

**PREDICTION TECHNIQUES OF ACID MINE DRAINAGE:  
A CASE STUDY OF A NEW POLY- METALLIC MINE DEVELOPMENT IN  
ERZİNCAN-İLİÇ, TURKEY**

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# ABSTRACT

## PREDICTION TECHNIQUES OF ACID MINE DRAINAGE: A CASE STUDY OF A NEW POLY- METALLIC MINE DEVELOPMENT IN ERZİNCAN-İLİÇ, TURKEY

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Acid Mine Drainage (AMD) is an environmental problem that eventually occurs in sulfide rich mine sites. In Turkey most of the metal mines are associated with sulphide minerals and are potential AMD generators. The purpose of this PhD thesis is to practice universally accepted tools for the prediction of AMD potential for a new metallic mine development.

This study involves evaluation of geological data, geochemistry, mineralogy, and acid-base accounting (static tests) data, obtained from the Erzincan-İliç Çöpler Gold Prospect case.

The mineralization in Çöpler is in sulfide and oxide types. The oxide is a supergene alteration and porphyry-copper type gold mineralization is classified as an intermediate sulfidation. The major lithologies observed in the study area are the regionally un-correlated meta-sedimentary lithologies, Munzur Limestone, and the Çöpler Granitoid.

Thirty-eight representative samples were tested for AMD prediction purposes. Sixteen more were included to the sampling scheme for site characterization.

Both acid producing and neutralizing lithologies are present in the mine site. Similarly it was revealed that the sulphate sulfur content of the samples were insignificant that any determined total sulfur amount can be directly considered as the factor for AMD production.

Geochemical data revealed arsenic enrichments up to 10000 ppm in the study area. Therefore, during the operational stage, in addition to the planning to avoid or minimize AMD, it is necessary to take precautions against arsenic mobilization during the design of the AMD neutralization scheme.

Both Kinetic studies and the heavy metal mobilization related to AMD are kept out of the scope of this investigation. Similarly, management and abatement stages of AMD are excluded.

Key Words: Acid Mine Drainage, Acid Base Accounting, Erzincan, Gold Mining, Environmental

# ÖZ

## ASİT MADEN DRENAJİ ÖNGÖRÜ TEKNİKLERİ: YENİ BİR POLİ-METALİK MADEN SAHASI ÜZERİNE VAKA ÇALIŞMASI ERZİNCAN-İLİÇ TÜRKİYE

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Asit Maden Drenajı (AMD), sülfidli sahalarda kaçınılmaz olarak ortaya çıkan bir çevresel sorundur. Türkiyede metalik madenlerin çoğu sülfidli mineralleri içerir ve bunlar potansiyel AMD üretim yerleridir. Bu tezin amacı, yeni açılacak polimetalik bir maden sahası örneğinde, küresel olarak kabul görmüş AMD öngörü tekniklerinin uygulanmasıdır.

Bu çalışma Erzincan-İliç Çöpler mevkiinde yer alan altın madenine ait jeolojik, jeokimyasal, mineralojik verilerin ve asit-baz muhasebesi ile ilgili (statik) deney sonuçlarının değerlendirilmesine dayanır. Çöpler madenindeki cevherleşme sülfid ve oksit tipidir. Oksit tipi cevherleşme süperjen bir bozuşma ile sahaya yerleşmiştir. Porfiri-bakır tipi cevherleşme ise orta dereceli bir sülfidleşme olarak sınıflandırılmaktadır. Çalışma sahasında gözlenen başlıca litholojiler bölgesel olarak korole edilemeyen meta-sedimanter birimler, Munzur Kireçtaşı ve Çöpler Granitoididir.

Sahayı temsil eden otuzsekiz adet örnek AMD öngörüsü amacıyla sınıanmış, ayrıca onaltı adet örnek de sahanın daha iyi karakterize edilmesi amacıyla örnekleme programına sonradan eklenmiştir.

Maden sahasında hem asit üreten, hem de asit tüketen litolojiler mevcuttur. Benzer şekilde sülfat türü kükürtün ihmal edilecek kadar az olması nedeniyle sahada jeokimyasal vb. analizlerle tespit edilecek toplam kükürt miktarının tamamının AMD üretimine katkıda bulunacağı anlaşılmıştır.

Jeokimyasal veriler sahada 10000 ppm'e varan seviyelerde arsenik zenginleşmesi olduğunu ortaya koymuştur. Bu nedenle, sahanın hazırlanması esnasında AMD oluşumunun engellenmesine yönelik yapılacak planlamaların yanısıra AMD oluşumunun giderilmesi esnasında tasarlanacak sistemde arsenik mobilizasyonuna karşı gerekli tedbirler de dikkate alınmalıdır.

Hem kinetik çalışmalar, hem de AMD ile ilişkili ağır metal mobilizasyonuna yönelik çalışmalar, ve benzer şekilde AMD'nin yönetimine ve iyileştirilmesine yönelik konular bu tezin kapsamı dışında bırakılmıştır.

Anahtar Kelimeler: Asit Maden Drenajı, Asit-Baz Muhasebesi, Erzincan, Altın Madeni, Çevresel.

To my grandmother **Beria Kesen** and to my parents who have supported me  
unconditionally...

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# TABLE OF CONTENTS

<b>ABSTRACT</b>	<b>iv</b>
<b>ÖZ</b>	<b>vi</b>
<b>ACKNOWLEDGMENTS</b>	<b>ix</b>
<b>TABLE OF CONTENTS</b>	<b>x</b>
<b>LIST OF TABLES</b>	<b>xiv</b>
<b>LIST OF FIGURES</b>	<b>xvi</b>
<b>ABBREVIATIONS</b>	<b>xix</b>
<b>CHAPTERS</b>	
<b>1.INTRODUCTION</b>	<b>1</b>
<b>1.1 Acid Mine Drainage</b>	<b>1</b>
<b>1.2 Acid Mine Drainage Chemistry</b>	<b>2</b>
<b>1.3 Examples of the AMD as an Environmental Problem in the World and in Turkey</b>	<b>6</b>
<b>1.4 Research Trends in AMD</b>	<b>8</b>
<b>1.5 Purpose and Scope</b>	<b>18</b>
<b>2.THE STUDY AREA</b>	<b>20</b>
<b>2.1 Location and Geographical Characteristics</b>	<b>20</b>
<b>2.2. Climatic Characteristics of the Study Area</b>	<b>22</b>
<b>2.3 Geology of the Study Area</b>	<b>24</b>
2.3.1 Previous Studies	24
2.3.2 Regional Geology	25
2.3.3 Stratigraphy	27
2.3.3.1 Keban Group – Kemaliye Formation.	30

2.3.3.2 Munzur Limestone	34
2.3.3.3 Ovacık Group	38
2.3.3.3.1 Eriç Ophiolitic Mélange	40
2.3.3.3.2 Uluyamaç Ophiolitic Member:	40
2.3.3.4 Post-Tectonic Tertiary Deposits	41
2.3.3.4.1 Subaşı Formation	41
2.3.3.4.2 Dedek Formation	43
2.3.3.4.2.1 Dolugün Member	43
2.3.3.4.2.2 Koçkar Volcanic Member	44
2.3.3.4.3 Kemah Formation	44
2.3.3.4.4 Quaternary Talus	45
2.3.3.4.5 Quaternary Alluvium	45
2.3.4 Structural Geology	45
2.3.4.1 Faults	46
2.3.4.2 Folds	47
2.3.5 Volcanic Activities and Magmatism	47
2.3.5.1 Çöpler Granitoid	47
2.3.5.2 Yakuplu Granitoid	49
2.3.6 Tectonic Deformation History	50
2.3.7 Ore Mineralization	52
2.3.7.1 Alterations	52
2.3.7.2 Jasperoids	52
2.3.7.3 Mineralization Zonations	53
2.3.7.3.1 Main Zone	54
2.3.7.3.1.1 Main Zone Oxide	55
2.3.7.3.1.2 Main Zone Sulphide	55
2.3.7.3.2 Manganese Mine Zone	56
2.3.7.3.2.1 Manganese Mine Zone Oxide	56
2.3.7.3.2.2 Manganese Mine Zone Sulphide	56
2.3.7.3.3 Marble Contact Zone	57
2.3.7.3.3.1 Marble Contact Zone Oxide	57

2.3.7.3.3.2 Marble Contact Zone Sulphide _____	58
2.3.8 Resource Estimate _____	59
2.3.9 Hydrogeology _____	61
2.3.9.1 Aquifer Systems: _____	63
2.3.9.1.1 The deep limestone aquifer _____	63
2.3.9.1.2 Local shallow aquifers _____	66
2.3.9.1.3 Alluvium Aquifer _____	67
2.3.9.2 Chemistry of the Groundwater _____	67
2.3.9.3 Surface Waters _____	70
<b>3.MATERIALS AND METHODS _____</b>	<b>73</b>
<b>3.1 Sampling Scheme _____</b>	<b>73</b>
<b>3.2 Methods Used _____</b>	<b>78</b>
3.2.1 Mineralogy and Petrography _____	78
3.2.2 Geochemistry _____	80
3.2.3 Acid Base Accounting _____	80
3.2.3.1 Components of ABA _____	80
3.2.3.1.1 The Maximum Potential Acidity (MPA) _____	81
3.2.3.1.2 The neutralization potential (NP) _____	82
<b>3.3 The Road Map Followed in the Case Study _____</b>	<b>82</b>
<b>3.4 ABA Tests Applied in the Study _____</b>	<b>85</b>
<b>3.5 Accuracy, Quality Control and Assurance in ABA tests _____</b>	<b>87</b>
<b>4.RESULTS _____</b>	<b>88</b>
<b>4.1 Mineralogy _____</b>	<b>88</b>
4.1.1 Polarized light Microscopy _____	88
4.1.1.1 Mineralogy of the Metasedimentary Unit _____	88
4.1.1.2 Mineralogy of the Munzur Limestone _____	91
4.1.1.3 Mineralogy of the Çöpler Granitoid _____	93
4.1.2 Ore Microscopy _____	95
4.1.3 X-Ray Diffraction _____	98

<b>4.2 Geochemistry</b>	<b>101</b>
<b>4.3 Acid Base Accounting</b>	<b>112</b>
4.3.1 Paste pH	112
4.3.2 Maximum Potential Acidity	115
4.3.3 Neutralization Potential	117
4.3.4 Net Neutralization Potential	118
4.3.5 Neutralization and Acid Potential Ratio (NPR):	119
<b>5.DISCUSSION</b>	<b>123</b>
<b>5.1. Sampling Scheme</b>	<b>124</b>
<b>5.2 Mineralogy and Petrography</b>	<b>125</b>
<b>5.3.Geochemistry:</b>	<b>126</b>
<b>5.4 Acid Base Accounting</b>	<b>127</b>
5.4.1 Maximum Potential Acidity (MPA)	127
5.4.2 Fizz Rating	129
5.4.3 Neutralization Potential	135
5.4.4 Interpretation of ABA data and AMD Potential Criteria	138
<b>6.CONCLUSIONS AND RECOMMENDATIONS</b>	<b>144</b>
<b>REFERENCES</b>	<b>152</b>
<b>APPENDICES</b>	
<b>A-LIST AND DETAILS OF THE SAMPLES INVOLVED IN THE STUDY</b>	<b>196</b>
<b>B-GEOCHEMICAL ANALYSIS RESULTS</b>	<b>200</b>
<b>C-ACID BASE ACCOUNTING_ METHODS AND CANMET STANDARD “NBM-1” UTILIZED IN THE STUDY</b>	<b>212</b>
<b>D-X-RAY DIFFRACTION ANALYSIS RESULTS</b>	<b>228</b>
<b>CURRICULUM VITAE</b>	<b>259</b>

## LIST OF TABLES

Table.2.1 Major stratigraphic units observed in the Munzur Mountains (After Özgül et al., 1981). _____	28
Table 2.2 The resource estimate of Çöpler Gold Prospect (MCI, 2005) _____	60
Table 2.3 Concentrations of selected metals and SO <sub>4</sub> in two different sampling periods. Note that the maximum amount allowed by Turkish Ministry of Health and by European Union Regulations are 0,2mg/L for Fe; 250 ppm for SO <sub>4</sub> and 0.1mg/L for As and Pb (concentration values are taken from Ekobil, 2005). _____	68
Table 3.1 Abbreviations used in the coding terminology of the studied samples. _____	73
Table 3.2 The well codes, sampling depth and lithologies of the collected samples and their lithologic properties RMH: Rock Mechanics Holes, CRC: Çöpler Rock Cuttings Drill Hole; CDD Çöpler Diamond Drill Hole (Refer to Appendix-A for more detail) ____	76
Table 3.3 Summary of the tests applied to the total 54 samples that were dealt with in the study. _____	78
Table 3.4 A summary of the ABA tests applied over each sample collected for AMD prediction. (MetaS: metasediments; Drt.: diorite; NP: Neutralization Potential; MPA: Maximum Potential Acidity; NNP: Net Neutralization Potential, CO <sub>2</sub> CD: Carbonate carbon determination, SO <sub>4</sub> SD, sulfate sulfur determination). _____	86
Table 3.5 Quality Control and Accuracy test indicators for ABA tests results. _____	87
Table 4.1 Summary of the major and trace element geochemical analysis Part-1. _____	102
Table 4.2 Major and trace element geochemistry results of the composite samples. Only the Average (Ave.), Minimum (Min.), Maximum (Max.) and Standard Deviation (St.Dev.) of the analyzed interval in depth are given. The full analyses of the indicated intervals are given in Appendix-B. _____	103
Table 4.3 Summary of the Acid Base Accounting Test Results _____	113
Table 4.4 Ratio of sulphate sulfur in total sulfur _____	115
Table 4.5 Samples with lower MPA values due to high content of sulphate. _____	116

Table 4.6 The difference between NP calculated from total CO <sub>2</sub> equivalent value and the laboratory tested NP. _____	117
Table 4.7 Summary of the NNP results of the samples classified according to NNP Criterion _____	119
Table 5.1 Fizz Rating Values compared with the literature indicated range of NP values provided by (Morin and Hutt, 2005). _____	134
Table 5.2 Neutralization Potential Ratio (NPR) Screening Criteria to Determine AMD Potential (Price et al., 1997). (AG: Acid Generating; PAG: Potentially Acid Generating; PAC: Potentially Acid Consuming; AC: Acid Consuming) _____	140

## LIST OF FIGURES

Figure 2.1 Location Map of the Study Area -----	21
Figure 2.2 A view from the study area and the Çöpler Village, looking towards Northwest. -	23
Figure 2.3 Distribution of the major tectonic units (After Özgül et al., 1981)-----	26
Figure 2.4 Map illustrating the regional geology in the vicinity of the study area (1:Quaternary alluvium, 2:Quaternary talus, 3:Kemah Formation, 4: Dedek Formation-Tdk: Koçkar volcanics member, Tdd: Dolugün Member, 5:Granite-Granodiorite intrusion, 6: Subaşı Formation, 7: Eriç ophiolitic mélangé-Ke: Undifferentiated, Keu: Uluyamaç member, 8: Pelagic Blocks of Kemaliye Formation, 9: Munzur Limestone) (After Özgül et al., 1981). -----	29
Figure 2.5 Detailed geology of the study area, ÇNF: Çöpler North Fault, ÇSF: Çöpler South Fault (Modified after Poyraz, 2005). -----	32
Figure 2.6 Meta-sedimentary units observed in the study Area. Soft sediment features such as slump folds and boudinaged chert bands are preserved. The unit interpreted to be a turbidite sequence, but not correlated regionally (Easterday, 2004). -----	33
Figure 2.7 Generalized stratigraphic columnar section of the Munzur Limestone (Özgül et al., 1981).-----	35
Figure 2.8 Munzur limestone exhibiting massive structures with indistinct bedding. It lies unconformably above the meta-sedimentary unit and its contacts display evidence of tectonic emplacement and soft-sediment flame structures (Easterday, 2004).-----	38
Figure 2.9 Ovacık Group's Generalized Schematic Stratigraphic Columnar Section (After Özgül et al., 1981)-----	39
Figure 2.10 A: Major neotectonic elements of Anatolia (from Elmas, 1996) B: Simplified neotectonic map showing major tectonic escape induced structures in Eastern half of Turkey and the adjacent areas (from Sial, 2004). -----	46
Figure 2.11 Hornblende-quartz-monzonite porphyry intruding the entire sequence. (Picture taken from Easterday, 2004).-----	48
Figure 2.12 Photography of the core sample from Main zone sample no: CDD-002; between 21.5 to 29.4 m. Oxide / Sulphide boundary shown at 25.45 m (Poyraz, 2005)---	55
Figure 2.13 Photography of the core sample from Mn Mine Zone – Oxide (a) and Sulphide (b) Mineralization. Core samples: CDD-066, CDD 256-5-274.35 m. Marble breccia (c) and argillized brecciated intrusives (d).-----	57
Figure 2.14 Core photo from the Marble Contact Zone, CDD-039, 45.9-60.6 m. Oxidized intrusive (a) and gossan (b). -----	58
Figure 2.15 Locations of springs, seeps, and groundwater monitoring wells in the study area on a topographic map from I41-d4 sheet, (Erzincan-İliç). SP: Spring, SZ: Seep, WMR: Groundwater Monitoring Well (Map modified after Ekobil, 2005). -----	62

Figure 2.16 Conceptual model for groundwater movement in Çöpler region and surroundings. Model shown on a 3D topographic elevation model). (From Ekobil, 2005).-----	65
Figure 2.17 Major drainage networks in the vicinity of the study area (N:River; D:Rivulet) (After Ekobil, 2005).-----	72
Figure 3.1 Acid Mine Drainage Core Sampling -----	74
Figure 3.2 Drill locations for samples collected for Acid Base Accounting (ABA), geochemical and mineralogical tests. Well numbers are indicated for most of the samples, in each well for details of the samples, refer to Appendix-A.-----	77
Figure 3.3 Flow Chart Summarizing Acid Base Accounting procedures and critical issues to be considered.-----	84
Figure 4.1 Fine clayey textures with boudinage like microstructures of a Metasedimentary rock sample (RMH02; 32.45-32.55) (Magnification 45X) -----	88
Figure 4.2 Metasedimentary lithology that exhibit major chalcedony veins, rock fragments and fine-grained clayey minerals. a: single nicole, b: cross nicole, magnification 45X (Sample from CDD334).-----	89
Figure 4.3 The thin section of the metasedimentary lithology that show rock fragments and small veinlets that indicate cataclastic activity; a: single nicole, b: cross nicole (Sample from CDD334) (magnification 100X).-----	90
Figure 4.4 Metasedimentary rock sample (RMH02; 32.45-32.55) exhibiting epidotization, a: single nicole, b: cross nicole (magnification 100X).-----	90
Figure 4.5 Microscopic view of a Marble sample (CDD-98;51.7-51.9) with large euhedral to subhedral calcite crystals, a: single nicole, b: cross nicole (Magnification 45X) -	91
Figure 4.6 A Limestone sample (CDD 91) exhibiting fractures lined with iron oxides and filled with recrystallized calcite, a: single nicole, b: cross nicole. (Magnification 45X).	92
Figure 4.7 Karstic voids and mineral boundaries lined with iron oxides in marbles, , a: single nicole, b: cross nicole. (Sample CDD-98; 13m). (Magnification 45X).-----	92
Figure 4.8 A sample (CDD-85) from Çöpler Granitoid exhibiting porphyritic texture with very fine grained silica matrix and highly deformed feldspar crystals, a: single nicole, b: cross nicole (Magnification 45X).-----	93
Figure 4.9 A Sample (CDD-99) from Dioritic Çöpler Granitoid exhibiting Phenocrysts with sericitization, opaques, kaolinitization, feldspath and ferromagnesian phenocrysts in a micro-silica matrix; a: single nicole, b: cross nicole. Magnification 45x. -----	94
Figure 4.10 Plagioclase phenocrysts with saursoritization and calcitization (from CDD-84); a: single nicole, b: cross nicole. Magnification 45X.-----	94
Figure 4.11 Disseminated rutiles (r) and pyrites (p)-----	95
Figure 4.12 Vein filling pyrite (p), subhedral chalcopyrite (cp) and marcasites (mc) engulfed in pyrite fillings (a: picture with single nicole; b: picture with cross nicole).-----	96
Figure 4.13 Subhedral to euhedral magnetite (m) with unehedral hematite (h) grains -----	97
Figure 4.14 A large euhedral magnetite grain-----	97

Figure 4.15 X-Ray diffraction pattern of the <170 mesh (bulk) fraction of the sample CRD 356. Qtz: Quartz, F: Feldspar, Ca: Calcite, S: Smectite; I: Illite, See Appendix-D for full size graphics. -----	99
Figure 4.16 X-Ray diffraction patterns of the clay fraction of the sample CRD 356 Qtz: Quartz, F: Feldspar, Ca: Calcite, S: Smectite; I: Illite, G: Gypsum See Appendix-D for full size graphics. -----	100
Figure 4.17 The change in Mo concentration with depth, in diorite drill hole samples. Elevated Mo concentrations indicate hydrothermal contribution. -----	104
Figure 4.18 Fluctuation of %Al, %Fe and %S with respect to depth. -----	105
Figure 4.19 Variation of Pb, Cu, Zn and As concentrations in ppm and S content in percentage with respect to depth for samples from drill holes CRC 255 and CRC 270 (The 10000 ppm is the upper detection limit of the reported analysis results, and 10% S is the upper detection limit of the reported results).-----	106
Figure 4.20 Variation of Pb, Cu, Zn and As concentrations in ppm and S content in percentage with respect to depth for drill hole samples CRC 271 and CRC 280 (The 10000 ppm is the upper detection limit of the reported analysis results, and 10% S is the upper detection limit of the reported results). -----	107
Figure 4.21 Change in Ca and K concentrations (in weight %) of drill hole samples (CRC 255, CRC 270, CRC 271 and CRC 280) with respect to depth. -----	109
Figure 4.22 Change in Ti, Na and Mg concentrations (in weight %) of drill hole samples (CRC 255, CRC 270, CRC 271 and CRC 280) with respect to depth. -----	111
Figure 4.23 Distribution of the samples based on NPR values. -----	120
Figure 4.24 Graph that shows the NPR distribution of the tested samples in a detailed scale. -----	122
Figure 5.1 Carbonate Carbon Neutralization Potential vs. tested Neutralization Potential of some marbles from the marble zone and one limestone sample from the manganese mine zone. -----	138
Figure 5.2 Graph indicating positive correlation between maximum potential acidity (MPA) and total sulfur content. -----	141
Figure 6.1 Significant issues that effect final drainage chemistry, modified after Morin and Hutt (2005). -----	145

## ABBREVIATIONS

<b>ABA</b>	Acid Base Accounting
<b>AC</b>	Acid Consuming
<b>AG</b>	Acid Generating
<b>AMD</b>	Acid Mine Drainage –Asit Maden Drenajı
<b>AMIRA</b>	Mineral Industries Research Association
<b>ARD</b>	Acid Rock Drainage
<b>CANMET</b>	Natural Resources Canada
<b>DOIT</b>	Department of Information Technology State of Connecticut
<b>EU</b>	European Union
<b>ICARD</b>	International Conference on Acid Rock Drainage
<b>MPA</b>	Maximum Potential Acidity
<b>MTA</b>	Maden Tetkik Arama Genel Müdürlüğü; General Directorate of Mineral Research and Exploration
<b>NAG</b>	Net Acid Generation
<b>NAP</b>	Net Acid Production
<b>NAPP</b>	Net Acid Production Potential
<b>NNP</b>	Net Neutralization Potential
<b>NP</b>	Neutralization Potential
<b>NPR</b>	Neutralization Potential Ratio
<b>PAC</b>	Potentially Acid Consuming
<b>PAG</b>	Potentially Acid Generating
<b>USEPA</b>	United States Environmental Protection Agency
<b>UNP</b>	Unavailable Neutralization Potential
<b>MCL</b>	Maximum Concentration Level
<b>amsl</b>	Average mean sea level

# CHAPTER 1

## INTRODUCTION

### 1.1 Acid Mine Drainage

Acid Mine drainage can be simply considered as an analogous problem of the well-known air pollution related acid rain problem. Acid rain forms as a result of atmospheric  $\text{SO}_2$  reacting with  $\text{H}_2\text{O}$  to form sulfuric acid. Similarly when sulfur present in rocks in the form of sulfide minerals is liberated and oxidized it generates sulfuric acid. This is one of the major impacts of mining activity related to coal and metal mining. Acid Mine Drainage (AMD) is a problem that occurs within time in sulfide rich mine sites. When in contact with oxygen or oxygenated waters, metal sulfides breakdown leading to acid generation. This leads to metal leaching. Although oxidation of sulfide bearing minerals can as well occur naturally as a result of weathering since mining activity accelerates sulfur exposure to air and water the problem is referred to as acid mine drainage (Peppas *et al.*, 2000). However it must be noted that in some North American especially Canadian literature it is also referred as Acid Rock Drainage (ARD) attributing to the possibility of acid drainage formation without human disturbance in areas where high sulfide bearing minerals are concentrated.

AMD is generally defined as the product formed by the atmospheric (i.e. by water, oxygen and carbon dioxide) oxidation of the relatively common iron-sulfur minerals such as pyrite ( $\text{FeS}_2$ ) and pyrrhotite ( $\text{FeS}$ ) in the catalyzing presence of *Acidithiobacillus ferrooxidans*, an acidophilic bacterium, and any other products generated as a consequence of these oxidation reactions (Mills, 1995; USEPA, 1994a, 1994b in Akçıl and Koldaş, 2006).

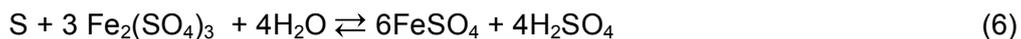
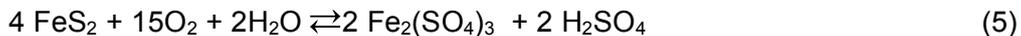
Problems that can be associated with mine drainage include contaminated drinking water, disrupted growth and reproduction of aquatic plants and animals and the corroding effects of the acid on parts of infrastructures such as bridges. In addition,

especially benthic macro invertebrate communities are severely restricted (Armitage, 1980; Dills and Rogers, 1974) and this has a knock-on-effect for higher organisms, especially fish. In addition, a number of socioeconomic impacts are associated with mine waters. Clearly, deposition of bright orange, iron-rich precipitates on streambeds has a devastating aesthetic impact. Apart from aesthetics, mine waters rising through deep mines (usually following mine closure) may result in flooding, subsidence, corrosion of foundations, and emissions of carbon dioxide and methane gases at the surface (Jarvis and Younger, 2000).

AMD is an environmental problem that has been extensively studied since 1950's (Leathen, et al, 1953). The causes, and formation of acid mine drainage as a major water quality degradation source (McCleary and Kepler, 1994) especially in coal mining regions is well documented by Stumm and Morgan (1970) Brodie et. al. (1993) Hedin et. al,(1994) and in Skousen and Ziemkiewicz(1995).

## 1.2 Acid Mine Drainage Chemistry

The following chemical reactions describe the oxidation and hydrolysis of the most Acid mine drainage prone mineral pyrite or marcasite ( $\text{FeS}_2$ ) to the products that constitute the contaminants generically termed Acid Mine Drainage (AMD). Similar reactions may be written for the oxidation of other AMD prone minerals such as pyrrhotite ( $\text{FeS}$ ) sphalerite ( $\text{ZnS}$ ) and Galena ( $\text{PbS}$ ) (Mills, 1995).



In general, the expression "bacteria" pointed out in the equations number (3) and (4) is generally site-specific strains of *Acidithiobacillus ferrooxidans*. The A.

*ferrooxidans* bacteria make use of the available sulfur as its source of energy. These are autotrophic bacteria, obtaining their nutritional needs such as nitrogen, oxygen, carbon dioxide and water, from the atmosphere and those others such as sulfur and phosphorus from Sulfide minerals such as pyrite, arsenopyrite, sphalerite etc. (Mills, 1995).

By true meaning, these bacteria are not catalysts, however they do act as accelerating agents if their habitat conditions are at or close to optimal and they make up one of the most important factors in the generation of AMD. In addition, these bacteria are also able to adapt themselves by mutation if their habitat is markedly changed. Studies related to the role of *A. ferrooxidans* bacteria date back to 1947 (Colmer and Hinkle, 1947) and a significant portion of the general AMD literature is dedicated to the studies related to *Acidithiobacillus ferrooxidans* or alike acidophilic bacteria, although some significant portion of these studies are dedicated to bio-metallurgical studies (based on data in Mills, 1995).

Mills (1995) suggests that in the absence of bacteria (usually *A. ferrooxidans*) Equations (1) (2) and (5) succeed, while in the presence of bacteria reactions are best described by Equation (5) which can be considered as a combination of Equations (1) and (3) or (2) (3) and (4) or (1) (2) (3) and (4).

Since for the sequence of the processes presence of oxygen and water is essential, removal of the oxygen source (e.g. by total submersion under water) or the water source (such as arid climatic conditions) is regarded to stop the progress of AMD production. AMD production would also be considerably slowed or stopped by the termination of *A. ferrooxidans* reproduction by an agent that will terminate bacteria. The final products are sulfuric acid and ferric sulphate. Sulfuric acid is, also, an important intermediate product. From the commencement of pyrite oxidation, pH falls rapidly and then stabilizes, typically at values around pH 2.5 to 3.0. The stabilization level of pH is generally determined by the optimal habitat requirement of the site-specific strain of bacteria (Mills, 1995).

In cases where pyrite and/or pyrrhotite are the only sulphide minerals open to atmospheric oxidation then the products of the oxidation process are those described above. Depending upon the availability of water and oxygen, reactions

may not always approach completion as indicated by equations 1 to 6, and in such cases intermediate phases of chemical compounds or minerals may remain at the oxidation site.

Presence of other metallic minerals such as galena, chalcopyrite, sphalerite in addition to pyrite and pyrrhotite, then there may be a secondary effect of the oxidation of the iron-sulfur minerals to sulfuric acid and ferric iron (Mills, 1995).

On the other hand, as indicated by Akçıl and Koldaş (2006) although other sulfide minerals such as pyrrhotite (FeS) and chalcocite (Cu<sub>2</sub>S) have other ratios of metal sulfide and metals other than iron, and even though other oxidants and sulfide minerals have varied reaction pathways, stoichiometries and rates, research related to these differences are not abundant.

After the starting of AMD reactions as the stable pH develops (2.5 to 3.0) the products of sulfuric acid and ferric sulphate create conditions where the ferric iron ion itself can act as an oxidant<sup>1</sup>. In the absence of ferric iron at pH 2.5-3.0, sulfuric acid will dissolve some heavy metal carbonate and oxide minerals, but has little reactive effect on heavy metal sulphides. However, ferric iron ion is capable of dissolving many heavy metal sulphide minerals, including those of lead, copper, zinc, and cadmium, by the general reaction (7) given below (Mills, 1995):



Where: MS = solid heavy metal sulphide; Fe<sup>+++</sup> = aqueous ferric iron ion; Mn<sup>+</sup> = aqueous heavy metal ion; S = sulfur; Fe<sup>++</sup> = aqueous ferrous iron ion.

It is by this process explained in equation (7) that significant amounts of heavy metals may become soluble as a result of AMD. In addition, many metallic elements are often present at trace levels within the minerals pyrite and pyrrhotite. Oxidation of these minerals can therefore release and mobilize these trace elements (Mills, 1995).

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<sup>1</sup> Between pH 2.3 to 3 the ferric ion is itself hydrolyzed to ferric hydroxide and jarosite (Akçıl and Koldaş, 2006) which precipitates as the familiar rust-colored stain associated with AMD

AMD does not only occur as a result of mining activity but it can as well occur as a natural alteration process. Hence, geochemists that measure the levels of metals in surface or ground waters can often infer the presence of a mineral deposit and predict its location. This procedure is generally considered to be a powerful exploration tool. The chemical processes of AMD are directly related to metal transport and the formation of metallic mineral deposits via the natural generation and neutralization of AMD such as gossans (Mills, 1995). Natural processes and natural state of the environment are equally important when a new mine is planned. In general under the global regulatory processes for new mine development, Environmental Impact Assessment process requires a "Baseline" study of water chemistry (in addition to many other requirements) before mine development begins, to determine the "natural" levels of metals and other constituents in surface and ground waters potentially affected by development.

Untreated (not neutralized) AMD creates two quite distinct environmental problems: First is the acidity from sulfuric acid, which is invariably a product by definition and the second is the heavy metals that become increasingly soluble as a result of ferric iron as explained above by equation (7). It is important that these two effects are recognized as separate, since their consequences to ecosystems are distinct, and because AMD generation and heavy metal transport are separate processes.

Major factors affecting AMD are pH, temperature, oxygen content of the porous media especially if water saturation is less than 100%; dissolved oxygen concentration in the water phase of the pore space, degree of water saturation, chemical activity of ferric ion, surface area of the exposed metal sulfide, chemical activation energy required to initiate acid generation, and bacterial activity (Akçıl and Koldaş, 2006).

Akçıl and Koldaş (2006) in their review article identifies primary sources of AMD as mine rock dumps, tailings impoundments, underground and open pit mine workings, pumped/nature discharged underground water, diffuse seeps from replaced overburden in rehabilitated areas, construction rock used in roads, dams, etc. and considers treatment sludge pounds, rock/road cuts, concentrated load-out stockpiles, concentrate spills along roads and emergency ponds as secondary AMD sources.

### **1.3 Examples of the AMD as an Environmental Problem in the World and in Turkey**

In Appalachian coal mining region, approximately 12,000 km of streams and 12,000 ha of impoundments, have rendered biologically overwhelmed due to AMD and associated heavy metal leaching (Appalachian Regional Commission, 1969).

Jarvis and Younger (2000) refer to estimates suggesting that more than 700 km of the UK's streams and rivers are detrimentally affected due to mine related contamination.

The numbers of abandoned and active mines that are degrading Turkish watersheds are not known, but there are mines that threaten high value infrastructures. Such as Muratlı Dam in Artvin, with an investment of about £169 million<sup>2</sup> is threatened by the AMD of Murgul Copper mine. Under construction, Havran Dam, investment worth approximately £90 million in Balıkesir is threatened by abandoned Balya Balıkesir Cu/Pb/Zn mine's old tailings' AMD.

Once initiated, metal leaching due to AMD may persist for hundreds of years. In North America, metal leaching and ARD have led to significant ecological damage, contaminated rivers, loss of aquatic life and multi-million dollars clean-up costs for industry and government (Price, 2003). The ARD liability associated with existing Canadian tailings and waste rock is estimated to be between 2 and 5 billion Canadian dollars (Feasby and Tremblay, 1995).

AMD is a long-term environmental problem that requires continuous information, monitoring and long-term performance follow-up, therefore this long term procedures also incur extra costs to the society as indicated by Price (2003). The needs for pro-active detection and for the mutually satisfactory site-specific solutions are other factors that challenge and increase AMD related costs. Price (2003) suggests, mitigation costs in the orders of 10s of millions of Canadian Dollars for the Capital investment and post-closure operating costs of \$1 million per year. I believe

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<sup>2</sup> Numbers are taken from Turkish Parliament : <http://www.tbmm.gov.tr/butce/htm/pbk16112005.htm> (Last visited 22/03/2006)

that this argument is exaggerated and needs to be reviewed based on better and cheaper long term solutions such as wetland construction as suggested by McCleary and Kepler (1994)<sup>3</sup>.

On the other hand the formation of AMD and metal leaching is controlled by the site-specific geological and climatic conditions, therefore it is not possible to transfer these damage costs from one region to another without studying the underlying calculations. There are several cost determination guidelines and even practical software developed for North America. These practical tools are developed to help mining industry calculate their environmental liabilities.

Although mine wastes are recognized to be amongst the largest waste streams in the European Union and although it ranks first in the relative contribution of wastes in many Central and Eastern European countries, the AMD damage that could be related to these wastes are not identified in EU. Similarly, even there exist a mining directive there is no specific stated policy regarding AMD abatement in EU.

Although AMD is a recognized problem by Ministry of Environment and Forestry and by the General Directorate of Mineral Research and Exploration (MTA) the only AMD studies are covered within the EIA projects (Eurogold, Bergama Gold Project, Tuprag- Uşak Eşme Gold Project) and MTA has two projects related to abandoned mines that deal with the impact of AMD produced by abandoned mine sites (MTA Project: Environmental Impact of Mining; MTA Project: Northern Black Sea Abandoned Mines Project). In addition, MTA is in process of developing a research laboratory for investigating AMD and water quality related problems. Although AMD is a recognized problem and covered in curricula of mining faculties in Turkey, there are not many researches related to AMD except some biological ore enrichment, hydrometallurgy and mine abatement studies (Akçıl and Çiftçi, 2003; Aytakin and Akdağı, 1996; Kesimal *et al.*, 2003,) and a recent review paper by Akçıl and Koldaş (2006).

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<sup>3</sup> This suggestion of Pierce relies on Feasby and Tremblay, 1995, probably missed the passive wetland study of McCleary&Kepler (1994). Same in British Columbia AMD Policy statement. Yet damage related to AMD is significant.

## 1.4 Research Trends in AMD

The Acid Mine Drainage or Acid Rock Drainage subject is widely studied mainly in North America. Appalachian region and Pennsylvanian coal mining regions are intensely studied by the mining schools and the earth scientists of the region. As a result an immense literature is present on this issue. Since 1990s the studies related to Acid Mine Drainage has been presented mainly in two international conferences regularly: Annual Conference on Tailings and Mine Waste and the International conference on Acid Rock Drainage (ICARD) that is organized in every three years since the ICARD 1<sup>st</sup> that was organized in 1988.

Studies related to AMD and especially the role of chemotropic bacteria date back to 1947 when Colmer and Hinkle (1947) identified the role of the bacteria in AMD formation, Temple and Colmer (1951) identified *Acidithiobacillus ferrooxidans* as a new iron oxidizing bacteria. Bacteria itself and its role in the formation of acid from certain sulfuric constituents associated with bituminous coal, or sulfide minerals was intensely studied in 1950s. (Colmer and Hinkle, 1947; Colmer *et al.*, 1950; Temple and Colmer 1951; Palache *et al.*, 1951; Temple and Delchamps, 1953; Leathen *et al.*, 1953, Temple and Koehler, 1954; Leathen *et al.*, 1956; Bryner and Jameson 1958; Silverman and Lundgren, 1959; Duncan *et al.*, 1967, Lau *et al.*, 1970; Ehrlich, 1972; Norris *et al.*, 1988; Norris, P.R., 1990).

Studies related to bacteria or in general the biogeochemistry of the AMD formation, the role of these chemotropic bacteria in metal gain and the use of bacteria in AMD abatement and management have continued to be studied in depth since '60s especially by Sutton and Corrick (1961a, 1961b, 1963, 1964); Hem (1963a, 1963b); Barnes *et al.* (1964) Torma *et al.* (1972) and Ferris, *et al.* (1989). Dugan (1975) studied the bacterial ecology of strip mine areas and revealed its relationship to the production of acid mine drainage. Kleinmann and Crerar (1979) exhibited relation of *Acidithiobacillus ferrooxidans* and the formation of acidity in the simulated coal mine environments.

Wilchlacz and Unz (1981) revealed Acidophilic, heterotrophic bacteria of acid mine waters. Ingledew (1982) revealed the bioenergetics of *Acidithiobacillus ferrooxidans*. Alexander *et al.* (1987) showed the relationship between chemi-osmotic parameters

and sensitivity to anions and organic acids in *Acidithiobacillus ferrooxidans*. Basaran and Tuovinen (1987) revealed the details of pyrite oxidation by *Acidithiobacillus ferrooxidans*, such as sulfur intermediates, soluble end products, and changes in biomass. Karamanev and Nikolov (1988) identified the influence of some physicochemical parameters on bacterial activity of biofilm ferrous iron oxidation by *Acidithiobacillus ferrooxidans*. Liu *et al.* (1988) exhibited the role of ferrous iron, dissolved oxygen, and inert solids concentrations on the growth of *Acidithiobacillus ferrooxidans*. Cravotta and Bird (1995) demonstrated the role of water saturation and microbial activity on acid production and metals transport from pyrite rich formations. Harvey and Crundwell (1996) revealed the role of As (III) on the growth of *Acidithiobacillus ferrooxidans* in laboratory conditions. Crundwell (1997) studied the kinetics of the chemi-osmotic proton circuit of the iron-oxidizing bacterium *Acidithiobacillus ferrooxidans*. Fowler *et al.*, (2000) also studied on the kinetics and mechanism of the dissolution of pyrite in the presence of *Acidithiobacillus ferrooxidans*. Elberling *et al.* (2000) studied bacterial and chemical oxidation of pyritic mine tailings at low temperatures. Pronk *et al.* (1990) studied the oxidation of reduced inorganic sulfur compounds by acidophilic thiobacilli. Yet, it was Wanner and Egli (1990) together with Pronk *et al.* (1991) who demonstrated energy transduction by anaerobic ferric iron respiration in *Acidithiobacillus ferrooxidans*.

Tuttle *et al.* (1969) introduced the possibility of using bacteria as an acid mine water pollution abatement system by microbial sulfate reduction. Later, others also suggested the use of microbiological treatment of AMD waters (Whitesell *et al.*, 1971; Dvorak *et al.*, 1992; Johnson, 1995; Lawrence and Poulin 1996). Elimination of sulfur content in coal using bacteria, thus mitigating AMD was also well studied (Beyer *et al.*, 1986; Bos *et al.*, 1986; Francis *et al.*, 1989; Bos *et al.*, 1990; Khalid *et al.*, 1990; Choi and Torma, 1990). Elimination of *Acidithiobacillus ferrooxidans* bacteria to avoid AMD was also studied as a mitigation option (Shuttleworth and Unz, 1988; Watzlaf, 1988; Suzuki *et al.*, 1989; Taylor and Schumam, 2001)

Other bacteria related researches involve studies by scientists such as Sutton, and Corrick (1961a,b) who revealed the uses of bacteria for metal ore extraction. Studies related to involvement of chemotropic bacteria after 60's have shown a trend including the effect of bacteria on the AMD production (Duncan *et al.*, 1967) use of bacteria for low grade ore extraction (Corrick, and Sutton, 1965). Schonborn

and Hartmann (1978) studied bacterial leaching of metals from sewage sludge, while McElroy and Bronstein (1978) demonstrated and made the economic analysis of continuous biological leaching of chalcopyrite concentrates. By 1980's microbiological mining, in other words role of chemotropic sulfide oxidizing bacteria in metal leach started to be more intensely studied (Brierley and Brierley, 1981; Brierley, 1982; Lawrence *et al.*, 1984; Lawrence *et al.*, 1985; Puhakka and Tuovinen, 1986; Sanmugasunderam *et al.*, 1986; Ehrlich, 1986; Lawrence *et al.*, 1986; Puhakka and Tuovinen, 1987; Lizama and Suzuki, 1987; Marchant *et al.*, 1989) Sanmugasunderam *et al.* (1985) suggested a growth model for the continuous microbiological leaching of a zinc sulfide concentrate by *Acidithiobacillus ferrooxidans*. Marchant (1986) demonstrated a commercial piloting and the economic feasibility of plant scale continuous biological tank leaching. By 1990s the principles of bioleaching processes started to be revealed (Brierley, 1990; Fowler and Crundwell, 1998; Fowler and Crundwell, 1999; Fowler *et al.*, 1999; Holmes, *et al.*, 1999.) such as Tuovinen (1990) who exhibited the biological fundamentals of mineral leaching processes. Recently, Haoran *et al.* (2005) suggested use of bacteria to gain metals from marine nodules under anaerobic condition.

Although the available literature is immense and deals with various aspects of the AMD, majority of the recent studies are concerned with the abatement of AMD. Hill and Wilmoth (1971) are one of the earliest to study Limestone treatment of AMD. Other abatement issues studied in 1970s include biochemical-iron-oxidation limestone-neutralization process (Lovel, 1972) re-vegetating bituminous strip-mine spoils with municipal wastewaters (Edgerton *et al.*, 1975). In 80s studies related to neutralization using lime and limestone continued and Erickson *et al.* (1985) introduced the idea of applying bactericides and eliminating the chemotropic bacteria to treat the AMD. Hue *et al.* (1988) tested application of sewage sludge as an abatement procedure for AMD via using plant and soil chemical compositions. Although Sopper *et al.* (1974) first introduced the idea of sludge utilization in mine reclamation in 1974, to establish grasses and legumes on bituminous strip-mine spoils, and Sopper and Seaker (1984) explained more about the strip mine reclamation using municipal sludge in their 1984 paper, the research related to usage of neutralization properties of alkaline sludge has gain popularity in 90's (Cravotta, 1996; Dugas *et al.*, 1993; Jianwei Z. 1995, Whitmire, 1995; Schultz,

1995). Fly ash is another material considered as a neutralizer to the AMD threat (Taylor and Schumam, 1988; Scheetz *et al.*, 1993; Aljoe, 1996). Nicholson *et a.* (1989) studied the use of moisture-retaining cover layers as oxygen barriers to prevent AMD. Although studies range from construction of wetlands as passive treatment for AMD (Kleinmann, 1985; Holm and Elmore, 1986; Girts and Kleinmann, 1986; Eger and Lapakko, 1988; Brodie *et al.*, 1989; Brodie *et al.*, 1991; Klusman *et al.*, 1993; Tarutis, *et al.*, 1992) or construction of anoxic limestone drains (Nairn *et al.*, 1991; Nairn *et al.*, 1992; Hedin and Watzlaf, 1994; Skousen, 1991; Skousen and Faulker, 1992; Watzlaf *et al.*, 1992) or a combination of these (Brodie *et al.*, 1992a; Brodie *et al.*, 1992b) the performance and type of abatement of the mitigation and abatement to be pursued is highly dependent on site specific conditions.

Environmental impact of AMD and the metal leach such as element concentrations toxic to plants, animals, and human have been widely studied since as early as 1930s (Redfield, 1934; Burrows, 1977; Gough *et al.*, 1979). Similarly Reuther (1981) and Hyman and Watzlaf (1997) shown the impact of sulfur in coal, especially impact of coal mine drainage on the aquatic life. Baker and Schofield (1982) demonstrated aluminum toxicity to fish in acidic waters. Burton and Allan (1986) revealed influence of pH, aluminum, and organic matter on stream invertebrates. Stubbles *et al.* (1996) exhibited the responses of foraminifera to the presence of heavy metal contamination and acid mine drainage. Kimball *et al.*, (1995) exhibited the effects of colloids on metal transport in a river receiving AMD. Sommerfield *et al.* (1994) demonstrated the change in benthic community structure as a result of an instantaneous discharge of waste waters from a tin mine. Sasowsky *et al.* (1995) revealed the impact of acid mine water in karst terrains. Environmental impact of metals derived from mining activities was widely studied by many scientists (Bain *et al.*, 1995; Drake *et al.*, 1995; Elberling and Langdahl, 1998; Salomons, 1995).

Mainly from a point of view of assessing cost of reclamation, Östensson (1991) Camm (1995) and Bird (1994) studied the significantly high economic cost of impact caused by AMD. However the economic damage caused by AMD is estimated to be a lot higher especially in North America as explained in the previous section.

Effect of AMD and metal leach over groundwater and water quality have also been studied widely (Barnes *et al.*, 1964; Barnes *et al.*, 1969; Buchanan and Somers *et al.*, 1969; Langmuir and Whittemore, 1971; Smith *et al.*, 1974; Whittemore *et al.*, 1975; Smith *et al.*, 1975; Gardner, 1982; Helsel, 1983; Koch, 1983; Bencala *et al.*, 1987; Bencala and McKnight, 1987; Bencala *et al.*, 1990; Clark, 1994). Blowes and Jambor (1990) studied the pore-water geochemistry and mineralogy of the capillary fringe above the water table of the mine tailings impoundment of the Waite Amulet. Similarly, Brady *et al.* (1992) has shown implications of carbonate weathering on hydrogeology, coal overburden chemistry, and groundwater quality. Cravotta *et al.* (1994) revealed the effects of selective handling of pyritic, acid-forming materials on the chemistry of pore gas and ground water at a reclaimed open pit coal mine. Brady *et al.* (1994) made an evaluation of acid-base accounting to predict the quality of drainage at surface coal mines in Pennsylvania. Potential metal contaminations, contaminant transport in AMD affected waters, water quality indicators, and other water and groundwater quality issues related to AMD were well studied and is a widely growing scientific interest area related to AMD (Karathanasis *et al.*, 1988; Kimball *et al.*, 1994; Hoffman and Wetzel, 1995; Brady *et al.*, 1997; Haefner and Rowe, 1997; Powell and Larson, 1985; Williams and Pattison, 1987; Brady and Hornberger, 1989; Williams *et al.*, 1992; Schueck *et al.*, 1996; Wood, 1996).

Modeling of AMD has also widely studied since late '70s (Plummer *et al.*, 1976; Nordstrom *et al.*, 1979; Velleman and Hoaglin, 1981; Hem and Lind, 1983; Ball *et al.*, 1987). Parkhurst, *et al.*, (1982) developed a computer program (BALANCE) for calculating mass transfer for geochemical reactions in ground water. Modular 3-D finite difference groundwater flow models were also utilized to analyze the impact of AMD (McDonald and Harbaugh, 1988). Hawkins and Aljoe (1990) demonstrated hydrologic characterization and modeling of a heterogeneous acid-producing coal mine spoil. In addition there are studies for the modeling of leachate quality from acid generating waste rock dumps (Broughton and Robertson, 1991; Cathles, 1994; Elberling *et al.*, 1994; Bigham *et al.*, 1996). Plummer *et al.* (1991) developed an interactive code (NETPATH) for modeling net geochemical reactions along a flow path. Guo (1993) applied a numerical simulation of coupled heat transfer and gas flow in porous media models to AMD. White III *et al.* (1994) revealed a chemical predictive model for acid mine drainage from waste rock and compared the modeled

output to experimental data. Lin (1996) studied modeling of AMD itself, and Lin *et al.* (1997) developed this model into a three-dimensional, three-phase geochemical kinetic model for AMD. Smith *et al.* (1998) developed a predictive double-layer modeling of metal sorption in mine-drainage systems. Runkel, *et al.* (1999) developed a surface complexation model approach for trace metal sorption to predict reactive solute transport in streams.

Chemical aspects of acid mine drainage (Barnes and Romberger, 1968; Peters and Bonelli, 1982; Blevins and Chafin, 1988; McKnight and Bencala, 1990; Alpers *et al.*, 1994) and geochemistry of coal-mine drainage or acid mine drainage were extensively studied (Alpers and Nordstrom, 1991; Cravotta, 1991; Cameron and Zentilli, 1997; Feetham *et al.*, 1997; Foos, 1997; Elberling *et al.*, 2001; Nordstrom and Ball, 1986; Nordstrom and Alpers, 1990; Sasowsky and White, 1993; Logsdon and Mudder, 1995; Falck, 1995; Plumlee *et al.*, 1995; Sterner *et al.*, 1998; Nordstrom and Alpers, 1998; Rose and Cravotta, 1998). Nordstrom, *et al.* (1979) studied redox equilibriums of iron in acid mine waters. Miller (1980) revealed the sulfur and hydrogen ion buffering in pyritic strip mine spoils. Nordstrom (1982) demonstrated the effect of sulfate on aluminum concentrations in natural waters. Taylor *et al.* (1984) in an experimental pyrite oxidation study demonstrated the stable isotope geochemistry of acid mine drainage. Similarly as an evidence for oxidation mechanisms, Taylor *et al.* (1984) revealed oxygen and sulfur isotope compositions of sulfate in acid mine drainage. Karathanasis *et al.* (1988) demonstrated aluminum and iron equilibriums in soil solutions and surface waters of acid mine watersheds. Fry *et al.* (1988) studied sulfur isotope effects associated with oxidation of sulfide by oxygen in aqueous solutions. Fritz *et al.* (1989) exhibited oxygen isotope exchange between sulphate and water during bacterial reduction of sulphate. Moses and Herman (1991) revealed pyrite oxidation at circumneutral pH. Cravotta (1994) demonstrated secondary iron-sulfate minerals as sources of sulfate and acidity as a result of a geochemical evolution of acidic ground water at a reclaimed surface coal mine. Ali and Dzombak (1996) has shown the interactions of copper, organic acids, and sulfate in goethite suspensions. Casiot *et al.* (2005) in their study on a stream impacted by AMD revealed the sorption redox potentials that are involved in the mobilization of arsenic and indicated that the arsenic concentration is highly related with the air temperature and heat waves. They have

revealed that arsenic was transported conservatively in the aqueous phase away from the confluence in the relatively colder months; therefore, dilution by unpolluted tributaries was the only route that decreased arsenic concentrations. They also showed that, As(III) is quickly oxidized and As(V) remained in the solution. On the contrary, during the warm months, desorption from arsenic-rich sediment takes place which leads in an increase of As(V) and As(III) concentrations along Amous river flow until they attain levels up to ~20 Ag/L each. Consequently, Casiot *et al.* (2005) concluded that Amous River appears not to be totally improved from mine-related arsenic pollution after 3.5 km and has the potential to affect further downstream freshwater resources such as the drainage basin of the Rhône river (Southern France).

Means of AMD production, pyrite oxidation, controls on ochre chemistry and precipitations from coal and metal mines were studied since '80s (Harvey and Dollhopf, 1986; Brown and Jurinak, 1989; Deissmann *et al.*, 1995; Bowell *et al.*, 1996; Broshears *et al.*, 1996). Lefebvre *et al.* (2001) demonstrated the importance of oxygen supply mechanisms to the rate of pyrite oxydation. Especially the involvement of bacteria and the acceleration of pyrite oxidation and the increased rate of AMD formation due to acidophilic bacteria is very well explained by Kuyucak (2002).

Factors affecting AMD formation and severity of AMD have been studied mostly in vitro laboratory studies, since '60s (Caruccio, 1967; Caruccio and Parizek, 1968; Smith *et al.* 1968; Williams *et al.*, 1982; Morrison, 1988; Bayless and Olyphant, 1993; Bayless and Olyphant, 1993; Elberling, 2001). In a bioreactor simulating acid mine drainage, Bayless and Olyphant (1993) studied the influence of pH on mineral speciation. Wels *et al.*, 1996 revealed the influence of specific surface area.

Characterization of AMD that is caused by coal, uranium and metal mine wastes was also widely studied (Lawrence *et al.*, 1982; Hawkins, 1984; Sturm *et al.*, 1984; Growitz *et al.*, 1985; Wetzel and Hoffman, 1989; Hawkins and Aljoe, 1991; Anonymous, 1994; Pendleton *et al.*, 1995; Soregaroli and Lawrence, 1997; Soregaroli and Lawrence, 1998). Phelps (1983) tried to characterize the mine spoil properties as a tool for pre-mining planning. As also mentioned by Smith (1995) Struhsacker (1995) and Robertson (1996) for the effective environmental planning,

project design and proper remediation of AMD, the role of geo-statistical characterization is very important. Henke (1985) contributed with a hydrogeologic characterization of a surface mining-impacted watershed in order to provide implications for acid mine drainage abatement.

Determination of AMD potential was studied at pre-mining stages and for abandoned mines especially in North America (Bruynesteyn and Duncan, 1979; Bruynesteyn, and Hackel, 1984; diPretoro, 1986; diPretoro, and Rauch, 1987; Diodato and Parizek, 1988; Kleinmann, 1989; Brodie *et al.*, 1991). Use of static tests or Acid Base Accounting as a determination technique for AMD potential was used since late '80s (diPretoro and Rauch, 1988; Bradham and Caruccio, 1990; Brady *et al.*, 1992; White *et al.*, 1997).

Sobek *et al.* (1978) developed a step-by step laboratory protocol for performing Acid Base accounting (ABA) for the prediction of AMD potential. However, earlier publications described the application of ABA principals to mine overburden testing (West Virginia University, 1971; Grube *et al.*, 1973; Smith *et al.*, 1974; Smith *et al.*, 1976). There were many studies to evaluate the prediction methods of AMD (Rose *et al.*, 1983; Wang, 1983; Erickson *et al.*, 1985; Renton *et al.*, 1985; Ott, 1986; Ferguson and Erickson, 1988; Lapakko, 1988; Brady *et al.*, 1988; Ott, 1988; Lawrence *et al.*, 1989a,b,c; Coastech Research Inc., 1989; Smith *et al.*, 1989; Lawrence, 1990a; 1990b; 1990c; 1990d; Morrison *et al.*, 1990b; Morrison *et al.*, 1990; O'Shay *et al.*, 1990; Smith *et al.*, 1991; Lawrence *et al.*, 1994; USEPA, 1994b; Lawrence, 1994; Lawrence, 1995; Edwards and Lawrence, 1995; Robertson and Ferguson, 1995; Lawrence and Wang 1996). Cagnetta and Jencks (1990) published an evaluation of lime requirement tests on pyritic mine soils. Elberling and Nicholson (1996) developed field measurement methods for oxygen diffusion and sulphide oxidation in mine tailings and micro-scale measurements of oxygen diffusion and consumption in sub aqueous sulfide tailings (Elberling and Damgaard, 2001). Skousen (1987) and Skousen *et al.* (1997) revealed the subjectivity of fizz-tests in a review of static techniques. Thus they suggested use of hydrogen peroxide for siderite correction. A technical guideline to predict AMD was published by Steffen, Robertson and Kirsten (B.C.) Inc., in 1989 and revised in 1992. Lawrence (1991) and Smith and Brady (1990) revealed the interpretation of AMD data, evaluation of static test or acid base accounting data. Lapakko and Lawrence (1993) later

published a modification to the Net Acid Production (NAP) Test. Lapakko (1994) published an evaluation of neutralization potential determinations for the metal mine waste and proposed an alternative method. Lawrence (1996) and Lawrence and Wang (1997) reviewed the developments in the measurement of neutralization potential of the mine wastes.

Studies related to the kinetics of oxidation of ferrous iron and the formation of AMD date back to late '60s. (Singer and Stumm 1968, 1970; Geidel and Gwendolyn, 1979; Plummer *et al.*, 1979; Lasaga and Kirkpatrick, 1981; Morse, 1983; Lasaga, 1984; Sjöberg and Rickard, 1984a; 1984b; Davies and Morgan 1989; Drever and Swoboda-Colberg, 1989; Bruno *et al.*, 1992a, 1992b; Elberling *et al.*, 1993; Elberling *et al.*, 1994; Ritchie, 1994; Arakaki and Mucci, 1995; Morin *et al.*, 1995; Aschenbach, 1995; Guard, 1997; Holmes and Crundwell, 2000). Banaszak (1981) revealed predicting changes in the mineralogy of mine spoil as a function of net neutralization potential and rate of flushing. Breen (1982) proposed control of Eh and pH to evaluate the rate of pyrite oxidation. Sjöberg and Rickard (1983) emphasized the significant influence of experimental design on the rate of calcite dissolution. Dresel (1989) in a laboratory study revealed the dissolution kinetics of siderite and its effect on acid mine drainage. Ahonen and Tuovinen (1994) used the column bioleaching to reveal solid phase alteration and iron transformation of a complex sulfide ore. Ziemkiewicz and Meek (1994) published long-term behaviors of acid forming rock: results of 11-year field studies.

Weber *et al.* (2004) in a project for acid mine drainage predictive test work allied with the Australian Mineral Industries Research Association (AMIRA), critically revised the static acid evaluation and the kinetic information from acid–base accounting techniques, including net acid production potential (NAPP) net acid generation (NAG) and column leach tests. In their study they provided comparison of results on two waste rock samples that contained significant amounts of fine-grained framboidal pyrite. In addition, similar research, results obtained by Weber *et al.* (2004) indicated that framboidal pyrite is more reactive than euhedral forms due to the greater specific surface area of framboidal pyrite. Weber *et al.* (2004) indicated that this was evidenced by optical microscopy of the reacted samples. In addition, they obtained results revealing that NAPP testing was influenced by the rapid acid generating oxidation of framboidal pyrite preceding, and throughout the

acid neutralization capacity test. Weber et al. (2004) pointed out that this could result in negative acid neutralization capacity values for the samples containing significant framboidal pyrite (usually “fixed” to zero kg H<sub>2</sub>SO<sub>4</sub>/t) when significant acid neutralization capacity is essentially available in the sample. Weber et al. (2004) also revealed that NAG testing that utilizes H<sub>2</sub>O<sub>2</sub> exhibited that samples containing a significant quantity of framboidal pyrite can result in the catalytic decomposition of the H<sub>2</sub>O<sub>2</sub> before total oxidation of the available sulfide minerals, necessitating sequential adding up of H<sub>2</sub>O<sub>2</sub> for completion. Weber et al. (2004) reminds the positive aspect of the NAG test, as it helps us evaluate the net acid generation capacity of the sample without prejudice towards acid generation as is observed using NAPP methods and adds that the kinetic NAG test also provides data on the reaction sequence of framboidal and euhedral pyrite. Weber et al. (2004) also performed kinetic analysis of sub-samples from column leach tests and revealed quick oxidation of the framboidal pyrite compared to the euhedral pyrite, as expected and correlated with the greater framboidal pyrite surface area.

In order to mitigate or reclaim AMD, management of the mine wastes is essential (Geidel *et al.*, 1984; Anonymous, 1991; Cravotta *et al.*, 1994; Lawrence, 1996; St-Arnaud, 1996; Environment Australia, 1997; Wels *et al.*, 1998). Waybrant et al. (1997) proposed a prevention technique for acid mine drainage using *in-situ* porous reactive walls. Integration of these techniques together with waste organization techniques is effective in management of the problem. Environmental management of mine wastes is not only important for new mine developments but also for abundant mines or closed mines (Anderson, 1994; USEPA, 1994a; Fytas and Hadjigeorgiou, 1995; Durkin and Herrmann, 1996; DOIT, 1996; USEPA, 1996).

Weber et al. (2005) in a study questioning the fly ash/biosludge cover for the mitigation of AMD in a closed Swedish mine, revealed that the high organic carbon concentrations detected in the leachate indicate a dissolved organic material from the cover of the mine wastes. They indicate that the pyrite oxidation rate appears to be slowed down, however they also pointed out the ambiguity that the mitigation measure may bring about if the biosludge component of the abatement system decomposes in time (Weber *et al.*, 2005).

Zagury et al. (2006) has showed that the effectiveness of the sulphate-reducing bacteria in acid mine drainage treatment process depends on the organic substrate preferred to provide the bacteria's carbon source, and demonstrated that the mixture of organic materials was most effective in encouraging sulphate reduction, with a metal deduction efficiency in batch reactors that are as high as 100% for Fe, 99% for Mn, 99% for Cd, 99% for Ni, and 94% for Zn depending on reactive mixtures.

There are many case studies that cover one or more issues explained above (Barnes, *et al.*, 1964; Brown and Parizek, 1971; Caruccio and Geidel, 1981; Hornberger, *et al.*, 1990, Cravotta, 1992; Kirkham *et al.*, 1995; Durkin, 1996; Miller and Hertel, 1997). Some of these case studies involved in critical assessment of AMD and tailings management practices by international mining companies (Mills, 1996). Elberling *et al.* (2001) in a relatively recent case study investigated the potential prevention of AMD regarding the reactivity of covered sulfidic waste near Maarmorilik in West Greenland due to cold surface temperatures. In another one Elberling *et al.* (2001) revealed the geochemical trends in metal-contaminated fiord sediments near a former lead-zinc mine in West Greenland.

## **1.5 Purpose and Scope**

As explained in section 1.3 AMD studies are wide spread in North America but are restricted to EIA studies related to gold mine developments in Turkey. Although there are many aspects of the problem, academically, prediction of AMD is not widely studied in Turkey.

From this point of view and taking into account the conditions present in Turkey, the purpose of this PhD thesis is to practice the static acid mine drainage tests on a newly developing poly-metallic mine relying on the globally preferred techniques as a valuable tool for AMD prediction and evaluation. Based on this case, It is also aimed to discuss the problems encountered and that may be encountered during the prediction of AMD.

The materials used in this thesis are obtained within the Environmental Baseline Study conducted by Ekobil Environmental Services and Consulting Ltd. in Çukurdere Madencilik Sanayi ve Ticaret Ltd.'s<sup>4</sup> Erzincan-Çöpler Gold Mine Prospect, under the operational License of IR-477. This study involves evaluation of geological data, geochemistry, mineralogy, and acid-base accounting (static tests) data. Both Kinetic studies related to the question of when or how a site will produce acid mine drainage and the heavy metal mobilization related to AMD are out of the scope of this study. The management and abatement stages of AMD are also excluded

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<sup>4</sup> To simplify will be referred to as the Çukurdere Ltd. or as the Company from this point forward.

## CHAPTER 2

### THE STUDY AREA

#### 2.1 Location and Geographical Characteristics

The study area is located at 120 km Southwest of Erzincan Province, approximately 650 km East of Ankara in eastern Anatolia geographical district of Turkey.

Relative to major settlements, it is situated at 35 km Northeast of Kemaliye (Erzincan), and about 7.5 km Southwest of İliç (Erzincan), on the Divriği-İliç motorway (Figure 2.1). Study area lies in the 1/25.000 scaled İ41-d4 sheet of Turkey between 57700-60900 Northing and 62750-65350 Easting gridlines. The known ore mineralization appears in the vicinity of Çöpler Village along the contacts between the limestone and plutonic rocks, and within the altered plutonic rocks.

The nearest town, 7,5 km away from the study area, is İliç with an approximate population of 2,700 people. The other considerable settlement in the area, Kemaliye, is approximately 40 km to the south of study area, with an approximate population of 3,000 people.

The study area is reached via a 4,5 km graded road after leaving the main Erzincan-Kemaliye tarred road from the junction, three kilometers South of İliç.

The main railway passes within 2 kilometers of Çöpler Village and runs parallel to the main road between İliç and Bağıştaş towns, along the bank of the Karasu River.

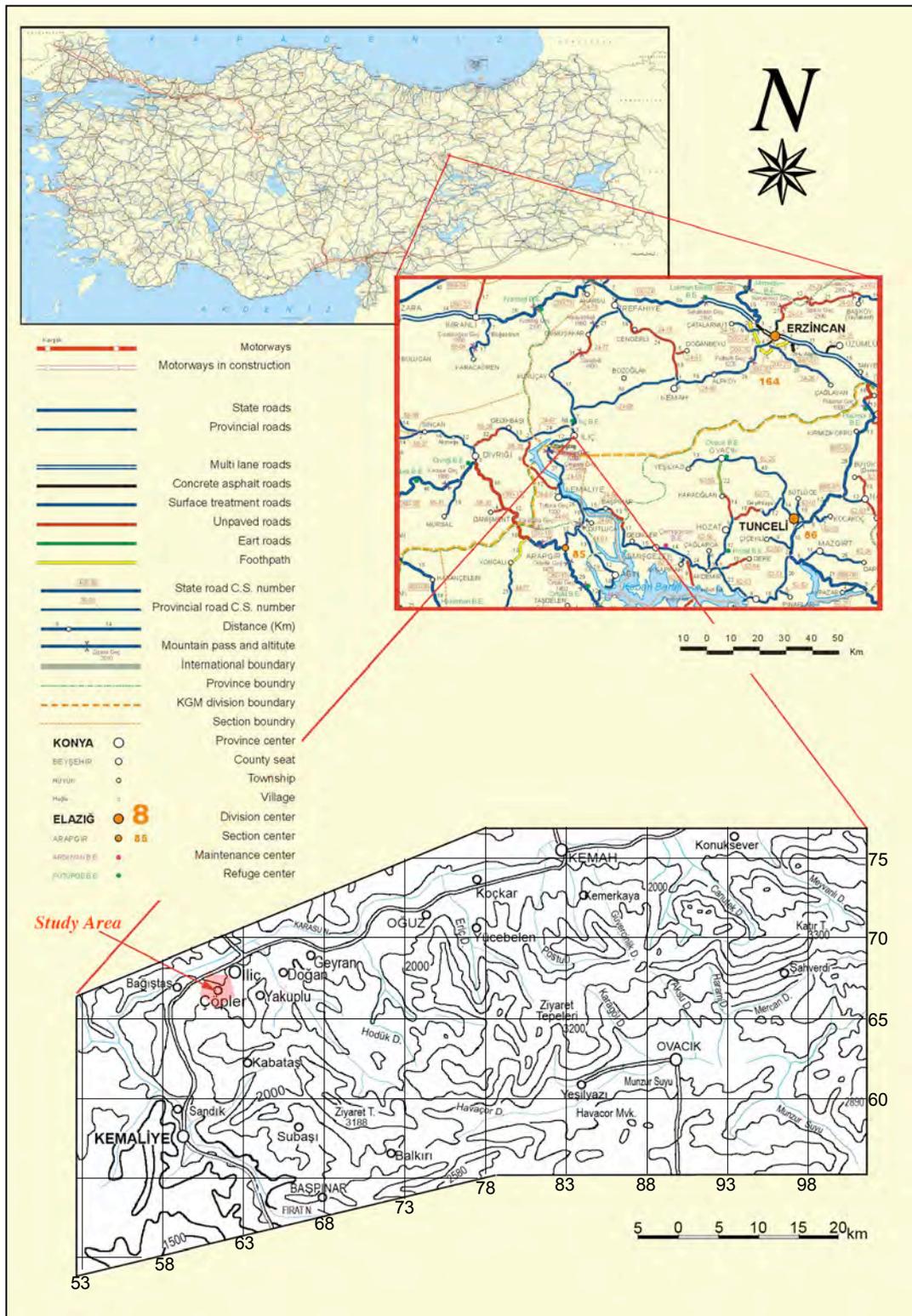


Figure 2.1 Location Map of the Study Area

## 2.2. Climatic Characteristics of the Study Area

At the study area the summers are dry and warm; the winters are relatively wetter and colder. Based on Koeppen classification the climate is considered to be a " Mid-latitude steppe, semiarid, cool or cold climate" - evaporation exceeds precipitation on average precipitation; and is more than half but less than potential evaporation; usually mid-latitude, with steppe/grassland/bush grasses (Figure 2.2). Mean average temp is below 18°C.

The climate in the study area is milder due to the Karasu River that borders the study area from its North. The climate in the study area is a transition between Central Anatolian type climate and Eastern Anatolian type climate. The climate exhibits local differences based on topographical changes (Erzincan Valliği , 2003) (Figure 2.2).

Based on meteorological records from 1935 to 1999, annual average temperature of the region is 10.6°C, the average temperature at the coldest month, which is January, is -3.7°C, the average temperature at the warmest month, which is August, is 23.9°C. Based on this long-term data the maximum and the minimum temperatures recorded were 40.5°C and -36.6°C, respectively. The average number of summer days is recorded to be 115 days (Between April and October). During winter, there occur very cold days due to the Siberia originated air masses. The average number of winter days is 30. Freezing, in general starts in November and can extent up to April. The average number of snowing days is 30, and the average number of days with snow cover is recorded to be 42 days. In general snowing starts towards the end of November and extends up to April (Erzincan Valliği ,2003).



Figure 2.2 A view from the study area and the Çöpler Village, looking towards Northwest.

Based on meteorological records from 1935 to 1999, the average precipitation in the region was recorded to be 366.6 mm. The maximum precipitation was recorded to be 630 mm and minimum was recorded to be 210 mm. The season with highest precipitation is spring when the 41% of the annual precipitation falls. About 22% of the annual precipitation falls during autumn, 15 % during summer and 22% during winter times. The second half of June, July, August and September are the arid months when almost no precipitation is recorded. In general the highest precipitation is recorded in April and the lowest in August. The average annual humidity for the region is recorded as 60% based on long run records (Erzincan Valiliği, 2003).

## 2.3 Geology of the Study Area

### 2.3.1 Previous Studies

The study area is located to the west of the Munzur Mountain Range. The geological studies along the Munzur Mountains are known to date back to 1940's. Ketin (1945), Baykal (1953), Nebert (1959) and Kurtman (1961) studied the geology of several parts of the Munzur Mountain Ranges. In addition to that, especially the North Western parts of the Munzur Mountain range, and the vicinity of the İliç town were studied by Aytuğ (1964), Aslan (1971), Kurt (1971), Durgun, (1972) and Maviş, (1977) for the iron ore mineralization. These local studies were useful in revealing the geological properties of the study area.

The most extensive unit in the region is the Mesozoic carbonates (Munzur Limestone). Previous studies related to these carbonates are limited to discussions on the age based on the fossil content. Ketin (1945), based on *Orbitolina conoidea* and *Orbitolina trochus* collected from the flanks of Ziyaret Tepe, assigns Lower Cretaceous age to these limestones. Ketin (1945) suggests the possibility that other levels of lower Cretaceous may be present, however, he does not support this argument with fossil data. Baykal (1953) states that the *Orbitolina conoidea* Grass bearing levels that he found on the Northern parts of Munzur Mountains are the lowest level of Munzur Limestone. Nebert (1959) on the other hand, considers a well bedded, gray colored *Havrania* bearing Upper Triassic limestone he observed overlying the serpentines in the northern parts of Munzur Mountain as the lowest part of the limestone that he calls "Munzur Unit". He further considers that the reefal limestones, which he suggests to consist of the main part of the unit, is of Cenomanian-Turonian age due to the *Trocholina* content of these rocks. Nebert (1959) suggests an Upper Jurassic age for the limestone that is situated in between these two units. Kurtman (1961) points out the presence of *Valvulinella Jurassica* Henson, as the evidence of Jurassic on the northern and southeastern flanks of the mountainous areas, and proposes Upper Cretaceous age based on the *Orbitolina* sp. content of the lithologies on the summit of the Munzur Mountains.

Özgül *et al.*, (1981) studied an extensive area that also includes the immediate study area. On the southern parts of the study area there are metamorphic rocks, which are not much studied previously. Nebert (1959) named these metamorphic rocks as “Başvartirik Unit” and defined goniatite in these rocks. In addition to that, based on the Fusulinides found in the limestone blocks intercalated that he considers to belong to the same metamorphic lithologies, he assigns Permo-Carboniferous age for these metamorphic units. Özgül (1981), however, considers these blocks to be part of an ophiolitic mélangé.

The previous studies about this ophiolitic mélangé contradict with each other. Ketin (1959) suggests that the diorite serpentine intrusion intersects the Lower Cretaceous carbonates and is overlain by the Eocene basal conglomerate, on the northeastern part of Ovacık Town. Nebert (1959) argues that the serpentines are emplaced under the Munzur Unit and thus he proposes that these lithologies are younger than Upper Triassic. Also he tries to define a relationship between these units and the middle Triassic Alpine lithologies that were initially igneous rocks. Kurtman (1961), suggest that serpentinites have silicified the limestones and therefore they are extrusive.

Transgressive Eocene units including volcanics in the north cover Munzur limestones, metamorphics and ophiolites. In addition to that presence of a second transgression in Burdigalian was indicated by all the previous studies. Nebert (1955) mentions presence of Oligocene without relying on fossil data. To the east of Ovacık-Tunceli, Ketin (1945) and Kurtman (1961) states that the Miocene rocks were cut by volcanics therefore, they point out volcanic activity in the Upper Miocene.

Nebert (1955, 1959), based on his regional investigations, suggests the presence of two different tectonic units namely “Munzur Unit” and the “Başvartirik Unit”. He also suggests the post-Eocene displacement of Munzur unit over the other tectonic units. Özgül (1981) finds this argument reasonable.

### **2.3.2 Regional Geology**

The study is located on the western end of the Munzur mountain range. This mountain range lies on the northeastern edge of the junction of Tauride orogenic

belt and the North Anatolian fault zone. Therefore study area displays some peculiarities of the fault zones.

The eastern end of the Tertiary basins that are observed between Central Anatolian and Tauride belts borders Munzur Mountains. These Tertiary basins exhibit serious volcanic activity. The Munzur Mountain range is connected on its south to the Keban–Tunceli region and probably to Pötürge-Bitlis Metamorphic zone through the Tertiary covering rocks. Therefore the study area lies in a region where three big regions of Anatolia, with totally different geological stories, have complex relations. These are namely Eastern Anatolia, Central Anatolia and Taurides (Poyraz, 2005).

Due to the complex tectono-stratigraphic features of the region, Özgül *et al.*, (1981) described each rock group within its time range instead of trying to describe each issue in a sequential geological time span. In their study they differentiated three tectonic lithologic groups and a group of post-tectonic rocks (Table 2.1).

The distributions of these groups are shown in Figure 2.3.

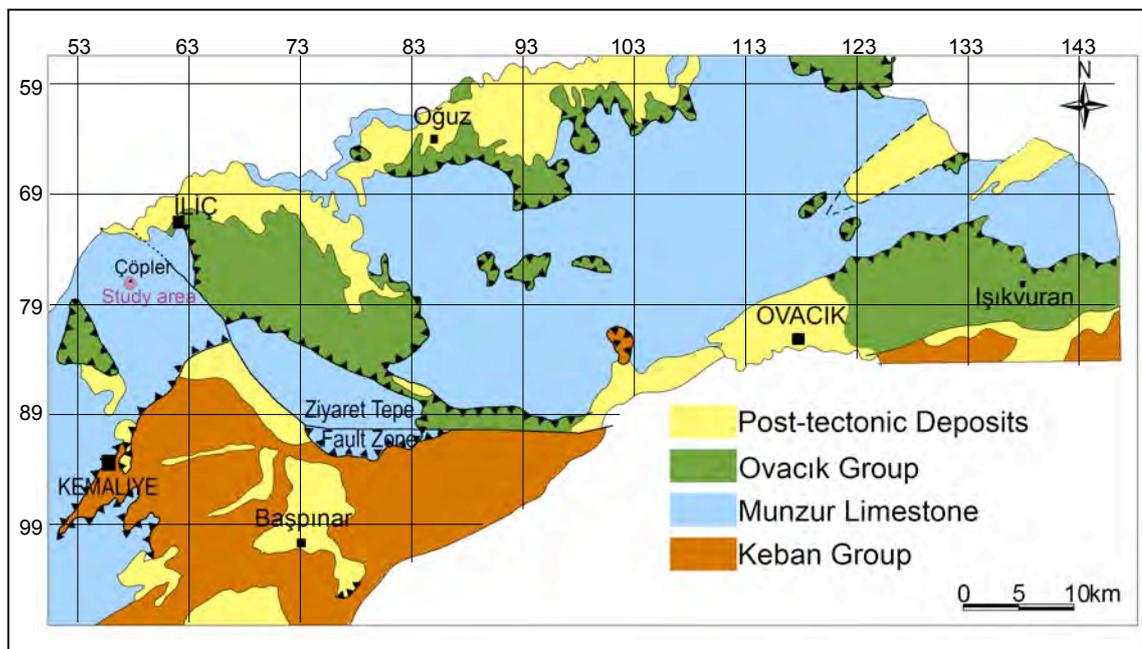


Figure 2.3 Distribution of the major tectonic units (After Özgül *et al.*, 1981)

### 2.3.3 Stratigraphy

Munzur Mountain range comprises Paleozoic and Mesozoic metamorphic units, thick neritic carbonates that represent most of the Mesozoic, Cenonian olistostromes and ophiolitic mélangé, Upper Cenonian and Tertiary transgressive sediments and Tertiary volcanics. The oldest unit determined based on its fossil content is Permian aged and the youngest is Miocene aged (Özgül *et al.*, 1981).

Özgül *et al.*, (1981) classifies Pre-Tertiary lithologies that exhibit post-tectonic properties, into three major tectonic groups due to their different stratigraphic, metamorphic and structural features that exhibit three different environmental settings. Each of these units has tectonic contact with each other and has their own tectonic and stratigraphic characteristics. In general, these types of units are also found in different parts of Taurides, and these laterally displaced units are generally called "lithologic groups". Özgül *et al.*, (1981) used the same terminology together with the geographical names where these groups were defined. Namely "Keban Group", "Munzur Limestone" and "Ovacık Group" reflects different environmental settings and Özgül *et al.*, (1981) explain these three tectonic groups not in a continuous age sequence but defines their stratigraphical attributes within each group. All the rock stratigraphic units defined in Munzur Mountain Range are summarized in Table 2.1, and their characteristics and positions in the study area are given starting from the Keban Group, and following the reverse order presented in Table 2.1.

Table.2.1 Major stratigraphic units observed in the Munzur Mountains (After Özgül *et al.*, 1981).

NAME OF THE UNIT	FORMATION	MEMBER	AGE	
POST-TECTONIC DEPOSITS	<u>Cover Sediments</u>		<u>Quaternary</u>	
	<u>Kemah Formation</u>		Burdigalian	
	<u>Başpınar Formation</u>			
	<u>Dedek Formation</u>	<u>Koçkar Volcanics</u>	Upper Lutetian	
		<u>Doluğun Member</u>		
	<u>Hopik Formation</u>		Lutetian	
<u>Subaşı Formation</u>		Upper lilerdian-Cuisian		
OVACIK GROUP	Arıkaya Limestone		Maastrichtian+ Paleocene	
				Çolaklar Formation
	Eriç Ophiolitic Melange	Neritic Limestone Blocks	Triassic, Jurassi, Cretaceous	Senonian (Age of Settlement)
		Pelagic Blocks	Upper Triassic	
		Yücebelen Member	Permian	
<u>Ulyamaç Ophiolitic Member</u>				
MUNZUR LIMESTONE	<u>Munzur Limestone</u>	Ayıkayası Limestone Member	Turonian-Campanian	
		Kabataş Limestone Member	Senomanian	
		Ziyaretbaşı Limestone Member	Aptian-Albian	
		Salihli Limestone Member	Upper Dogger-Malm	
		İnin Deresi Limestone Member	Lower Dogger	
		Kurudere Limestone Member	Liassic-Upper Triassic	
KEBAN GROUP	Gözerek Formation		Maastrichtian	
			Senonian	
	Balkırı Group	Kale Tepe Limestone		Liassic-Upper Cretaceous
		Alıçlı Formation		Lower Triassic
		Çay Dere Limestone		Permian
		Yoncayolu Formation		Permian or pre-Permian

Detailed information about the above listed units can be found in Özgül *et al.*, (1981). In this study only the units that are observed in the immediate study area will be defined in detail. These units are indicated as underlined in Table 2.1 and their distribution is given in Figure 2.4.

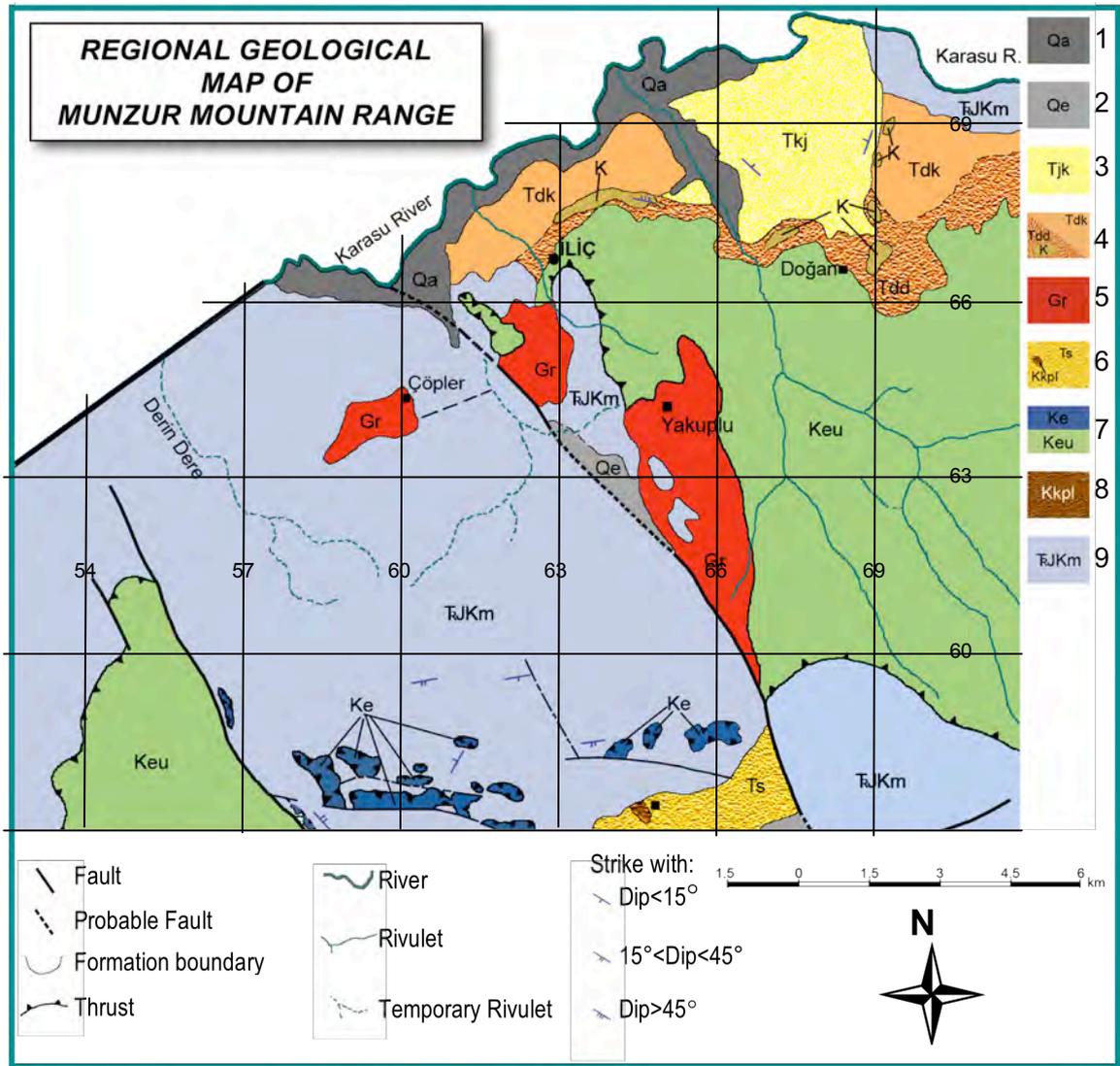


Figure 2.4 Map illustrating the regional geology in the vicinity of the study area (1:Quaternary alluvium, 2:Quaternary talus, 3:Kemah Formation-Tdk: Koçkar volcanics member, Tdd: Dolugün Member, 5:Granite-Granodiorite intrusion, 6: Subaşı Formation, 7: Eriç ophiolitic mélangé-Ke: Undifferentiated, Keu: Uluayamaç member, 8: Pelagic Blocks of Kemaliye Formation, 9: Munzur Limestone) (After Özgül *et al.*, 1981).

### 2.3.3.1 Keban Group – Kemaliye Formation.

Keban Group is described to include Paleozoic and Mesozoic metamorphic rocks derived from shelf type, clastic and carbonaceous lithologies (Özgül *et al.*, 1981). The members of the Keban Group crops out on the southern sections of the Munzur Mountain range between Kemaliye and Ovacık towns, and further south around Keban, Arapgir towns and in vicinity of Tunceli, covering extensive areas. The group is named after Keban town (Özgül *et al.*, 1981). From oldest to youngest, the Keban Group is made up of Balkırı Group (Yoncayolu Formation, Çay Deresi Limestone, Alıçlı Formation, Kale Tepesi Limestone), Kemaliye Formation and Gözerek Formation (Özgül *et al.*, 1981). In the study area Keban Group is only represented by Kemaliye Formation.

Kemaliye Formation is made up of clastic rocks of different ages, sedimentary blocks of different type and size and ophiolitic blocks of olistostromal facies. Kemaliye formation is named after Kemaliye town where it was defined. Kemaliye Formation exhibits olistostromal properties. Sedimentary rocks of different size, type and age and ophiolitic blocks are found in a matrix of clay, sand and gravel. In general the bedding is not easily differentiated and matrix to rock block ratio differs from place to place. Bedding becomes more perceptible in places where matrix ratio is higher than the block ratio (Özgül *et al.*, 1981).

Özgül *et al.* (1981), explain the blocks to be originated from all the three tectonic units that are observed in the region namely: Keban Group, Munzur Limestone and Eriç Ophiolitic Mélange. In addition to that there are also totally exotic blocks such as the Permian micro-fauna rich, non-metamorphosed limestone blocks. The sizes of these blocks differ extremely. The relatively smaller blocks have rounded corners whereas larger blocks have angular and faulted edges. Özgül *et al.*, (1981) differentiates six commonly encountered blocks-olistoliths within the Kemaliye Formation: Dolomitic limestone blocks, metamorphic blocks, non-metamorphosed Permian limestone blocks, Doğankaya limestone blocks, pelagic blocks and ophiolitic blocks.

Özgül *et al.*, (1981) admits that there is no evidence to assign a direct age for Kemaliye Formation. Therefore, based on observations about the age of the blocks

present in Kemaliye Formation and based on the evidences (i.e. transgressional and contact relations) between the Kemaliye and Balkırı Formations they suggest that this formation is of Upper Campanian and Lower Maastrichtian age. In the rock table for stratigraphic relationships (Table 2.1) they state Cenonian as the age of Kemaliye Formation.

In the study area Keban Group is represented by the Kemaliye formation's pelagic blocks. Özgül *et al.*, (1981) mapped these blocks within the post-tectonic Subaşı formation on the South of the study area (Figure 2.4).

In the immediate study area it is not possible to trace any member of the Keban Group. However a thick meta-sediment sequence forms the structural base of the Çöpler area and is confined to the western extent of the study area, bound between the Çöpler North and Çöpler South Faults (Figure 2.5).

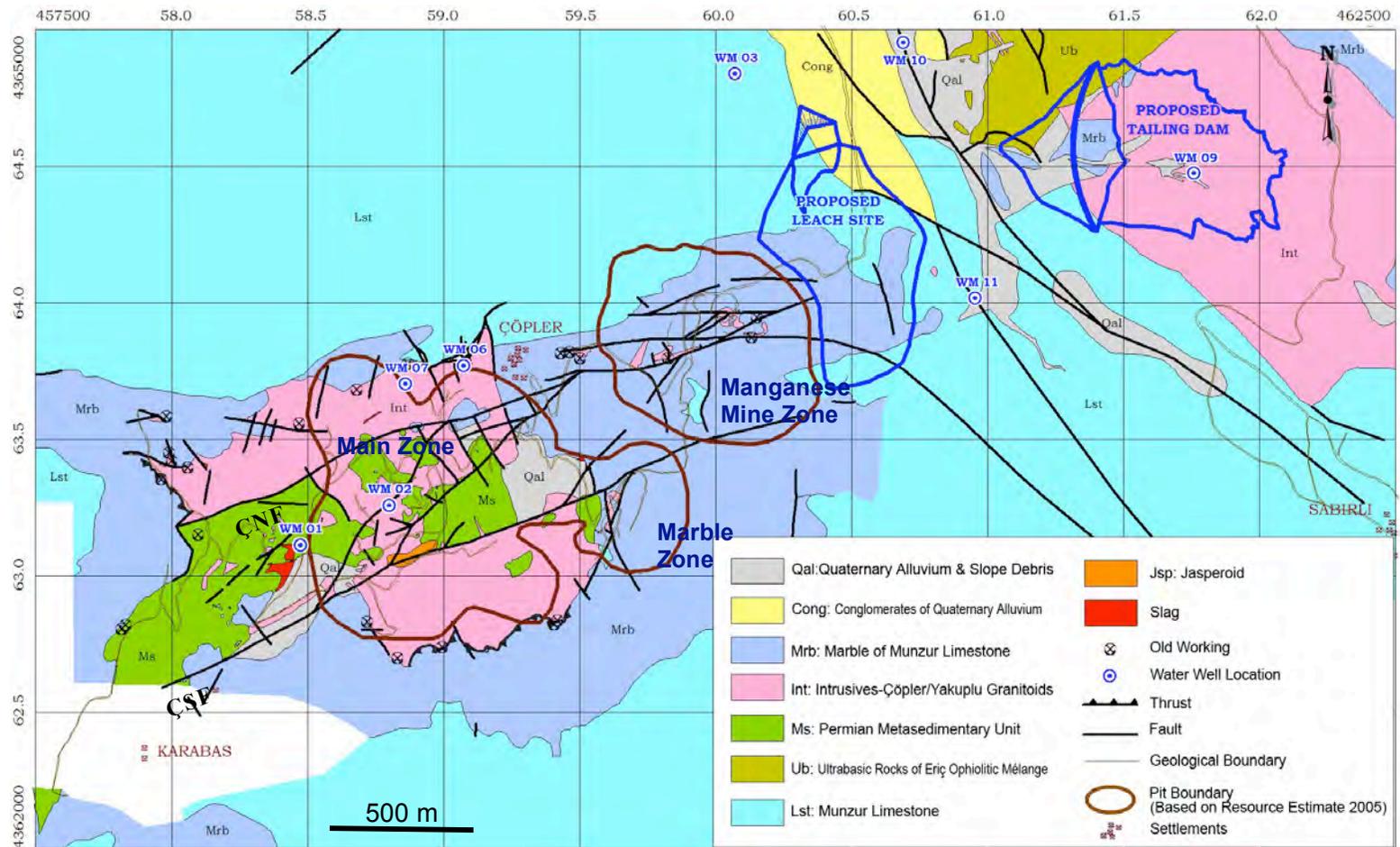


Figure 2.5 Detailed geology of the study area, ÇNF: Çöpler North Fault, ÇSF: Çöpler South Fault (Modified after Poyraz, 2005).

This meta-sedimentary unit is not shown on published geological maps, and it does not appear to be related to the Munzur Formation with which it shows a remarkable contrast in facies. It occurs structurally below the Munzur Formation, with which it has a tectonic contact. Its age is unknown, but it is probably concurrent and often referred to as Permian. The meta-sediments typically display alternating micro- to meso-scale siliciclastic bedding comprising siltstone, pelite and chert. Bedding within the meta-sediment is often indistinct, but where present, graded bedding (including reverse grading) and soft-sediment features such as slump folds and boudinaged chert bands are preserved (Figure 2.6) (Poyraz, 2005).



Figure 2.6 Meta-sedimentary units observed in the study Area. Soft sediment features such as slump folds and boudinaged chert bands are preserved. The unit interpreted to be a turbidite sequence, but not correlated regionally (Easterday, 2004).

Although these meta-sedimentary lithologies were not shown on published geological maps or they were not reported by previous MTA reports, the author suggests that they may be correlated metamorphics of Keban Group. However during the detailed geological exploration studies by Çukurdere geologists, they were not keen to correlate this formation with any Permian aged formations in the region.

### **2.3.3.2 Munzur Limestone**

Munzur Limestone, which is mainly made up of continental shelf type carbonates, is described to be a thick unit that represents majority of the Mesozoic (Upper Triassic to Upper Cretaceous). This unit has its own exclusive tectono-stratigraphic characteristics and is in tectonic relation with the other geologic groups in the region. However since significant changes and disruptions are not observed along the deposition process it was possible to name the entire unit under a single rock stratigraphic unit (Özgül *et al.*, 1981).

Munzur limestone extensively surrounds the southern and western parts of the study area. This formation makes up a significant portion of the Munzur Mountain range. Özgül *et al.*, (1981) describes in detail all the members of Munzur Limestone and provides a generalized stratigraphic columnar section of the Munzur Formation (Figure 2.7).

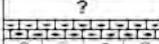
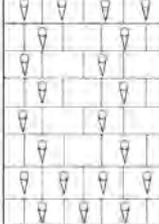
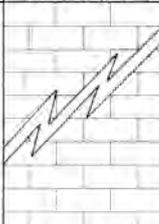
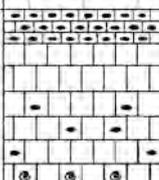
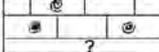
System	Stage	Name of the Member	(m)	Lithology
CRETACEOUS	Turonian-Campanian	AYIKAYASI LIMESTONE	1200	 Biomicrotic, pelagic limestone
	CENOMANIAN	KABATAŞ LIMESTONE	900	 Reefal limestone with rudists
	APTIAN-ALBIAN	ZİYARETTEPE LIMESTONE	520	 Thickly bedded micritic, biomicritic, pel-micritic limestone with gastropoda and lamellibranchia and with minor amount of chert
JURASSIC	MALM	SALIHLI LIMESTONE	350	 Algal Limestone
	BATONIAN		320	
	BAJOCIAN	İNİNDERE LIMESTONE	320	 Oolithic Limestone
	MIDDLE-UPPER	KURUDERE LIMESTONE	100	 Biosparitic type algal limestone with lamellibranchia
TRIA-SSIC	LADINIAN-RAESIAN		?	

Figure 2.7 Generalized stratigraphic columnar section of the Munzur Limestone (Özgül *et al.*, 1981).

The oldest member of Munzur limestone observed in the region is Kurudere Limestone, a bio-sparitic limestone based on Folk Classification. This formation contains algae and neritic organisms such as lamelli branchia. According to the fossil content of the formation its age is determined to be Upper-Triassic (Ladinian-Resian) to Liassic. Kurudere Limestone conformably passes to İnindere Limestone member. İnindere Limestone is a fully oolithic, ash colored thick-layered limestone,

which can be classified as an oospartic limestone. This member of Munzur limestone contains relatively fewer amounts of fossils but based on the available foraminifera its age is determined to be Lower Dogger (Bajocian) (Özgül *et al.*, 1981).

The Salihli Limestone is a gray to ash colored, medium to thick-bedded limestone that bears algae and bryozoa at its lower levels and in some levels it contains chert nodules or intercalations of chert. The fossil content of the Salihli Limestone reveals that the deposition of the unit starts from Upper Dogger and continues up to Upper Jurassic (Özgül *et al.*, 1981).

Ziyaretbaşı Limestone member follows Salihli Limestone conformably. This is a micritic, bio-micritic, pel-micritic laminated limestone with abundant lamelli-branchia and gastropodic micrite and with rare chert nodules. Although the boundary between Salihli Limestone and the Ziyaretbaşı limestone is conformable, the transition between Ziyaretbaşı Limestone and the Kabataş Limestone that overlies this member was not observed (Özgül *et al.*, 1981). Although the fossil content of the Ziyaretbaşı limestone was difficult to identify, Özgül *et al.*, (1981) attributes Lower Cretaceous (Aptian-Albian) age to this limestone based on its limited microfossil content.

The Kabataş Limestone member is made up of dark to light ash colored, thick bedded, reefal carbonates with abundant rudists and large sized orbitolina that makes this unit easily differentiable from the other members of the Munzur Limestone in the field. The Kabataş limestone in general has biocalcaranite characteristics due to the presence of broken shell pieces, micritic pieces, black and white reefal fragments. These fragments are nicely rounded and sorted and the darker organic clasts give the rock a spotted appearance. The rich fossil content of Kabataş Limestone indicates it to be Senomanian in age (Özgül *et al.*, 1981).

The Ayıkayası Limestone, the uppermost Member of the Munzur Limestone, conformably overlies the Kabataş Limestone, which is a pelagic limestone with chert intercalations. The major characteristic lithology of this unit is a pelagic limestone with *Globotruncana sp.* This thinly bedded limestone has a light brownish rusty color with brownish chert intercalations. The pelagic microfossil contents of the Ayıkayası

limestone indicates that it was deposited throughout Turonian-Upper Campanian in a pelagic, low energy environment (Özgül *et al.*, 1981).

In general the Munzur limestone has the highest coverage in the study area and surrounds the southern and western parts of the study area. The Munzur limestone lies unconformably above the meta-sedimentary lithologies observed in the study area and represents the enveloping lithology that defines the Çöpler erosional – geomorphologic window. The contact between the two units is irregular and where observed, indications of tectonic movement are obvious.

In the study area the Munzur limestone is mapped but not differentiated into its members. Instead the carbonaceous lithologies observed in the immediate study area are differentiated into sub-units based on the dominant petrography such as limestone, recrystallized limestone and marble. The marblization and recrystallization observed in the vicinity of Çöpler is attributable to contact metamorphism.

In the study area the Munzur limestone is mapped but its members are not differentiated. Instead, the carbonaceous lithologies observed in the immediate study area are differentiated into sub-units based on the dominant petrography such as limestone, recrystallized limestone and marble. The marbling and recrystallization observed in the vicinity of Çöpler may be due to contact metamorphism.

In the study area, at the vicinity of the mineralization zones, bedding within the Munzur limestone is indistinct and the majority of the unit appears massive. The vast majority of the Munzur limestone within the central Çöpler erosional window is marbleized. The marble does not display a normal affiliation to the underlying meta-sediment or the Çöpler Granitoid. The marble contains medium to coarse sized calcite crystals, and shows no relict bedding. Texturally, it is massive to incipiently brecciated, though the fracturing and breccia texture was healed and predates the recrystallization event (Poyraz, 2005) (Figure 2.8).

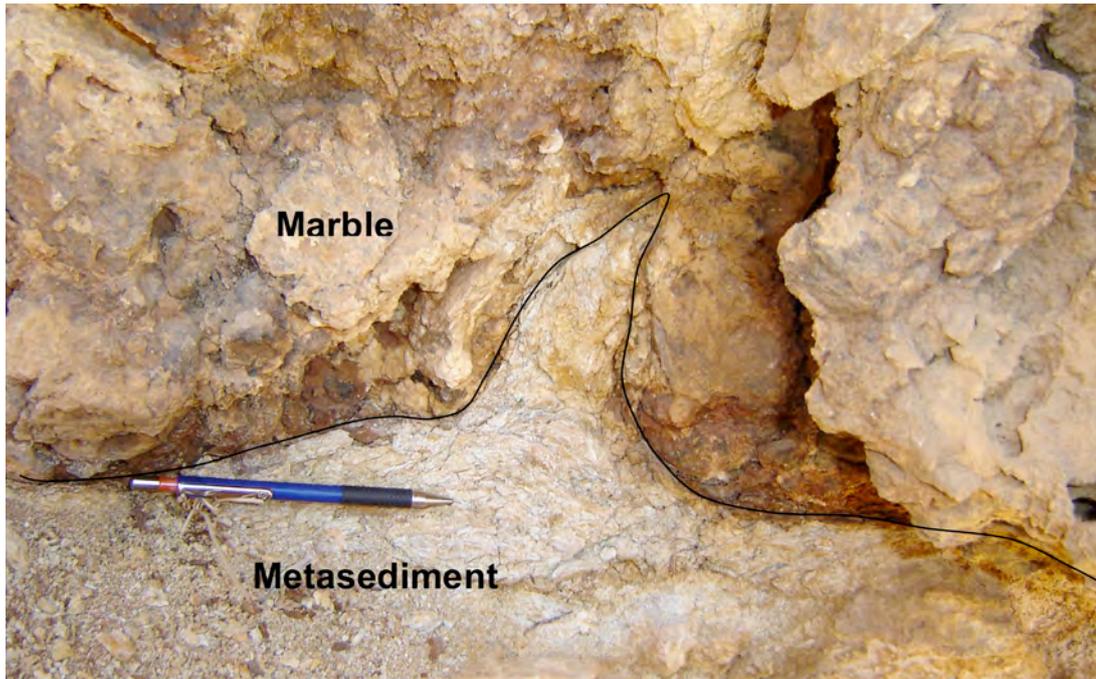


Figure 2.8 Munzur limestone exhibiting massive structures with indistinct bedding. It lies unconformably above the meta-sedimentary unit and its contacts display evidence of tectonic emplacement and soft-sediment flame structures (Easterday, 2004).

A major dissolution event resulted in mass degradation (“rubbing down”) of the marbles. The matrix to the breccias has become permeated with iron oxides and clay, suggesting a significant degree of permeability during the hydrothermal event. The presence of vugs and open breccia texture cause intrusion of the hydrothermal fluids, have resulted in the dispersion of patchy gold anomalies throughout a large volume of the marble (Poyraz, 2005).

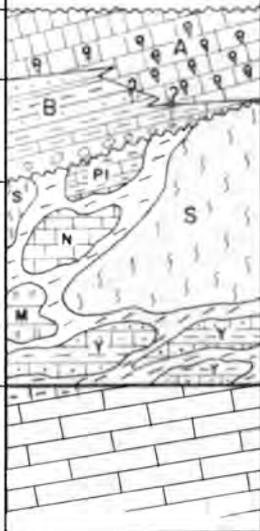
The Munzur Limestone is highly karstified in the study area. This feature of the Munzur Limestone is discussed in the hydrogeology part of this study.

### **2.3.3.3 Ovacık Group**

Ovacık Group is made up of Eriç Ophiolitic Mélange, the Çolaklar Formation and Arıkaya Limestone that overlies this mélange by unconformity (Figure 2.9) (Özgül *et al.*, 1981). Ovacık Group mainly consists of ophiolites and mélanges that contain

sedimentary blocks that were deposited in different facies and environmental settings within Permian-Upper Cretaceous time frame. It also contains post-tectonic deposits that covers ophiolitic mélangé transgressionally, and that contain foraminifera spp. Representing Maastrichtian. Another characteristic of Ovacık Group is that the ophiolitic mélangé is allochthonously positioned over the Munzur Limestone (Özgül *et al.*, 1981).

In the study area only the undifferentiated sections of the Eriç Ophiolitic Mélangé and the Yücebelen Member is observed. More detailed information about the other units of the Ovacık Group can be found in Özgül *et al.* (1981).

Name of Group	AGE	FORMATION	(m)*	LITHOLOGY
OVACIK GROUP	Maastrichtian +Paleocene	Unconformity ARIKAYALIMESTONE	150 m	 <p>A-Reefal Limestone B-Shale, sandstone, limestone, conglomerate</p> <p>S: Serpentine PI: Pelagic Limestone N: Neritic Limestone M: Metamorphics Y: Yücebelen Member</p>
	Maastrichtian	ÇOLAKLAR FORMATION	100 m	
	Blocks of Permian, Triassic, Jurassic, Cretaceous	Unconformity ERİÇ OPHIOLITIC MÉLANGE	400-500 m	
	Triassic-Upper Campanian	Tectonic Contact MUNZUR LIMESTONE		

\*The thickness is given as an approximation.

Figure 2.9 Ovacık Group's Generalized Schematic Stratigraphic Columnar Section (After Özgül *et al.*, 1981)

### **2.3.3.3.1 Eriç Ophiolitic Mélange**

The Eriç Ophiolitic Mélange is observed extensively to the south and east of the study area. In the study area, it is composed of mostly serpentinized ultrabasic, and basic rocks such as peridotite, gabbro, diabase and split (Poyraz, 2005).

Yılmaz (1985) describes Eriç ophiolitic mélange as a mixture of dark green, pale, brownish, smoky, bluish colored lithology with blocky parting, dunite peridotite, serpentinite, amphibolite and gabbro. Özgül *et al.*, (1981) define four different members for Eriç Ophiolitic Mélange: Ulyamaç ophiolitic member, Yücebelen member, pelagic blocks and neritic blocks. Among these, undifferentiated Eriç Ophiolitic Mélange and Ulyamaç ophiolitic member are observed in the study area.

Eriç ophiolitic mélange was emplaced in the region within the lower Campanian-Lower Maastrichtien period (Özgül *et al.*, 1981; Aktimur, 1986). However the lateral movements of the ophiolitic mélange continued for several periods, discontinuously until Lower Miocene (Arpat and Tütüncü, 1978; Aktimur, 1986; Tütüncü and Aktimur, 1988).

The unit has a tectonic contact with the Munzur limestones and its blocks can be seen in it. West of study area the ophiolitic mélange was thrust onto the Upper Campanian Munzur Limestone, (Özgül *et al.*, 1981).

Özgül *et al.*, (1981) identifies four different members comprising the Eriç Ophiolitic Mélange: “Ulyamaç Ophiolitic Mélange”, “Yücebelen Member”, “Pelagic Blocks” and “Neritic Blocks”. In the study area only the “Ulyamaç Ophiolitic Mélange” member is observed to the west and southeast of the study area (Figure 2.4) and this member is described in more detail below.

### **2.3.3.3.2 Ulyamaç Ophiolitic Member:**

This is one of the most widespread members of the Eriç ophiolitic mélange. It consists of dunite, serpentinite, spilitic diabase and gabbro. The most dominant lithology of the serpentinites constitutes the most dominant lithology of the Ulyamaç ophiolitic mélange. These are dark to lighter green, bluish in color, shiny and sliperry in appearance. They are reported to contain serpentine minerals with

braided texture, lower amounts of olivine, bastite, enstatite, chromite and minor amounts of opaque minerals such as magnetite (Özgül *et al.*, 1981).

The diabase and dunite dykes cut the serpentinites from place to place. The green colored diabases, have hyalocrystaline ophitic texture. They consist of partially albitized andesine, and labradorite phenocrysts in a matrix of plagioclase microlithes (Özgül *et al.*, 1981).

Gabbro appears also as dykes within the serpentinites. It appears as green to dark ash colored with a brown alteration color. They constitute the resistant small mound-like geographic features in the study area. They mainly contain unaltered pyroxenes, amphiboles and plagioclases dominated by labradorites (Özgül *et al.*, 1981).

Spilites usually occur in a mixed state with pelagic limestones, radiolarites and shales. In general they exhibit a metamorphism of almandine to amphibolite facies (Özgül *et al.*, 1981).

#### **2.3.3.4 Post-Tectonic Tertiary Deposits**

The Post-Tectonic Tertiary deposits that are observed in the vicinity of the study area are summarized below:

##### **2.3.3.4.1 Subaşı Formation**

The Subaşı formation mainly consists of clastic and volcanic lithologies. It comprises of conglomerate, sandstone, and agglomerate intercalations at the lower levels followed by tuff, agglomerate and andesite on the upper levels. In all its outcrops, it starts with a basal conglomerate. Although the grain size decreases towards the upper levels it is still possible to observe conglomerate as intercalations. The agglomerates and tuffs that start as thin intercalations at the lower levels of the formation turn out to be the major lithology at the upper levels of the formation (Özgül *et al.*, 1981).

The basal conglomerate of the Subaşı Formation consists of the dark ash colored recrystallized limestone pebbles of the Balkırı Group s Limestone<sup>5</sup>. The grain size ranges from 1 cm to 1 m, with angular, poorly sorted grains. The thickness of this level is about 3 meters in the type section of the formation, being entirely constituted of the pebbles and blocks of the Balkırı Group with almost no matrix. The pebbles are lithified by fine carbonate cement. Towards upper levels grain size decreases and an increased ratio of a buff matrix of sand grains can be observed. This matrix contains significant amounts of microfossils such as *Nummulites*, *Alveolina*, *Discocyclus* and shells of *Ostrea* (Özgül *et al.*, 1981).

This level is followed by a sandstone, shale, calcarenite and agglomerate intercalation that exhibits a decreasing grain size towards the upper levels. This clastic level also consists of conglomerate levels with small pebbles. The sandstone level is distinct with its buff color. It consists of sand sized recrystallized limestone and volcanic grains in a matrix of calcareous clay. This turns into calcarenite as the ratio of the calcareous cement increases. It is rich in fossil content. Shales usually appear bluish with a weathering color of pale ash color, and distinct parting. As the calcite ratio increases it turns into a finely bedded clayey limestone. The shale is finely bedded with sandstone and limestone intercalations. Within this clastic intercalating level, there are also 3 to 5 m thick agglomeratic volcanic sandstone levels (Özgül *et al.*, 1981).

The volcanics of the Subaşı Formation that makes up its upper most levels consists of agglomerate, tuff and andesite. They are violet, purple and dark ashy colored. Andesites are reported to exhibit porphyritic texture with large phenocrysts of feldspar (Özgül *et al.*, 1981).

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<sup>5</sup> Balkırı Group Limestone consists of the Yoncayolu Formation (Permian or older), Çay Deresi Limestone (Permian), Alıçlı Formation (Lower Triassic) and Kale Tepesi Limestone (Liassic-Upper Cretaceous). It is a part of Keban Group (See Table 2.1). Balkırı Group is not observed in the close vicinity of the study area and therefore not mentioned in detail in this thesis. More Information about these limestone formations can be found in Özgül *et al.*, (1981).

Subaşı formation overlies the Kemaliye Formation transgressively. Based on extensive studies its thickness in the region is reported to be around 1000m. Subaşı formation started to be deposited in a shallow environment with relatively lower wave energy but with a high rate of transgression, in a steep fiord type coastal morphology. The decreasing grain size is reported to indicate a decreasing rate of transgression and a more stable environment with a wider coastal morphology, and presence of volcanics on the upper levels are reported to be the indications of a volcanic activity, which is concurrent with the deposition. Based on its fossil content the age of the formation is reported to be Ileridian-Cuisian (Özgül *et al.*, 1981).

#### **2.3.3.4.2 Dedek Formation**

Dedek formation mainly consists of clastics, limestones and volcanics. In the study area it is widely observed towards the North of İliç. Lower levels of Dedek formation is identified as Dolugün Member and it consists of clastics and limestones that intercalate with tuff and agglomerate. Upper levels are differentiated as Koçkar Volcanic Member and it consists of andesitic and basaltic volcanics (Özgül *et al.*, 1981).

##### **2.3.3.4.2.1 Dolugün Member**

This lower member of the Dedek formation in general starts with a basal conglomerate or a buff, yellowish colored sandy limestone. At the upper levels it exhibits intercalation of different ratios of sandy limestone, limestone and sandstone. It also contains tuff-agglomerate intercalations. The lithologies that constitute the Dolugün Member exhibit lateral and vertical changes (Özgül *et al.*, 1981).

To the south of the İliç, the Dolugün Member overlies the Ulyamaç Ophiolitic Mélange. It starts with ash colored shales and passes onto buff colored medium thick-bedded limestones that make up a steep ridge. Agglomerates belonging to Koçkar Volcanic Member are also observed to overly the Dolugün member at the outcrop in İliç. The limestone part does not exhibit large foraminifera specimens but in its thin sections it is reported to contain a nummulite rich fauna (Özgül *et al.*, 1981).

Avcı et al., (1995) suggests that the Dolugün Member is Lower-Middle Eocene aged due to its fossil content and due to its relation with other formations. Özgül et al. (1981) more precisely suggests Upper Lutetian as the age of Dolugün Member.

#### **2.3.3.4.2.2 Koçkar Volcanic Member**

Koçkar volcanics consists of tuff, agglomerate, andesite and basaltic volcanics. This unit that overlies the Dolugün Member constitutes the upper levels of the Dedek Formation. These two sub-units exhibit lateral and vertical transitions between each other.

The andesites of the Koçkar Volcanics are purple green and dark ash colored. They have porphyritic texture with andesine and hornblende phenocrysts and parted plagioclase microliths in a glassy matrix. The basalts are black-dark ash colored and porphyritic in texture. They exhibit labradorite, hornblende, augite, hydroxidized olivine, and from place to place biotite phenocrysts in a glassy matrix. Agglomerates consist of large blocks of andesite and constitute the most dominant lithology of this member (Özgül *et al.*, 1981).

The Koçkar Volcanics cut the older formations and appears as an east – west elongated eruptive structure. Avcı *et al.*, (1995) suggests that it to be Late Eocene in age since it cuts through the Eocene sediments but is overlain discordantly by Neogene aged Kemah Formation.

#### **2.3.3.4.3 Kemah Formation**

Özgül *et al.*, (1981) named Kemah formation after Kemah Town where it crops out widely. Mainly limestone and clay, silt and sand sized clastics constitute the formation. At the bottom Kemah Formation begins with a thick and nicely bedded, fossiliferous, yellow ash colored algal limestone of approximately 20 m thick. This is followed by an alternating sequence of red ash and bluish colored claystone, sandstone, siltstone and limestone together with basalt intercalation. This clastic upper level which is in general medium to thin in thickness, nicely bedded with plenty of cross bedding, also contains from place to place some gypsum lenses and coal seams that range from 5 cm to 1m. The upper most levels of the Kemah

Formation constitute a limestone that contains large fossil shells and that has a fragmented character.

Kemah formation covers discordantly all other formations in the region, and is overlain from place to place by the quaternary deposits. The Kemah formation is Neogene in age and deposited in shallow marine, lagoonal, and deltaic environments (Özgül *et al.*, 1981).

#### **2.3.3.4.4 Quaternary Talus**

At the steep slopes of the Munzur Mountain alluvial fans and Quaternary talus can be observed. This is mainly made up of loose angular pebbles and blocks (Özgül *et al.*, 1981).

#### **2.3.3.4.5 Quaternary Alluvium**

Alluvial deposits are observed to be fine or coarse-grained deposits that are either loose or loosely cemented. Pebble and sand size particles are dominant. They are generally observed as terraces of conglomerates or sandstones along the riverbanks. They are deposited along riverbanks as a result of river flooding (Özgül *et al.*, 1981).

### **2.3.4 Structural Geology**

The eastern part of the central Anatolia is dominated by NE-SW trending-left lateral transcurrent structures. In this region where the study area also takes part, there are also numerous second-order tectonic escape structures that shape the neotectonic framework of eastern Turkey (Figure 2.10). These are: (1) dextral to sinistral intracontinental strike-slip faults and subfault zones, and (2) strike-slip basins, and (3) ramp basins. Most of the strike-slip faults and subfault zones are displaced off from the NAF near Erzincan and Niksar, trending in WSW and NE directions, and cutting across the Anatolian Plate and East Anatolian plateau which then form numerous smaller structural blocks. (Sial, 2005)

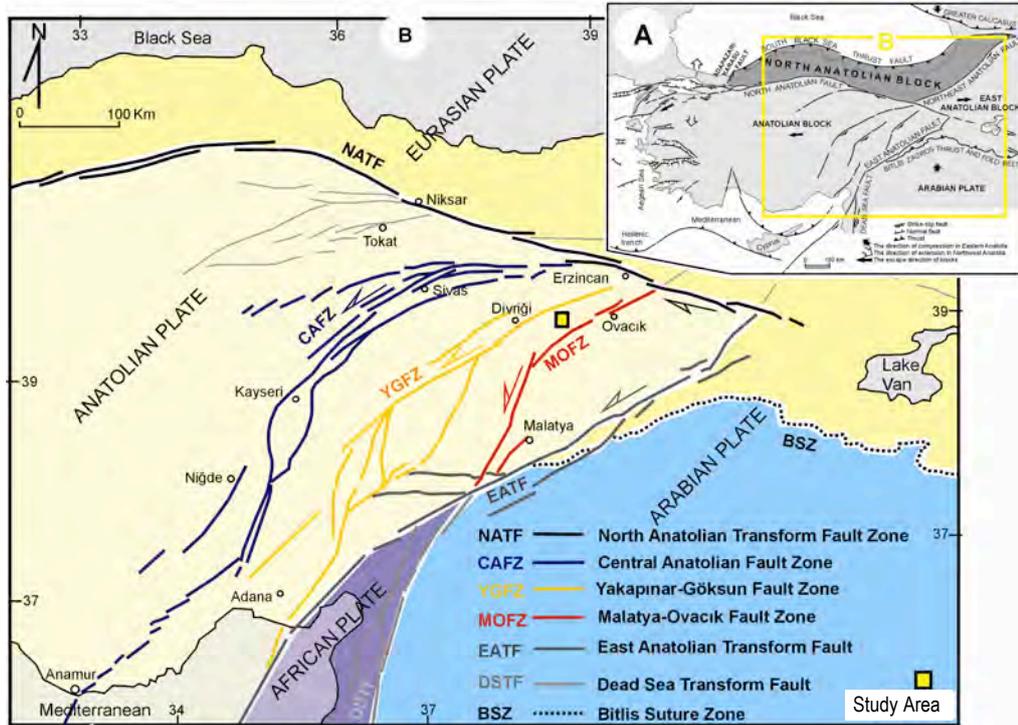


Figure 2.10 A: Major neotectonic elements of Anatolia (from Elmas, 1996) B: Simplified neotectonic map showing major tectonic escape induced structures in Eastern half of Turkey and the adjacent areas (from Sial,2004).

### 2.3.4.1 Faults

There are several faults in the vicinity of the study area. These faults represent the Ziyaret Tepe Fault zone (See Figure 2.3, and location Map at Figure 2.1). It is morphologically the most prominent fault system in the study area (Poyraz, 2005).

The Ziyaret Tepe fault zone is an approximately 30-km-long and 2-km-wide, sinistral strike-slip fault zone, which is located between Karasu River in the North and the Ziyaret Tepe, which is the Western peak of the Munzur Mountain (Poyraz, 2005).

There are two parallel normal faults identified in the immediate study area (Figure 2.5). These are named as Çöpler North and Çöpler South Faults by the Çukurdere Ltd. geologists during the exploration stage.

### **2.3.4.2 Folds**

In their extensive studies Özgül *et al.*, (1981) was unable to identify a folding system in the region. They attribute this to the block-faulted nature of the Munzur Limestone and the thrust and gravitationally complicated nature of the ophiolitic mélanges and the olistostromal units.

However within the uncorrelated meta-sedimentary units observed in the study area, it is possible to observe local foldings as soft sedimentary features such as slump folds and boudinages (Figure 2.6).

### **2.3.5 Volcanic Activities and Magmatism**

Özgül *et al.* (1981) describes andesitic dykes that cut through Eriç Ophiolitic Mélange and describe them to be brownish, with shades of green and porphyritic in texture. They report these andesites to contain biotite, hornblende and feldspar phenocrysts in a fine crystalline matrix.

Özgül *et al.* (1981) also mapped the granitic intrusions in Çöpler and Yakuplu but they did not name these intrusions but described them. They described the intrusion in the Çöpler Village to be a biotite-hornblende Granodiorite. They also describe the contact metamorphism observed along the contact between the intrusive body and Munzur Limestone and the ophiolitic mélange, and they have also recognized the hematite, magnetite and manganese ore formation along this contact.

#### **2.3.5.1 Çöpler Granitoid**

Avcı (1991) was the first to name the granitic intrusion in Çöpler village. They suggest that it was developed as a relatively small intrusion in the form of sub-volcanic to hypabyssal intrusions with porphyritic texture.

Avcı *et al.* (1995) describes the lithologies of Çöpler granitoid as diorite, quartz diorite and their porphyritic equivalents. As they also suggest, the Çöpler granitoid exhibits an extensive disintegration and alteration. The alteration is in general in the form of argillization and carbonatization and to a relatively less extend in the form of chloritization. In addition to these intense alterations, in the contact zones

silicification as well as limonitization and hematitization are common as a result of hydrothermal activity. Also in these contact zones, manganese and copper oxide minerals are relatively commonly observed.

Poyraz (2005) describes the Çöpler Granitoid as a porphyry intrusion, central to the erosional window, extending to the east and west as dikes and sills cutting through the Munzur Limestone and meta-sedimentary parts, respectively (Figure 2.11).



Figure 2.11 Hornblende-quartz-monzonite porphyry intruding the entire sequence. (Picture taken from Easterday, 2004).

Poyraz (2005) describes the Çöpler intrusion to be comprised of hornblende-quartz-monzonite porphyry that exhibits strong argillic alteration especially in the SW to southern parts. The majority of this intrusive body is highly weathered; however, fresh-transitional equivalents can be observed in exploration cores and in locally resistant areas.

Poyraz (2005) suggests multiple intrusive phases to be interpreted from tectonic relationships constrained to local deformation within the center of the SW to southern parts. A distinctly resistant (to both weathering and veining) and highly chlorite-magnetite altered monzonite porphyry part of the Çöpler granitoid also exists in these locations.

The Çöpler granitoid is observed to be cut by late aplitic dykes with characteristic pyrite disseminations (Poyraz, 2005). The previous studies showed that they contain up to 300 ppb gold (Avcı *et al.*, 1996). During exploration studies, Çukurdere Ltd. geologists reported that the Çöpler intrusive were intensively altered and silicified. In general, they reported the alteration to tend to increase from East to West. The unaltered relicts and/or remnants of Çöpler granitoid are observed as unreplaced or unaltered islands only to the south of Cirit Meydanı (Poyraz, 2005). Although, it is hard to name the rock by naked eye without microscopic and chemical studies, the unaltered islands of plutonic rocks within the altered zones are referred to as granite and diorite (field description).

The Çöpler intrusive forms two large, distinct, sub parallel lobes to the North and South of the Çöpler north and Çöpler south faults, respectively (Figure 2.7). Within the SW to southern parts, the aerial distribution of the intrusive is preserved as remnant shallow bodies enveloped within the meta-sedimentary unit. Small- to large-scale xenoliths of both meta-sediment and limestone/marble are commonly observed within the monzonite porphyry (Poyraz, 2005).

### **2.3.5.2 Yakuplu Granitoid**

Although Özgül *et al.*, (1981) mapped the granitic intrusion along the Yakuplu Village they did not name it, however Avcı (1991) names and describes (Avcı *et al.*, 1995) Yakuplu Granitoid as a NW-SE elongated, 7 km long and about 2 km wide plutonic intrusion at the South of İliç Town near Yakuplu Village (Figure 2.4). Avcı *et al.*, (1995) observed this intrusion as a highly altered, degraded granodiorite, quartz diorite porphyry type granitoid formation. They described it to be relatively granular, less porphyritic, with mafic inclusions exhibiting porphyritic texture.

Yakuplu Granitoid exhibits contact metamorphism evidences in its surrounding due to the pressure, temperature and solutions that caused metamorphism during its

intrusion. This has resulted in not only the recrystallization of Munzur limestone but also it lead to the, epidotization, garnet, corundum and feldspar formation in the form of silisification. In the Eriç ophiolitic Mélange on the other hand, it resulted in schistositic features together with serpentization, carbonatization, and formation of minerals such as talc and fucsite that indicates metasomatic and hydrothermal effects (Avcı *et al.*, 1995).

Avcı *et al.*, (1995), suggests Late Cretaceous-Paleocene for the age of Yakuplu Granitoid by indicating that Yakuplu Granitoid cuts through Munzur Limestone and Eriç Ophiolitic Mélange and pointing out that there are pebbles from Yakuplu Granitoid in Eocene and Neogene Formations,

### **2.3.6 Tectonic Deformation History**

During the exploration studies, Çukurdere Ltd.'s geologists have identified five stages of deformation within the Çöpler area. These have been cross-correlated in each of the three mineralization zones that were mapped based on the reserve estimations and also correlated with the regional geology to a certain extent.

The deformation history involves first an early tectonic emplacement of the Munzur thrust sheet. This early deformation is recorded at the contact between the Munzur limestone and the Çöpler meta-sedimentary unit. Although it is only possible to observe the soft-sediment slump structures in locations where this contact locally dips shallowly north, a number of low-angle thrust faults mapped within the Munzur limestone where fault brecciation and shearing lineation are evident. However NE-directed vergence is not keeping with regional setting (S-directed) thus was noted to be problematic by the structural investigators of the exploration team of Çukurdere Ltd., (such as Easterday, 2004). Tectonic emplacement of the Munzur thrust sheet occurred as a result of NE directed thrusting, as revealed by the soft-sediment deformation that was observed at the contact indicating pre-diagenetic (meta-sedimentary) emplacement (Easterday, 2004).

The second stage of the deformation history involves a lengthened period of uplift and proximal extension. This is associated with the main phase of grano-diorite intrusion event. Two prominent ENE-WSW trending faults; Çöpler North and Çöpler South faults dragged out uplift event associated with intrusion of the Çöpler intrusive

body. Early extension along these faults was followed by progressive uplift. Development of E-W splay faults off the Çöpler North fault. This represents the final stages of the second phase of the deformation (Easterday, 2004).

At the third stage of the deformation history involves SSE-NNW compression and intrusion of the Çöpler stock. This stage appears to be localized and non-persistent. Also some small offset, conjugate faults that was well constrained in timing were observed in a number of locations. These are brittle-ductile/brittle in nature. During the intrusion of the Çöpler stock, the second stage still continued; Intrusive sills along meta-sediment/limestone contact were emplaced of and vertical feeder dykes along the Çöpler north and south, first-order bounding faults were placed and marbleized forming exoskarns proximal to the intrusive body (Easterday, 2004).

The fourth stage of the deformation history involved localised sinistral activation of Çöpler north fault SE-directed compression and also involved the possible mineralization event. The main mineralization event relates to SE-directed compression and the reactivation of earlier, favorably oriented fault sets. While the second stage continued E-W sinistral splay faults formed along the Çöpler north fault. Grano-diorite intrusion phase was also continued at this stage as well as the continuation of marble development as an exoskarn proximal to the intrusive body. At this stage NE-trending link thrust faults was formed and earlier faults including second stage faults were reactivated (Easterday, 2004). At this stage gold bearing jasperoids were also formed along Çöpler north and south faults most probably at the possible reactivation points and active fault intersections points. Easterday (2004) suggests that mineralized vein styles include stock work, sheeted and micro veining and NW-SE-trending vein populations are distinctly thicker. He also interprets that the intersections of these gossan type vein populations plunge moderately towards the WSW and SW. He suggests that this represents the maximum fluid flow direction (Easterday, 2004).

The final stage of the deformation history involves a Late Stage Brittle Faulting. At this final stage brittle faulting cross cuts and offsets earlier faults, formed in previous stages. These faults are oriented E-W and NW-SE, are small-scale, and brittle. They display no evidence of fault brecciation texture on their surfaces. They are colloform and cockade, and they exhibit late open-space veining. However, it is not certain as

to their relationship with this late deformation event. Southeast directed compression and mineralization also continued at this stage. Although the main mineralization event was associated with the formation of NE-trending link thrusts, late-phase monzonite-diorite intrusives as vertical dykes along linking faults continued. At this stage re-activation and fluid focusing along favorable fault orientations and geological contacts took place (Easterday, 2004).

This interpretation of the Çöpler fault architecture highlights the main fault controls on gold distribution within the three mineralized zones at Çöpler Two fault orientations are critical for the localization of the mineralization; namely the E-W and NE-SW faults (Poyraz, 2005).

### **2.3.7 Ore Mineralization**

In this section the alterations, jasperoids, the type of ore mineralization and the zonation of the ore mineralization defined by the mine operators are explained.

#### **2.3.7.1 Alterations**

Two main phases of alteration are observed throughout the mineralization system: First phase is the Porphyry Copper style of alteration, represented by the presence of quartz-magnetite-chalcopyrite facies where quartz-pyrite-molybdenite veins may be associated with early Cu-porphyry type of alteration (Poyraz, 2005). Later a retrogressive alteration recognised as a primary bleach assemblage, associated with quartz-carbonate-pyrite veinlets and magnetite destruction. This represents transitional- to late-stage argillic alteration associated with the main epithermal event (Poyraz, 2005).

#### **2.3.7.2 Jasperoids**

The jasperoids are located either at the contacts of the Çöpler Granitoid, or at the metasediment-carbonate contacts at up to several hundred meters (in plan) from the Çöpler Granitoid. This suggests that permeability and in particular solution cavities at the meta-sediment-carbonate contact were the primary control on formation of the jasperoids (Poyraz, 2005).

In addition to this, Jasperoid lenses also appear in other places of the Çöpler Deposit and they are not localized in structures or contacts, which may suggest that they occupy hydrothermal karst or paleokarst features (Kociumbas and Macfarlane, 2003).

The presence of Jasperoids in the study area is a good evidence for the metasomatic hydrothermal alteration of the Çöpler Intrusion.

### **2.3.7.3 Mineralization Zonations**

Poyraz, (2005) defines three mineralization zones and two mineralization types (Figure 2.5) at the Çöpler Gold Prospect based on an extensive drilling and exploration programme conducted by Çukurdere Ltd. The zones are defined according to practical mining purposes, grouping similar lithologies and ore bodies with similar gold tenures. These three zones were also illustrated in Figure 2.5. These zones are as follows:

1. Main zone: Located at the West of the study area with an average area of 700 X 800 m extending in the East – West direction. Main zone consists mainly of diorites of Çöpler Granitoid and the metasediments.
2. Manganese Mine Zone: Located at the East of the study area with an average area of 450 X 700 m extending in East – West direction. Manganese Mine Zone consists mainly of marble of Munzur Limestone.
3. Marble Contact Zone: Located in the middle of these two zones with an average area of 250 X 400 m extending in the North East-South West direction. Marble Contact Zone is consists mainly of marble and the metasediments.

As shown in Figure 2.5 these mineralization zones follow also the proposed pit boundaries.

The two identified mineralization types are sulphide and Oxide type mineralizations. Sulphide type mineralization is observed in three distinct types in the study area as first the disseminated sulphides in stock work quartz veined metasediments and quartz monzonites. This type occurs in the Main Zone, and in the Marble Contact

Zone. Secondly as disseminated sulphides in clay altered, brecciated and carbonatized quartz monzonite. This type of mineralization occurs in the Manganese Mine Zone. Finally and thirdly as massive sulphide replacement bodies along the marble contacts. This type, occurs in the Main Zone contacts, Marble Contact Zone, and Manganese Mine Zone (Poyraz,2005)..

Oxide type mineralization, is a supergene oxidation and it was resulted in the formation of gossans, massive manganese oxide and goethite-jarosite assemblages hosting fine-grained free gold in the marble, meta-sediment and the diorites (Poyraz,2005).

Porphyry copper-gold mineralization associated with K-silicate alteration is confirmed to be occurring at Çöpler, and its characteristics are compatible with its being a gold-rich albeit low-grade system. The overprinted gold mineralization is of base metal-rich, low-sulphidation type, recently assigned to a newly created intermediate-sulphidation class. The gold occurrence is reported to be not of high-sulphidation affiliation type unlike its commonplace counter parts in telescoped porphyry copper systems occurring worldwide (Poyraz, 2005). Two styles of overprinted gold mineralization are recognized: arrays of quartz-manganese carbonate-barite veinlets in which tennantite and chalcopyrite appear to be closely related to gold, and quartz-pyrite replacements of either limestone or prograde calcic skarn.

Manganese oxides develop from the manganese carbonates during weathering, whereas gossan type quartz and even true gossan are the oxidation products of the replacement-style mineralization (Poyraz, 2005).

In the following sections these mineralizations are discussed in more detail within the context of defined mining zones.

### **2.3.7.3.1 Main Zone**

As explained above the Main zone consists mainly of diorites of Çöpler Granitoid and the metasediments. The main zone oxides and main zone sulfides are explained below.

### 2.3.7.3.1.1 Main Zone Oxide

The Çukurdere exploration studies revealed, supergene oxidation of sulphides to be penetrated to a maximum depth of 35 meters with the thickest development being over the ridges and thinning in the intervening valleys. The contact between oxide and sulphide is reported to be invariably sharp with apparent insignificant penetration to a depth along high angle structures (Figure 2.12) (Poyraz, 2005).



Figure 2.12 Photography of the core sample from Main zone sample no: CDD-002; between 21.5 to 29.4 m. Oxide / Sulphide boundary shown at 25.45 m (Poyraz, 2005)

### 2.3.7.3.1.2 Main Zone Sulphide

Poyraz (2005) describes this zone as an epithermal gold mineralization within the Main Zone, which is largely hosted by fractured, sheared and quartz stock worked, metasediments and quartz monzonite

The Main Zone opaque mineral assemblage is mainly composed of marcasite together with subordinate pyrite, arsenopyrite, chalcopyrite and magnetite as well as trace amounts of sphalerite, tennantite/tetrahedrite and molybdenite. The ore minerals are texturally complex and are characterized by the widespread development of fine-grained arsenopyrite that forms micro-scale intergrowths with marcasite, and as disseminations. Gold has not been seen and is assumed to occur as sub-micron inclusions in arsenopyrite (Poyraz, 2005).

### **2.3.7.3.2 Manganese Mine Zone**

The marble lithology of the Munzur Limestone makes up the majority of the Manganese Mine Zone. The oxide and sulfide mineralizations of the manganese mine zone is explained below:

#### **2.3.7.3.2.1 Manganese Mine Zone Oxide**

Oxide mineralization is hosted by marbles, as well as manganese oxides, gossans and oxidized intrusives at the marble contact. Manganese oxides and gossans are considered to be the up-dip and up-plunge lateral equivalents to the massive sulphides. As a consequence, the highly permeable marbles have allowed penetration of meteoric fluids to depths, and oxidation has locally penetrated to depths of hundreds of meters along intrusives and marble (Poyraz, 2005).

#### **2.3.7.3.2.2 Manganese Mine Zone Sulphide**

The Manganese Mine Zone sulphide mineralization is hosted by carbonatized, argillized and brecciated intrusives at places close to the marble contact or exactly over the marble contact as massive sulphides (Poyraz, 2005).

The Manganese Mine Zone opaque mineral suite is dominated by pyrite and marcasite that are characterized by a wide range of grain size and variety of forms. The associated opaque minerals are commonly fine-grained and generally consist of complex intergrowth of aggregates of galena, sphalerite and compositionally zoned grains of tennantite/tetrahedrite. Locally, subordinate amounts of stibioluzonite (famatinite) and other Pb-Sb-As-S sulphosalts are also present.

Realgar and orpiment occur as disseminations and coatings on fractures in altered intrusive and marble lithologies (Figure 2.13) (Poyraz, 2005).



Figure 2.13 Photography of the core sample from Mn Mine Zone – Oxide (a) and Sulphide (b) Mineralization. Core samples: CDD-066, CDD 256-5-274.35 m. Marble breccia (c) and argillized brecciated intrusives (d).

### **2.3.7.3.3 Marble Contact Zone**

As explained above Marble Contact Zone also contains marbles of Munzur Limestone and Metasediments. The oxide and sulfide mineralizations of the Marble Contact zone are explained below.

#### **2.3.7.3.3.1 Marble Contact Zone Oxide**

In the Marble Contact Zone, marbles and gossans, host gold mineralization for oxide mineralization zone. The sub-vertical to shallow angled juxtaposition of highly permeable marble allowed penetration of meteoric fluids resulting in penetration of oxidation to greater depths compared to what is observed in the Main Zone (Poyraz, 2005).

Mineralogical investigation of a composite sample submitted by Çukurdere Ltd. for metallurgical test work showed that the secondary oxide ore mineral suite consists largely of goethite and jarosite together with very much lesser amounts of heullandite and plumbojarosite (Poyraz, 2005).

### 2.3.7.3.3.2 Marble Contact Zone Sulphide

Quartz stockworked metasediments, quartz-monzonite and massive pyrite-marcasite host gold mineralization for the sulphide type of the mineralization in the Marble Contact zone (Poyraz, 2005).

The core samples obtained during exploration studies, exhibit minor amounts of malachite, cuprite, chalcophanite and tripuhyite. The relict sulphides consist largely of pyrite and marcasite together with minor to trace amounts of chalcopyrite, supergene Cu-sulphides, enargite, tennantite and cinnabar. (Figure 2.14) (Poyraz, 2005).



Figure 2.14 Core photo from the Marble Contact Zone, CDD-039,45.9-60.6 m. Oxidized intrusive (a) and gossan (b).

### 2.3.8 Resource Estimate

Based on a September 2005 news release published in Anatolia Minerals Web Site<sup>6</sup> an updated estimate of gold resources for Çöpler gold deposit is provided in this section. Based on a study by Independent Mining Consultants Inc. (IMC), of Tucson, Arizona, the Measured and Indicated (M&I) in-pit oxide resources are estimated to be 11.6 million tonnes of mill-feed averaging 2.96 grams per tonne (gpt) gold, plus 30.9 million tonnes heap-leach at 0.70 gpt gold, aggregating 1.8 million ozs. gold (75% Measured). The Inferred oxide resource totals 4.5 million tonnes at 0.84 gpt gold, containing 121,600 ozs. of gold.

Based on the same news release the sulfide resources total 28.0 million tonnes of in-pit Measured & Indicated at 2.22 gpt gold (2.0 million ozs. gold), plus 15.5 million tonnes of Inferred at 3.00 gpt gold (1.5 million ozs. gold).

Overall Çöpler measured and indicated resources total 70.5 million tonnes at a grade of 1.68 gpt gold (3.8 million oz.) as contained in conceptual pit shapes. In addition to the measured and indicated resource, an inferred resource of 20.0 million tonnes at 2.52 gpt gold (1.6 million ozs. gold) was defined. This compares to the 359,000 ozs. of measured and indicated and 3.6 million ozs. of inferred reported last year.

The update follows a 171-hole, 29,564-meter, grid drilling campaign completed earlier in year 2005 as part of Anatolia's program to complete a feasibility study by end of first quarter of 2006 and lead to a production decision shortly thereafter.

A summary of the recently completed IMC resource estimate for Çöpler is given in Table 2.2.

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<sup>6</sup> Anatolia Minerals Development Limited owns Çukurdere Ltd. and the Exploration and operation licences of Çöpler Gold Deposit. This information is taken from a news release downloaded from their web site : [www.anatolia-minerals.com](http://www.anatolia-minerals.com) (Last visited in 25.01.2007). Name of the downloaded file is:PR 09-26-2005 Copler Resource Update.pdf (Çöpler Project, Resource Estimate, Technical Report. Prepared by Independent Mining Consultants, Inc., October 2005.)

Table 2.2 The resource estimate of Çöpler Gold Prospect (MCI, 2005)

	Measured			Indicated			Measured + Indicated M+I				Inferred			
	Tonnes (000)	Au (Gpt)	Ag (Gpt)	Tonnes (000)	Au (Gpt)	Ag (Gpt)	Tonnes (000)	Au (Gpt)	Ag (Gpt)	Au oz (000)	Tonnes (000)	Au (Gpt)	Ag (Gpt)	Inferred Au ozs (000)
<b>Oxides-Mill Only</b>														
Main	1,047	2.85	5.06	1,083	2.82	3.92	<b>2,130</b>	<b>2.83</b>	<b>4.48</b>	<b>194</b>	290	2.57	0.92	24
Manganese	7,189	2.74	10.69	600	2.33	9.24	<b>7,789</b>	<b>2.71</b>	<b>10.55</b>	<b>679</b>	255	1.90	0.35	15
Marble Contact	1,424	4.21	4.89	247	4.77	4.66	<b>1,671</b>	<b>4.29</b>	<b>4.85</b>	<b>230</b>	9	2.90	0.19	1
<b>Total Mill Oxide</b>	<b>9,660</b>	<b>2.97</b>	<b>9.22</b>	<b>1,930</b>	<b>2.92</b>	<b>5.67</b>	<b>11,590</b>	<b>2.96</b>	<b>8.61</b>	<b>1,103</b>	<b>554</b>	<b>2.27</b>	<b>0.65</b>	<b>40</b>
<b>Oxides-Leach Only</b>														
Main	2,539	0.95	2.08	4,813	0.91	1.80	<b>7,352</b>	<b>0.92</b>	<b>1.90</b>	<b>217</b>	1,552	0.80	0.73	40
Manganese	14,793	0.65	0.63	5,843	0.54	0.33	<b>20,636</b>	<b>0.62</b>	<b>0.55</b>	<b>411</b>	2,146	0.55	0.26	39
Marble Contact	2,081	0.75	0.68	824	0.71	1.28	<b>2,905</b>	<b>0.74</b>	<b>0.85</b>	<b>69</b>	251	0.53	2.50	4
<b>Total Leach Oxide</b>	<b>19,413</b>	<b>0.70</b>	<b>0.83</b>	<b>11,480</b>	<b>0.71</b>	<b>1.01</b>	<b>30,893</b>	<b>0.70</b>	<b>0.90</b>	<b>697</b>	<b>3,949</b>	<b>0.65</b>	<b>0.59</b>	<b>83</b>
<b>Oxides-Total</b>														
Main	3,586	1.50	2.95	5,896	1.26	2.19	<b>9,482</b>	<b>1.35</b>	<b>2.48</b>	<b>411</b>	1,842	1.08	0.76	64
Manganese	21,982	1.33	3.92	6,443	0.71	1.16	<b>28,425</b>	<b>1.19</b>	<b>3.29</b>	<b>1,090</b>	2,401	0.69	0.27	54
Marble Contact	3,505	2.15	2.38	1,071	1.65	2.06	<b>4,576</b>	<b>2.04</b>	<b>2.31</b>	<b>299</b>	260	0.61	2.42	5
<b>Total Oxides</b>	<b>29,073</b>	<b>1.45</b>	<b>3.61</b>	<b>13,410</b>	<b>1.03</b>	<b>1.68</b>	<b>42,483</b>	<b>1.32</b>	<b>3.00</b>	<b>1,800</b>	<b>4,503</b>	<b>0.84</b>	<b>0.59</b>	<b>123</b>
<b>Sulfides-Total</b>														
Main	4,664	2.33	5.90	14,038	2.24	5.75	<b>18,702</b>	<b>2.27</b>	<b>5.80</b>	<b>1,365</b>	15,046	3.03	5.41	1,466
Manganese	4,749	2.01	10.90	3,687	1.92	0.03	<b>8,436</b>	<b>1.98</b>	<b>10.54</b>	<b>537</b>	454	2.01	5.24	29
Marble Contact	610	3.63	2.11	258	3.61	1.96	<b>868</b>	<b>3.61</b>	<b>2.06</b>	<b>101</b>	28	5.55	2.52	5
<b>Total Sulfides</b>	<b>10,023</b>	<b>2.26</b>	<b>8.04</b>	<b>17,983</b>	<b>2.19</b>	<b>6.57</b>	<b>28,006</b>	<b>2.22</b>	<b>7.11</b>	<b>2,003</b>	<b>15,528</b>	<b>3.00</b>	<b>5.40</b>	<b>1500</b>
<b>Total Resource</b>														
Main	8,250	1.97	4.62	19,934	1.95	4.70	<b>28,184</b>	<b>1.96</b>	<b>4.68</b>	<b>1,776</b>	16,888	2.82	4.90	1,531
Manganese	26,731	1.45	5.16	10,130	1.15	4.39	<b>36,861</b>	<b>1.37</b>	<b>4.95</b>	<b>1,627</b>	2,855	0.90	1.06	82
Marble Contact	4,115	2.37	2.34	1,329	2.03	2.04	<b>5,444</b>	<b>2.29</b>	<b>2.27</b>	<b>400</b>	288	1.09	2.43	10
<b>Total Resource</b>	<b>39,096</b>	<b>1.66</b>	<b>4.75</b>	<b>31,393</b>	<b>1.70</b>	<b>4.49</b>	<b>70,489</b>	<b>1.68</b>	<b>4.64</b>	<b>3,803</b>	<b>20,031</b>	<b>2.52</b>	<b>4.32</b>	<b>1,623</b>

The resource estimate prepared by IMC reflects metallurgical test-work performed by Research Development Inc (RDi) of Denver, Colorado. Recoveries for oxide ores are based on available test results. Approximate average mill recoveries for gold were 88% for the Manganese Zone, 83% for the Marble Contact Zone and 78% for the Main Zone. Recoveries used for the heap leach ores were generally between 66% and 76%. Heap leach test work was in progress when this thesis study was prepared. Sulfide mill recoveries were estimated at 75% based on preliminary test work that was reported in the December 2003 Conceptual Study (Cliff and Boast, 2003).

### **2.3.9 Hydrogeology**

Within the framework of the environmental baseline study (in 2005) of the Çöpler Mine operation the hydrogeology of the study area is studied in considerable detail by Dr. Yolcubal (Ekobil, 2005). The information provided in this section is based on these studies that involved sampling and monitoring of 14 different springs and 8 water monitoring wells that 6 of which were drilled for the environmental baseline study and 2 were old water wells that supplied water needed for exploration drilling activities.

Based on their location (Figure 2.15), springs sampled in the Çöpler region can be categorized under three groups:

1. Springs up gradient from mining site, namely SP01 and SP02;
2. Springs down gradient from mining site
  - a. Springs in Gözeler, alongside the Karasu river, namely SP13 and SP14
  - b. Spring in Bahçe Mahallesi, namely SP12
3. Springs in the mining site namely, SP03 to SP11

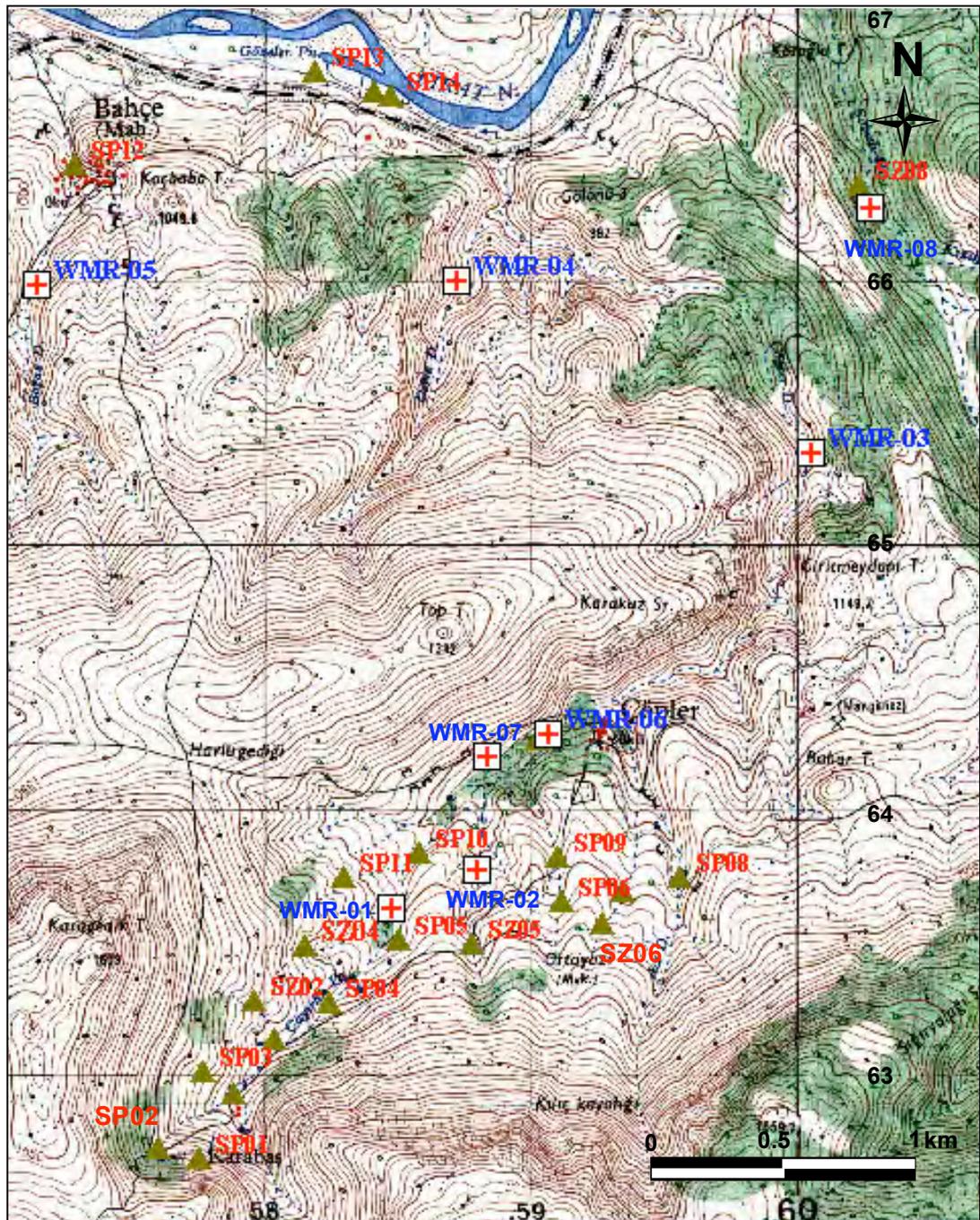


Figure 2.15 Locations of springs, seeps, and groundwater monitoring wells in the study area on a topographic map from İ41-d4 sheet, (Erzincan-İliç). SP: Spring, SZ: Seep, WMR: Groundwater Monitoring Well (Map modified after Ekobil, 2005).

### **2.3.9.1 Aquifer Systems:**

The groundwater in the study area is controlled by three characteristically different aquifer systems. These are namely: the deep limestone aquifer, the local shallow aquifers in the main zone, and finally alluvium aquifer near Karasu River. A conceptual model indicating the groundwater movement directions is shown in Figure 2.16 (Ekobil, 2005).

#### ***2.3.9.1.1 The deep limestone aquifer***

The deep limestone aquifer is the major aquifer system in the study area. Although to the east it is bound by the impermeable ophiolitic and intrusive units via the strike slip Sabırlı fault, along Sabırlı stream, the boundaries of this system continue beyond the study area (Ekobil, 2005).

The NE-SW trending fault contact between Munzur limestone and Eriç ophiolitic Mélange and/or the intrusive units let the Groundwater in the deep limestone aquifer to flow northwards towards the Karasu River. To the South of Sabırlı village at an elevation of around 1550 m (amsl<sup>7</sup>), many springs appear along this fault contact, Along the Sabırlı stream. At the lowest elevation near Karasu River a significant discharge called “Gözeler” also appear along the same fault line. This is identified as the major discharge point of the deep limestone aquifer system (Ekobil, 2005).

The water table level in the deep limestone aquifer is determined to be around 870 m (amsl), which is about the same level as the main discharge point at Gözeler.

To the south of the study area, within the Munzur Limestone, hundreds of karstic enclosed depressions are located in a considerably large area at higher elevations (2000-2200 m (amsl)). This region is attributed to be the main recharge area of the deep karstic aquifer system. During the spring, in this karstic depression, the recharge of the deep limestone aquifer begins with an increase in snowmelt and

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<sup>7</sup> amsl: average mean sea level

precipitation, The increase in the amount of discharge in response to the recharge process in summer is attributed to be a clear indication of connection between the karstic depression fields and the deep limestone aquifer system (Ekobil, 2005).

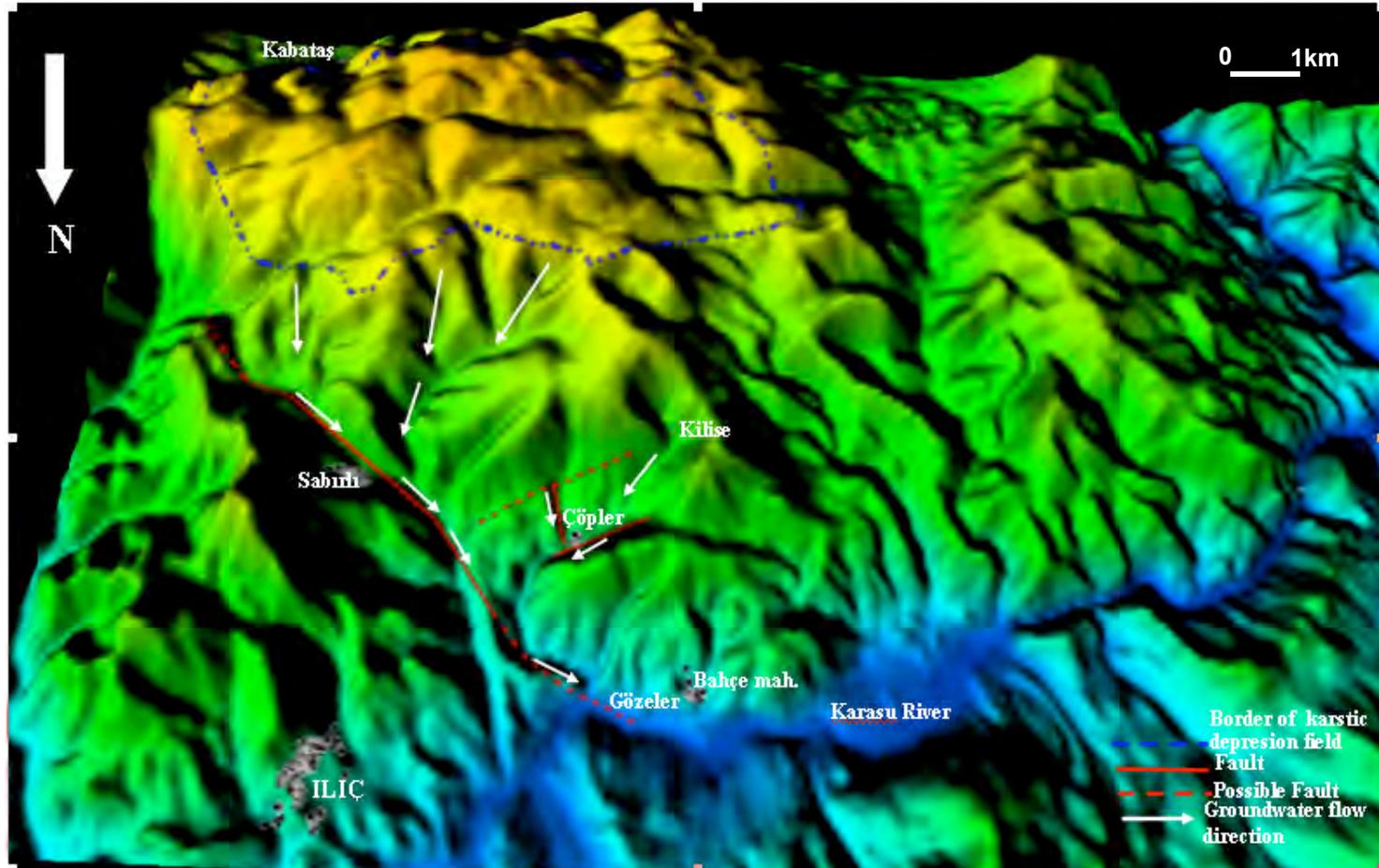


Figure 2.16 Conceptual model for groundwater movement in Çöpler region and surroundings. Model shown on a 3D topographic elevation model). (From Ekobil, 2005).

Besides the deep limestone aquifer, at higher elevations in limestone, there are indications of a perched water table. Fractures that are not connected directly to the deep limestone aquifer, result in development of such local water tables in limestone. At the contact of limestone and meta-sediment near Karabaş, at an elevation of 1490m (amsl) (SP01 and SP02) and at down gradient locations along Çayırılık Dere on the west of Çöpler (SP03 and SP04), the springs make up obvious examples of such discharges from such local perched limestone aquifers (Ekobil, 2005).

### **2.3.9.1.2 Local shallow aquifers**

Within the permeable zones of fractured and/or altered metasediments and granite-granodiorite intrusions along the contact zone there are local shallow aquifers in the main zone (Ekobil, 2005).

Hydraulic conductivities of the altered granite-granodiorite zones range from  $1 \times 10^{-5}$  cm/s to  $9 \times 10^{-4}$  cm/s, whereas, hydraulic conductivities of metasediments range from  $2.9 \times 10^{-4}$  cm/s to  $8.8 \times 10^{-4}$  cm/s (Ekobil, 2005).

These units enclose numerous faults trending NW-SE directions and diagonal to those. In the main zone, the groundwater flow towards the Çöpler stream is thought to be controlled by these well developed dense fracture/fault systems. Near the faults, there are relatively high permeability zones in these units, as in the example of water monitoring wells WMR-02 and WMR-06. These local systems have limited recharge opportunities and their recharge mainly occurs through snowmelt and precipitation in the spring period. The local aquifer systems (i.e. meta-sediment aquifer), are observed to be recharged via up gradient discharges from perched limestone aquifers (SP01, SP02, SP03, and SP04) from the main zone and via the recharge through flood sediments along Çayırılık Dere (Ekobil, 2005).

Water balance calculation for the entire shallow aquifer systems in the main zone indicates that the amount of recharge to these systems is limited and is estimated to be approximately 580,000 m<sup>3</sup> per year. Based on pumping tests applied in the field studies, this amount is approximately equal to the total annual safe yields of the wells in the main zone. In spite of the fact that these aquifers are low in capacity, the

existence of such fluid bearing bodies in the main zone can bring about serious problems during the mining practice. For that reason, the capacity and nature of these systems must be carefully evaluated considering the possibility of their connection with the perched limestone aquifer in the area (Ekobil, 2005). This connectivity also brings about the contamination risk to the down gradient wells from the mining zone.

### **2.3.9.1.3 Alluvium Aquifer**

The Quaternary alluvial deposits along the Karasu River have the hydraulic properties to be potential aquifer system. Based on some test holes that were drilled in these sediments to find the potential for the required process water. During this survey, some holes were dry, while the others were not productive enough to supply process water. It must be noted that, if these systems are planned to be mined for groundwater in the future, their relation with Karasu River needs to be clarified to ascertain that water is not exclusively withdrawn from Karasu River (Ekobil, 2005).

### **2.3.9.2 Chemistry of the Groundwater**

The springs and the water monitoring wells exhibit two distinct water chemistries in the study area. One group originating from the deep limestone aquifer is classified as Ca-HCO<sub>3</sub> type and those originating from the local aquifers are classified as Ca-SO<sub>4</sub>. During winter, the temperature of groundwater is measured to be approximately 12 °C and 13 -14 °C in the spring (Ekobil, 2005).

The groundwater originating from deep limestone aquifer exhibits a water chemistry typical of karst aquifers with an average pH and conductivity of about 7.4 and 325 µS/cm, respectively. This is considered as an indication of a rapid flow in the karstic deep aquifer system (Ekobil, 2005).

The groundwater originating from the mining area has distinctive water chemistry and displays the indication of mineralization in its water chemistry. This distinct water chemistry fallout from the circulation of groundwater through the oxide and alteration zone. This groundwater is considered to be an extremely hard Ca-SO<sub>4</sub> type water with a slightly acidic pH (6.7) and relatively high electrical conductivity (2453 µS/cm) compared to karstic groundwater. This relatively low pH and high

electric conductivity is an indication of an already started acid mine drainage. The sulfide minerals in the main zone are oxidized and decrease the pH resulting in dissolving of heavy metals and increasing the electric conductivity.

The baseline studies conducted by Ekobil Ltd. reveals the elevated As, Fe, Zn, Pb and SO<sub>4</sub> concentrations in monitoring wells and in springs located in the main zone, compared to the concentrations observed outside the Çöpler gold prospect (Table 2.3).

Table 2.3 Concentrations of selected metals and SO<sub>4</sub> in two different sampling periods. Note that the maximum amount allowed by Turkish Ministry of Health and by European Union Regulations are 0,2mg/L for Fe; 250 ppm for SO<sub>4</sub> and 0.1mg/L for As and Pb (concentration values are taken from Ekobil, 2005).

Well/ Spring No:	As (mg/L)		Fe (mg/L)		Zn (mg/L)		Pb (mg/L)		SO <sub>4</sub> (ppm)	
	25/03/05	17/06/05	25/03/05	17/06/05	25/03/05	17/06/05	25/03/05	17/06/05	25/03/05	17/06/05
WMR 02	32.8	28.3	1177	354	133.8	<0.02	1.9	0.1	808	687
WMR 03	2.4	2.3	98	37	542.8	<0.02	2.2	16	4.89	5.70
WMR 04	4.2	4.1	115	14	374.7	<0.02	2.2	7.9	15.80	15.8
WMR 06	*	438		17705		<0.2		4.3		1580
WMR 07	71.7	12.1	1270	2382	26492	<0.02	7.5	6.4	1550	1350
WMR 08	1.6	3.8	115	26	1107.4	<0.02	7.0	0.9	34.60	31.6
SP 01	0.7	0.7	108	<10	7.1	2.5	0.9	0.1	3.67	4.67
SP 02	<0.5	<0.5	115	30	5.2	1.5	0.4	<0.1	19.3	19.8
SP 03	1.1	1.1	414	<10	8	<0.5	3.2	<0.1	36.4	36.6
SP 04	1.3	1.1	197	<10	8.9	4.1	1.3	0.3	62.2	72.80
SP 05	3.8	3.9	205	<10	47.4	48.9	0.3	<0.1	260	257
SP 06	15.2	17.7	557	<100	10.5	25.5	4.3	<1	939	1050
SP 07	134.9	203.6	3023	4100	21.2	25.3	1.1	<0.1	380	417
SP 08	1.9	1.4	205	<10	78.5	63.4	1.7	0.2	253	260
SP 09	39.4	32.1	670	<100	20.6	21.9	4.4	<1	866	950
SP 10	12.9	15.9	160	<10	10.6	9.2	0.5	0.1	194	198
SP 11	0.9	0.9	161	<10	7.9	4.7	0.3	<0.1	365	363
SP 12	0.9	<0.5	1086	<100	10.3	8	0.3	<1	1390	1360
SP 13	3.2	3.2	122	<10	5.5	1.2	0.3	<0.1	10.9	10.80
SP 14	3.7	3.8	114	<10	6	2.1	0.6	0.1	12.9	12.20

As can be observed in table 2.3 especially the metal and SO<sub>4</sub> concentrations in water monitoring wells WMR 06 and WMR 07, and in springs SP 07, SP 09 and SP

10 are significantly high. These springs and monitoring wells are located in the main zone (Figure 2.15),

The water samples from the water monitoring wells located within the main mineralization zone, exhibit very similar water chemistry with the springs from the mining area. The springs in the main zone is most likely to be the discharge point of local shallow aquifers (Ekobil, 2005).

The quality of groundwater from deep limestone aquifer is classified as drinkable, based on Turkish Ministry of Health standards, Since this ground water is not in contact with the sulfide ore body. However, the quality of groundwater in the mining zone is relatively low in quality compared to others in the study area and is classified to be not drinkable. Because, the mineralization in the main zone increases metal concentrations of the groundwater. As a result, trace metal concentrations of the groundwater (such as As, Hg, Fe, and Mn and Ni) exceed the permitted mean concentration levels, As levels being as high as 246.9 ppm at the spring SP07 (Ekobil, 2005). As mentioned above this can as well be attributable to an ongoing acid mine drainage.

During the comparison of the major ion chemistry of the groundwater, through the dry and wet seasons no significant change was observed in the groundwater chemistry, indicating that the aquifer systems are in equilibrium in the Çöpler area (Ekobil, 2005).

Regarding that the water from the deep limestone aquifer is not contaminated by the presence of the ore body in Çöpler, it is important to assess the risk of contamination of the waters from this aquifer, in the proposed mining area. Therefore, understanding the link between local and deep aquifer systems is essential. The extent of a potential contamination is dependent on the thickness and the size of the intrusion beneath the mining area and on the depth of the fracture systems (Ekobil, 2005). The detailed investigation of these hydrogeological links needs to be considered by the mine operators.

It was observed that the groundwater sampled from WMR-03 and WMR-04 wells have relatively higher zinc concentrations compared to springs at Gözeler. This situation was especially pronounced during the spring sampling event. The zinc

concentration in the waters sampled from the mining area is significantly high. Therefore this is considered to be a possible indication of a mixing between local and deep aquifer systems. No such evidence of a signature of comparable mixing is noticed in the zinc concentrations of Gözeler springs, which are the main discharge point of deep limestone aquifer. This can be attributed to a dilution effect or it may also be possible that the groundwater discharging through Gözeler follows a different flow path than those that flow through WMR-03 and WMR-04. In order to reveal the flow path and the possibility of an interaction between the two aquifers can be proved by further in depth studies, however this risk needs to be considered in management and planning of mining activities (Ekobil, 2005).

Along the tectonic contact of formation boundaries (such as the contact of meta-sedimentary unit and Munzur Limestone and the contact of Çöpler Granitoid with Meta-sedimentary Unit and Munzur Limestone) and along the faults surrounding Çöpler Prospect there are several springs and seeps. In general these springs are observed to be at the tectonic contact or along the fault lines and in the main drainages in the mining site. As clearly marked by their chemical compositions, a number of these springs discharge via limestones while others discharges via the altered meta-sediment/intrusive zones. Varying seasonally, the discharge rate of these springs reach to a maximum during the spring period as a result of snow melt (Ekobil, 2005).

In the study area, the unique water source is the springs. Some of these springs serve as the drinking water and basic household water supply of the Çöpler village. Other springs serve mostly to irrigation purpose and used to water the livestock. Çöpler village obtain its drinking water from a karstic spring near Karabaş Church, although this spring itself is insufficient to meet the drinking water requirements of Çöpler, especially during the dry winter and summer periods when the precipitation is lacking (Ekobil, 2005).

### **2.3.9.3 Surface Waters**

Karasu River that bound the study area from its North is a major branch of Euprates and is the largest surface water body. On the down stream direction this water body flows towards Keban (848 m amsl), Karakaya (698 m amsl), Atatürk (549 m amsl),

Birecik (389 m amsl) and Karkamış Dams (344 m amsl). Based on EİE's past 32 years of data, average flow rate of Karasu River was recorded to be 150 m<sup>3</sup>/s, with the highest flow rate recorded in this period was 1320 m<sup>3</sup>/s on the thirteenth of May 1969. The lowest recorded flow rate was during the same data period was 43.8 m<sup>3</sup>/s on the ninth of January 1974. In general, peak flows in the Karasu River occur in April or May in response to precipitation and snow melt. Very rarely, peak flows (~400 m<sup>3</sup>/s) also be observed in December and June (Ekobil, 2005).

Using the EİE data, the flood recurrence analysis for the Karasu River revealed flow rates of 25, 50 and 100-year floods as 1219 m<sup>3</sup>/s, 1406 m<sup>3</sup>/s, 1592 m<sup>3</sup>/s, respectively. Recurrence interval of the highest flow rate recorded during the past 32 years period is estimated to be 36 years (Ekobil, 2005).

Due to the dry summers and winters other ephemeral rivers in the study area such as the Sabırlı and Çöpler streams do not exhibit any significant runoff except for March to June period. The flow that occur during that spring-early summer period is dependent and reflection of the precipitation and snowmelt during the spring. Sabırlı river flows along a major fault line, whereas, the flow in the Çöpler stream usually disappears underground along its flow path due to the highly porous nature of the streambed. The major surface waters including ephemeral rivers and rivulets in the study area are given in Figure 2.17 (Ekobil, 2005).

The Karasu River is the largest branch of Euphrates and it is already receiving contaminated mine waters from the Divriği Iron Mine. Both the contamination via the Divriği iron mine and the surface runoff that washes the Çöpler ore body and flows to Karasu River are in the upstream direction of most of the Turkey's major hydroelectricity producing dams such as Keban, Karakaya, Atatürk, Birecik and Karkamış Dams. Therefore it is very important to manage the mining operations in order to avoid acid mine drainage and its potential damage to these mega structures.

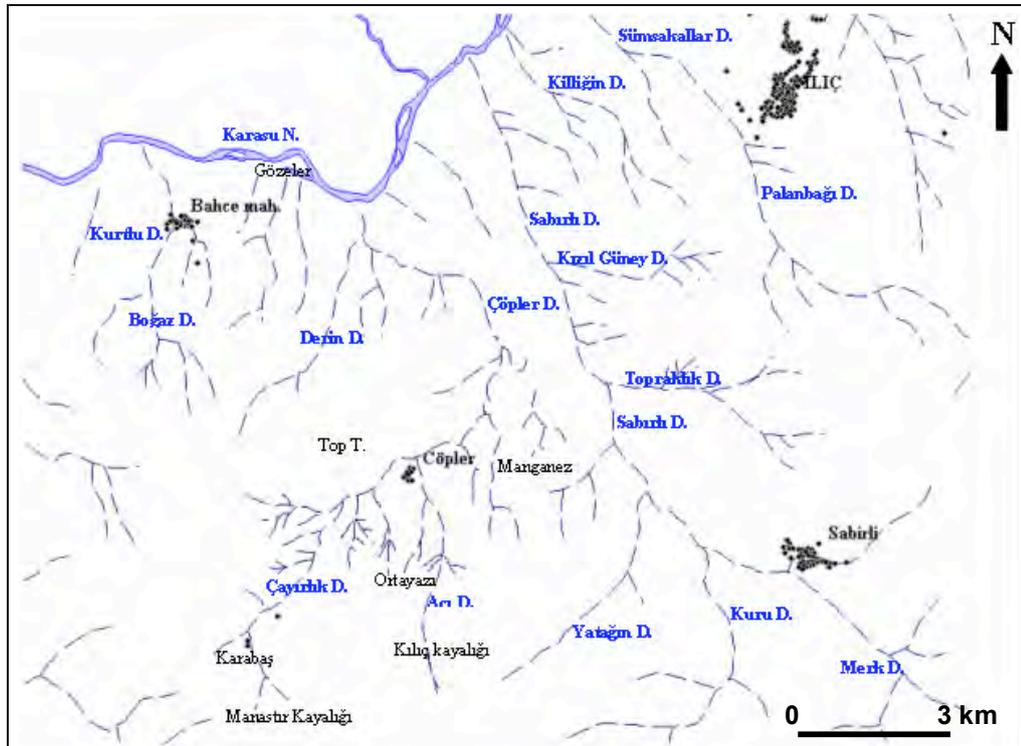


Figure 2.17 Major drainage networks in the vicinity of the study area (N:River; D:Rivulet) (After Ekobil, 2005).

## CHAPTER 3

### MATERIALS AND METHODS

#### 3.1 Sampling Scheme

In this study the author paid attention to represent all the lithologies observed in the study area during the sampling. All the samples are fresh core samples obtained through the exploration-drilling scheme of the Çöpler gold mining project. The list of samples, their coordinates and the depth intervals that they were taken are given in Appendix-A. Throughout the study the samples are mentioned using their drilling code and depth interval. When ever necessary the mining/mineralization zone is also mentioned. Within the sampling code terminology the abbreviations used are given in the following table (Table 3.1).

Table 3.1 Abbreviations used in the coding terminology of the studied samples.

Code	Explanation
CDD	Çöpler Diamond Drill
CRC	Çöpler Rock Cuttings
CRD	Çöpler Diamond Drill and Rock Cutting (A drill hole started as Rock cutting turned into diamond drill or vice a versa)
RMH	Rock Mechanics and Acid Mine Drainage study drill hole

In order to evaluate the Acid Mine Drainage potential of different lithologies, 26-diamond core (Figure 3.1) and 12 rock-cutting composite samples were collected from the study area.

The three diamond drill holes that were drilled for the Rock Mechanics testing also served for the AMD intact sample collection purpose. Two of the drill holes were

located in the Main Mineralization Zone, and one was located in the Marble zone. These drill holes targeted to sample the major lithologies in the study area, namely the Marble in RMH-01, Metasediments and diorite in drill holes RMH-02 and RMH-03. In addition to these 24 systematic diamond drill samples, 10 composite rock-cutting samples were collected during the exploration stage from the Manganese Mine Zone. In addition, to these two diamond drill core samples from the Marble lithology, and 2 composite samples from marble/limestone boundary were evaluated. In total there are 38 samples representative of all lithologies, transitions, and different mineralization zones (Table 3.2).



Figure 3.1 Acid Mine Drainage Core Sampling

Core samples were sealed as soon as they were taken from the holes to prevent oxidation. Later a batch of about 400 g was dried under low heat conditions (<40°C) overnight to get rid of excess moisture. The moisture content of each sample was noted. Samples were ground to 400 Mesh size and reserved in airtight plastic containers to be analyzed for Acid Base Accounting.

There are five marble core samples from the “Marble Contact Zone”, two core samples from the “Manganese Mine Zone”. In addition, there are another one limestone and four marble composite rock-cutting samples again from the “Manganese Mine Zone”.

From the main zone, there are nineteen diamond drill samples, nine of which are diorites, and nine of which are meta-sedimentary rocks and there is one sample that represents the metasediment-diorite contact.

Other seven composite rock-cutting samples are taken from the Manganese mine zone, seven of these are from the diorite lithology and two of them are from carbonate lithologies (limestone and marble). The well codes, sampling depths and lithologies of the collected samples and the lithologic properties of these samples are summarized in Table 3.2. Most of the locations of the collected samples are also given in Figure 3.2.

Table 3.2 The well codes, sampling depth and lithologies of the collected samples and their lithologic properties RMH: Rock Mechanics Holes, CRC: Çöpler Rock Cuttings Drill Hole; CDD Çöpler Diamond Drill Hole (Refer to Appendix-A for more detail)

<b>Number</b>	<b>Well Code and meters :</b>	<b>LITHOLOGY</b>	<b>MINERALIZATION ZONE</b>	
1	RMH01;0-0.10	Marble	Marble Zone	
2	RMH01;0.17-0.30			
3	RMH01;1.50-1.77			
4	RMH01;4.50-4.62			
5	RMH01;30.4-30.55			
6	RMH02;0.5-0.65	Metasediment	Main Zone	
7	RMH02;1.6-1.72			
8	RMH02;4.38-4.50			
9	RMH02;11.1-11.2			
10	RMH02;13.9-14.0			
11	RMH02;14.5-15.1			
12	RMH02;19.4-19.6			
13	RMH02;25.3-25.5			Metasediment+Diorite
14	RMH02;29.25-29.35			Diorite
15	RMH02;30.75-30.90			Metasediment
16	RMH02;32.45-32.55			Diorite
17	RMH03;0.85-1.05			
18	RMH03;1.85-1.95			
19	RMH03;15.1-15.3			
20	RMH03;21.75-21.95			
21	RMH03;25.20-25.33			
22	RMH03;26.80-27.00			
23	RMH03;32.0-32.1			
24	RMH03;35.0-35.2			
25	CRC246;0-128	Limestone	Manganese Mine Zone	
26	CRC246;128-139	Diorite		
27	CRC247;0-163	Marble		
28	CRC248;0-157			
29	CRC 255;44-75	Diorite		
30	CRC 255;96-115			
31	CRC 257; 42-115			
32	CRC270; 108-205			
33	CRC271; 78-100			
34	CRC280; 80-165			
35	CDD98;51.7-51.8	Marble		
36	CDD91; 294.0-295.7			
37	CRC388; 69-119			
38	CRC391; 0-197			

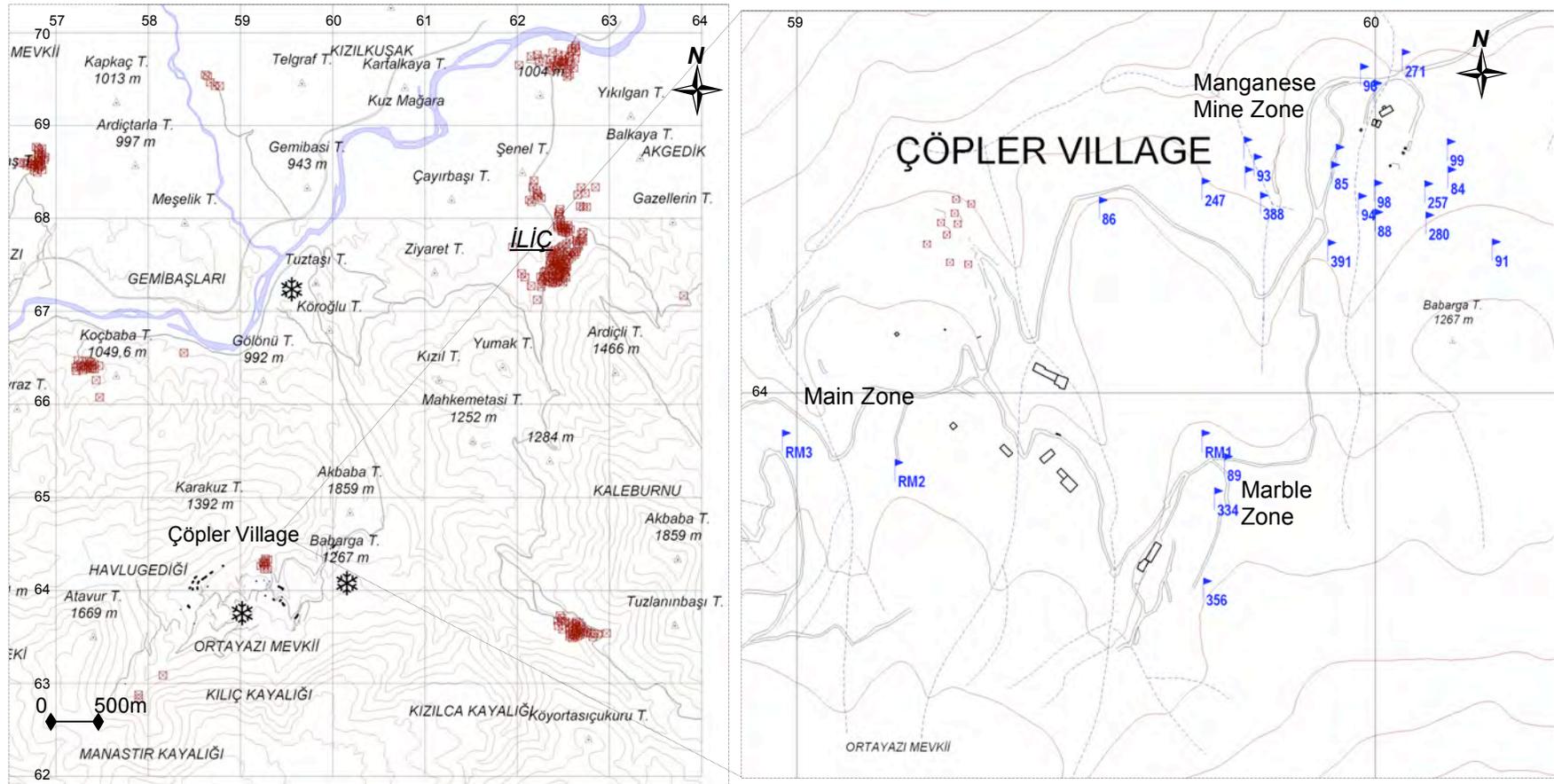


Figure 3.2 Drill locations for samples collected for Acid Base Accounting (ABA), geochemical and mineralogical tests. Well numbers are indicated for most of the samples, in each well for details of the samples, refer to Appendix-A.

In addition to the samples collected and analyzed for Acid Base Accounting, some samples that are not analyzed for ABA were added to the sample characterization studies for major element and trace element geochemistry, thin section and polished section petrography and X-ray Diffraction analysis. In total 54 samples were dealt with in this study. The summary of the tests applied is given in Table 3.3. Which analysis is applied on which sample is given in Appendix-A.

Table 3.3 Summary of the tests applied to the total 54 samples that were dealt with in the study.

	<b>Test Applied</b>	<b>Number of Samples</b>
Sample characterization-mineralogy and geochemistry	Major and Trace Element Geochemistry	17
	Thin Section	14
	Polished Section	4
	XRD	7
AMD Potential determinations: Acid Base Accounting	Paste pH	38
	CO <sub>2</sub>	6
	Total Sulfur	38
	Sulphate Sulfur	29
	Maximum Potential Acidity	38
	Neutralization Potential	38
	Fizz Rating	38

## 3.2 Methods Used

The methods used for the characterization of the samples and determination of the acid mine drainage potential are given below.

### 3.2.1 Mineralogy and Petrography

Petrographic studies were conducted to determine primary and secondary mineralogy and alteration variations

For the mineralogical studies in addition to petrographic thin section investigations, ore microscopic studies and X-ray diffraction (XRD) analysis were also used for the identification of minerals in the samples.

For Petrographic analysis Nikon Lbaphot pol. Type 104 microscope, available in METU Department of Geological Engineering, for ore microscopy Leica DMLP polarized and reflective microscope and for X-Ray Diffraction Rigacu D-Max III TC X-Ray Diffractogram were used. The ore microscopy and X-Ray diffraction studies were performed in General Directorate of the Mineral Research and Exploration.

In order to obtain the basal reflections of clay minerals, oriented samples were prepared. Clay fraction of the samples have been concentrated by sedimenting the samples in a water column for approximately 4 h 15 m at 20°C (determined based on the Stoke's Law), and first 5 cm is piped after that to obtain the less than 2 µm sized particles that are in suspension (Tanner and Jackson, 1947). A small amount of Natrium Pyrophosphate is added during this process to avoid flocculation. Subsequently the clay fraction is precipitated by centrifugation at 6000 rpm for 15 minutes and smeared on glass slides. These slides are prepared in quadruples. First is allowed to air dry, second is ethylene glycolated in a desiccator filled with ethylene glycol and placed in an oven at about 60°C overnight, the third and the fourth are placed in a furnace at 300°C and 500°C, respectively for one hour. These slides have been X-Rayed hereafter immediately (Jackson, 1975).

Also unoriented mounts have been prepared by placing them into an aluminum holder, in order to determine especially the non clay mineral content of the samples. Later the x-ray diffraction patterns are obtained and studied to determine the mineralogical composition of the samples.

Cu K $\alpha$  radiation with a Ni Filter, at 30 kV, 24 mA, with a slit aperture of 0.2, at a speed of 0.05° per second is used for the determination of diffraction patterns of both oriented and unoriented samples. The 2 $\theta$  range for oriented samples was 2° to 30°, and range for un-oriented samples was between 2° to 40°.

### **3.2.2 Geochemistry**

Major and trace element geochemistry data were obtained through the mine's exploration studies. The samples were analyzed in ALS Chemex Laboratories. Samples were analyzed via inductively coupled plasma emission spectrography (ICP-ES) delivering concentrations for 27 different elements. Sample solutions are aspirated into a plasma operating at 8000 °K. Light emitted by excited atoms returning to the ground state is split into its spectral wavelengths by an Eschelle grating. The intensities of the various wavelengths are measured by ICP-ES. Linear range is five orders of magnitude with detection limits in the ppm to ppb level (Downing *et al.*, 2001) (Geochemical data are given in Appendix-B).

In addition to the 27 elements analyzed via ICP-ES, gold was analyzed using Atomic Absorption Spectroscopy in the same laboratory.

### **3.2.3 Acid Base Accounting**

ABA is based on the premise that the propensity for a site to produce acid mine drainage can be predicted by quantitatively determining the total amount of acidity and alkalinity that the strata on a site can potentially produce (Mills, 1995).

#### **3.2.3.1 Components of ABA**

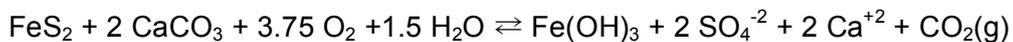
The maximum potential acidity (MPA) (expressed as a negative) and total potential alkalinity (termed neutralization potential) (NP) are summed. If the result is positive, the site should produce alkaline water, if it is negative, the site should produce acidic water. Later the results of the Net Neutralization Potential are calculated by subtracting the Maximum Potential Acidity from Neutralization Potential or the Neutralization Potential Ratio (NPR). NPR is calculated as a the ratio of Neutralization Potential over Maximum Potential Acidity and compared to the criteria provided by the acknowledged literature.

The standard and accepted ABA suit consists of determination of the: Fizz Rating, paste pH, total sulfur and sulfate sulfur, Neutralization Potential and calculation of Maximum Potential Acidity and Net Neutralization Potential or Neutralization

Potential Ratio (Details provided in Appendix-C). However, the two major components of ABA are Maximum Potential Acidity and Neutralization Potential.

### **3.2.3.1.1 The Maximum Potential Acidity (MPA)**

The maximum potential acidity (MPA) is stoichiometrically calculated from the percent sulfur in the lithology. The appropriate calculation factor is somewhat controversial. Sobek et al. (1978), noting that 3.125 g of CaCO<sub>3</sub> is theoretically capable of neutralizing the acid produced from 1 g of S (in the form of FeS<sub>2</sub>), suggested that the amount of potential acidity in 1000 tons of overburden could be calculated by multiplying the percent S times 31.25. This factor is derived from the stoichiometric relationships in the following equation and carries the assumption that the CO<sub>2</sub> exsolves as a gas.



Cravotta *et al.*, (1990) suggested that, in backfills where CO<sub>2</sub> cannot readily exsolve, the CO<sub>2</sub> dissolves and reacts with water to form carbonic acid and that the maximum potential acidity in 1000 tons of overburden should then be derived by multiplying the percent S times 62.50.

The approach by Sobek et al. (1978), as to take the 31.25 factor to determine the MPA is generally and more widely accepted. This was the factor utilized in MPA calculations.

Determination of the total sulfur is essential for the calculation of the MPA. If the sample contains significant amounts of sulfate, depending on the characteristics of the samples, sulfate content is subtracted from the total sulfur amount and the %sulfide is used in the calculations to determine MPA.

Total sulfur is determined via analysis by infrared adsorption using a Leco C244 Carbon-Sulfur analyzer. After precise weighing, induction flux is added and the sample is ignited at >1650°C in an induction furnace. A carrier gas sweeps up released carbon and sulfur to be measured by adsorption in an infrared spectrometric cell. Results are total and attributed to the presence of carbon and sulfur in all forms details of the analytic procedure is provided in Appendix-C.

For sulphate-sulfur analysis, 5 g of pulverized sample is treated with 20 mL of 3 N hydrochloric acid in a beaker. The beaker is covered with a watch glass and heated to a boil. The sample is allowed to cool and is made up to a final volume of 100 mL. The clear supernatant is then submitted for sulphate analysis by the turbidimetric method. The results are expressed in percent sulphate-sulfur. Details of sulphate sulfur determination procedure are given in Appendix-C.

### **3.2.3.1.2 The neutralization potential (NP)**

The neutralization potential (NP) is determined by digesting a portion of the prepared sample in hot acid, and then by titrating with a base to determine how much of the acid the sample consumed. NP represents carbonates and other acid neutralizers and is commonly expressed in terms of tons CaCO<sub>3</sub> per 1000 tons of overburden (ppt). Negative NP values are possible, and are sometimes derived from samples of weathered rock that contain residual weathering products that produce acidity upon dissolution.

Neutralization Potential is determined by in general by Modified EPA method, (Sobek *et al.*, 1978) that is also referred to as “modified NP Lawrence method”. The details of the method are provided in Appendix-C.

In determining neutralization potential, considering calcite as the major neutralizer, in order to determine the full neutralization capacity also carbonate carbon is taken into account.

In order to determine the total amount of carbonaceous carbon, the pre-treated sample in a bottle is attached to the Leco 244 Carbon and Sulfur Analyzer via the stopcocks. The stopcocks are opened and the CO<sub>2</sub> gas is swept into the analyzer with an O<sub>2</sub> carrier gas. The instrument determines the CO<sub>2</sub> as total carbon, which is then calculated to total CO<sub>2</sub>. The details of the method are provided in Appendix-C.

## **3.3 The Road Map Followed in the Case Study**

Figure 3.3 is a flow chart that summarizes the methods utilized and explained above in the course of this case study and other potential methods or issues that are necessary to know for different circumstances.

This flow chart can be considered as a road map that may be utilized for the evaluation of acid mine drainage production potential of a mining site.

The chart is color-coded. The sample preparation stage is represented in green. The studies involving sample characterization are given in purple. The ABA tests are given in blue and their interpretation criteria are given in peach color. The boxes and arrows involving mixed colors are utilized to represent the transition between these stages.

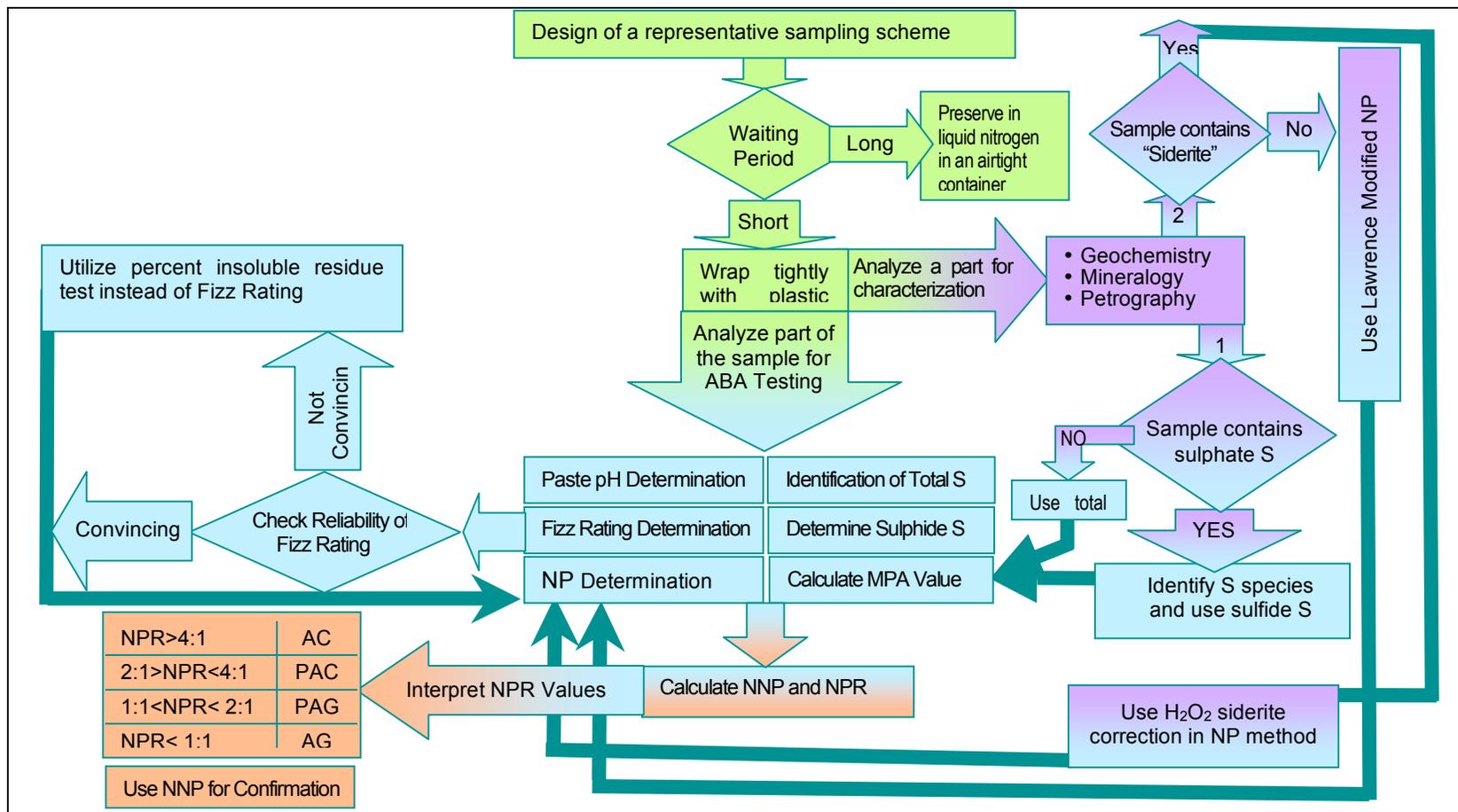


Figure 3.3 Flow Chart Summarizing Acid Base Accounting procedures and critical issues to be considered.

### **3.4 ABA Tests Applied in the Study**

In this study, the following ABA tests were applied on the collected samples: Fizz Rating, Neutralization Potential, Maximum Potential Acidity, Net Neutralization Potential, Paste pH and Sulfate Determinations. Over selected carbonate rock samples Carbonate Carbon determinations were also performed. All the tests are performed in VIZON SCITEC Laboratories, which is an accredited laboratory that uses CANMET ABA Standards for quality control assurance. The detailed procedures about ABA tests are provided in the Appendix-C.

In addition to that, the following table presents a summary of the ABA tests applied over each sample (Table 3.4). As can be seen in Table 3.4 sulfate sulfur content is not tested over samples such as marbles and limestones, since these samples are not expected to contain sulfur. Carbonate carbon testing only applied to marbles and limestone samples, considering not only carbonates are present in particularly meta-sedimentary lithologies but also other silicate and clay minerals that are potential neutralizers.

Table 3.4 A summary of the ABA tests applied over each sample collected for AMD prediction. (MetaS: metasediments; Drt.: diorite; NP: Neutralization Potential; MPA: Maximum Potential Acidity; NNP: Net Neutralization Potential, CO<sub>2</sub>CD: Carbonate carbon determination, SO<sub>4</sub>SD, sulfate sulfur determination).

Number	Well Code and meter	LITHOLOGY	ZONE	TEST APPLIED			
				NP, MPA, NNP, paste pH and fizz rating	CO <sub>2</sub> CD	SO <sub>4</sub> SD	
1	RMH01;0-0.10	Marble	Marble	✓	✓	-	
2	RMH01;0.17-0.30			✓	✓	-	
3	RMH01;1.50-1.77			✓	✓	-	
4	RMH01;4.50-4.62			✓	✓	-	
5	RMH01;30.4-30.55			✓	✓	-	
6	RMH02;0.5-0.65	MetaS	Main	✓		✓	
7	RMH02;1.6-1.72			✓		✓	
8	RMH02;4.38-4.50			✓		-	
9	RMH02;11.1-11.2			✓		✓	
10	RMH02;13.9-14.0			✓		✓	
11	RMH02;14.5-15.1			✓		✓	
12	RMH02;19.4-19.6			✓		✓	
13	RMH02;25.3-25.5			MetaS+Drt.	✓		✓
14	RMH02;29.25-29.35			Diorite	✓		✓
15	RMH02;30.75-30.90			MetaS	✓		✓
16	RMH02;32.45-32.55				✓		✓
17	RMH03;0.85-1.05	Diorite	Main	✓		✓	
18	RMH03;1.85-1.95			✓		✓	
19	RMH03;15.1-15.3			✓		✓	
20	RMH03;21.75-21.95			✓		✓	
21	RMH03;25.20-25.33			✓		✓	
22	RMH03;26.80-27.00			✓		✓	
23	RMH03;32.0-32.1			✓		✓	
24	RMH03;35.0-35.2			✓		✓	
25	CRC246;0-128	Limestone	Manganese Mine	✓	✓	-	
26	CRC246;128-139	Diorite		✓		✓	
27	CRC247;0-163	Marble		✓		-	
28	CRC248;0-157	Marble		✓		-	
29	CRC 255;44-75	Diorite		✓		✓	
30	CRC 255; 96-115	Diorite		✓		✓	
31	CRC 257; 42-115	Diorite		✓		✓	
32	CRC270; 108-205	Diorite		✓		✓	
33	CRC271; 78-100	Diorite		✓		✓	
34	CRC280; 80-165	Diorite		✓		✓	
35	CDD98; 51.7-51.8	Marble		✓			
36	CDD91; 294.0-295.7	Marble		✓			
37	CRC388; 69-119	Marble		✓			
38	CRC391; 0-197	Marble		✓			

### 3.5 Accuracy, Quality Control and Assurance in ABA tests

Selected duplicate results and internal laboratory standards, and CANMET standards were used to compare the obtained test results. The properties of the CANMET standard NBM-1 is given in Appendix-C and other in-house standards used by the laboratory and the comparative results of the duplicates are given in Table 3.5.

As indicated in Table 3.5 the accuracy of the results ranges from 91% to 100 %.

Table 3.5 Quality Control and Accuracy test indicators for ABA tests results.

<b>QA/QC for NP Determination (Modified ABA NP Method)</b>			
<b>Sample</b>	<b>NP<sub>First Run</sub> (kgCaCO<sub>3</sub>/Tone)</b>	<b>NP<sub>Second Run</sub> (kgCaCO<sub>3</sub>/Tone)</b>	<b>% Accuracy<sup>8</sup></b>
<b>Duplicates - NP</b>			
RMH02; 14.50-15.10	-14.8	-14.3	99.50
RMH02; 30.75-30.90	92.8	92.3	99.50
RMH03; 1.85-1.95	0.3	0.5	99.80
CRC 248; 0-157	903.0	894.0	91.00
NBM-1 Reference (NP = 46.6)	42.6	-	96.00
<b>QA/QC for Sulfur Speciation</b>			
<b>Sample</b>	<b>Sulfur (Wt.%)</b>	<b>Sulfur (Wt.%)</b>	
<b>Total Sulfur</b>			
RMH03; 1.85-1.95	0.75	0.78	99.97
CRC 246; 0-128	0.07	0.07	100.00
CRC 248; 0-157	<0.02	<0.02	100.00
CRC 280; 80-165	5.19	4.83	99.64
In-house Ref. (0.11% TS)	0.12	0.13	99.99
Std. CSB (5.3% TS)	5.29	5.3	99.99
<b>Sulphate-sulfur</b>			
RMH03; 32.00-32.10	0.04	0.02	99.98
In-house Ref. (0.27% SO <sub>4</sub> -S)	0.27	-	100.00
<b>QA/QC for CO<sub>2</sub> Determination</b>			
<b>Sample</b>	<b>CO<sub>2</sub> (Wt.%)</b>	<b>CO<sub>2</sub> (Wt.%)</b>	
CRC 246; 0-128	43.9	43.5	99.60
Std. CSB (1.50% CO <sub>2</sub> )	1.47	-	99.97

<sup>8</sup> Accuracy is calculated based on repeatability of the result or compared to reference material's result.

## CHAPTER 4

### RESULTS

#### 4.1 Mineralogy

The results of the polarized light and ore microscopic studies are summarized in the following sections.

##### 4.1.1 Polarized light Microscopy

As indicated in detail in the Geology section, there are four main lithologies in the study area. Thin sections representing these lithologies are selected to investigate these lithologies under polarized microscopy and the findings are summarized below:

##### 4.1.1.1 Mineralogy of the Metasedimentary Unit

The oldest lithology is the metasediment, which is not regionally correlated. The samples that represent the metasedimentary units exhibit very fine grained clayey, banded, slightly folded or boudinaged micro structures (Figure 4.1).



Figure 4.1 Fine clayey textures with boudinage like microstructures of a Metasedimentary rock sample (RMH02; 32.45-32.55) (Magnification 45X)

There are also secondary microstructures such as veins filled with chalcedony and pores that appear to be indications of fallen or lost rock fragments. Although it is possible to recognize rock fragments, in thin sections it is not possible to identify fossils. The sand and fine gravel sized grains recognized in these sections are generally sub angular to rounded (Figure 4.2). In the thin sections of the metasedimentary lithology it is possible to observe the clay as a matrix (Figure 4.2) or as the entire body of the rock with folded or boudinaged microstructures (Figure 4.1).

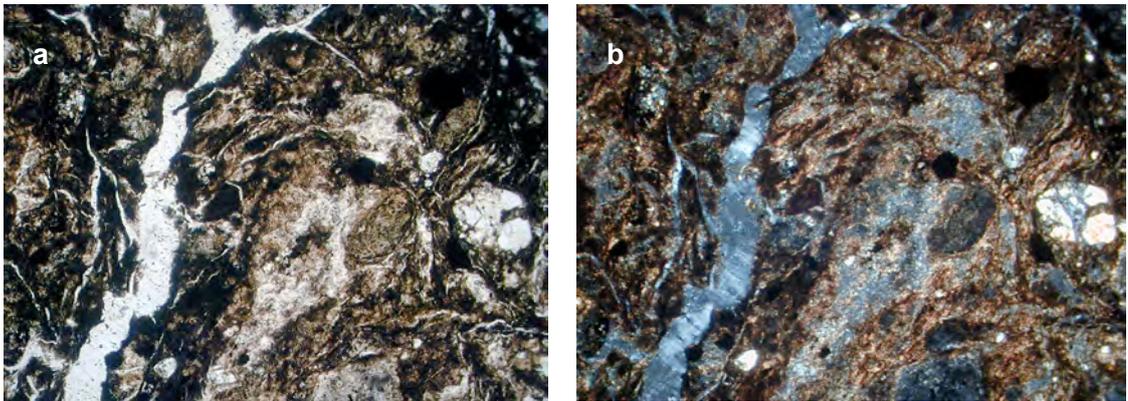


Figure 4.2 Metasedimentary lithology that exhibit major chalcedony veins, rock fragments and fine-grained clayey minerals. a: single nicole, b: cross nicole, magnification 45X (Sample from CDD334).

The thin sections of the metasedimentary lithology also show the evidences of metamorphism by the small veinlets that indicate cataclastic activity (Figure 4.3).

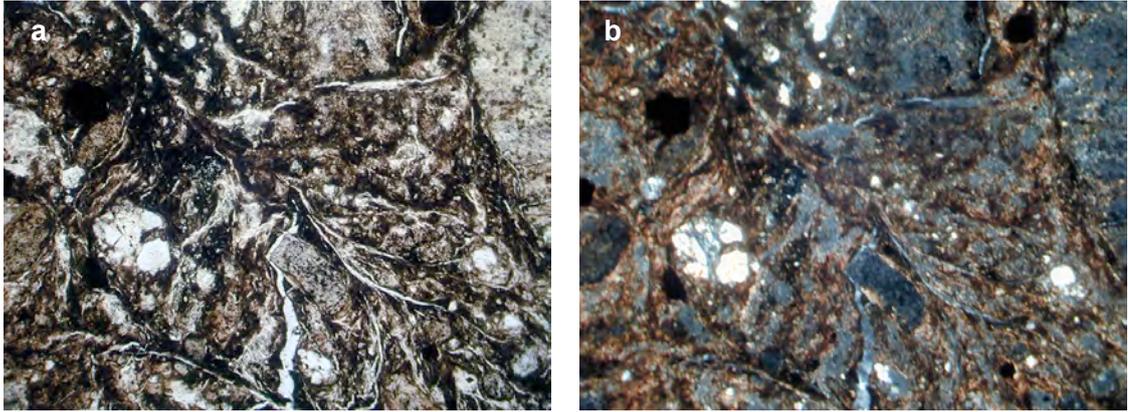


Figure 4.3 The thin section of the metasedimentary lithology that show rock fragments and small veinlets that indicate cataclastic activity; a: single nicole, b: cross nicole (Sample from CDD334) (magnification 100X).

The thin sections of the metasedimentary unit also exhibit alterations such as epidotization and kaolinitization (Figure 4.4).

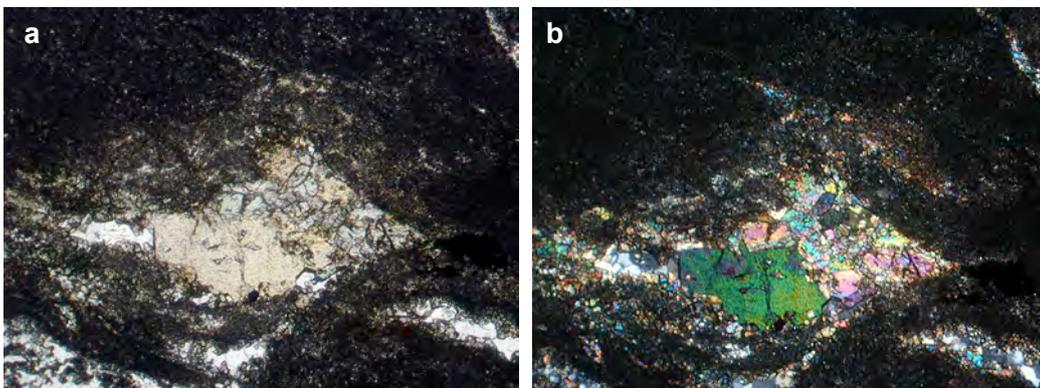


Figure 4.4 Metasedimentary rock sample (RMH02; 32.45-32.55) exhibiting epidotization, a: single nicole, b: cross nicole (magnification 100X).

Due to the grain size and disturbed nature of the metasedimentary unit sulfide minerals that may have acid production potential were not identified in the thin sections. However the secondary calcite minerals that fill the veins and veinlets and

to some extent the clay minerals that constitute the matrix and in some parts the majority of the metasedimentary lithology can be considered as neutralising minerals in case of an acid production. The ABA test results of the metasedimentary rock sample (RMH02; 32.45-32.55) are also matching these mineralogical findings.

#### 4.1.1.2 Mineralogy of the Munzur Limestone

Munzur Limestone, which is the most extensive lithology in the study area is represented by limestones and marbles (Figure 4.5.). The calcite grains in the marble sample are large enough to be recognized on an hand specimen. The shapes of the calcite crystals are euhedral to subhedral due to secondary hydrothermal activities.

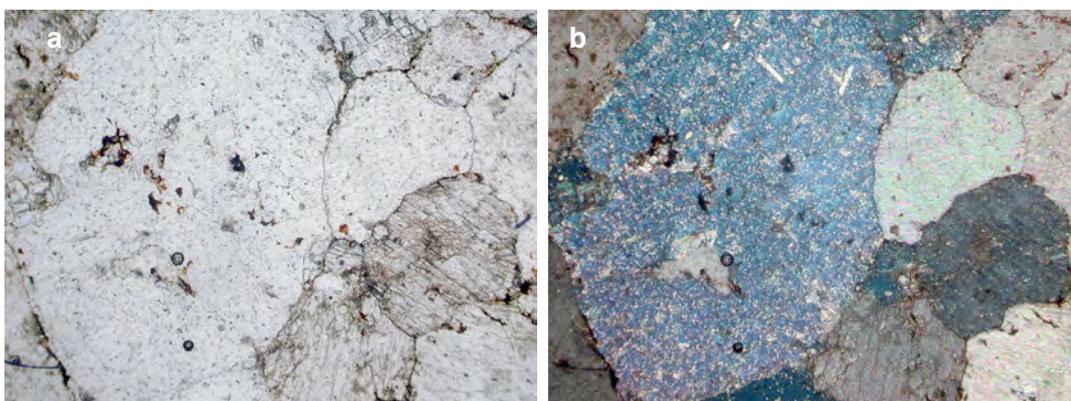


Figure 4.5 Microscopic view of a Marble sample (CDD-98;51.7-51.9) with large euhedral to subhedral calcite crystals, a: single nicole, b: cross nicole (Magnification 45X)

The hydrothermal activities also lead to the formation of veins that are lined by iron oxides, or that are filled by recrystallized calcite (Figure 4.6). The limestones are differentiated from marbles by their smaller grain size. In the thin sections, however, it was not possible to observe micritic or fossiliferous parts of the Munzur Limestone. The thin sections studied were not intended to identify the lithologies and facies described for Munzur Limestone but to help identify the mineralogy of the ABA tested samples. These thin sections revealed different grain sizes of the calcite minerals that constitute the Munzur Limestone. However during the sample

preparation for ABA tests the samples were pulverized, and thus the grain size of calcite minerals have no significant effect on the ABA test results. However in evaluating an acidic contamination circulating via Munzur limestone the grain size differences and presence of fractures and cavities may effect the final chemistry of the circulating water.

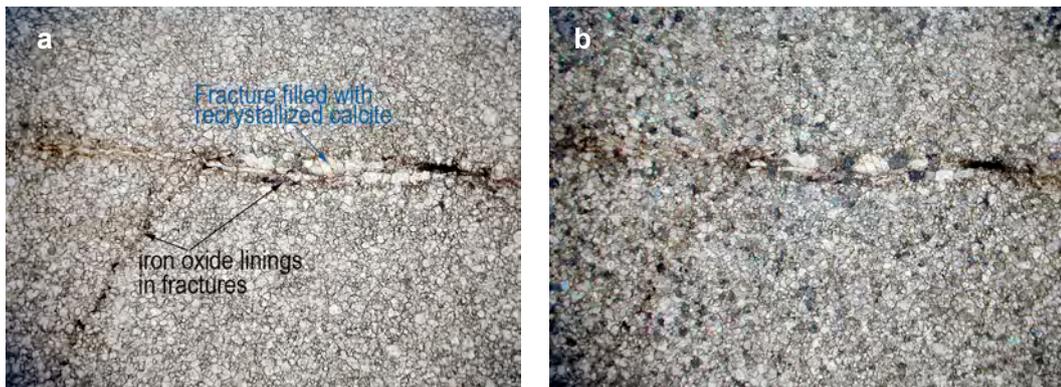


Figure 4.6 A Limestone sample (CDD 91) exhibiting fractures lined with iron oxides and filled with recrystallized calcite, a: single nicole, b: cross nicole. (Magnification 45X).

As shown in Figure 4.7, it is also possible to identify large pores and cavities in marbles and limestones. These cavities and fractures increase the permeability of the Munzur Limestone and is the microscopic evidence of its karstic nature.

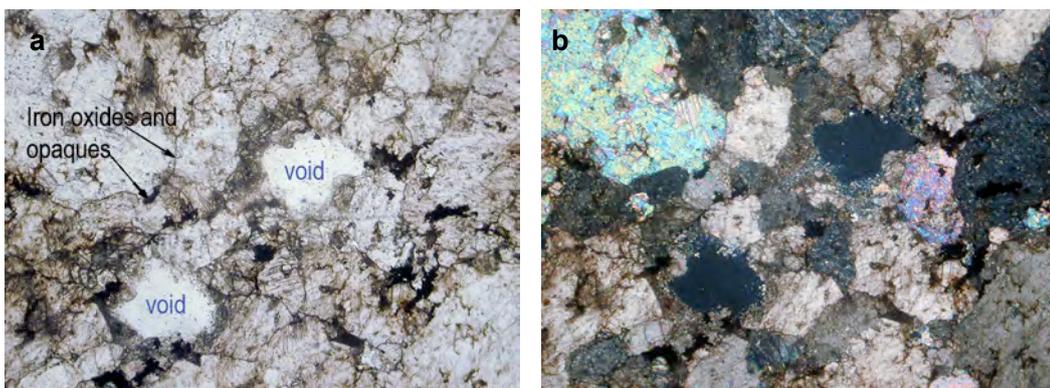


Figure 4.7 Karstic voids and mineral boundaries lined with iron oxides in marbles, , a: single nicole, b: cross nicole. (Sample CDD-98; 13m). (Magnification 45X).

### 4.1.1.3 Mineralogy of the Çöpler Granitoid

The porphyritic texture of the Çöpler Granitoid that is a dioritic intrusion is clearly visible in thin section (Figure 4.8).

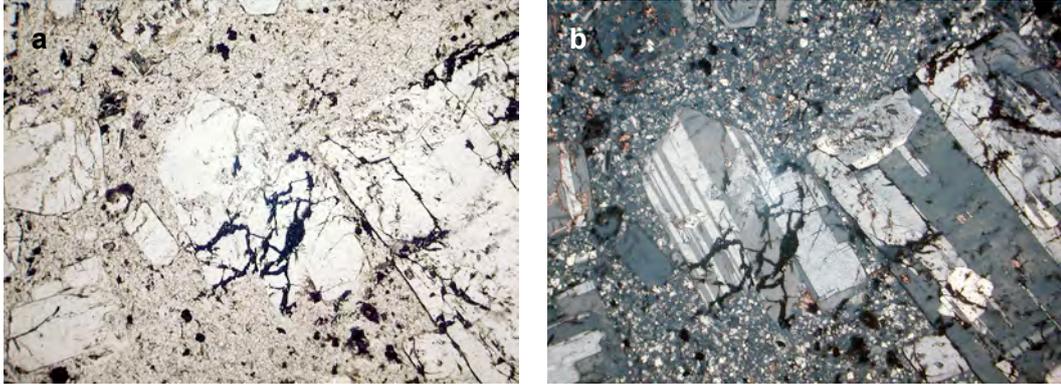


Figure 4.8 A sample (CDD-85) from Çöpler Granitoid exhibiting porphyritic texture with very fine grained silica matrix and highly deformed feldspar crystals, a: single nicole, b: cross nicole (Magnification 45X).

The feldspar phenocrysts are euhedral to subhedral in shape. However, these phenocrysts also exhibit traces of intense deformation, in the form of parting. The space occurred after parting is usually filled with opaque very fine grained or unhedral minerals. The matrix of the dioritic lithology is made up of very fine grained silica. The highly deformed feldspar and ferromagnesian phenocrysts do also display epidotic replacements, and intense kaolinitization along their parting (Figure 4.9).

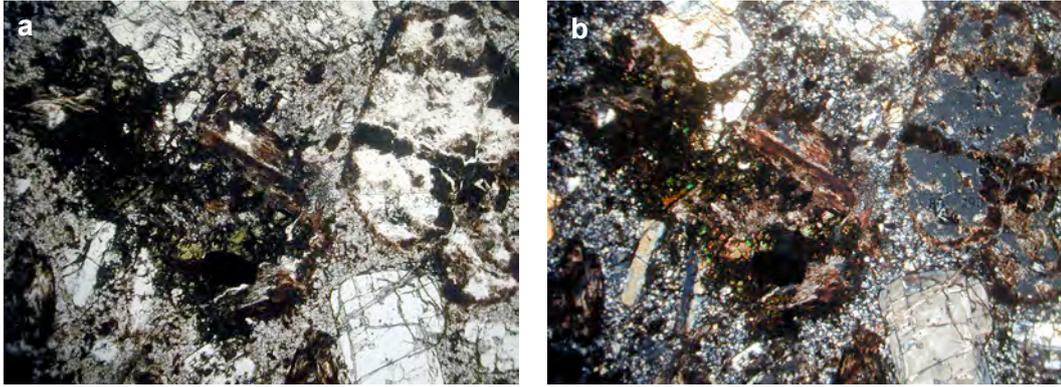


Figure 4.9 A Sample (CDD-99) from Dioritic Çöpler Granitoid exhibiting Phenocrysts with sericitization, opaques, kaolinitization, feldspath and ferromagnesian phenocrysts in a micro-silica matrix; a: single nicole, b: cross nicole. Magnification 45x.

The Çöpler Granitoid is observed to be highly deformed especially along the faults and along its contact with other lithologies in the study area such as the metasedimentary unit and the Munzur Limestone. The observed alteration is accelerated by hydrothermal fluids. The major alteration products are the opaque minerals, hematite formation, silisification, and argillization. However, it was also possible to recognize other alteration products such as saursoritization and calcitization in the thin section examinations (Figure 4.10).

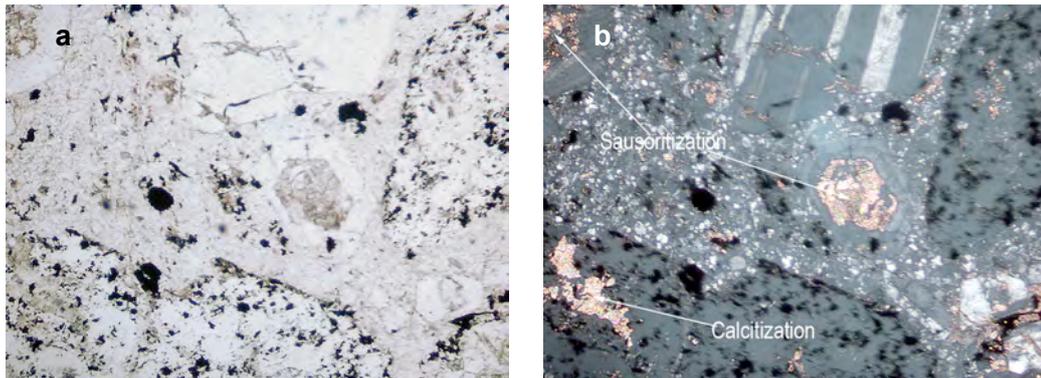


Figure 4.10 Plagioclase phenocrysts with saursoritization and calcitization (from CDD-84); a: single nicole, b: cross nicole. Magnification 45X.

### 4.1.2 Ore Microscopy

Some of the diorite samples are selected for ore microscopic investigations. The selection of the specimen is based on the intense presence of opaque minerals detected in thin sections, and visual presence of pyrite veins in hand specimens.

These ore microscopic investigations revealed presence of disseminated pyrite grains together with disseminated rutiles (Figure 4.11).

In addition to that vein filling fine grained pyrites and marcasites together with larger subhedral chalcopyrite grains (Figure 4.12a and b), subhedral to euhedral magnetite and unhedral hematite grains are identified (Figure 4.13).

Pyrite is the most abundant and marcasite is the youngest vein filling mineral identified in the polished sections. Magnetites are relatively larger grained (Figure 4.14) whereas pyrites and marcasites are detected to be relatively fine grained. Chalcopyrites are noticed not only as individual minerals, but also as inclusions in pyrite veins.

The fine grain size of sulfide minerals such as pyrite and marcasite indicate the an increased surface area for oxidation and acid formation by sulfide minerals.

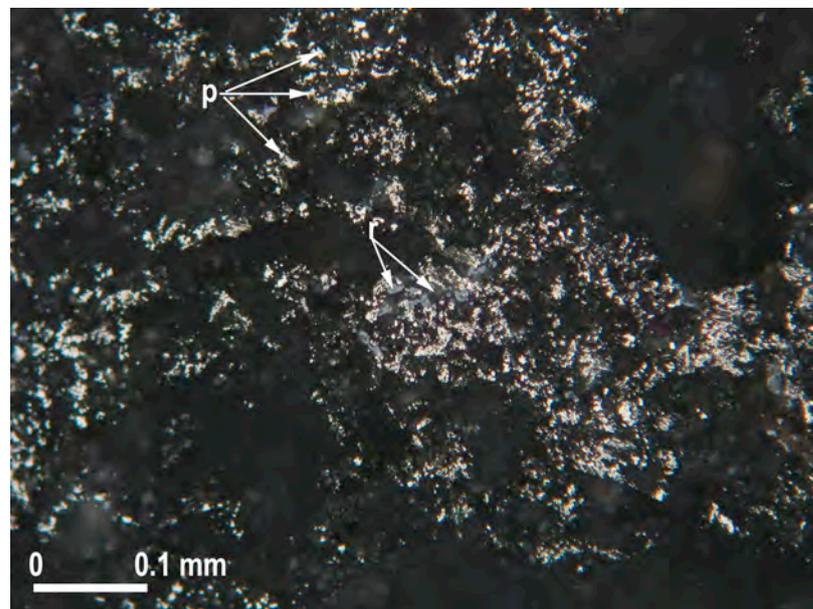


Figure 4.11 Disseminated rutiles (r) and pyrites (p)

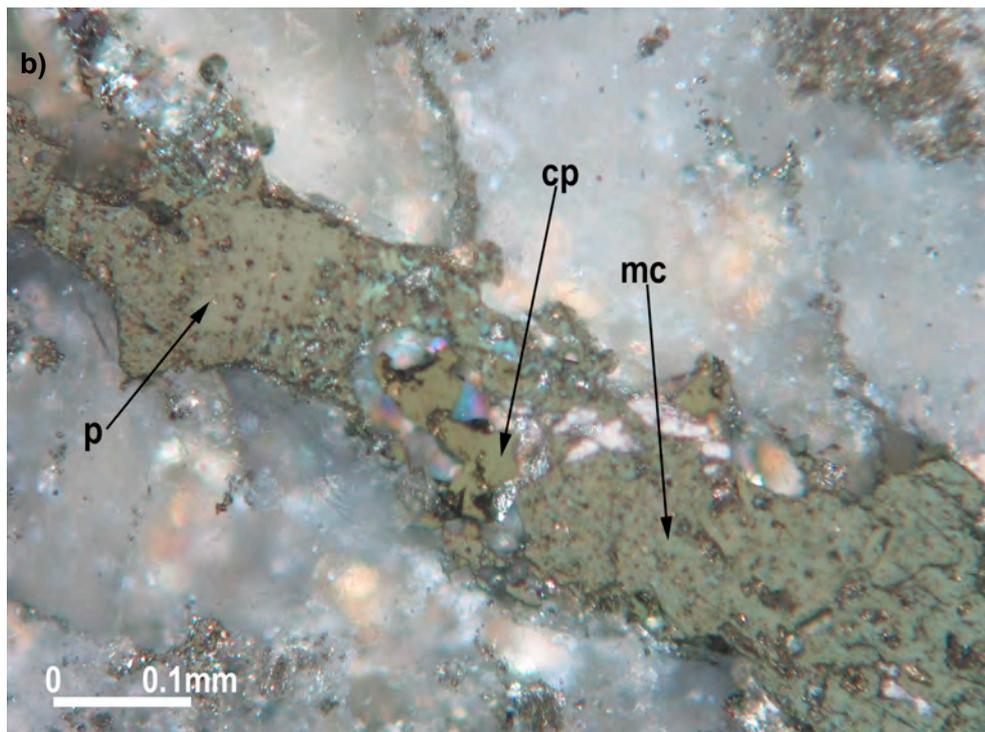
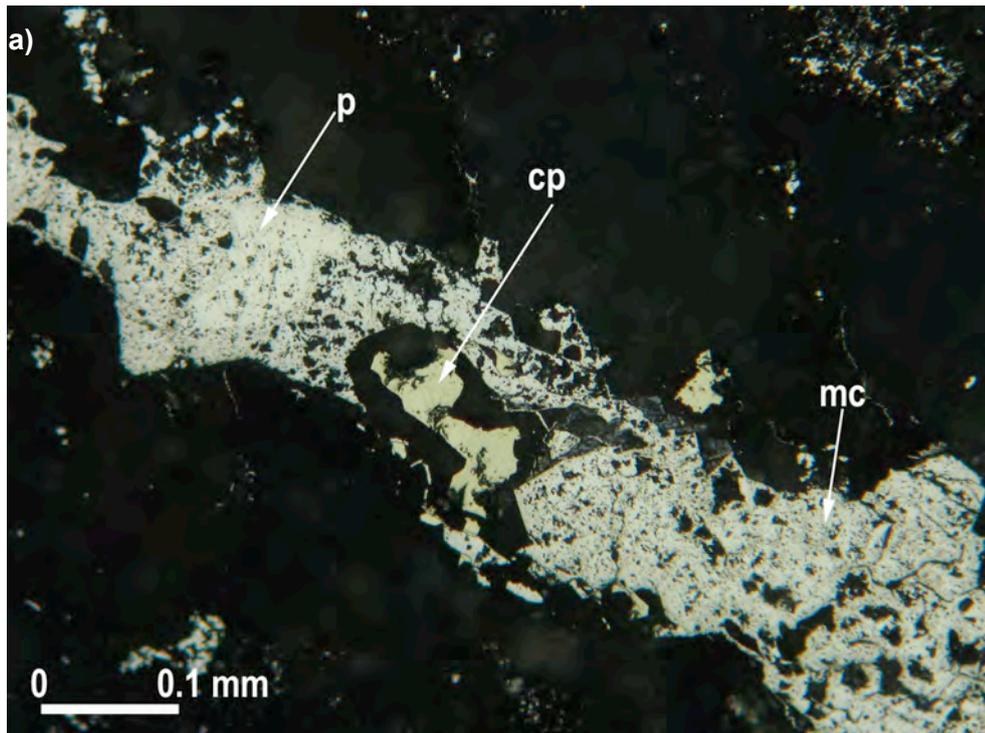


Figure 4.12 Vein filling pyrite (p), subhedral chalcopyrite (cp) and marcasites (mc) engulfed in pyrite fillings (a: picture with single nicole; b: picture with cross nicole).

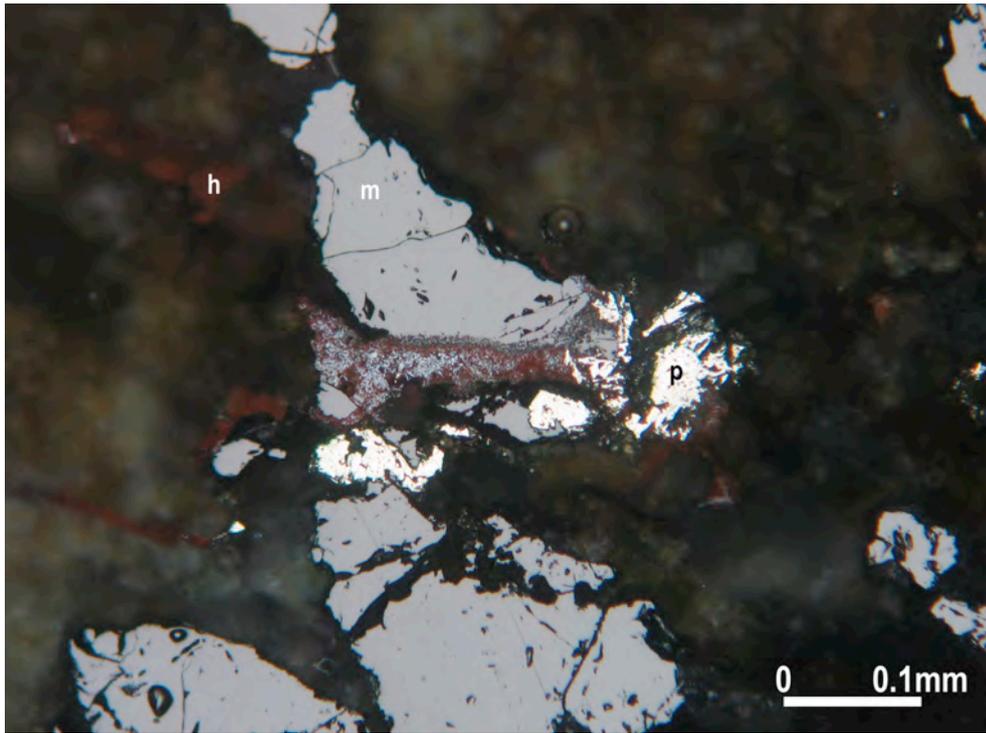


Figure 4.13 Subhedral to euhedral magnetite (m) with unhedral hematite (h) grains

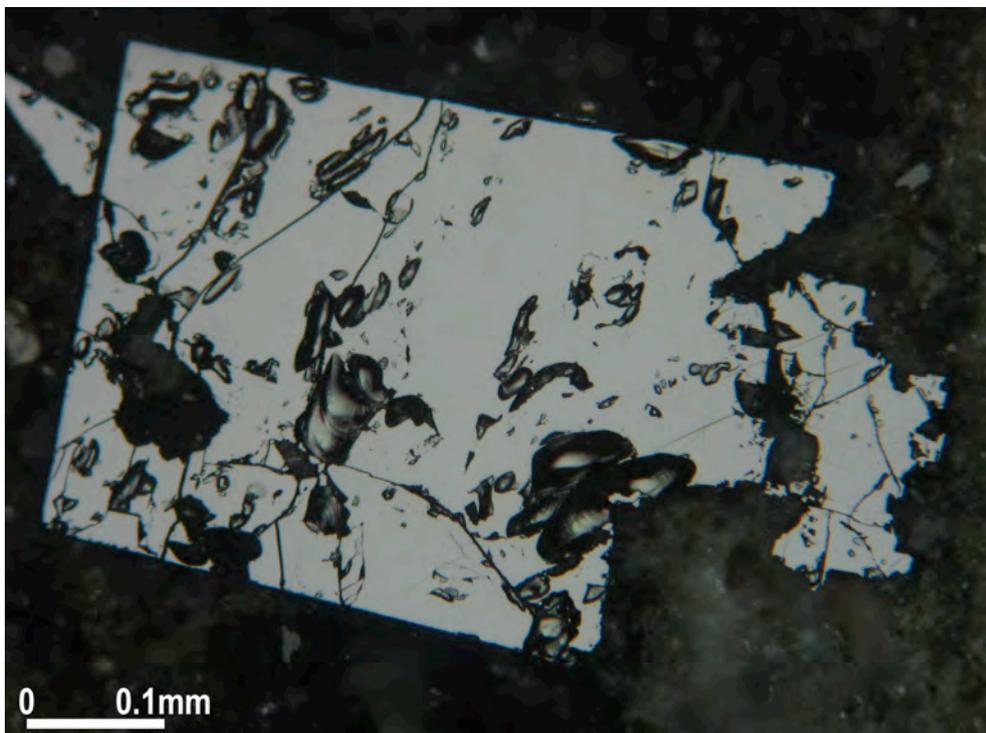


Figure 4.14 A large euhedral magnetite grain

### 4.1.3 X-Ray Diffraction

X-Ray Diffraction analysis was performed in order to reveal the alteration products and the characteristic clay minerals in the study area. The selected samples' bulk fractions are sieved below 170 mesh and their un-oriented XRD graphs are obtained. The oriented clay fraction in air dried, glycolated, heated to 300 °C and heated to 550 °C of the highly altered samples are analyzed. The full sized detailed XRD graphs of bulk and oriented clay fractions are given in Appendix-D.

Among the analyzed samples the bulk XRD pattern of the sample RMH01 revealed presence of quartz, feldspar and Mg-calcite minerals; whereas, in clay fraction (<2µm), some minor amounts of poorly crystallized smectite is detected.

Similarly un-oriented XRD pattern of sample CRD 356 indicates presence of quartz (d=3.30), calcite (d=3.02), feldspar (d=3.22), smectite (d=14.25) and mica/illite (d=9.94) in an amorphous silica background (Figure 4.14 and 4.15). In the clay fraction, air dried, glycolated and heated to 300°C and to 550°C patterns this sample indicates presence of smectite, illite and gypsum (d=7.56 after glycolation) (Figure 4.15).

Sample CDD 99 also indicates presence of quartz, feldspar, calcite, hematite (d=2.70) and pyrite (d=1.63) and presence of smectite (d=14.85) and gypsum (d=7.64) are detected at their air-dried oriented XRD pattern (See Appendix-D).

In general the samples, examined for their clay fraction, do not exhibit a well-developed, well crystallized clay mineral structure. Samples are rather relatively amorphous. For instance sample CDD 92, in its clay fraction, exhibits disordered smectite as indicated by less swelling after glycolation. The disordered smectite, which is identified as Illite/smectite mixed layering can only be recognized by a broad peak at d=11.55 in the oriented air dried XRD pattern.

Presence of kaolinite is indicated in sample CDD 92 by the consistent peaks at d=7.19 and d=3.58 in air-dried and glycolated XRD patterns respectively. Other than these, quartz, feldspar and pyrite (d=1.63), are identified, in bulk XRD pattern (See Appendix-D).

In sample CDD 99, quartz, hematite and calcite, are identified in bulk XRD pattern, and in clay fraction smectite and gypsum are detected.

In sample CDD 86, kaolinite, feldspar, hematite and pyrite are also identified in un-oriented bulk XRD graph.

On the other hand, in clay fraction, presence of kaolinite and some minor amounts of illite are also observed in air-dried oriented XRD patterns. In the bulk un-oriented XRD pattern, the presence of feldspar, quartz and smectite is revealed. In the oriented clay fraction, glycolated XRD graph smectite, kaolinite and gypsum are detected, (Appendix-D).

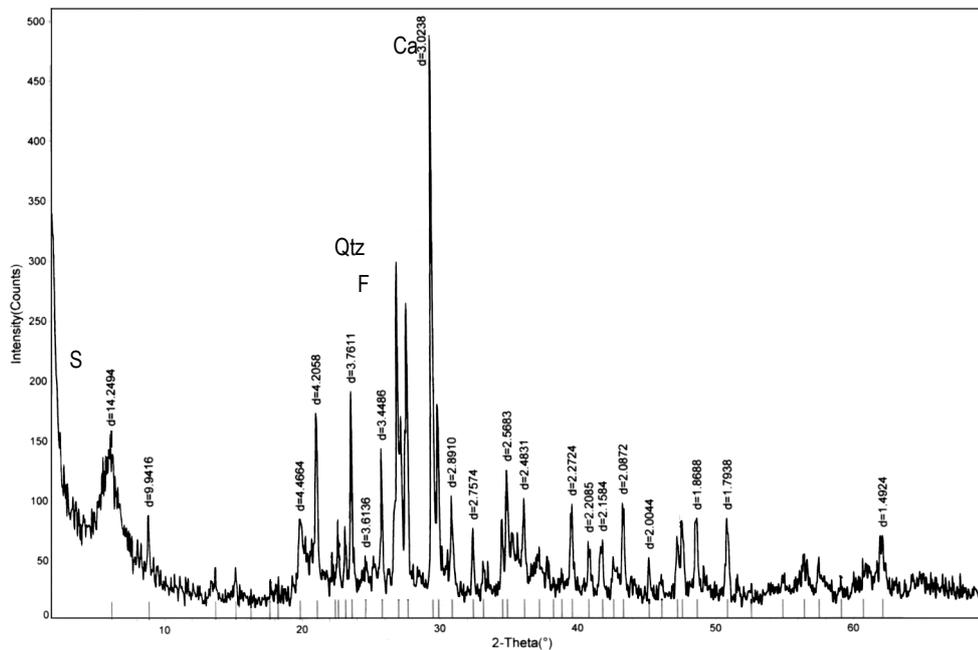


Figure 4.15 X-Ray diffraction pattern of the <170 mesh (bulk) fraction of the sample CRD 356. Qtz: Quartz, F: Feldspar, Ca: Calcite, S: Smectite; I: Illite, See Appendix-D for full size graphics.

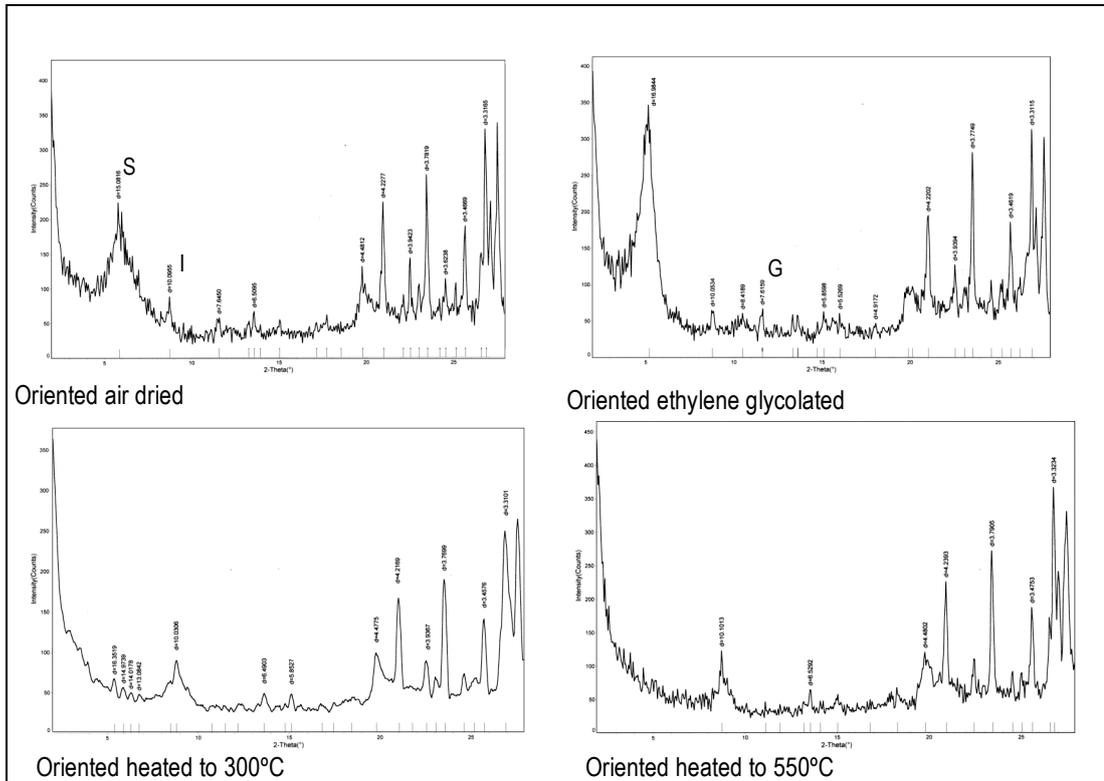


Figure 4.16 X-Ray diffraction patterns of the clay fraction of the sample CRD 356 Qtz: Quartz, F: Feldspar, Ca: Calcite, S: Smectite; I: Illite, G: Gypsum See Appendix-D for full size graphics.

The X-ray diffraction patterns of the clay fraction of CRD 356 exhibits presence of quartz, feldspar, calcite, smectite, illite, and gypsum (Figure 4.16).

As indicated above, the un-oriented and oriented XRD graphs of the analyzed samples also support the presence of sulphide minerals such as pyrite. The calcite minerals detected can be attributed to the presence of secondary calcite minerals that developed as vein fillings, as a result of hydrothermal circulations. Similarly presence of gypsum can be attributed to a secondary mineral formation as an interaction between sulfide minerals and waters rich on carbonates.

## 4.2 Geochemistry

The summary of the geochemical analysis results is presented in Table 4.1. The entire analysis results are given in Appendix-B. The results of the composite samples are given for every meter within the interval the sample was composite. (Appendix-B). In addition to that the average, minimum, maximum values and the standard deviation in elemental concentrations of the composite samples are given in Table 4.2, to provide an idea about the composition of these samples.

The geochemical results were mainly considered from an acid base accounting point of view. As it can be seen in Table 4.1, the %S value is significantly high in dioritic samples.

The results of geochemical analysis are also given as plots of change of certain elemental concentrations versus depth, based on the detailed analysis results of the composite core samples.

As can be seen from the Acid Base Accounting results in Table 4.3 there is very limited amount of %SO<sub>4</sub> in the samples and almost the entire sulfur identified in a sample as % Sulfur in geochemical analysis has the potential to contribute to the potential of acid production.

Table 4.1 Summary of the major and trace element geochemical analysis Part-1.

LITHOLOGY	DIORITE									METASEDIMENTARY			MARBLE	
	HOLE NO and meter	CDD_84 43 to 44	CDD_85 177 to 178	CDD_86 246 to 247	CDD_88 165 to 166	CDD_88 166-167	CDD_92 135 to 136	CDD_93 145 to 146	CDD_94 109 to 110	CDD_96 223 to 224	CDD_89 121 to 122	CRD_334A 140 to 141	CRD_334A 141 to 142	CDD_91 291 to 292
Au (ppm)	0.017	1.35	0.1	0.16	0.07	1.12	0.14	0.35	0.18	0.05	0.13	0.18	0.1	0.06
Ag (ppm)	<0.5	9.9	<0.5	<0.5	<0.5	7.6	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
Al (%)	8.06	4.7	9.16	8.27	8.61	8.26	7.12	8.77	9.94	7.81	9.23	9.05	0.21	0.33
As (ppm)	108	1110	110	147	186	827	89	337	190	18	24	175	28	146
Ba (ppm)	760	40	360	70	250	110	380	160	10	200	480	260	30	170
Be (ppm)	1.1	<0.5	0.9	0.9	1	0.6	0.8	0.5	<0.5	1.9	1.1	1.4	<0.5	<0.5
Bi (ppm)	<2	3	<2	<2	<2	3	<2	<2	<2	<2	2	<2	2	<2
Ca (%)	7.57	0.77	0.3	1.74	1.58	0.97	7.68	4.05	13.7	2.23	0.61	0.54	37.2	38.8
Cd (ppm)	<0.5	<0.5	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	59.8	15.9	1.2	3
Co (ppm)	12	6	10	11	12	13	13	11	9	14	33	32	1	3
Cr (ppm)	3	4	6	4	4	2	7	7	6	53	54	58	5	8
Cu (ppm)	29	298	507	824	235	376	1365	961	311	198	202	256	15	286
Fe (%)	2.91	3.68	2.28	7.44	4.01	5.39	2.96	7.4	5.87	4.55	2.96	3.82	0.16	1.08
K (%)	2.79	1.74	1.5	1.16	2.2	2.2	1.51	0.75	0.1	3.75	3.67	2.76	0.03	<0.01
Mg (%)	0.34	0.22	0.11	1.12	1.28	0.14	0.32	0.79	0.55	4.7	0.71	0.46	0.17	0.23
Mn (ppm)	1490	>100000	219	849	538	42800	3940	834	773	286	96	118	286	2180
Mo (ppm)	3	8	84	32	4	13	59	4	7	2	21	12	<1	2
Na (%)	1.42	0.01	0.05	0.08	0.3	0.02	0.07	0.07	0.01	0.05	0.19	0.15	<0.01	<0.01
Ni (ppm)	6	<1	4	5	6	5	1	7	5	38	49	54	12	44
P (ppm)	1120	80	1170	780	1150	1050	950	650	920	640	740	700	90	190
Pb (ppm)	24	83	16	7	9	25	20	45	56	2	6	4	57	85
S (%)	3.23	4.12	2.48	8	4.27	6.51	3.56	8.65	6.17	2.73	2.61	3.18	0.02	<0.01
Sb (ppm)	<5	36	10	<5	<5	20	5	<5	<5	<5	<5	<5	<5	5
Sr (ppm)	610	23	33	74	123	44	71	77	30	29	447	137	69	33
Ti (%)	0.34	0.19	0.32	0.32	0.35	0.37	0.3	0.36	0.37	0.38	0.45	0.43	0.01	0.01
V (ppm)	139	51	145	122	130	160	240	164	164	117	138	148	10	28
W (ppm)	<10	<10	<10	10	<10	<10	<10	10	<10	<10	<10	<10	<10	30
Zn (ppm)	28	77	162	66	33	238	18	106	114	303	1160	1325	137	604
MnO (%)														

Table 4.2 Major and trace element geochemistry results of the composite samples. Only the Average (Ave.), Minimum (Min.), Maximum (Max.) and Standard Deviation (St.Dev.) of the analyzed interval in depth are given. The full analyses of the indicated intervals are given in Appendix-B.

HOLE NO:	CRC 270; 108 to 205 m				CRC 271; 78 to 100 m				CRC 255; 47 to 76 m				CRC 255; 96 to 116 m				CRC 280; 80 to 165m			
	Ave.	Min	Max	St.Dev.	Ave.	Min	Max	St.Dev.	Ave.	Min	Max	St.Dev.	Ave.	Min	Max	St.Dev.	Ave.	Min	Max	St.Dev.
Au (ppm)	4.4	0.4	15.0	0.4	0.8	0.1	3.7	0.9	4.4	0.4	15.0	3.3	0.4	0.1	2.4	0.5	2.2	0.0	34.4	5.4
Ag (ppm)	3.4	0.5	25.8	8.7	0.8	0.5	2.8	0.6	5.8	0.5	25.8	7.2	0.6	0.5	1.2	0.2	4.9	0.5	72.4	14.0
Al (%)	7.23	3.58	9.77	1.61	9.19	7.36	11.25	1.06	7.23	3.58	9.77	1.49	7.68	3.58	8.48	0.53	8.01	2.80	9.76	1.30
As (ppm)	995	301	2090	1071	531	224	1055	242	995	301	2090	402	311	116	789	160	876	59	8530	1311
Ba (ppm)	261	40	730	196	306	40	4100	850	261	40	730	157	458	40	660	111	406	30	4760	565
Be (ppm)	0.53	0.50	0.80	0.23	0.51	0.50	0.60	0.03	0.58	0.50	0.80	0.07	0.79	0.50	1.00	0.16	0.74	0.50	1.20	0.20
Bi (ppm)	2.4	2.0	13.0	0.0	2.2	2.0	3.0	0.4	4.6	2.0	13.0	2.1	2.0	2.0	2.0	0.0	3.3	2.0	43.0	5.3
Ca (%)	9.4	0.8	25.5	5.4	8.2	1.1	20.8	6.6	9.4	0.8	25.5	6.3	9.6	0.8	13.1	2.0	2.3	0.3	8.8	1.9
Cd (ppm)	5.0	0.5	47.8	2.6	7.0	0.5	63.2	14.8	6.6	0.5	47.8	11.3	0.9	0.5	7.0	1.4	2.4	0.5	61.7	7.6
Co (ppm)	11.7	5.0	17.0	4.2	20.5	5.0	53.0	13.5	11.7	5.0	17.0	2.9	10.6	5.0	21.0	3.0	13.1	7.0	23.0	2.9
Cr (ppm)	7.9	3.0	12.0	5.9	9.3	5.0	18.0	3.4	7.9	3.0	12.0	2.1	4.4	3.0	8.0	1.3	8.5	2.0	50.0	9.2
Cu (ppm)	341	32	2420	329	692	83	3770	919	341	32	2420	503	99	32	369	81	537	6	6450	1099
Fe (%)	5.6	2.8	15.4	1.6	5.3	3.3	7.6	1.3	5.6	2.8	15.4	2.4	3.8	2.5	7.1	1.0	4.2	2.0	13.3	1.8
K (%)	1.22	0.27	2.96	0.87	0.89	0.23	2.22	0.49	1.22	0.27	2.96	0.70	2.17	0.27	3.47	0.77	2.22	0.42	4.92	0.90
Mg (%)	0.30	0.17	0.57	0.90	0.19	0.06	0.29	0.07	0.30	0.17	0.57	0.08	0.33	0.11	0.58	0.11	0.29	0.02	0.70	0.18
Mn (ppm)	1780	751	5320	4065	1636	326	9570	1935	1780	751	5320	965	2176	751	3760	650	5127	114	94300	12697
Mo (ppm)	23	4	267	9	34	14	78	17	23	4	267	48	14	4	32	7	10	2	59	10
Na (%)	0.08	0.02	0.50	0.26	0.04	0.01	0.11	0.03	0.08	0.02	0.50	0.09	0.36	0.02	1.00	0.32	0.11	0.01	1.17	0.14
Ni (ppm)	8.4	2.0	34.0	4.1	21.8	5.0	53.0	13.1	8.4	2.0	34.0	5.5	10.0	2.0	55.0	14.0	9.8	2.0	75.0	13.0
P (ppm)	1170	480	1620	305	1428	910	1880	272	1170	480	1620	304	1148	480	1310	73	1098	330	1430	173
Pb (ppm)	199	14	2290	154	33	13	100	23	199	14	2290	475	35	13	106	22	126	6	3480	464
S (%)	6.19	3.73	8.57	1.55	5.49	0.84	8.77	2.05	6.19	3.73	8.57	1.11	4.49	2.12	9.63	1.71	4.79	2.48	9.96	1.61
Sb (ppm)	22	8	113	70	16	5	51	12	22	8	113	19	8	5	22	5	106	5	2210	350
Sr (ppm)	92	49	197	82	45	19	138	24	92	49	197	32	166	49	340	88	125	21	434	77
Ti (%)	0.34	0.12	0.46	0.07	0.46	0.33	0.60	0.08	0.34	0.12	0.46	0.09	0.31	0.12	0.36	0.02	0.33	0.11	0.39	0.05
V (ppm)	179	65	293	31	215	152	281	38	179	65	293	48	163	65	219	19	139	60	195	19
W (ppm)	15	10	30	1	12	10	20	4	15	10	30	6	11	10	20	2	12	10	40	5
Zn (ppm)	560	22	5090	518	280	98	880	249	560	22	5090	1168	132	22	445	117	251	7	6500	811
MnO (%)								0.28												

Plots of Molybdenum versus depth from four different drill hole samples that were tested for Acid Base Accounting as composite samples (CRC 255 47-76m, 96-116m; CRC 270, CRC 271 and CRC 280) exhibit influences of hydrothermal activity as indicated by the elevated Mo values (Figure 4.17).

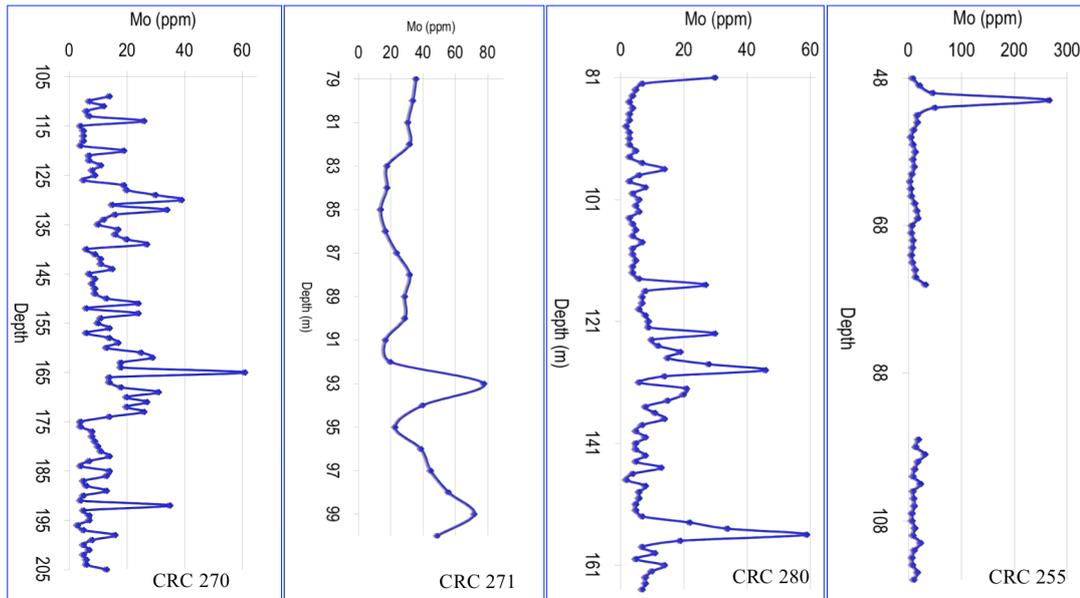


Figure 4.17 The change in Mo concentration with depth, in diorite drill hole samples. Elevated Mo concentrations indicate hydrothermal contribution.

As the %Al, Fe and S values of the same samples (CRC 270, CRC 271, CRC 255, CRC 280) are plotted against depth; there appears a strong correlation between Fe and S indicating presence of pyrite and/or marcasite. There are levels where this correlation is reversed. This behavior can be attributed to an alteration process that may have oxidized the pyrite and consumed the Fe into iron oxides and S into sulphate minerals (Figure 4.18).

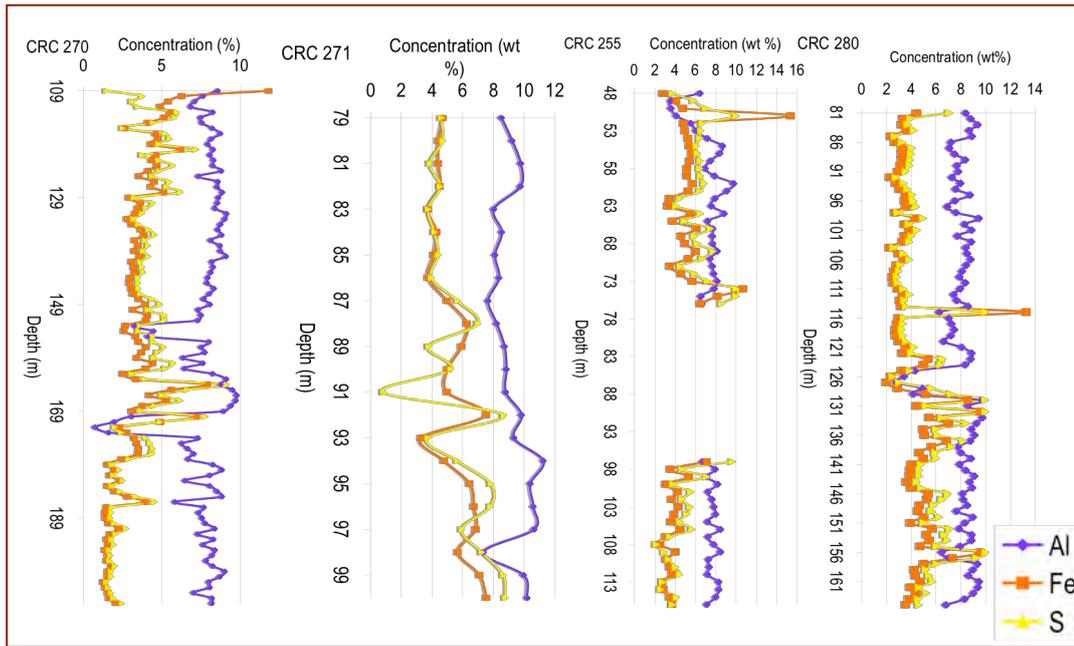


Figure 4.18 Fluctuation of %Al, %Fe and %S with respect to depth.

The relation and change of Pb, Cu, As, Zn and S with respect to depth is investigated on samples from drill holes CRC 255, CRC 270, CRC 271 and CRC 280 (Figure 4.19 and 4.20). In these graphs, Pb, Cu, As, and Zn are given at the primary axes as concentration in ppms, and S is presented at the secondary axis as %S.

At drill hole CRC 255 around 50m, a parallel enrichment of Cu and Zn is observed. Also Cu is observed to be enriched where there are higher amounts of %S. This parallel enrichment of S and Cu are also observed in other drill hole samples. This can be attributed to the presence of chalcopyrite mineral. Similarly where there is an As enrichment it was possible to observe relatively higher amounts of S. In addition, However in drill hole CRC 270 at around 91 m As reaches up to 933 ppm whereas %S is as low as 1%. This may be attributed to an alteration that oxidized and depleted S but left As behind.

Other heavy metal enrichments are all considered to be indicating the effect of hydrothermal alteration and trace element mobilization within the dioritic lithology (Figure 4.19 and 4.20).

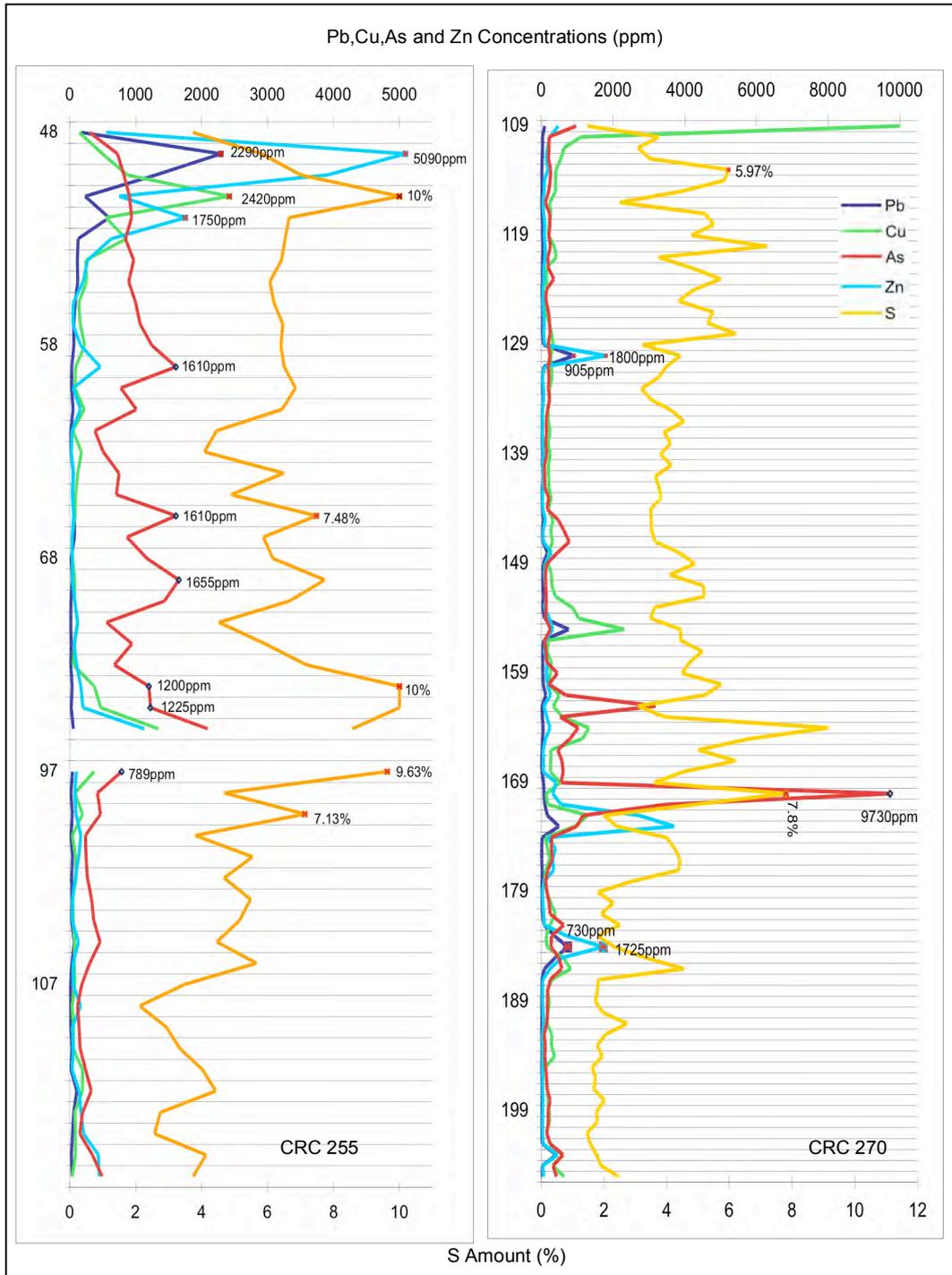


Figure 4.19 Variation of Pb, Cu, Zn and As concentrations in ppm and S content in percentage with respect to depth for samples from drill holes CRC 255 and CRC 270 (The 10000 ppm is the upper detection limit of the reported analysis results, and 10% S is the upper detection limit of the reported results).

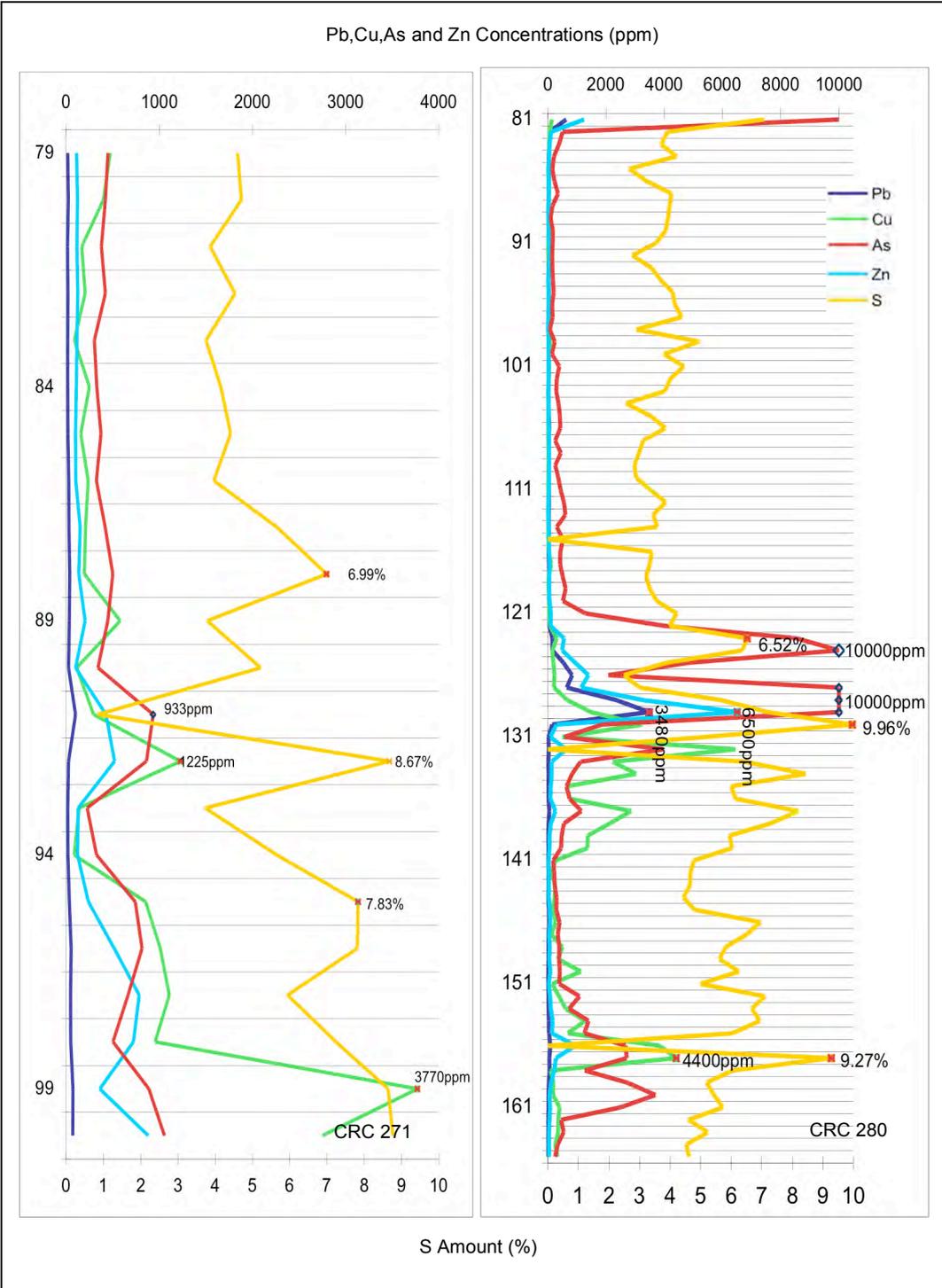


Figure 4.20 Variation of Pb, Cu, Zn and As concentrations in ppm and S content in percentage with respect to depth for drill hole samples CRC 271 and CRC 280 (The 10000 ppm is the upper detection limit of the reported analysis results, and 10% S is the upper detection limit of the reported results).

In drill hole CRC270 Ca concentration enrichments ranges around 10 % up to 17% (Figure 4.21), The maximum Ca enrichment at drill hole CRC 270 is observed between 153m to 155 m with a Ca concentration of 22%. In the same drill hole K enrichment ranges up to 3%. However the K level is depleted up to about 0 between 120m and 121m. In drill hole CRC271 Ca enrichment reaches up to 20.8%. Similarly K level only increases up to the 2 % range (Figure 4.21). Drill hole CRC 255 (Figure 4.21) exhibits significant amounts of Ca, at 50 m. Drill hole CRC280 exhibits relatively less Ca concentrations compared to other samples with an average of 2.3 %. These Ca enrichments can be attributed to the influence of hydrothermal waters that circulate through Munzur Limestone and carry the Ca to the fractures.

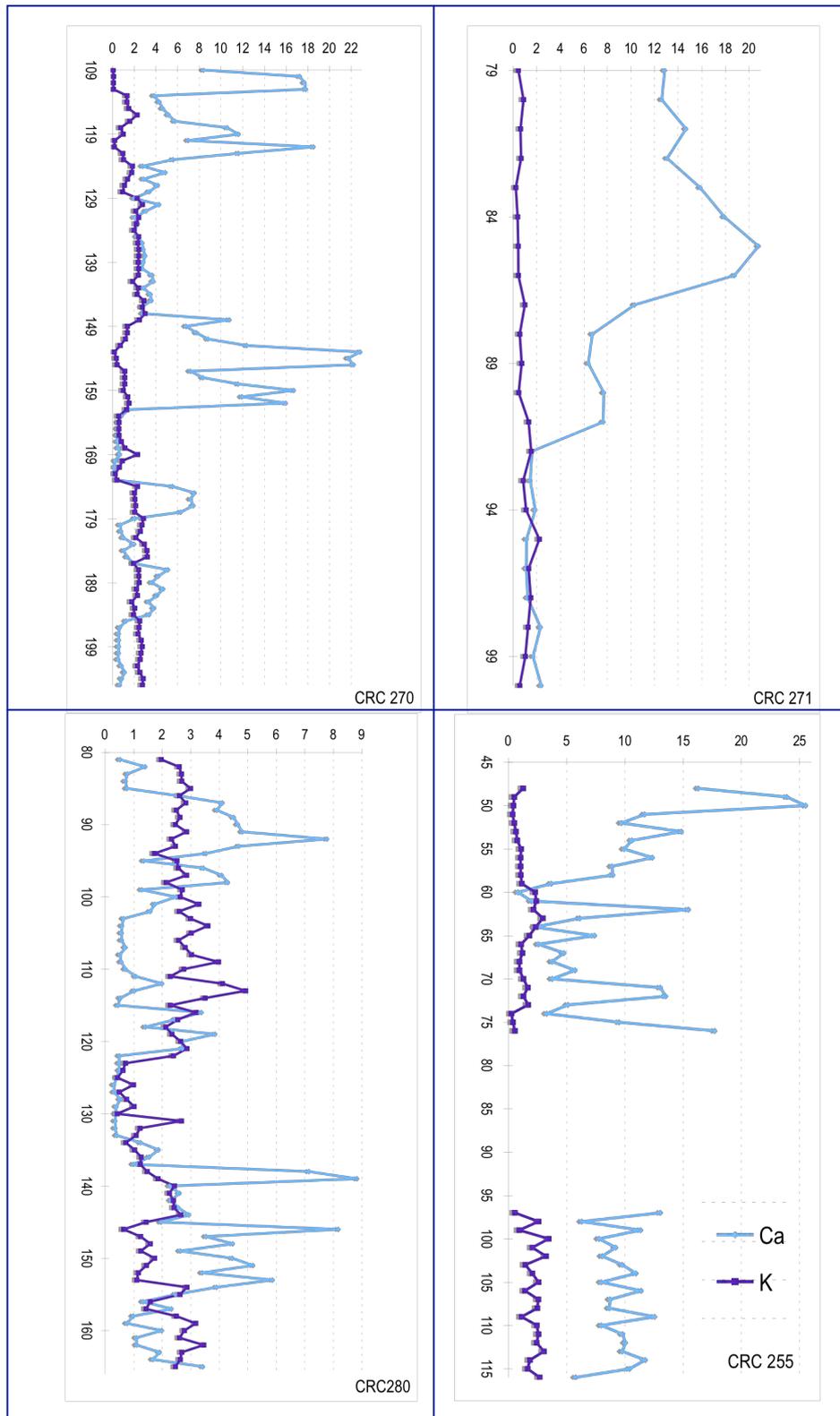


Figure 4.21 Change in Ca and K concentrations (in weight %) of drill hole samples (CRC 255, CRC 270, CRC 271 and CRC 280) with respect to depth.

When the Ti, Na and Mg concentrations are plotted against depth, for the drill hole CRC270 the highest Ti concentration is observed at 166 m with 0.42%, and has an average concentration of 0.3% (Figure 4.22).

For the same drill hole (CRC 270) the Na concentration is 0.22% in average and reaches up to 1.02% at 125m. Mg is observed to exhibit great fluctuations in CRC 270, ranging from 0.01% and 4.3 % (Figure 4.22).

In drill hole CRC271 the Mg concentration ranges from 0.07% at 184th m and 2.6% at 190th m. Na level is observed to be very low and is less than 0.11 % and the average Na concentration is around 0.04%. Average Ti concentration is about 0.46 % (Figure 4.22).

In drill hole CRC280 the Na concentration is very low with an average of 0.11% and a maximum level of 1.17%. The drill hole CRC280 also has a relatively low Ti concentration with an average of 0.33%. The drill hole CRC280 has an average Mg concentration of 0.29% (Figure 4.22).

The drill hole CRC255 has Mg concentrations ranges from 0.11% to 0.58%. In the drill hole 255 Ti concentration ranges between 0.12 and 0.46%. In the drill hole CRC255 the Na concentration ranges around 0.2% and 0.17% and makes peaks at 63m with 0.5 % and at 108th m with 1% (Figure 4.22).

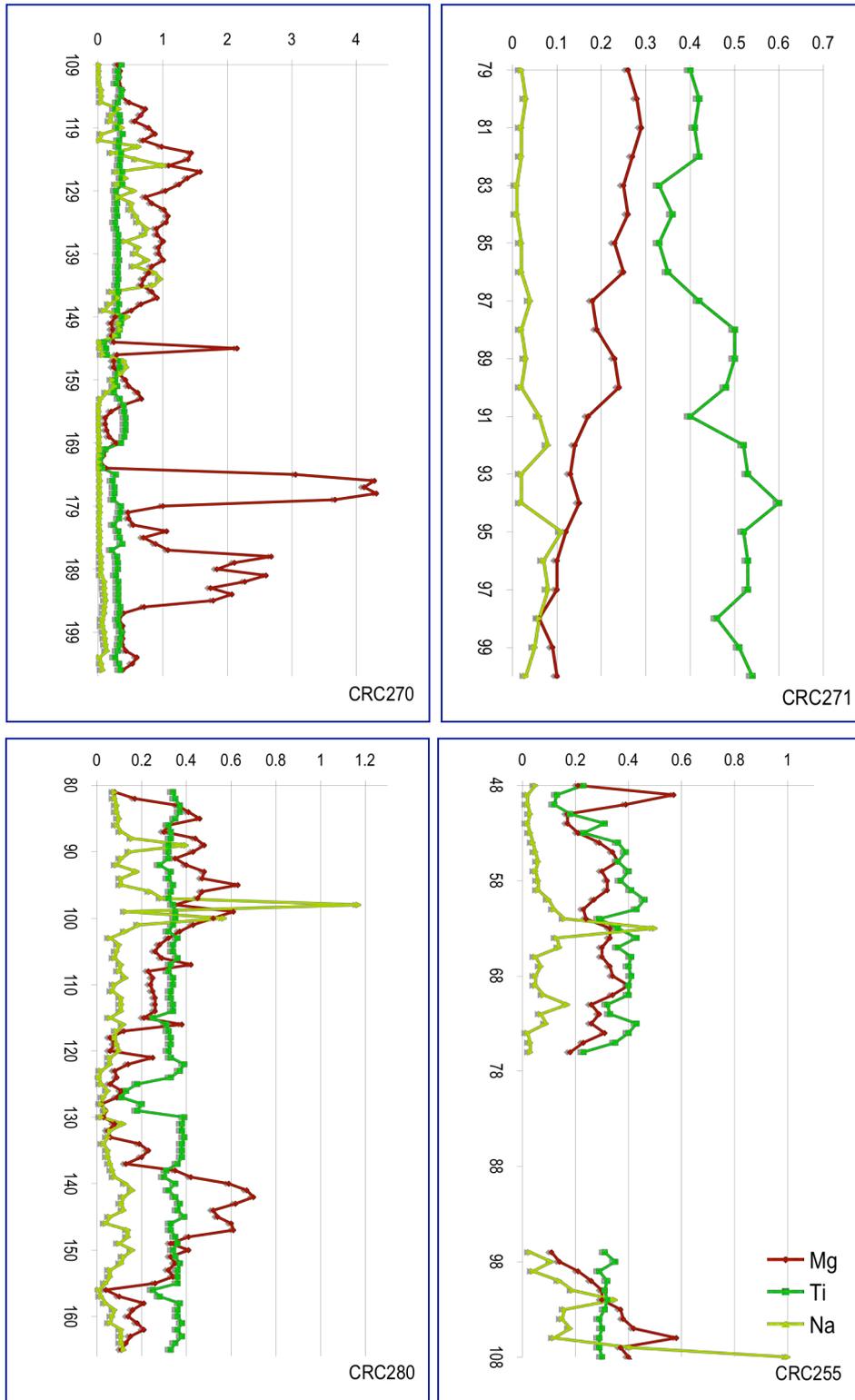


Figure 4.22 Change in Ti, Na and Mg concentrations (in weight %) of drill hole samples (CRC 255, CRC 270, CRC 271 and CRC 280) with respect to depth.

## 4.3 Acid Base Accounting

The summary of the ABA test results is given in Table 4.3. These results are evaluated based on the lithology and the test applied.

### 4.3.1 Paste pH

The elimination criterion for paste pH is  $< 4.0$ , where samples with paste pH less than 4.0 are considered acid toxic.

Out of 38 samples tested for ABA eleven samples exhibit a paste pH value greater than or equal to 7.9, indicating high acid consuming capacity. These samples are mainly from marble and limestone lithologies. Among these lithologies four samples belong to the marble zone, and the seven samples belong to the manganese mine zone.

Six samples exhibit a pH value slightly greater than 7, indicating relatively low risk of acid generation. One of such samples is a marble (RMH01; 4.50-4.62 m) and the others are metasediments taken from the main zone. Some samples with "Paste pH" values ranging from 3.2 to 4.2 exhibit strong acidity.

The transition zone that was sampled between diorite and metasediment lithologies (RMH02; 25.3-25.5) exhibits the strongest acidity with a paste pH of 2.7. The paste pH of diorite samples ranges from 3.9 to 6.9 depending on the alteration degree of the samples. The less altered diorite samples exhibit relatively higher pH values that range from 5.9 to 6.9, while rather more altered diorite samples exhibit a pH value ranging from 3.9 to 5.7 (Table 4.3).

Out of the 38 tested samples only three samples were determined to have a paste pH value less than 4.0. All of these samples are from the main zone. RMH03; 25.2 to 25.33m was a diorite sample with a paste pH value of 3.9, RMH02; 14.50 to 15.10 was a metasediment sample with a paste pH value of 3.2, and the one with the lowest paste pH value of 2.7 was RMH02; 25.30 to 25.50 m that was positioned at the transition boundary between diorite and metasediment. Sample RMH02; 11.0 to 11.2m was also a metasediment sample from the main zone that exhibited a paste pH value of 4.2, which is very close to the critique level of pH 4.0 (Table 4.3).

Table 4.3 Summary of the Acid Base Accounting Test Results

Sample Codes	Paste pH	CO <sub>2</sub> Wt.%	CaCO <sub>3</sub> Equiv. KgCaCO <sub>3</sub> /Tonne	Total Sulfur Wt.%	Sul-phate Sulfur Wt.%	Sul-phide Sulfur* Wt.%	Max.Potential Acidity** KgCaCO <sub>3</sub> /Tonne	Neutralization Potential KgCaCO <sub>3</sub> /Tonne	Net Neutralization Potential KgCaCO <sub>3</sub> /Tonne	Fizz Rating	Neutralization Potential Ratio
RMH010.00-0.10	8.4	46.7	1060.7	<0.02		<0.02	<0.6	991.0	991.0	strong	1651.7
RMH010.17-0.30	8.5	45.9	1042.5	<0.02		<0.02	<0.6	795.0	795.0	strong	1325.0
RMH011.50-1.77	8.3	46.3	1051.6	<0.02		<0.02	<0.6	879.0	879.0	strong	1465.0
RMH014.50-4.62	7.3	15.4	349.5	0.02		0.02	0.6	334.0	333.4	strong	556.7
RMH0130.40-30.55	8.2	45.9	1042.5	<0.02		<0.02	<0.6	813.0	813.0	strong	1355.0
RMH020.50-0.65	7.4			2.61	2.42	0.19	5.9	3.0	-2.9	none	0.5
RMH021.60-1.72	7.2			0.14	0.14	0.00	0.0	1.8	1.8	none	-
RMH024.38-4.50	7.2			<0.02		<0.02	<0.6	2.0	2.0	none	3.3
RMH0211.10-11.20	4.2			0.86	0.74	0.12	3.7	-3.5	-7.2	none	-1.0
RMH0213.90-14.10	6.1			0.83	0.67	0.16	4.9	0.8	-4.1	none	0.2
RMH0214.50-15.10	3.2			5.76	0.68	5.08	158.9	-14.8	-173.7	none	-0.1
RMH0219.40-19.60	6.0			7.98	0.05	7.93	247.9	30.3	-217.6	none	0.1
RMH0225.30-25.50	2.7			7.32	0.21	7.11	222.2	-0.5	-222.7	none	0.0
RMH0229.25-29.35	5.5			3.49	0.12	3.37	105.4	62.3	-43.1	none	0.6
RMH0230.75-30.90	7.2			2.88	0.07	2.81	87.9	92.8	4.9	moderate	1.1
RMH0232.45-32.55	7.4			2.42	0.04	2.38	74.4	160.6	86.2	moderate	2.2
RMH030.85-1.05	6.4			0.49	0.43	0.06	2.0	0.8	-1.2	none	0.4
RMH031.85-1.95	6.3			0.75	0.67	0.08	2.6	0.3	-2.3	none	0.1

\* Based on difference between total sulfur and sulphate-sulfur

\*\* Based on sulphide-sulfur

Table 4.3 Continued

Sample Codes	Paste pH	CO <sub>2</sub> Wt. %	CaCO <sub>3</sub> Equiv. KgCaCO <sub>3</sub> /Tonne	Total Sulfur Wt. %	Sul-phate Sulfur Wt. %	Sul-phide Sulfur* Wt. %	Max.Potential Acidity** KgCaCO <sub>3</sub> /Tonne	Neutralization Potential KgCaCO <sub>3</sub> /Tonne	Net Neutralization Potential KgCaCO <sub>3</sub> /Tonne	Fizz Rating	Neutralization Potential Ratio
RMH0315.10-15.30	6.8			0.78	0.66	0.12	3.7	1.2	-2.5	none	0.3
RMH0321.75-21.95	6.9			0.1	0.08	0.02	0.7	1.5	0.8	none	2.2
RMH0325.20-25.33	3.9			2.65	0.06	2.59	80.9	-1.5	-82.4	none	0.0
RMH0326.80-27.00	5.4			4.45	0.10	4.35	136.0	11.0	-125.0	none	0.1
RMH0332.00-32.10	5.7			3.08	0.04	3.04	95.0	36.2	-58.8	none	0.4
RMH0335.00-35.20	5.6			4.71	0.08	4.63	144.7	5.7	-139.0	none	0.0
CRC2460-128	8.0	43.9	997.0	0.07		0.07	2.2	896.0	893.8	strong	409.6
CRC246128-139	5.5			7.17	0.47	6.70	209.4	84.9	-124.5	moderate	0.4
CRC2470-163	8.2			<0.02		<0.02	<0.6	880.0	880.0	strong	1466.7
CRC2480-157	8.1			<0.02		<0.02	<0.6	903.0	903.0	strong	1505.0
CRC25544-75	6.2			5.78	0.30	5.48	171.4	287.8	116.4	moderate	1.7
CRC25596-115	6.7			3.66	0.16	3.50	109.4	166.5	57.1	moderate	1.5
CRC25742-115	6.5			3.12	0.04	3.08	96.3	126.6	30.4	moderate	1.3
CRC270108-205	6.7			3.06	0.06	3.00	93.8	183.8	90.0	moderate	2.0
CRC27178-100	6.3			5.25	0.19	5.06	158.2	135.5	-22.7	moderate	0.9
CRC28080-165	5.9			5.19	0.12	5.07	158.4	32.5	-125.9	slight	0.2

\* Based on difference between total sulfur and sulphate-sulfur

\*\* Based on sulphide-sulfur

### 4.3.2 Maximum Potential Acidity

Maximum potential acidity (MPA) is mainly calculated based on the total sulfur content of the samples. Twenty-five samples were tested for their sulphate content, and sulphate sulfur was subtracted from the total sulfur to determine the “sulfide sulfur” that will contribute to the maximum potential acidity. The effect of sulphate sulfur is observed to range from 0.58 % to 100%.

For samples that contained a very little amount of sulfur such as sample RMH02;1.60 to 1.72m, a metasedimentary sample from the Main Zone, the amount of sulfur detected was 0.14 % and identified to be entirely sulphate sulfur. Samples that contained relatively higher amount of total sulfur such as sample RMH02; 19.40 to 19.60m, with a total sulfur content of 7.98%, was identified to have only 0.05 % of sulphate sulfur, which contributes only 0.58 % to the total sulfur (Table 4.4).

Table 4.4 Ratio of sulphate sulfur in total sulfur

Sample Code	Total Sulfur	Sulphate Sulfur	% Sulphate Contribution
RMH020.50-0.65	2.61	2.42	92.72
RMH021.60-1.72	0.14	0.14	100.00
RMH0211.10-11.20	0.86	0.74	86.40
RMH0213.90-14.10	0.83	0.67	81.08
RMH0214.50-15.10	5.76	0.68	11.74
RMH0219.40-19.60	7.98	0.05	0.58
RMH0225.30-25.50	7.32	0.21	2.87
RMH0229.25-29.35	3.49	0.12	3.38
RMH0230.75-30.90	2.88	0.07	2.33
RMH0232.45-32.55	2.42	0.04	1.61
RMH030.85-1.05	0.49	0.43	87.14
RMH031.85-1.95	0.75	0.67	88.80
RMH0315.10-15.30	0.78	0.66	85.00
RMH0321.75-21.95	0.1	0.08	78.60
RMH0325.20-25.33	2.65	0.06	2.37
RMH0326.80-27.00	4.45	0.10	2.22
RMH0332.00-32.10	3.08	0.04	1.30
RMH0335.00-35.20	4.71	0.08	1.67
CRC246128-139	7.17	0.47	6.56
CRC25544-75	5.78	0.30	5.12
CRC25596-115	3.66	0.16	4.37
CRC25742-115	3.12	0.04	1.28
CRC270108-205	3.06	0.06	1.86
CRC27178-100	5.25	0.19	3.58
CRC28080-165	5.19	0.12	2.31

Among the 38 tested samples, eleven samples had total sulfur content equal or less than the detection limit (0.02 wt % S) and accordingly calculated to have a Maximum Potential Acidity value of  $\leq 0.6$  kg CaCO<sub>3</sub>/tonnes. These are composed of five marble samples (RMH01s) collected from the Marble Zone, one metasedimentary sample collected from the Main Zone (RMH02; 4.38 to 4.50m) and five limestone samples (CRC247;0 to 163 m; CRC248; 0 to 157m; CDD98;51.7 to 51.8 m; CDD91;294 to 294.7 m; CRC391; 0 to 197m) collected from the Manganese Mine Zone and exhibit a similar MPA value. Sample RMH0321.75-21.95, with a sulphate amount of 0.0786 % with a sulfide sulfur value of 0.0214%, exhibited a MPA value of 0.66875 kg CaCO<sub>3</sub>/tonnes (Table 4.4). Thus this sample can be considered as one of the other samples that exhibit a minimum amount of MPA. In addition, the sulphate value of sample RMH02; 1.6 to 1.72 m revealed that the total sulfur was entirely sulphate and thus there were no sulfur to contribute acidity. This sample was ended with a nil MPA.

Similarly the sulphate content of sample RMH02; 0.50 to 0.65m was determined to be 2.42 % out of a total sulfur value of 2.61 %. Therefore the effective sulfide value was calculated to be 0.19% that yielded a MPA value of 5.9 kg CaCO<sub>3</sub> /tonnes. Similar reductions happened in samples RMH02;11.10-11.20 m, RMH02; 13.90-14.10 m, RMH03; 0.85-1.05m, RMH03;1.85-1.95 m, and RMH03;15.10 to15.30 m, the MPA values calculated to be < 5 kg CaCO<sub>3</sub>/tonne (Table 4.5).

Table 4.5 Samples with lower MPA values due to high content of sulphate.

<b>Sample Code</b>	<b>Total Sulfur (wt. %)</b>	<b>Sulphate Sulfur (wt. %)</b>	<b>Sulphide Sulfur (wt. %)</b>	<b>MPA Kg CaCO<sub>3</sub>/tonne</b>
RMH02;11.10-11.20	0.86	0.743	0.117	3.65625
RMH02;13.90-14.10	0.83	0.673	0.157	4.90625
RMH03;0.85-1.05	0.49	0.427	0.063	1.96875
RMH03;1.85-1.95	0.75	0.666	0.084	2.625
RMH03;15.10-15.30	0.78	0.663	0.117	3.65625

Two of the above mentioned samples are metasedimentary samples collected from the main zone (RMH02;11.10-11.20 m, RMH02; 13.90-14.10 m) and the other three

are diorite samples from the main zone (RMH03; 0.85-1.05m, RMH03;1.85-1.95 m, and RMH03;15.10-15.30 m).

The MPA values of other metasedimentary samples collected from the main zone range from 74.4 (RMH02;32.45-32.55m) to 249.4 (RMH02;19.4-19.6m) kg CaCO<sub>3</sub>/tonnes (Table 4.3) .

The MPA values of the other diorite samples collected from the main zone range from 80.9 (RMH03;25.20-25.33m) to 147.2 (RMH03;35-35.2m) kg CaCO<sub>3</sub>/tonnes. The MPA values of the composite diorite samples collected from the Manganese Mine Zone range from 93.8 (CRC270;108-205m) to 209.4 kg CaCO<sub>3</sub>/tonnes (CRC246;128-139m). The sample that exhibits the highest MPA value is the diorite-metasediment transition sample (RMH02;25.30-25.50m) that was collected from the Main Zone with an MPA value of 222.2 kg CaCO<sub>3</sub>/tonnes (Table 4.3).

### 4.3.3 Neutralization Potential

The NP values of the limestone samples collected from the Marble zone range between 334 kg CaCO<sub>3</sub>/tonnes (RMH01; 14.5-14.62m) to 991 kg CaCO<sub>3</sub>/tonnes (RMH01; 0.00-0.10m), and the NP values of the composite samples collected from the Manganese Mine Zone ranges between 880 kg CaCO<sub>3</sub>/tonnes (CRC247;0-163m) to 989 kg CaCO<sub>3</sub>/tonnes (CDD98; 51.7-51.8m).

Compared to the CaCO<sub>3</sub> equivalents of the samples analyzed for wt % CO<sub>2</sub>, it is observed that there is about 4.4% (RMH014.50-4.62) to 23.7% (RMH010.17-0.30) (Table 4.6) less, if consumption of all the available CaCO<sub>3</sub> is considered.

Table 4.6 The difference between NP calculated from total CO<sub>2</sub> equivalent value and the laboratory tested NP.

Sample	CO <sub>2</sub> (Wt.%)	CaCO <sub>3</sub> Equiv. (KgCaCO <sub>3</sub> /Tonne)	Neutralization Potential KgCaCO <sub>3</sub> /Tonne	% Difference
RMH010.00-0.10	46.7	1060.7	991.0	6.6
RMH010.17-0.30	45.9	1042.5	795.0	23.7
RMH011.50-1.77	46.3	1051.6	879.0	16.4
RMH014.50-4.62	15.4	349.5	334.0	4.4
RMH0130.40-30.55	45.9	1042.5	813.0	22.0
CRC2460-128	43.9	997.0	896.0	10.1

It is also revealed that the metasediments that exhibit low MPA values also have low NP values that range from -3.5 kg CaCO<sub>3</sub>/tonnes (RMH02;11.10-11.20m) or 0.8 kg CaCO<sub>3</sub>/tonnes (RMH02;13.90-14.10m) to 3.0 kg CaCO<sub>3</sub>/tonnes. Similarly, some of the diorite lithologies from the main zone that also exhibit low MPA values also exhibit low but negative NP values such as sample RMH03; 0.85-1.05m that exhibit an NP value of -1.2 CaCO<sub>3</sub>/tonnes (Table 4.3). This can be attributable to

Some of the metasedimentary samples from the main zone, with moderate MPA values such as RMH02; 30.75-30.90m with a MPA value of 87.9 CaCO<sub>3</sub>/tonnes, and RMH02; 32.45-32.55m with a MPA value of 74.4 CaCO<sub>3</sub>/tonnes, exhibit moderate NP values of 92.8 CaCO<sub>3</sub>/tonnes and 160.6 CaCO<sub>3</sub>/tonnes, respectively. A similar situation was observed in some of the composite diorite samples from the manganese mine zone such as CRC246; 128-139 m, that exhibited a MPA value of 209.4 CaCO<sub>3</sub>/tonne and a NP value of 84.9 CaCO<sub>3</sub>/tonnes. CRC280; 80-165m exhibited a NP value of 32.5 CaCO<sub>3</sub>/tonnes whereas it exhibited a MPA value of 158.4 CaCO<sub>3</sub>/tonnes (Table 4.3).

#### **4.3.4 Net Neutralization Potential**

Net neutralization potential is the difference between MPA and NP values. NNP value is one of the differentiation criterion used to determine acid production potential of a sample (See Table 4.3). If the net neutralization potential is less than -20 kg CaCO<sub>3</sub>/tonnes then the sample is said to have an acid production potential, if the sample has a NNP value greater than +20 kg CaCO<sub>3</sub>/tonnes, then the sample is said to have an acid neutralizing potential. If the NNP value is in between these boundaries in other words if  $-20 < \text{NP} < +20$  then the NNP criterion is not enough to decide about the acid production or neutralizing potential of the sample.

When the NNP values of all the 38 samples are considered, 17 of the tested samples have NNP values greater than +20 kg CaCO<sub>3</sub>/tonnes. All the marble samples collected from the Marble Zone, one metasedimentary sample collected from the Main Zone and the limestone and marble samples from the Manganese Mine Zone fall into this category. According to Net Neutralizing Potential criteria, ten of the tested samples fall into the  $-20 < \text{NP} < +20$  kg CaCO<sub>3</sub>/tonnes zone where it is not possible to decide about acid producing or neutralizing potential. Four of these

are diorite samples from the Main Zone and six of them are metasedimentary samples from the Main Zone. Eleven of the studied samples fall in to the  $NNP < -20$  kg  $CaCO_3$ /tonnes, three of the diorite samples and two of the metasedimentary samples from the Main Zone and four diorite samples from the Manganese Main Zone fall into this category (Table 4.7).

Table 4.7 Summary of the NNP results of the samples classified according to NNP Criterion

NNP > +20 Neutralizing Potential		-20 < NNP < +20 No decision on acid production potential		NNP < -20 Acid Producing Potential	
Sample Code	NNP kg $CaCO_3$ / tonne	Sample Code	NNP kg $CaCO_3$ / tonne	Sample Code	NNP kg $CaCO_3$ / tonne
RMH01;0.00-0.10	991	RMH03;0.85-1.05	-1.2	CRC271;78-100	-23
RMH01;0.17-0.30	795	RMH03;1.85-1.95	-2.3	CRC280;80-165	-126
RMH01;1.50-1.77	879	RMH03;15.10-15.30	-2.5	CRC246;128-139	-125
RMH01;4.50-4.62	333	RMH03;21.75-21.95	0.8	RMH03;25.20-25.33	-82
RMH01;30.40-30.55	813	RMH02;0.50-0.65	-2.9	RMH03;26.80-27.00	-125
RMH02;32.45-32.55	86	RMH02;1.60-1.72	1.8	RMH03;32.00-32.10	-59
CRC246;0-128	894	RMH02;4.38-4.50	2	RMH03;35.00-35.20	-139
CRC247;0-163	880	RMH02;11.10-11.20	-7.2	RMH02;14.50-15.10	-174
CRC248;0-157	903	RMH02;13.90-14.10	-4.1	RMH02;19.40-19.60	-218
CRC255;44-75	116	RMH02;30.75-30.90	4.9	RMH02;25.30-25.50	-223
CRC255;96-115	57			RMH02;29.25-29.35	-43
CRC257;42-115	30				
CRC270;108-205	90				
CDD98;51.7-51.8	989				
CDD91;294-295.7	987				
CRC388;69-119	925				
CRC391; 0-197	949				
Marble in Marble Zone		Limestone/Marble in Mn Mine Zone		Diorite in Mn mine zone	
Metasediment in Main Zone		Diorite in Main Zone		Metasediment+Diorite Transition in Main Zone	

#### 4.3.5 Neutralization and Acid Potential Ratio (NPR):

One extremely useful graphical method for the assessment of ABA data is a plot of Neutralization Potential Ratio, NPR (NP/MPA). It is considered that "...using the NP/MPA ratio, ABA is a good tool to assess overburden quality before mining and to predict post-mining drainage quality after mining...". The NPR was shown to be 89% correct (Skousen *et al.*, 2002).

If the NPR is <1:1 the sample is said to be Acid Generating (AG). If the sample's NPR is between 1:1 and 2:1 ( $1:1 < \text{NPR} < 2:1$ ) then the sample is considered to be Potential Acid Generating (PAG). If the sample is from 2:1 to 4:1 then the sample is said to be potentially acid consuming (PAC) finally if the sample has a NPR ratio greater than 4:1 then it is said to be Acid Consuming (AC) (See Figure 4.23).

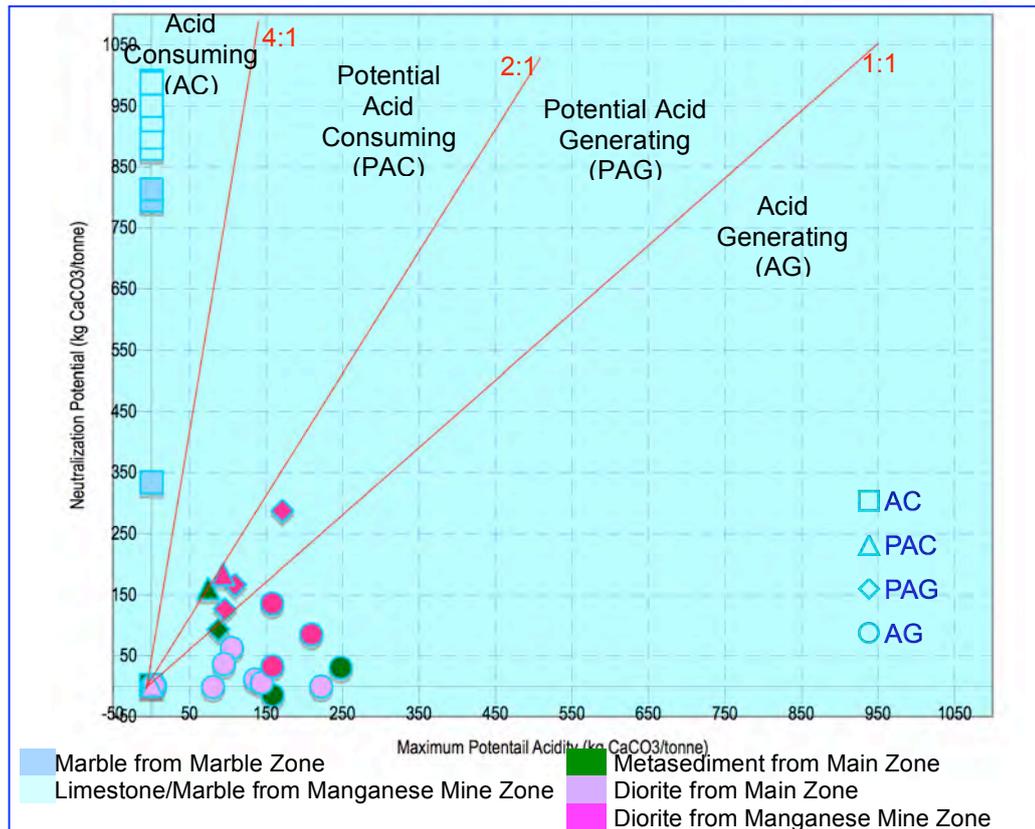


Figure 4.23 Distribution of the samples based on NPR values.

Among the tested samples all the limestone and the marble lithologies (All RMH01 samples from Marble Zone and CRC246;0-128m, CRC247;0-163m, CRC248;0-157m, CDD98; 51.7-51.8m, CDD91;294.0-295.7m, CRC388; 69-119m, CRC391;0-197m) have NPR values much higher than the 4:1 ratio. In addition, one metasediment sample (RMH02;1.60-1.72 m) from the main zone that has zero MPA value and only 1.8 kg CaCO<sub>3</sub>/tonne plot into this (>4:1 NPR) zone and can be

considered to be Acid Consuming since it has a MPA value less than 0.45 kg CaCO<sub>3</sub>/tonne.

In total there are 13 samples categorized as Acid Consuming (Figure 4.24). On the other hand 16 of the tested samples have an NPR ratio less than 1:1, thus they fall into the Acid Generating category. Out of this 16 samples, 8 of them are diorite samples collected from the Main zone (RMH03; 0.85-1.05m, RMH03;1.85-1.95, RMH03;15,10-15,30m, RMH03; 25.20-25.33, RMH03;26.80-27.00m, RMH03;32.00-32.10m; RMH03;35.00-35.20m, RMH02;29,25-29,35) and one of the samples is from the transition from diorite to metasediment from the main zone (RMH02;25.30-25.50m). Three diorite samples from the Manganese Mine Zone (CRC280;80-165m, CRC271;78-100m and CRC246;128-139m) and 4 metasedimentary samples from the main zone fall into the Acid Generating category (RMH02;11.10-11.20m, RMH02;13.90-14.10; RMH02;14.50-15.10, RMH02;19,40-19.60m).

There are 4 samples with NPR values that fall into 1:1 to 2:1 and these are considered as potentially acid generating. Three of these samples are diorites (CRC255;44-75m, CRC255;96-115m, CRC257;42-115m) collected from the manganese mine zone, and one of them is a metasedimentary sample collected from the main zone. In addition to this, there is one metasedimentary sample collected from the main zone (RMH02;30.75-30.90m).

There are 4 samples that fall into the Potentially Acid Consuming category with their NPR values ranging from 2:1 to 4:1. Two of these samples are metasedimentary samples (RMH02;4.38-4.50m, RMH02;32.45-32.55m) from the main zone. The distribution of the samples according to NPR criteria is shown in Figure 4.23 and in more detail in Figure 4.24.

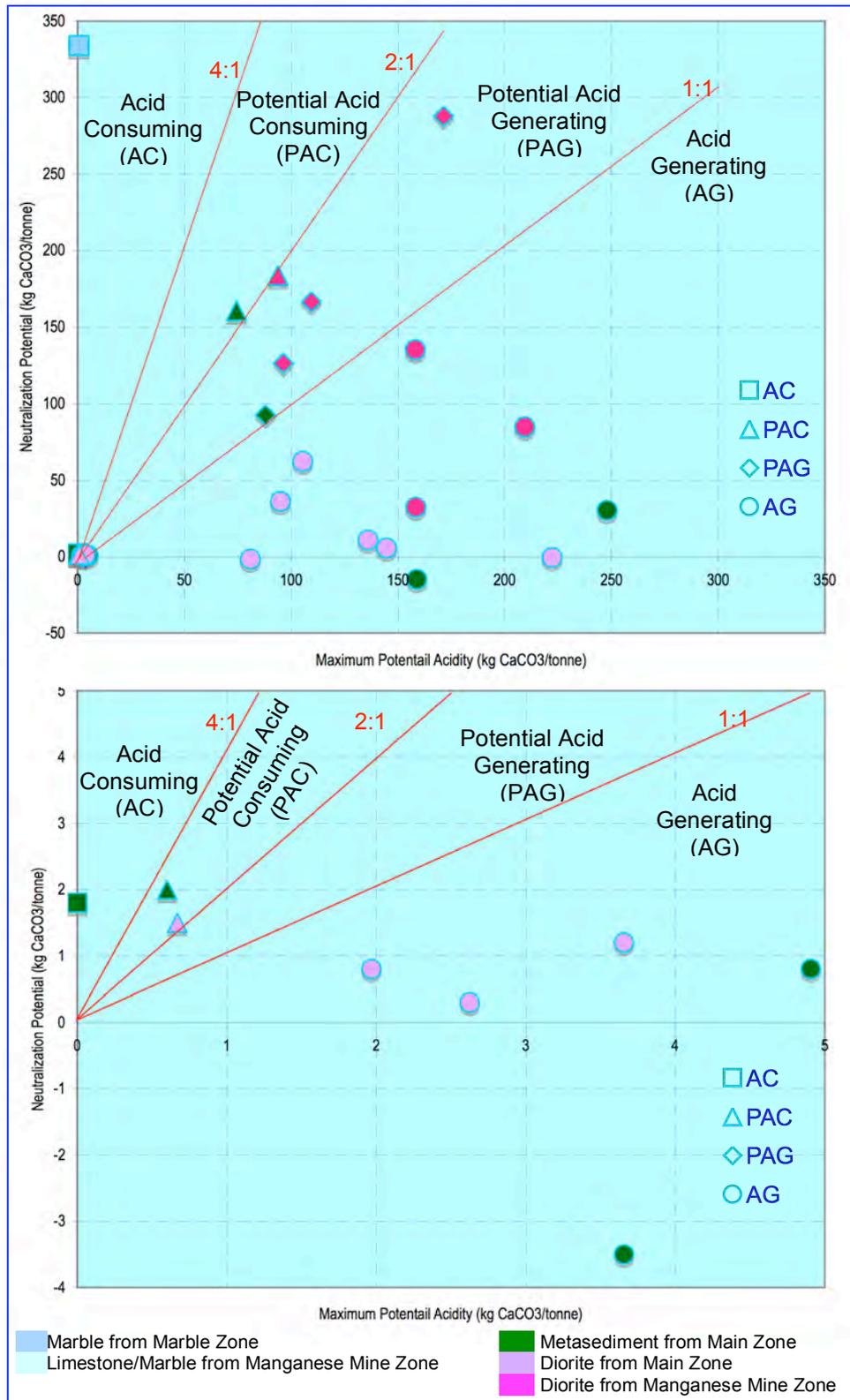


Figure 4.24 Graph that shows the NPR distribution of the tested samples in a detailed scale.

## CHAPTER 5

### DISCUSSION

Acid Mine Drainage and prediction of the final drainage chemistry after operation of a mine site is a problem studied since 1940s. The prediction techniques using stoichiometric relations of the Acid Mine Drainage chemistry was developed towards the end of 70s and the guidelines were developed in the North America by EPA and by British Columbia AMD Policy Statement. The acid base accounting is one of the widely accepted approaches that is being used internationally. However even this approach is not enough on its own to predict the post mining drainage chemistry. Because, as emphasized by *Morin and Hutt, (2005)* in most scientific work, executors would be contented with a 90 to 95 percent success rate. However, in AMD prediction and prevention, any failure that leads in significant environmental impact is intolerable. Therefore, in order to improve the drainage chemistry predictions to a nearly 99 % accurate level, within a holistic approach, all of the following issues are advised be considered as potential pitfalls and therefore are advised to be scrutinized (*Morin and Hutt, 2005*):

- On-Site Water Chemistry Monitoring Data
- Acid-Base Accounting
- NAG Testing
- Total Metals and Whole Rock Geochemistry
- Mineralogy and Petrography
- Laboratory Kinetic Testing
- Field Kinetic Testing
- Retention Tests

In this case study, most of the above steps except the kinetic testing was applied. It was revealed that every bit of data collected during the course of this study was useful. For instance, the geochemistry and XRD investigations gave a better understanding of the minerals that may be involved in AMD production. Most of the

sulfide minerals such as orpiment and realgar were not recognized in optical and ore microscopy studies, however simultaneously elevated levels of As and S observed in geochemical analysis revealed the presence of these minerals. Morin and Hutt, (2005) also, provide examples of the errors made in visual mineralogical interpretations such as petrographic measurements of pyrite being unrecognized but presence of pyrite being revealed by XRD techniques. Morin and Hutt, (2005) reminds that there can be significant mineralogical variations on small to medium scales, even within the samples duplicates. Conventional mineralogical techniques have significant error bars and are not necessarily consistent with each other. They also remind that XRD cannot detect amorphous phases, which can be important in some samples. Small impurities and solid solutions can affect the solubility and leaching rates of minerals, and affect the elements released by dissolution of a mineral.

Engineering expertise can help for a coarse prediction of the final drainage chemistry using only mineralogy or on-site water chemistry monitoring data, however in order to improve the completeness of the final picture a site must be investigated including all the above mentioned issues, as much as possible. One must also consider all the possible errors that can be made in these steps, such as the accuracy of the modal mineralogy and geochemistry.

In this study mineralogy, geochemistry and acid base accounting stages of a drainage prediction process were completed and investigated in detail. These data were provided to the mine planners and operators in order to accurately predict the drainage chemistry. The following sections provide a discussion about the techniques used for the mineralogy, geochemistry and acid base accounting stages of this prediction process starting with the sampling of the material.

## **5.1. Sampling Scheme**

The sampling scheme is designed to define acid generating and non acid generating and acid neutralizing material, to determine spatial differences in lithologies and to generate enough data points for waste rock block modeling. In general, the waste rock block modeling is produced by the project mining

engineering team since waste rock is generally defined by the project mining engineer (Downing and Giroux, 1993).

It is a rule of thumb that the samples selected should be representative of the study area or the mining operation. In our case, samples were selected not only to represent all the different available lithologies in the study area but also to represent the different mining zones.

Another point that must be considered very carefully is the preservation of the collected samples. To be able to represent field conditions the collected samples were immediately packed tightly to avoid further oxidation of the sulfur bearing minerals. Depending on the availabilities the best option is to preserve the samples in liquid nitrogen bearing airtight containers, however it is a costly preservation technique. In our case the samples are collected, oven dried overnight at a low temperature (40°C) and pulverized and placed in tightly closed plastic containers, and sent immediately to Vison Scitec laboratories for analysis. However well they may be packed samples have a chance to lose their properties within weeks unless they are preserved in liquid nitrogen (Mills, 1995).

## **5.2 Mineralogy and Petrography**

In order to understand mineral integration of the sampled medium, it is essential to consider the behavior of a mineral and its metal component(s) during weathering (Borsch, 1995). Therefore, petrographic studies were conducted as a part of the ABA procedure to determine the primary and secondary minerals and alteration variations that could impact the determination of neutralization potential. Mineralogy and petrography was also used to examine sulphide mineralogy, to determine mineralogy for rock classification, and finally to study grain size and grain boundaries as reaction sites for acid rock generation.

As indicated in the previous section, all the studied lithological samples were under the effect of cataclastic and hydrothermal alteration due to highly active tectonic nature of the study area and due to hydrothermal activities that occurred during the intrusion of the Çöpler Granitoid. The X-ray studies revealed lack of euhedral crystals but rather presence of imperfect crystals, the thin sections of limestone and marble samples indicated high ratios of recrystallization of calcite. In addition to that

we have observed calcification and sericitization as alteration products in dioritic lithologies. The ore microscopic studies revealed presence of disseminated pyrite and pyrite as vein filling material, as well as presence of oxide minerals such as magnetites and rutiles. This mineralogical investigation revealed presence of pyrites and chalcopyrite as sulfide minerals. In a previous study done during the exploration stage presence of arsenopyrite was also identified (Cliff et. al., 2003) but being in harmony with this study relative abundance of pyrite and marcasite was also indicated.

Pyrite and its polymorph marcasite are identified to be the most prominent minerals that have the potential for acid drainage production.

### **5.3.Geochemistry:**

All litho-geochemical studies were performed to determine the bulk chemistry of the non-ore material, which is a direct indication of mineralogy and alteration; to correlate chemistry with petrographic studies, to determine complimentary prediction method(s) in conjunction with the conventional and regulatory NNP ABA Procedures (Downing and Madeisky, 1998).

The tectonic environment of the formation of volcanogenic massive sulphide deposits and porphyry tin, gold and copper-molybdenum deposits can be identified from the geochemical characteristics of the associated igneous rocks (Pearce and Gale,1975). The incorporation of trace elements into minerals occurs at the time of formation but can be altered over geologic time with changes in temperature, pressure and alteration resulting from hydrothermal fluids (Raiswell and Plant, 1980 and Madeisky, 1995). From this point of view geochemical investigations are essential in understanding prediction of the final drainage chemistry.

In this study the porphyry copper-gold deposit is observed to be affected by hydrothermal alteration as indicated by molybdenum enrichments (Figure 4.16). Geochemical investigations also revealed the linear relation between Fe and S as another evidence of presence of pyrite (Figure 4.17). Although arsenopyrite or minerals such as orpiment and realgar were not revealed in mineralogical studies, geochemical data showed presence of such minerals by the parallel enrichment of As and S (Figure 4.19 and Figure 4.20).

## 5.4 Acid Base Accounting

Acid Base Accounting (ABA) is a stoichiometric approach and for a proper understanding one must consider the peculiarities of the methods used for determination of the "Acid Mine Drainage Potential".

### 5.4.1 Maximum Potential Acidity (MPA)

Since acid mine drainage results from accelerated weathering of sulfide minerals, the amount of sulfur in a sample, or in an overburden column, is obviously an important component of Acid Base Accounting (ABA). ABA uses the percent sulfur to predict the "Maximum Potential Acidity" (MPA) that a particular overburden sample or column could produce if all the sulfur reacts.

Sulfur determinations for ABA are often performed for total sulfur only, however, determinations for forms of sulfur are sometimes included. Sulfur generally occurs in one of three forms in the rock strata: sulfide sulfur, organic sulfur in case of coal mining, and sulfate sulfur. Sulfide sulfur is the form which reacts with oxygen and water to form acid mine drainage. The sulfide minerals most commonly involved in the study area and in general in coal and metal mining environments are pyrite and marcasite, both of which are  $\text{FeS}_2$ , in chemical composition. Other sulfide minerals such as chalcopyrite ( $\text{CuFeS}_2$ ) and arsenopyrite ( $\text{FeAsS}$ ) may also contribute to AMD in relatively minor amounts (Mills, 1995).

Organic sulfur is that sulfur which occurs in organic remnant, carbon-based molecules in coal and other rocks with significant carbon content; since organic sulfur is tied up in compounds that are stable under atmospheric conditions, it is not considered as a contributor to acid mine drainage. Organic sulfur can represent a significant fraction of the total sulfur found in coal seams (Mills, 1995).

Sulfate sulfur is often overlooked because in humid climates it is generally found in relatively low concentrations due to its high solubility (sulfate is washed away with precipitation). However, sulfate sulfur often occurs in partially weathered samples as the reaction by-products of sulfide mineral oxidation. When dissolved, these weathering by-products are the source of the contaminants found in acid mine drainage, so when determinations for forms of sulfur are done, sulfate sulfur must

be considered in the calculation of MPA. Alkaline earth sulfate minerals such as gypsum ( $\text{CaSO}_4$ ) can also contribute to the sulfate sulfur fraction. Where they are present, the alkaline earth sulfate minerals do not contribute to acidity.

Theoretically, the total of the sulfate and sulfide sulfur components should be a better indicator of the amount of reactive sulfur in a sample than total sulfur<sup>9</sup> should. However, a laboratory study (Hedin and Erickson, 1988) showed that total sulfur was related more strongly to leachate test results than was pyrite related sulfur. Since pyrite related sulfur is the form which contributes most significantly to acid mine drainage, these results indicate problems with pyrite related sulfur determinations. A review of the methods for sulfur determinations described by Noll *et al.*, (1988) reveal that the methods for total sulfur determinations have a relatively high degree of precision with few notable interferences and precautions, while the forms of sulfur determination methods described involve lesser degrees of precision and relatively more numerous potential interferences and precautions.

Brady and Smith (1990) compared total sulfur and forms of sulfur determinations performed by various laboratories. While the results generated by each laboratory were internally consistent in terms of the ratio of pyrite related sulfur to total sulfur, there were significant differences between laboratories in the median percent pyrite related sulfur/total sulfur. Where duplicate samples were available from different laboratories, differences were noted in the pyrite related determinations, but total sulfur determinations were comparable (Mills, 1995).

Within the studied samples sulfate sulfur contribution to total sulfur amount ranged from 0.58 % to 100 %. In samples with low total sulfur amounts the contribution of sulfate sample revealed to be significant, however in samples with high sulfur content the effect of sulphate sulfur was insignificant. Therefore the wt% sulfur values detected in exploration geochemistry can be directly converted to MPA and in the block model<sup>10</sup> design total sulfur values can be converted and used as the MPA values.

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<sup>9</sup> Total sulfur indicates sulfide sulfur plus sulphate sulfur.

<sup>10</sup> A block model is a 3-D model used in mine planning. These models are created on mine planning softwares that utilize geostatistical techniques and they are based on a vast amount of geocoded data.

Total sulfur determinations are typically simple to do, are reproducible, and can be calibrated and verified using available standards; pyrite related sulfur determinations are done using a variety of methods (sometimes not standardized, and at least one of which is considered inappropriate for rock samples), produce results which are often not reproducible between laboratories, and cannot be calibrated and verified using available standards. Given these considerations, and that pyrite related sulfur is the most abundant form in coal overburden (but not necessarily in the coal), total sulfur determinations currently provide the best basis for calculating MPA (Mills, 1995).

In this study the total sulfur and sulfate sulfur amounts are determined separately using LECO furnace and Wet Chemical methods respectively and the sulfide sulfur calculated by the difference is used in MPA calculations. The precision and accuracy of the determinations are checked via CANMET standard NBM-1 details of which are provided in Appendix-C. The Quality Control and Quality assurance tests performed on the selected samples indicated 99% to 100% accuracy (Table 3.5).

#### **5.4.2 Fizz Rating**

The significance of the fizz rating on ABA results is much underrated and has often not acknowledged suitable consideration. The fizz test is usually demonstrated as a minor element of the neutralization potential test; however the fizz test can have a considerably significant influence on the reliability and reproducibility of NP value, therefore a separate discussion is dedicated to fizz rating.

The fizz rating can be used as a confirmation on the NP determination, since there should be a qualitative correlation between the two. Even more significantly, the fizz rating ascertains the volume and the normality and volume of the acid, which is used to digest the sample, which in turn can affect the NP determination results (Evans and Skousen, 1995; Skousen *et al.*, 1997). The NP result is subsequently rather dependent on the fizz test results, however, the fizz test results are somewhat subjective human judgments.

The fizz test is performed by adding a couple of drops of 25% HCl to a small part of the prepared sample (Sobek *et al.*, 1978). The extent of reaction is observed and

evaluated, based on a four-ranked system where the reaction is judged to be none (0), slight (1), moderate (2) and strong (3).

There is a further concern, which additionally causes difficulties to the subjective nature of the fizz test. In general, in interpreting ABA, there are thresholds that are used for NP and percent sulfur. The strata which produce NP or percent sulfur values below the thresholds are considered to have little impact on post mining water quality. This is the reason behind using thresholds. Nevertheless, these same strata often correspond to the largest mass of the overburden and can "attenuate" the effects of the strata with significant NP and percent sulfur if they are included in the calculations of total NP and MPA for the considered site.

Mills (1995) reported that in Pennsylvania Coal Mining District of USA, a threshold value of 30 is often used for NP and a threshold value of 1 (slight fizz) is also frequently used for the Fizz Rating, designating samples below these values as "bad" or acid producible. The fizz threshold has a propensity to label a 0 or no fizz as being "bad" and higher fizz ratings as being "good." Strata identified to process a 0 fizz will not be considered to contribute to the potential alkalinity of the post mining water quality which could result in a negative permitting decision.

In addition to this, even with the best intentions of the laboratory employees performing the test, one cannot expect unbiased and repeatable results from a subjective test with a particular outcome pre-tagged as either good or bad. This is not to advocate that the use of thresholds is inappropriate, but to designate another precaution regarding stated fizz test results.

Evans and Skousen (1995) proposed a two-ranked fizz rating system, which would combine the 0 and 1 fizz ratings into a single category and a 2 or 3 fizz rating into a second category. They stated that during a round robin sample testing study accomplished by representatives of West Virginia University, Consolidation Coal Company (Consol), and the Pennsylvania Department of Environmental Protection on samples processed at the Penn State Materials Research Laboratories, the fizz ratings varied significantly between laboratories for certain samples. The laboratories thus used different normalities and volumes of acid to perform the NP determinations on those samples, as commanded by the fizz ratings. The NP values

varied significantly, and generally were higher when a larger volume of acid was used to digest the samples. When the Consol lab ran the NP determinations for each sample twice, with a different volume of acid each time, the analysis that was made with the higher volume of acid resulted in with a higher NP in each instance. The differences were often vast enough to alter the interpretation one would make concerning the alkaline producing potential of the sample. Skousen *et al.*, (1997) reported that when three different laboratories performed fizz determinations on replicates of 31 samples, all three laboratories assigned the same fizz rating to only 13 of the 31 samples which corresponds to only about one third of the samples.

Reducing the number of tiers in the fizz test is expected to reduce the amount of judgment required and consequently the subjectivity of the test. However, running the NP test with a reduced number of fizz test possibilities means that some samples would be digested in different volumes of acid than they would using the methods in Sobek *et al.* (1978) and Noll *et al.* (1988). Users of NP data need to be aware that changing the volume of acid used to digest a sample can change the NP results.

Skousen *et al.* (1997) described a protocol for a quantitative method of fizz rating of overburden samples based on the percent insoluble residue. Twenty ml of 10% HCl is added to 2.0 g of the prepared sample that was dried at low temperature (40-50°C) oven for about two hours. The solution is agitated until evolution of CO<sub>2</sub> is observed to cease. The solution is passed through a weighed filter, the filter plus residue are then dried and weighed, and the percent insoluble residue is calculated. The rating is then used to determine the volume and strength of acid used in the NP digestion; for that purpose the carbonate rating numbers are considered to be equivalent to the fizz rating values described in Sobek *et al.* (1978) and Noll *et al.*, (1988). The NP and fizz determinations reported in Skousen *et al.*, (1997) were run on replicates of the overburden samples, but the percent insoluble residue test was only run by one of the labs. As noted by the authors of the later study, the method needs to be further tested to validate the proposed rating system and to provide a yardstick for comparing NPs based on the fizz test to those based on the percent insoluble test. Mills (1995) notifies one potential problem with the percent insoluble residue test as for some samples, the results may vary significantly when the percent HCl used in the digestion is changed. The samples studied by Skousen *et*

al. (1997) were subjected to X-ray diffraction and characterized as belonging to one of four groups, based on their mineral and elemental content: Fe, Ca, S, and Si. When the percent insoluble residue test was performed on replicates of some of the samples using differing percents HCl, the results changed significantly for the iron-rich samples (Fe group), which included the samples with relatively high siderite content. The results for one of the carbonate-rich samples ( $\text{Ca}^{2+}$ ) also changed significantly. These results raise questions concerning which % HCl should be used to achieve results which rate the carbonate in the samples in an accurate and reproducible way.

Taking into account the difficulties that the current fizz rating system introduces into NP determinations, a reproducible, objective carbonate-rating test could significantly improve the reproducibility of NP data. Until such a test is refined, individuals who generate and interpret ABA data need to be much more aware of the influence of the fizz test values on the NP determinations. Where fizz test results and NP values seem to be at odds, further testing would be practical.

Since the widely used four ranked fizz test is not replaced yet globally, in this study as well as the Vison Scitec Laboratories an accredited highly experienced laboratory was asked to use Modified Neutralization Potential test procedure (Lawrence, 1997), but they were asked to report the fizz testing separately so that the above mentioned objectiveness of the test can be taken into account at the interpretation stage.

In addition, Vison Scitec is one of the preferred and accredited laboratories in AMD prediction tests that their expertise were relied upon to provide possibly the most reliable fizz rating and NP values. This idea is then tested by the fizz rating values compared with the literature sited NP range (Morin and Hutt, 2005) as shown in Table 5.1. Taking into account that if the compared NP value is below the appropriate range, then too much acid was utilized in the NP test procedure and the NP value may be overestimated; if the compared NP value is above appropriate range, then insufficient acid was utilized in the NP procedure and thus NP value may be underestimated (Morin and Hutt, 2005). In general most of the NP values

are within the expected range<sup>11</sup>. The limestone and Marble lithologies that are observed to be above the appropriate range are interpreted to be normal, in other words, considered to be not underestimated since they have the maximum fizz rating rank. However, those samples indicated with red color (CRC255;44-75m, CRC255;96-115m, CRC257;42-115m, CRC270;108-205m, CRC271;78-100m and RMH02; 29.25-29.35m) in Table 5.1 can be considered to be truly above appropriate range with underestimated NP. Regarding the four samples that appear to be below range indicated as underlined (RMH02;11.10-11.20m, RMH02;14.50-15.10m, RMH02;25.30-25.50m, RMH03;25.20-25.33m) in Table 5.1, may be considered to have an overestimated NP values but they are already either negative or very low NP values of the samples that have significant MPA values.

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<sup>11</sup> Sixteen of samples are within the range and 13 of the above range samples are carbonate lithologies that are expected to exhibit above range values.

Table 5.1 Fizz Rating Values compared with the literature indicated range of NP values provided by (Morin and Hutt, 2005).

<b>Sample</b>	<b>NP</b>	<b>Fizz Rating</b>	<b>NP Range</b>	<b>Range Comparison</b>
RMH01;0.00-0.10	991.0	3	100-500	Above Range
RMH01;0.17-0.30	795.0	3	100-500	Above Range
RMH01;1.50-1.77	879.0	3	100-500	Above Range
RMH01;4.50-4.62	334.0	3	100-500	Within Range
RMH01;30.40-30.55	813.0	3	100-500	Above Range
RMH02;0.50-0.65	3.0	0	0-50	Within Range
RMH02;1.60-1.72	1.8	0	0-50	Within Range
RMH02;4.38-4.50	2.0	0	0-50	Within Range
RMH02;11.10-11.20	-3.5	0	0-50	<u>Below Range</u>
RMH02;13.90-14.10	0.8	0	0-50	Within Range
RMH02;14.50-15.10	-14.8	0	0-50	<u>Below Range</u>
RMH02;19.40-19.60	30.3	0	0-50	Within Range
RMH02;25.30-25.50	-0.5	0	0-50	<u>Below Range</u>
<b>RMH02;29.25-29.35</b>	<b>62.3</b>	<b>0</b>	<b>0-50</b>	<b>Above Range</b>
RMH02;30.75-30.90	92.8	2	50-100	Within Range
RMH02;32.45-32.55	160.6	2	50-100	Above Range
RMH03;0.85-1.05	0.8	0	0-50	Within Range
RMH03;1.85-1.95	0.3	0	0-50	Within Range
RMH03;15.10-15.30	1.2	0	0-50	Within Range
RMH03;21.75-21.95	1.5	0	0-50	Within Range
RMH03;25.20-25.33	-1.5	0	0-50	<u>Below Range</u>
RMH03;26.80-27.00	11.0	0	0-50	Within Range
RMH03;32.00-32.10	36.2	0	0-50	Within Range
RMH03;35.00-35.20	5.7	0	0-50	Within Range
CRC246;0-128	896.0	3	100-500	Above Range
CRC246;128-139	84.9	2	50-100	Within Range
CRC247;0-163	880.0	3	100-500	Above Range
CRC248;0-157	903.0	3	100-500	Above Range
<b>CRC255 ;44-75</b>	<b>287.8</b>	<b>2</b>	<b>50-100</b>	<b>Above Range</b>
<b>CRC255 ;96-115</b>	<b>166.5</b>	<b>2</b>	<b>50-100</b>	<b>Above Range</b>
<b>CRC257;42-115</b>	<b>126.6</b>	<b>2</b>	<b>50-100</b>	<b>Above Range</b>
<b>CRC270;108-205</b>	<b>183.8</b>	<b>2</b>	<b>50-100</b>	<b>Above Range</b>
<b>CRC271 ;78-100</b>	<b>135.5</b>	<b>2</b>	<b>50-100</b>	<b>Above Range</b>
CRC280;80-165	32.5	1	0-50	Within Range
CDD98; 51.7-51.8	989	3	100-500	Above Range
CDD91; 294-295.7	988	3	100-500	Above Range
CRC388; 69-119	926	3	100-500	Above Range
CRC391; 0-197	950	3	100-500	Above Range

However, if the tests will be performed in a newly establishing laboratory instead of the common four-ranked subjective fizz rating test the percent insoluble test procedure proposed by Skousen *et al.*, (1997) is more appropriate to be able to obtain a more reliable NP value.

### 5.4.3 Neutralization Potential

The widely accepted NP procedure used in this study is the modified NP-Lawrence (1997) procedure that is detailed in the Appendix-C. NP results make up an important base for the assessment of AMD and the first step of the NP test is to conduct a qualitative fizz test on a small amount of the prepared sample as discussed above. Based on the fizz test results, an appropriate volume and normality of HCl is selected and utilized for the digestion of the sample.

In general, carbonate minerals, such as calcite and dolomite, are known to be the major contributors to groundwater alkalinity. The acid-digestion step of the NP test is suspected to dissolve various silicate minerals, besides carbonates, which results in an NP determination that overestimates the amount of carbonate minerals in a sample. Lapakko (1993), working with rock samples from metals ore in Minnesota, reported that silicate minerals such as plagioclase, dissolve and neutralize acid at relatively low pH values such as those occurring in acid mine drainage or during a NP titration; however, he also noted that since this dissolution will only take place at low pH values, it is unlikely to help maintain a drainage pH of acceptable quality. His test results, based on leaching studies, also indicated that the rate of acid neutralization by silicate minerals was not adequate to maintain a drainage pH of 6.0 or above. Therefore the contributions of other silicate minerals are relatively insignificant compared to calcite minerals.

Siderite ( $\text{FeCO}_3$ ) has long been suspected of interfering with the accuracy of NP determinations and of complicating the interpretation of the data (Morrison *et al.*, 1990). Noll *et al.*, (1988) indicated that samples with significant amounts of siderite can make it difficult to hold the final end point of the titration with NaOH. If iron in solution from the siderite is not completely oxidized, the titration is terminated, then the calculated NP value will be over estimated, since complete oxidation of the iron would produce additional acidity. An uncertain titration end point can obviously affect the reproducibility of the NP results. Skousen *et al.* (1997) also revealed that laboratories tended to assign different fizz ratings to the replicates of samples with high siderite content.

Morrison *et al.*, (1990) recommended adding a hydrogen peroxide step to the NP determination procedures to get rid of the problems with the method caused by siderite. Morrison and Scheetz (1994) executed ABA tests on four samples using both the method described in Noll *et al.* (1988) and their modified approach. The NP for each sample was lower when the modified method was used, and was drastically lower for the three samples known to contain a significant amount of siderite.

Evans and Skousen (1995) revealed that NP values were not noticeably different when samples were analyzed both with and without the hydrogen peroxide step; however they revealed that reproducibility between laboratories did get better when the hydrogen peroxide step was used. They also revealed that when the hydrogen peroxide step was executed without filtering the solution, the results sometimes did not compare well with other ABA methods, most likely due to the oxidation of pyrite in the residue by H<sub>2</sub>O<sub>2</sub>. As a matter of fact, oxidation of pyrite with H<sub>2</sub>O<sub>2</sub> has been used as a method of predicting the acid-producing potential of overburden (O'Shay, *et al.*, 1990). Morrison and Scheetz (1994) utilized samples known to include a significant amount of siderite (determined by X-ray diffraction) in their comparative study, which may be why their results showed that the hydrogen peroxide step reduced NP.

Skousen *et al.* (1997) subjected 31 overburden samples of known mineralogy (determined by X-ray diffraction) to four variations of the NP test. The variations were named after the authors of that methodological paper or after the step that made the difference. These differences are indicated below:

- 1) (Sobek), the standard Sobek method (Sobek *et al.*, 1978);
- 2) (Boil), a method that includes boiling of the sample for five minutes during the digestion step (Noll *et al.*, 1988);
- 3) (H<sub>2</sub>O<sub>2</sub>), the same as the boil method except that after digestion the sample is filtered and treated with H<sub>2</sub>O<sub>2</sub> before titration;
- 4) (SobPer), the same as the Sobek method apart from peroxide (H<sub>2</sub>O<sub>2</sub>) added to the sample (no filtration) after the first titration. Among their findings the Skousen *et al.*, (1997) concluded that, the four variations on the NP test

resulted in similar findings for samples containing little pyrite or siderite. Skousen *et al.*, (1997) also revealed that the SobPer method resulted in lower NP values than the other methods for samples that contained significant amounts of pyrite, due to oxidation of the pyrite by H<sub>2</sub>O<sub>2</sub> in the unfiltered samples. Skousen *et al.*, (1997), shown that, compared to the other three methods, the H<sub>2</sub>O<sub>2</sub> method provided: the lowest NP values for samples with significant siderite content; the best reproducibility between the laboratories which participated in the study; results which were the most consistent with soxhlet leachate results. They have also concluded that auto titration at a slow setting is preferable to hand titration, especially for samples with significant siderite content.

Skousen *et al.* (1997) briefly described a method to perform NP determinations with the H<sub>2</sub>O<sub>2</sub> step. If the hydrogen peroxide step performs according to its intent, it should generally decrease the NP's of strata with a significant siderite content, but should not appreciably affect the NP values of strata that do not include significant amounts of siderite. It should also lead to better reproducibility of NP data between laboratories, especially for samples with significant siderite content.

In our case there is no significant siderite content determined or reported to be present in our sampled lithologies therefore the Vison Scitec laboratories was not asked to perform a siderite correction or boiling step in the determination of NP and the Modified Acid Base Accounting Procedure for Neutralization Potential (Lawrence, and Wang, 1997 ) was used instead ( See Appendix-C).

The NP test has been adapted and widely used to approximate the carbonate content of mine overburdens largely because it is relatively quick, inexpensive, and easy to perform. However, as noted above, it may not always provide results, which are accurate and reproducible. Other methods of determining carbonate content have occasionally been used in high risk-sites or on sites where the NP test provided questionable results.

In situations where NP data provide ambiguous results and/or where mining presents a risk to significant uses of nearby groundwater or surface water sources, tools such as X-ray diffraction and CO<sub>2</sub> coulometry are suggested to be considered

to verify the NP results. In this study the carbonaceous samples are analyzed for their total CO<sub>3</sub> C content. In this study Carbonate carbon is determined via Leco furnace combustion. As indicated in Figure 5.2. there is a linear relation between Carbonate NP and tested NP. Tested NP are 4.3% to 23.7% lower than Carbonate NP.

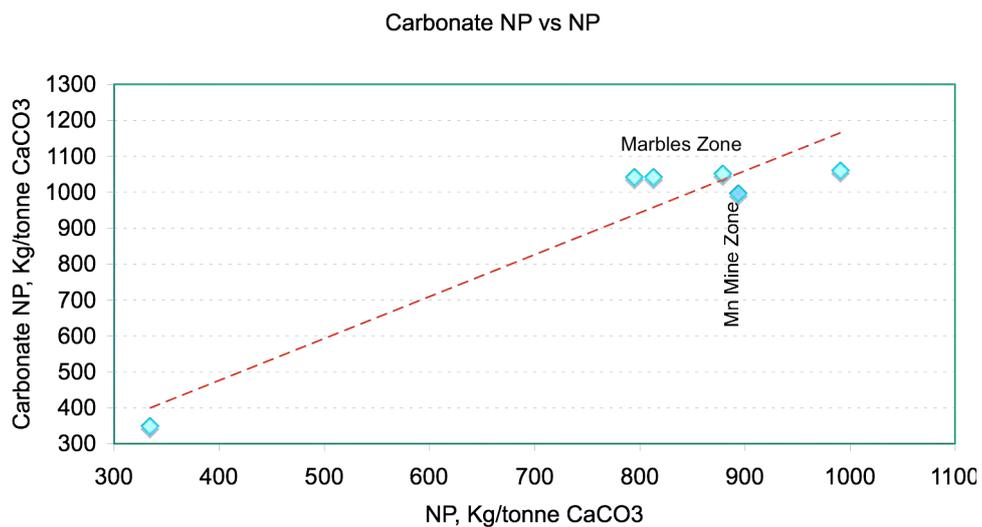


Figure 5.1 Carbonate Carbon Neutralization Potential vs. tested Neutralization Potential of some marbles from the marble zone and one limestone sample from the manganese mine zone.

#### 5.4.4 Interpretation of ABA data and AMD Potential Criteria

Interpretation of ABA data involves the application of numerous assumptions; some of the more significant assumptions often used are:

- all sulfur in a sample will react to form acid;
- all material in the sample which consumes acid during digestion in the lab will generate alkalinity in the field;

- the reaction rate for the sulfur will be the same as the dissolution rate for the neutralizing material.
- NP and percent sulfur values below certain threshold levels do not influence water quality.

As these assumptions imply, interpretation of ABA data is far more complicated than simply summing the MPA and NP values.

The two commonly used criteria for AMD potential assessment are:

1. The difference in value between NP and AP, or Net Neutralization Potential ( $NNP = NP - AP$ ), where if NNP is negative the sample is indicated to produce acidity;
2. The ratio of NP value to MPA value, or Neutralization Potential Ratio ( $NPR = NP/MPA$ )

In a detailed study, Skousen et. al, (1990) gathered geologic and geographic data for 56 mined sites in West Virginia, USA, which allowed them to estimate total overburden amounts. They determined values for maximum potential acidity (MPA), neutralization potential (NP), net neutralization potential (NNP), and NP/MPA ratios for each site based on Acid Base Accounting. These values were correlated to post-mining water quality from springs or seeps on the mined property.

Skousen et. al. (1990) showed that there existed a poor relationship between MPA and post-mining water quality, NP was intermediate, and NNP and the NP/MPA ratio showed the best prediction accuracy. In their study, NNP and the NP/MPA ratio gave identical water quality prediction outcomes (Skousen et. al,1990). Using NP/MPA ratios, Skousen et. al. (1990) separated values into categories: <1 should produce acid drainage, between 1 and 2 can produce either acid or alkaline water conditions, and >2 should produce alkaline water. On their 56 sites, NP/MPA ratios varied from 0.1 to 31, and six sites (11%) did not fit the expected pattern using this category approach. Two sites with ratios <1 did not produce acid drainage as predicted (the drainage was neutral), and four sites with a ratio >2 produced acid drainage when they should not have. These latter four sites were either mined very slowly, had inaccurate ABA data, received water from an adjacent underground

mine, or included some mining practice that degraded the water. Skousen et. al. (1990) revealed that, in general, an NP/MPA ratio of <1 produced mostly acid drainage sites, between 1-2 produced mostly alkaline drainage, while sites with a NP/MPA ratios of >2 produced alkaline drainage with a few exceptions (Table 5.2). Using the NP/MPA ratio, ABA is a good tool to assess overburden quality before mining and to predict post-mining drainage quality after mining, and was correct in 50 out of 56 cases (89%) (Skousen et. al. 1990).

Table 5.2 Neutralization Potential Ratio (NPR) Screening Criteria to Determine AMD Potential (Price *et al.*, 1997). (AG: Acid Generating; PAG: Potentially Acid Generating; PAC: Potentially Acid Consuming; AC: Acid Consuming)

Potential For AMD	Initial NPR Screening Criteria	Comments
Likely (AG)	< 1:1	Likely to generate AMD
Possibly (PAG)	1:1 - 2:1	Possible to generate AMD if NP is insufficiently reactive or is depleted at a faster rate than sulphides
Low (PAC)	2:1 - 4:1	Not potentially AMD generating unless significant preferential exposure of sulphides along fracture planes, or extremely reactive sulphides in combination with insufficiently reactive NP
None (AC)	> 4:1	No further AMD testing required unless materials are to be used as a source of alkalinity

However the rate of AMD production or neutralization is not possible to be interpreted by only ABA studies. In addition to that Morin and Hutt (2005) reminds us to take into account the unavailable neutralization potential value that can be determined as a result of humidity cell kinetic tests. The UNP value can range between 10 kg CaCO<sub>3</sub>/tonne to up to 60 kg CaCO<sub>3</sub>/tonne. The UNP value is not considered in this study since kinetic tests are out of scope of this study.

In addition, one must remember that paste pH can only help us detect the readily available H<sup>+</sup> ions and even though it can provide us an idea about the acid producability of a lithology, it cannot be used as a screening tool on its own.

As mentioned above, the ABA that is used as a screening tool for the prediction of potential of acid mine drainage production, is a stoichiometric approach that

assumes simultaneous occurrence of acid production or acid neutralization. However, it is a fact that sulphide mineral disintegration, thus acid production is a considerably slow event. One of the factors affecting the rate of acid production is the grain size of the sulphide minerals. In the case of the study area the grain sizes are small enough to ease acid production.

The Çöpler gold Prospect has mainly four different types of lithologies, in three distinctly different petrographic composition: limestone-marble, meta-sediments and diorites at different degrees of alterations.

It is a fact that all the limestone-marble lithologies have strong capability of acid consuming in other words have high neutralization potential. On the other hand other lithologies are prone to produce acidity at a wide range depending on their sulfur content. The sulfide minerals may be present in all of these three lithologies. As indicated by the mineralogical and geochemical studies the most abundant sulfide minerals are pyrites and marcasites. The maximum acid potential vs. % sulfur plot (Figure 5.2), indicates that there is a positive correlation between maximum acid potential and the total sulfur content of the sample. Therefore the sulfur bearing rocks should be considered carefully during the mine planning stage.

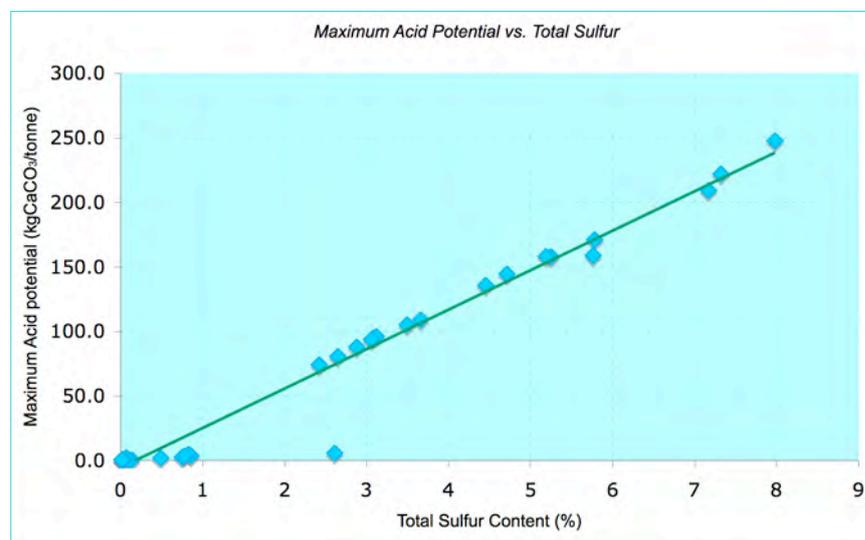


Figure 5.2 Graph indicating positive correlation between maximum potential acidity (MPA) and total sulfur content.

On the other hand most of the acid producing lithologies, especially diorites also have a certain amount of acid consuming/neutralizing capacity, due to the presence of silicate minerals such as feldspars and the micro-silica matrix of the diorite.

Acid mine drainage leads to the reduction of the pH and thus causes the mobilization of most of the metals such as Fe. On the other hand, as recently revealed by Lengke and Tempel (2005), arsenic can be mobilized via a relatively different path than the other heavy metals. As the pH is increased As may still continue to be mobilized.

As indicated by the geochemical analysis the arsenic levels in the studied samples are also significantly high (in some samples as high as 10000 ppm). In their study Lengke and Tempel (2005) indicated that, in a relatively short time span (approximately in 200–300 days), arsenic release from orpiment and realgar oxidation go beyond the current U.S. National Drinking Water Standard (0.05 ppm) even at the lowest initial dissolved oxygen concentration (3 ppm) and a reactivity factor of 1%. Another agonizing solution from their study is that the simulations of orpiment oxidation in the presence of albite and calcite show that calcite can act as an effective buffer to the acid water produced from orpiment oxidation within relatively short periods (days/months), but the release of As continues to increase. Lengke and Tempel (2005) shown that pyrite oxidation rates are faster than orpiment and realgar within pH 2.3 to 8; however, pyrite oxidation rates are slower than  $\text{As}_2\text{S}_3$  (am) and AsS (am) at pH 8. The activation energies of arsenic sulfide oxidation range from 16 to 124 kJ/mol at pH 8 and temperature 25 to 40°C, and pyrite activation energies are 52 to 88 kJ/mol, depending on pH and temperature range. They revealed that the magnitude of activation energies for both pyrite and arsenic sulfide solids indicates that the oxidation of these minerals is dominated by surface reactions, except for  $\text{As}_2\text{S}_3$  (am). Low activation energies of  $\text{As}_2\text{S}_3$  (am) indicate that diffusion may be the factor controlling the reaction rate.

In a mining environment to prevent acid drainage formation, Limestone is commonly mixed with acid prone sulfide minerals. However, the oxidation rates of arsenic sulfides increase as solution pH rises and result in a greater release of As (Lengke and Tempel, 2005).

Furthermore, carbonate minerals (i.e., calcite, aragonite, and dolomite) last much shorter than those of arsenic sulfide and silicate minerals. Thus, within a geologic time scale, carbonate minerals are generally consumed at the initial stages and may not be present to act as a pH buffer for acid mine waters. Additionally, the presence of silicate minerals such as pyroxenes (wollastonite, jadeite, and spodumene) and Ca-feldspars (labradorite, anorthite, and nepheline) may not be significant for buffering acid solutions because these minerals dissolve relatively more rapidly and survive relatively shorter periods compared to sulfide minerals. However, other silicate minerals such as Na and K-feldspars (albite, sanidine, and microcline), quartz, pyroxenes (augite, enstatite, diopside, and  $\text{MnSiO}_3$ ) have much longer lifetimes than arsenic sulfide minerals that may be present in a system (Lengke and Tempel, 2005).

The results of the modeling studies of arsenic sulfide mineral oxidation reveal that these minerals potentially can liberate significant concentrations of dissolved As to natural waters, and the factors and mechanisms involved in arsenic sulfide oxidation are still under investigation (Lengke and Tempel, 2005).

Therefore, especially regarding the high arsenic concentrations observed in certain levels in the study area, the arsenic levels should be thoroughly modeled and monitored in the study area during the mine planning and operating stages.

## CHAPTER 6

### CONCLUSIONS AND RECOMMENDATIONS

Acid Mine Drainage (AMD) is an environmental problem that leaves behind detrimental hazards that last for long periods of time and are a very costly to abate. As mentioned in Chapter 1, due to the abandoned mine sites such as Balya, and operating mines such as Murgul this problem is threatening strategic energy investments such as the Havran Dam in Balıkesir and the Muratlı Dam in Artvin. The investment values of these structures are about £260 million and the threat over their water basin is invaluable. Similarly, the study area is located within the catchments of the Euphrates, next to the Karasu River a major branch of Euphrates. This international water body is critical for our country and it passes through most of our very important energy dam investments such as the Keban Dam, Karakaya Dam, Atatürk Dam, Birecik Dam and Karkamış Dam. Therefore damage to the catchments will potentially affect all these investments.

Therefore prediction of the potential for AMD is required to be as accurate as possible, and is very important prior to mining operations that involve sulfide bearing metal ores or sulfide rich coal mining.

Prediction of AMD requires an integrated and holistic approach. Even though this study only deals with the proper realization of the acid base accounting component of this system one must consider all the eight issues that contribute to the final drainage chemistry prediction as indicated in Figure 6.1.

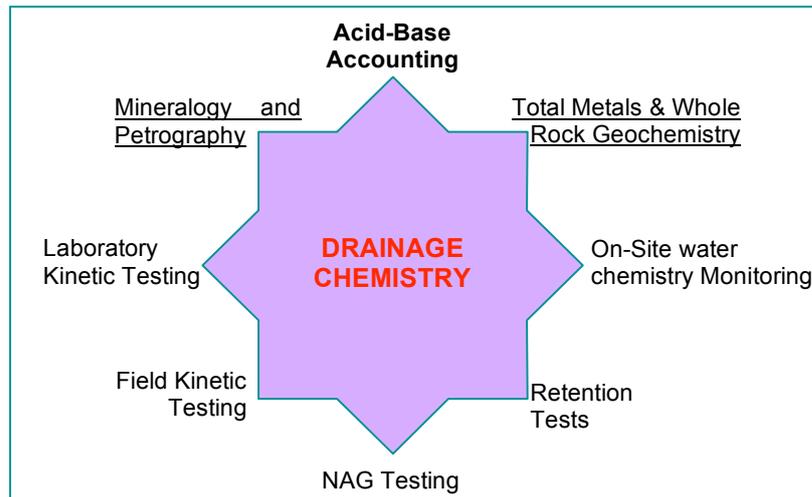


Figure 6.1 Significant issues that effect final drainage chemistry, modified after Morin and Hutt (2005).

The sampling scheme is the starting point of a drainage chemistry prediction process. The collected samples should be able to represent all the lithologies including ore bearing strata and the overburden. In addition to that the samples need to be preserved properly in order to retain the original humidity and to avoid post sampling oxidation of the collected samples. If the analysis will be performed immediately it can be acceptable to tightly wrap the samples by plastic film, if the samples will be conserved for longer periods it is advised to preserve the samples in liquid nitrogen filled vacuumed special containers. Samples collected from the Çöpler gold prospect were wrapped with plastic and sent to the analysis immediately, and the diamond drill and rock cutting composite samples were representative to all the lithologies in the study area. The results obtained through the samples analyzed for AMD revealed the importance of total sulfur content as explained in Chapter 4 and Chapter 5. The Çukurdere mine operators are strongly recommended to consider in their mine design, the total %S values they have obtained through their exploration studies as an indication of acid generating lithologies.

Sample characterization is an other important stage for the accurate determination of the final drainage chemistry. This stage involves mineralogical examination using

not only everyday techniques such as optic mineralogy and ore microscopy studies but also usage of XRD techniques to reveal nature of the alteration products and the components of the overburden rocks.

Geochemical studies are also very significant in the sample characterization stage and not only to provide the distribution of the total sulfur that has great chance to contribute to the acid production, but also to show the traces of the hydrothermal alteration levels. It is very important to know these mineral enrichment levels to be able to block model<sup>12</sup> the removal and placement of the acid producing or arsenic rich strata during the mine site planning stage to avoid rapid disintegration of the altered acid producing rocks. Mineralogical and geochemical characterization of the samples is also important at the interpretation stage of acid base accounting data. In addition, identification of sulphate bearing minerals or problematic minerals such as siderite is also very important for the accurate determination of the MPA and NP at the acid base accounting stage as explained in the flow chart given in Chapter 3 and as discussed in Chapter 5.

In the study area the geochemical data revealed the presence of minerals such as orpiment, realgar, chalcopyrite and arsenopyrite as indicated by the parallel enrichment of elements such as Cu - S, and As- S.

ABA or static tests are the next stage for the drainage chemistry prediction. Both determination of the MPA and NP has peculiar pitfalls one must take into consideration. Most of these pitfalls were discussed in Chapter 5, for instance, the effect of total sulfur versus sulfide sulfur. Even though the total sulfur may be considered as the maximum amount that may be potentially oxidized to form acidity, identification of the sulfide species present in the sample is very important. In the case of coal mines and/or in the presence of sulphate minerals it is known that organic sulfur and sulphate sulfur is not involved in the acid production. The total sulfur value yields higher MPA values than the real sample can produce if the sample contains sulphate sulfur or organic sulfur that will not react to form sulfuric acid. In the case of Çöpler Gold Prospect, although the effect of sulphate sulfur was

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<sup>12</sup> As explained in previous chapters a block model is a three dimensional geocoded mine site model where the mine operators design their operations from the overburden removal stage up to reclamation stage.

up to 100% for some samples, since these samples were very low in sulfur the actual affect was insignificant, and in case of Çöpler total sulfur values can be directly taken into MPA calculations.

Similarly, presence of siderite yields more acid consumption during the determination of neutralization potential and therefore the neutralization potential value is overstated. If the presence of siderite is detected during the sample characterization stage, a siderite elimination stage using hydrogen peroxide is advised in order to determine the realistic neutralization potential value. In case of Çöpler Gold prospect the samples are identified to lack siderite, thus siderite correction was not applied to the ABA procedures.

Determination of the appropriate fizz rating value is another important issue that needs to be considered for the determination of neutralization potential. If the fizz rating is determined less than the appropriate value than it leads to addition of too much acid and results in an overstated NP value, and if the fizz rating is determined above the appropriate value then less than sufficient amount of acid may be used in the digestion and the NP value will be understated. Therefore the NP value obtained at the end needs to be checked with the appropriate range, in other words expected range of NP value with respect to Fizz rating. Another option may be to compare visually judged Fizz rating values with the objective carbonate-rating test that relies up on percent insoluble residue as proposed by Sukousen et al. (1997). The reproducibility and accuracy of the results can be improved by paying attention to the determination of the fizz rating. In the case of Çöpler gold prospect the fizz ratings are determined by the conventional subjective techniques. Yet, as discussed in Chapter 5, the fizz rating determinations did not affect the results. However, in an NP determination practice that will be preformed in Turkey it is strongly recommended to base the fizz rating determinations on percent insoluble residue approach.

Interpretation criteria that will be used can be categorized into two: Net Neutralization Potential (NNP) and Neutralization Potential Ratio (NPR). These criteria are usually classified against thresholds. One of the accepted thresholds for NNP is  $>+20$  kg  $\text{CaCO}_3$ /tonne being non acid producing and  $<-20$  kg  $\text{CaCO}_3$ /tonne being acid producing, the values that fall in between are considered to be

unpredictable. The NNP criteria is not reliable on its own especially if the unavailable neutralization potential (UNP) value is considered since the subtraction of the UNP value determined after kinetic tests would push more samples into the unpredictable zone. It was not possible to perform kinetic tests in this case study. In the second stage it is recommended to do further studies to determine UNP values.

However, NNP values can be utilized as a cross check during the interpretation stage, just like the Paste pH value that can only provide us an idea about the immediately available free H<sup>+</sup> ions.

Neutralization Potential Ratio is the essential criterion that needs to be utilized in the classification of the samples as acid producing, potentially acid producing, acid neutralizing, and potentially acid neutralizing.

The next stage is testing of the data obtained in ABA determinations using laboratory and field kinetic tests. Since this stage takes longer time in parallel to this stage it is recommended to use the ABA data during the block modeling and mine planning process in order to be aware of the abatement and prevention plans and costs that will be applied during mining and at the post mining stages.

In the study area, 16 samples are identified to be "Acid Generating". In addition 4 more samples are determined to be "Potentially Acid Generating". On the contrary, 4 samples are identified to be "Potentially Acid Consuming" and 14 samples are identified to be "Acid Consuming". However, two of these samples exhibit very low NP values and therefore, are not considered as really acid consuming. The acid generating and consuming characteristics were explained in full detail in Chapter 4. From a lithological point of view all the limestone and marble lithology, which is abundant in the area, have a great potential to neutralize a potential AMD that may be produced by diorites and in some cases by metasedimentary lithologies. Metasedimentary lithologies can be expected to stay neutral or acid producing but diorites exhibit high affinity to produce acidity. Therefore during planning stage the exposure and placement of the limestones/marbles, diorites and metasediments after the removal of the ore they contain should be considered carefully taking into account the Acid Production ability or Acid consumability potential of the subject strata.

In general the porphyry copper and gold deposits in Turkey are relatively rich in arsenic as in the case of the study area (Uşak-Eşme Gold mine is another example). Therefore the behavior of arsenic in pre- and post- mining stages also needs to be considered carefully. As indicated by Lengke and Tempel (2005), the factors and mechanisms involved in arsenic sulfide oxidation are still under investigation however it is also known that As has higher reaction rates for oxidation even though the pH approaches to 8 compared to pyrite. Therefore, during the abatement stage, when the acid production is neutralized arsenic minerals such as orpiment, realgar will still continue their oxidation. In this case all the acid generating phases consume the neutralizing materials such as limestone, or lime, relatively quicker. Later the acid producing materials are no longer neutralized and pH is lowered again resulting in the mobilization of As and other heavy metals. Therefore, the presence of arsenic in overburden strata should be scrutinized and needs to be considered in detail. The mobilization of arsenic and other heavy metals by means of colloids or fine-grained sediment can lead in the contamination of the aquatic habitats in the catchment areas. Therefore, it is strongly recommended to do a research that will investigate arsenic mobilization in relation to AMD for Çöpler gold prospect case and for operating and abandoned mine sites.

In order to prevent high costs of abatement an accurate prediction and planning in AMD can be obtained if the above-mentioned critical points are taken into account. However, an other problem in our country is the abandoned sulfide bearing mine sites. Although this case study is the first academic approach to the AMD problem, more research is needed for the proposed, active and abandoned Turkish mine sites. The future research areas can be listed as follows:

- Kinetic studies: Especially for the study area kinetic studies such, as humidity cell tests are needed to be performed.
- Arsenic mobility in relation to AMD: As explained above the Turkish mines have an already existing arsenic background the relation of this arsenic mobility and AMD, including prediction of what might happen after abatement of AMD should be studied in depth.

- Reference Material Development: In this study a Canadian reference material was used (CANMET standard NBM-1 see Appendix-C). Since the geology of Turkey and the ore bodies are different than those in Canada, it is strongly recommended to develop a research scheme for the development of reference materials specific to the nature of Turkish mines.
- Hydrogeologic studies: The contamination and damage related to AMD over surface and groundwaters is very important, therefore it is necessary to do hydrogeological research related to mining activities and AMD.
- Resource economics studies: The contribution of mine operations to our economy is important, however there is a research need to reveal the damage caused by AMD. Such a study may involve calculation of existing or potential AMD damage due to abandoned mines. Such a research may lead in realization of a regulatory framework in order to avoid AMD damage by determining science based economic sanctions.
- Abatement and Management Studies: The best way to reduce the cost of AMD damage is to plan and manage a site based on AMD prediction techniques. Therefore research related to abatement of AMD in abandoned and active sites and research related to the management of AMD is very important.
- Standard development studies: The ABA methods utilized to predict acid production and acid neutralization potential of the lithologies in the study area are available in international literature. However for the adaptation of international quality standards it is strongly recommended to perform necessary steps to standardize these methods for Turkey, in cooperation with Turkish Standards Institute.

As regards to the conclusions to be drawn from this case study, as indicated by the ground water chemistry, geochemistry results and taking into consideration the ABA test results, the existence of Çöpler ore body is already creating an abnormally high metal concentration in the waters sampled during the baseline study by Ekobil (2005). Therefore the AMD problem can be considered to be already existing in the study area to a certain extent as can be expected from a metallic resource.

However, we are unable to observe very low pH values, since the large limestone bodies are able to neutralize the system. Therefore, in case of disturbing the site and operating the mine, the AMD problem of the Çöpler Gold Prospect needs to be scrutinized and managed during the operational and post-operational stages of the mining activity. If not controlled the heavy metals that will be mobilized due to lowered pH will be carried away by colloids and fine sediments.

Concerning that the water from the deep limestone aquifer is not contaminated by the presence of the ore body in Çöpler, it is important to assess the risk of contamination or mixing of the waters from this aquifer, in the proposed mining area. Therefore, understanding the link between local and deep aquifer systems is essential. As indicated in the baseline report, (Ekobil, 2005) the extent of a potential contamination is dependent on the thickness and the size of the intrusion beneath the area to be mined and on the depth of the fracture systems. The detailed investigation of these hydrogeological links needs to be considered by the mine operators.

Regarding the surface water bodies, The Karasu river is the largest branch of Euphrates and it is already receiving contaminated mine waters from the Divriği Iron Mine. Both the contamination through the Divriği iron mine and any future surface run off that will wash the Çöpler gold prospect and flows to Karasu River are in the upstream direction of most of the Turkey's major hydro electricity producing dams such as Keban, Karakaya, Atatürk, Birecik and Karkamış Dams. Therefore it is very important to manage the mining operations in order to avoid acid mine drainage and its potential damage to these mega structures.

As a final recommendation, concerning that "diorite" is a lithology with a relatively high probability for acid production, the site proposed as the tailing dam needs to be re-considered due to underlying diorite lithology and the danger of elevated AMD potential in case of a leakage. Otherwise, that particular area needs to be re-investigated from an AMD point of view.

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## **APPENDIX-A**

### **LIST AND DETAILS OF THE SAMPLES INVOLVED IN THE STUDY**

In Appendix-A a list of all the samples involved in this study is provided. In the following table, the samples are indicated by the name and number of the exploration well and by the meter or meter interval the sample was collected. CDD indicates “Çöpler Diamond Drill”, CRC indicates “Çöpler Rock Cutting” and CRD is utilized for the exploration wells that have started as rock cutting and transformed into diamond drill. Finally RMH indicates “Rock Mechanics Holes”. The locations of the drill holes are also provided in this table. The sample characterization tests that reveal the mineralogy and geochemistry of the samples and the applied ABA tests are indicated by an “X” symbol.

SAMPLE INFORMATION			COORDINATES			MINERALOGY				ACID BASE ACCOUNTING TESTS						
Sample Code and meter	Lithology	Mineral zone	East	North	Elevation	Geochemistry	Thin Section	Polished Section	XRD	Paste pH	CO2	Total Sulphur	Sulphate Sulphur	Maximum Potential Acidity	Neutralization Potential	Fizz Rating
CDD 84; 43.2-43.4m	Diorite		460125.043	4364350.965	1191.015	X	X	X(13)								
CDD 85; 177-178 m	Diorite		459924.091	4364358.679	1180.882	X	X	X (6)								
CDD 86; 246-247 m	Diorite		459523.964	4364298.979	1206.569	X	X		X							
CDD 88;; 166-167 m	Diorite		459999.275	4364277.590	1183.689	X										
CDD 92; 135-136 m	Diorite		459932.342	4364388.596	1176.994	X	X		X							
CDD 93; 145-146	Diorite		459790.676	4364372.663	1128.138	X	X									
CDD 94; 109-110	Diorite		459971.645	4364305.107	1176.192	X										
CDD 96; 223-224 m	Diorite		459974.729	4364526.808	1159.097	X										
CRD-334A;140.9-141.1m	Metasediment		459722.665	4363801.325	1279.257	X	X		X							
CDD-89; 121-122			459739.698	4363860.167	1269.864		X									
CDD91; 294.0-295.7	Marble	Mn Mine Zone	460202.00	4364226.00	1224.00		X			X		X	X	X	X	X
CDD-98;13			459998.886	4364327.435	1181.076		X									
CDD98; 51.7-51.8	Marble	Mn Mine Zone	459998.886	4364327.435	1181.076					X		X	X	X	X	X
CDD-98; 51.7-51.9	Marble	Mn Mine Zone	459998.886	4364327.435	1181.076		X									
CDD-99; 163-163.3			460124.877	4364398.638	1181.619		X		X							
CRC 255; 44-75	Diorite		459997.304	4364498.629	1160.425	X				X		X	X	X	X	X
CRC 255; 96-115	Diorite		459997.304	4364498.629	1160.425	X				X		X	X	X	X	X
CRC 257; 42-115	Diorite	Mn Mine Zone	460085	4364326						X		X	X	X	X	X
CRC246; 0-128	Limestone	Mn Mine Zone	459775	4364350						X	X	X		X	X	X
CRC246;128-139	Diorite	Mn Mine Zone	459775	4364350						X		X	X	X	X	X
CRC247; 0-163	Marble	Mn Mine Zone	459700	4364330						X		X		X	X	X
CRC248; 0-157	Marble	Mn Mine Zone								X		X		X	X	X
CRC270; 108-205	Diorite	Mn Mine Zone	459773.888	4364401.777	1121.938	X				X		X	X	X	X	X
CRC271; 78-100	Diorite	Mn Mine Zone	460046.737	4364551.984	1156.371	X				X		X	X	X	X	X
CRC280; 80-165	Diorite	Mn Mine Zone	460087.911	4364272.091	1204.400	X				X		X	X	X	X	X

SAMPLE INFORMATION			COORDINATES			MINERALOGY				ACID BASE ACCOUNTING TESTS						
Sample Code and meter	Lithology	Mineral zone	East	North	Elevation	Geochemistry	Thin Section	Polished Section	XRD	Paste pH	CO2	Total Sulphur	Sulphate Sulphur	Maximum Potential Acidity	Neutralization Potential	Fizz Rating
CRC388; 69-119	Marble	Mn Mine Zone	459801.060	4364306.950	1152.113					X		X	X	X	X	X
CRC391; 0-197	Marble	Mn Mine Zone	459918.668	4364225.338	1197.414					X		X	X	X	X	X
CRD_334A;141-142	Metasediment		459722.665	4363801.325	1279.257	X										
CRD_356	Marble		459703.859	4363647.529	1294.090	X			X							
RMH01;0.17-0.30	Marble	Marble Zone	459700	4363900					X	X	X	X		X	X	X
RMH01;0-0.10	Marble	Marble Zone	459700	4363900			X		X	X	X			X	X	X
RMH01;1.50-1.77	Marble	Marble Zone	459700	4363900						X	X	X		X	X	X
RMH01;30.4-30.55	Marble	Marble Zone	459700	4363900						X	X	X		X	X	X
RMH01;4.50-4.62	Marble	Marble Zone	459700	4363900						X	X	X		X	X	X
RMH02;0.5-0.65	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;1.6-1.72	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;11.1-11.2	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;13.9-14.0	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;14.5-15.1	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;19.4-19.6	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;25.3-25.5	Metasediment+Diorite	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;29.25-29.35	Diorite	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;30.75-30.90	Metasediment	Main zone	459170	4363850			X	X(17)		X		X	X	X	X	X
RMH02;0.5-0.65	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;1.6-1.72	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;11.1-11.2	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;13.9-14.0	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;14.5-15.1	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;19.4-19.6	Metasediment	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;25.3-25.5	Metasediment+Diorite	Main zone	459170	4363850						X		X	X	X	X	X
RMH02;29.25-29.35	Diorite	Main zone	459170	4363850						X		X	X	X	X	X

SAMPLE INFORMATION			COORDINATES			MINERALOGY				ACID BASE ACCOUNTING TESTS						
Sample Code and meter	Lithology	Mineral zone	East	North	Elevation	Geochemistry	Thin Section	Polished Section	XRD	Paste pH	CO2	Total Sulphur	Sulphate Sulphur	Maximum Potential Acidity	Neutralization Potential	Fizz Rating
RMH02;30.75-30.90	Metasediment	Main zone	459170	4363850			X	X(17)		X		X	X	X	X	X
RMH02;32.00-32.10	Metasediment	Main zone	459170	4363850			X	X(14)		X		X	X	X	X	X
RMH02;4.38-4.50	Metasediment	Main zone	459170	4363850						X		X		X	X	X
RMH03;0.85-1.05	Diorite	Main zone	458975	4363900						X		X	X	X	X	X
RMH03;1.85-1.95	Diorite	Main zone	458975	4363900						X		X	X	X	X	X
RMH03;15.1-15.3	Diorite	Main zone	458975	4363900						X		X	X	X	X	X
RMH03;21.75-21.95	Diorite	Main zone	458975	4363900						X		X	X	X	X	X
RMH03;25.20-25.33	Diorite	Main zone	458975	4363900						X		X	X	X	X	X
RMH03;26.80-27.00	Diorite	Main zone	458975	4363900						X		X	X	X	X	X
RMH03;32.0-32.1	Diorite	Main zone	458975	4363900						X		X	X	X	X	X
RMH03;35.0-35.2	Diorite	Main zone	458975	4363900						X		X	X	X	X	X

## **APPENDIX -B**

### **GEOCHEMICAL ANALYSIS RESULTS**

In Appendix-B the detailed results of the geochemical analysis are provided. The name of the drill hole and the meter interval that was geochemically analyzed are indicated at the top row. The analyses are performed at every meter indicated on the first column.

CRC 255 47m to 76m																															
Sample No	From	To	Au ppm	Ag ppm	Al %	As ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	K %	Mg %	Mn ppm	Mo ppm	Na %	Ni ppm	P ppm	Pb ppm	S %	Sb ppm	Sr ppm	Ti %	V ppm	W ppm	Zn ppm	Ag ppm
03052	47	48	0.77	2.7	6.45	301	330	<0.5	<2	16.3	3	6	7	140	2.79	1.28	0.21	1230	9	0.05	7	740	172	3.73	8	104	0.23	112	10	552	
03053	48	49	3.1	19.6	3.58	724	100	<0.5	13	23.9	47.8	5	8	494	4.11	0.52	0.57	1460	22	0.02	8	490	2290	5.82	36	92	0.13	65	<10	5090	
03054	49	50	3.56	25.8	3.6	821	80	<0.5	4	25.5	41.1	6	9	871	4.79	0.45	0.39	1130	47	0.02	7	480	1305	7	42	97	0.12	72	10	3910	
03055	50	51	1.56	25.5	4.12	905	110	<0.5	<2	11.7	5.7	16	8	2420	15.4	0.37	0.17	1880	267	0.03	5	650	231	>10.0	32	49	0.18	122	10	749	
03056	51	52	2.5	7.6	5.55	936	190	<0.5	2	9.7	13.5	9	9	548	4.84	0.51	0.17	1000	51	0.02	9	1080	594	6.65	19	57	0.31	166	10	1750	
03057	52	53	4.04	1.7	6.06	842	320	<0.5	<2	14.85	4	12	8	856	4.99	0.66	0.21	2230	18	0.03	9	770	127	6.53	21	61	0.23	131	10	627	
03058	53	54	3.59	1.3	7.17	969	310	<0.5	<2	10.6	2.1	11	8	243	5.29	0.78	0.29	2590	18	0.04	7	1130	114	6.42	16	62	0.36	194	20	270	
03059	54	55	5.81	1.1	8.66	892	280	<0.5	<2	9.95	1.4	12	10	255	5.4	1.11	0.34	2110	11	0.05	9	1280	121	6.07	20	84	0.39	198	20	201	
03061	55	56	8.63	<0.5	8.4	1000	230	<0.5	<2	12.35	0.5	12	7	136	5.64	1.06	0.36	2230	6	0.06	7	1490	82	6.19	19	83	0.36	198	20	52	
03063	56	57	8.36	<0.5	7.49	1065	340	<0.5	<2	8.89	0.5	13	11	159	5.45	1.06	0.3	2220	10	0.05	7	1200	60	6.46	18	94	0.4	194	10	47	
03064	57	58	7.73	<0.5	6.96	1245	390	<0.5	2	8.97	0.6	12	8	225	5.19	1.08	0.32	2160	14	0.06	9	1140	62	6.4	19	87	0.37	183	20	164	
03065	58	59	4.8	0.6	7.9	1610	250	<0.5	<2	3.7	1.9	13	8	89	5.17	1.16	0.32	998	10	0.06	6	1200	30	6.5	20	87	0.41	207	20	464	
03066	59	60	2.56	0.6	9.77	774	70	0.5	<2	0.84	<0.5	16	8	77	5.73	2.31	0.27	920	12	0.1	6	1380	27	6.85	22	90	0.46	209	10	50	
03067	60	61	4.92	0.9	9.1	1010	70	<0.5	<2	1.98	1.1	15	9	219	5.32	2.41	0.23	1670	8	0.12	8	1360	51	6.44	21	128	0.43	209	20	162	
03068	61	62	0.43	<0.5	7.93	381	390	0.5	<2	15.45	<0.5	10	3	44	3.46	2.17	0.24	3630	4	0.16	5	1050	14	4.45	11	114	0.29	134	20	33	
03069	62	63	0.56	<0.5	7.57	507	460	0.8	<2	6.13	<0.5	14	8	177	3.29	2.96	0.33	1110	6	0.5	6	1160	18	4.08	8	197	0.36	162	10	22	
03070	63	64	6.76	<0.5	8.83	747	270	0.6	<2	2.28	0.8	17	7	119	5.51	2.35	0.33	751	7	0.13	7	1260	52	6.49	11	87	0.43	206	10	53	
03071	64	65	1.75	0.9	7.21	705	420	0.6	<2	7.39	<0.5	12	4	89	3.74	1.81	0.3	2560	13	0.14	2	1230	40	4.89	16	95	0.36	172	10	38	
03072	65	66	5.23	0.5	7.7	1610	170	0.5	<2	2.6	0.5	12	9	78	6.11	1.1	0.3	971	17	0.05	10	1560	73	7.48	22	81	0.41	216	20	59	
03073	66	67	1.14	<0.5	7.67	866	240	0.6	<2	4.77	<0.5	12	5	32	4.61	1.22	0.33	812	19	0.07	5	1510	70	5.87	10	70	0.4	198	10	35	
03074	67	68	2.19	<0.5	7.71	1170	230	0.6	<2	3.76	<0.5	12	6	41	4.99	0.96	0.34	1290	8	0.05	6	1470	21	6.16	11	64	0.41	207	10	37	
03075	68	69	3.98	0.6	8.15	1655	200	0.6	<2	5.73	<0.5	12	9	72	6.05	0.96	0.4	1625	7	0.05	10	1620	36	7.73	21	92	0.4	203	20	37	
03076	69	70	4.33	<0.5	7.45	1435	230	0.5	<2	3.77	1.1	14	6	72	5.32	1.3	0.34	1330	10	0.08	7	1400	18	6.66	21	81	0.4	206	10	72	
03077	70	71	0.83	<0.5	7.67	557	730	0.6	<2	13.05	0.8	10	4	122	3.48	1.68	0.26	2100	9	0.17	9	1170	14	4.52	8	128	0.32	148	20	116	
03079	71	72	5.68	<0.5	7.8	943	530	0.6	<2	13.5	0.8	10	7	74	4.6	1.3	0.29	2510	7	0.07	5	1250	21	5.92	20	98	0.33	175	10	64	
03080	72	73	2.15	0.6	8.14	675	160	0.5	<2	5.12	<0.5	12	9	52	5.71	1.7	0.26	1100	9	0.09	7	1550	16	7.18	9	85	0.43	228	20	102	
03081	73	74	6.49	<0.5	7.85	1200	40	<0.5	<2	3.29	1.4	10	12	372	10.7	0.27	0.31	1100	14	0.02	12	1160	35	>10.0	16	58	0.4	293	20	166	
03083	74	75	9.42	<0.5	6.55	1225	60	<0.5	<2	9.5	2.1	9	10	468	8.21	0.4	0.23	1570	15	0.03	16	1160	21	>10.0	34	78	0.35	234	30	200	
03084	75	76	14.95	2.7	6.64	2090	360	<0.5	2	17.7	8.9	15	11	1340	6.49	0.58	0.18	5320	33	0.03	34	980	54	8.57	113	166	0.23	148	20	1130	

CRC 255 47m to 116m																															
Sample No	From	To	Au ppm	Ag ppm	Al %	As ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	K %	Mg %	Mn ppm	Mo ppm	Na %	Ni ppm	P ppm	Pb ppm	S %	Sb ppm	Sr ppm	Ti %	V ppm	W ppm	Zn ppm	Ag ppm
03107	96	97	2.35	<0.5	6.7	789	370	<0.5	<2	13.05	0.7	21	8	369	7.1	0.58	0.11	1735	20	0.03	55	1310	40	9.63	12	73	0.31	219	20	99	
03109	97	98	0.91	<0.5	7.95	420	620	<0.5	<2	6.31	0.6	12	6	75	3.54	2.6	0.14	1045	15	0.11	37	1280	19	4.68	6	108	0.35	184	10	77	
03110	98	99	0.8	<0.5	7.14	466	400	0.5	<2	11.35	0.5	11	3	192	5.38	0.95	0.21	2380	32	0.04	23	1160	38	7.13	12	66	0.29	170	<10	95	
03111	99	100	0.52	<0.5	8.19	236	660	0.6	<2	7.78	<0.5	9	5	37	3.08	3.47	0.26	1740	19	0.14	5	1150	18	3.8	<5	132	0.32	152	<10	168	
03112	100	101	0.3	<0.5	7.25	246	420	0.8	<2	9.22	<0.5	10	4	89	4.28	2.07	0.3	1895	13	0.19	6	1160	40	5.54	5	122	0.31	164	<10	134	
03113	101	102	0.45	<0.5	7.63	266	590	0.9	<2	8.06	<0.5	13	4	98	3.66	3.24	0.3	1985	10	0.35	2	1160	27	4.68	5	176	0.32	150	<10	82	
03114	102	103	0.4	<0.5	7.83	332	340	0.8	<2	9.78	<0.5	8	3	40	4.34	1.46	0.37	2520	24	0.16	3	1160	31	5.48	6	93	0.31	158	<10	40	
03115	103	104	0.23	0.5	7.99	362	410	0.8	<2	10.95	<0.5	10	3	53	3.92	2.07	0.38	3050	10	0.15	3	1080	27	5.14	10	104	0.29	154	<10	36	
03116	104	105	0.92	1.2	7.2	460	520	0.8	2	7.98	<0.5	10	5	73	3.58	2.6	0.42	3760	11	0.18	5	1080	66	4.46	22	121	0.3	156	10	132	
03117	105	106	0.15	<0.5	8.47	302	250	0.8	<2	11.4	<0.5	8	3	68	4.53	1.44	0.58	2920	12	0.12	4	1140	33	5.66	5	94	0.29	168	<10	49	
03118	106	107	0.17	<0.5	7.25	181	460	0.9	<2	8.75	<0.5	9	5	75	3.07	2.58	0.37	1885	8	0.41	3	1100	13	3.47	5	174	0.29	142	<10	49	
03119	107	108	0.08	<0.5	7.82	116	530	1	<2	8.67	0.7	7	6	36	2.54	2.5	0.4	1545	8	1	2	1120	16	2.12	<5	340	0.3	142	<10	164	
03120	108	109	0.15	<0.5	8.48	142	270	1	<2	12.55	<0.5	8	4	55	4.04	1.14	0.43	2180	13	0.94	3	1090	16	2.93	5	300	0.29	152	<10	37	
03121	109	110	0.16	<0.5	7.3	156	470	0.9	<2	7.99	<0.5	9	4	50	3.1	2.45	0.38	1390	10	0.67	4	1060	31	3.34	<5	250	0.3	149	<10	52	
03124	110	111	0.12	<0.5	7.37	241	440	0.7	<2	9.8	<0.5	13	4	194	3.47	2.59	0.35	2010	24	0.29	2	1090	17	4.03	<5	152	0.29	161	<10	34	
03125	111	112	0.19	0.9	7.19	324	540	0.8	<2	10.05	1.2	12	4	191	3.71	2.43	0.33	3080	12	0.37	2	1110	106	4.43	17	171	0.3	170	<10	140	
03126	112	113	0.39	<0.5	8.29	192	560	0.9	<2	9.78	<0.5	10	5	75	2.74	3.05	0.38	1845	8	0.75	3	1130	60	2.75	8	287	0.31	151	<10	170	
03127	113	114	0.09	<0.5	8.32	152	390	0.9	<2	11.75	<0.5	10	5	84	2.88	1.86	0.37	2060	9	0.94	4	1110	40	2.57	<5	334	0.29	144	<10	208	
03128	114	115	0.4	<0.5	8.02	344	540	0.9	<2	10.4	<0.5	10	3	85	3.47	1.66	0.36	2560	18	0.23	12	1150	23	4.13	9	124	0.31	168	<10	432	
03129	115	116	0.21	<0.5	7.13	488	380	0.7	<2	5.79	7	12	4	39	3.71	2.7	0.21	1935	11	0.08	21	1310	35	3.74	<5	95	0.36	198	<10	445	

**CRC 270 108m to 205m**

Sample No	From	To	Au	Ag	Al	As	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb	Sr	Ti	V	W	Zn	Ag
			ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	ppm	%	%	%	ppm	ppm	%	ppm	ppm	ppm	%	ppm	ppm	%	ppm
02552	108	109	1.6	7.8	8.58	967	1740	0.5	<2	8.38	1.4	23	19	>10000	11.85	0.04	0.3	2270	14	<0.01	18	750	87	1.46	<5	29	0.36	199	10	471	1.08
02553	109	110	0.49	<0.5	7.64	211	420	<0.5	<2	17.25	<0.5	10	17	1105	6.3	0.08	0.34	2950	7	<0.01	19	330	26	3.75	<5	26	0.3	109	<10	237	
02554	110	111	0.34	<0.5	7.1	210	400	<0.5	<2	17.7	<0.5	9	12	629	5.43	0.07	0.33	2980	12	<0.01	13	450	28	3.08	<5	28	0.31	107	<10	170	
02555	111	112	0.35	<0.5	6.86	191	380	<0.5	<2	17.8	<0.5	7	9	536	4.91	0.07	0.32	3290	6	<0.01	9	490	19	3.47	<5	32	0.28	109	<10	126	
02556	112	113	0.17	<0.5	8.26	255	190	0.8	<2	3.81	<0.5	16	5	400	5.53	1.32	0.38	1505	7	0.05	11	1200	12	5.97	<5	40	0.36	136	<10	182	
02557	113	114	0.14	<0.5	7.49	241	150	0.8	<2	4.3	<0.5	14	4	392	5.18	1.31	0.34	1445	26	0.05	12	1100	11	5.82	<5	41	0.35	137	<10	81	
02558	114	115	0.18	<0.5	7.57	196	180	0.9	<2	4.61	<0.5	14	6	390	4.12	1.48	0.48	2610	4	0.05	8	1020	18	4.44	<5	44	0.3	134	10	71	
02559	115	116	0.12	<0.5	8.22	110	520	1	<2	5.15	<0.5	9	7	234	2.65	2.26	0.73	907	5	0.32	12	1080	7	2.49	<5	90	0.26	121	<10	36	
02561	116	117	0.11	<0.5	8.74	224	330	0.8	<2	5.73	<0.5	11	6	260	4.62	1.57	0.66	1935	5	0.21	12	1000	15	5.21	<5	80	0.33	122	<10	59	
02562	117	118	0.08	<0.5	8.17	235	190	0.7	<2	10.55	<0.5	12	9	211	4.77	0.74	0.56	2950	5	0.19	9	970	31	5.5	<5	105	0.34	134	<10	91	
02563	118	119	0.09	<0.5	7.94	201	260	0.8	<2	11.6	<0.5	11	4	195	4.31	0.97	0.78	3300	4	0.37	10	880	22	4.78	<5	156	0.3	121	<10	81	
02565	119	120	0.1	<0.5	8.29	248	70	0.7	<2	6.96	<0.5	13	10	357	6.21	0.18	0.88	2500	19	0.06	10	780	38	7.2	<5	68	0.38	140	<10	102	
02566	120	121	0.12	0.5	8.08	175	30	0.5	<2	18.5	<0.5	6	12	414	4.64	0.15	0.69	6430	7	0.02	8	300	29	3.73	<5	52	0.32	80	<10	100	
02567	121	122	0.03	<0.5	8.31	191	260	0.9	<2	11.6	<0.5	10	5	132	4.35	0.93	0.98	4040	7	0.63	14	850	23	4.81	<5	184	0.31	104	<10	57	
02568	122	123	0.07	<0.5	8.26	345	230	0.9	<2	5.56	<0.5	12	5	143	4.71	1	1.44	2670	11	0.22	7	940	29	5.72	<5	110	0.35	125	<10	67	
02569	123	124	0.03	<0.5	8.81	132	150	1	<2	2.76	<0.5	10	5	152	4.15	1.82	1.39	1075	8	0.6	10	1020	13	4.84	<5	176	0.34	136	<10	35	
02570	124	125	0.01	<0.5	7.33	123	280	0.9	<2	4.84	<0.5	10	5	92	3.55	1.76	1.09	1140	9	1.02	8	1080	24	4.38	<5	229	0.33	139	<10	32	
02571	125	126	0.02	<0.5	8.59	195	200	1.1	<2	2.84	<0.5	13	5	116	4.54	1.36	1.58	1455	5	0.29	12	1080	26	5.47	<5	117	0.37	127	<10	54	
02572	126	127	0.08	0.6	8.53	226	320	1.1	<2	4.16	<0.5	12	5	211	4.32	1.09	1.38	3310	19	0.43	13	1160	30	5.3	<5	164	0.36	140	<10	75	
02573	127	128	0.1	<0.5	8.87	238	230	1	<2	3.37	<0.5	15	7	283	5.14	0.9	1.25	1645	20	0.29	7	1180	23	6.2	<5	128	0.37	146	<10	59	
02574	128	129	0.05	1	8.62	189	510	1.1	<2	1.98	<0.5	10	8	321	2.9	2.26	1.04	622	30	0.56	10	1110	59	3.22	13	161	0.27	137	<10	92	
02576	129	130	0.26	6.3	8.56	240	310	1.1	<2	4.28	21.5	11	9	252	3.66	2.74	0.73	1770	39	0.31	10	1110	905	4.43	47	150	0.29	135	<10	1800	
02577	130	131	0.04	1	8.4	189	320	1.2	<2	3.08	<0.5	12	6	271	3.48	2.12	0.83	1100	15	0.52	5	1090	62	3.98	<5	156	0.29	128	<10	89	
02578	131	132	0.08	<0.5	9.14	209	270	1.2	<2	2.01	<0.5	10	6	294	3.32	2.4	1.02	808	34	0.51	7	1090	23	3.73	<5	147	0.28	125	<10	16	

CRC 270 108m to 205m																															
Sample		Au	Ag	Al	As	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb	Sr	Ti	V	W	Zn	Ag	
No	From	To	ppm	ppm	%	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	%	%	%	ppm	ppm	%	ppm	ppm	ppm	%	ppm	ppm	%	ppm	ppm	ppm	ppm
02579	132	133	0.11	<0.5	9.03	190	420	1.2	<2	2.31	<0.5	10	6	222	2.79	2.19	1.08	1485	16	0.59	3	1070	30	3.19	<5	176	0.29	126	<10	57	
02580	133	134	0.09	<0.5	8.75	227	260	1.2	<2	2.05	<0.5	8	5	222	3.09	1.97	1.05	736	12	0.63	6	1060	38	3.5	<5	162	0.26	120	<10	59	
02581	134	135	0.04	<0.5	8.58	164	220	1.2	<2	2.24	<0.5	10	9	179	3.67	2.4	0.9	683	10	0.76	6	1060	20	4.15	<5	198	0.28	127	<10	22	
02582	135	136	0.02	<0.5	8.82	129	230	1.1	<2	2.73	<0.5	11	8	184	3.89	2.31	0.91	904	17	0.72	9	1140	17	4.54	<5	196	0.31	124	<10	25	
02583	136	137	0.02	<0.5	8.12	142	290	1.1	<2	2.83	<0.5	9	6	244	3.28	2.41	1.01	1025	16	0.42	6	1080	19	3.91	<5	135	0.31	115	<10	21	
02585	137	138	0.04	<0.5	8.72	113	200	1.1	<2	3	<0.5	12	9	178	3.51	2.41	0.93	907	20	0.63	8	1150	17	4.12	<5	182	0.31	118	<10	26	
02586	138	139	0.08	0.9	8.74	150	230	1.2	<2	2.82	<0.5	9	8	250	3.26	2.35	0.94	3090	27	0.58	9	1100	32	3.79	<5	173	0.3	123	<10	57	
02587	139	140	0.03	<0.5	9.11	82	220	1.3	<2	2.71	<0.5	11	7	187	3.6	2.39	1.01	1135	6	0.77	10	1150	19	4.14	<5	217	0.32	127	<10	23	
02588	140	141	0.05	<0.5	8.21	90	370	1.2	<2	3.63	<0.5	11	6	199	3.08	2.37	0.83	1340	9	0.56	8	1090	55	3.63	<5	189	0.3	129	<10	55	
02589	141	142	0.03	<0.5	8.29	91	450	1.2	<2	3.74	<0.5	11	6	205	3.22	1.84	0.78	1195	11	0.88	10	1050	19	3.75	<5	275	0.3	119	<10	32	
02591	142	143	0.08	<0.5	8.13	202	380	1.3	<2	2.85	<0.5	11	10	268	3.28	2.37	0.7	1140	11	0.97	5	1130	19	3.81	<5	286	0.31	136	<10	25	
02592	143	144	0.05	<0.5	7.94	155	420	1.2	<2	3.48	<0.5	11	9	191	2.98	2.25	0.67	1535	15	0.86	8	1060	20	3.48	<5	263	0.29	126	<10	33	
02593	144	145	0.24	1	7.9	469	390	1.1	<2	3.56	<0.5	11	7	324	2.94	2.88	0.83	3390	7	0.21	10	1100	57	3.5	<5	120	0.31	132	<10	106	
02594	145	146	0.19	<0.5	8.34	627	410	1.2	<2	2.69	<0.5	11	6	252	3.07	2.73	0.91	2330	9	0.31	10	1110	24	3.51	<5	133	0.29	130	<10	38	
02595	146	147	0.32	<0.5	8.05	773	390	1.2	<2	2.78	<0.5	11	8	306	3.15	2.98	0.66	2560	8	0.18	7	1160	36	3.63	<5	108	0.32	143	<10	53	
02596	147	148	0.27	0.5	7.68	450	330	0.9	<2	10.75	<0.5	10	4	201	3.54	2.46	0.51	3580	9	0.09	9	990	169	4.39	<5	104	0.29	129	<10	276	
02597	148	149	0.08	<0.5	8.08	143	370	1.1	<2	6.77	<0.5	11	6	186	3.97	1.35	0.26	930	9	0.46	12	1140	45	4.89	<5	344	0.36	148	<10	89	
02598	149	150	0.09	<0.5	7.33	110	400	0.9	<2	7.73	<0.5	10	6	284	3.17	1.35	0.2	819	13	0.32	8	1170	32	4.09	<5	237	0.35	153	<10	82	
02599	150	151	0.14	<0.5	7.51	117	340	0.9	<2	8.79	<0.5	13	6	288	4.11	1.17	0.22	1600	24	0.34	10	1070	42	5.16	<5	252	0.33	153	<10	116	
02600	151	152	0.22	<0.5	7.31	129	230	0.9	<2	12.35	<0.5	10	7	392	4.02	0.7	0.21	2100	6	0.26	7	930	51	5.19	<5	226	0.3	117	<10	135	
02601	152	153	0.3	<0.5	3.27	128	60	<0.5	<2	22.8	<0.5	11	13	862	2.7	0.16	0.24	4050	24	0.02	11	140	35	3.6	<5	94	0.09	44	<10	82	
02602	153	154	0.3	<0.5	4.49	118	90	<0.5	<2	21.7	<0.5	10	9	1040	2.6	0.33	2.15	4670	11	0.03	10	100	80	3.49	<5	95	0.12	37	<10	219	
02603	154	155	0.45	<0.5	4.11	247	150	<0.5	<2	22.2	<0.5	14	8	2310	3.36	0.4	0.29	3450	10	0.07	10	330	757	4.44	<5	122	0.13	58	10	315	
02606	155	156	0.13	<0.5	8.02	87	340	0.9	<2	7.16	<0.5	10	5	191	3.53	1.12	0.24	930	14	0.4	4	1050	55	4.43	<5	284	0.34	140	<10	108	

CRC 270 108m to 205m																															
Sample No	From	To	Au ppm	Ag ppm	Al %	As ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	K %	Mg %	Mn ppm	Mo ppm	Na %	Ni ppm	P ppm	Pb ppm	S %	Sb ppm	Sr ppm	Ti %	V ppm	W ppm	Zn ppm	Ag ppm
02607	156	157	0.16	<0.5	7.51	127	350	1	<2	8.31	<0.5	11	5	153	4.02	1.11	0.24	1875	6	0.44	4	1080	34	5.13	<5	311	0.33	143	<10	78	
02608	157	158	0.15	<0.5	7.76	145	330	0.8	<2	11.55	<0.5	12	5	280	3.72	1.12	0.31	2140	14	0.35	8	890	33	4.72	<5	270	0.3	123	<10	158	
02609	158	159	0.2	<0.5	6.36	445	260	0.6	<2	16.7	<0.5	9	4	247	3.42	0.98	0.42	2810	17	0.22	8	760	42	4.48	<5	190	0.26	124	<10	140	
02610	159	160	0.29	<0.5	7.63	199	280	0.9	<2	11.9	<0.5	8	6	191	4.45	1.39	0.47	1790	13	0.25	8	910	47	5.73	<5	212	0.29	138	<10	166	
02611	160	161	0.42	<0.5	6.45	672	190	0.8	<2	15.95	<0.5	9	5	505	3.99	1.5	0.61	11400	25	0.14	9	620	120	5.22	<5	143	0.24	103	<10	252	
02612	161	162	1.47	0.8	8.26	3190	420	0.7	<2	1.49	<0.5	9	5	327	2.51	1.28	0.67	3700	29	0.04	12	1080	17	3.07	5	36	0.33	138	10	68	
02613	162	163	0.62	<0.5	9.12	519	220	0.6	<2	0.79	<0.5	14	6	585	3.37	0.55	0.38	1110	18	0.01	7	1260	23	3.93	<5	50	0.39	156	<10	150	
02614	163	164	0.93	<0.5	8.76	1025	10	0.6	<2	0.52	<0.5	33	4	1325	7.94	0.58	0.2	765	18	0.01	10	1200	43	9.16	12	68	0.4	222	<10	239	
02615	164	165	0.58	<0.5	9.52	798	60	0.5	<2	0.46	<0.5	20	5	1145	5.64	0.57	0.11	658	61	0.01	10	1420	29	6.63	6	29	0.42	203	<10	111	
02616	165	166	0.2	<0.5	9.79	455	140	0.5	<2	0.42	<0.5	15	5	260	4.2	0.58	0.11	610	14	0.01	8	1460	16	5	<5	32	0.42	170	10	48	
02617	166	167	0.5	<0.5	9.73	572	50	0.6	<2	0.43	<0.5	13	5	260	5.32	0.79	0.13	794	14	0.01	3	1200	8	6.19	<5	33	0.42	164	<10	53	
02618	167	168	0.92	<0.5	9.41	606	270	0.7	<2	0.51	<0.5	14	6	251	3.79	1.13	0.17	661	18	0.02	8	1410	9	4.52	<5	24	0.4	159	<10	43	
02619	168	169	0.85	3.4	8.96	546	320	0.6	<2	0.66	0.7	11	7	515	3.1	2.3	0.28	6900	31	0.02	8	1160	55	3.59	37	33	0.35	135	<10	405	
02621	169	170	2.65	8.1	3.08	9730	40	<0.5	<2	0.23	2.2	9	27	129	7.23	0.89	0.12	861	20	0.02	13	240	70	7.8	641	128	0.11	47	<10	311	
02622	170	171	1.06	9.2	1.98	3490	40	<0.5	<2	0.14	<0.5	11	32	178	4.94	0.61	0.08	1145	27	0.02	13	80	92	4.89	115	21	0.05	45	10	547	
02623	171	172	1.49	43.5	0.74	1160	40	<0.5	<2	0.12	3.4	7	37	1285	2.33	0.23	0.03	1325	20	0.01	18	<10	164	1.99	116	86	0.02	18	<10	2720	
02625	172	173	1.18	68	1.62	982	40	<0.5	<2	0.4	4	5	35	937	2.79	0.39	0.12	4010	26	0.01	13	130	485	2.4	199	200	0.06	38	<10	3700	
02626	173	174	0.16	0.9	7.31	276	240	0.6	<2	5.52	<0.5	9	4	106	3.25	2.28	3.06	13000	14	0.02	2	840	16	3.99	17	33	0.27	105	<10	160	
02627	174	175	0.38	0.9	6.28	275	80	0.6	<2	7.54	<0.5	10	5	167	3.41	2	4.28	16050	4	0.03	1	400	8	4.25	14	30	0.22	70	<10	393	
02628	175	176	0.25	0.6	6.66	299	50	0.6	<2	7.19	<0.5	9	4	229	3.53	2.05	4.12	13700	4	0.02	3	570	6	4.42	12	30	0.25	93	10	308	
02629	176	177	0.09	<0.5	7.06	176	60	0.7	<2	7.43	<0.5	9	6	117	3.51	2.12	4.31	11000	8	0.03	2	670	18	4.37	8	32	0.25	106	<10	338	
02630	177	178	0.06	<0.5	6.69	119	90	0.7	<2	6.27	<0.5	8	8	80	2.45	2.03	3.67	10300	8	0.02	1	720	16	2.9	5	29	0.23	99	<10	66	
02631	178	179	0.05	<0.5	8.27	148	100	0.9	<2	2.04	<0.5	4	7	160	1.53	2.84	1	2900	9	0.03	2	1120	14	1.8	5	29	0.35	99	<10	22	
02632	179	180	0.11	<0.5	8.85	216	320	0.9	<2	0.68	<0.5	7	5	255	1.99	2.7	0.46	657	10	0.03	3	1160	19	2.29	8	30	0.34	124	<10	37	
02633	180	181	0.21	2.5	8.07	240	400	0.8	<2	0.76	<0.5	7	6	393	1.67	2.55	0.47	1160	11	0.02	3	1050	23	1.9	20	28	0.32	127	<10	59	
02634	181	182	0.68	7.6	6.5	620	110	0.6	<2	0.97	<0.5	6	6	239	2.32	2.13	0.54	2920	14	0.02	5	780	74	2.5	41	20	0.24	116	10	80	
02636	182	183	0.26	3.7	8.07	275	130	0.8	<2	1.96	5.8	3	6	129	1.54	2.91	1.06	5850	7	0.03	4	1040	362	1.8	42	26	0.31	119	20	706	
02637	183	184	0.33	4.4	8.53	268	140	0.9	<2	1.02	14.4	6	6	153	1.98	3.16	0.7	2160	4	0.03	3	1100	730	2.32	26	28	0.33	136	20	1725	

<i>CRC 270 108m to 205m</i>																															
Sample No	From	To	Au ppm	Ag ppm	Al %	As ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	K %	Mg %	Mn ppm	Mo ppm	Na %	Ni ppm	P ppm	Pb ppm	S %	Sb ppm	Sr ppm	Ti %	V ppm	W ppm	Zn ppm	Ag ppm
02638	184	185	0.29	15.9	8.85	486	90	0.9	<2	1.34	2	10	7	611	2.8	3.19	0.89	3060	14	0.03	3	1090	377	3.33	94	26	0.37	134	10	565	
02639	185	186	0.39	3.2	5.85	564	130	0.6	<2	1.92	<0.5	14	9	816	3.98	1.92	1.08	4730	13	0.02	5	650	78	4.55	39	24	0.21	118	<10	237	
02640	186	187	0.1	<0.5	7.69	242	100	0.8	<2	5.09	<0.5	5	3	285	1.48	2.39	2.68	10950	5	0.05	4	950	11	1.82	8	38	0.29	106	<10	35	
02641	187	188	0.08	<0.5	7.36	175	130	0.8	<2	4.22	<0.5	4	3	155	1.4	2.41	2.11	8530	6	0.05	2	1000	9	1.78	7	37	0.3	108	<10	27	
02642	188	189	0.07	<0.5	7.58	166	150	0.9	<2	3.6	<0.5	4	4	222	1.4	2.43	1.84	7980	13	0.05	3	980	8	1.72	7	36	0.3	101	<10	29	
02643	189	190	0.05	<0.5	7.78	165	170	0.9	<2	4.65	<0.5	5	4	178	1.62	2.18	2.6	8080	5	0.05	3	920	13	1.96	5	39	0.27	106	<10	44	
02645	190	191	0.04	<0.5	8.39	149	120	0.9	<2	4.1	<0.5	6	3	145	2.27	2.28	2.27	5160	4	0.1	1	980	14	2.73	6	56	0.31	113	<10	54	
02646	191	192	0.06	<0.5	7.3	74	190	0.8	<2	3.32	<0.5	5	4	288	1.7	1.75	1.74	3850	35	0.1	4	1000	8	2.04	<5	62	0.31	108	<10	20	
02647	192	193	0.06	<0.5	8.3	103	180	0.9	<2	3.82	<0.5	6	4	271	1.5	2.03	2.07	4220	5	0.11	2	1000	12	1.78	8	70	0.31	102	<10	26	
02648	193	194	0.06	<0.5	7.65	88	200	0.8	<2	3.36	<0.5	4	5	370	1.6	1.92	1.78	4820	7	0.12	3	1050	9	1.94	7	64	0.31	110	<10	27	
02649	194	195	0.06	<0.5	8.4	116	240	0.9	<2	1.22	<0.5	5	5	111	1.38	2.49	0.71	1765	7	0.1	2	1130	7	1.62	7	63	0.34	112	<10	22	
02651	195	196	0.17	0.9	8.22	143	380	0.8	<2	0.66	<0.5	6	6	132	1.56	2.42	0.39	508	3	0.1	2	1040	13	1.72	12	68	0.33	116	<10	27	
02652	196	197	0.15	<0.5	7.83	152	210	0.8	<2	0.54	<0.5	4	5	177	1.5	2.34	0.32	338	5	0.07	2	1010	17	1.66	11	55	0.3	109	<10	30	
02653	197	198	0.24	1.5	8.26	235	190	0.8	<2	0.55	<0.5	6	5	180	1.79	2.63	0.38	377	16	0.07	4	1060	17	2.01	13	48	0.32	116	<10	40	
02654	198	199	0.11	<0.5	9.03	181	370	0.8	<2	0.55	<0.5	6	4	217	1.56	2.73	0.38	139	8	0.1	3	1160	13	1.76	12	69	0.36	122	<10	28	
02655	199	200	0.1	<0.5	8.71	194	250	0.8	<2	0.54	<0.5	5	4	222	1.57	2.6	0.38	188	5	0.11	3	1130	10	1.78	8	72	0.34	122	<10	29	
02656	200	201	0.06	<0.5	8.01	145	210	0.9	<2	0.5	<0.5	5	5	136	1.28	2.53	0.37	265	7	0.12	4	1050	11	1.45	8	80	0.33	114	<10	26	
02657	201	202	0.22	5.6	8.07	239	280	0.8	<2	0.79	<0.5	4	4	248	1.4	2.28	0.43	4300	5	0.14	2	1010	25	1.56	27	89	0.3	111	<10	48	
02658	202	203	0.3	28.9	7.05	608	350	0.7	<2	1.1	1.4	6	5	587	1.58	2.51	0.6	27900	6	0.02	2	820	412	1.76	122	25	0.26	106	<10	449	
02659	203	204	0.32	1.8	8.2	321	260	0.8	<2	0.84	<0.5	7	5	309	1.65	2.81	0.53	2040	6	0.05	2	1060	25	1.9	18	41	0.32	122	<10	34	
02660	204	205	0.16	<0.5	8.19	418	410	0.8	<2	0.64	<0.5	8	5	629	2.1	2.74	0.38	538	13	0.07	3	1100	20	2.46	22	52	0.34	129	<10	56	

CRC 271 78m to 100 m																															
Sample No	From	To	Au ppm	Ag ppm	Al %	As ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	K %	Mg %	Mn ppm	Mo ppm	Na %	Ni ppm	P ppm	Pb ppm	S %	Sb ppm	Sr ppm	Ti %	V ppm	W ppm	Zn ppm	Ag ppm
02704	78	79	0.29	<0.5	8.53	448	160	0.5	<2	12.85	1	13	7	471	4.72	0.45	0.26	2000	36	0.02	14	1380	16	4.6	8	40	0.4	198	<10	110	0.26
02705	79	80	0.3	<0.5	9.21	419	150	0.5	3	12.6	<0.5	13	6	397	4.42	0.88	0.28	1900	34	0.03	5	1300	21	4.7	13	50	0.42	192	10	120	0.24
02707	80	81	0.22	<0.5	9.78	376	80	<0.5	<2	14.65	<0.5	10	5	165	4.41	0.62	0.29	1705	31	0.02	15	1320	13	3.86	5	39	0.41	189	<10	114	0.22
02708	81	82	0.23	<0.5	9.76	420	100	<0.5	<2	13.05	0.5	13	6	202	4.52	0.68	0.27	1755	32	0.02	14	1280	18	4.53	9	40	0.42	192	10	122	0.23
02709	82	83	0.26	<0.5	8.02	302	40	<0.5	<2	15.85	<0.5	9	6	87	3.75	0.23	0.25	2140	18	0.01	13	1060	14	3.75	6	29	0.33	158	10	114	0.32
02710	83	84	0.37	<0.5	8.54	326	60	<0.5	<2	17.9	0.5	12	7	247	4.3	0.38	0.26	2320	18	0.01	14	1060	16	4.15	10	35	0.36	168	10	108	0.32
02711	84	85	0.45	<0.5	8.1	372	80	<0.5	<2	20.8	<0.5	7	6	154	4.13	0.44	0.23	3040	14	0.02	15	910	18	4.41	6	42	0.33	152	10	99	0.4
02712	85	86	0.29	<0.5	8.37	323	70	<0.5	<2	18.75	<0.5	11	7	235	3.76	0.45	0.25	2400	17	0.02	17	1090	25	3.96	6	42	0.35	156	10	102	0.32
02713	86	87	0.46	<0.5	7.65	418	170	<0.5	<2	10.3	0.7	15	9	206	5	1	0.18	1470	24	0.04	14	1340	27	5.66	15	43	0.42	211	10	149	0.19
02714	87	88	0.47	<0.5	8.22	500	90	<0.5	<2	6.72	1.7	16	9	193	6.29	0.56	0.19	945	32	0.02	23	1380	37	6.99	18	32	0.5	259	10	133	0.12
02715	88	89	0.32	0.9	8.72	445	110	0.5	<2	6.37	1.1	12	9	578	5.93	0.73	0.23	636	29	0.03	18	1440	32	3.78	11	35	0.5	261	<10	203	0.07
02716	89	90	0.22	<0.5	8.84	341	90	<0.5	<2	7.69	0.5	16	12	112	5.03	0.47	0.24	823	29	0.02	14	1420	24	5.22	8	29	0.48	259	10	98	0.11
02717	90	91	0.91	2.8	8.8	933	4100	0.5	<2	7.64	1.6	5	15	293	4.99	1.32	0.17	9570	17	0.06	13	1220	100	0.84	51	138	0.4	186	10	427	1.39
02718	91	92	1.44	<0.5	9.83	860	90	0.5	3	1.61	6.1	28	12	1225	7.54	1.53	0.14	742	20	0.08	19	1540	24	8.67	24	53	0.52	241	10	519	0.1
02719	92	93	0.1	0.7	9.34	224	70	0.6	2	1.46	1	15	7	138	3.31	0.85	0.13	326	78	0.02	8	1680	14	3.73	6	19	0.53	212	<10	127	0.04
02720	93	94	0.29	<0.5	11.25	325	110	0.6	<2	1.88	<0.5	17	8	83	4.8	1.1	0.15	483	40	0.02	17	1880	17	5.65	<5	26	0.6	240	10	120	0.06
02723	94	95	0.85	0.5	10.4	740	120	<0.5	3	1.14	4.8	31	9	851	6.45	2.22	0.12	670	23	0.11	32	1820	33	7.83	25	74	0.52	241	20	237	0.1
02724	95	96	2.06	0.5	10.6	814	240	<0.5	3	1.12	13.3	46	13	1010	6.74	1.32	0.1	721	39	0.07	37	1700	51	7.81	34	51	0.53	236	20	515	0.1
02725	96	97	1.19	0.9	10.65	662	300	<0.5	2	1.23	63.2	38	9	1105	6.86	1.5	0.1	502	45	0.08	37	1820	45	5.94	22	61	0.53	256	10	784	0.06
02726	97	98	1.51	<0.5	7.36	501	190	<0.5	2	2.33	15	33	10	953	5.69	1.26	0.06	507	56	0.06	40	1410	48	7.24	15	48	0.46	213	10	721	0.07
02727	98	99	3.69	1.1	9.96	887	200	<0.5	<2	1.68	5.1	53	14	3770	7.11	1.04	0.09	649	72	0.05	47	1640	70	8.64	31	45	0.51	237	20	359	0.09
02728	99	100	2.38	2.4	10.2	1055	120	<0.5	<2	2.39	34.2	38	18	2750	7.56	0.56	0.1	686	49	0.03	53	1720	69	8.77	33	27	0.54	281	20	880	0.09

CRC 280 80 m to 165 m																															
Sample No	From	To	Au ppm	Ag ppm	Al %	As ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	K %	Mg %	Mn ppm	Mo ppm	Na %	Ni ppm	P ppm	Pb ppm	S %	Sb ppm	Sr ppm	Ti %	V ppm	W ppm	Zn ppm	Ag ppm
04677	80	81	13.85	10.1	8.41	>10000	30	<0.5	9	0.52	10.2	15	28	135	4.46	1.96	0.08	197	30	0.08	45	1200	626	7.07	924	266	0.34	164	20	1245	
04678	81	82	0.58	0.8	8.81	504	550	0.6	<2	1.4	0.9	13	8	51	3.35	2.59	0.17	193	7	0.08	6	1220	58	3.91	16	117	0.35	146	<10	106	
04680	82	83	0.33	0.5	9.38	375	690	0.7	<2	0.78	<0.5	12	7	37	3.25	2.67	0.36	326	5	0.09	6	1210	43	3.7	8	119	0.37	151	<10	51	
04681	83	84	0.08	<0.5	8.68	206	520	0.8	<2	0.71	<0.5	14	47	43	3.63	2.68	0.41	305	4	0.09	25	1320	24	4.2	<5	106	0.37	156	<10	34	
04682	84	85	0.05	<0.5	8.91	153	790	0.9	<2	0.76	<0.5	8	6	10	2.37	2.99	0.46	184	3	0.1	3	1200	24	2.66	6	123	0.35	145	<10	13	
04683	85	86	0.08	<0.5	7.22	216	490	0.9	<2	2.54	<0.5	10	6	16	2.7	2.6	0.32	609	4	0.09	4	1000	24	3.23	6	125	0.32	134	<10	25	
04684	86	87	0.05	<0.5	7.09	346	350	0.9	<2	4.11	<0.5	11	5	25	3.26	2.82	0.3	1270	3	0.11	3	1030	27	4.04	7	132	0.33	133	<10	25	
04685	87	88	0.03	<0.5	7.51	154	440	1.1	<2	3.91	<0.5	10	4	27	3.25	2.49	0.44	1355	3	0.16	3	1080	17	3.98	<5	131	0.33	133	<10	13	
04686	88	89	0.01	<0.5	8.37	90	550	1.2	<2	4.5	<0.5	10	4	23	3.25	2.62	0.48	1510	2	0.4	2	1060	19	3.93	<5	196	0.32	125	<10	10	
04687	89	90	0.05	<0.5	7.69	169	500	1	<2	4.65	<0.5	9	4	15	3.15	2.46	0.43	1370	3	0.15	3	1050	23	3.85	<5	124	0.32	129	<10	18	
04689	90	91	0.06	<0.5	7.81	161	600	1	<2	4.8	<0.5	11	5	9	2.94	2.85	0.35	1255	3	0.11	4	1090	20	3.54	<5	155	0.32	132	<10	39	
04690	91	92	0.05	<0.5	7.3	138	670	1	<2	7.77	<0.5	7	3	6	2.28	2.32	0.4	1860	3	0.09	2	990	21	2.76	<5	162	0.28	116	<10	55	
04691	92	93	0.03	<0.5	7.98	150	590	1.2	<2	4.68	<0.5	10	5	34	2.77	2.46	0.48	1345	5	0.18	3	1080	19	3.38	5	155	0.33	134	<10	26	
04692	93	94	0.04	<0.5	7.6	163	470	1.2	<2	3.53	<0.5	14	4	10	3.06	1.72	0.47	1095	3	0.11	3	1060	16	3.68	<5	95	0.32	123	<10	12	
04693	94	95	0.04	<0.5	8.75	197	240	1.1	<2	1.35	<0.5	11	5	17	3.58	2.51	0.63	682	7	0.11	3	1120	25	4.08	5	102	0.34	137	<10	16	
04695	95	96	0.06	<0.5	7.54	144	190	1.1	<2	3.44	<0.5	12	4	19	3.5	2.56	0.47	1210	14	0.24	3	1030	19	4.15	5	149	0.33	131	<10	14	
04696	96	97	0.11	<0.5	6.93	162	270	1.1	<2	4.08	<0.5	12	4	23	3.6	2.85	0.45	1235	6	0.29	2	1120	21	4.38	<5	184	0.32	135	<10	12	
04697	97	98	0.02	<0.5	7.62	59	590	1.2	<2	4.3	<0.5	13	5	28	2.71	2.13	0.35	1005	3	1.17	4	1160	13	2.89	<5	434	0.34	139	<10	12	
04698	98	99	0.14	<0.5	9.47	230	240	1	<2	1.28	<0.5	15	5	66	4.36	2.7	0.61	505	8	0.13	5	1210	33	4.95	6	122	0.35	149	<10	17	
04699	99	100	0.04	<0.5	8.32	129	470	1.1	<2	2.48	<0.5	14	5	21	3.48	2.63	0.52	674	4	0.57	4	1230	14	3.79	<5	263	0.35	145	<10	14	
04700	100	101	0.2	<0.5	8.88	386	240	0.8	<2	1.74	<0.5	13	5	34	3.86	3.28	0.43	762	6	0.19	3	1190	27	4.45	12	165	0.34	145	10	18	
04701	101	102	0.16	<0.5	7.73	296	460	0.8	<2	1.58	<0.5	11	4	27	3.47	2.59	0.37	722	5	0.13	4	1090	22	4	5	115	0.32	138	10	15	
04702	102	103	0.07	<0.5	8.86	285	480	0.8	<2	0.64	<0.5	11	5	8	3.32	2.99	0.32	176	6	0.06	5	1210	21	3.82	5	148	0.36	152	10	10	
04703	103	104	0.09	<0.5	8.42	359	840	0.7	<2	0.59	<0.5	9	6	11	2.27	3.6	0.28	138	3	0.1	4	1110	22	2.56	<5	179	0.34	136	<10	14	

CRD 280 80 m to 165 m

	Au	Ag	Al	As	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb	Sr	Ti	V	W	Zn	Ag	
Sample No	From	To	ppm	ppm	%	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	%	%	%	ppm	ppm	%	ppm	ppm	ppm	%	ppm	ppm	%	ppm	ppm	ppm	ppm
04704	104	105	0.13	<0.5	8.53	403	610	0.7	<2	0.57	<0.5	15	5	10	2.98	3.01	0.26	196	4	0.09	4	1150	28	3.35	<5	134	0.34	138	<10	15
04705	105	106	0.28	<0.5	8.81	422	310	0.7	<2	0.58	<0.5	18	5	12	3.4	2.57	0.29	155	5	0.08	8	1170	43	3.84	6	120	0.36	145	<10	25
04706	106	107	0.11	<0.5	8.45	246	630	0.7	<2	0.71	<0.5	15	5	10	2.83	2.8	0.42	114	4	0.11	5	1100	20	3.11	<5	139	0.33	138	10	31
04707	107	108	0.1	<0.5	8.12	442	670	0.7	<2	0.52	<0.5	13	5	15	2.65	3.02	0.23	155	7	0.1	7	1070	34	2.98	5	150	0.32	134	<10	31
04710	108	109	0.05	<0.5	7.9	249	580	0.7	<2	0.56	<0.5	14	6	17	2.52	3.97	0.25	160	4	0.13	5	1130	25	2.83	<5	203	0.34	144	10	34
04711	109	110	0.15	<0.5	8.38	350	750	0.8	<2	0.71	<0.5	12	5	9	2.56	2.75	0.24	217	4	0.08	5	1090	30	2.89	<5	117	0.34	140	<10	32
04712	110	111	0.03	<0.5	7.95	433	500	0.8	<2	1.07	<0.5	13	5	7	2.92	2.28	0.25	389	5	0.07	3	1120	27	3.35	<5	103	0.33	140	<10	28
04713	111	112	0.17	<0.5	7.44	545	160	0.7	<2	1.99	<0.5	18	6	9	3.34	4.11	0.26	1560	4	0.11	6	1070	34	3.85	8	218	0.33	138	<10	22
04714	112	113	0.05	<0.5	7.69	602	250	0.7	<2	1.02	<0.5	13	6	6	3.09	4.92	0.26	949	4	0.11	6	1090	25	3.44	<5	275	0.34	138	10	7
04715	113	114	0.15	<0.5	8.6	297	360	0.7	<2	0.53	<0.5	16	5	11	3.19	3.5	0.26	173	6	0.11	6	1130	25	3.57	<5	155	0.34	136	<10	24
04716	114	115	0.21	<0.5	6.27	513	120	0.5	12	0.45	<0.5	17	10	12	13.3	2.28	0.21	116	27	0.06	11	830	33	>10.0	8	108	0.25	119	10	34
04717	115	116	0.11	<0.5	7.03	427	500	0.8	<2	3.37	<0.5	12	5	26	2.97	3.18	0.38	2240	8	0.12	7	1020	17	3.4	<5	161	0.31	127	<10	33
04718	116	117	0.22	<0.5	7.26	418	560	0.7	<2	2.44	<0.5	14	6	109	2.87	2.54	0.12	1315	7	0.09	8	1050	34	3.33	9	123	0.32	136	<10	66
04719	117	118	0.47	<0.5	7.48	502	320	0.6	<2	1.41	<0.5	16	5	16	2.74	2.12	0.06	1595	7	0.08	6	1090	34	3.21	11	102	0.33	136	10	44
04720	118	119	0.36	<0.5	7.22	607	490	0.6	<2	3.85	<0.5	16	5	16	2.76	2.34	0.08	2790	6	0.09	3	1060	31	3.32	8	128	0.33	132	<10	35
04721	119	120	0.47	<0.5	6.62	513	160	0.5	<2	2.71	<0.5	15	4	40	2.99	2.64	0.06	1795	8	0.1	7	1000	37	3.56	<5	124	0.32	133	<10	55
04722	120	121	0.98	4.9	8.08	1290	280	0.6	<2	2.7	0.6	15	7	36	3.59	2.86	0.25	3260	9	0.06	5	1050	54	4.21	20	92	0.33	154	<10	100
04723	121	122	3.82	3.6	8.88	4000	90	<0.5	<2	0.5	0.7	13	10	69	3.29	2.39	0.14	4620	9	0.06	9	1280	44	3.98	40	92	0.39	174	10	88
04725	122	123	23.5	18.9	8.82	8530	50	<0.5	8	0.49	4.6	16	25	298	5.38	0.71	0.08	12700	30	0.02	19	1250	151	6.52	304	113	0.37	195	30	544
04726	123	124	11.05	5.6	8.37	>10000	490	<0.5	<2	0.5	3.6	20	14	149	5.02	0.62	0.09	9790	10	0.01	16	1430	151	6.36	125	184	0.33	144	20	485
04727	124	125	9.31	21	4.32	4820	4760	<0.5	4	0.41	7.9	12	16	186	3.25	0.43	0.06	23700	12	0.02	22	640	527	3.88	343	201	0.18	90	10	932
04729	125	126	7.77	48.8	3.43	2070	380	<0.5	5	0.31	12.9	8	24	224	2.38	0.99	0.11	661	19	0.05	29	520	826	2.48	571	256	0.13	75	20	1390
04730	126	127	7.17	72.4	2.8	>10000	310	<0.5	5	0.32	10.5	8	16	204	2.02	0.5	0.09	14150	15	0.03	22	330	642	3	2210	333	0.11	60	10	1135
04731	127	128	9.92	69.1	4.9	>10000	2390	<0.5	10	0.53	30.2	12	29	664	2.9	0.75	0.02	52900	28	0.02	36	840	2330	5.64	1150	407	0.2	116	10	3240
04732	128	129	34.4	66.3	4.17	>10000	710	<0.5	24	0.39	61.7	17	50	1475	5.16	1.01	0.04	13500	46	0.04	75	840	3480	7.2	1865	277	0.18	121	10	6500
04733	129	130	5.9	3.9	9.64	1860	70	<0.5	<2	0.36	2.7	20	15	3250	8.56	0.42	0.03	1505	14	0.02	15	1260	141	9.96	139	65	0.39	177	20	292

CDD 280 80 m to 165 m																															
Sample No	From	To	Au ppm	Ag ppm	Al %	As ppm	Ba ppm	Be ppm	Bi ppm	Ca %	Cd ppm	Co ppm	Cr ppm	Cu ppm	Fe %	K %	Mg %	Mn ppm	Mo ppm	Na %	Ni ppm	P ppm	Pb ppm	S %	Sb ppm	Sr ppm	Ti %	V ppm	W ppm	Zn ppm	Ag ppm
04734	130	131	1.08	1	8.57	564	110	0.5	<2	0.35	<0.5	14	6	494	4.43	2.67	0.08	451	6	0.12	6	1220	14	5.16	21	74	0.38	152	20	78	
04735	131	132	18.85	3.8	9.57	3960	80	<0.5	<2	0.35	8	23	38	6450	9.5	1.22	0.05	1000	21	0.06	58	1030	29	>10.0	273	49	0.38	166	40	614	
04736	132	133	3.38	1.1	9.76	1120	240	<0.5	<2	0.41	1.2	17	10	2220	5.47	1.08	0.06	750	20	0.05	13	1250	12	6.44	38	36	0.39	156	20	121	
04737	133	134	1.31	1.5	9.29	831	40	0.5	<2	1.24	1.1	14	9	3030	7.03	0.72	0.19	1745	15	0.03	12	1180	17	8.44	22	37	0.38	171	20	124	
04738	134	135	0.73	0.8	8.88	634	60	0.6	<2	1.87	0.7	13	6	645	4.98	1.03	0.23	2250	8	0.05	7	1220	17	6	26	53	0.38	162	10	99	
04740	135	136	1.21	1.4	9.12	740	50	0.5	<2	1.54	0.7	15	7	753	5.09	1.26	0.2	1995	11	0.05	5	1240	22	6.13	47	60	0.38	162	10	83	
04741	136	137	1.93	1.7	8.78	1145	60	0.5	<2	0.99	2.5	17	19	2850	6.87	1.23	0.13	884	14	0.06	30	1200	44	8.2	38	49	0.36	154	20	256	
04742	137	138	0.78	1.2	7.79	545	190	0.6	<2	7.14	1	12	6	2110	5.67	1.47	0.35	4120	7	0.07	15	1010	15	7.27	20	73	0.31	123	10	100	
04743	138	139	0.46	0.7	8.03	470	240	0.6	<2	8.82	0.6	11	5	1365	4.66	1.85	0.42	4070	5	0.08	7	980	12	5.94	9	73	0.3	115	<10	55	
04744	139	140	0.57	0.5	8.84	447	180	0.8	<2	2.26	0.5	13	6	1360	5	2.43	0.59	1770	8	0.13	6	1110	17	6.02	7	88	0.35	140	10	54	
04745	140	141	0.25	<0.5	7.92	173	240	0.9	<2	2.6	<0.5	12	4	253	4.01	2.25	0.67	1795	5	0.16	3	1080	9	4.77	9	98	0.32	131	<10	21	
04746	141	142	0.11	<0.5	8.42	209	270	0.9	<2	2.3	<0.5	12	4	124	3.92	2.39	0.7	1480	5	0.12	5	1140	14	4.66	8	98	0.35	137	<10	23	
04747	142	143	0.15	<0.5	9.11	227	290	0.8	<2	2.56	<0.5	12	5	247	3.89	2.41	0.62	1395	8	0.11	3	1210	15	4.65	6	90	0.37	143	<10	28	
04749	143	144	0.11	<0.5	8.74	287	300	0.7	<2	2.93	<0.5	12	4	229	3.64	2.65	0.52	1280	5	0.12	4	1250	12	4.43	6	98	0.36	129	<10	24	
04750	144	145	0.16	0.7	8.94	279	300	0.8	<2	1.95	<0.5	12	5	163	3.98	1.43	0.54	1155	13	0.06	4	1280	25	4.8	5	68	0.39	156	<10	61	
04751	145	146	0.22	<0.5	8.16	398	160	0.7	<2	8.17	<0.5	10	4	268	5.39	0.64	0.6	2160	4	0.04	3	920	34	6.95	7	66	0.33	142	10	82	
04752	146	147	0.27	<0.5	8.23	335	160	0.8	<2	3.53	<0.5	11	4	113	5.3	1.24	0.61	1315	2	0.14	4	970	19	6.49	<5	92	0.33	134	<10	39	
04753	147	148	0.07	<0.5	8.54	386	180	0.8	<2	4.47	<0.5	12	4	492	4.68	1.58	0.41	1860	8	0.14	4	1210	17	5.81	<5	90	0.35	142	<10	60	
04755	148	149	0.3	<0.5	7.65	382	200	0.9	<2	2.63	<0.5	12	5	347	4.55	1.25	0.33	1535	6	0.1	5	1160	14	5.61	<5	70	0.36	142	<10	45	
04756	149	150	0.73	0.5	8.99	407	170	0.9	<2	4.45	0.5	14	5	1130	5.05	1.73	0.41	2180	6	0.16	8	1160	11	6.25	5	104	0.34	140	<10	76	
04757	150	151	0.13	<0.5	8.35	388	310	0.9	<2	5.18	<0.5	11	4	138	3.94	1.44	0.33	2570	5	0.12	3	1210	11	4.98	<5	93	0.35	141	<10	23	
04758	151	152	0.56	<0.5	7.87	1080	100	0.9	<2	3.4	<0.5	13	5	383	5.72	1.16	0.35	1925	5	0.11	5	1100	15	7.1	9	78	0.37	156	<10	72	
04759	152	153	0.56	0.5	8.89	723	230	0.8	<2	5.86	0.6	13	5	606	5.25	1.11	0.32	4270	7	0.06	5	1180	19	6.67	8	68	0.36	145	<10	101	
04760	153	154	1.65	2.2	8.87	1390	180	0.7	<2	3.9	0.8	13	5	1270	5.5	2.86	0.34	23700	22	0.06	8	1190	29	6.93	48	72	0.36	142	10	158	
04761	154	155	2.52	8.1	7.96	1250	190	0.6	3	2.46	0.5	9	3	678	4.72	2.62	0.26	36400	34	0.04	5	1160	34	6.04	40	50	0.36	145	10	136	
04762	155	156	5.11	22.2	6.47	2670	70	<0.5	43	1.33	6.2	21	29	3830	9.56	1.58	0.04	94300	59	0.01	54	750	77	>10.0	97	21	0.25	135	20	932	

<i>CDD 280 80 m to 165 m</i>																															
			Au	Ag	Al	As	Ba	Be	Bi	Ca	Cd	Co	Cr	Cu	Fe	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Sb	Sr	Ti	V	W	Zn	Ag
Sample No	From	To	ppm	ppm	%	ppm	ppm	ppm	ppm	%	ppm	ppm	ppm	ppm	%	%	%	ppm	ppm	%	ppm	ppm	ppm	%	ppm	ppm	%	ppm	ppm	ppm	ppm
04763	156	157	5.58	12.1	7.02	2700	60	<0.5	9	2.32	0.9	13	2	4400	7.32	1.43	0.1	>100000	19	0.02	27	630	43	9.27	90	34	0.28	116	10	270	
04764	157	158	2.15	1.5	9.36	1260	220	0.6	<2	0.98	0.6	12	3	91	5.03	2.49	0.21	8050	7	0.04	4	1200	52	6.04	42	42	0.37	149	<10	209	
04765	158	159	0.88	2	9	2720	380	0.6	<2	0.77	0.5	13	4	185	4.26	3.17	0.16	7990	11	0.08	3	1210	25	5.19	57	64	0.36	146	10	110	
04766	159	160	0.91	1.4	8.63	3690	240	0.7	<2	1.98	<0.5	13	4	165	4.36	2.77	0.14	3860	5	0.07	3	1270	15	5.43	51	57	0.36	147	<10	56	
04767	160	161	1.03	2.1	9.48	2480	270	0.7	<2	1.09	<0.5	12	4	398	4.74	2.6	0.18	8910	14	0.06	5	1250	18	5.72	39	51	0.38	151	10	71	
04770	161	162	0.71	2	9.4	449	230	0.7	<2	1.1	<0.5	13	4	351	3.92	3.45	0.21	17600	10	0.11	2	1220	12	4.6	22	77	0.36	139	<10	56	
04771	162	163	0.88	0.6	9.03	541	220	0.7	<2	1.91	<0.5	14	4	354	4.39	2.68	0.15	7950	8	0.11	4	1260	12	5.23	13	75	0.38	148	<10	39	
04772	163	164	0.57	<0.5	8.32	338	330	0.6	<2	1.67	<0.5	13	5	244	3.81	2.63	0.13	3350	8	0.11	4	1160	12	4.53	6	80	0.35	135	<10	31	
04773	164	165	0.37	<0.5	6.81	248	190	0.6	<2	3.42	<0.5	11	5	324	3.56	2.46	0.11	3930	7	0.12	5	1040	6	4.61	<5	88	0.33	132	<10	33	

## **APPENDIX -C**

### **ACID BASE ACCOUNTING METHODS AND CANMET STANDARD “NBM-1” UTILIZED IN THE STUDY**

In Appendix-C the “Acid Base Accounting” methods are provided. Vizon SciTec Inc provided the methods. The references of the standard operating procedures are also provided at the end of each method when ever necessary. The NBM-1 is the reference material utilized in this study; its properties are also given in Appendix-C.

**Vizon SciTec Inc.**

**STANDARD OPERATING PROCEDURE**

**for the**

**The Modified Acid Base Accounting Procedure for Neutralization  
Potential (Lawrence - 1997)**

**SOP: 7140      VERSION: 1.0**

Written by: Terri-Lynn Ferguson

Reviewed by: \_\_\_\_\_ Date: \_\_\_\_\_

**Rik Vos**

Authorized by: \_\_\_\_\_ Date: \_\_\_\_\_

**Tim O'Hearn**

Controlled Copy Number

Original SOP Issue Date: July 14, 2004  
\_\_\_\_\_

Last Revision Date: \_\_\_\_\_

Next Revision Date: July 14, 2008  
\_\_\_\_\_

## Scope and Application

This SOP pertains to authorized ARD Group personnel. The Vizon SciTec Inc. (Vizon) management is responsible for ensuring compliance with this document.

## Labware Cleaning Requirements

General cleaning procedure is described in Vizon's SOP for Labware Cleaning, EQP 8, current version.

## Health and Safety Concerns

There are no special health and safety concerns related to this procedure. Normal prudence and good laboratory techniques should be exercised. Refer to MSDS for safety precautions for all products used.

## Test Procedure

1. Add a few drops of 25% HCl to 1 to 2 g of pulverized sample on a watch glass or in plastic boat. Observe the degree of reaction and assign a fizz rating as "none, slight, moderate, or strong fizz".
2. Weigh  $2.00 \pm 0.02$  g of pulverized sample into a 250 ml conical flask and add approximately 90 ml of distilled water.
3. At the beginning of the test (time = 0), add a volume of certified or standardized 1.0 N HCl according to the fizz rating as follows:

Fizz	Volume of 1.0 N HCl (m)	
	At time = 0 hrs	At time = 2 hrs
None	1.0	1.0
Slight	2.0	1.0
Moderate	2.0	2.0
Strong	3.0	2.0

4. Place the flask on a shaking apparatus such a reciprocating shaker, maintained at room temperature. After approximately 2 hours, add the second acid quantity as indicated in the above table. Note: If initial paste pH is low 2<sup>nd</sup> quantity may not be needed check pH and discuss with client/manager if this will be added.
5. After approximately 22 hours, check the pH of the pulp. If it is greater than 2.5, add a measured volume of 1.0 N HCl to bring the pH into the range 2.0 to 2.5. If the pH is less than 2.0, too much acid was added in steps 2 and 3. In this case, repeat the test adding a reduced volume of HCl.
6. After 24 hours, terminate the test and add distilled water to the flask to bring volume to approximately 125 ml. Measure and record the pH, making sure it is in the required range of 2.0 to 2.5.
7. Titrate the contents of the flask to a pH of 8.3 using certified or standardized 0.5 N or 0.1 N NaOH.

## Calculation of Results

Modified NP (kg CaCO<sub>3</sub>/t) = [(N x vol (ml) of HCl) – (N x vol (ml) NaOH) x 50] / [weight of sample (g)]

The acid generating potential of the sample should be calculated on the basis of the sulphide-sulphur content (AP = S = x 31.25). Sulphide-sulphur is typically determined as the difference between total sulphur and sulphate-sulphur, although analysis of other sulphur species such as elemental sulphur and barite-sulphur is sometimes justified. Caution should be exercised for certain samples in interpreting sulphate-sulphur analyses as this form can be either inert (e.g. gypsum) or essentially stored products of acid drainage that could become mobilized if conditions within a waste change. Reference to the MEND Report 1.16.1c is suggested (Norecol Environmental Consultants, 1991) for a discussion of sulphur species.

## **Quality Control**

### **Blanks**

Blank will be run to verify normality of the each titrant.

### **Replicates**

Replicate 10% of samples for groups of 10 or more samples or 1 duplicate for smaller batches.

### **Reference Standards**

The CANMET reference material NBM-1 or KZK-1 should be run with each batch.

## **Method Performance**

### **Detection Limit**

A detection limit is not applicable for this test. Samples may not consume acid and may even generate acid and therefore may consume more base than the added acid on back titration, in which case the result will be 0 kg/tonne or negative. Readability of the burette is 0.1 ml therefore results are read to within ±0.25 or 1.25 kg/tonne depending on the normality of the titrant used.

### **Analytical Range**

Theoretical based on 100% CaCO<sub>3</sub> = -1000 to 1000 kg/tonne

### **Precision**

Insufficient data to calculate

### **Accuracy**

Insufficient data to calculate

### **Bias**

Insufficient data to calculate

## **References**

- Lawrence, R.W. and Wang, Y. (1997), Determination of Neutralization Potential in the Prediction of Acid Rock Drainage, Proc. 4th International Conference on Acid Rock Drainage, Vancouver, BC, p449-464.
- see also: Coastech Research (1991), Acid Rock Drainage Prediction Manual, MEND Project Report 1.16.1b, MEND, Ottawa, Ontario.

## **Method Revision History**

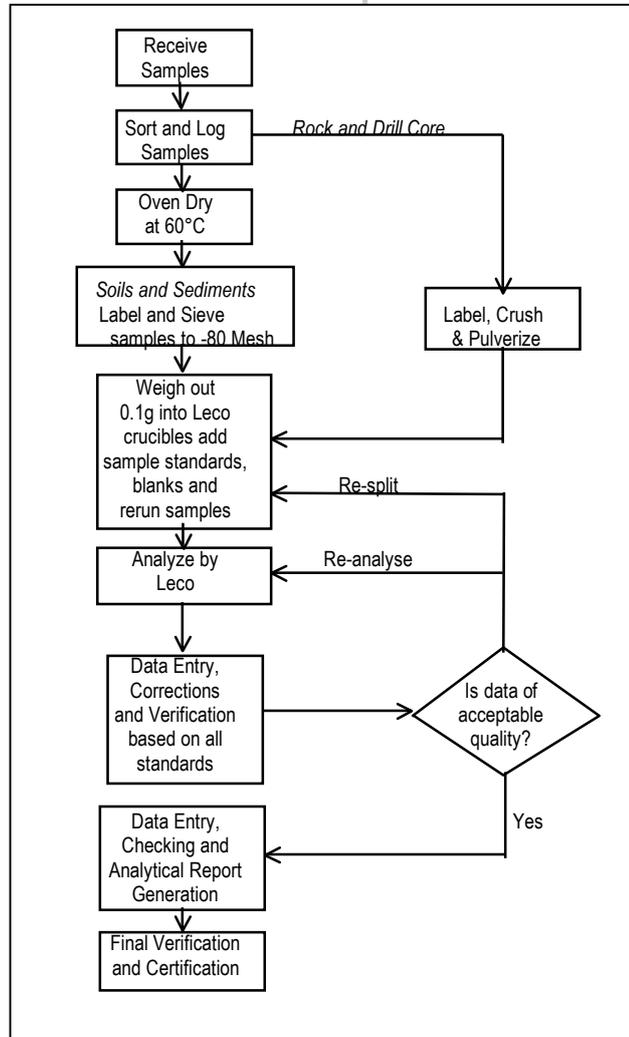
**Version 1.0 April, 2004**

**Procedure formally documented.**

# METHODS AND SPECIFICATIONS FOR ANALYTICAL PACKAGE

## GROUP 2A: TOTAL CARBON & SULPHUR

### Analytical Process



## **Comments**

### **Sample Preparation**

Soils and sediments are dried (60°C) and sieved to -80 mesh ASTM (-177 microns), rocks and drill core are crushed and pulverized to -150 mesh ASTM (-100 microns). Moss-mat samples are dried (60°C), macerated then sieved to recover -80 mesh sediment or ashed at 550°C (upon a client's request). Sample splits (0.1 g) are placed in Leco crucibles. Duplicate splits of crushed (rejects duplicate) and pulverized (pulp duplicate) fractions are included with every 34 drill core or trench samples to define sample homogeneity (reject duplicate) and analytical precision (pulp duplicate). Duplicate pulp splits (only) are included in every batch of soil, sediment and routine rock samples. A blank and in-house standard material STD CSB are carried through weighing, ignition and analytical stages to monitor accuracy.

### **Sample Analysis**

Analysis is by infrared adsorption using a Leco C244 Carbon-Sulphur analyser. After precise weighing, induction flux is added and the sample is ignited at >1650°C in an induction furnace. A carrier gas sweeps up released carbon and sulphur to be measured by adsorption in an infrared spectrometric cell. Results are total and attributed to the presence of carbon and sulphur in all forms.

### **Data Evaluation**

Raw and final data from the Leco Carbon-Sulphur analyser undergoes a final verification by a British Columbia Certified Assayer who must sign the analytical report before release to the client.

**Vizon SciTec Inc.**  
**STANDARD OPERATING PROCEDURE**  
**for the**  
**Sulphate–Sulphur**  
**SOP: 7410 VERSION: 3.0**

Written by: T. Ferguson

Revised by: \_\_\_\_\_ Date: \_\_\_\_\_

D. Cheng

Reviewed by: \_\_\_\_\_ Date: \_\_\_\_\_

T. O'Hearn

Authorized by: \_\_\_\_\_ Date: \_\_\_\_\_

J. Albright

Controlled Copy Number :  
Original SOP Issue Date : July 15, 2004  
Last Revision Date : March 3, 2006  
Next Revision Date : March 3, 2010

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## 1. Introduction

Chemical analysis can estimate the content of acid-producing minerals in mine waste samples. A significant acid-producing component are sulphur species that include iron sulphide minerals and metal sulphate minerals. These minerals are of interest because they can contribute trace metals to drainage. An analytical scheme to quantitate acid-soluble sulphate in mining wastes is useful in estimating their potential for acid production. The difference between total sulphur content and acid leached sulphate value is used to determine sulphide content of the sample.

## 2. Principle of Method

For sulphate-sulphur analysis, 5 g of pulverized sample is treated with 20 mL of 3 N hydrochloric acid in a beaker. The beaker is covered with a watch glass and heated to a boil. The sample is allowed to cool and is made up to a final volume of 100 mL. The clear supernatant is then submitted for sulphate analysis by the turbidimetric method according to Standard Methods (1992). The results are expressed in percent sulphate-sulphur.

## 3. Scope and Application

This SOP is applicable to all ARD soil, rock, and tailings samples.

## 4. Method Performance

This method is fit for its intended use for determining the % sulphate-sulphur of soil, rock, and tailings samples. Method performance parameters were determined by replicate analysis using an in-house soil sample (ARG-Viceroy) for precision, accuracy, and bias. The sulphate sulphur content was crossreferenced against extracts run by ICP-OES (0.27 %SO<sub>4</sub>-S) and CANMET Reference Materials NBM-1 and KZK-1. Reference values for these two standards are below method detection limits used.

### 4.1. Detection Limit

0.01% Sulphate Sulphur. Sulphate in the extraction can be measured to 1 mg /L or 0.0006% however since total S is measured to 0.01% this is adopted as the DL.

### 4.2. Analytical Range

0 - 50 mg/L and 0 - 200 mg/L in the digested extract (extendable by dilution).

### 4.3. Precision

0.02 (6.76%)

### 4.4. Accuracy

0.0% and 100% Recovery

#### **4.5. Bias**

0.00 (0.00%)

#### **4.6. Combined Uncertainty**

(U(95%)) For example, a combined uncertainty was calculated to be 0.045% for a modified neutralization potential of 0.27%. For more information on calculating uncertainty, refer to current version of the Vizon SOP for the Calculation and Reporting of Measurement Uncertainty (ADM 25).

#### **5. Sample Requirements**

Air dry wet samples, or oven dry on low heat (<40oC) if necessary. Riffle and split a representative portion of the sample and pulverized to a target size of 80% minus 180 mesh (Tyler). For instructions on sample preparation, refer to the current version of the Vizon SOP for the ARD Sample Preparation (EQP 33). Tailings and pulps can be used as received. There are no specific sample storage conditions, sample containers, or holding times required for this test method. Typically, samples are stored at ambient room temperature.

#### **6. Interference**

Alternate methods can be used to determine sulphur species depending on rock mineralogy. Barite, jarosite and alunite mineralogy may not totally dissolve in the digestion and have been noted to underestimate sulphide content.

#### **7. Apparatus and Equipment**

- Beakers (e.g., 250 mL)
- Plastic bottles (e.g., 125 mL)
- Watchglasses
- Balance, read to 0.01 g
- Hotplate
- Water bath

#### **8. Labware Cleaning Requirements**

No special cleaning is required for glassware used in this procedure. General information on lab ware is described in the current version of the Vizon SOP for Lab Ware Cleaning (EQP 8).

#### **9. Reagents and Supplies**

- Purity of water – references to water, deionized or DI water are understood to mean reagent water conforming the specifications for Type II DI water I. For more information on deionized

water, refer to the current version of the Vizon SOPs for the Operation of the Milli-Q/RiOs 16 Water Purification System (EQP 05) and Operation/Calibration of Laboratory Water Purification System Milli-RO 60 and Super Q (EQP 06).

- 3 N (25%) Hydrochloric Acid
- Hydroxylamine hydrochloride – Reagent Grade

## 10. Health and Safety Concerns

There are no special health and safety concerns related to this procedure. Normal prudence and good laboratory techniques should be exercised. Refer to MSDS for safety precautions for all products used.

## 11. Test Procedure

### 11.1. Analysis

1. Place 5.00 g of sample in a beaker (e.g., 250 mL).
2. Add 20 mL of 3 N HCl.
3. Heat until it just boils on hotplate.
4. Remove from heat, cool and transfer digest to a plastic bottle of known weight. Make up to  $105 \pm 0.1$  g total weight using DI water.
5. Allow solids to settle overnight. If liquid is clear continue to step 6, filter to remove solids if not clear. If liquid is uncoloured go to step 8.
6. For coloured (yellow/orange) samples transfer an aliquot of solution to plastic vial 20 mL (e.g., 20 mL) containing one scoop of hydroxylamine hydrochloride reagent (approximately 0.15 g).
7. Heat vial in  $\sim 80^{\circ}\text{C}$  water bath for 1 hour or until color disappears.
8. Analyse for sulphate by turbidimetric method, according to the current version of the Vizon SOP for the Automated Turbidimetric Analysis of Sulfate in Water and Wastewater (5380).

### 11.2. Calculation of Results

$$\%SO_4 - S = \left( \frac{\left( \frac{\text{mg}SO_4}{L} \times \frac{1L}{1000\text{ml}} \times \frac{1}{3} \right) \times \text{final volume (ml)}}{\text{sample weight (mg)}} \right) 100\%$$

## 12. Quality Control

### 12.1. Blanks

A method blank is run with each batch of samples.

### 12.2. Replicates

Replicate 10% of samples for groups of 10 or more samples or 1 duplicate for smaller batches. Repeat the duplicates if the duplicates disagree by  $\pm 10\%$  relative difference.

### 12.3. Reference Standards

An In-house soil sample (ARG-Viceroy) is used as a control reference material with every batch of 10 or more samples. CANMET NBM-1 and KZK-1 reference values are estimated at values below method detection limits for sulphate sulphur but can be used for other sulphur speciation analytical schemes. The results of the reference or control standards should be within 2 standard deviations of the mean of previous results. If not, the standards and the samples in the same batch are re-tested. Information on tracking the results of reference samples is described in the current version of the Vizon SOP for the Calculation and Reporting of Measurement Uncertainty (ADM 25).

## 13. References

Vizon SciTec Inc. Standard Operating Procedure for Labware Cleaning. EQP 08. Current Version. Vancouver, BC.

Vizon SciTec Inc. Standard Operating Procedure for the ARD Sample Preparation. EQP 33. Current Version. Vancouver, BC.

Vizon SciTec Inc. Standard Operating Procedure for the Automated Turbidimetric Analysis of Sulfate in Water and Wastewater. 5380. Current Version. Vancouver, BC.

Vizon SciTec Inc. Standard Operating Procedure for the Calculation and Reporting of Measurement Uncertainty. ADM 25. Current Version. Vancouver, BC.

Vizon SciTec Inc. Standard Operating Procedure for the Operation of the Milli-Q/RiOs 16 Water Purification System. EQP 05. Current Version. Vancouver, BC.

Vizon SciTec Inc. Standard Operating Procedure for the Operation/Calibration of Laboratory Water Purification System Milli-RO 60 and Super Q. EQP 06. Current Version. Vancouver, BC.

## 14. Appendices

None

## **15. Method Revision History**

### **15.1. Version 1.0 July 2004**

Procedure formally documented.

### **15.2. Version 2.0 October 2005**

This document replaces SOP 7410, Version 1.0.

Added a reference section (Section 10).

Added reference to the Standard Operating Procedure for the Automated Turbidimetric Analysis of Sulfate in Water and Wastewater.

Added 125 mL plastic bottles and Balance, read to 0.01 g to Section 6.

The following sentence from Section 7.4, Make up to weigh using DI water so liquid volume equals 100 mL. was changed to Make up to weight using DI water so that total weight is 105 g.

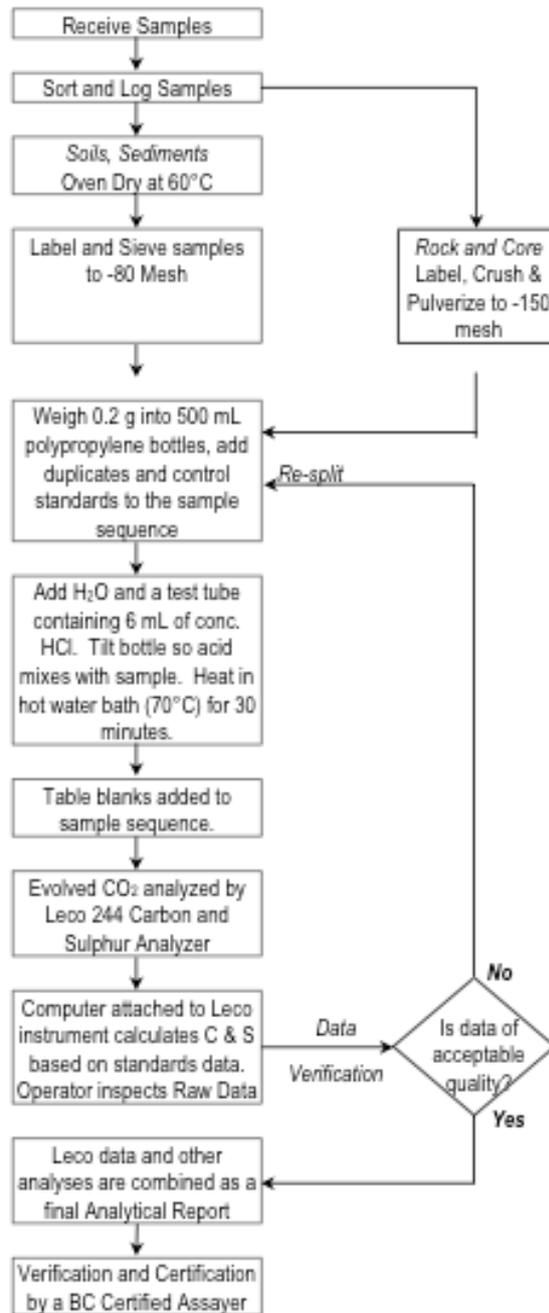
### **15.3. Version 3.0 March 2006**

This document replaces SOP 7410, Version 2.0.

- An introduction was added.
- The scope was updated to include the types of samples for which this method can be used.
- Minor revisions were made to correct errors in spelling, grammar, and sentence clarity.
- Method performance information was updated and estimates of uncertainty were listed.
- The sample preparation (EQP 33), uncertainty calculation (ADM 25) and deionized water SOPs (EQP 05 and EQP 06) SOPs were cited.
- Apparatus, equipment, reagent and supplies were updated to reflect current practices.
- Additional information was added to Section 11.1 Analysis.
- Quality Control section was updated to reflect current practices.

**METHODS AND SPECIFICATIONS FOR ANALYTICAL PACKAGE  
GROUP 2A - CO<sub>2</sub> CARBON**

**Analytical Process**



## **Comments**

### **Sample Preparation**

Soil and sediment samples are dried (60°C) and sieved to -80 mesh (-177 microns), rocks and drill core are crushed and pulverized to -150 mesh (-100 microns). Sample splits (0.2g) are placed in 500 mL polypropylene bottle.

Duplicate splits of crushed (rejects) and pulverized (pulp) fractions are included with every 34 rock samples to define sample homogeneity (reject split) and analytical precision (pulp split). Duplicate pulp splits are included in each batch of 34 soil or sediment samples. A blank and standard STD CSB are included in each batch of samples to monitor accuracy.

### **CO<sub>2</sub> Evolution**

Water (34 mL) is added. A test tube containing 6 mL of HCl is placed in the bottle and the cap fitted with two stopcocks is screwed on tightly. The bottle is tilted to allow the acid and sample to mix. The bottle is placed in a hot water bath (70°C) for 30 minutes to help evolve CO<sub>2</sub> into the gas phase.

### **Sample Analysis**

The bottle is attached to the Leco 244 Carbon and Sulphur Analyzer via the stopcocks. The stopcocks are opened and the CO<sub>2</sub> gas is swept into the analyzer with an O<sub>2</sub> carrier gas. The instrument determines the CO<sub>2</sub> as total C which must then be calculated to total CO<sub>2</sub>. Data Evaluation Raw and final data undergoes a final verification by a British Columbia Certified Assayer who then signs the Analytical Report before it is released to the client.

## **CANMET STANDARD NBM-1**

NBM-1 is a reference material for acid rock drainage (ARD) prediction technologies. The standard acid base accounting (EPA 600 or Sobek) method for the determination of the net neutralization potential (NNP) was employed to standardize NBM-1 for a static prediction test.

The raw material was crushed, milled and sieved in a series of batches until 86 % of the original 410 kg was finer than 74 :m (200 mesh). The powdered material was blended in a 570-L conical blender for 16h and bottled into 3429 100-g bottles. These were sealed under nitrogen in laminated mylar-foil pouches to provide long-term protection from oxidation.

### **RECOMMENDED VALUE**

Constituent Total S

wt %

Mean 0.298

95% confidence limits  $\pm$  0.015

### **PROVISIONAL VALUES**

Parameter NP NNP

t CaCO<sub>3</sub> 1000t

Mean 52 42

### **INFORMATION VALUES**

Parameter

Paste pH 8.6

Modified AB Accounting NNP 42 t CaCO<sub>3</sub> / 1000t

BC Research Initial Test 9.2 kg/t

acid producing potential

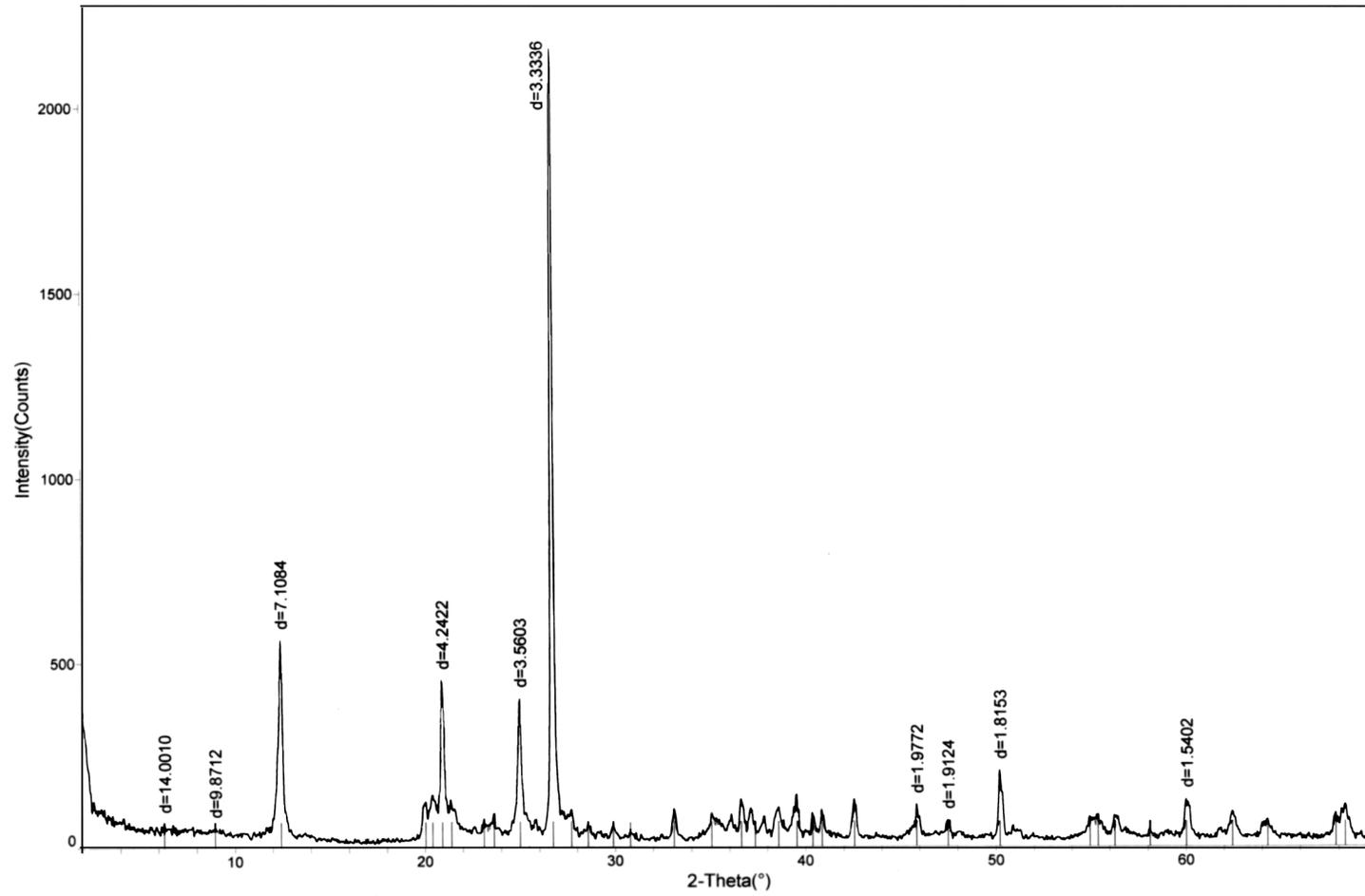
acid consuming ability 35.8 kg/t

## **APPENDIX -D**

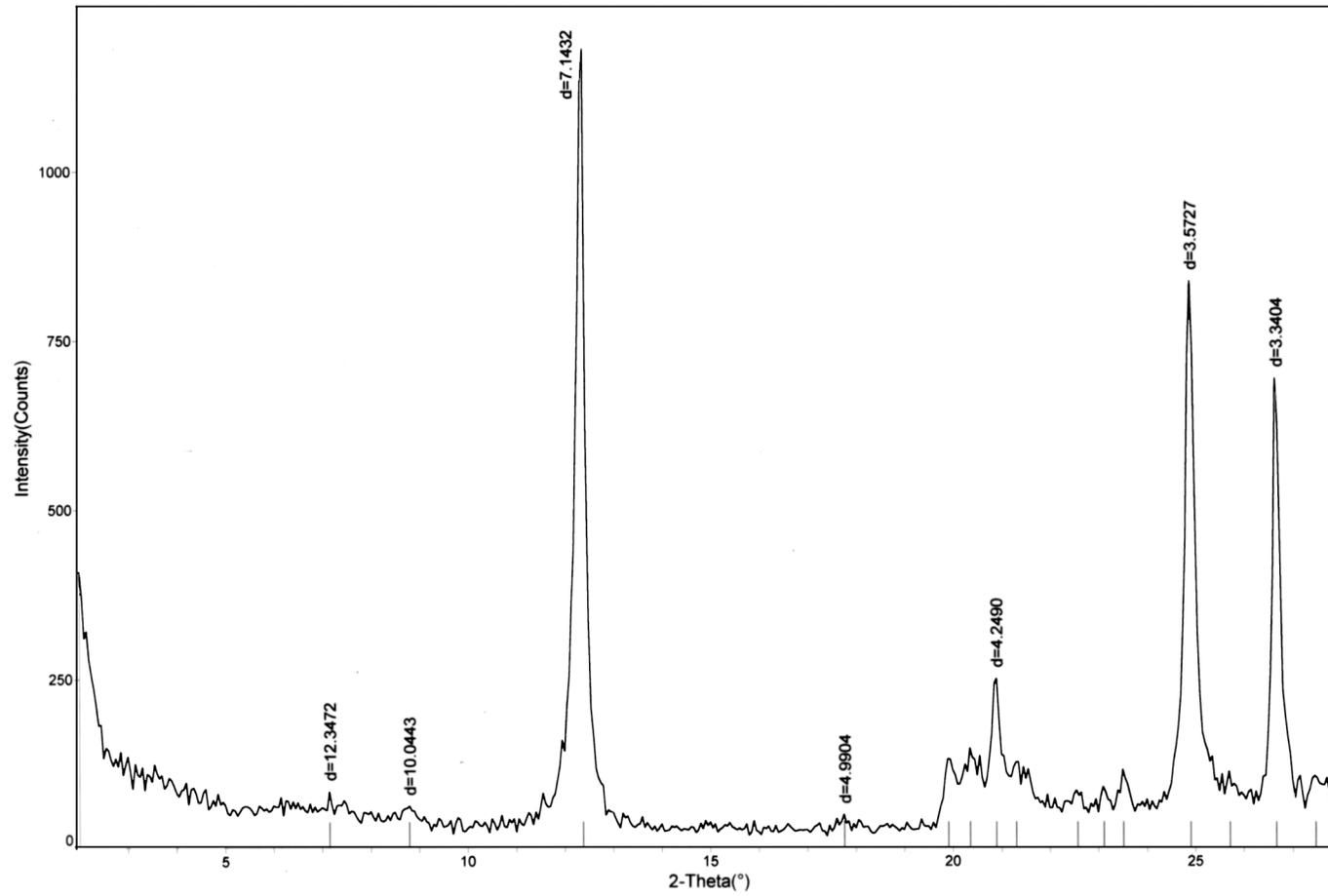
### **X-RAY DIFFRACTION ANALYSIS RESULTS**

In Appendix-D X-Ray Diffraction analysis results are provided. The well name of the sample and the type of X-Ray graph is indicated on top of each graph. Bulk indicates un-oriented powder samples; air-dried indicates that the oriented sample was dried under normal room temperatures, exposed to air. Ethylene Glycolated indicates that the oriented sample was treated with ethylene glycolade over-night. Samples heated to 300°C and 550°C is heat treated for one hour at the corresponding temperature.

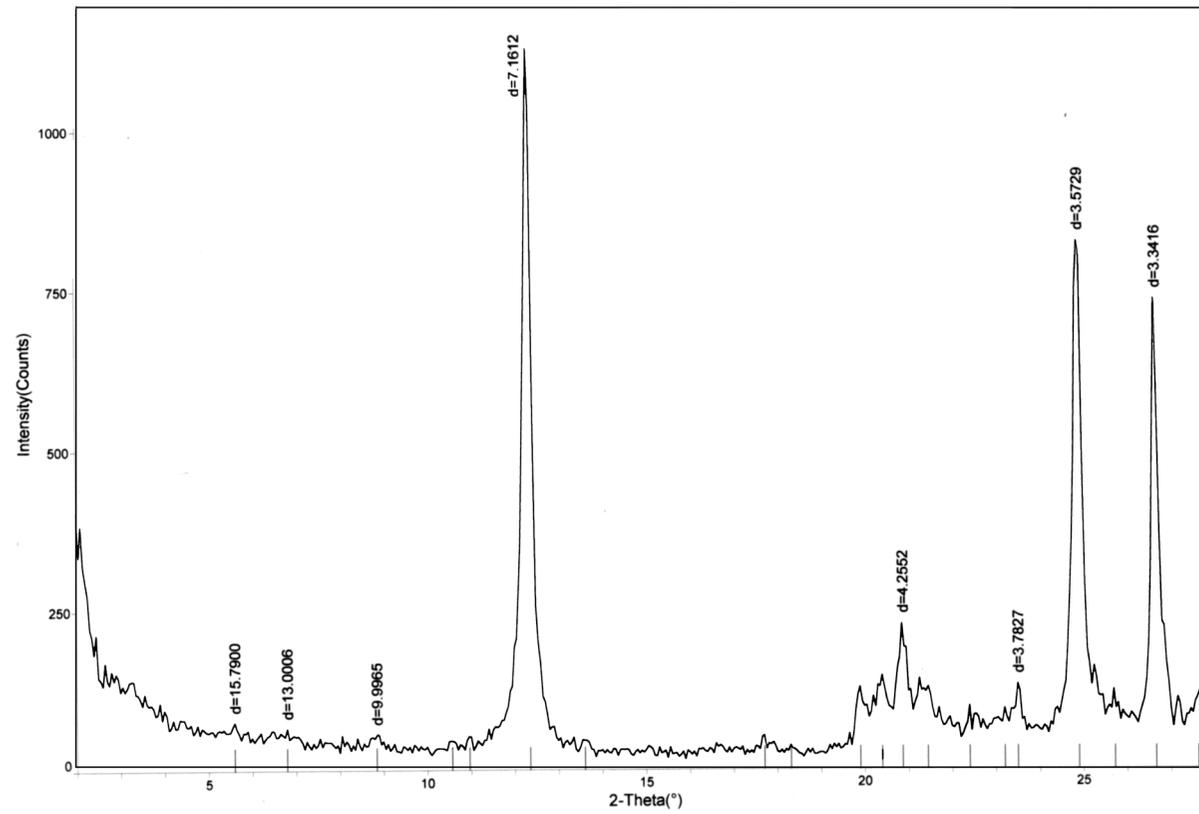
# CDD 86 BULK



# CDD86 AIR DRIED



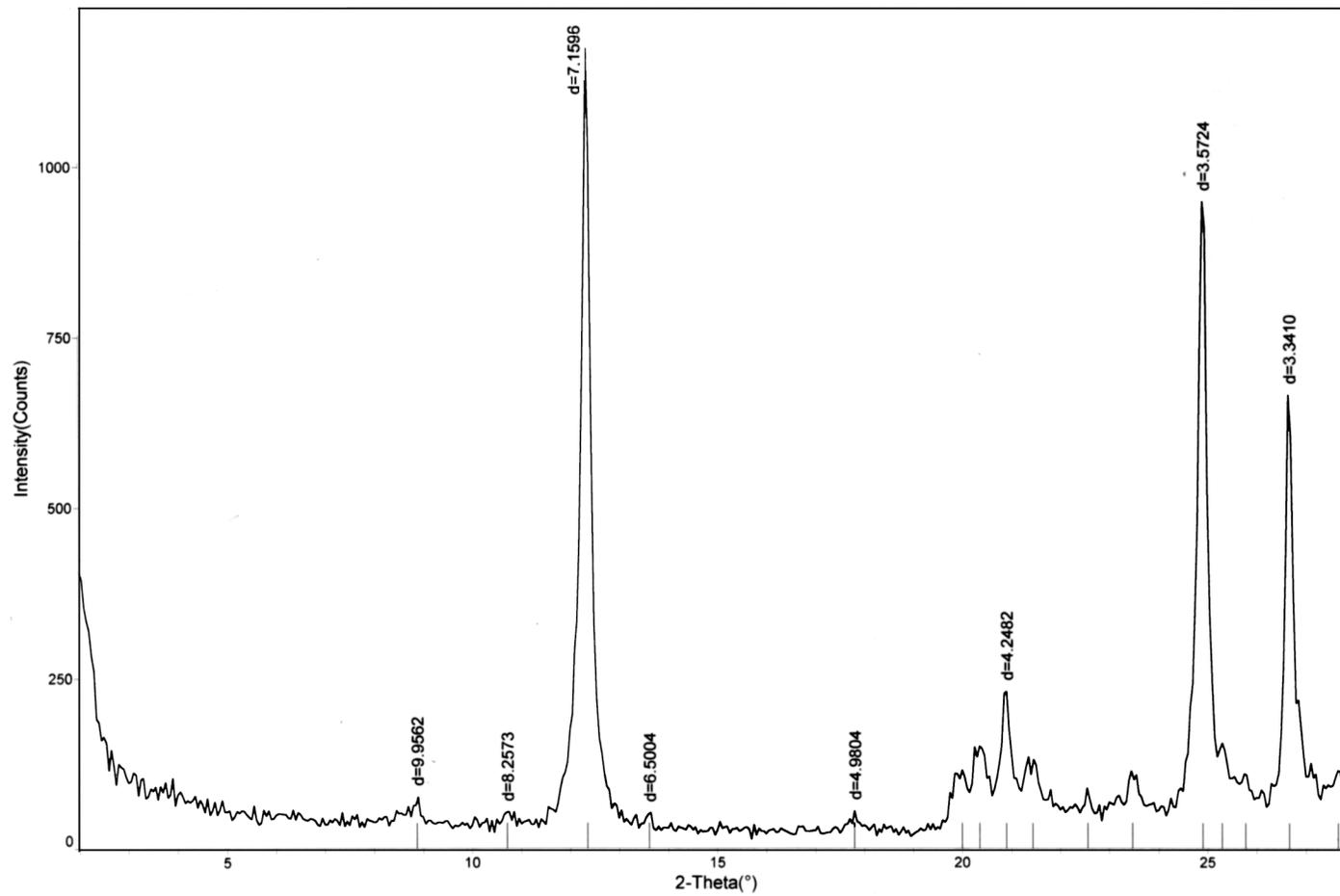
# CDD86 ETHYLENE GLYCOLATED



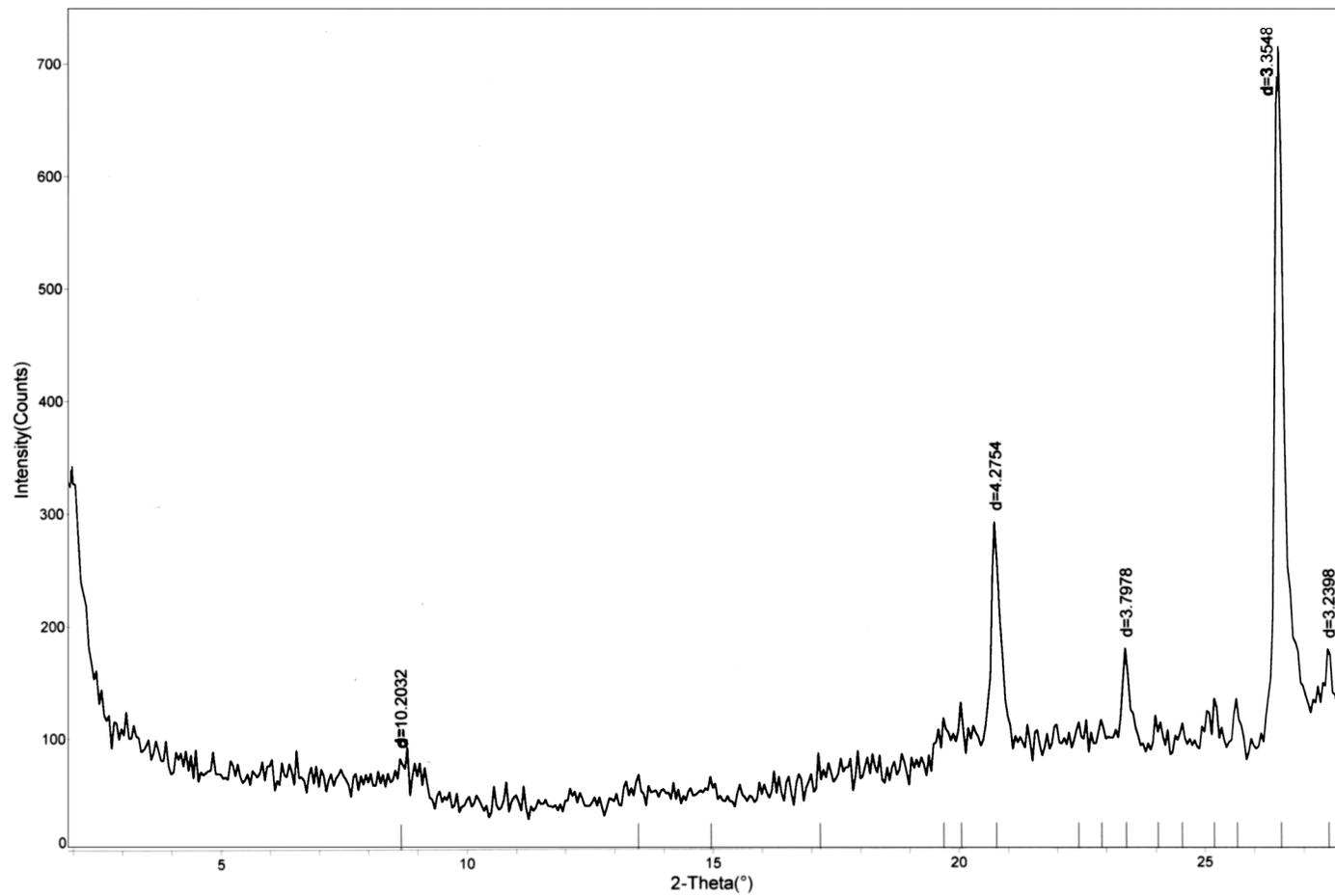
Mininn Res Inst

[MTA]MTA]-a-> Perpembe, Pub 23, 2006 02:25p (MDI/JADE6)

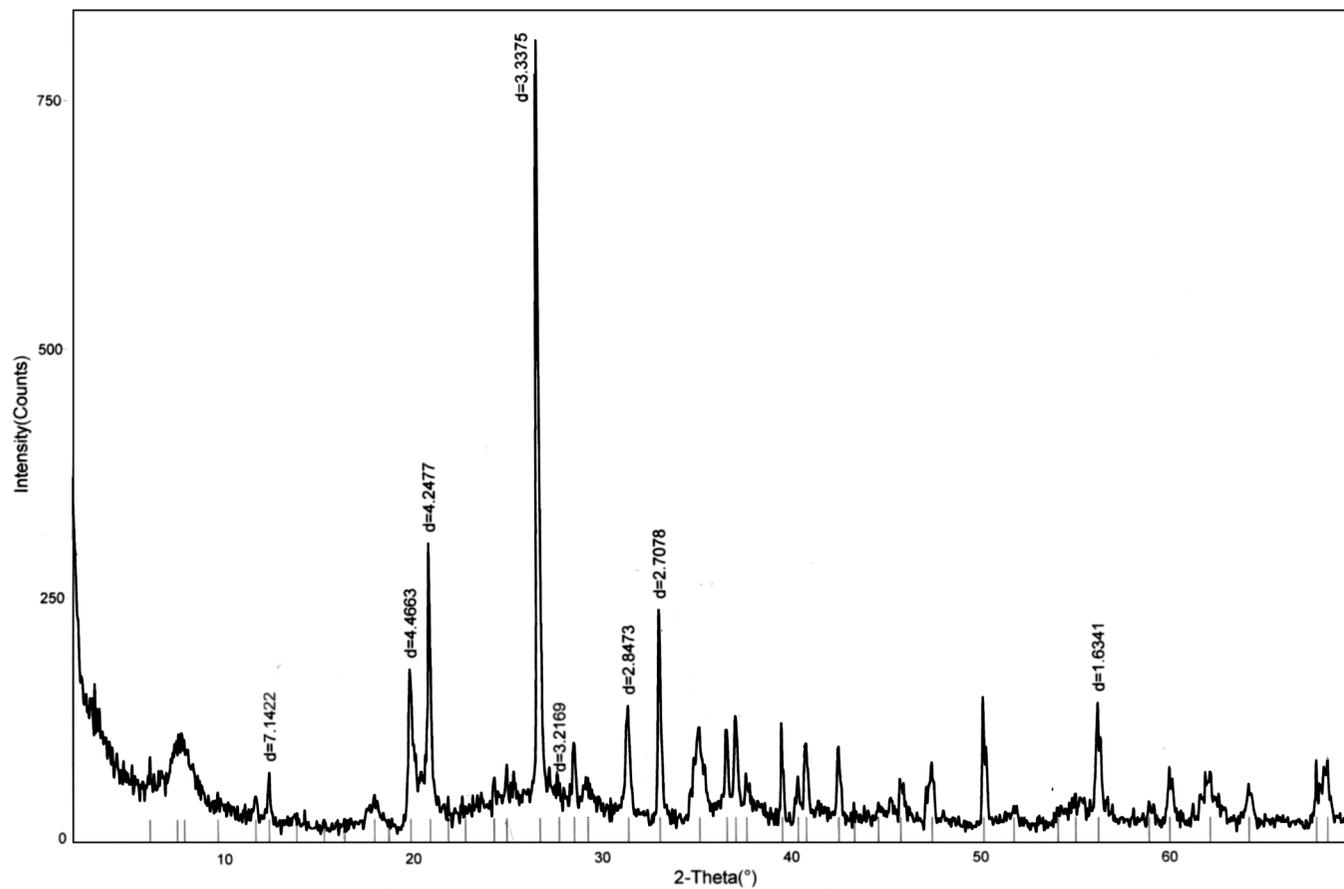
CDD86 HEATED TO 300 °C



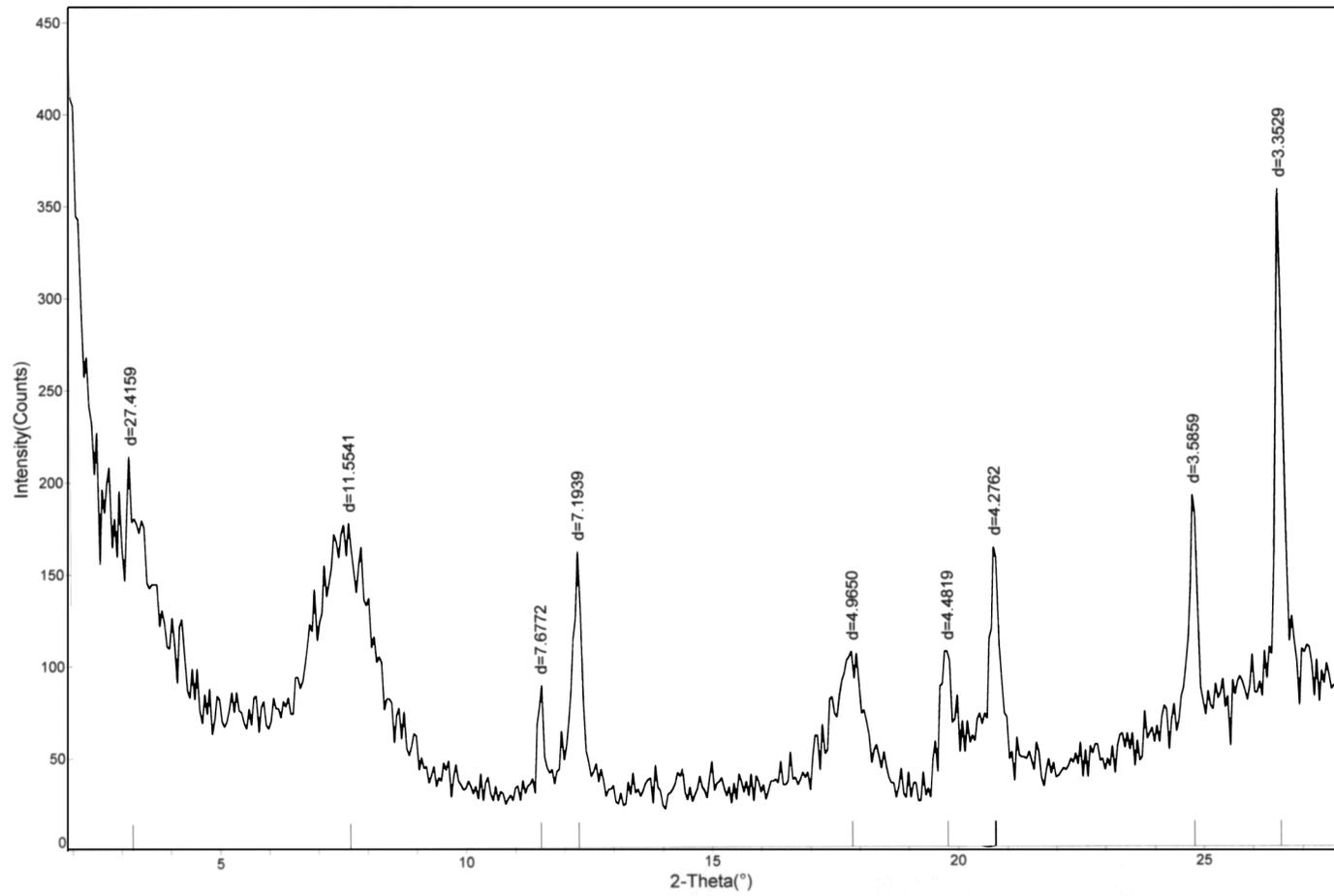
CDD86 HEATED TO 550 °C



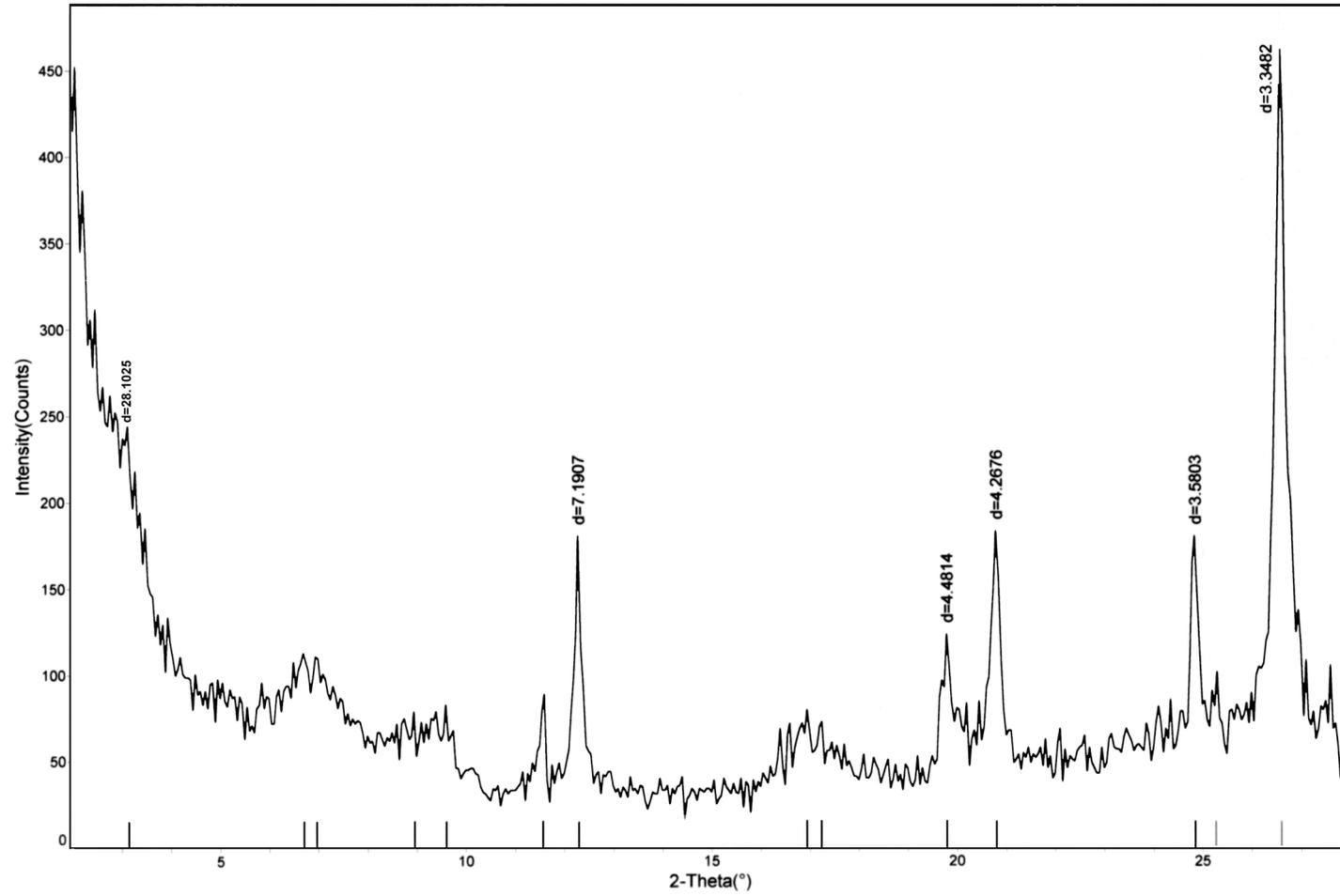
# CDD92 BULK



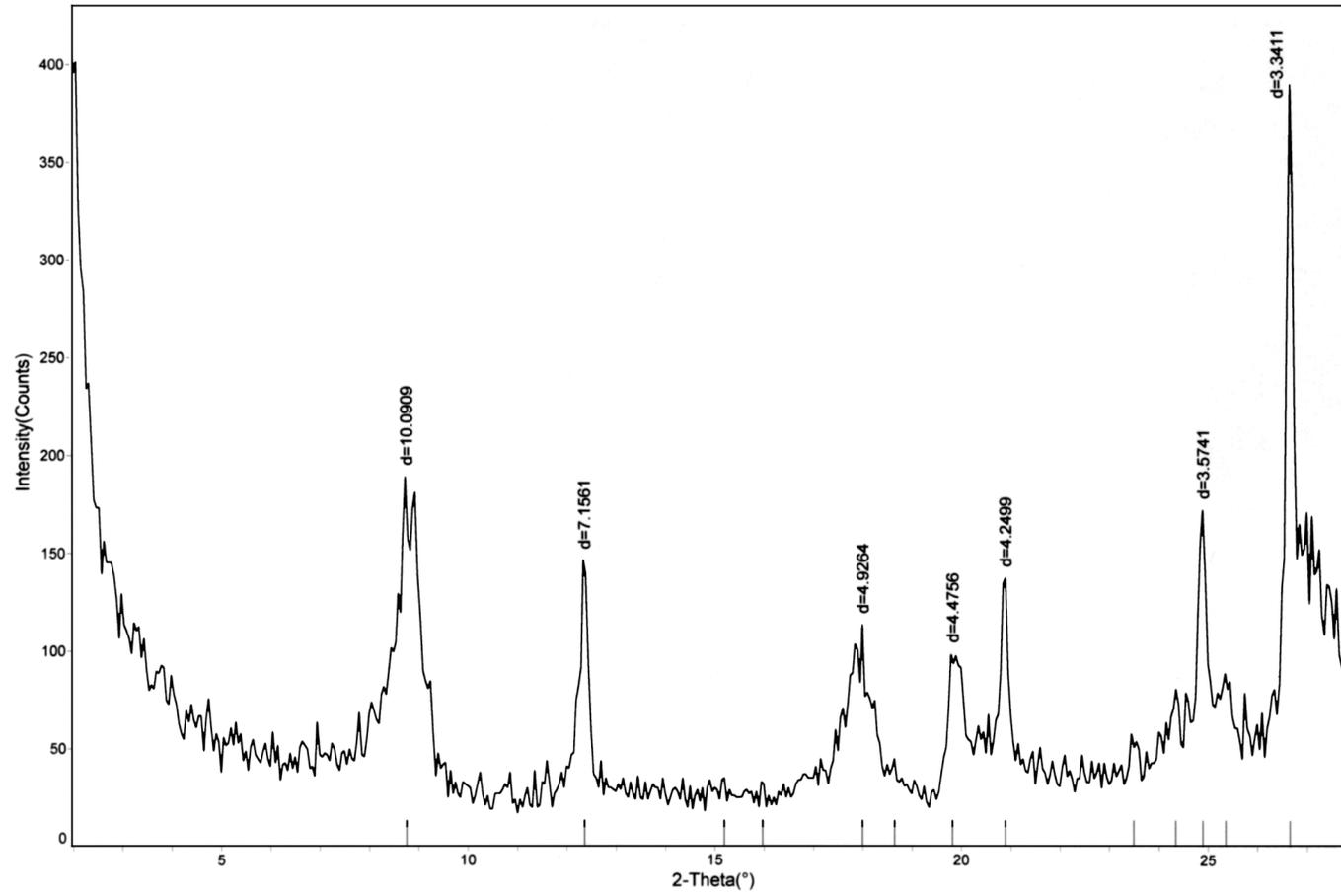
# CDD92 AIR DRIED



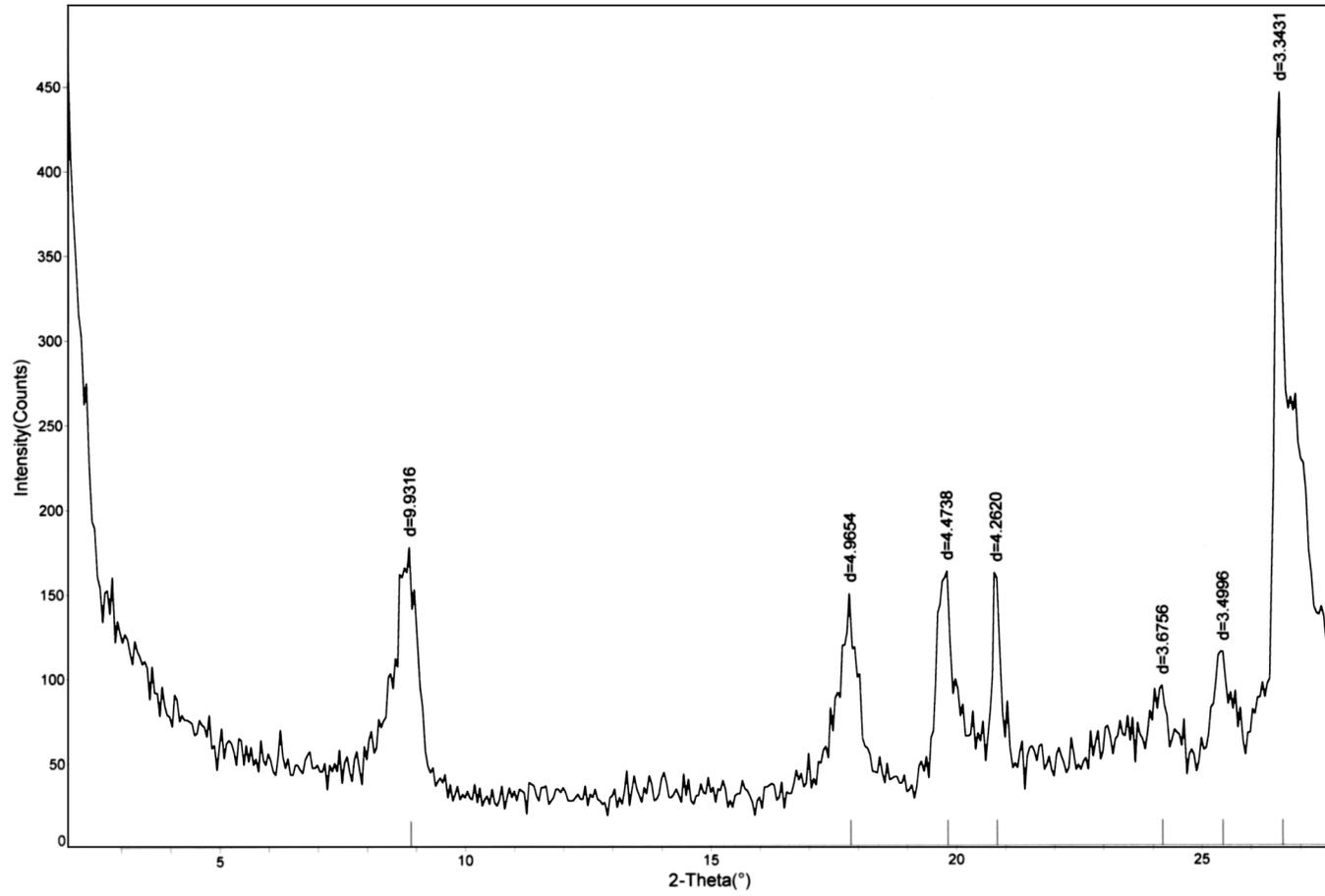
# CDD92 ETHYLENE GLYCOLATED



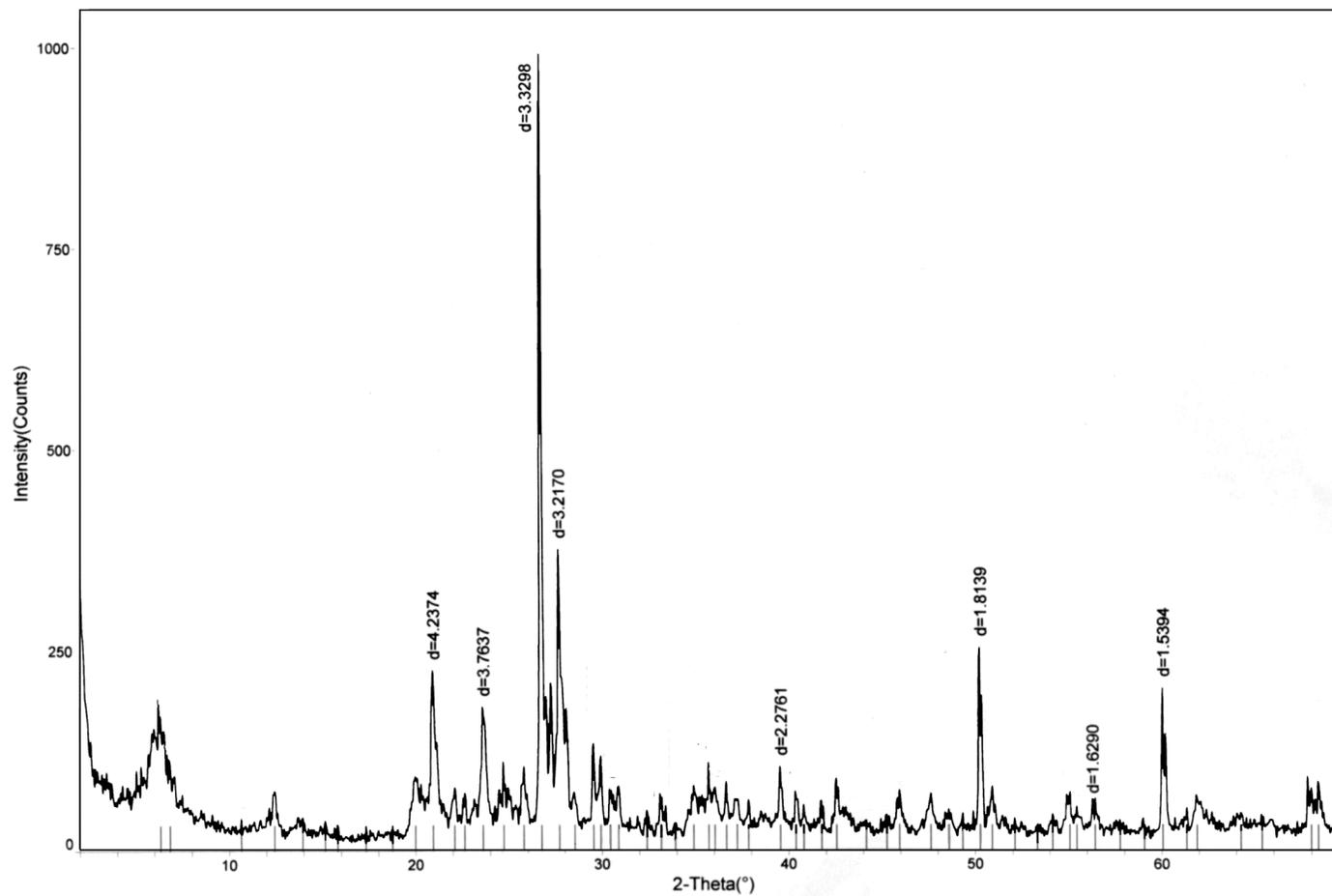
### CDD92 HEATED TO 300°C



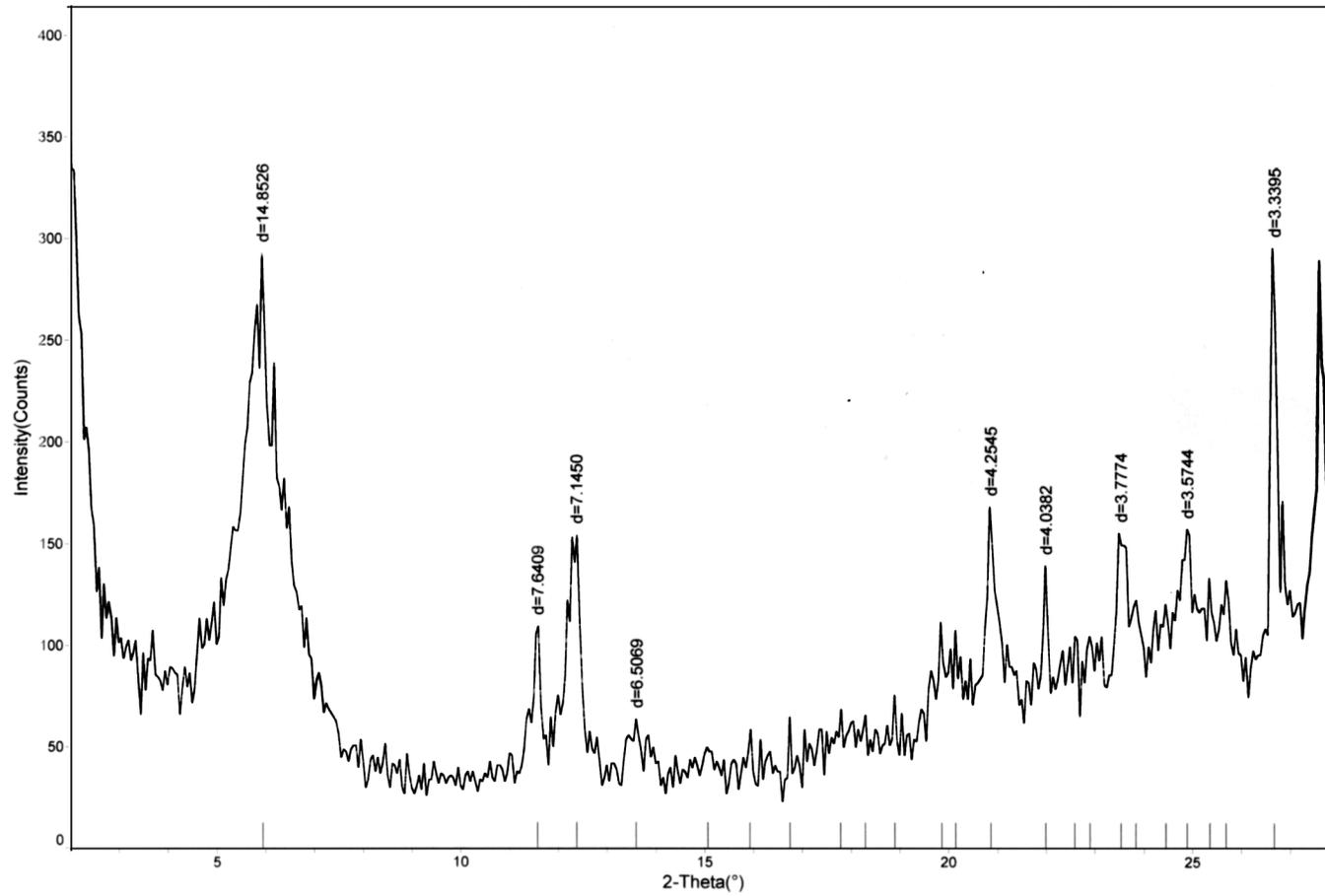
CDD92 HEATED TO 550°C



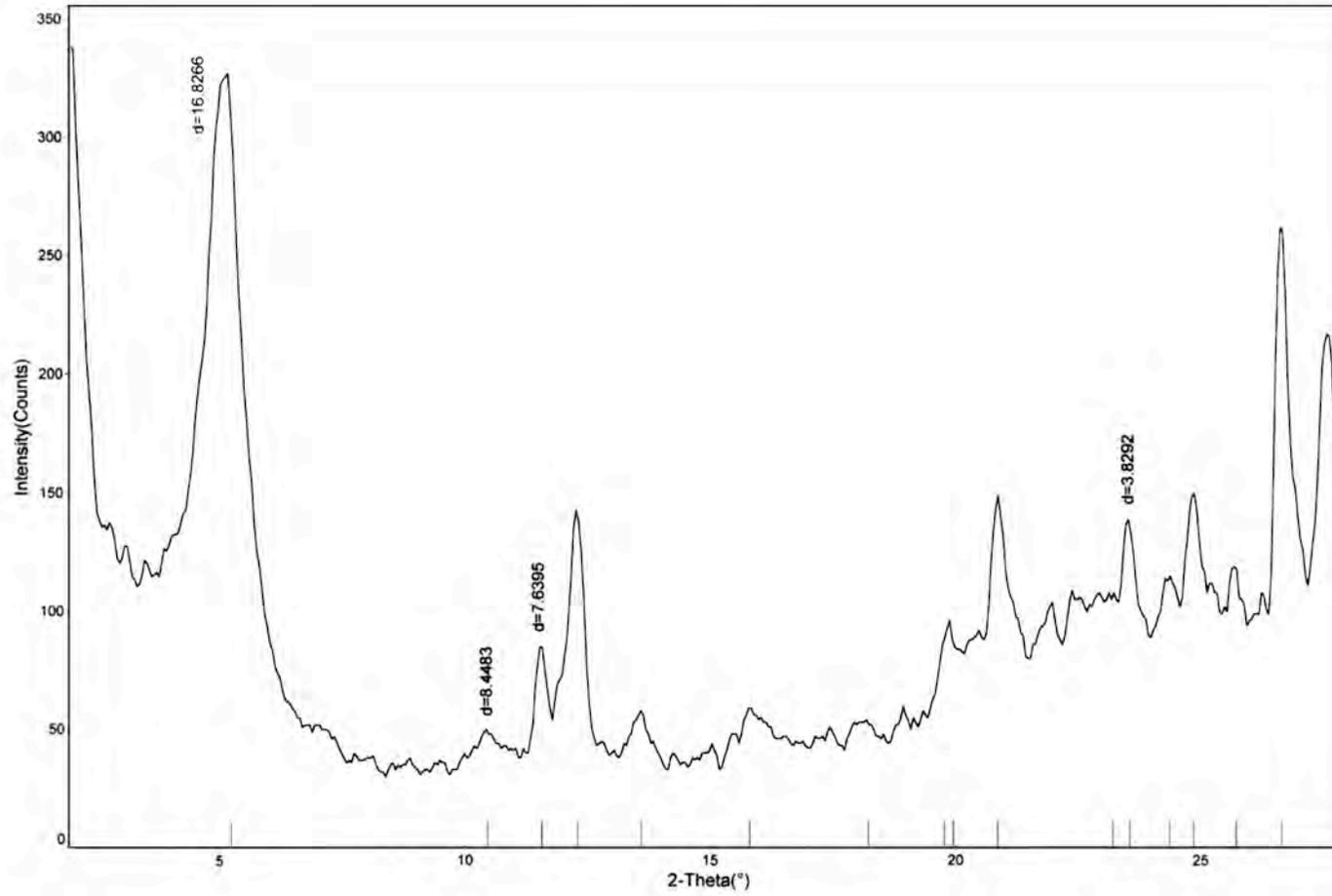
# CDD99 BULK



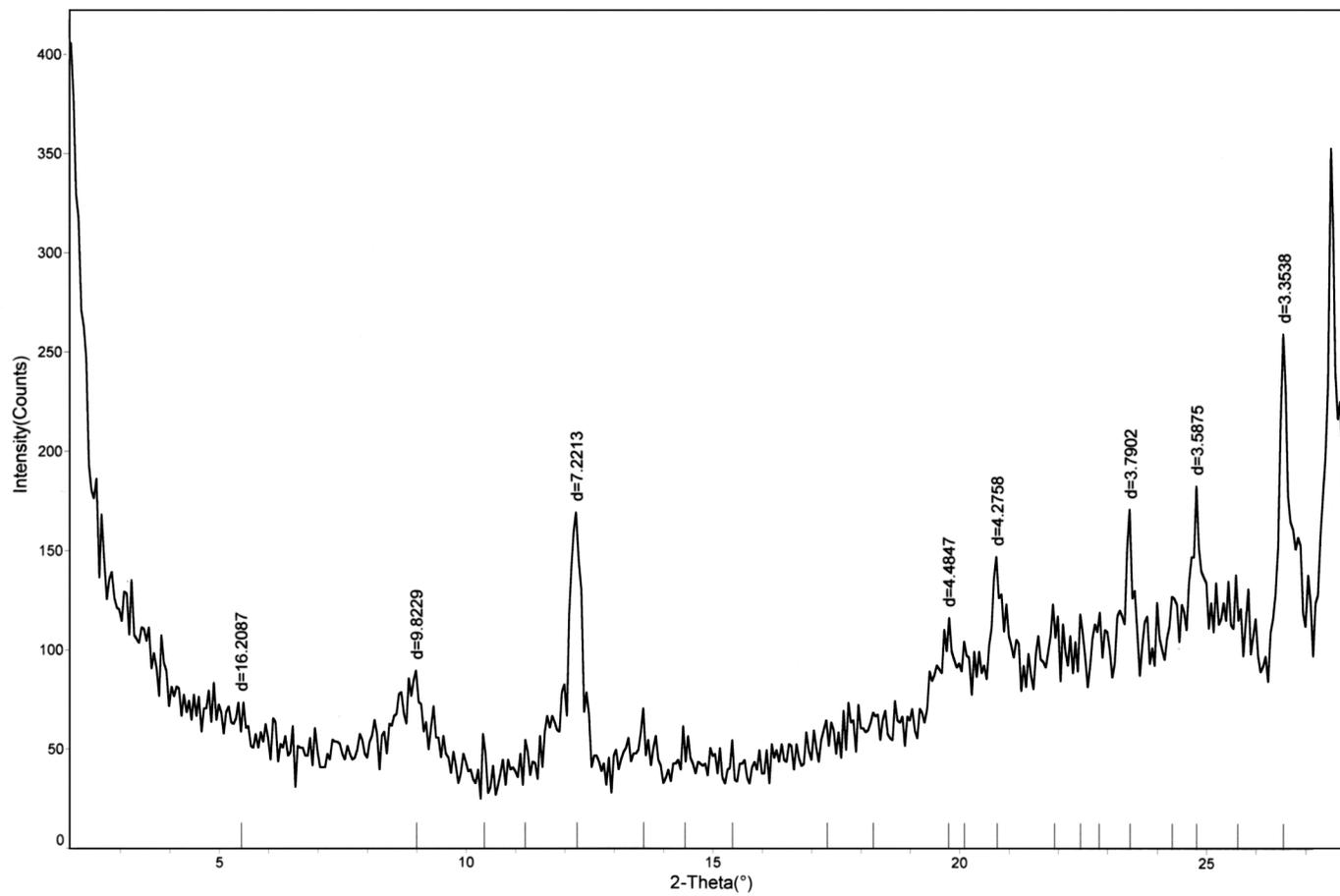
# CDD99 AIR DRIED



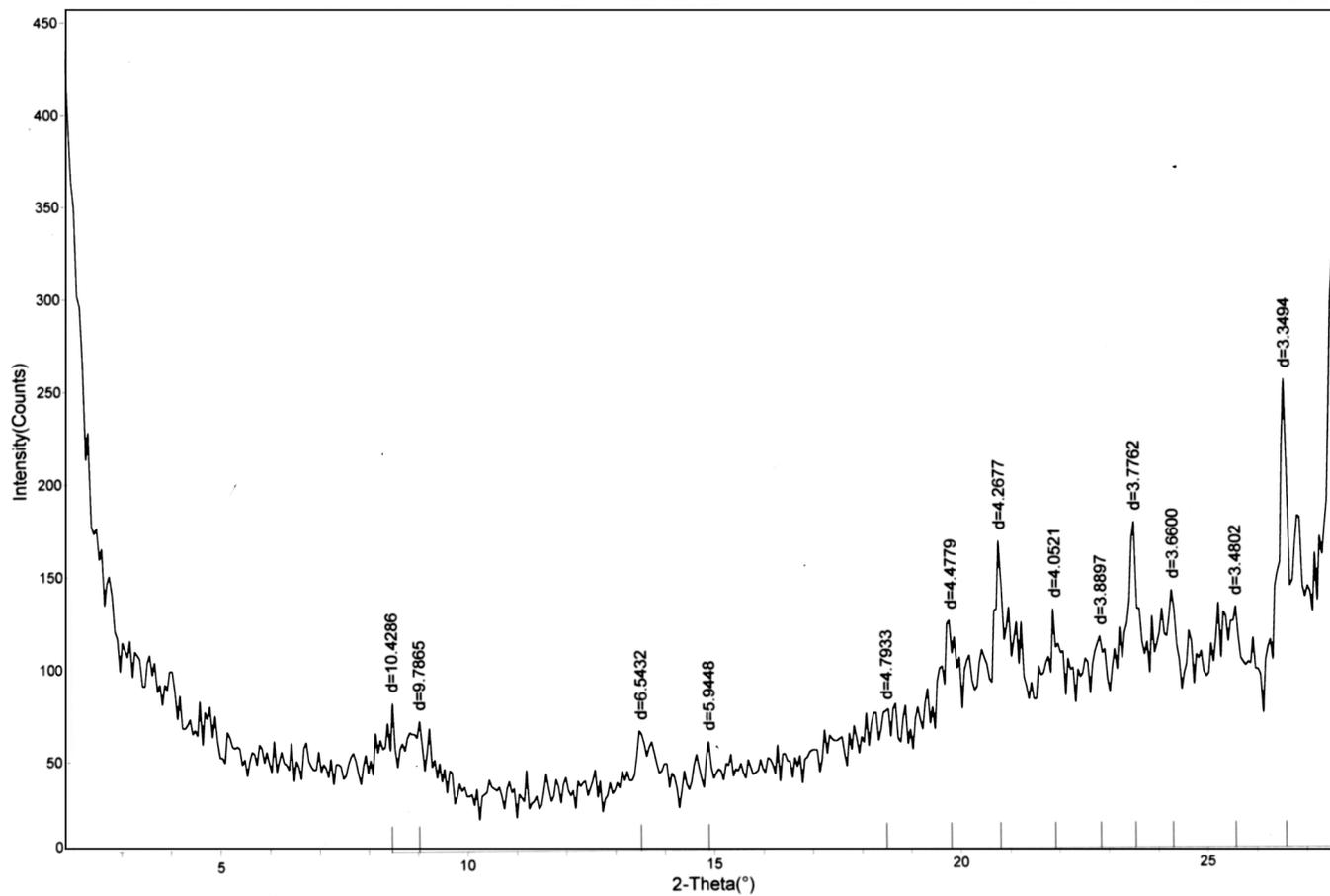
# CDD99 ETHYLENE GLYCOLATED



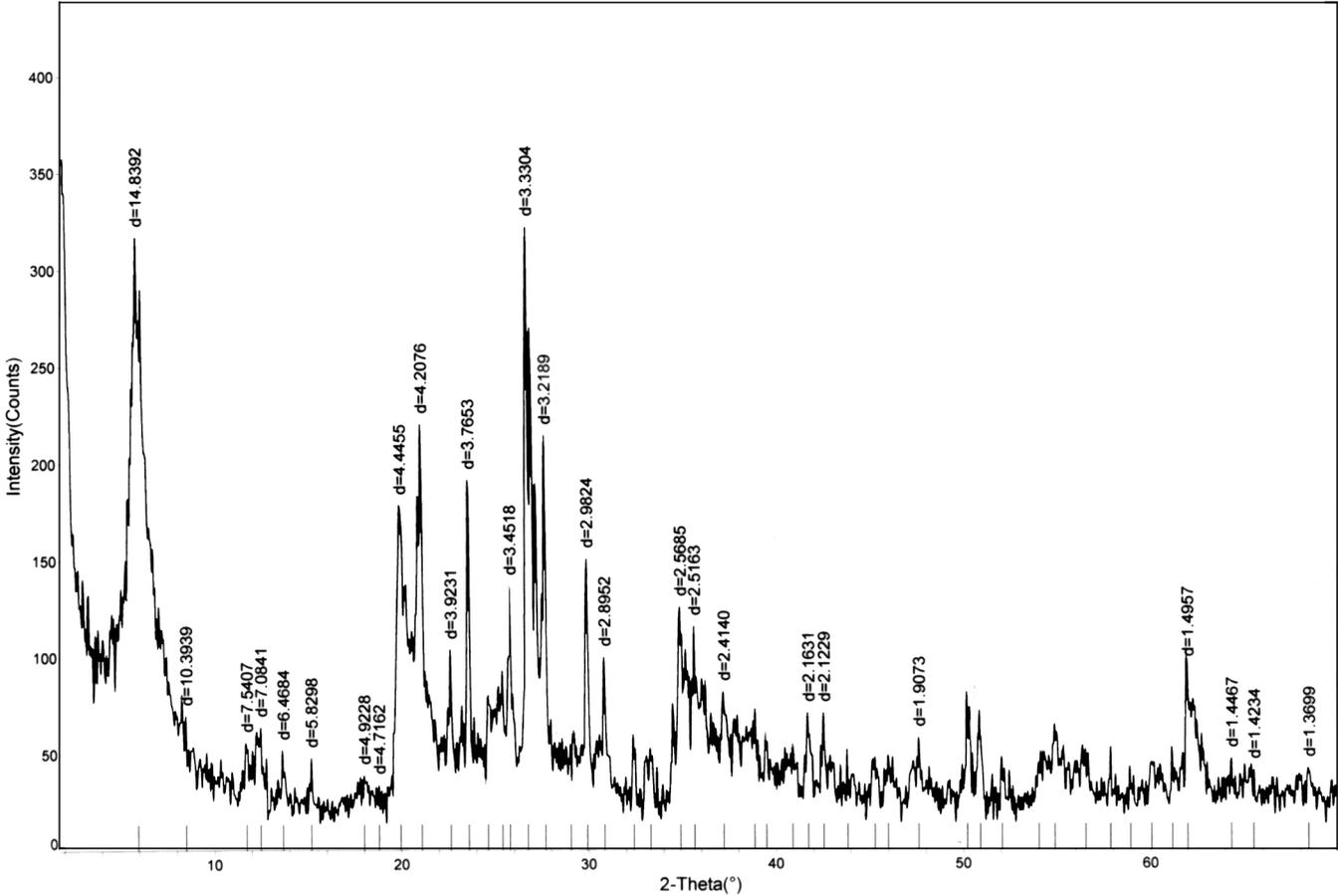
CDD99 HEATED TO 300°C



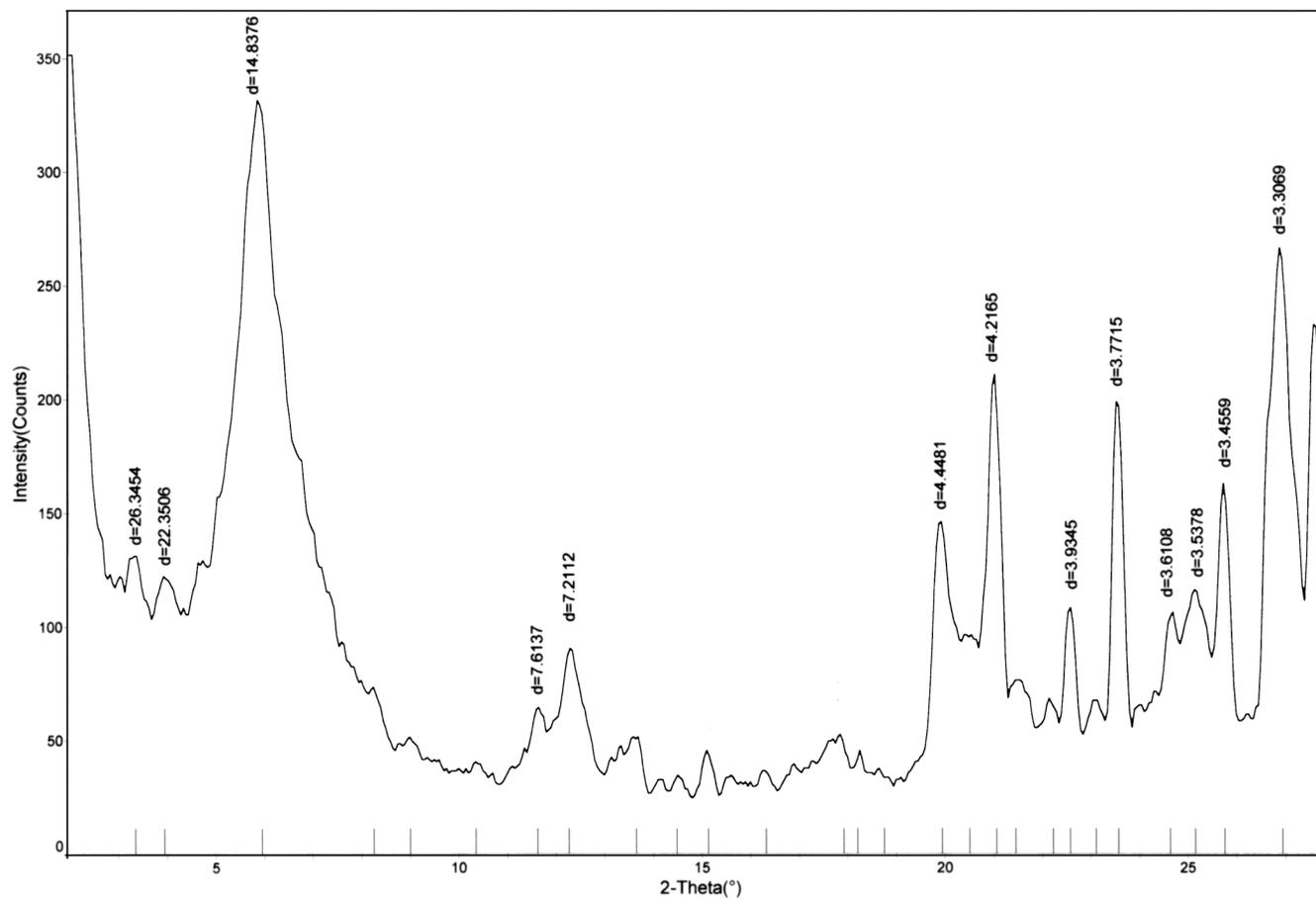
# CDD99 HEATED TO 550°C



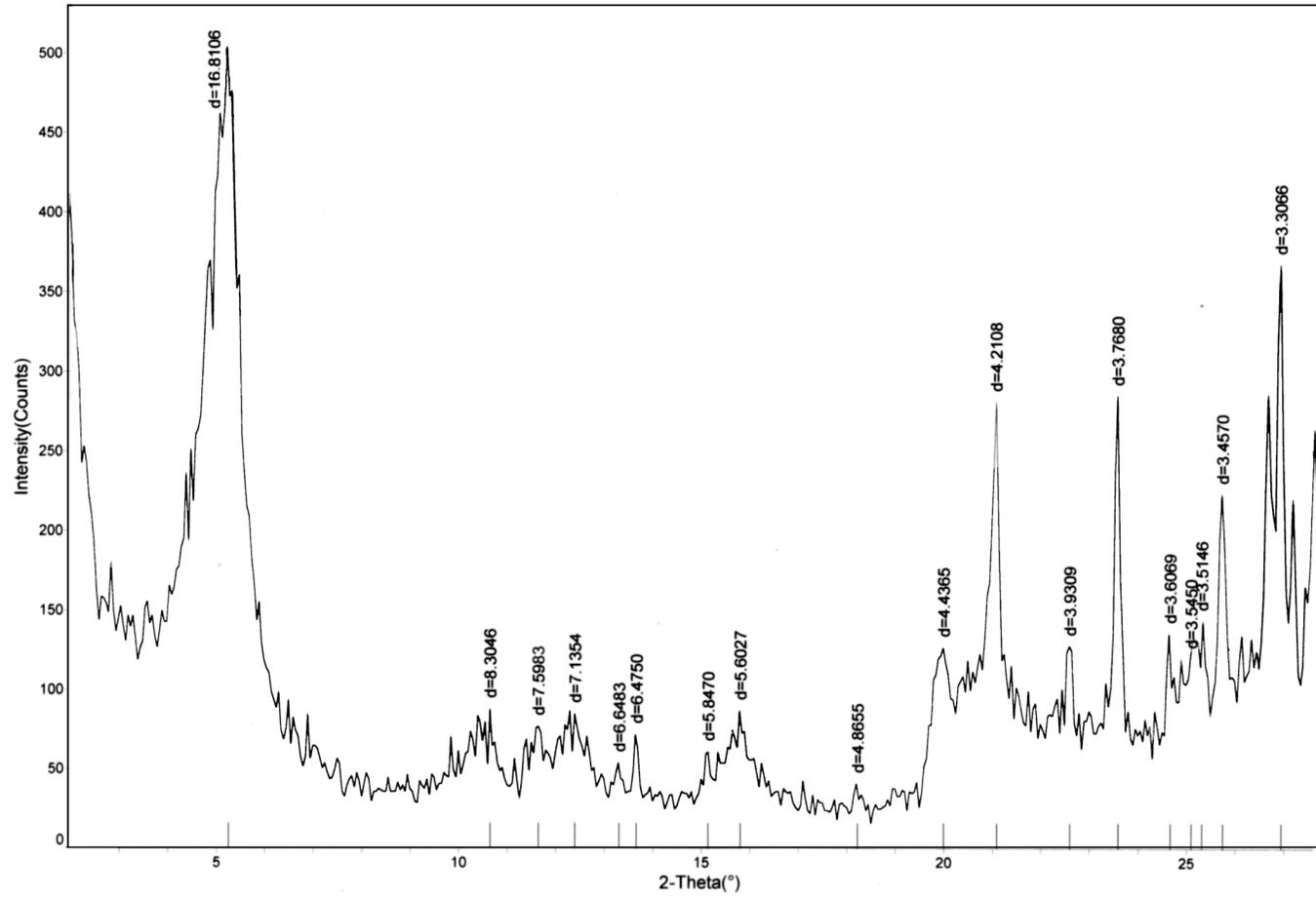
CDD334A BULK



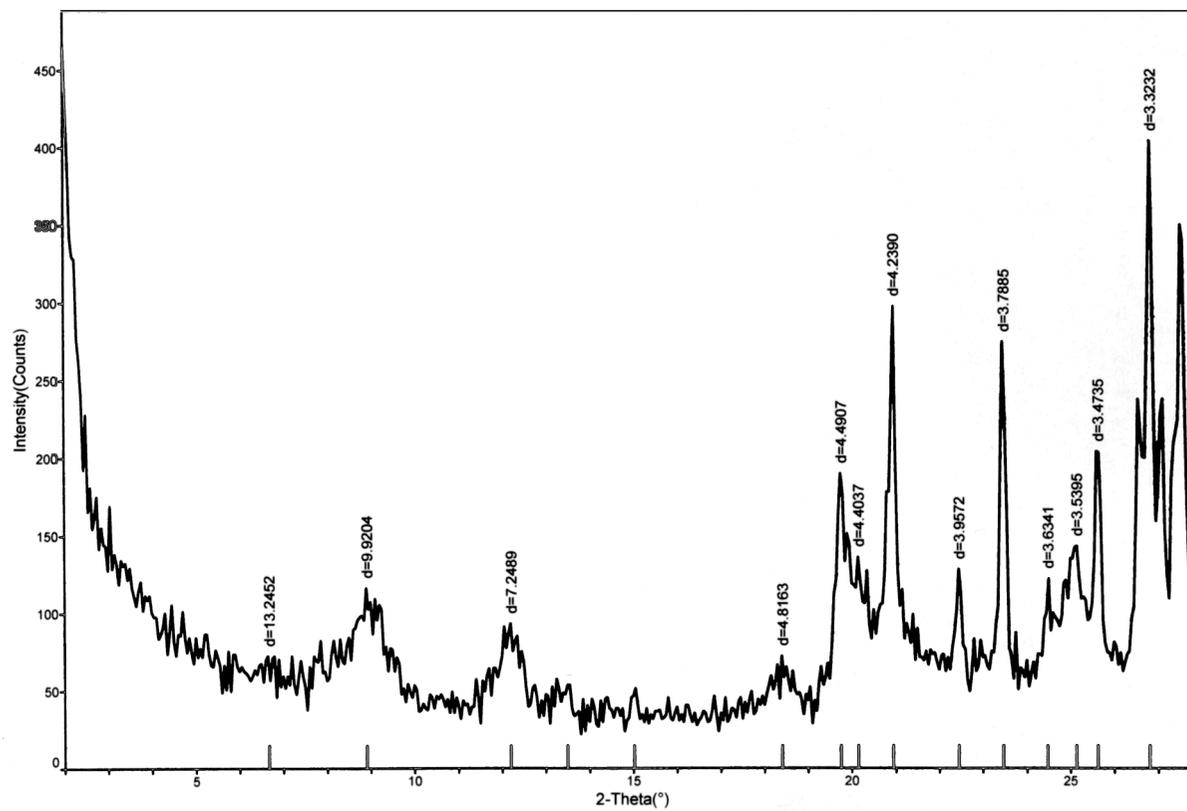
# CDD334A AIR DRIED



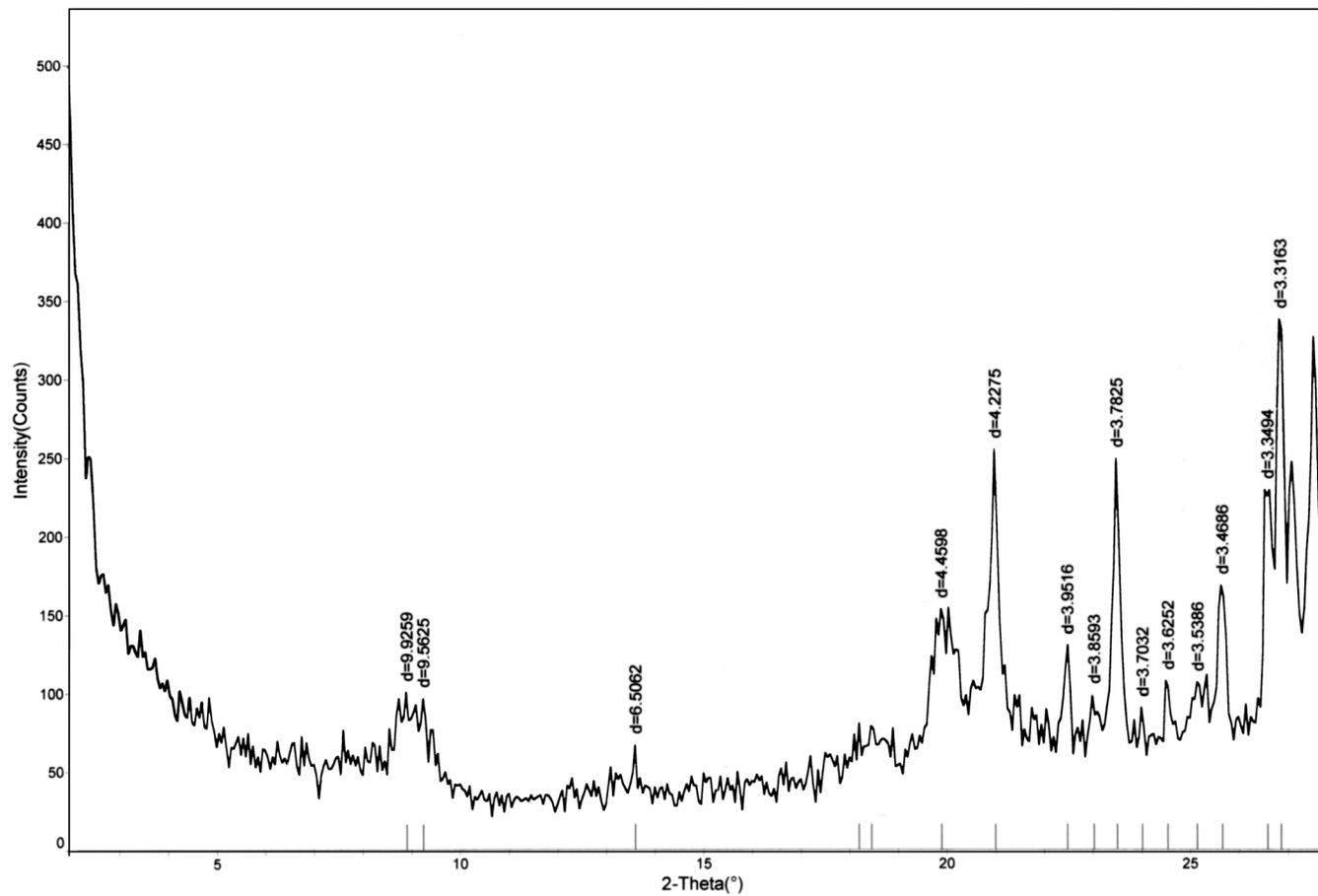
# CDD334A ETHYLENE GLYCOLATED



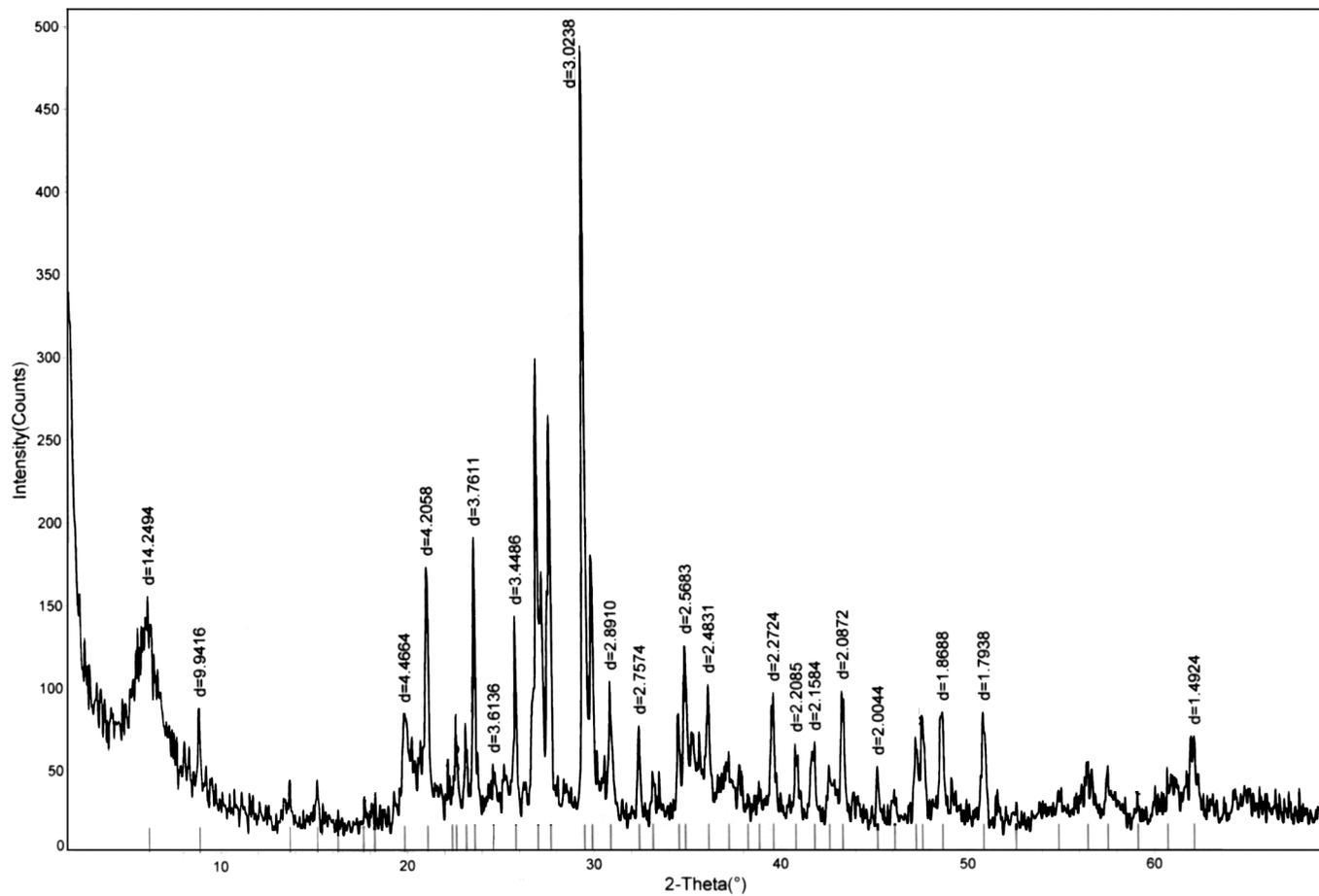
# CDD334A HEATED TO 300°C



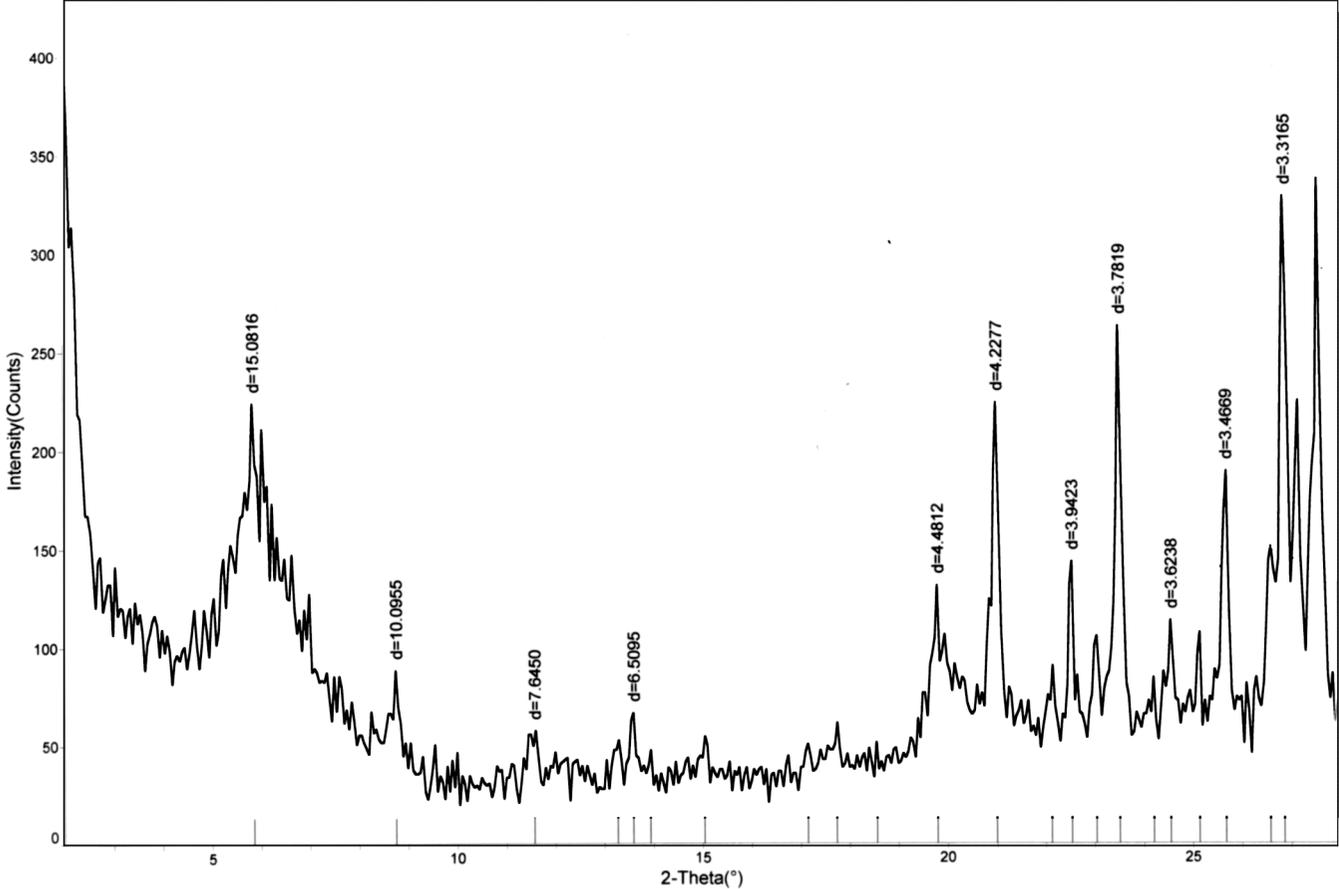
CDD334A HEATED TO 550°C



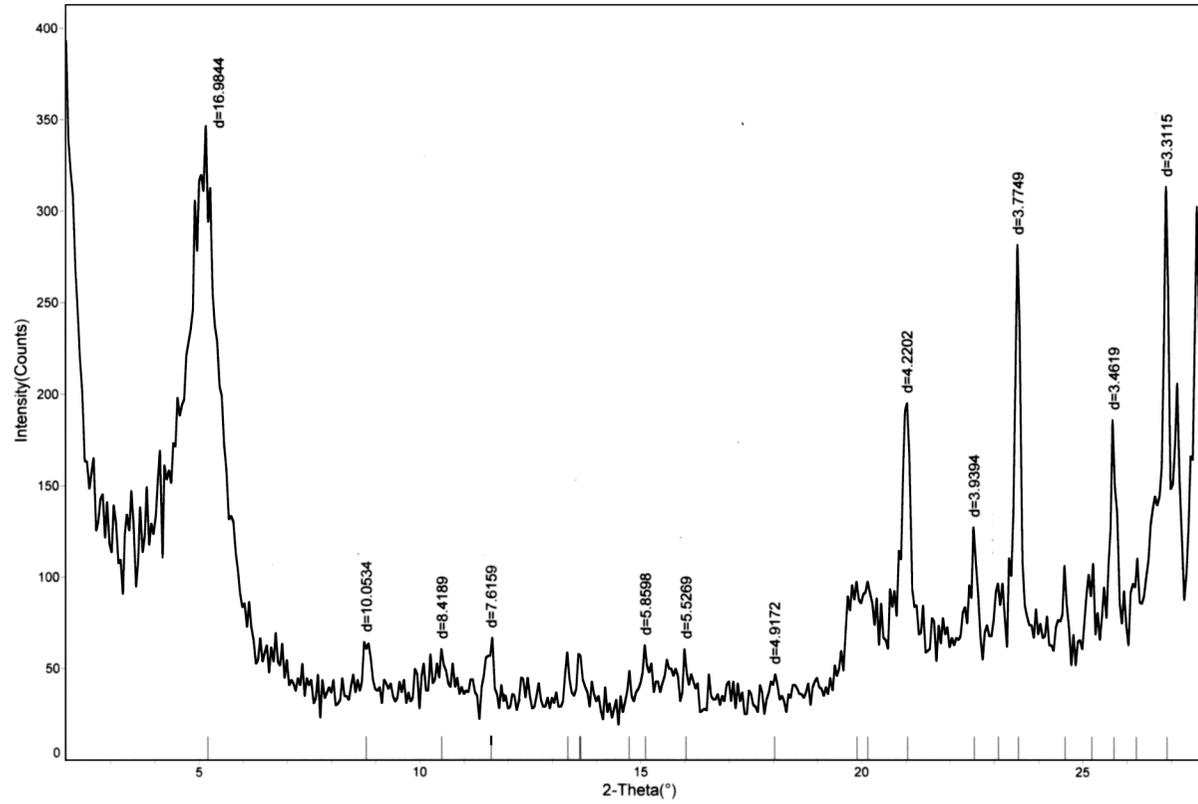
# CRD356 BULK



CRD356 AIR DRIED



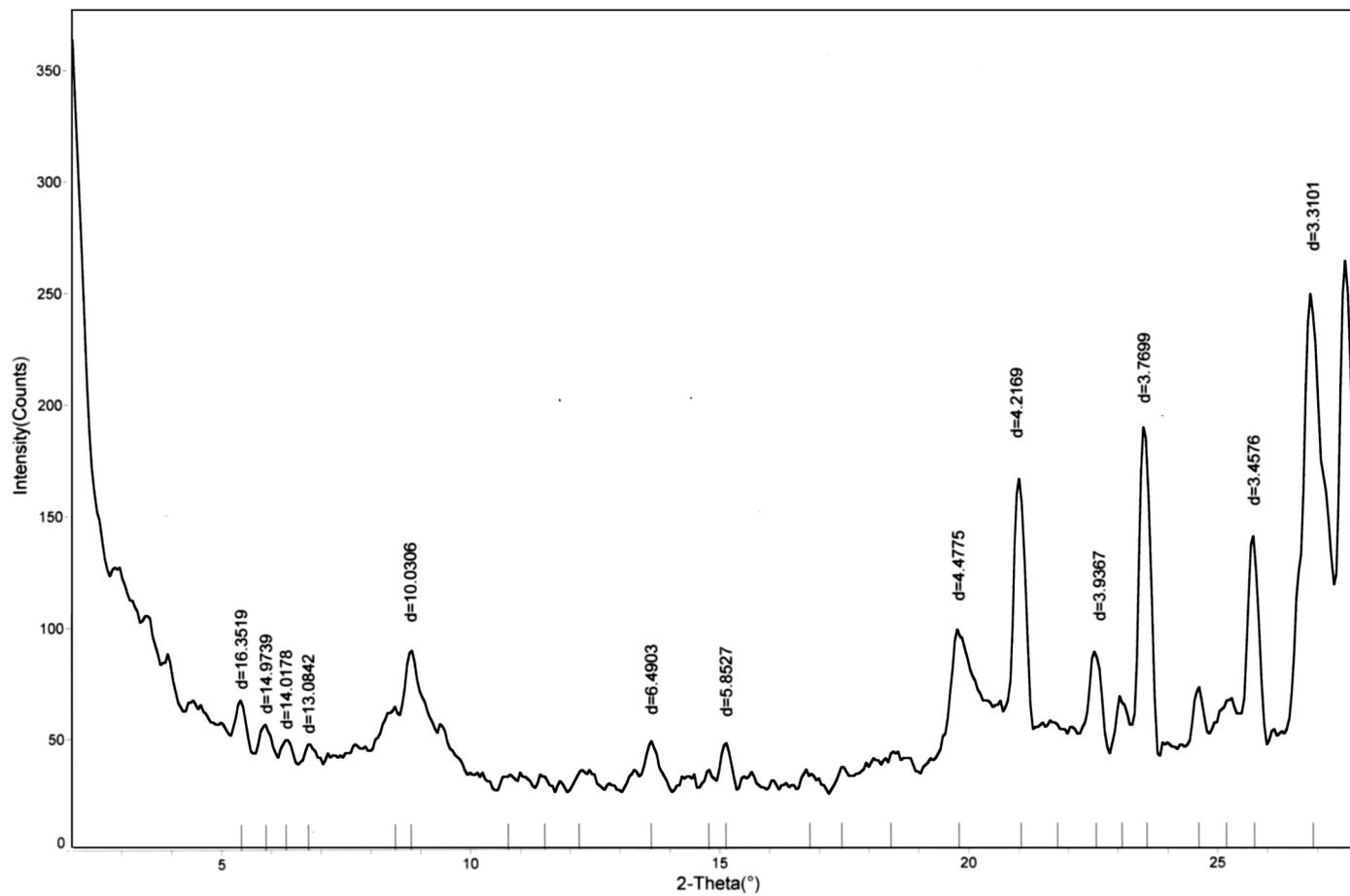
# CRD356 ETHYLENE GLYCOLATED



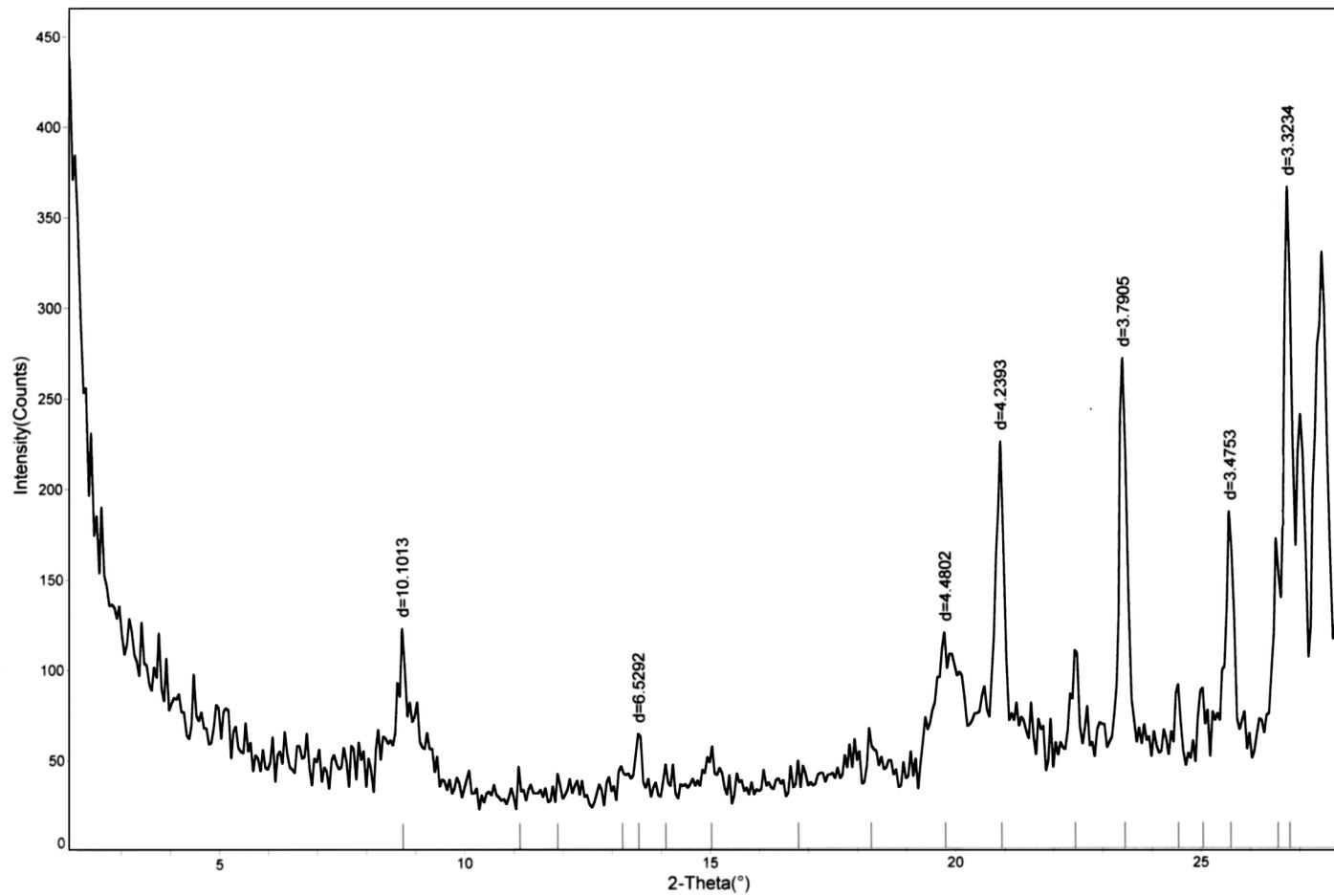
Mining Res Inst.

[MTAIMTA]<a> Perbembe, Pub 23, 2006 02:19p (MDI/JADE6)

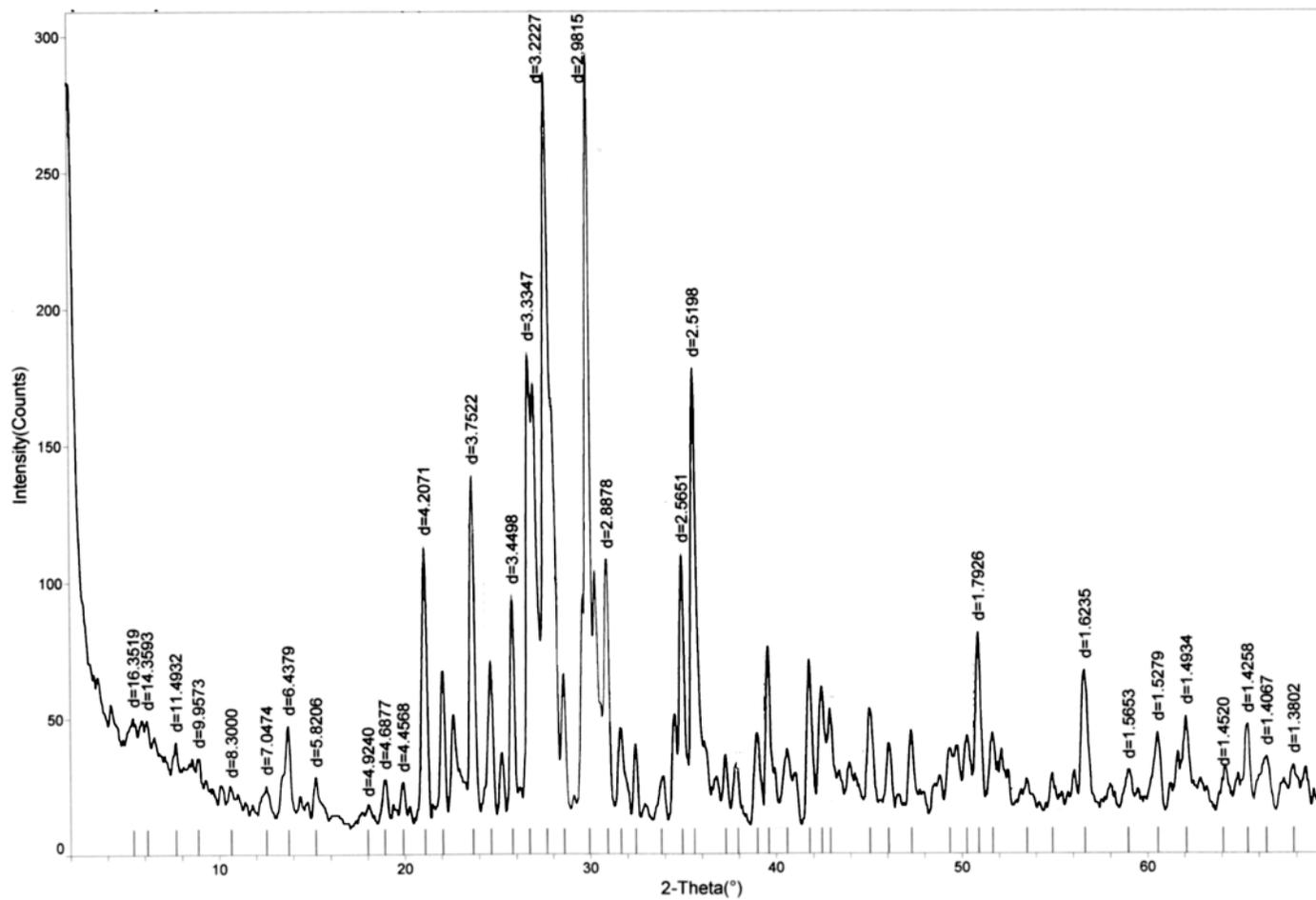
CRD356 HEATED TO 300°C



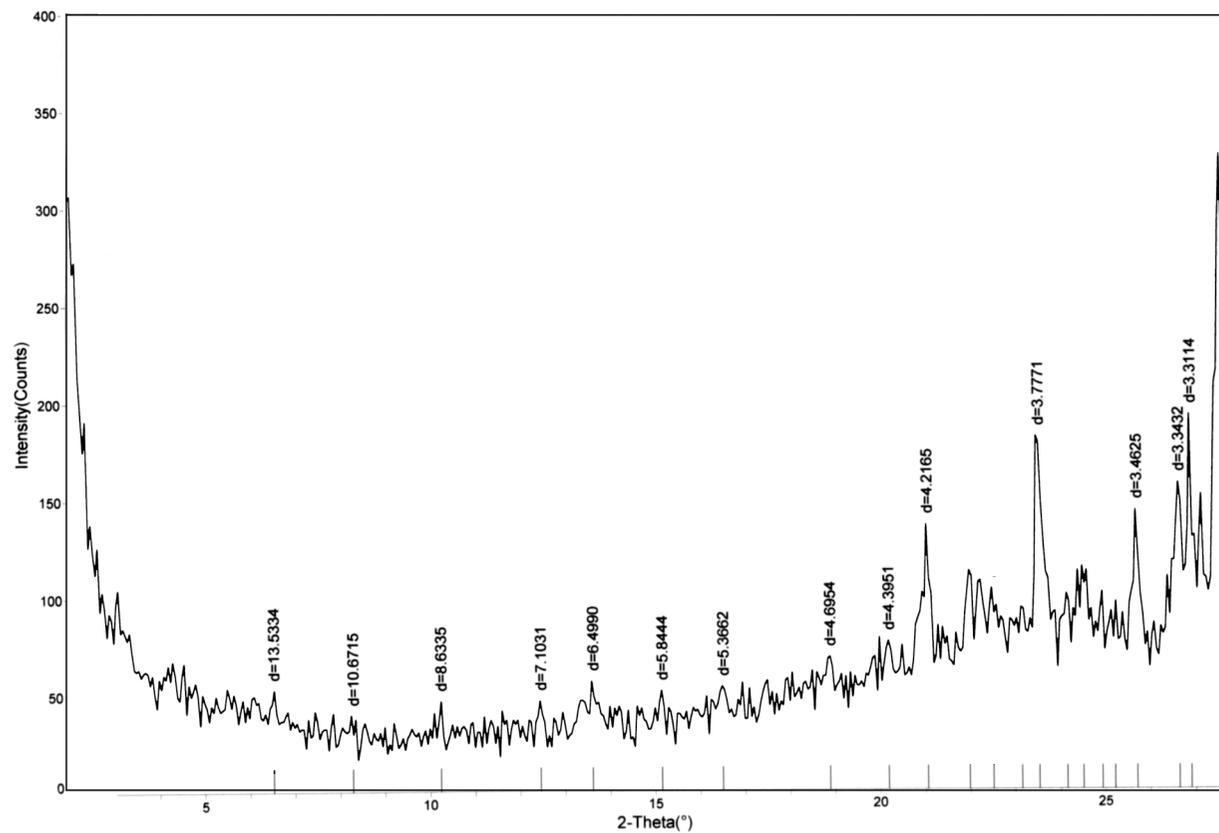
CRD356 HEATED TO 550°C



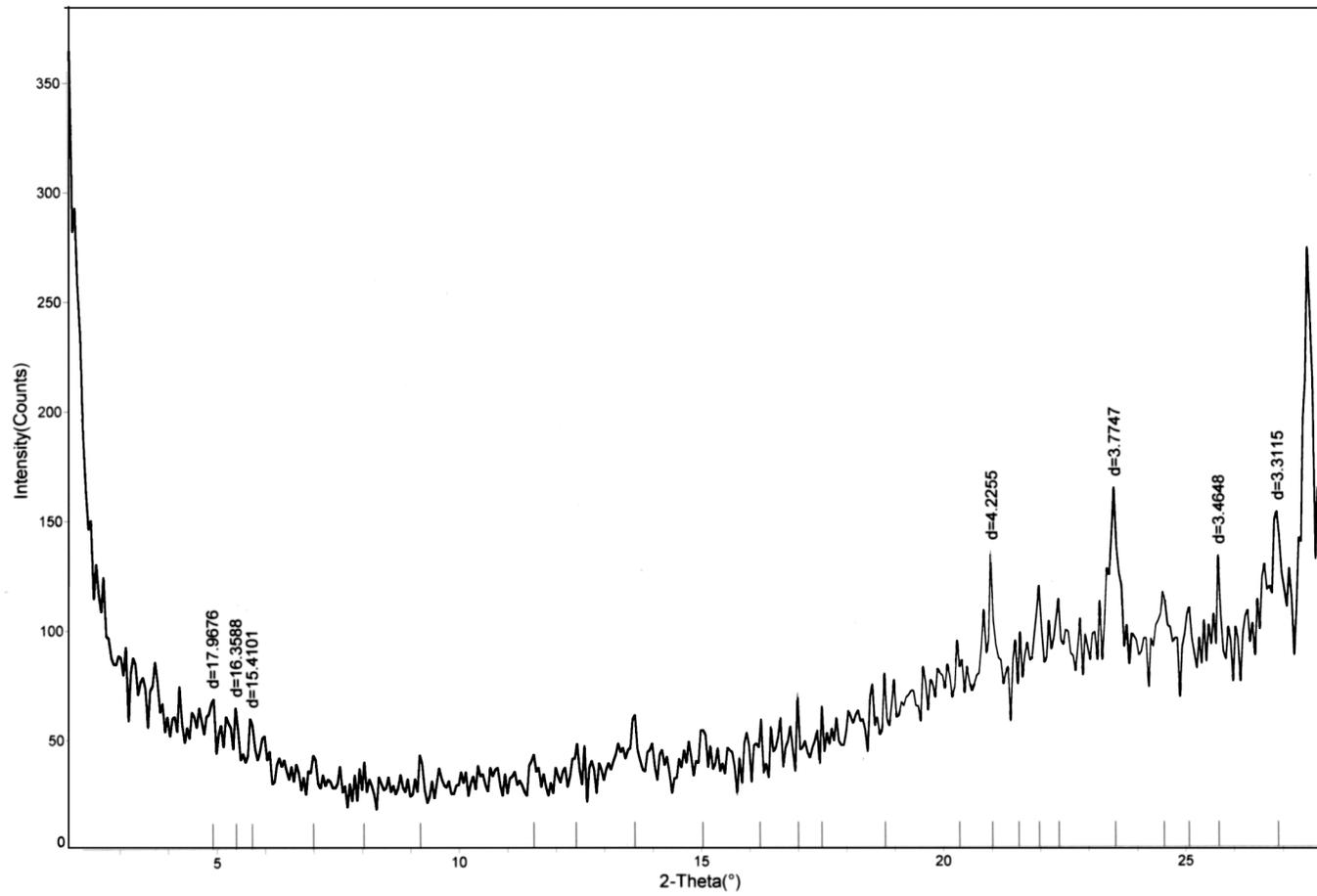
# RMH01 BULK



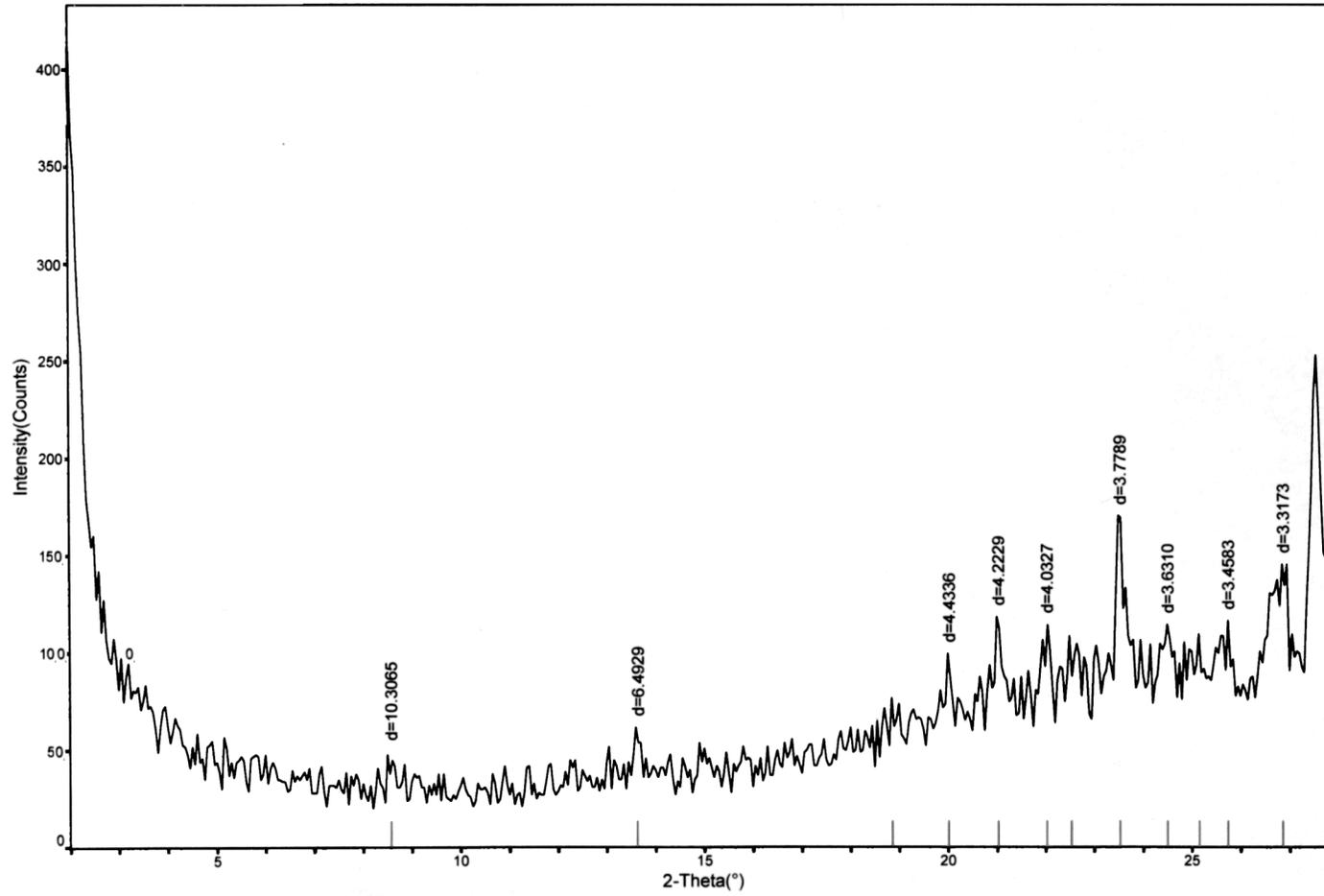
# RMH01 AIR DRIED



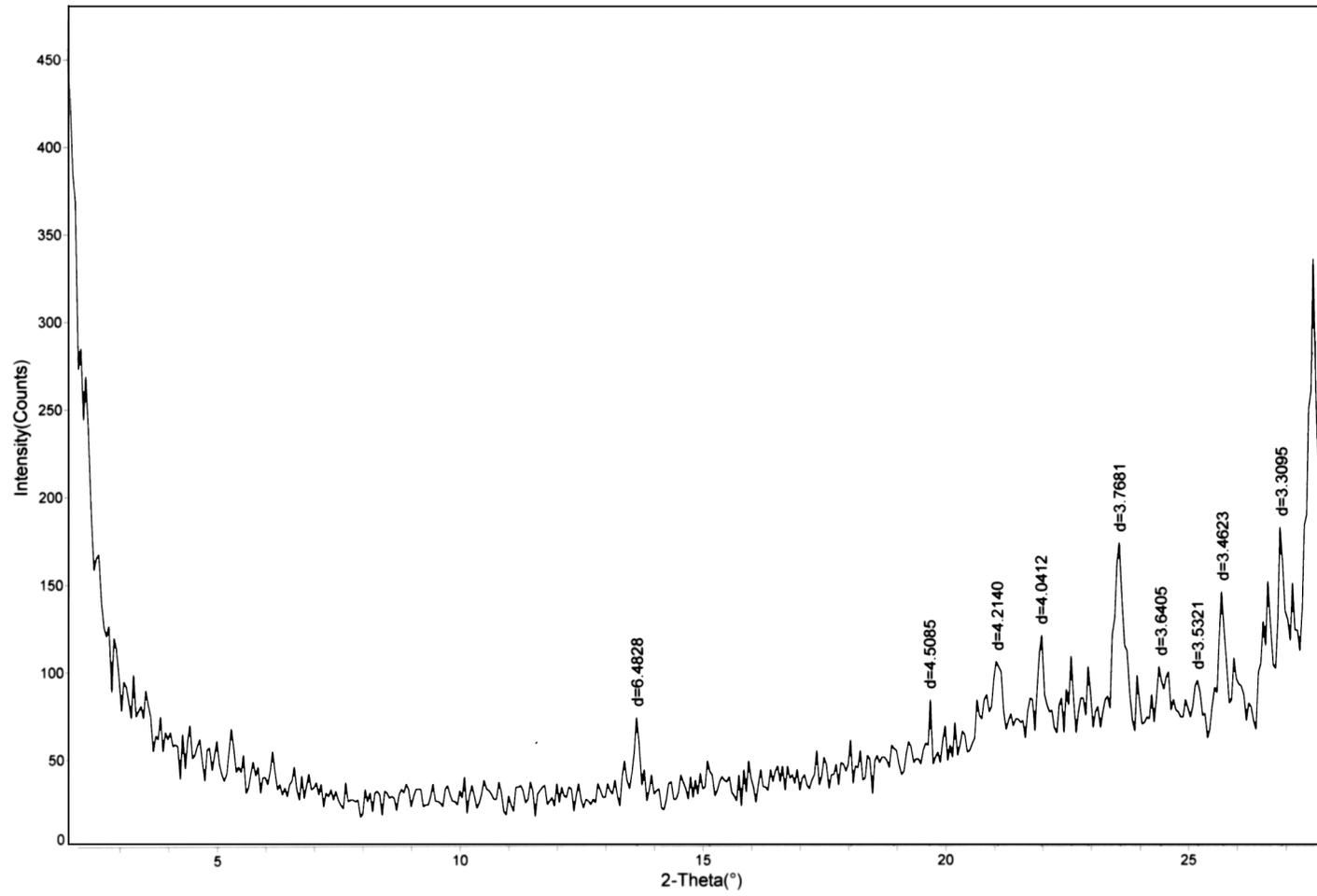
# RMH01 ETHYLENE GLYCOLATED



RMH01 HEATED TO 300°C



RMH01 HEATED TO 550°C



# CURRICULUM VITAE

## PERSONAL INFORMATION

Surname, Name: Sezer Özçelik, Ganime Aslı
Nationality: Turkish (T.C.)
Date and Place of Birth: 24 March 1970, Ankara
Marital Status: Married
Phone: +90-312-489 13 38
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## EDUCATION

Degree	Institution:	Year of Graduation
MSc	Oxford University, Environmental Change Institute, UK	2006
MSc	METU, Geological Engineering	1998
MSc	Ankara University, MED Campus-Environmental Management	1995
Minor Degree	METU, Biology	1994
BSc	METU, Geological Engineering	1994
High School	Ankara Anadolu High School-French Teaching Div., Ankara	1989

## WORK EXPERIENCE

Year	Place	Enrollment
2002-Present	General Directorate of Mineral Research and Exploration, Department of Mining Analysis and Technologies	Geological Engineer
1994-2002	METU, Department of Geological Engineering	Research Assistant
1992 - 1994	Turkish Association for the protection of Nature and Natural Resources	Project Assistant

## FOREIGN LANGUAGES

Advanced English and French

## PUBLICATIONS:

1. Asatekin, G., Brackman, P., Deruytter, M., Erdoğan, M., Ersoy, B., Karadeniz, N., Karaoğlu, N., Knockaert, J.P., Özcan, Z., Öztan, Y., Pauwels, M., Perçin, H., **Sezer, A.** , Vanmoerkerke, A., Vermander, C., Vural, M., 1996, Along Ancient Trade Roads, Seljuk Caravansaries and Landscapes in Central Anatolia, Maasland VZW. , Kanaal Straat 10, 3621, Rekem-Lanaken, Belgium. Salto nv. , 157pp
2. **Sezer, G.A.**, Türkmenoğlu, A.G, and Göktürk,, E.H., Mineralogical and sorption characteristics of Ankara Clay as a landfill liner, *Applied Geochemistry, Volume 18, Issue 5, May 2003, Pages 711-71.*
3. Özçelik M. F.& **Sezer G. A.**, "The Ornitho-tourism Concept, The Ornitho-touristic potential of Turkey and the Sultan Marshes Model", International Symposium for the Conservation of Wetlands, 27/09/1995-01/10/1995-Kapadokya, 25 pp.
4. **Sezer, G.A.**, Türkmenoğlu A. G., Göktürk, H., Volkan, M.; Heavy Metal Exchange And Fixation Property Of Some Clay Materials Tested As Landfill Liners For Ankara Sanitary Landfill, 9th Biennial Meeting of European Union of Geosciences, Union Symposia 22: Environmental Geoscience: From Resource to Recycling, Poster Presentation, 23 - 27 March 1997, Strasbourg - France.
5. **Sezer,G.A.**, Türkmenoğlu, A.G., Göktürk, E.H., ve Volkan, M., 1997, A research on the uptake behavior of some polluting cations by Ankara Clay, VIIIth National Clay Sympozium, 24-27 Eylül 1997, DPÜ, Kütahya,s.521-528.

## HOBBIES

Birdwatching, Nature Photography, Ecotourism (within the frame of wetland management), Cooking, Cat Breeding (with special interest to Turkish Vankedisi).