AN INVESTIGATION ON THE MINERALOGICAL, PETROGAPHICAL AND CHEMICAL PROPERTIES OF STONE OBJECTS FROM KARAİN CAVE, ANTALYA-TURKEY

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Approval of the thesis

AN INVESTIGATION ON THE MINERALOGICAL, PETROGAPHICAL AND CHEMICAL PROPERTIES OF STONE OBJECTS FROM KARAİN CAVE, ANTALYA-TURKEY

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ABSTRACT

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The archaeological and technical questions about ancient stone tools lead to various research activities such as chemical and petrographical analysis.

Considering research areas and publications it can be suggested that mineralogical studies of stone samples of ancient stone tools have disclosed useful information concerning identification of the stone.

Within this context, aim of this study is to determine the chemical, mineralogical and petrographical identities of the stone samples of Karain Cave (Antalya).

Most paleolithic caves show one specific time interval layer but Karain Cave shows lower-upper and middle layers which give information about the migration ways between Near East and Europe.

Stone tools excavated from Karain Cave are not only first human remainings in Anatolia but also first artworks of Anatolian people.Most of the stone tools excavated from Karain Cave are cherts. These cherts were analysed for archeological aspects but mineralogical, petrographical, and chemical contents have not been analysed yet. During the excavations at the Karain Cave in Antalya many stone pieces in different sizes and colors had been found. In this study ten samples were examined. The methods used consists of thin section, X- ray powder diffraction , scanning - electron microscopy coupled with energy dispersive X-ray analysis , differential thermal analyses and inductively coupled plasma mass spectrometry to determine material characteristics of the samples.

Petrographically the nine of the samples are chert with some including radiolarian fossils. Microcrystalline α - quartz is the major mineral in the chert. Only one sample is composed calcite and is identified as micritic limestone. Chemical analysis reflect the typical composition of chert with the average values of; 40.9% Si and 1 sample is limestone, which is composed of 35.7% Ca . Minor elements are Fe, Al, K, and Ti in the samples. Thermal analysis is also supported the thin section studies.Further research is suggested for provenance analysis of stone tools from the Karain Cave.

Keywords: Chert, Limestone, Karain Cave, Stone Tools, Paleolithic, Antalya.

ÖZ

KARAİN MAĞARASI, ANTALYA (TÜRKİYE)‘ DA ELE GEÇEN TAŞ OBJELERİN MİNERALOJİK PETROGRAFİK VE KİMYASAL ÖZELLİKLERİNİN ARAŞTIRILMASI.

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Tarihi taş aletler hakkında arkeolojik ve teknik sorular çeşitli araştırma faaliyetlerine yol açmaktadır. Bunlar taş aletlerin yapımında seçilen kayaçların tanımlanması ,kaynakların bulunması gibi alanlardır.

Taş örneklerinin bileşimlerinin belirlenmesinin, bu taşların kaynağı ile ilgili yararlı bilgiler ortaya çıkaracağı ifade edilebilir. Bu çalışmanın amacı Karain Mağarası’ndan (Antalya) elde edilen taş örneklerin mineralojik yapısının ve petrografik özelliklerinin belirlenmesidir. Paleolitik mağaraların çoğu tek bir zaman aralığını barındırırken Karain Mağarası alt, orta ve üst katmanları ile farklı dönemlere ait kalıntıları barındırmakta ve bu kalıntılar Asya ve Avrupa arasındaki göç yolları hakkında bilgiler vermektedir. Kazılarda elde edilen taş aletler Anadolu’nun en eski buluntuları ve anadolunun ilk sanat eserleridir. Karain Mağarası’ nda yapılan kazılarda farklı renk ve

büyüklüklerde taş parçaları elde edilmiştir. Bu çalışmada bunlardan on adet örnek mineralojik ,petrografik ve kimyasal açılardan incelenmiştir. Kullanılan analiz metodları, ince kesit analizi, X - ışınları toz difraktometresi , elektron mikroskobu ve endüktif eşleşmiş plazma-kütle spektrometresi (ICP-MS) ,ve termal analizi içermektedir. Petrografik olarak dokuz örnek çört olarak belirlenmiş ve bazılarında radiyolarya fossil kalıntılarına rastlanmıştır. Çörtledeki ana mineralin ise α- Kuvars olduğu anlaşılmıştır.

Diğer örneğin ise kalsitten olduğu anlaşılmış ve mikritik kireç taşı olarak tanımlanmıştır. Termal analizler petrografik analizlerin verdiği sonuçları desteklemiştir. Konuyla ilgili sonraki araştırma Karain Mağarası' nda bulunan taş kalıntıların kaynaklarının bulunması için çalışmalara devam edlilebilir.

Anahtar Kelimeler: Çört, Kireç Taşı, Karain Mağarası, Taş aletler, Paleolitik, Antalya.

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I am very grateful to Prof. Dr. Harun Taşkıran and Assoc. Prof. Dr. Metin Kartal for giving the chert samples from Karain cave, Antalya.

Very special thanks to Prof. Dr. Emine N. Caner - Saltık and Res. Asst. Evin Caner, for their valuable helps for the XRD analysis.

Special thanks to staff members of the Central Labrotary of METU for taking SEM photomicrographs of the samples and Orhan Karaman from the Department of Geological Engineering prepared the thin sections of the chert samples.

Finally, I owe special thanks to Prof. Dr. Ay Melek Özer who always guided and encouraged me during my graduate studies in the Archaeometry Department.

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INTRODUCTION

1.1. The Aim and Scope of the Thesis

Raw material sources of chert were extensively exploited during prehistoric times dating back to more than one million years ago. This fact is because of the suitability of chert for shaping during tool making, and its physical properties like conchoidal fracture, high hardness and durability. Chert tools were widely manufactured during Paleolithic and Neolithic times in Asia, Near East , Europe, Australia and America.

Stone tools provide very valuable information about the past behaviour of human societies (Ewen, 2003).

Topological aspects of them provide dating of archaeological sites based on the trends in production technology (Whittaker, 1994). Functional analysis such as use-wear and residue analysis help to understand what people did with stone tools.

Other aspects of studying stone tools are their technological analysis and provenance analysis by means of which technological level, trade and movements of ancient people and societies can be enlighted in Turkey.

Paleolithic age studies are attracting the interests of archaeologists especially after 20th century (Kartal, 2005). Since Anatolia has possible cultural connections with Balkans and Levant, archaeological and archaeometric investigation of the Paleolithic stone tools (eg. cherts) exploited in Paleolithic sites in Anatolia, are highly expected to play important role in establishing the cultural sequence during Pleistocene and Holocene times (Kartal, 2005).

The aim of this thesis is to reveal material properties of chert tool samples collected from the Karain Cave (Antalya) excavations. For this purpose a limited number of chert samples are investigated to reveal their mineralogical , petrographical, chemical properties using a number of scientific methods including petrographic microscope (PM), scanning electron microscope equipped with energy dispersive X-ray analysis (SEM-EDX), thermal analysis (DTA) and major and trace element chemical analysis with Inductively Coupled Plasma- Mass Spectrometry. The results obtained will be a preliminary basis for the provenance studies of chert tools from Karain Cave, as a further research project.

1.2. Karain Cave and Previous Archaeological Investigations

The Karain Cave is found within the borders of Yağca Village which is at 5 - 6 km. from to the old Antalya - Burdur highway, 30 km northwest of Antalya (Fig.1.1). The Cave is situated 30 km. North-Nortwest of Antalya.

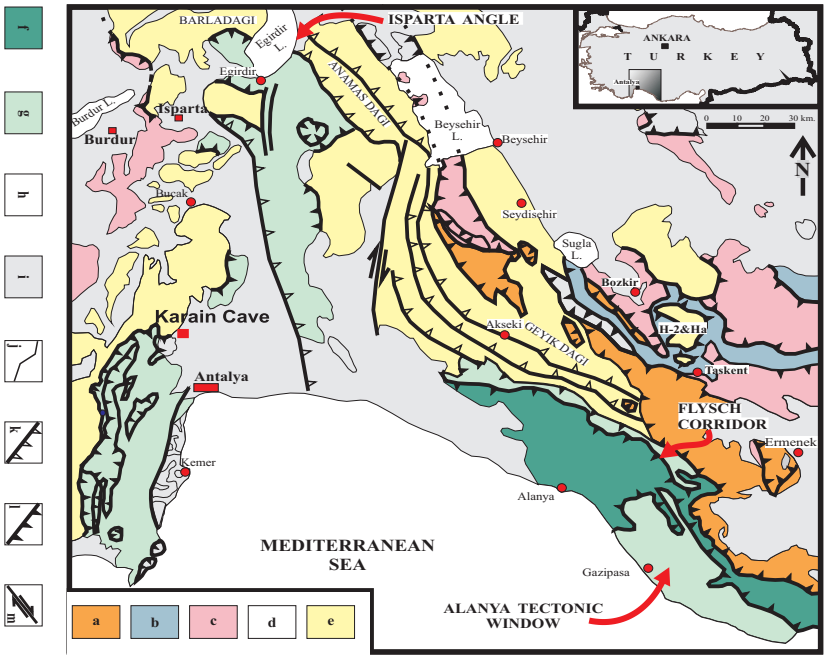


Figure 1.1. Geologoical map of Antalya showing the location of Karain Cave a. Hadim Nappe, b. Bolkardagi Nappe, c. Beysehir-Hoyran Nappe, d. Ophiolitic Nappes belonging to the Northern Branch of Neo-Tethys (Dipsizgol Ophiolite etc.), e. Beydaglari-Anamas-Akseki Autochthon, f. Alanya Nappe, g. Antalya Nappes, h. Ophiolitic Nappes belonging to the Southern Branch of Neo-Tethys (Tekirova Ophiolitic Nappes), i. Post-Eocene cover rocks, j. Normal contact, k. Thrust, l. Overthrust, m. Strike-slip fault (after Tekin 1999, as revised from Özgul, 1984)

It is on the east slope of Katran Mountain which is in the range of western Taurus mountains. The Karain Cave was carved in the Jurassic - Cretaceous age limestone with abundant fractures which control cave devolopment within a karstic topography.

There are fine water springs where the plain meets the mountains.Geological and geomorphological researches in the recent years revealed a lake in the middle of the plain in Pleistocene time; and many open air settlements in Paleolithic period. This is proved by the fossils of hippopotamus bones and shells of invertebrata found in the fauna of the Karain Cave. The location of the Cave is near the strait of Çubuk which is an important passage connecting the Mediterranean region with inner Anatolia and the Region of Lakes . Karain is a complex of caves rather than a single cave. It consists of seven chambers .These chambers are separated by limestone walls and passageways (Figure 1.2).

Figure 1.2. A view from the Karain Cave

The Karain Cave was occupied in the period of the beginning of the history of the mankind, as the cavern was continuously accommodated by early humans during prehistoric and classic periods starting from early Paleolithic , Neolithic , Chalcolithic and Ancient Bronze stages. As a natural result of this, the cave contains a thick cultural layer which can be 11 meters thick.

But the longest and most important accommodation period of the cave is relevant with the Paleolithic period. The usage at the classical period is more likely as an Offering Cave (Temple) and there are Greek inscriptions and niches at the cave exterior walls.(http://www.kultur.gov.tr/TR/belge/2-16184/caverns-of-antalya.html.)

1.3.Silicous Rocks and Varieties of SiO_2 Group

1.3.1.Macrocrystalline Quartz

Quartz is a very common mineral, a chemical compound of silicon and oxygen silicon dioxide SiO_2, commonly called silica. Quartz occurs in a great number of varieties that differ in form and color. It occurs as massive aggregates, dense nodules, or crystals in druses. Quartz is colorless if pure, but may assume any color due to inclusions of other minerals or built-in trace elements.Macrocrystalline varieties are those that form crystals having a macroscopical crystal structure, like amethyst, rock crystal, rose quartz and citrine.

1.3.2 Microcrystalline and Granular Varieties of SiO_2 Group

These varieties may have fibrous or granular morphologies. The granular varieties are chert, flint and jasper. Chert is a fine-grained silica-rich microcrystalline sedimentary rock that may contain small fossils such as radiolarian cherts.It varies greatly in color but most oftenly occur light colors. Its color is an expression of trace elements and impurities ,such as iron and hematite, present in the rock. Red colored chert is called jasper.

It is very hard compact material (H=7) that fractures conchoidally when struck .Dark siliceous nodules , usually found in chalk are called flint, which includes carbon . The exact mode of formation of flint is not yet clear but it is thought that it occurs as a result of chemical changes in compressed sedimentary rock formations, during the process of diagenesis.

Chert can form both organic and inorganic geological process. It is clear that the chemical and physical variation among chert types result from the differing modes of the origin and mainly by chemical composition of the adjacent rock (Klein , 2002).

There is much confusion concerning the exact meanings and differences among the terms "chert" and "flint" (as well as their numerous varieties). In petrology the term "chert" is used to refer generally to all rocks composed primarily of microcrystalline, cryptocrystalline and microfibrous quartz.

Strictly speaking, the term "flint" is reserved for varieties of chert which occur in chalk and marly limestone formations. Among non-geologists (in particular among archaeologists), the distinction between " flint " and " chert " is often one of quality - chert being lower quality than flint.

1.3.3. Microcrystalline and Fibrous Variety of SiO_2 Group

Chalcedony is the term applied to fibrous varieties.It has brown to gray color, translucent and has waxy luster. Chalcedony is deposited from aqeous solutions and is found lining cavities in rocks. Agate is a banded variety of chalcedony Silicified wood is also variety of agate.(Klein, 2002)

1.4. Prehistoric Uses of Chert

Chert is the most common raw material in the lithic technology of prehistoric peoples.

Many prehistoric group learned that when raw chert was slowly heated and slowly cooled in the sand , marked improvements in knapping properties resulted. Heating chert above about 375 °C causes internal changes favorable for tool production.

These thermal alterations increase the compressive strength, reduce the point tensile strength and allow a more effective control of fracture for flaking. Chert was used for the manufacture of flint tools during the Prehistory as it splits into thin, sharp splinters called flakes or blades (depending on the shape) when struck by another hard object (such as a hammerstone made of another material). This process is referred to as knapping (Rapp ,2002).

CHAPTER 2

MATERIALS AND METHODS

The first archaeological excavations of the Karain Cave started in 1946 by Dr. I. Kılıç Kökten. After 26 digging seasons, in 1974 the excavations were stopped because of the death of Kılıç Kökten. The excavations of Karain Cavewere started again in 1985 by Prof. Dr. Işın Yalçınkaya and Archeology Department of Ankara University.Today digging continue in two sections, E and B.In present study, 10 chert samples have been collected from the section E (Figure 2.1)

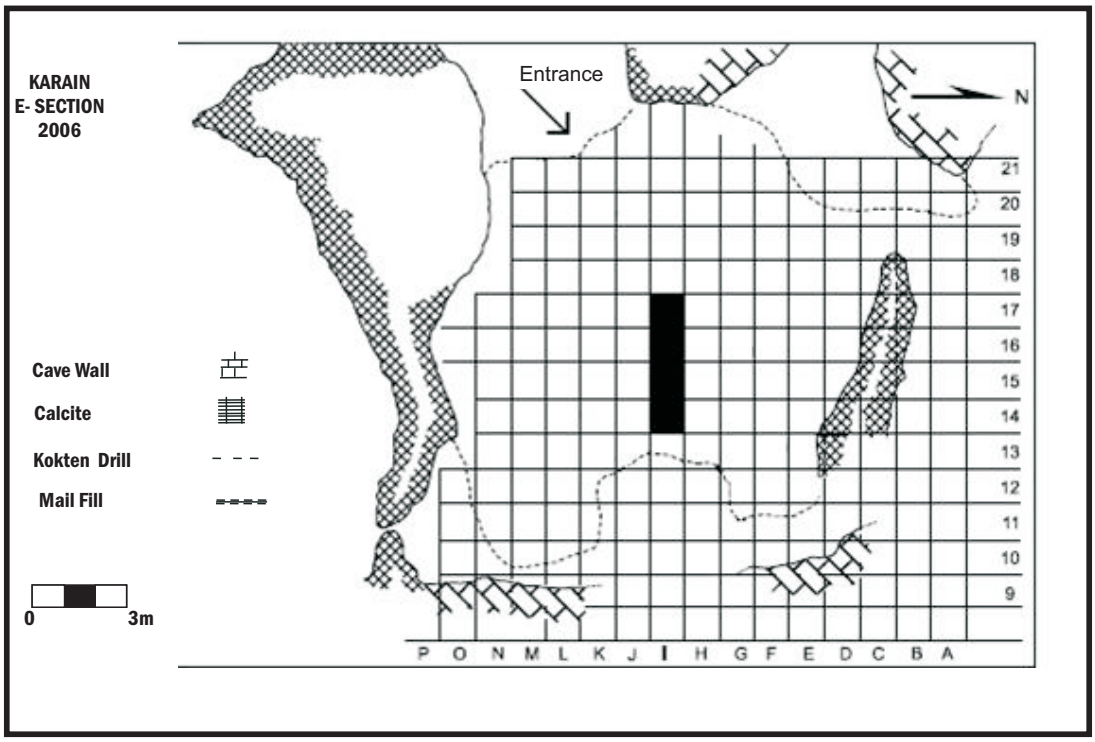
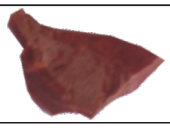


Figure 2.1.Karain Cave section E plan view

2.1. Sampling and Visual Descriptions of the Chert Samples

Ten samples are analysed during this thesis study.The samples are given by Prof. Dr. Harun Taşkıran and Assoc. Prof. Dr. Metin Kartal from the Archeology Department of Ankara University.Hand specimen descriptions are given Table 2.1

Table 2.1: Hand specimen descriptions of analysed chert samples

Field Sample No	Laboratory Sample No	Hand specimen descriptions	cm 1 2 3 4
KE 1999 18H/23 II2	1	Vitrous luster and brown color. Sharp edges with conchoidal fracture. There are black colored spot like patched.	
KE 2000 G18/39 III.3	2	White with brown patches. Hard, brittle with sharp edges smooth surfaces.	
KE 1999 18H/23 II2	3	Red colored. Hard, brittle with sharp edges	
KE 1999 18H/23 II2	4	Brown colored. Hard and brittle with sharp edges. Smooth surface	
G16/32 III.2	5	Gray brown colored. Hard, brittle with sharp edges	
KE 1999 18H/23 II.2	6	White colored.Hard and brittle with sharp edges.Conchoidal fracture.	
KE 2002 18H/4 VI1	7	Yellowish - grayish color. Sharp edges. Conchoidal fractures. Very smooth surface.	
KE 2008 I/4 IV	8	Dark black in color. Hard and brittle with sharp edges.	
KE 1999 18H/234 II2	9	White colored carbonate rock (reacts with dilute HCl acid)	
KE 1999 18H/23 II2	10	Brown colored. Hard and brittle with sharp edges. Smooth surfaces.	

The longest dimensions of the samples vary between 2 to 4 cm.Thickness of the samples are variable and allow thin sectioning. Most of the samples have sharp edges,hard and brittle. Flakes become thicker at their middle parts.

2.2. Method of Analysis

2.2.1 Petrographic Analyses (PA)

Thin section of the chert samples prepared by cutting, grinding , abrading processes in the thin section labarotory of the Department of Geological Engineering at METU. A thin uniform slice 0,03mm thick was obtained in the form of thin sections (Kerr , 1977). All samples have been analysed and thin section photographs are taken by using Nikon 2 Petrographic Microscope.

2.2.2 X-Ray Powder Diffraction Analysis(XRD)

Mineralogical analysis of the chert samples have been done by using XRD technique. XRD analysis were carried out in Materials Conservation Laboratory of METU using the Bruker D 8 Advanced X-Ray Diffractometer. Six chert samples were characterized by performing X-ray powder diffraction on randomly oriented powdered specimens (whole rock).

Diffraction patterns are obtained between 2 -70° 2θ with a scan speed of 2 degrees / min^{-1} using Cu Kα radiation.

2.2.3 Scanning Electron Microscopy Analysis (SEM-EDX)

Three samples (5, 7 and 9) have been analysed by means of SEM analysis using QUANTA 400F Field Emission SEM coupled with EDX

2.2.4. Thermal Analysis (DTA)

Six samples (1,5, 6,7,9,10) are analysed by means of DTA. Analysis have been done in Central Laboratory of METU by using Setaram Labsys TGA/DTA.

2.2.5. Chemical Analysis (ICP-MS)

Chemical analyses of the six samples (1,5,6,7,9,10) are analysed for their Si, Al, Fe, Mg, K, Ca, Na and Ti contents.Chemical analysis have been done in the Central Laboratory of METU by using Perkin Elmer DRC II model ICP-MS.

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Thin- section Analyses with Petrographical Microscopy (PM)

Sample 1 is microcrystalline quartz. There are some micritic calcite observed as clusters which may be the relicts of radiolarian fossils. Microfractures are alsoseen (Figure 3.1).

Sample 2, is microcrystalline quartz and there are chalcedony formations within the microcracks, veins and pores (Figure 3.2)

In sample 3 radiolarian fossils are seen (U.K.Tekin, personal communication, 2012). These fossils, are embedded in a red colored clayeychert matrix (Figure 3.3).

Sample 4 is chert including clay and few radiolarian fossils can be observed. It has a banded texture like clay rich and silica rich parts (Figure 3.4).

Figure 3.1.Thin section photograph of sample 1
showing micritic calcite in chert (cross nicol, x10)

Figure 3.2. Thin section photograph of sample 2
with chalcedony (CH) formations (cross nicol, x10)

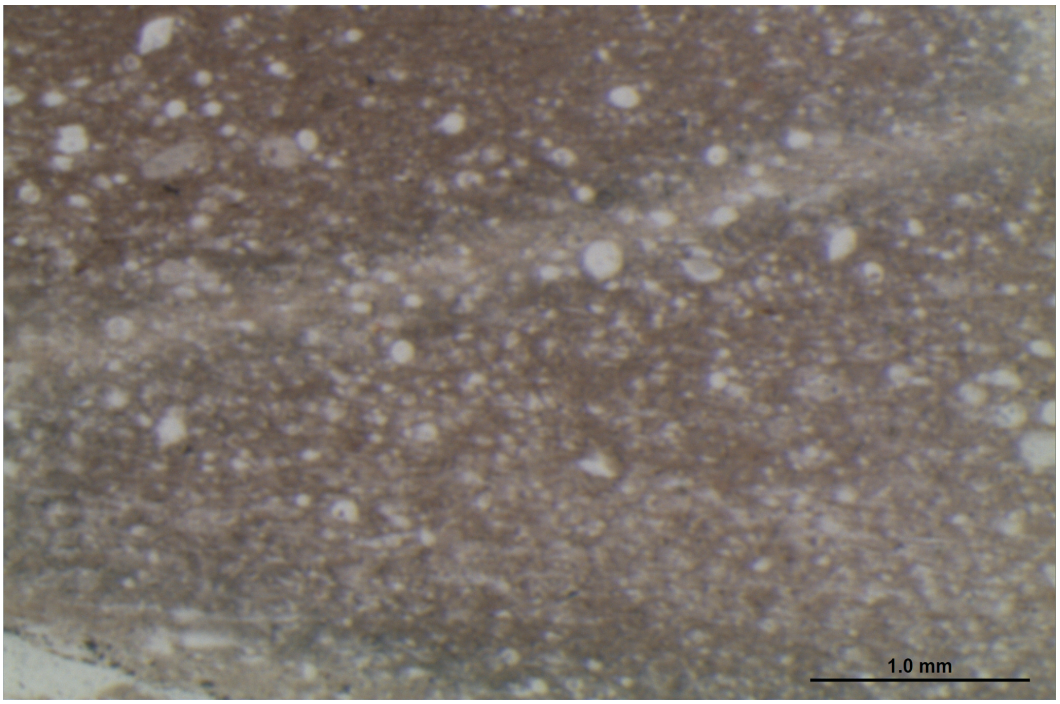


Figure 3.3. Thin section photograph of sample 3
with relict fossils (cross nicol, x10)

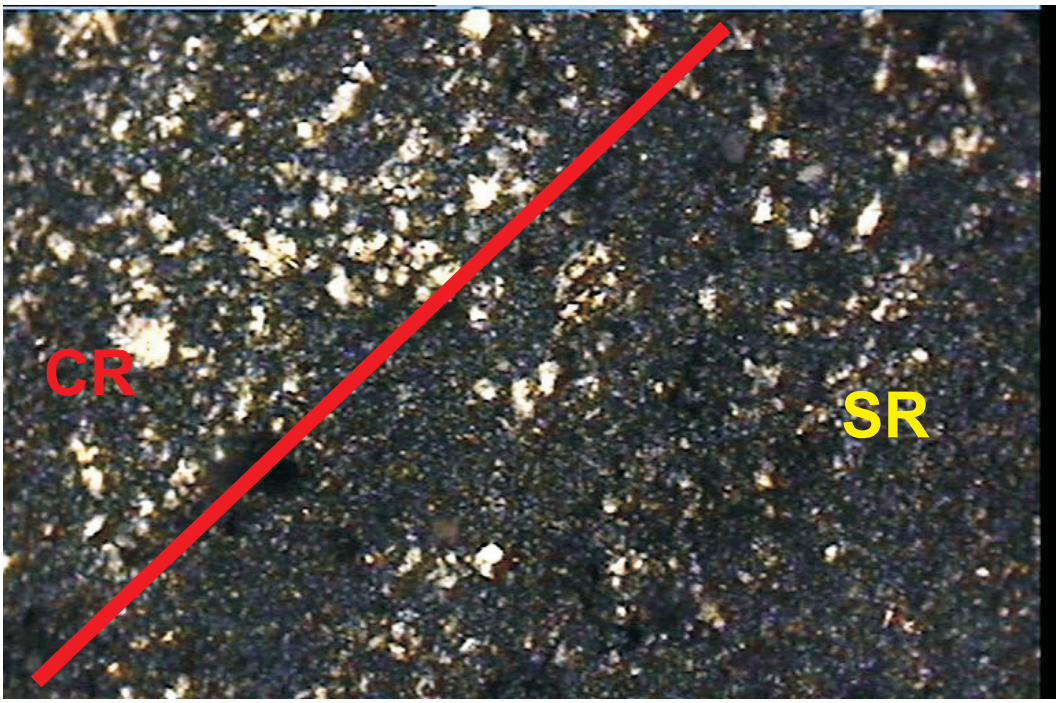


Figure 3.4. Thin section photograph of sample 4
showing clay rich (CR) and silica rich (SR) parts (cross nicol, x10)

Sample 5 is microcrystalline quartz and there are a lot of radiolarian fossils which are replaced with chalcedony and green glacony (Figure 3.5).

Sample 6 is recrystallised microcrystalline quartz including chalcedony formation. (Figure 3.6).

Sample 7 is microcrystalline quartz. Fossils and hematite minerals are observed (Figure 3.7).

Sample 8 is microcrystalline quartz and there are lots of fossils that are replaced with the chalcedony and glauconite which is a green colored hydrous silicate mineral of iron and potassium (Figure 3.8).

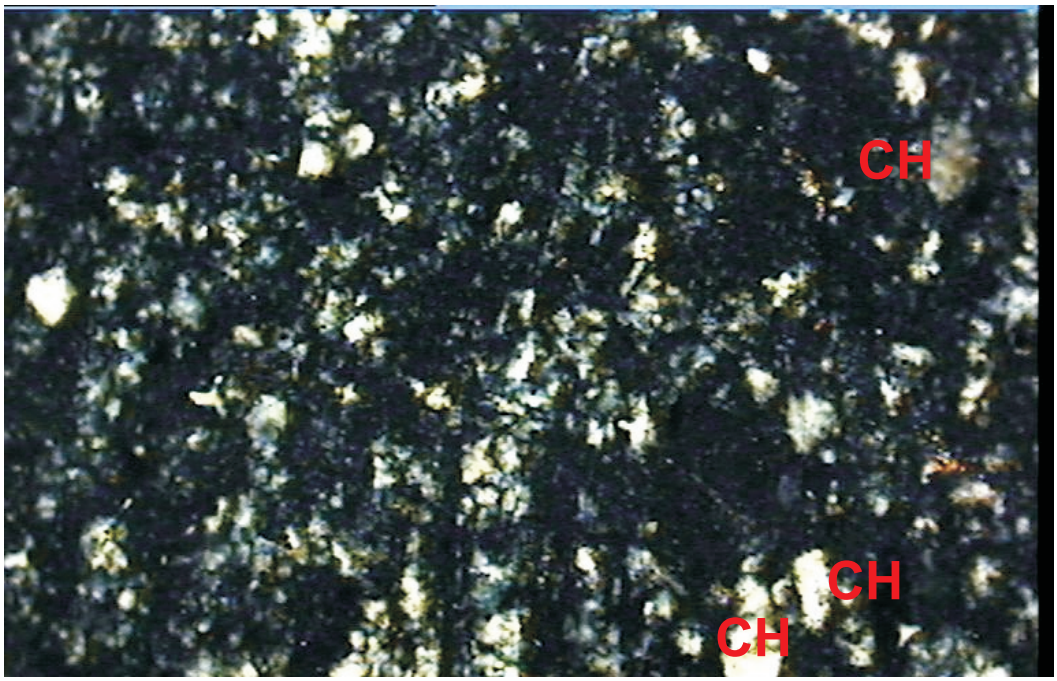


Figure 3.5. Thin section photograph of sample 5
showing microcrystalline chert with radiolarian fossils (cross nicol, x10)

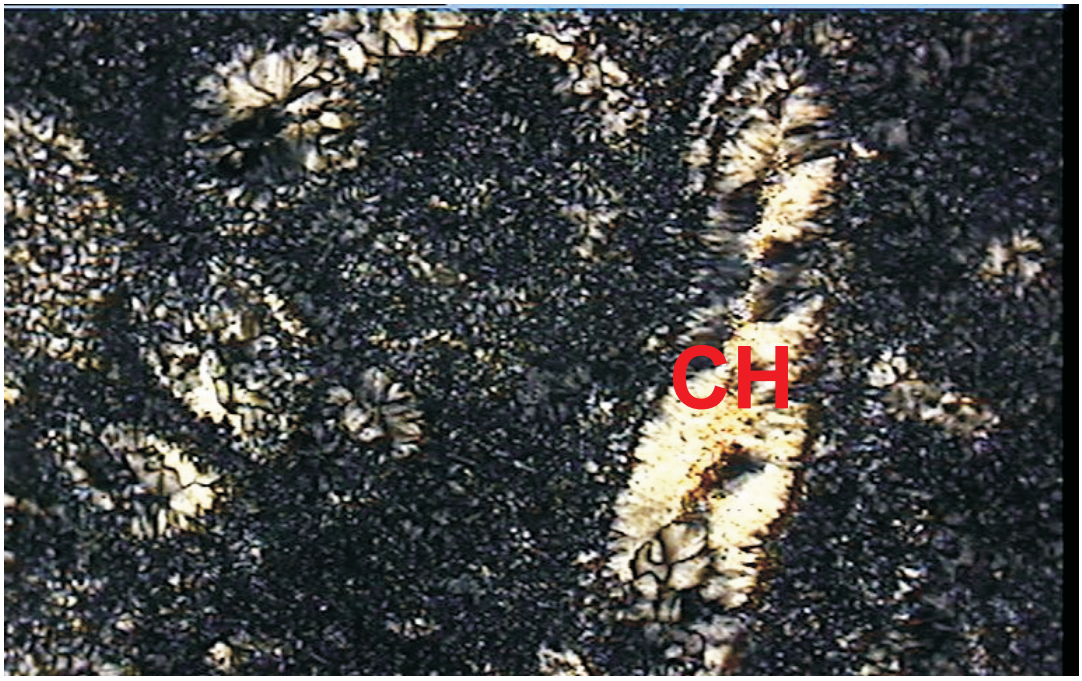


Figure 3.6. Thin section photograph of sample 6
showing recrystallization and chalcedony (CH) formation (cross nicol, x10)

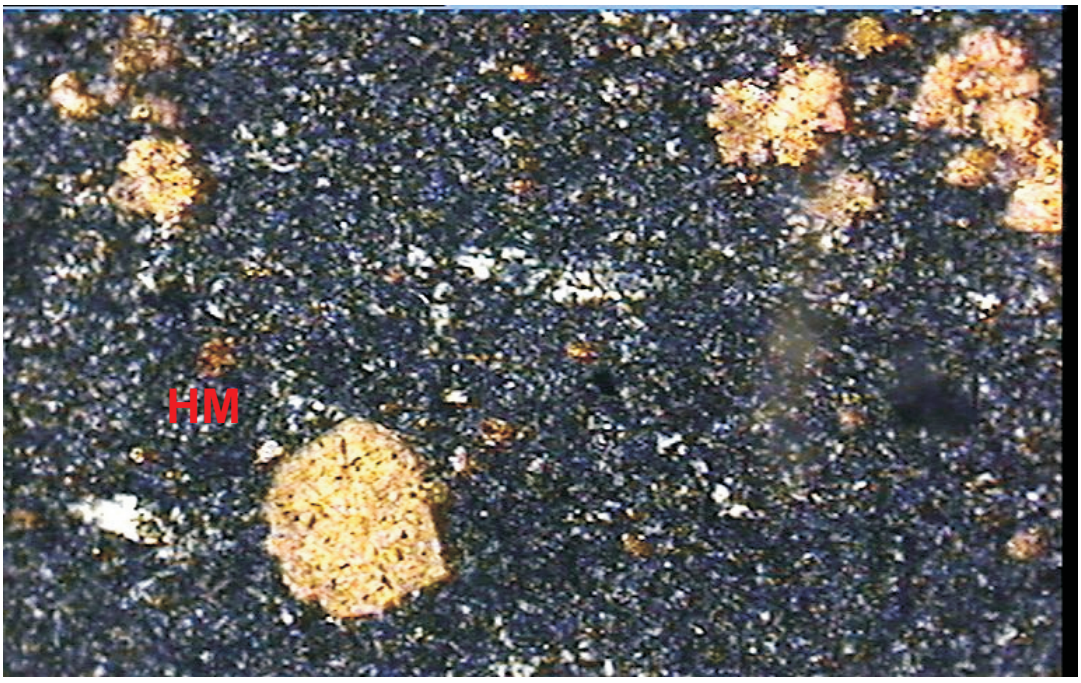


Figure 3.7. Thin section photograph of sample 7 which shows microcrystalline
texture and hematite (HM) formation (cross nicol, x10)

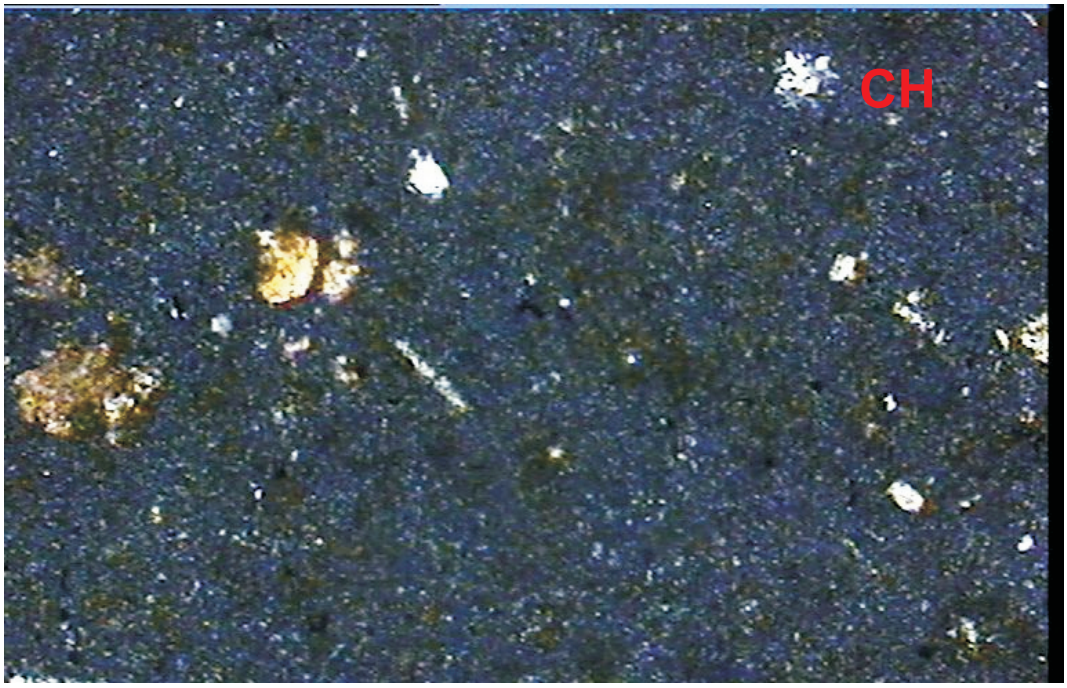


Figure 3.8. Thin section photograph of sample 8
including chalcedony (CH) , fossils and glaconite (cross nicol, x10)

Sample 9 is micritic limestone with vein like sparry calcite , and fossils are observed inside the micro veins (Figure 3.9).

Sample 10 is microcrystalline quartz. There are some micritic calcite observed as clusters. These are fossil remainings and micro fractures present (Figure 3.10).

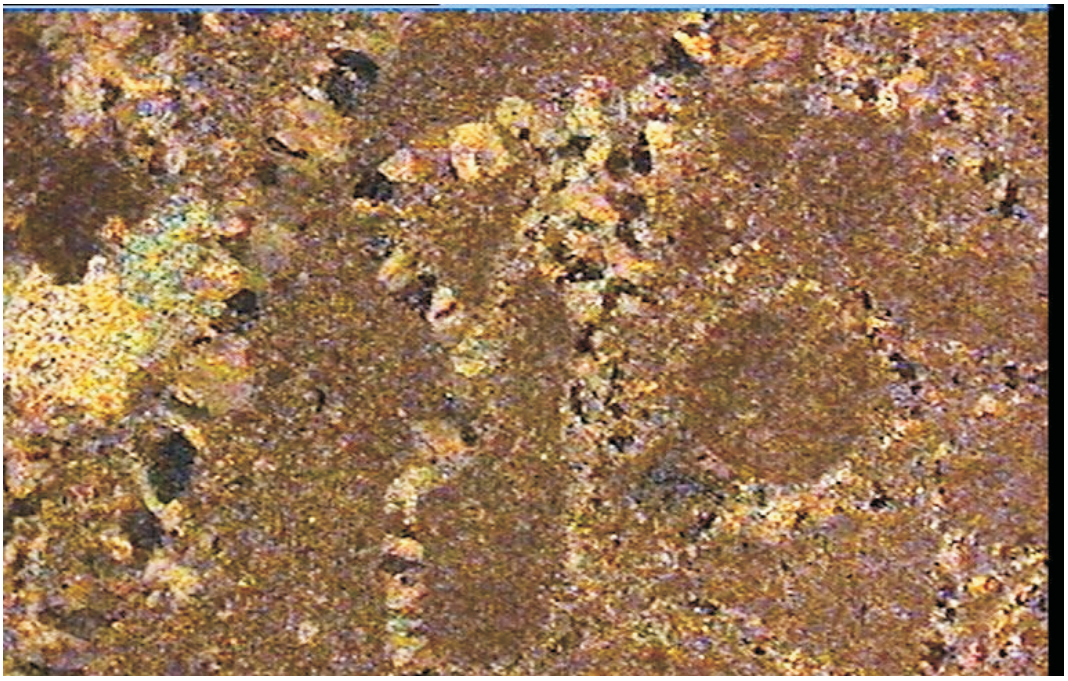


Figure 3.9. Thin section photograph of sample 9
micritic limestone with sparry calcite veins (cross nicol, x4)

Figure 3.10 Thin section photograph of sample 10
with micritic calcite and relict fossil textures. (cross nicol, x4)

3.2 XRD Analysis:

X-ray powder diffraction provides a positive means to identify silica polymorphs and most other rock forming minerals like feldspars and calcite. Quartz, cristobalite, tridymite, and disordered phases exhibit a unique set of XRD maxima. Quartz is easily identified because it yields a characteristic X-ray pattern with abundant intense and well defined peaks.(Table 3.1 and Figure .3.11).

Table 3.1 : Major diffraction peaks of quartz ,tridymite , cristobalite,albite and calcite (Drees et al, 1989) I : Intensity

Quartz		Tridymite		Cristobalite opal c & opal (CT)		Albite		Calcite	
d(Å)	*I*	d(Å)	*I*	d(Å)	*I*	d(Å)	*I*	d(Å)	*I*
0,426	35	0,430	90	0,404	100	0,403	35	38.6	12
0,334	100	0,410	100	0,313	12	0,318	35	3.04	100
0,246	12	0,381	50	0,283	14	0,284	35	2.57	14
0,228	12	0,325	W	0,248	20	0,252	35	2.29	18
0,182	17	0,297	25	0,212	6	----		2.10	16

Well-ordered cristobalite, exhibits a well defined XRD pattern with sharp symetric peaks (Figure 3.11). Opal-CT gives a pattern resembling that of well ordered cristobalite ,except for slight line broadening and minor evidence of tridymite stacking (Jones & Segnit,1971).

Opal-CT usually exhibits broad cristobalite peaks at about 0,41 and 0.25 nm with evidence of tridymite stacking at about 0.43 nm (Figure 3.11). Opal - A has a diffuse X-ray spectrum centered at about 0.41.

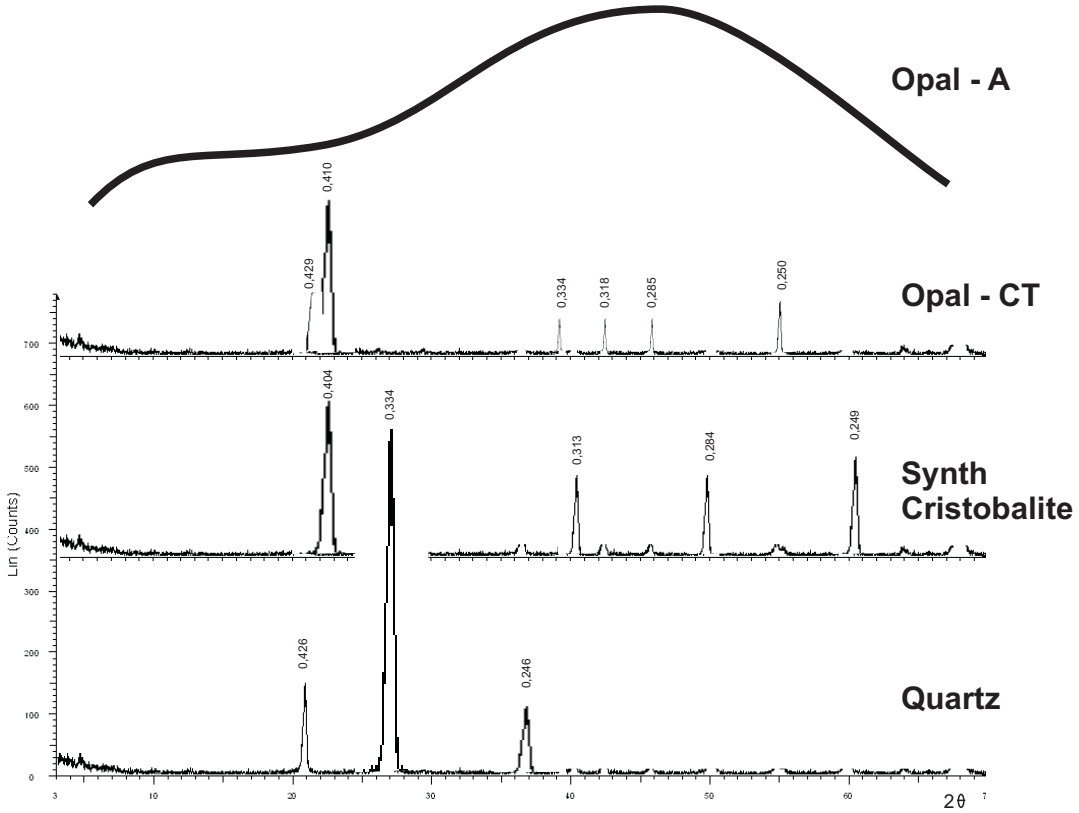


Figure.3.11. Comparison of Xray diffraction spectra of quartz synthetic cristobalite, disordered cristobalite and opal (Drees et al ,1989).

Diffractograms of all samples were obtained and they all resemble to each other and consist of microcrystalline quartz except sample 9 for which calcite is the only mineral .Diffractograms obtained are included in Appendix A , only two of them will be involved in the text. X-ray diffraction of sample 5 provides identification of quartz as seen Figure. 3.12 and Table 3.2 .

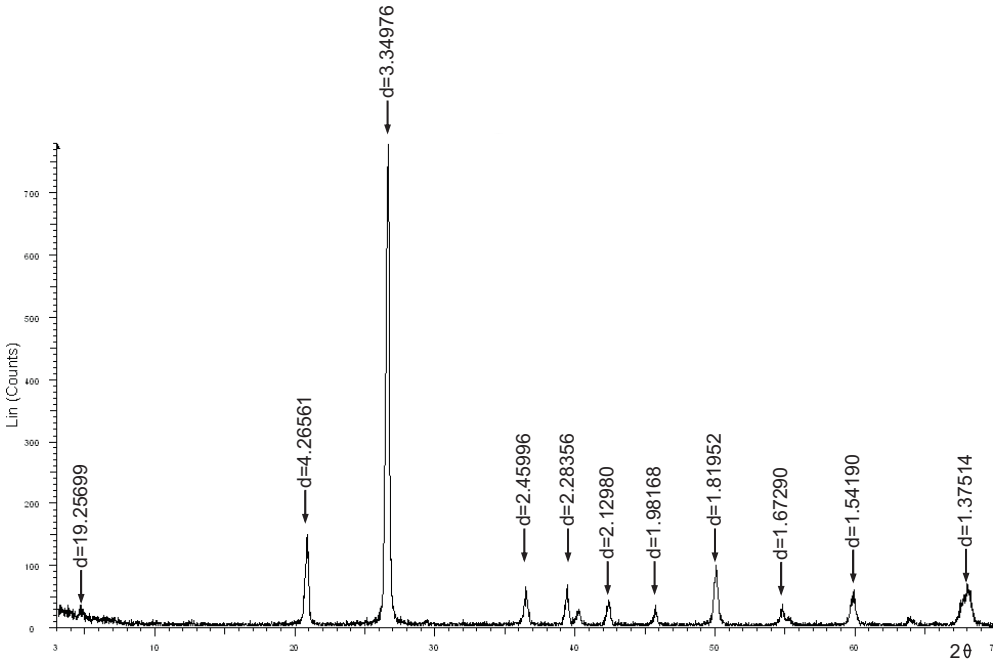


Figure 3.12. X ray diffraction spectra of sample 5 indicating quartz as the only mineral in the sample

Table 3.2 : XRD results of sample 5

Intensity	d-value	angle 2θ
100	3,34976	26,58
17.1	4,26561	20,80
12.6	1,81952	50,09
8.1	1,37514	68,13
7.1	2,28356	39,42
6.6	2,45996	36,49
6.2	1,54190	59.94
4.7	2,12980	42.40
3.6	1,98168	45.74
3.5	1,67290	54.83
2.7	2,24016	40.22
1.5	1,45435	93.96
1.3	1,66129	55.24
1.3	19,25699	4.585
0.6	27,13646	3.253
0.4	1,43890	64.73
0.4	1,43150	65.11
0.4	1,49312	62.11

On the other hand analysis of sample 9 shows that it mainly consists of calcite (Figure 3.13 and Table 3.3).All other samples are chert similar to sample 5.

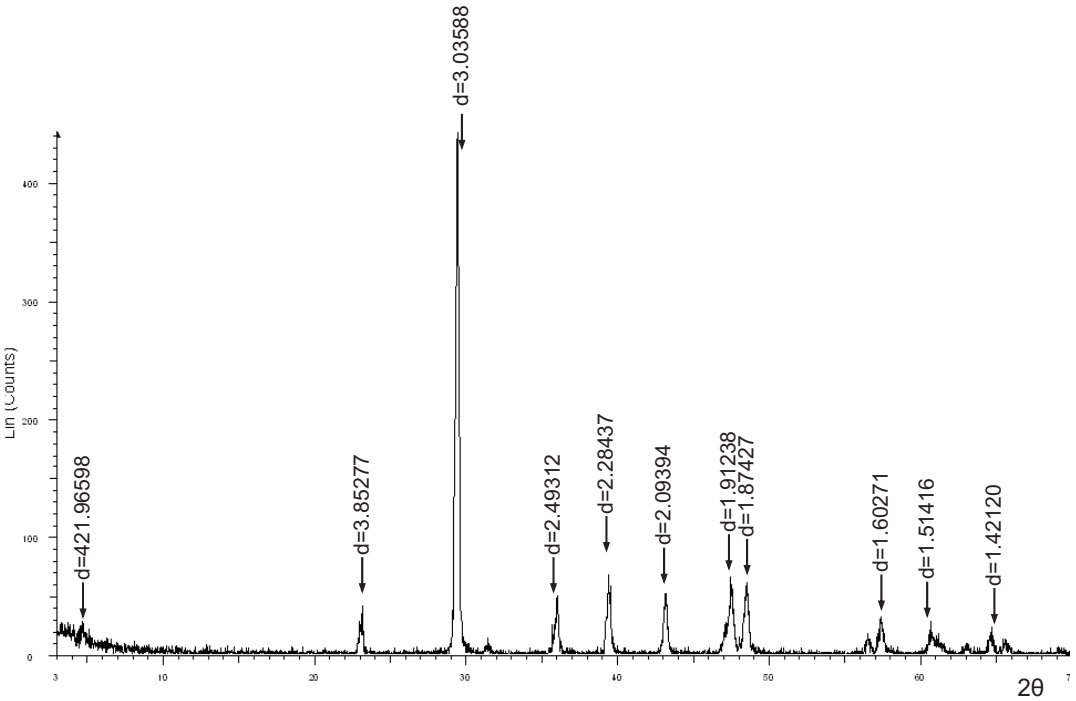


Figure 3.13. X-ray diffraction spectra of sample 9

Table 3.3. XRD results of sample 9

Intensity	d-value	angle 2θ
100	3.03588	29.39
14.2	2.28437	39.41
14.0	1.87427	48.53
13.8	1.91238	47.50
12.5	2.09394	43.16
11.4	2.49312	35.99
7.2	3.85277	23.06
7.1	1.60271	57.45
4.5	1.52377	6073
4.4	1.43938	64.71
4.4	2.98855	29.87
3.4	19.12457	4.617
2.8	1.62584	56.56
2.8	1.51416	61.15
2.7	1.42210	65.64
2.3	1.47074	63.16
2.1	2.84237	31.44
1.8	24.26003	3.693
1.8	1.41477	65.99
1.6	21.96598	4.019
0.8	27.38897	3.223

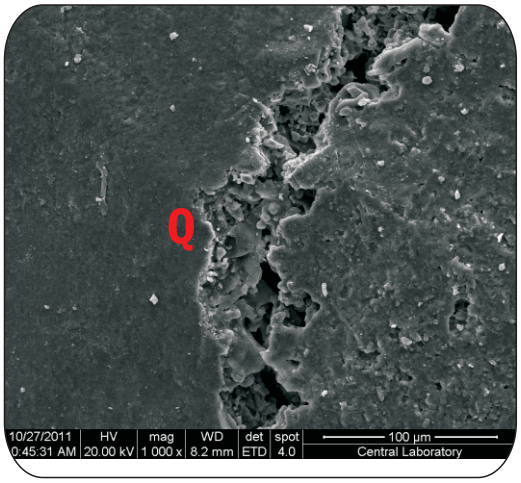
3.3 Scanning Electron Microscopy (SEM-EDX)

Three samples (5,7,9) have been analysed by SEM-EDX. Sample 5 shows specific microcrystalline structure and recrystalliation are present with in pores most probably due to diagenetic effect. (Figure 3.14.A). The shape of crystals appeared to be anhedral with sizes varying between 50-200 nm (Figure 3.14.B).The micro-chemical investigation by EDX presents that the fresh crystals have pure silicon and oxygen content (Figure 3.14.C).

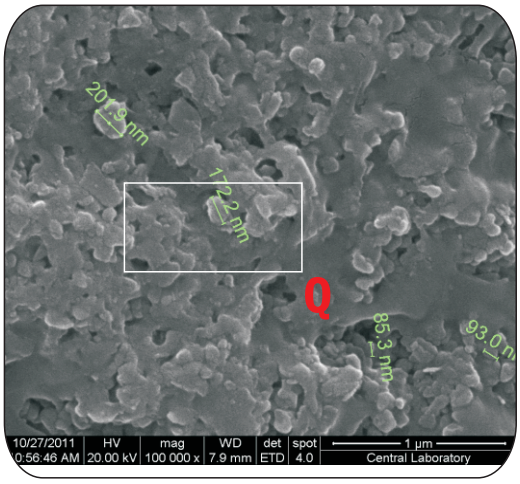
Sample 7 is also recrystallized microcrystalline quartz and fossils remainings are present (Figure 3. 15.A) and (Figure 3.1 5.B).The micro-chemical investigation present fresh crystals have almost pure silicon and oxygen content (Figure 3.15.C). In this sample clay impurities are observed during SEM studies(Figure 3.15.B).

Sample 9 is micritic limestone (Figure 3.16.A and B). Euhedral calcite crystals have larger dimensions in the pores (Figure 3.16.B) .They exhibit mainly prismatic forms.

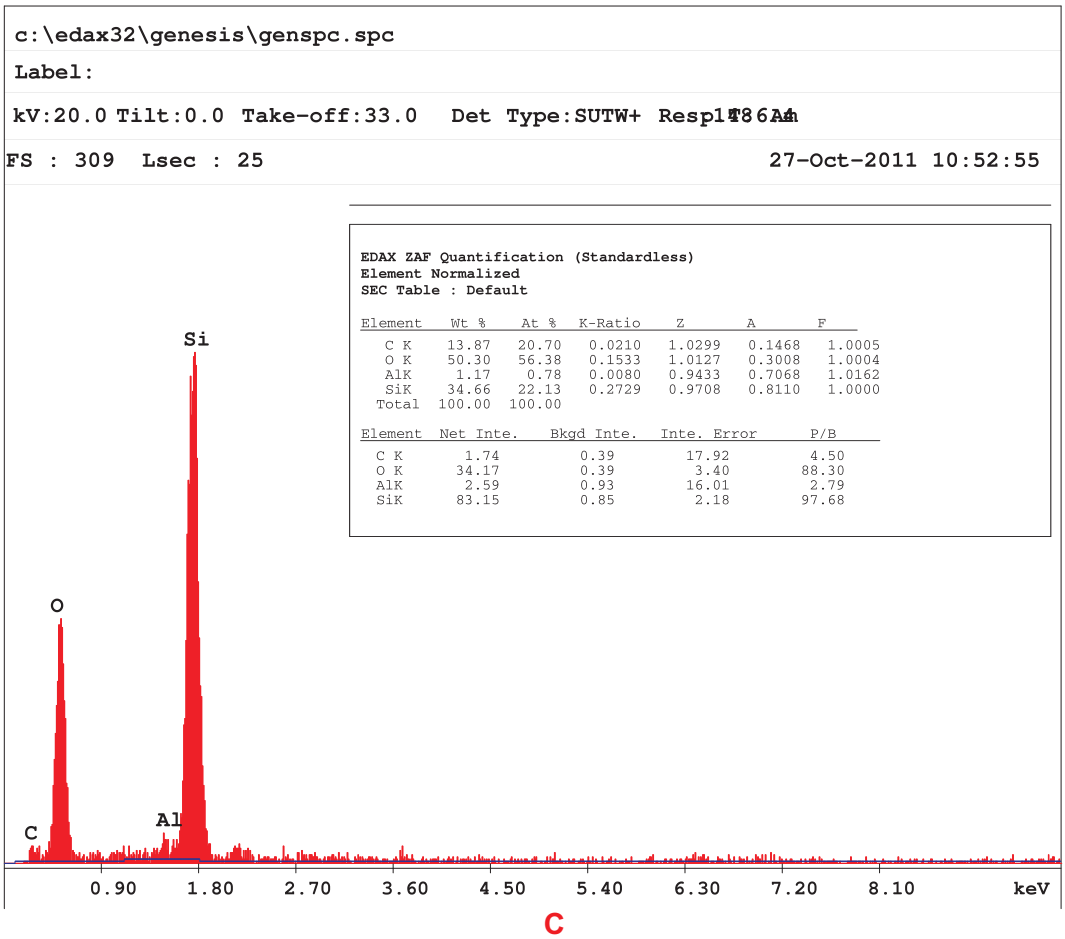
Coarser calcite crystals occuring within the pores and most probably have diagenetic origin due to dissolutions -recrystalliation effect of this process.



A

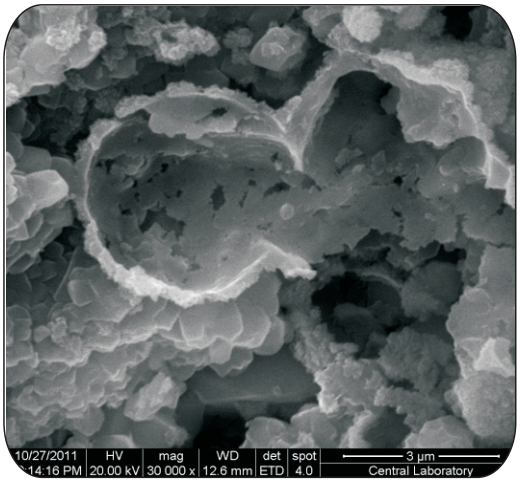


B

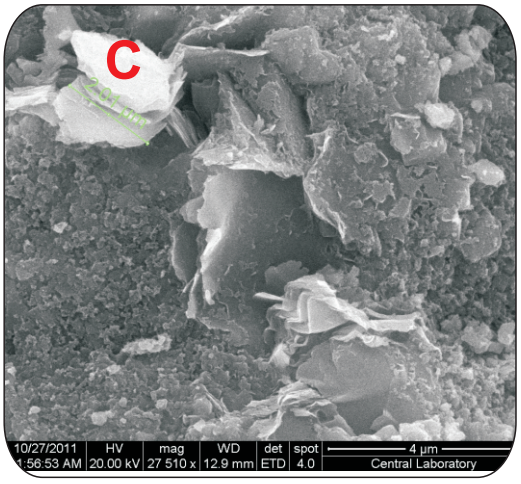


C

Figure 3.14.A) SEM photo micrograph of quartz grain (Q) Sample 5
B) SEM photo micrograph of quartz grain (Q)Sample 5
C) Semi quantitative EDX analysis of the quartz grain from the pore including various sizes of quartz(Q) grains (Figure 3.14.B) of Sample 5)



A



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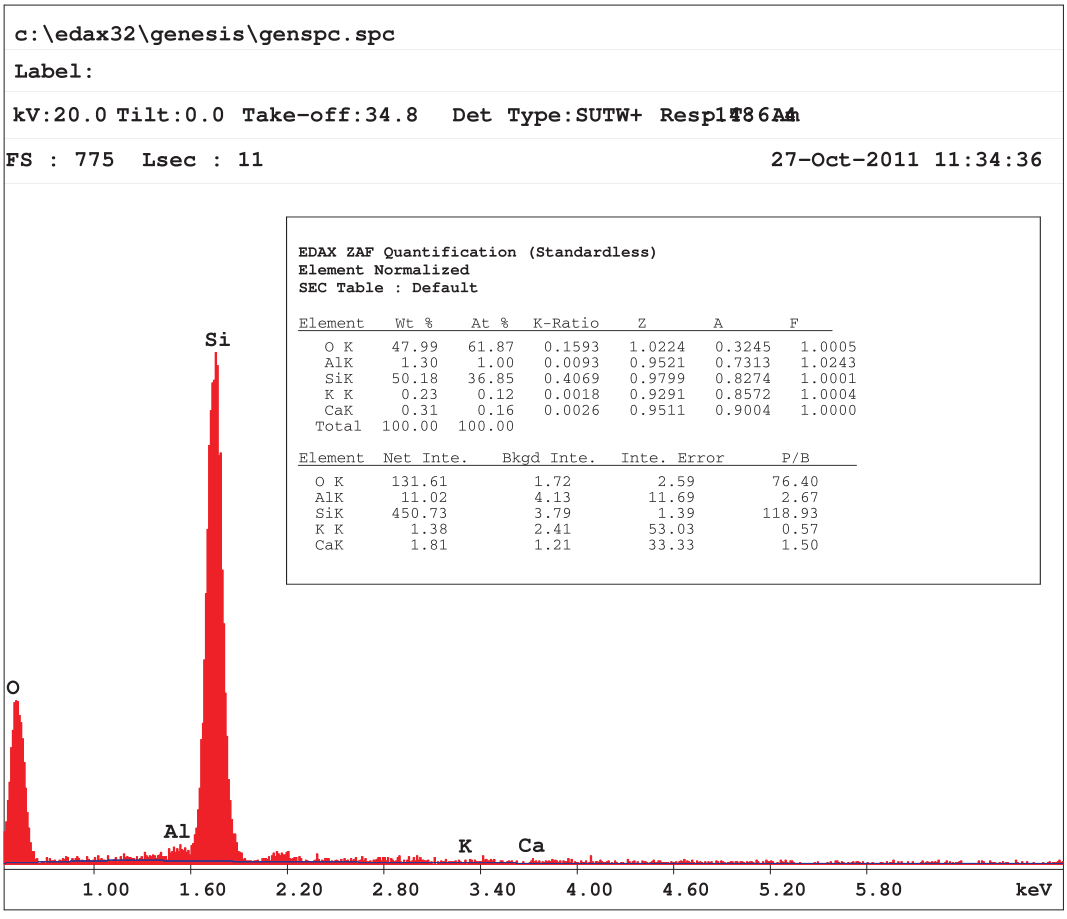
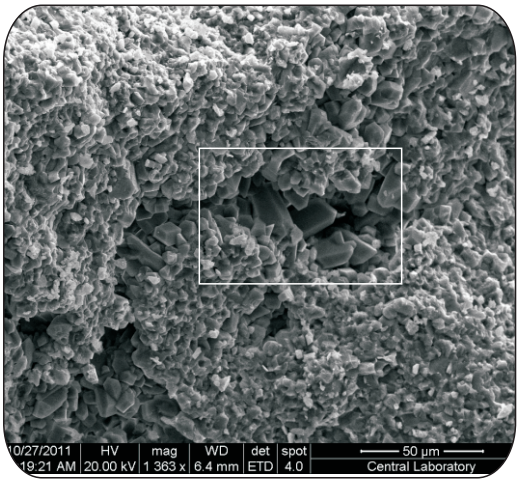
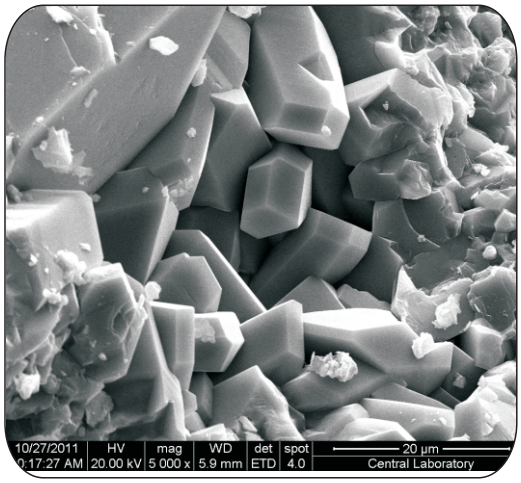


C

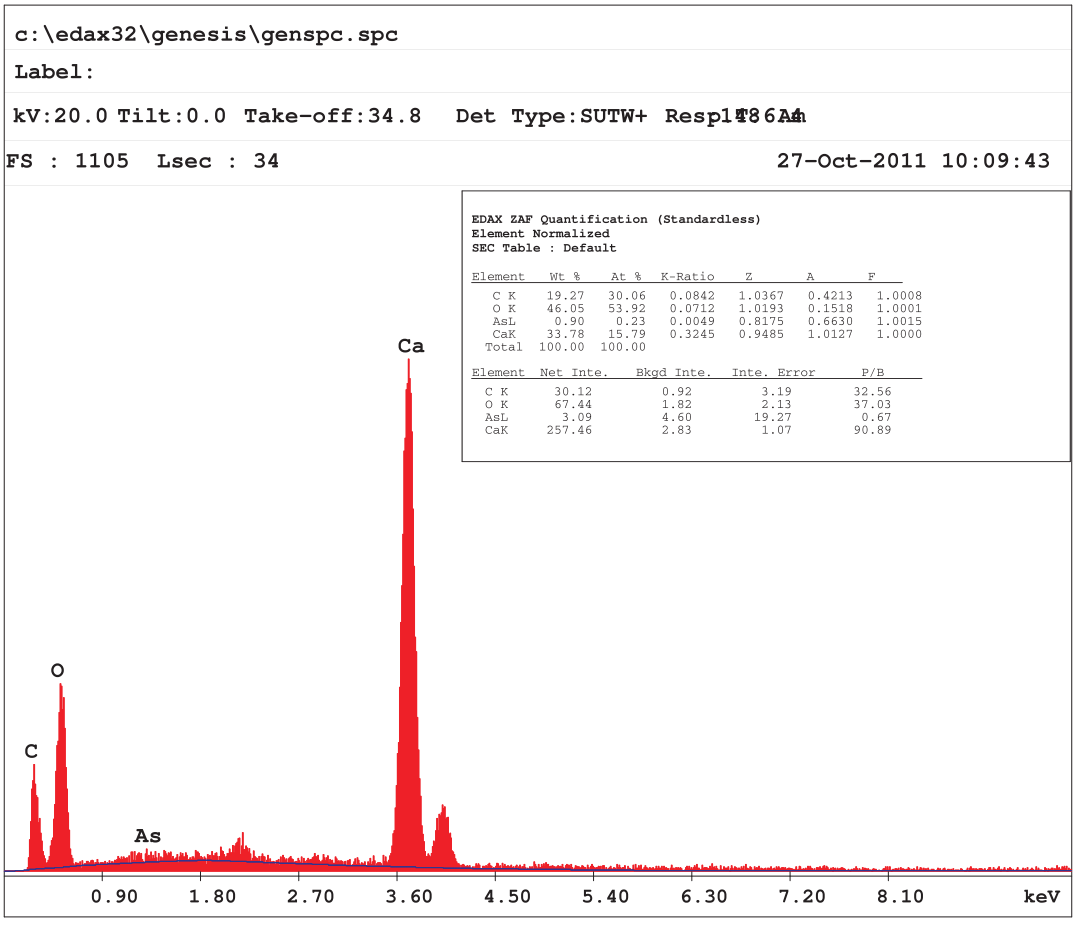
Figure 3.15. A) SEM photo micrograph of chert including a fossil relict structure Sample 7
B) SEM photo micrograph of Sample 7 with clay impurity (C)
C) Semi quantitative EDX analysis of silica in chert
clay mineral flakes which are the impurity in chert
(Figure 3.15.B) of Sample 7)



A



B



C

Figure 3.16. A) SEM micrograph of general view Sample 9
B) SEM micrograph of quartz grain,Sample 9
C) Semi quantitative EDX analysis of quartz grain (Figure 3.16.A) of Sample 9)

3.4 Chemical Analysis (ICP-MS)

Six samples have been examined and ICP-MS data reflect the typical composition of them(Table 3.4).

All chert samples other than sample 9 consist of Si which varies between 23% - 42% .

On the other hand,sample 9 contains %38.6 Ca.The other elements Al ,Fe, Mg,K, and Na, are in the trace quantities.

Ti contents are found to be varying between 47-465 mg/kg.

Table 3.4. ICP-MS results of sample 1,5,6,7,9,10

Sample / Element	1	5	6	7	9	10
Si(%)	42.5 ± 0.4	40.5 ± 0.4	41.7 ± 0.8	41.2 ± 0.4	0.23 ± 0.001	37.2 ± 0.6
Al(%)	0.56 ± 0.01	1.02 ± 0.01	0.203± 0.001	0.591± 0.007	0.077 ± 0.001	0.452 ± 0.003
Fe(%)	0.041 ± 0.001	0.67 ± 0.01	0.997± 0.001	0.100± 0.002	0.068 ± 0.002	0.046 ± 0.001
Mg(%)	0.013 ± 0.001	0.1691± 0.001	0.054± 0.001	0.035± 0.001	0.233 ± 0.001	0.043 ± 0.001
K(%)	0.142 ± 0.002	0.211± 0.001	0.078± 0.002	0.183± 0.004	0.029 ± 0.001	0.131 ± 0.002
Ca(%)	0.124 ± 0.002	0.503 ± 0.003	0.348± 0.003	0.825± 0.003	38.6 ± 0.6	4.87 ± 0.02
Na(%)	0.023 ± 0.001	0.121 ± .001	0.053± 0.001	0.069± 0.002	0.023 ± 0.001	0.029 ± 0.002
Ti(mg/kg)	49.1 ± 1.4	465.3 ± 2.0	125.8± 4.1	128.8± 2.0	47.6 ± 0.3	58.8 ± 1.8

3.5 Thermal Analysis:

The crystalline silica polymorphs (quartz ,tyridmite , cristobalite,opal) show low-high temperature inversions related to structural linkage as shown in (Figure 3.17)(Mitchell, 1975).

In theory, at normal pressure trigonal quartz (α-quartz) will transform into hexagonal β-quartz at 573°C, upon further heating the SiO_2 will transform into hexagonal β-tridymite at 847°C and later to cubic β-cristobalite at 1470°C. At 1700°C β-cristobalite finally melts(Table 3.5).

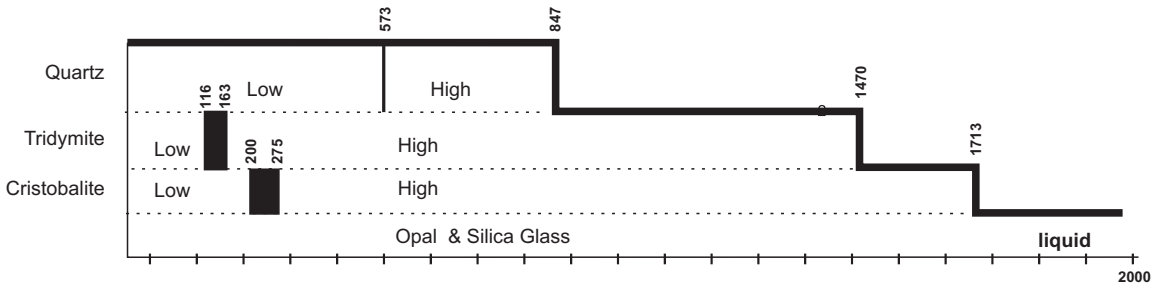


Figure 3.17. Relationship between the silica polymorphs with temperature (Dress et al, 1989)

All quartz undergoes the low-high inversion between 572 and 574°C.Quartz generally exhibits a sharp endothermic DTA peak near 573°C (Figure 3.17)

Well ordered synthetic cristobalite has a characteristic endothermic DTA peak at about 260°C resulting from the conversion of low to high cristobalite (Fig.3.17)

The inversion temperature ranges from 200 °C to 275 °C Opal CT yields a fairly flat DTA pattern with no characteristic endotherm below 600 °C (Fig.3.18).

When heated to higher temperatures , Opal- CT can recrystallize to well ordered cristobalite at about 1100 °C (J.B. Jones & Segnit , 1971)

Thermal responses do not provide diagnostic criteria for opal identification (Figure 3.18).

A comparison of DTA curves of quartz ,synthetic cristobalite, disordered cristobalite (opal -CT) and opal is given (Figure 3.18).

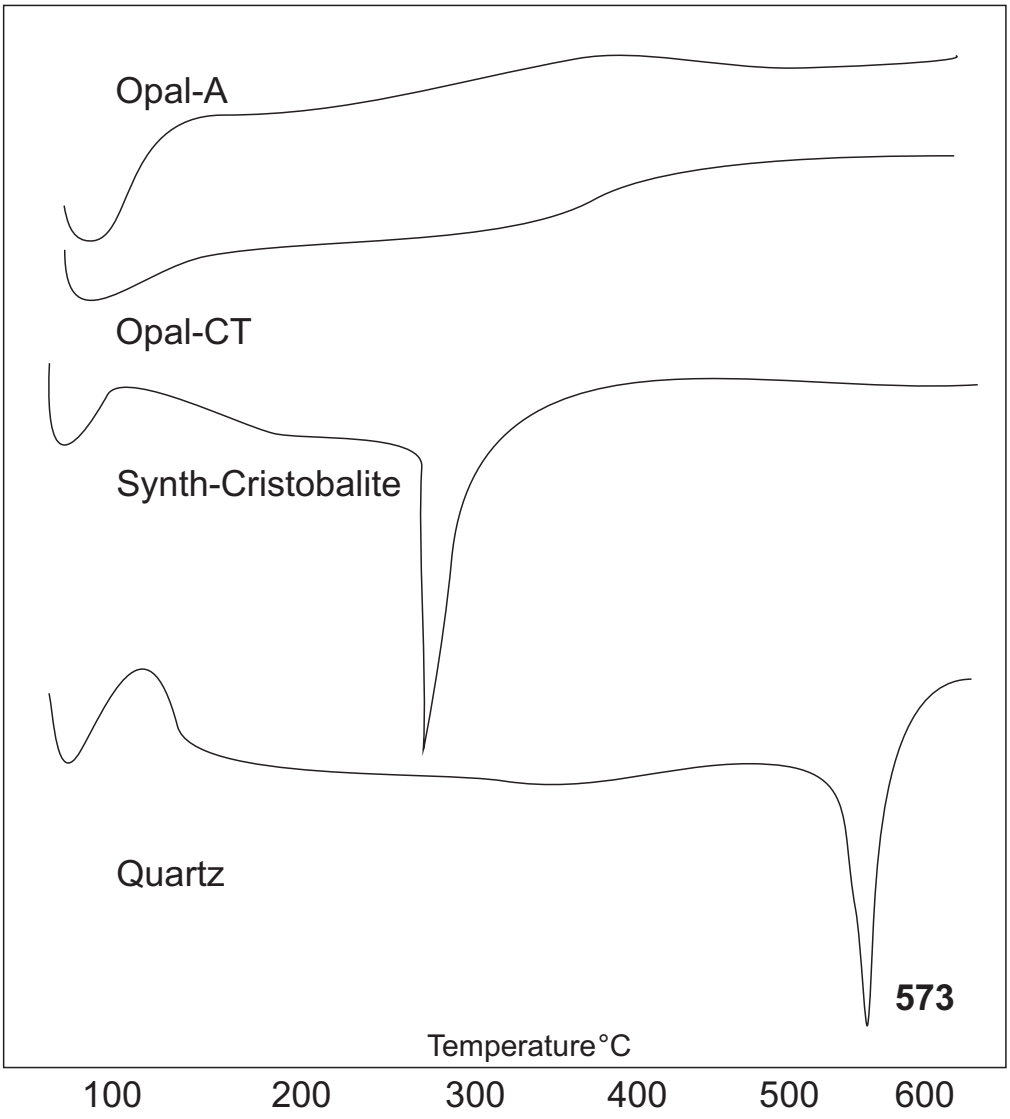


Figure 3.18 Relationship between the silica polymorphs with temperature (Drees et al , 1989)

6 samples (1,5,6,7,9,10) were analysed by means of DTA between 25°C -900°C and heating rate of 12 °C / minute. 5 samples slightly underwent the low-high inversion between 572°C and 574°C. Using this DTA thermographs our samples were identified as quartz. DTA curve of sample 5 is given (Figure 3.19) and others are given in Apeendix B.

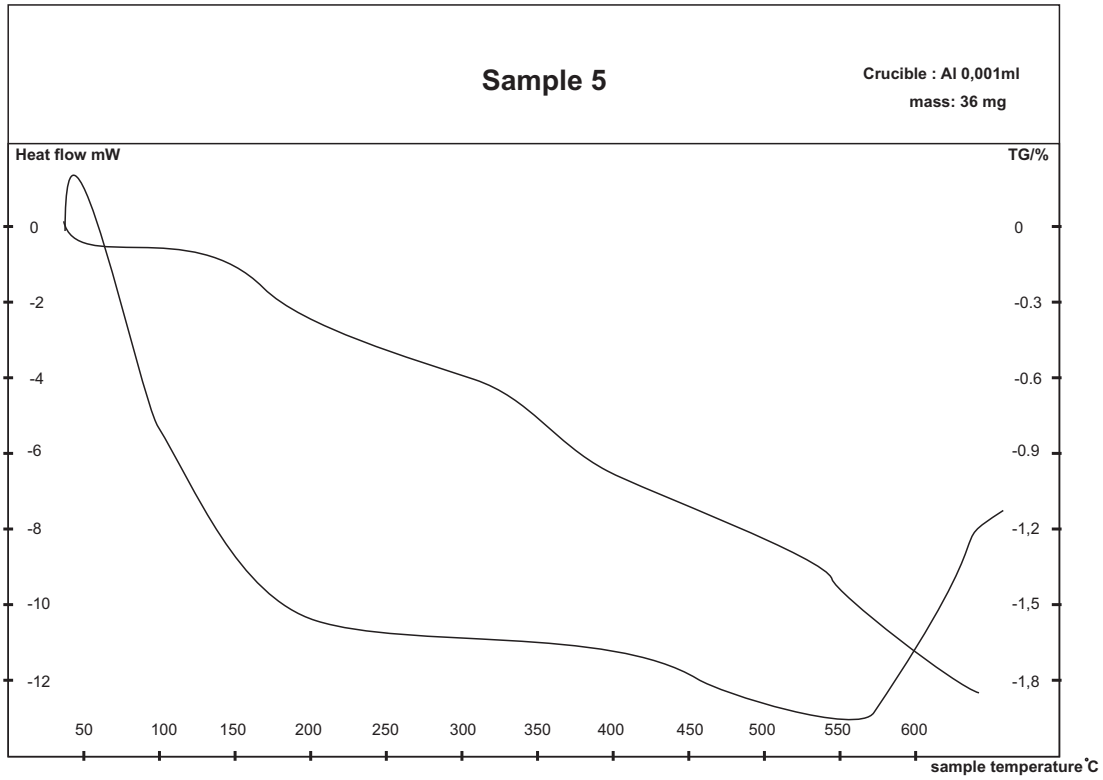


Figure 3.19. Thermal Analysis of Sample 5

Thermal analyses data showed that silica polymorphs in the sample transforms low to high quartz with specific point around 570°C. This provide us to identify that our chert samples are mainly consist of α - quartz.

During the diagenesis the paragenetic sequence of silica polymorphs proceeds from Opal A to micro crystalline opal - CT , and then with increasing depth of formations microcrystalline quartz forms. The latter has morphologically fibrous quartz varieties also. The standart chert sample seem to transform the latest variety of polymorphs,quartz according to data collected by means of XRD and DTA analyses.

Thermal analysis of sample 9 which is microcrystalline limestone exhibits an endothermic peak near 860 °C . This peak indicates that carbonate mineral is calcite.

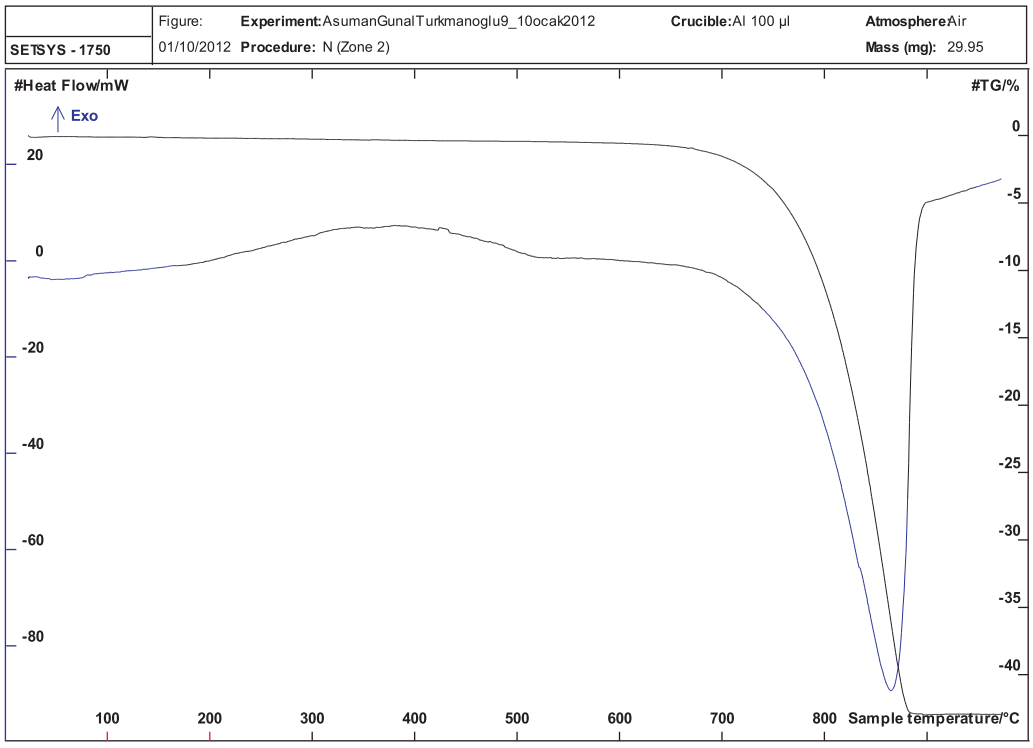


Figure 3.20. Thermal Analysis of Sample 9

CHAPTER 4

CONCLUSION

In this study ten stone artifacts which are collected from the Karain Cave in Antalya are examined archeometrically,for the first time, in order to determine their mineralogical petrographical and chemical properties.The following conclusions are obtained based on the thin -section, XRD,SEM-EDX,DTA and ICP-MS analysis .

1.All of the samples except sample 9 are composed of microcrystalline quartz chert.Sample 9 ismicritic limestone.

2.Chert samples are mainly consist of microcrstalline quartz, and may contain radiolarian fossils.

3.Sample 9 is composed of micritic calcite and partly sparry calcite as the major mineralogical component.

4. ICP-MS and XRD data reflect the typical composition of samples with an average of 40.6 % Si as average value.and also a major XRD peak at 3.34 Å Sample 9 is an petrographically as exceptional sample as also indicated by 38.6% Ca and 3.03 Å XRD peak which correspond to calcite ($CaCO_3$).

5.In thin section chert samples show quite similar textures. They also exhibit similar chemical compositious. Although the provenance analysis is out of the scope of this thesis based on this similarity of chert samples a preliminary conclusion can be made so that these artifact samples may have the same raw material source. On the contrary, sample 9 might be coming from another locality.

6. Samples exhibit some effects of diegenesis such as dissolution recrystallization of silica (chalcedony formation) and carbonate (sparry calcite formation) phases. Presence of microcrystalline alpha quartz of the silica polymorph forming chert mineralogy may indicate that the geological formations from which these chert samples were collected had undergone deeper diagenetic transformations.

Further studies can be suggested as follows: A precise provenancing of raw material such as chert and limestone should be carried on by means of detailed archeological, geological and archeometrical studies.

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APPENDIX A

XRD SPECTRUMS

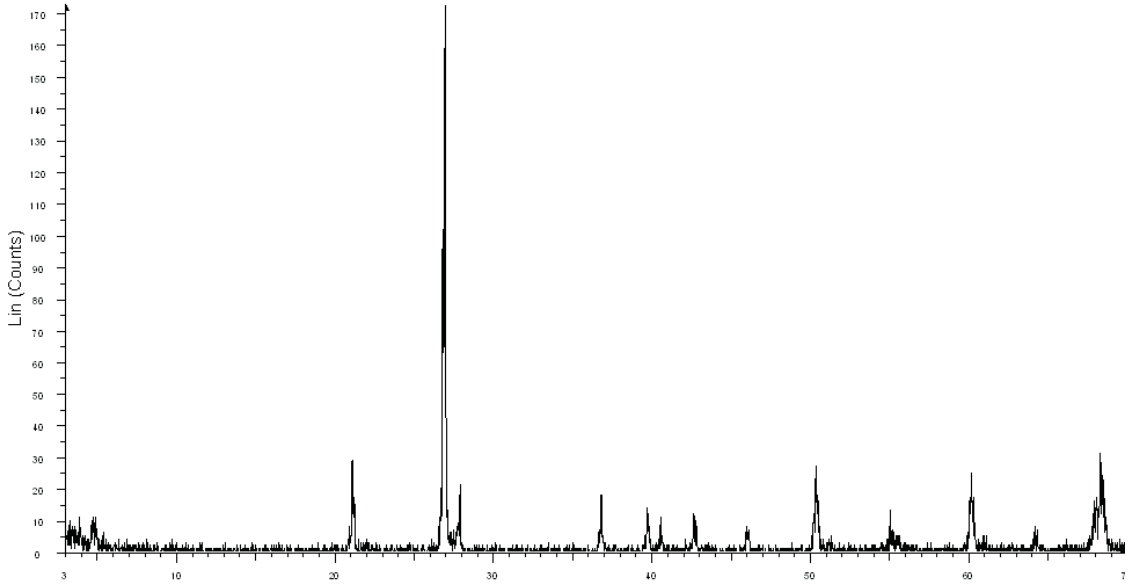

Figure A.1. X ray diffraction spectra of sample 1

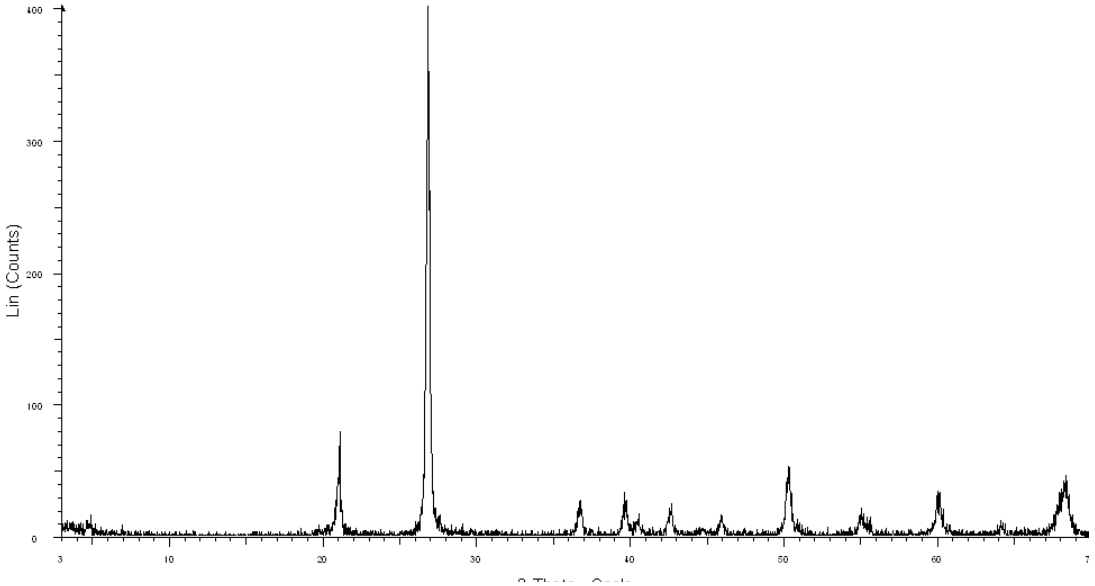

Figure A.2. X ray diffraction spectra of sample 6

Table A.1 Xrd results of sample 6

Intensity	d-value Å	angle 2θ
100	3.32301	26.807
14.4	4.22113	21.029
13.9	1.81202	50.315
10.1	1.37037	68.384
6.6	1.53835	60.097
5.7	2.11800	42.654
5.6	2.44520	36.725
4.1	3.32034	27.592
3.8	1.66785	55.013
3.8	1.97337	45.952
3.4	2.22455	40.519
2.8	1.44847	64.255
2.5	1.79099	50.947
2.3	1.65261	55.564
2.1	2.10096	43.017
1.5	18.45835	4.784
1.3	25.00625	3.530
1.0	1.52106	60.852

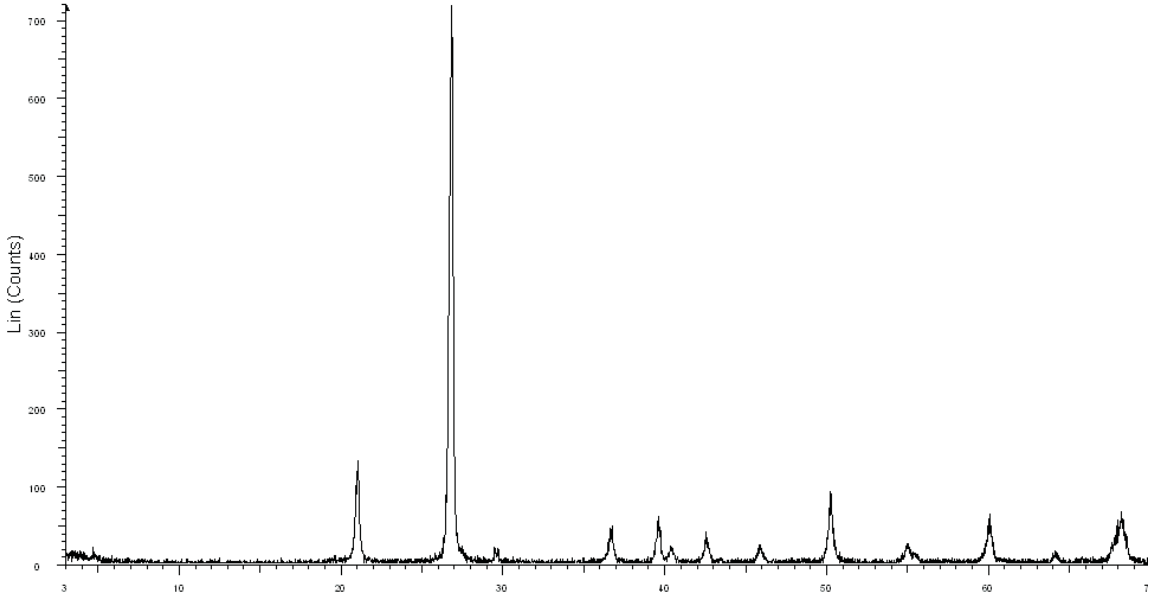

Figure A.3. X ray diffraction spectra of sample 7

Table A.2 Xrd results of sample 7

Intensity	d-value Å	angle 2θ
100	3.32533	26.788
17.3	4.22934	20.988
12.7	1.81309	50.283
8.4	1.37208	68.307
7.5	2.27339	39.612
7.3	1.53781	60.120
5.6	2.44705	39.969
4.7	2.12167	42.577
3.2	1.66737	55.030
2.6	1.97460	45.922
2.6	1.36588	68.660
2.4	2.22934	40.428
2.1	1.65559	55.456
1.8	3.02269	29.528
1.8	1.45022	64.168
1.6	18.68517	4.275
1.3	1.79278	50.893
0.7	1.35879	69.069

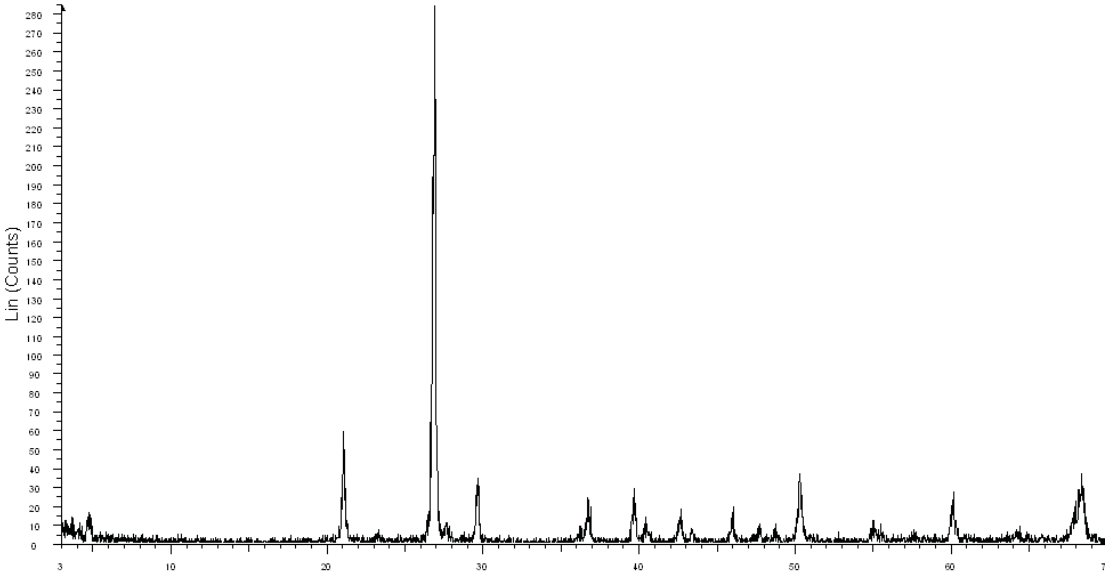

Figure A.4. X ray diffraction spectra of sample 10

Table A.3. Xrd results of sample 10

Intensity	d-value °A	angle 2θ
100	3.31900	26.840
15.8	4.22028	21.034
13.0	1.81130	50.336
11.5	3.01309	29.624
11.1	1.37032	68.407
8.4	1.53657	60.174
8.2	2.26954	39.682
7.3	2.44476	36.732
5.6	1.37952	67.894
4.5	1.97165	45.995
4.5	2.11773	42.660
3.9	18.96474	4.656
3.6	2.23028	40.410
3.3	3.23024	27.592
3.0	1.90341	47.744
2.9	1.86752	48.721
2.8	1.65261	55.564
2.6	1.66583	55.086
2.5	2.08343	43.398
2.1	1.44847	64.255
2.0	1.43336	65.015

APPENDIX B

DTA SPECTRUMS

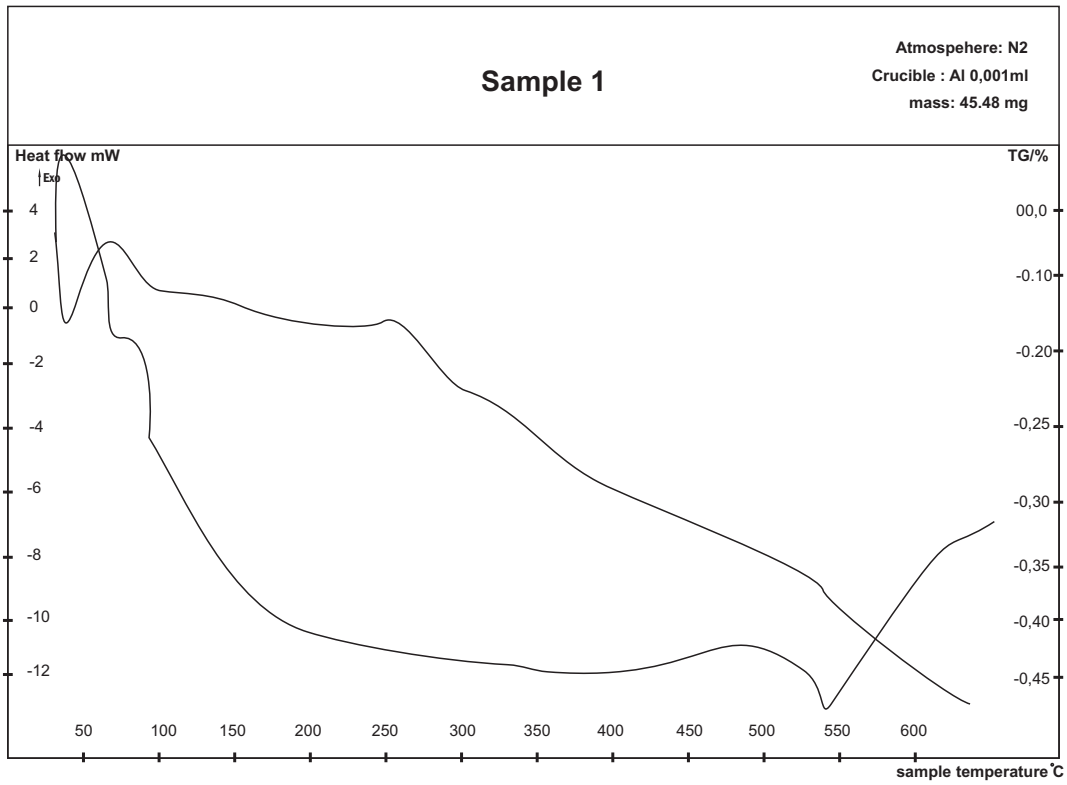

Figure B.1.Thermal Analysis Diagram of Sample 1

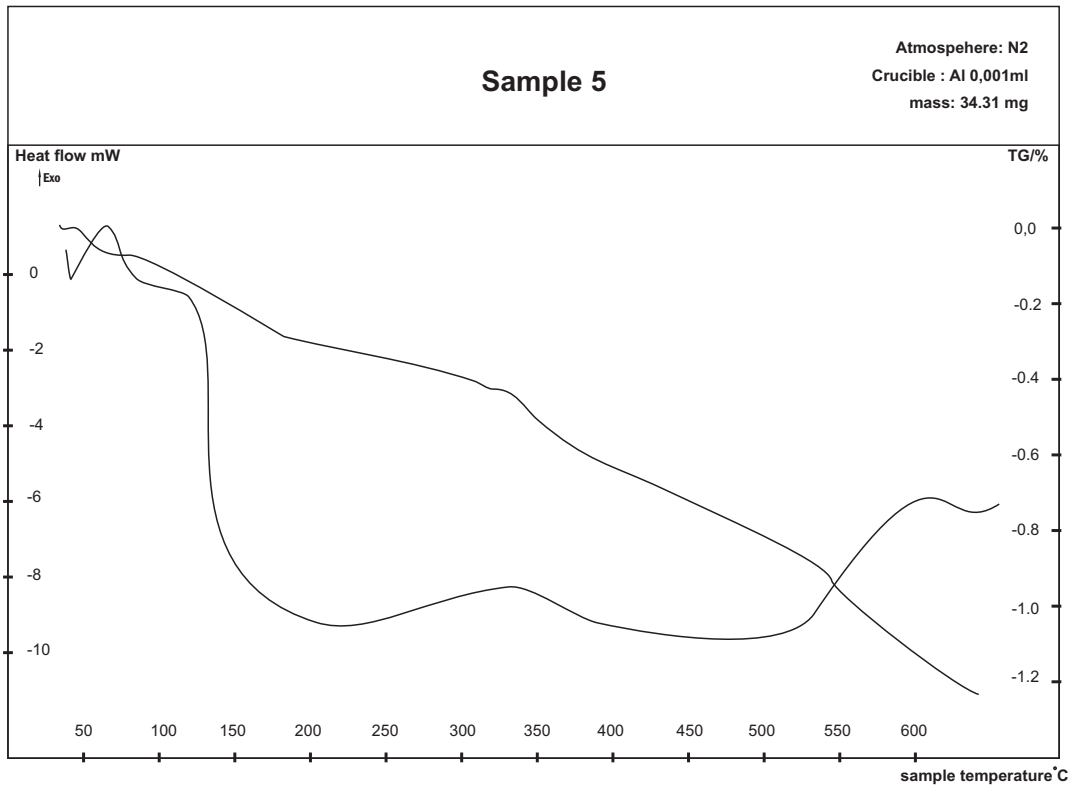

Figure B.2. Thermal Analysis Diagram of Sample 5

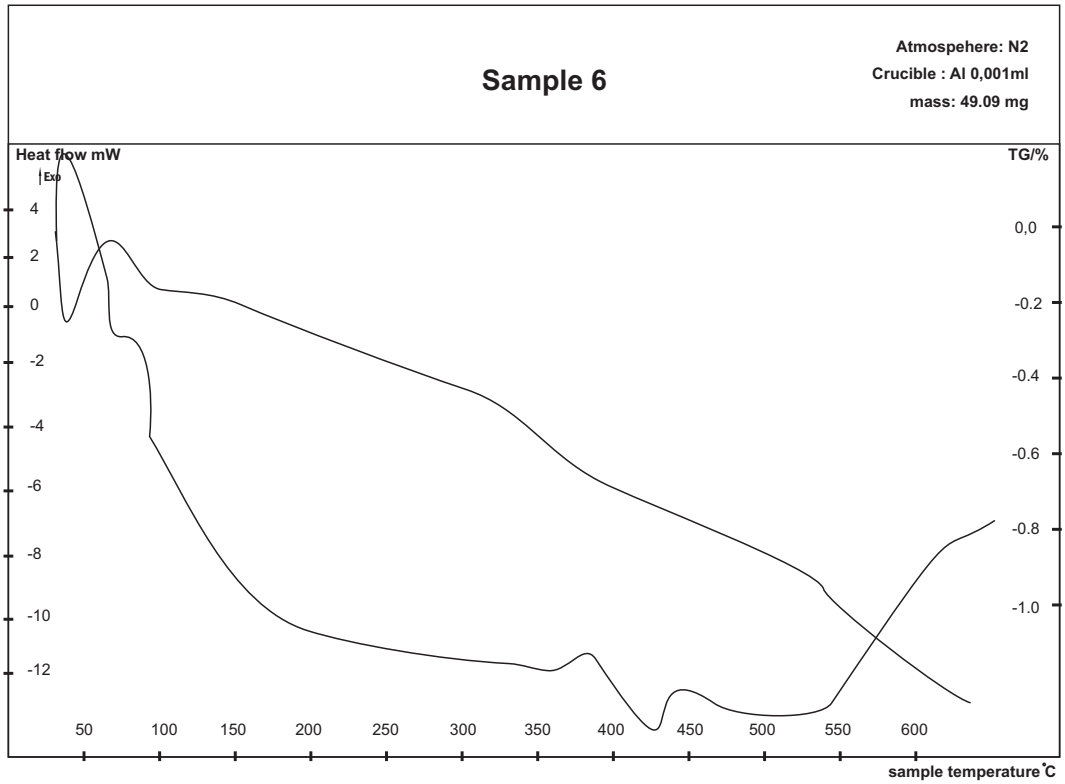

Figure B.3.Thermal Analysis Diagram of Sample 6

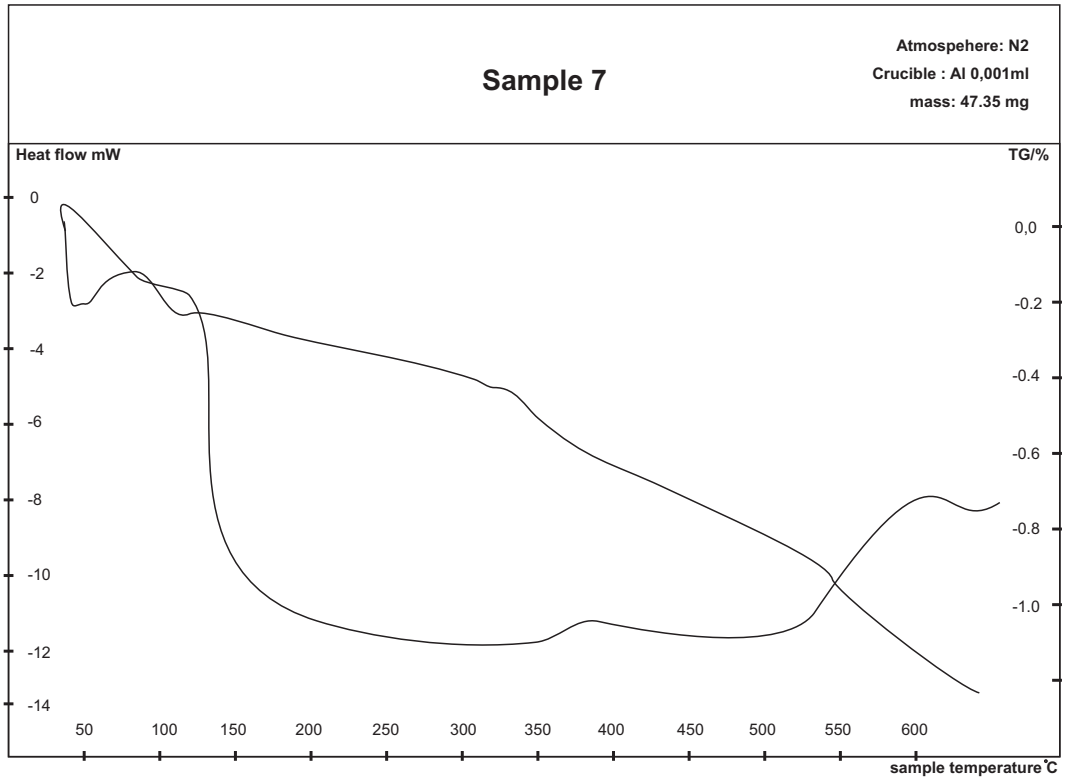

Figure B.4. Thermal Analysis Diagram of Sample 7

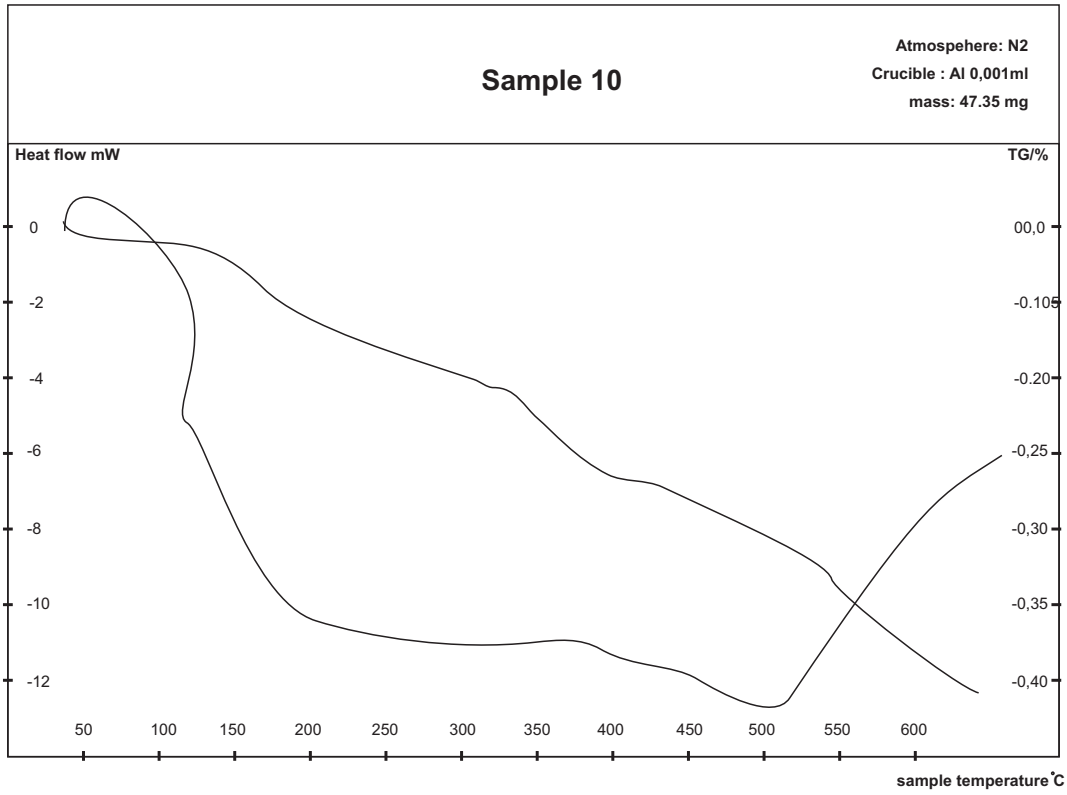

Figure B.5.Thermal Analysis Diagram of Sample 10