The Classification, Genesis, and Structural Characteristics of the Ankara Agates of Igneous Origin in Turkey

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ABSTRACT

The name agate is derived from the river called “Achates” in Sicily. The cutting of agate as an ornament goes to the date back to 4000 BC in Anatolia and 2000 BC in Mesopotamia.

Although the agates and their occurrences have been known for thousands of years, essential hypothesise about agate origins have only proposed for the last two centuries.

The area where the agates are largely obtained in Anatolia is placed in the northern part of the town “Çubuk” in Ankara. In the geologically investigated area, there are generally metamorphic, sedimentary, volcanic and alluvial cover units available, formed in different geological ages. Ankara agates have been found in the “volcanic sequence” of Miocene aged.

The agates found in this area mainly appear in two types of country rocks: 1) Andesite (basalt), 2) rhyolite. The agates in the andesites were deposited as open-space fillings in crevice- and fissure-vein cavities. Their settling positions are stratiform, but not nodular. They have the barred inclusions as solid chalcedony and quartz pseudomorphs, and concentric bands, but not Uruguay-bands. These agates are individual and first called “barred agates”. The agates in the rhyolites were deposited as cavity fillings in regular or irregular vesicles. Their settling positions are nodular. Most of them have sagenitic or moss-like inclusions with tubiform structures, and both concentric and Uruguay-bands. These agates are called “moss-agates”.

The macroscopic, petrographic and electron optical morphologies of the bands in the agates are dissimilar. The main process which reveals the formation of the concentric banding is the development of radial fibrous texture. The fibrous texture is often represented by the spherulites under the polarizing microscope, but electron optical examination shows that the fibres are not single quartz crystals because they were formed from the infinitesimal silica particles and were consummately contorted. The Uruguay-banding in the agates is a result of the precipitation of relatively coarse silica grains as horizontal layers by gravitation.

The most plausible assumption as the medium in agate formation is the colloidal silica system in the presence of hydrothermal circulation under lower P-T conditions.

The individual inclusions in the barred agates found in the fissure zone of andesites are doubtless of replacement origin, and these crystalline inclusions were originally of the mineral zeolite (scolecite). The tubiform inclusions in the agates found in the cavities of rhyolites are particular origin. Moss-like or sagenitic growths were formed from silica-gel including alkali-silicate. In the Ankara agates, whereas these silicate growths could be formed alone, they could also be developed around the replaced zeolite bars.

ÖZET

Agat ismi Sicilya'daki "Achates" nehrinden türetilir. Süsleme amacıyla agatın işlenmesi, Anadolu' da M.Ö. 4000 ve Mezopotamya'da ise M.Ö. 2000 yıllarına kadar uzanır.

Agat ve türleri binlerce yıldır bilinmesine rağmen, agatların oluşum kökenine ilişkin önemli hipotezler sadece son iki yüzyıldır ortaya atılmıştır.

Anadolu'da agatların bolca bulunduğu alan Ankara ilinin, Çubuk ilçesinin kuzeyinde yer alır. Jeolojik incelemesi yapılan bu bölgede, genellikle metamorfik, tortul, volkanik ve alüvyon örtü birimleri bulunur. Bu birimler farklı jeolojik zamanlarda oluşmuştur. Ankara agatları Miyosen yaşlı " volkanik seri" içerisinde bulunmuştur.

Bu bölgedeki agatlar başlıca iki tip çevre kayası içerisinde gözlenir: 1) Andesit (bazalt), 2) riyolit. Andezitler içerisindeki agatlar, yarık ve çatlak damar boşlukları içerisinde, açık boşluk dolguları olarak yataklanmışlardır. Bunların yerleşme pozisyonu, yumrusal olmayıp katmansıdır. Bu agatlar, kalsedon ve kuvars psödomorfları olarak çubuklu kapanımlar ve konsantrik bandlar içerirler, ancak yatay tabakalı (Uruguay) bandlarına sahip değildirler. Bu agatlar özel olarak ve ilk defa "çubuklu agatlar" olarak adlandırılmışlardır. Riyolitler içerisindeki agatlar ise, düzenli ya da düzensiz gözenekler içerisinde boşluk dolguları olarak yataklanmışlardır. Yerleşme pozisyonları, yumrusaldır. Birçoğu, borumsu yapılarda çalı yada yosun benzeri kapanımlara ve hem konsantrik hem de Uruguay bandlarına sahiptir. Bu agatlar da, "mos-agat" olarak adlandırılmışlardır.

Agatlar içerisindeki makroskopik, petrografik ve elektron optiksel morfolojiler birbirine benzemez. Konsantrik bandların oluşumunu ortaya çıkartan ana işlem ışınsal, lifsi dokunun gelişmesidir. Lifsi doku genelde polarizan mikroskopu altında küreciklenme ile temsil

edilir. Ancak elektron mikroskobik incelemeler, liflerin tek kuvars kristalleri olmadığını göstermiştir. Çünkü bunlar çok küçük silis parçacıklarından meydana gelmişlerdir ve bükülmüşlerdir. Agatlar içerisindeki Uruguay bandları ise göreceli olarak daha iri silis tanelerinin, yer çekiminin etkisiyle yatay olarak çökeliminin bir sonucudur.

Agat oluşumunda aracı olarak en makul varsayım, düşük P-T koşulları altında, hidrotermal sirkülasyonun varlığında, koloidal silis sistemidir.

Andezitlerin çatlak zonu içerisinde bulunan çubuklu agatlar içindeki özgün kapanımlar, ornatma kökenli olup, başlangıçta zeolit (skolezit) mineraliydiler. Riyolitlerin gözenekleri içerisinde bulunan agatlar içindeki borumsu yapıya sahip kapanımlar, özgün büyüme kökenine sahiptirler. Bu yosun benzeri yada çalımsı büyümeler, alkali-silikat içeren silis jelinden oluşmuştur. Ankara agatlarında bu silikat büyümeleri tek başına oluşabildiği gibi, ornatılmış zeolit çubuklarının etrafında da gelişebilir.

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CHAPTER ONE

INTRODUCTION

Anatolia has a high potency as both quality and variety of the gems. However, these gems are not known throughout world, as they have not been enough examined and presented. The main aim of this thesis is to be the initiator of such kinds of investigations. So, the subject has been chosen particularly and thought that the most convenient mineral has been agate. When the criteria considered why agate has been chosen, is indicated below:

Nowadays, more than 2500 minerals are known and most of them can be produced in synthetic forms. Agate is one of the samples of which can not be synthesized. Because having produced a mineral in synthetic form, the mechanism of its natural formation should be followed. But it has not been clarified how the formation mechanism of the agate in nature, yet. This caused increasing the interest in agates all over the world. A new logical mode of the agate formation has been tried to put forward by joining the principles colloidal chemistry with the geological and optical findings based on the thoughts of the formation of colloidal solutions. This is the second aim of the study.

Agates, economically, are only found in the following countries: USA, Germany, England, Mexico, Uruguay, Brazil, India and Turkey. During the study about this mineral the findings of the sources from Turkey has gained a great importance to introduce the agates from the region of Ankara in details is the third aim in order to provide the existence in the agates of the world as the agates from Turkey .

The mineral agate has a great respect in the history of the humanity by different civilisations. However, this mineral is not rarely found in the world. The reason of the interest on this is due to the formation of its mechanism which has not been analysed. The importance given to the agates during the history has been explained in the first section of

this thesis. The fourth aim of this study is a wish to examine the mineral which has been seen respect during the ages.

There are different theories and discussions for 200 years how the agates have been formed. It is hardly difficult to classify the formation of the agates as they have been attributed as different origins. The investigators are divided into two groups in articles examined and the publications. The first group, widely, is the ones who approached to the theory according to the “infilled cavity theory” (regarding external rhythm) and the second group is the ones who certainly refused this theory (regarding internal rhythm).

CHAPTER TWO

ACQUAINTANCE WITH AGATES

1. ORIGIN OF THE NAME AGATE

The name agate belongs to the group of ancient Greek mineral names Mitchell (1979). The name agate was derived from the river called “Achates”, today the Carabi or the Cannitello in Sicily (Italy). But, the most types of quartz and chalcedony which are known in different names today were used under this name in ancient times. Although the first gravels of agate have found in the river which has given its name to agate, it is also thought that they came from India and Anatolia according to beads of agates which were found in the archaeological excavations made in these places.

In Turkish this mineral is called “akik”.

2. HISTORY OF AGATE CUTTING AND ITS USES

The cutting of agate as an ornament goes to the date back to 4000 BC in Anatolia and 2000 BC in Mesopotamia. Necklaces and ear-rings which are belonged to the Chalcolithic period found in Hacılar and Tilkitepe (Anatolia), and other ones which are belonged to the Early Bronze age found in Alacahöyük and Horoztepe (Anatolia) excavations are exhibited in Hittite Museum in Ankara.

In Mesopotamia, the agate has been polished after having cut in various shapes, on which was engraved the figures of worship. In that period agates were formed being rubbed on the flat or slightly curved sandstones; afterwards they were polished with

quartz-powder or another oxides. Engraving was made with a piece of corundum or diamond which was attached on a pointed pin. While Assyrian were cutting agate in cylindrical or in cone shape, ancient Egyptians were cutting it in a rounded shape. Agate was first cut as an ornament object in Crete in 2000 - 1800 BC in the late period of

Minoan civilization, flourished on that island, agates could be cut in lens shape. Urartus who ruled on East Anatolia in 1000 BC cut agate as an ornament object.

Art of agate cutting largely developed in ancient Greek in 7th and 6th centuries before Christ. In these periods it was designed on the gem, mythological descriptions, war coaches, and animal motives. The most picturing which was designed on the agate were Venus and Eros. In Hellenistic period art of agate cutting into cabochon shape instead of engraving it flourished.

In 7th century before Christ in Etrüks civilization, most of the agates were cut into the shape of an insect (Scarabaeus Socer) and sometimes were written on them. In Early Christian and Late Rome periods agates were used as a magical spell of Gnosticism sect by writing on them. A big block of agate on which has St. John's figure was in Benedictine Monastery in Toul (France). After that it is exhibited in Louvre Museum as one of the private pieces of French Kings.

Agate has quite a history. Over the ages there has been more interest in this gem than in any other. Agates are known to have been used back in ancient Egypt, Sumeria and Anatolia as ornamental trinkets such as beads, rings, bracelets etc. The Sumerian axe-head which was made nearly 5000 years ago, in New York's National History Museum is the first object from agate (Quick, 1974). The Egyptians used agate for cylinder seals, ring stones, cameos, and vessels at least 3000 years ago. The agates have been used in trade among the Arabians since 500 BC It is probable that these agates were brought from India and Anatolia. Mohammed had a signet ring of Yemen agate.

The agate literature in the history was written by Theophrastus about 300 BC called "On Stones", and then by Pliny (Pilinius) about at the beginning of the Christianity called

"Libri Naturalis Historial" (Quick, 1974). The investigated documents demonstrate a wide belief in the efficacy wearing agates because of their wonderful virtues, in ancient times. The agates the prices of which are cheap now were in the past extremely valued. It was the accepted tradition to own an agate cup or bowl which would keep the vine cool, for was not crystal. The Romans loved and used the agates widely. Many Romans had

special keepers for their cabinets of agate cups and some even had individual names for each cup. Agates served as mortars and pestles, and were held in the mouth to quench a thirst. They were a cure for snake and spider bite (Quick, 1974).

After Caesar had conquered Gaul (Gallia, old name of France), he pressed on north to a valley near the Rhine. His soldiers came upon a little village called Hidera, now Idar (Germany), where a stream ran between rock walls. The peasants here were hunters, but in winter they practised lapidary. The Romans were captivated by their agates and brought them gigantic grindstones and polishing wheels. At the village of Idar, such water-powered wheels are still exhibited with the workmen lying on their stomachs to handle the stones. The interest was not intense after the departure of the Romans until the 12th Century. The Count of Oberstein (Germany) owned the agate quarries then, and the workers formed a guild to look after their rights. As the agates became scarce, scouts went out of the valley in search of new material (Quick, 1974).

When one are said the cutting and polishing of agate, Idar-Oberstein (Germany) occurs to the mind. The biggest industry of gems in the world, as to come first the agates, has developed there. The main centre of the art is Idar-Oberstein, where more than 90% of the world's engraved gems are made the bases for this development were deposits of agate, good local sandstone for the production of cutting and polishing wheels, and water power to work the wheels. Agate cutting has been modern made in and near Idar-Oberstein since the first part of the 16th Century, and today in Idar-Oberstein area, there are thousands of people who are all artisans and who have family roots in practically every country in the world where agates is found.

CHAPTER THREE

THEORIES OF FORMATION OF AGATES

1. INFILLED CAVITY THEORY

This theory was firstly proposed by Werner, Dolomieu and Hutton respectively at the end of 1700's years, and then Cleaveland related the theory completely (Shaub, 1983). This theory which was based on the external rhythm basement has been accepted by investigators since the beginning of 1800's years.

According to the infilled cavity theory, pre-existing cavities with rounded shapes were filled by the filtration of siliceous solutions, and successive deposited thin layers formed the agate nodules. When the cavities were not completely filled with siliceous particles, the centre of the nodule was lined with other quartz varieties with crystalline shape. The theory implied that agate amygdales were formed in relatively low-viscosity molten lava with gas bubbles and the amygdale was flattened on the bottom and more bulbous towards to top. In this theory, nodular agate formations were based on the action of water and aqueous solutions.

2. THEORY OF HAIDINGER, NOEGGEARATH, AND KENNGOTT

In the middle of 1800's years, petrological interpretation of agate genesis was made by Haidinger, Noeggearath, and Kenngott (Landmesser, 1984). According to this; Volcanic mass with vesicles cools and cracks. After, agate formation materialised with precipitation of SiO2 alternately from the solution contained CO_2, cause of late effects of volcanic activity, in gas cavities and fissures in solidified igneous rocks. They assumed that external rhythms effected the whole rock environment of the nascent agate, and that the flow

of solutions and SiO_2 deposition controlled by external rhythms. In addition, SiO_2 deposition was supposed to result from changes in the physical or chemical conditions (such as composition, temperature etc.) of silica solutions.

3. THE GEYSER THEORY

In the second half of 1800's years, the geyser theory was defended by Reusch, Lange, Bauer and Erdmann (Landmesser, 1984). This theory was entirely based on the source of siliceous solutions which were carried to the empty cavities by heated waters from hot springs, the cavities being located in strongly weathered igneous rocks; even to the extent the fresh rocks are free from filled cavities. The existence of the theory is assumed of hot intermittent springs. Essential event for the agate formation regarding the theory is that hot water rises and sinks. All kinds of emptiness in the solid rock are filled with chalcedony layer by layer depending on the action of hot water. In this theory, hot water was accepted as an agent that dissolved the silica and other constituents in the rock.

4. THEORY OF DANA

At the end of 1800's years, Dana was exposed the approach of the infilled cavity theory and internal rhythm (Shaub, 1983; Landmesser, 1984). But, in this theory the source of the siliceous solution and its action into the site of the empty was not explained. According to the theory, the siliceous solution passes from the outer chalcedony layer by osmosis, and it is denser than the inner weaker solution. Dana accepted that the colors of agate's bands with delicate parallel lines were produced by organic matter or oxides of iron, manganese or titanium. Dana expressed that the different layers in agate could be account for with the etching process by fluoric acid which accomplished the porosity and its rate.

5. THEORY OF HEDDLE AND GOODCHILD

In this theory proposed by Heddle and Goodchild, the geyser was opposed and it was claimed that SiO_2 formed becoming full with solution movement. Heddle and Goodchild defended a genesis based on mineral charged liquid passing in and out of the chalcedony

layers. According to their theory; the first happening is intrusion into gas cavity of green earthy minerals derived from augite or ferro-magnesian minerals within the lavas, and called by Heddle celadonite and delessite, which seeps in and coats the walls of the cavity. This is followed in like fashion by zeolitic material which has been derived from feldspars. Then, the cavity is filled with hot siliceous liquid which, coming through the

walls and the two previous deposits, lays down a coating on top as chalcedony (Landmesser, 1984). This theory is the first theory which implied the hydrothermal alteration before agate formation, which proposed at the beginning of 1900's years.

6. THEORY OF LIESEGANG

Liesegang did an experimental study on the origin of banding in agates, and published in 1915 an account of his experiments with the diffusion of silvernitrate when submerged into the kaliumbichromate solution. The silvernitrate diffused through the gelatine transformed chromate solution producing an unusual banding of silverchromate. Liesegang proceeded to compare the banding produced in the silverchoromate with that in the agate and concluded that the banding in agate could be due to a diffusion process in silica. The disturbance in the outer bands of the agate he considered to be an inflowing canal through which additional material would be added to the interior of the agate in the cavity in the rocks. Liesegang seized upon this experimental production of concentric bands to postulate that the banding in the agates was developed in the identical manner, that is, by the diffusion of salts into the gelatinous mass of the colloidal silica nodules. He assumed that the surrounding rock contained salts that entered the colloidal silica gel within the nodule through the outward bulges of the agate bands that frequently appear within the agate nodule (Landmesser, 1984).

7. THEORY OF NACKEN

In 1917, Nacken at the first put forward the idea of the special importance of the critical temperature of water for the explanation of both concentric and horizontal layer bands in agates, whereas he has changed then his opinion on the formation of agate bands completely. Nacken accepted infilled cavity theory, and tried to explain the formation of banding in the agates concerning the critical temperature of water (374°C).

He stated that colloidal silica solutions injected into the cavities of cooling lava under high pressures and at a temperature near the critical temperature of water. He conceived that agate nodules with bastion-like edges formed at temperatures above the critical temperature of water from one phase filling the whole cavity; but if the temperature dropped under this value, the phase would split into two phases one of which could form agate nodule with even layers due to its higher specific gravity (Landmesser, 1984).

8. THEORY OF BROCKMEIER

Brockmeier put forward in his theory a different approach for agate formation in 1927 (Landmesser, 1984). According to Brockmeier, migration of SiO_2 is formed cause of filtration of aqueous solution. Agate genesis takes place largely in the field of sedimentation and partly in the environment which the formation of soil happened. Brockmeier estimated that the solution which agate was formed became in particular from humus in the tropical forests.

9. THEORY OF HEINZ AND LINCK

Rhythmic structures of agates by Heinz and Linck in 1930 were established a connection with rhythm of seasons (Landmesser, 1984). They took into consideration that hot weather with humid influenced on the formation of agates. According to this idea; during dry weathers, siliceous acids are hold down between fissures and crevices. From there they fill into cavities by diffusion, and settle. In humid times, solutions with alkali /earthalkali metals, carbonates/ sulphates, or solutions enriched with CO_2 infiltrate into cavities and vesicles, and meet with silica. In conclusion, these events frequently continue until the interior of them has been fully filled as a gelatinous mixing.

10. EXPERIMENTAL STUDY OF PELTO

Pelto (1956) investigated chalcedony as chemical, and under microscope. He stated that chalcedony consisted of fibrous quartz crystallites with pores including water. According to Pelto; “Heat effects are masked near the high-low inversion point of quartz because of the strained state of the material and because of the pressure gradient”.

11. EXPERIMENTAL FINDINGS OF WHITE AND CORWIN

White & Corwin (1961) did an experimental study to produce chalcedony, and compared to natural one. These investigators expressed that synthetic chalcedony could be produced by transformation of silica glass in slightly alkaline solutions in the presence of hydrothermal solutions at moderate P-T. In their observation, nucleation and growth of silica fibres began from a surface and continued to other parts of the material producing the typical fibrous and radial textures. According to them, the formation of crystalline quartz with submicroscopic holes is due to negative volume change. The conversion proceeds by a series of steps:

Glass $\rightarrow$ cristobalite $\rightarrow$ keatite $\rightarrow$ chalcedony $\rightarrow$ quartz.

However, it was proved by Landmesser (1992) that the morphology of chalcedony formed by transformation seen under the scanning electron microscope was different from natural chalcedony; so we can say that the agate formation is not account for with transformation of solid silica.

12. OBSERVATIONS OF MONROE

Monroe (1964) examined the fine-grained silica minerals such as chert, flint, jasper, chalcedony-agate and opal, by the electron and light microscopes, and X-ray diffraction. The investigator in his study compared the morphologies of those mineral under the electron and polarizing microscopes, and observed that the polarizing microscope displays

granular or poorly defined fibrous regions in the chalcedony-agate whereas the electron microscope shows both porous and granular regions.

13. OBSERVATIONS OF FINKELMAN

Finkelman (1974) demonstrated in the table the minerals and their mineralogical features those of which were in about 500 geodes after having examined under the

electron microscope the minerals in geodes from Chihuahua, Mexico. The list of minerals which were observed by Finkelman are as follows: Quartz, chalcedony, opal, calcite, gypsum, mordenite, hematite, goethite, todorokite, ramsdellite, hollandite etc.

14. OBSERVATIONS OF DANIELS

Daniels (1974) examined the SiO_2 formations found in Brazil, that are different to ordinary quartz form morphologically, that include agate structures, and called quartz polyhedrons, and tried to work out their origin. He thought that the shapes of the objects were the result of fairly random system of joints. According to him, the process of filling of joint pattern with silica-rich solutions in early stage of agate formation was hydrothermal signifying proximity to volcanic activity. The investigator state that "the conditions varied during the infilling process to an extent that amorphous and crystalline silica were both deposited, often in alternate bands". The formation theory proposed by Daniels (1974) for agate-like quartz polyhedrons is quite reasonable for the agate genesis in volcanic regions, at least in its early stages.

15. EXPERIMENTAL FINDINGS OF OEHLER

Oehler (1976) did an experimental study called hydrothermal crystallization of silica gel and he exposed that these findings would enlighten the mechanism of pattern formation in silica in nature. With this aim, he investigated the behaviour of nonbiogenic cherts under hydrothermal conditions. Oehler disapproved the explanations that the origin of natural silica formations is cause of transformations of silica under hydrothermal conditions, and stated that "the principal significance of pervasive quartz microspheres in cherts is that

they are relic structures indicator of crystallization from viscous colloidal precursors". The experimental study of Oehler is important development for agate genesis in nature.

16 . OBSERVATIONAL FINDINGS OF FRONDEL

Frondel (1978) studied the varied types of fibrous quartz and single quartz, and proposed the principle of general occurrence of microscopic fibres in quartz and of

euhedral or anhedral quartz crystals. He expressed that quartz formed microscopic fibres in low-temperature environments and formed macroscopic euhedral or anhedral single crystals in high-temperature environments.

17 . THEORY OF SIM

Sim (1979, 1982) thought that the rise and fall of the water table in the rocks was the main factor governing the development of agates. This theory is a newly expression of the infilled cavity theory. Sim in his theory defended that agates were indicators of nature of the rocks beneath because of agate-forming solutions came from deeper.

18. THE SYNGENETIC AGGLUTINATED COLLOIDAL SILICA THEORY OF SHAUB

Shaub (1979, 1983) has rejected all theories, and approaches regarding the infilled cavity theory, and differently has developed a mechanism on the origin of agates. The syngenetic theory proposed by Shaub based on the origin of agates directly from the very high siliceous magma which supplied the silica and various materials for the forming of the agates and other siliceous nodules. Shaub's intramagmatic theory includes agates, geodes, thunder-eggs and Bruneau type jasper from the Oregon Region in USA While earlier expressions accounted for the origin of agates and other siliceous nodules as epigenetic, or formed in cavities after the solidification of surrounding rock, Shaub's study holds that they are syngenetic, or were formed contemporaneously with the other rock in a deposit. However, Shaub was not account for barred and moss-agate found in linings of volcanic cavities and fissures.

19. THEORY OF LANDMESSER

Landmesser (1984) published a monograph on the problems of explaining the origin of agates. In his study he systematically examines all the important explanations proposed since 1850 and, on the basis of careful, modern, scientific study, displays why most of these theories do not hold up. After having investigated the agates with various structures under the polarizing and scanning electron microscopes. Landmesser (1984-1995) elaborated the elements of a model of agate genesis. He assumed that the medium of

agate formation has been a polydispersed colloidal silica system , and believed that the agates were formed as cavity fillings under the P-T conditions of sedimentation/ diagenesis. In addition , he explained the structure of the infiltration channels by deformation processes in gelatinous media. Landmesser has attributed that the rhythms of agate banding may be caused by internal rhythms developed in the agate forming solution, but external rhythms are inconstant or periodic changes of the conditions in the environment around the nascent agate. Thus "agate formation is an example of a natural self-ordering process in the wide sense defined by the term , internal rhythm. External rhythms can not be regarded as the essential causes of the characteristic bandings in the agates". Landmesser assumed that the formation of gel-like zones which born ordinary banding starts at different points and proceeds to all directions forming hemispherical aggregates, later becoming spherulites of chalcedony. Moreover, he emphasized that the critical temperature of water or aqueous solutions had not to consider at the formation of band types of agate.

CHAPTER FOUR

GEOLOGY OF ÇUBUK (ANKARA) AREA

1. GEOGRAPHIC SITUATION OF THE INVESTIGATED AREA

The geological investigated area is placed in the northern part of the town called "Çubuk" in Ankara (fig.4.1). It is near 25 km away from the town Çubuk and near 40 km away from Ankara. From topographical maps drawn with 1/25000 scale, you can find the area in sections "Çankırı $H30_{a3,a4}$ ".

The main morphological features of the place are low flat hills, large flat wadis and occasionally small forests. The average altitude is 1200 m.

In the summer weather is dry and nominal temperature is about 25 ^{0}C. On the contrast the winters are snowy and the temperature is 0-5 ^{0}C.

2. STRATIGRAPHY

2.1 GENERAL SETTING

While the area was studying as geological, special attention was given to volcanic units in which agates exist. The geological units which settled down in the area were named without any discipline. Those names were just based on relation with the similar lithological forms.

In the study area, there are generally metamorphic, sedimentary, volcanic and alluvial cover units available, formed in different geological ages. The oldest ones consist mainly of schists, meta-greywackes of Palaeozoic age, called "Basement Rocks". These are unconformably overlain by mainly sedimentary rocks of Mesozoic age, with melange feature, called "Mixed Series". Upon these units is the Miocene (Neogene) aged "Volcanic Sequence" available with its unconformable tuffs, pyroclastic materials, intermediate and basic lava flows (andesite, basalt) and acidic stocks (rhyolite, dasite) which cut those rocks. Next sequence upon these with an unconformity is the

“Sedimentary Sequence” which consists of slightly consolidated conglomerate with lava, limestone and sandstone gravels; limestone and sandstone, Pliocene aged. Finally an alluvial cover of Quaternary takes unconformably place upon these.

Generalized stratigraphic columnar section of the investigation area, without scale (fig.4.2), geological map and its cross-sections, in 1/25000 scale are presented (appendix 1).

2.2 LITHOLOGIC FORMATIONS

2.2.1 Basement Rocks

The Palaeozoic aged basement is actually very disputatiously and still has been known with all details. It has been processed in many treatises with different formations and lithological definitions.

-Erol (1954) accepted that the unit consisted of schists and greywackes is Palaeozoic aged and he named it Dikmen Greywackes. He mentions of Silurian and older aged schists, Carboniferous and Permian aged limestones inside this unit.

-Ünsal (1973) distinguished the Palaeozoic aged rocks as: 1) Severe metamorphic schists and greywackes, 2) scarcely metamorphic, dark colored, grained schists.

-Norman (1975) notified that there was Palaeozoic aged melange with metamorphic, limestone and ophiolitic blocks in the area.

-Tatlı (1975) separated the greywackes and spilities from Palaeozoic basement and he named green schists.

-Akyürek, Bilginer, Çatal, Değer, Soysal, & Sunu (1980) found Carboniferous and Permian aged blocks in the formations which they distinguished as Lower Triassic aged.

-Tankut (1985) determined that the basement consisted of schists and greywackes in the area is Palaeozoic aged.

-Helvacı , İnci, & Yağmurlu (1989) expressed that the metamorphic rocks in the basement of the region are Palaeozoic aged.

These rocks accepted as Palaeozoic aged are placed in the North, Northwest and Northeast of the study area. The unit consists mainly of green and yellow colored, sometimes stronger, sometimes scarcely metamorphosed schists and meta-greywackes. The lower sections of the unit are green and getting darker to the upper sections. Especially in the upper sections there are black schists including 5-10 cm coarsen strata. It includes, on some places, grey-white colored massive limestones.

Scarcely metamorphosed green schists have granoblastic texture and include a lot of quartz, chlorite and calcite, a little muscovite, serisite and plagioclase (albite, oligoclase), and also opaque minerals in trace quantity (Tatlı, 1975). There are on some places inside the schists black coloring, crystallised limestones in the form of lens. These crystallized limestones demonstrate large numbers of pressure-twins (Tatlı, 1975).

The schists here appear together with the complicated Karacakaya Formation (Tatlı,1975; Suludere, 1976) and they are very hard to separate from each other. Upon them is older aged “Mixed Series” unconformably available. But on geological map these both units are seen together.

Because the basement of the unit is not being seen, it can not be said something decisive about its thickness.

2.2.2 Mixed Series

It is sedimentary series including mainly sandstone, meta-greywacke, claystone, serpentinite, chert, ophiolite, chalk and more or less metamorphic fragments. It has been seen, on some places in it, volcanic products such as tuff etc.

This series takes specially place in the North, East and Southeast of the study area. The Mixed Series is generally seen as interlaced with the Basement Rocks at the bottom. The units of this series at the Basement Rocks where they appear in the most hills of the region morphologically were marked together on the geological map. Different geologists

studied this Mixed Series in the surrounding areas, where it is more clearly to see and they distinguished it with different formation names;

-Erol (1954) collected in two portions the series as; a) Chalks; marbled and pseudo-oolitic chalks with a few fossils. b) Mixed series; serpentinites, rare chalk blocks and andesites.

-Tatlı (1975) distinguished the complicated units in this series as follows: a)Karacakaya Formation: Main units are sandstone, greywackes, ultrabasic lava (peridotite, serpentinite), limestone, and radiolarite. b) Kapak Limestone. c) Mesozoic Ophiolites consist of peridotite including crystallised limestone blocks, serpentinite, diabase, gabro, radiolarite, and chert. d) Yaşmeşe Formation includes limestones consisted of volcanic materials.

-Suludere (1976) determined that there are a lot of kinds of units inside this series and they are given without distinguishing with details under the title Karacakaya Formation. And he said that there are sandstones and clays with schists, crystallized limestone with and without stratum, on some places brown radiolarite, green serpentinites and cutting these dasitic, andesitic volcanic materials as the units formation of this formation.

-Akyürek et al. (1980) studied as the most details about the units including to this series.

Below the series is complicated with Palaeozoic basement. There is an unconformable contact because of lithological differences and age relations. Volcanic materials take unconformably place upon the series.

The different ages were determined for the Mixed Series as a result of collecting and defining in different formations of it by various researchers. The reason of this is that, the materials of very different geological environments were mixed there. Therefore, it is difficult to determine the age of the series exactly. Because it includes the block of limestones accepted by many researchers as Triassic, Permian and even Carboniferous aged; it can be expressed that the series is younger than Palaeozoic, older than Tertiary. As a general definition, it has Mesozoic age.

This series is a part which consists of ocean floor units pressed between two colliding continental crusts, and of sediments precipitated into this region; and it is a part of mixage that was brought here by dragging, called “Ankara Melange” by many geologists.

2.2.3 Volcanic Sequence

In the investigation area, Volcanic Sequence also displays very complicated characteristics like the Mesozoic aged Mixed Series. This sequence in which the mineral agate was formed was examined in detail to take some information about the formation of agates. In this area volcanic activity is widespread. In large scale, all of them take into consideration in Ankara volcanics. As studied in the surrounding regions, it is known that older igneous activity existed, which are not available in the investigation area, and the materials belonging it took place in the Mesozoic aged Mixed Series. But the young volcanic products formed at the last phase of the volcanic activity which effected the area from the Jurassic until the end of Neogene are mainly here the subject. These have different compounds and characters, which will be explained below, and are seen in the field as elevations which built the hills.

Erol (1954) and Ünsal (1973) used the title volcanic series in a general meaning. Tatlı (1975), in his studies belonging to the region, was the subject from the Pazar Formation including nodular limestones with clays, sandstones, conglomerates, tuffites as interval strata, and said that it was the same aged as the volcanics and in an intricate situation. Suludere (1976) worked in the same region, and collected all the volcanics and some

sediments under the title Pazar Formation. Akyürek et al. (1980) distinguished the Volcanic Sequence in two formation as Kurtsivrisi Volcanics and Aydos Basalt.

Volcanic Sequence, that covered the big part of the investigation area, that siliceous products such as nodular and stratiform agates, crystalline quartz fillings were deposited in its crevices and cavities consisted of lava flows (andesite, basalt), lava domes (rhyolite, dasite), pyroclastic materials, tuffs and tuffites. Generally the outer surfaces of those rocks were weathered and lost on some places their individual features.

Çalgın, Pehlivanoğlu, Ercan, & Şengün (1973) separated the Ankara Tertiary volcanics in two groups as Lower Eocene and Miocene aged volcanics with the help of stratigraphic relations, and they determined that these were seen in different geographical areas.

Tankut (1985) examined the petrochemical features of Neogene aged volcanics seen in four different places around Ankara, and expressed that they can be summarized into two groups as a) intermediate-acidic calcalkaline and b) basic alkaline. She classified them according to main and trace element contents.

Tankut & Türkmenoğlu (1989) stated that the mafic lava flows in Ankara region were the last products of volcanic activity which began in the Middle Miocene and continued until the Upper Pliocene, and that their contents were alkaline character. They resulted that the magma chamber of basic rocks according to rare earth elements, Cr and Sc data was formed with partial melting of lerzolitic mantle.

The Volcanic Sequence can be petrographically classified in three groups:

2.2.3.1 Pyroclastic materials

Complicated structured tuffs, tuffites, aglomerates and turbidites

Agglomerates which yielded with volcanic activity, seen in the West and East of investigation area have red-brown and purple coloring and were fairly altered. They were

volcanic mud and turbidite seeming in many places as lahaar with their mixage (Ünsal, 1973; Tatlı, 1975; Suludere, 1976). White-yellow, light green, light red, and brown colored tuffs and tuffites are in different structures and forms. They have big grains.

These are the pyroclastic deposits in which the materials of different sizes were brought together. The pieces from each size, from the thinnest ash (about 1/4mm) to thickest blocks (about 250 mm) are together available. These interwove with tuffs, on some places with lavas. It can be thought that these materials came dependent to the viscosity and gas contents of magma chamber during the volcanic activity as red hot cloud, red hot avalanche, volcanic breccias and also lahaar on to the surface (Tatlı,

1975). Those kinds of materials could come on to the surface with the gas pressure increasing sometimes, but they could not spread widely in the area. The mud flows in the west of investigation area, seeming brown, like mud, are typical. They include some different volcanic materials like basalt, andesite consist generally of angled particulars and the thinnest and the thickest materials.

Aglomerates and tuffs

These are products very often seen in the investigation area. Akyürek et al. (1980) named the ones with aglomeratic characters as Eregez Aglomerate.

Tuffs interwoven with pyroclastics, on some places with lavas are grey, yellowish-white and red colored. Aglomerates are usually rounded and half angled, most of them consist of nailing of pebbles and blocks of the tuffs. Tuffities and siltstone strata are between the aglomerates widely available. They usually have different colors.

By the microscopic researches of the tuffs from surrounding regions, volcanic rock grains, plagioclase parts, biotite, opaque mineral and zircon were observed and they were silicified, dyed with ironoxide, and tied with glassy material (Ünsal 1973). In addition, it was determined that these tuffs which included augite, andesine and biotite parts; quartz, zeolite and chlorite fragments, in a glassy matrix were the andesitic composition (Tatlı, 1975). Otherwise, it was found out that there were a lot of quartz, chalcedony, agate, opal

parts in the silicified tuffs and that the pulp consisted of glassy material (Suludere, 1976). As those units formed in distinct times and with distinct explosions, and defined in two different groups, intercalate with each other. They were shown together on the geological map.

This unit belonging to the Volcanic Sequence takes unconformably place upon the Mesozoic aged, sedimentary included Mixed Series. They also have lateral perpendicular transitions with the other units of Volcanic Sequence. Akyürek et al. (1980) determined that the formation including these units, named by them as Eregez Aglomerate was unconformably covered with Aydos Basalt and Büyükyakalı Formation, and it was laterally intercalated with Hançili and Karakoçaş Formation.

In the investigated area the thicknesses of these intricate structured units are different. Akyürek at al. (1980) measured that Eregez Aglomerate is about 400 m in thickness. In the investigated area these units are on some places max. 200 m in thickness. But this thickness could not have been measured with details.

There could not be found evidences to determine the age this unit. But, Keskin, Tatlı, Balkaş, Ünlü, & Erişen (1975) have determined that tuff, tuffite and agglomerate are Miocene in age, and also Tatlı (1975) determined, according to the Miocene sediments outside the investigated area, in the east of Kınık village of sub-district Güven in the north of Kızılcıhamam, the Miocene age. Akyürek et al. (1980) have determined that Eregez Aglomerate is the Upper Miocene in age, because it had the same age and was intricate with Hançili and Karakoçaş Formation found outside the investigated area. In the light of these data we can say that this unit has a Miocene age.

We think that the gas pressure of magma chamber was not very high because the tuffs in the investigated area are not very widespread. Also depending on the volcanic activity the middle section was filled with a faster coming of materials. On some places here are seen andesite flows upon the aglomerate.

2.2.3.2 Intermediate and basic lavas

They are spread in a big part of the investigated area, specially on the hills. Most of them appear as andesitic on some places in northern and southern parts as basaltic lava flows. They are widespread on Kapak, Koyun, Göz, Üçbaş, Çadırkaya, Sarıklı, and Kale hills. Also around Kargın , Tahtayazı, Kızılöz villages , the lava flows are seen as interwoven with tuffs. It is hard to separate them from each other. Here and there the lava flows were weathered and the tuffs were clayed.

Suludere (1976) determined that there were lava flows often between tuffs, tuffites and aglomerates with very different thickness and characteristics, that there were mainly

two lava layers found and the both two layers were basalt. One of them is black and hard, and gains the green colored secondary depositions partially because of weathering. The other lava appears brown, reddish and greenish-black colored; on some places it was cracked up into pieces with regular fissures and crevices. On the other hand, in the fissure-veins and crevice-cavities siliceous precipitations formed by hydrothermal activity were seen. Suludere (1976) observed silicification and analsime-formation (zeolite) in these lavas of andesitic composition.

Dark colored lava flows of this unit, which are seen on some places in the north of the investigated area (but outside of it) were accepted as the last products of volcanic activity and classified under the title Aydos Basalt by Akyürek et al. (1980). These are dark-black colored, with cooling joints, hard, sharp and bright fracture-surfaced; their flowing-structures with gas cavity are on some places wholesome. Akyürek et al. (1980) have observed the idiomorph-hypidiomorph augite (pyroxene) phenocrystals in glassy matrix, formed by plagioclase and pyroxene microlites in the dark colored basaltic lava flows. The color close to white seen in the andesites partially were generally former from the result of weathering. The products of weathering which can be defined is mostly clay formed from feldspars. Weathering depth is on some places up to 1 m. Phenocrystals in the andesites are mostly feldspar and quartz.

The lava flows with basic and intermediate characters are on many places intricate with pyroclastic products and they often take place upon them. The lava flows and the others were also cut by the acidic intrusions and their narrow spreading lavas.In the upper side on some places,Pliocene sediments and alluvium take unconformably place (Kasapoğlu,1980).

The thickness of the unit could not be measured with detail because these lava flows are intricate with tuffs, pyroclastic materials and also on many places with sediments, and their thickness change on every place. On some places it is 3-5 m., on some places it is 400 m.

In the previous studies, Erol (1954) claimed that the basalts and andesites should be connected with the part belonging to Miocene of Köroğlu Massif, and that the units belonging to Eocene ceased to exist because the connection between these lava flows and the mountain Aydos was eroded. Ünsal (1973) accepted that Aydos Basalt is Upper Miocene-Pliocene in age. Tatlı (1975) expressed that the volcanism has been very hardly activated during Miocene, because these lava flows were intricate with the Miocene sediments.

The lava flows with andesitic and basaltic character, coming out of regional pipes and fractures, are the rocks which were arisen on the surface following pyroclastics during different periods. Probably after the pyroclastic products a stagnancy phase began in the region; inner gas pressure of magma chamber decreased. It is a probability that the lava flows which became clear to come out of different pipes are the products of split portions of the same magma chamber. Next, it can be thought that the magma chamber was middle- viscosity. The pyroclastic materials and lava flows came out a long North-South directed fractures and were cut by the acidic stocks in the form of dome, which are well preserved on the hills.

After andesitic and basaltic lava flows in this area became solid, tension joints with NWW-SEE direction, and shear with NE-SW and NNW-SSE direction developed in these rocks because of stresses formed by the arising of the acidic stocks. This fissure and joint zone acted as a receiver to the stratiform agate aggregates with radial, pseudomorph, crystalline bars and other siliceous occurrences (fig. 4.3 and 4.4).

2.2.3.3 Acidic lavas

Acidic lavas are not widely spread because of their high-viscosity and they exist as domes signifying the pipes from which they came out. They occur in the investigated area around Susuz and Kuyumcu villages (fig.4.5 and 4.6).

The rocks usually appear as rhyolite; on some places as rhyodasite and dasite. Their phenocrystals are rather large quartz, mica and feldspar. They are pinkish-red colored and rich with silica minerals and siliceous occurrences. There are inside the high-viscosity

rhyolites a lot of small cavities left by the gas gone away, a result of sudden pressure decreases inside the atmosphere.

Acidic lavas cut the other volcanic products inside the investigated area. These are already no other units upon them because they are in the form of dome on the hills.

Acidic lavas appearing narrow spreading are 5-10 m. in thickness, in the pipe they have about 250-350 m. in thickness.

Acidic lavas are probably Upper Miocene-Lower Pliocene in age, because the volcanic activity in the area continued from the end of Miocene until the beginning of Pliocene and these acidic stocks cut the other volcanic products.

The pipes from which the acidic stocks and intermediate-basic lava flows came out are very close to each other, and this phenomenon reveal that these volcanics are the products of different phase of the same magma chamber. There happened exothermic gas reactions in the upper sections of the magma chamber rest inside the reservoir and splits after the coming out of high-viscosity lavas during long continuing stagnancy, they made it hotter and became fluid (Tatlı, 1975). It is probability that they came out through the pipes and with the load pressure of collapsed reservoir ceiling and so they consisted of the narrow-spread acidic lavas and the domes.

Cavities (vesicles) and cooling crevices with various dimensions, some of them jointly, in the contact zone of the rhyolitic massif acted as a receiver to the nodular agates with rounded or irregular shapes, moss-agate and crystal-lined cavity aggregates (agate geode).

2.2.4 Sedimentary Sequence

This sequence in the east and south of the investigated area was named by the different researchers under different formation names though its components look like each other.

Even though Tatlı (1975) studied it in two parts as Pazar and Sinap Formations. Suludere (1976) named the Volcanic Sequence as Pazar Formation, the Sedimentary Sequence as Sinap Formation. Akyürek et al. (1980) used the name Büyükyakalı Formation for this sequence.

The sequence consists mainly of conglomerate, sandstone, claystone, limestone with clay and tuffite. It has yellowish, grey, brown colored, slightly consolidated pebbles and volcanic parts, with different sizes and origins widely spread. The cement which found in slightly consolidated parts is clay and tuff. It has a few pores; so it can be crumbled easily in the hand. It was laminated and in some portions has cross bedding. With short intervals it sharply appears the lateral and perpendicular changing of unit.

This sequence which covered the Volcanic Sequence with an unconformity was also cut in lateral and perpendicular directions on some places. Its upper boundary can not be seen inside the investigated area.

It is about 200-300 m. in thickness. Tatlı (1975) determined that Sinap Formation is 300 m., Pazar Formation is 500-600 m. in thickness. Akyürek et al. (1980) also determined that Büyükyalı Formation is about 200 m. in thickness.

Any fossil necessary for age determination was not encountered in this unit. From the surrounding regions, a tooth belonging to *Hipparion ankyranum* OZANSOY and a horn belonging to *Paleoreas brachyceras* OZANSOY, *Paleoreas elegans* OZANSOY show

that the sequence has a Lower Pliocene age (Tatlı , 1975). Many other researchers also determined that the similar formations comprising this sequence are Pliocene in age (Suludere , 1976; Akyürek et al. 1980).

It is symbolizing a subsidence in a lacustral environment that the sequence is containing the pebbles of loose concreted, different rock groups and horizontal bedding. It is also appearing that the lacustral environment occurred in Miocene continued with occasionally drying until Pliocene, and that the volcanic activity in the surrounding frequently continued because the sequence is intricate with volcanic products on some places.

2.2.5 Alluvium

In dried and some flowing stream beds in the investigated area, there are alluviums consisted of conglomerate, sands, clays and river subsidence available, in Quaternary age. Their pebbles generally are the units of the metamorphic, volcanic and sedimentary rocks in the region.

3. STRUCTURAL GEOLOGY

There are angular unconformability between the rock units of Palaeozoic, Mesozoic, and Cenozoic ages.

The main structural forms seen in the area are folds and small faults. Alpine folds are most clearly seen in the tectonic activity of the region. The region gained its recent picture with the Walachian Phase (Tatlı, 1975).

Foldings are usually observed in schists, in limestones of the Mixed Series and lesser in the Pliocene aged Sedimentary Sequence.

Ankara-Çubuk plain is a depression basin.There are big faults in the eastern and western parts of the plain, but these are out of the investigation area. The small faults seen in the area are the faults which were most probably formed with the affect of the local volcanism.

The units in the Mixed Series have generally NW-SE direction with a high dip angle to the West. Sandstones have irregular fractures and joints. Dark colored limestones have good bedding whereas light colored ones have fractures and joints as massive looking blocks. Intermediate volcanics and tuffs have roughly N-S tending with dips of 5-15° to the West. Various crevice and fissure sets and alteration zones are seen inside of them. Acidic lavas were extruded along the fractures with N-S directions. The Sedimentary Sequence is rather horizontal.

The crevices and fissures in the andesitic lava flows from systematic sets. In addition, randomly developed fissures and joints were also formed during cooling. In general,

NNW-SEE and NE-SW directed sets are assumed to be `shears joints`, whereas the NWW-SEE striking sets are `tension joints` (Karacan & Kasapoğlu, 1986). As the matter of fact by the field observations, the fissures and joints which were shearing, have flat surfaces, high graded constancy and small parallel lines; the ones accepted as tension fissures have flat, rough surface and less constancy.

4. GEOLOGIC EVOLUTION AND PALEOGEOGRAPHY

In a wide scope there happened in the region very different metamorphism, volcanism and sedimentation activities during a long geologic period.

There is a very widespread igneous massif in the north of Çubuk (Ankara). Volcanic mass has a syncline appearance closed in large Termaçay-Çubuk (Ankara) groove (Erol, 1954) running across the Ankara Anticline. It separates the Çubuk plain from Termeçay basin (Erol, 1954).

Palaeozoic aged metamorphic units, the basement of the investigated area, are probably the rest of the materials left by the collision of plates of Eskişehir and Kırşehir. During Triassic the compression forces influenced the basin, and the result of this, sedimentary originated of the end Palaeozoic and the beginning of Mesozoic were folded and metamorphosed in green-schist facies. There was a sea in the region getting partially deeper at the beginning of Mesozoic. Blocking activities developed in the basin with the

influence of the tension pressure characterize the basin; Carboniferous and Permian aged units came in blocks to the bottom of the basin. As the another result of the tension, although it is not seen in the investigation area, the product of basic volcanism coming up the surface through the tectonic lines were spread intricately with the detritic materials.

During the Middle Triassic the sea flooded the region transgressively and it got deeper. The ophiolites which took place in the region coming by the tectonic movement during Lower Cretaceous completed in a subduction zone which was assumed that it existed in the northern parts, then they became melange character, taking older block within, and finally they settled down in the Austrian Phase (Akyürek et al. 1980). The ophiolitic

melange settled down on the continent edge where the deposition of flysch type sediments continue in the basin and alkali-basaltic volcanism is still activated (Çapan, Lauer & Whitechurch, 1983).

As a result of the influence of Laramian Phase the orogenesis and erosion stages were active in the region (Akyürek et al. 1980). At the beginning of Miocene the region was a lacustral environment. At the same period tectonic phase of Upper Oligocene or Lower Miocene age (Çapan et al .1983) caused the young volcanic activity to begin. Later, the volcanics, in which the Ankara agates were deposited, were come up with this volcanic activity and they spread inside the lacustral environment. But, before this volcanic activity, in Palaeocene the volcano-clastics which took place in the surrounding area somewhere outside the investigated area (Kazancı & Gökten, 1988), were carried with the other basic lava rests in the Ankara Melange from West to East and then settled down in the same lacustral basin in Miocene. Therefore, the volcanics of Miocene and volcano-clastics of Palaeocene are seen alternately and intricately each other .

At the end of Miocene and especially during Pliocene , sedimentary units were deposited in the shallow lacustral basin after the volcanism had stagnated. Most of the elements of these units are volcanic products.

In conclusion, the topography was occurred with fluvial erosion.

CHAPTER FIVE

CLASSIFICATION AND DESCRIPTION OF THE AGATES IN ÇUBUK (ANKARA) AREA

In classification and description of the agates in Çubuk (Ankara) area, it has been taken into consideration the following properties:

-Type of surrounding rock in which the agates were deposited , and their settling position.

- Macroscopic external shapes of the agates.
- Macroscopic internal structures and inclusion in the agates.
- Geodal structures.

The agates found in this area mainly appear in two types of surrounding rocks (host rocks) : 1) Andesite (basalt), 2) rhyolite.

The agates in the **andesites** were deposited as open-space fillings (crevice - and fissure -vein cavities) (fig. 5.1 and 5.2). Settling position of these agates is stratiform, but not nodular. The strata including agate aggregates continue along the vein zone in the andesites, but generally not parallel. Width of these veins including agates is about 1 mm. up to 10 cm. Length of the cracked zone is about up to 1 km. The agates set free by the decomposition of andesite rock were widespread as irregular blocks on the field. On the upper and bottom walls of some specimens, green colored zone, so-called chloritic zone, exits; even this green zone filled fully with the very fine fissure veins (fig. 5.1 and 5.2).

Agates in the andesites consist of solid and banded chalcedony material. They have concentrically banding, generally in fortification pattern (patterned like the ground-plain of
an old-fashioned fortress), but neither has horizontally banding (Uruguay-banding).

The agates in the andesites have characteristically inclusions. These agates often include the bars with rectangular prism shape or needle-like (acicular) shape, whatever mineral is now gone leaving solid chalcedony and quartz pseudomorphs and, on some places, hollow tubes, keeping original framework; so, these agates have been individual and first called “Barred Agate”. The agates with these individual inclusions have been only found in Çubuk (Ankara) area in the world In the case of the barred agates, radial mineral was formed earlier than agate formation. Bars or needles show no particular orientation in respect to the chalcedony host, indicating that they grew first and were enveloped later. These inclusions are sometimes so abundant that the agate material are

little more than them (fig.5.3). Sometimes, some of the bars were dissolved and they left spaces and hollow tubes (fig. 5.4.).

It should also be stressed that barred agates show evidences of both replacement and open-space filling and thus an overlap two processes.

In some specimens, randomly oriented columnar and acicular crystals which they exist at the bottom of vein were first replaced by silica, and then they were covered by a fine layer of solid chalcedony. These specimens are not real agate because they have not botryoidal chalcedony layers. The bars are often brownish in all specimens, but solid chalcedony membrane can be various in colors; principal colors are white (fig .5.5.a) dark yellow (fig 5.5.b) and red-brown (fig .5.5.c.).

In real agate specimens, vein-space including replaced bars was completely filled with the agate building material; the color of which is dark blue (fig. 5.6.a), or yellow (fig.5.6.b), or red-brown (fig. 5.6.c). However, the bars in these specimens also have brownish.

In other agate specimens, large open-spaces that have radial barred crystals were not completely filled with chalcedony. The most important characteristic is that various colored chalcedony bands which perched upon projecting points of the bars furnish nearly perfect spheres on the surface of agate block. Barred agate blocks, therefore, have botryoidal-reniform-mamillary surface. These terms in fact refer to the outward of appearance of fibrous aggregates of agate. Botryoidal means ‘grape-like’, reniform means `kidney-like` and mamillary means `breast-like`. The spherulites developed on the surface

give rise to the turtleback structure seen in cross-section of these agates. Diameters of these spherulites vary about from several mm to several cm. Some of the spherulites are seen as separated from each other (fig.5.7 and 5.8), most of them, as interlocked (fig .5.9-5.14). There is a thin crust on the spherulites. This crust is dominantly brown-yellow (fig.5.7), blue-white (fig.5.9), yellow (fig.5.11), or grey-black (fig.5.13) colored.

Examination of sections cut across of the agates shows that spherulite formation begins upon projecting points of the bars, and they give rise to an appearance called concentric

banding (fig.5.15-5.18). If the spherulites separated from each other, concentric banding can be clearly seen and it has fortification pattern (fig.5.15-5.18). If the spherulites close-set , concentric banding is seen as flatter(fig.5.14).

In some agate specimens, empty spaces which remained between the spherulites or latest concentric bands were lined with sparkling quartz crystals (fig.5.15 and 5.17). In these specimens, chalcedonic material has varies colors. They are in general blue-grey, yellow-brown colored.

Lastly, in some agate specimens in the andesites, vein-spaces where the bar inclusions were not formed in appreciable amounts were completely filled with chalcedonic material bearing the concentric banding. The individual bands are multi-colored (fig.5.19).

The agates in the **rhyolites** were deposited as cavity fillings (regular or irregular vesicles). Settling position of these agates is nodular. These nodules have rounded or irregular shapes. Gas cavities occur of bread-loaf shape or amygdaloidal in reference to the almond shape which is sometimes more common.

Some cavities remained unfilled, but most of them contain fillings or linings of chalcedony material on which may be further deposited drusy quartz, commonly rock crystal .

Macroscopic external shapes of the agates in the rhyolites in the area generally sign the different internal structures . Most of nodules are of a general spherical outline, and the

average size ranges between 7.5 and 20 cm. in diameters. The surfaces vary greatly from being relatively smooth to extremely rough with coarse, warty projections. They may be collected in various groups according to their external shapes:

The first group: The agates have an irregular shape pointed at the sharp corners (fig.5.20 and 5.21). The second group: The external shape of the agates is oval-nodular, has crater-from structures, and in most specimen outer shell is blue colored (fig.5.22-5.24). The third group: The agates have an external shape as spiri-structure, snail-like

(fig.5.25). The fourth group: The external shape of the agates is oval-nodular; but; on the surface there are dents (fig.5.26) The fifth group: The external shape of the agates is a general oval outline and kidney-like; but their surfaces is extremely rough with coarse, warty projections and generally blue colored (fig.5.27). The sixth group: The agates are nearly spherical rounded, but their surfaces are rough with coarse. Thick outer crust of the nodules has generally pink-red colored fine-grained perlitic rock material. Inner part of nodules, the five or six-pointed star-like central cavity resulted from a shear pattern with pyritohedral symmetry (fig.5.28-5.31).

In many agate interiors the structures are characteristically and extremely variable and strikingly unique. The agates found in the rhyolites in this area have a great range of color and patterns.

In these agates, concentric and horizontal (Uruguay) banding developed separately or they came in a number of different combination as concentric or Uruguay-banding initially, then followed by a combination of the two and ending with either type of banding. In addition some of them include sagenitic or moss-like structures.

In some specimens the individual layers, sometimes delicately fine but with uniform thickness and color, were arranged concentrically parallel to the walls of the cavity. Because this surface is angular and irregular, the layers in cross-section or slabs show mimetic patterns to which names such as fortification or bastion-like edges are given (fig 5.33 and 5.34).

In some rhythmically banded agate specimens, the laminated chalcedony bands and

comb quartz bands alternate in the same specimen (fig.5.35). In addition in these kinds of the agates there is a large central opening to be filled with the comb structured quartz (fig. 5.35). The central opening in some specimens was filled with the Uruguay-banding (fig.5.37).

In some agates there are both concentric and Uruguay-bandings. These kinds of the agates display different combination as the banding. The first one; The agates consist of the Uruguay-bands following initially very thin laminated chalcedony bands on the surrounding rhyolitic crust material (fig. 5.38). The second one: The concentric bands on

the walls are thicker. Both concentric and Uruguay-bands are dominantly grey-blue colored (fig.5.39). The third one: The agates with grooved surface consist of the concentric bands, Uruguay-bands and comb structured crystalline quartzes (fig.5.40 and 5.41). In these specimens, large space in the concentric bands next to the walls were filled the Uruguay-bands at the bottom. The upper part of the space were also filled with the quartz crystals terminated with the points oriented to the centre. The fourth one: The agates included tubular inclusions. These structures have long and short radial tubiforms and called sagenitic or moss-like growth (fig.5.42). Tubiform inclusions generally settled down at the bottom of the cavities and radiated to the centre. In some specimens of this kind, the inclusions are quite a few and these agates have both concentric and Uruguay-banding (fig.5.43). In some agates, tubiform inclusions are so abundant that the crystals enclosing them are little more than a chalcedony cement (fig.5.30, 5.31, 5.44 and 5.45). Some agates contain inclusions were filled the concentric bands and have a central opening filled with quartz crystals (fig. 5.46). Most agates contain big tubiform inclusions were filled with solid chalcedony, completely (fig.5.28) or partially (fig.5.29). Some of them show the Uruguay-banding (fig.5.47). The last ones also formed mossy colonies at the bottom of the cavities and have multi-colored concentric bands in the fortification pattern, sometimes including a crystalline filling (fig.5.48 and 5.49).

Some specimens are surprisingly spherical in outline. These agates consist of botryoidal, one colored chalcedony spherulites (fig.5.50). Some of them contain dendrites in the spherulites (fig.5.51). All of them may be named as geodal aggregates because empty spaces remained in their centres.

CHAPTER SIX

MINERALOGICAL, CHEMICAL AND MICROSCOPICAL DISTINGUISHING FEATURES OF THE AGATES FOUND IN ÇUBUK (ANKARA) AREA

1. GENERAL MINERALOGICAL CHARACTERS OF THE AGATES

Agate, from the point of view of mineralogical, is a solid and banded chalcedony, sometimes containing siliceous substances such as opal-CT. Yet, its chemical composition and crystal structure show that they are quartz. Agates have fibrous texture which can be only seen under the polarizing microscope. These fibres are both chalcedony (optically length-fast) and quartzine (optically length-slow), and represent cryptocrystalline texture as formal. The tiny fibrous particles of which they are composed are so intimately intergrown as to give a homogenous texture to the aggregate. Due to fibrous texture, some physical features of the agates such as specific gravity, Mohs' hardness, refractive index are numerically lower than those of quartz. Cryptocrystalline quartz varieties offer a huge diversity of pattern and colors. The most generally widespread of these materials is known as chalcedony. Names within the cryptocrystalline quartz family are generally based on colors and patterns. Banded varieties, and materials with moss-like inclusions, are known as agate. Therefore, the mineral agate in fact is a member of a large family, head of which is chalcedony. If the consistency evolution of the silica is accepted as following:

Silica gel $\rightarrow$ opal-CT $\rightarrow$ chalcedony $\rightarrow$ quartz

where the site of the agate is between amorphous and crystalline, sometimes containing opal-CT and quartz.

Agate occurs rhythmic alternating of banding of chalcedony and / or quartzine, sometimes quartz, showing between several microns to several millimetres in thickness. The individual bands are arranged either concentrically parallel to the walls or horizontally parallel to the bottom, or both.

Although the material is often strongly banded , the polished material is very smooth and nearly as hard as quartz, but never harder. The outer wall and outermost layer may form a white or brownish crust due to weathering. Banding formed concentric to cavity

walls the rule, but horizontal bands (Uruguay- bands), botryoidal growth, with or without coating of drusy quartzes, are also common.

Where the core of agate is not filled, well-developed crystals can form in the remaining spaces; rock crystal, amethyst, or smoky quartz, sometimes accompanied by calcite, hematite, and zeolite. A nodule with crystals in the core is called agate-geode.

The agates have also pseudomorphic inclusions as sagenitic, dendritic, barred etc. textured.

In conclusion, the variations in mode of formation, inclusions, colors, and patterns for the agates are almost endless.

2. METHODS FOR BEING STUDIED OF THE AGATES

The purpose of this investigation is to describe the structures seen in the agates found in Çubuk (Ankara) area and to elucidate the mechanism of the agate genesis.

In this study ,mainly two terms were used; "structure" and "texture": The term structure refers the patterns formed by the position of alternating bands, crystalline fillings and some inorganic residues in the agates. They were called macroscopic structures. The term texture refers both the petrographic patterns seen under the polarizing microscope and electron optical patterns seen under the scanning electron microscope . They were called submicroscopic textures . The textural nomenclature should be as descriptive as possible and classification made as to whether petrographic or electron optical

observations are concerned .

It is just possible to elucidate the mechanism of agate genesis by studies of petrographic, electron optical, and submicroscopic textures. The structures formed by alternating bands and some inorganic residues and crystalline filling in the agates inform on the condition and the process of agate formation.

In the mechanism of agate genesis is talked about the dissolution, transportation, and accumulation of SiO_2. Therefore the environment conditions such as pH, P-T, the electrolytes, the surrounding rock type are affective in the different steps of the process of agate formation.

Consequently, the geological data as well as morphological observations were also taken into consideration in the classification and description of the agates found in Çubuk (Ankara) area .They were in detail given in 'chapter five', as illustrated.

The chemical, X-ray diffraction, petrographic and electron optical as well as the geological data were taken into consideration to elucidate the role of trace elements, the origin of inorganic barred crystals, the mechanism, and the physico-chemical conditions of agate formation. They also will be in details given in this chapter. The terms used in this study are as following: fibrous, fibre, radial, spherulite etc. for the petrographic, and porous-spongy, infinitesimal particles, grains etc. for electron optical textures.

3. ALTERATION OF THE MINERALS AND REPLACEMENTS

In general, two types of changes frequently occur in minerals, 1) chemical alteration, 2) dissolution, sometimes both.

A mineral alters when some influence in its environment causes it to change its chemical composition, either by losing or adding constituents. If a crystal changes chemically or structurally, yet keeps the shape of the original, it is called a pseudomorph; it looks like a crystal of one species but is composed of another. Pseudomorphs also occur when one species is replaced by another which is in no way related chemically. Each cell, each pore

of the original is sometimes so faithfully preserved in the atom-by-atom replacement process that the original materials are easily and positively identified.

In the case of Çubuk (Ankara) area, there happened alterations and replacement. Rhyolitic dyke which had risen, depending on tectonic directions increased the temperature in the contacts of the andesite and basalt cooled in the lacustral basin. By the action of aqueous environment, amphiboles, pyroxenes and feldspars in these rocks were

exposed to a hydrothermal alteration corresponding to green-schist facies, and were alterated to the secondary minerals along the cracked zone as mentioned before. Macroscopic and microscopic data demonstrate to be ordered from the outer walls to the center as follows:

Tremolite-actinolite → chlorite → zeolite.

This observation accords with begin ordered in table 6.1.

Alteration products in shallow deposits are ordinarily fine-grained, and many are difficult to separate for identification. Chalcedony is doubtless of replacement origin in many instances of pseudomorphism being the replacement of wood, coral and even dinosaur bones by chalcedonic form. Details of the replacement process are obscured and has not become clear exactly.

Table 6.1 Orderly some minerals formed in hydrothermal alteration, according to temperature and pH (from Barrer, 1982).

4. REPLACED CRYSTALS IN THE AGATES FOUND IN ÇUBUK (ANKARA) AREA

The agates , so called barred agate in this study , includes constantly barred crystals in splintery columnar forms, forming original agate structure in Çubuk (Ankara) andesites.

During the field study, the primary mineral is sought, but not found. However, conspicuous constellated crystals which were fully silicified, preserving original framework were found out (fig. 6.1 and 6.2). Their colors are often cream and dark yellow. Next , red-brown colored, hollow, rectangular prism in shape specimens also are found in the area (fig .5.5). Some of them were dissolved, but their original moulds were preserved (fig. 5.4). Characteristics of the crystals with the barred structure are as follows:

-They are in the forms likely to splintery columnars (fig. 6.1 and 6.2).

-The cross-sections of the bars in the thin sections are seen rectangular or lozenge-shaped (fig . 6.20).

-Crystals were often formed fragile looking clusters of slim bars in the agates (fig.5.3).

-Parallel cords running along the long axis are seen on the outer surface of the pseudomorph crystals (fig. 5.5. c).

-The bars in some specimens were dissolved and their sites remained as hollow tubes (fig.5.4.).

This mineral which shows the barred structure may be hypothetical given various names. However, if the geological data of region and the paragenese and type of the hydrothermal alteration corresponding the mineralogical compound of the surrounding rocks are taken into consideration, it will be thought that we encountered a mineral of the zeolite group.

By the microscopic investigation of the andesites and basalts in the near environment to the region the mineral analsime (zeolite) was observed by Tatlı (1975) and Suludere (1976). Kostow emphasized a zoning of zeolites in a series of basic volcanics, similar to a typical zoning in a low metamorphic sequence, even if the zeolites are clearly of

hydrothermal deposition, namely crystallized in amygdales and veins (Sand & Mumpton, 1978). This interpretation is largely refered to the Srednogorian Zone and the Rhodopes, where volcanics ranging from andesitic to rhyolitic, including both lavas, tuffs and contain fibrous zeolites. Tankut (1985), who studied in the surrounding fields around Çubuk (Ankara), observed that the cooling gas cavities of the lavas found in the region were filled with zeolite and chlorite which are secondary minerals.

Thin sections of fifty-five different samples were firstly made to reveal whether this mineral in the agates with the barred structure was a zeolite. Residue of the original mineral has never been seen during the examination of these sections under the polarizing microscope. The interiors of the all bars were seen to be filled with quartz and chalcedonic silica.

One bar plucked out from the specimen seen in fig.6.1 was determined the whole surface analysis by the scanning electron microscope (fig.6.3), (table 6.2). According to distribution of the major elements, the formation of the zeolite as chemical components are possible even if their ratio was low.

The powders prepared from the barred agates, silicified bars and residues on the bars were taken X-ray diffraction patterns (fig.6.4-6.6). According to X-ray diffraction, almost all of the peaks corresponded to α-quartz whereas some of them remained vacantly.

In conclusion , we may contend that the original mineral is contingently **SCOLECITE** (zeolite), $Ca(Al_2Si_3O_{10}).3H_2O$, (SiO_2 : 46.63) (Al_2O_3 : 25.68) (CaO : 13.89) (Na_2O : 0.05) (H_2O: 13.75), according to the following data:

-The chemical components as determined with the scanning electron microscope correspond to scolecite (table 6.2).

-To its macroscopic growth shape (fig.6.1 and 6.2).

-To angle between cleavages seen on the bar in thin section under the polarizing microscope ; β_0 is about 90^0 , angle between (100) and (001).

-As determined with the trace element analysis , the element strontium is abundant which is markedly enriched in the residues on the bars. The enrichment of strontium is

accounted for by assuming that Sr^{2+} substitutes readily for the very similar ion Ca^{2+} , just as it does in the minerals of igneous rocks.

5. REGULARITIES OF DISTRIBUTION OF THE TRACE ELEMENTS IN THE BARRED AGATES, SILICIFIED BARS, AND RESIDUES ON THE BARS

Table 6.3 shows average concentrations of trace elements in three different sample groups concerning the agates found in the andesites. The first group, BA-1 to 5, consists of averages for the barred agates; the other three, SB-6 to 8, give analysis for the samples plucked out from the specimen seen in fig.6.1 and 6.2; and the last two give analysis for the residues on the bars plucked out from the specimens seen in fig.6.1 and 6.2. Thus, these three sets of analysis enable us to compare the distribution of trace elements in three different kinds of sampling with the average distribution for the agates with bars in general. Cursory examination of the data shows that the distribution has a certain amount of irregularity. Nevertheless, it can be drawn useful conclusions from the analysis about general patterns of trace element behaviour. Important features of this distribution are the followings:

One generalization about the distribution stands out immediately: Zinc and lead are about equal abundant in every sample. All elements except yttrium, shown in table 6.3, exist in the residues on the bars. The outstanding exceptions are nickel, barium, which are concentrated in the residues on the bars, zirconium which is markedly enriched in the barred agates, rubidium, gallium and niobium, which are absent. Lead, zinc, cupper, nickel, zirconium, strontium and barium exist in every sample, but they are irregular abundant.

An equally effective explanation for the distribution could be given by assuming that the principal features of trace element distribution in the barred agates, silicified bars and residues on the bars in the specimens found in the cracked zone of the andesites in Çubuk (Ankara) area can be explained by the simple rules of substitution based on ionic charge and radius, and by the mechanical concentration of the resistant minerals. But probably the chief process that leads to enrichment of trace elements in these samples is adsorption. The order of adsorption is somewhat dependent on the nature of the adsorbent and on the conditions under which adsorption takes place, but in general we might except

a fine-grained chalcedony, agate, to have a sufficient variety of small particles and to have experienced enough changes of environment during accumulation, so that rare elements of most kinds can be firmly held.

6. PETROGRAPHIC OBSERVATIONS OF THE AGATES IN ÇUBUK (ANKARA) AREA

Petrographic examination of the thin sections of the agates found in Çubuk (Ankara) area shows that the interior of solid, and concentric banding of the agates consists of completely fibres of silica (fig.6.7-6.13), the interior of the agates filled or lined with quartz crystals consists of dominantly fibres and partially grains of silica (fig.6.15-6.18), the interior of the agates with columnar bars consists of both fibres and grains of silica (fig.6.19-6.26). Therefore, the agates found in this area have both fibrous and granular texture. But, the granular texture is only seen the inside of the columnar bars and of the lining and filling regions. The main agate body has completely the fibrous texture, typically chalcedonic texture. Therefore, what is primarily of interest here are the characters of chalcedony, as upon a planer surface or the wall of a spheroidal or lining cavity, to occur parallel-fibrous or radially-fibrous aggregates.

6.1 CHARACTERS OF SILICA FIBRES FORMED FIBROUS TEXTURE

The fibres are usually a few microns in diameter and several hundred microns long and have both straight (fig.6.7) and undulatory (fig.6.8 and 6.9) extinction. The fibres range from approximately parallel to strongly divergent groups. The color ranges from colorless, to a distinct brown, to murky a long. Some of the fibre clusters denote to be piled up the straws of cereal-like (fig.6.19). The fibres were generally separated into two groups according to speed of light in optic long axes; fast in long axis (length-fast) and slow in long axis (length-slow), those of length-slow were collected under the name “quartzine” (fig.6.10-6.13). Because each quartzine (fibrous quartz) was composed of a large number of quartz crystallites always arranged with c-axes parallel to the length of the fibre. Commonly, one or the other predominates in a zone, but in view of general, both also arise as interwoven (fig.6.13). Main mode of the fibre aggregation is spherulitic. If the fibre groups display a texture of radiating bundles of fibre and blades, or of interwoven short

glades or fibres, they are called spherulites. The agate composing these spherulites was either length-slow, length-fast, or both.

If the nucleation and growth started from the irregular walls, it was seen that nucleation and growth generally started from a surface or wall and proceed to other parts of the material producing the typical fibrous and radial spherulites. The spherulites enlarged to the centre of the cavity could form the concentric banding as both microscopically and macroscopically. In addition, rhythmic banding is commonly present. Some fibre clusters showing the spherulitic aggregation are seen in shapes fan-like, sheaf-like (fig.6.8). Bundles of elongate fibres (spherulites) show abrupt termination with adjacent bundles (fig.6.9).

The three cases observed in the spherulitic formation are as follows: 1) Nucleation at a single point gives rise to hemi-spheres (fig.6.14.a). 2) Fibre clusters elongated from hemi-spheres on a smooth and flat surface formed a parallel-fibrous upper crust (fig.6.14.b). 3) Semi-spheres on the wall of irregular or inwardly-convergent cavity surface occur an inwardly convergent radial aggregate and its upper crust is botryoidal, kidney-like or mamillary-like (fig.6.14.c).

At the radial aggregates observed in the agates in Çubuk (Ankara) area, nucleation generally begins both as isolated fibres and as minute, hemispherical, divergently fibrous spherulites scattered over the interface (fig.6.7, 6.8, and 6.10). As the spherulites grow in size, they abut and interfere laterally, with those fibres more nearly perpendicular to the interface surviving competition. At a flat interface the last result is a shell of fibres in approximately parallel array perpendicular to the interface (fig.6.14.a and b). In the spheroidal case the fibres become radial inwardly-convergent (fig. 6.14.c).The surface of juncture of adjoining spherulites also converge inwardly depending on the actual shape of the cavity, and the number and arrangement of the sites of nucleation.

As seen in the thin sections, when distinct undulatory extinction bands and periodic striations are present, they are continuous through the various sectors (fig.6.10 and 6.26). Initially they are concentric around the various sites of spherulitic nucleation, but as growth continues they ultimately appear as shells concentric to the walls of the space

(fig.6.10 and 6.23-6.26). The degree to which these features in phase in adjoining sectors of fibre clusters, giving a more or less zigzag appearance (fig.6.9), has to depend on the timing in the formation of the initial spherulites. If the fibres in adjoining sectors are inclined at different angles to the plane of the thin section (fig.6.9), the continuity of the

undulatory band is broken, and at large angular differences they seem to stop at the boundary (fig.6.10). Sometimes finely disseminated foreign material such as iron, copper etc. becomes included during the growth of the fibres, giving thin pigmented band that serve as marker horizons (fig.6.11-6.13).

6.2 GRANULAR TEXTURE

A quite general feature of agates formed as vesicle- and vein-cavity fillings is the presence of a central opening that is crusted by (fig.6.15-6.18) or filled with quartz crystals. Otherwise, the interior of the columnar bars was filled with mostly grain, partially fibres of silica (fig.6.19-6.26). On the planer, outer side of the bars, a fibrous shell (quartzine) in approximately parallel array as perpendicular to the wall of the bar are seen (fig.6.19, 6.21, and 6.22). When the outer side of the bars was irregular, spherulitic fibre aggregate was developed, and cavity left between the granular texture was filled with the spherulites formed microscopically the concentric banding (fig.6.23-6.26). On the other hand, the crystalline grains signifying the granular texture in the space regions were observed on the spherulites (fig.6.17 and 6.18).

7. ELECTRON OPTICAL PROPERTIES OF THE STRUCTURES IN THE AGATES FOUND IN ÇUBUK (ANKARA) AREA

7.1 PREPARATION OF THE SAMPLES

A silicified bar and five characteristic agate specimens were selected for this purpose. The bar sample was plucked out by mechanical method and cut into 3x7 mm dimensions. Likewise, the agate samples also were cut into 3x4 dimensions using a diamond saw.

All the samples were firstly cleaned with alcohol and then washed with pure water to be become clear from dirtiness. After, the samples were set on the cylindrical shaped brass columns, so-called holder, with 10x10 mm dimensions. After then, to make them gain conductivity, the carbon conductive solution was spread the top surface of the brass holder and the bottom surface of the samples. Next, after having been put into a cull-spatter coater, marked 'Polaran E5100', the top of the samples was plated with gold approximately 200 A^o in thickness. The purpose of this procedure is that samples are brought in suitable position to be easily investigated by the electron microscope.

After this procedure, the samples were investigated by the scanning electron microscopes, being in M.T.A.I. marked Jeol 840A, being in T.P.A.O. marked Jeol JSM-5200, being in D.E.U. Fac. of Enginee., marked Jeol 540A, being in E.U. Fac. of Dentistry, marked Jeol 540A. But, because of lacking of transmission feature of these microscopes, it was not possible to determine the lattice sites of the elements in the samples.

7.2 ELECTRON OPTICAL OBSERVATIONS AND DISCUSSION

7.2.1 Concentric Bands

As examined the banding in the agates under the scanning electron microscope, it is understood that explanation of the formation of the bandings according to macroscopic and even the polarizing microscopic observations give often rise to wrong results. It is interesting to note that a discrepancy also exists between the petrographic and electron

optical textures. In conclusion, the macroscopic, petrographic and electron optical morphology of the bands in the agates are dissimilar.

The main process which reveals the formation of the concentric banding commonly found in the agates is the development of radial fibrous texture. The fibrous texture is often represented by the spherulites whereas both randomly and parallel arrayed of the

fibres exist, under the polarizing microscope. To understand this formation, the interior of the fibres is necessary to investigate under the electron microscope. The polarizing microscope as seen in fig.6.27 and 6.28 displays the radial fibres formed a spherulite, as magnified gradually. As seen in these microphotographs, the fibres are not separated each other by sharply lines. The same fibres can also be observed under the electron microscope. Electron photographs enlarged gradually of the fibres formed two adjacent spherulites seen as the regions of dark and light hues are displayed in fig. 6.29. In the microphotographs magnified up to x3500, numbered as 206 and 208 in fig.6.29, it is observed that the fibres in fact were formed the infinitesimal particles of silica and hollows in different dimensions. Consequently of this observation, electron optical examination shows that the fibres are not real quartz crystals; because the fibres formed the infinitesimal silica particles were consummately contorted. The contortion fibres are clearly seen at the boundaries of the regions of dark and light hues in fig.6.29, numbered as 203 and 204 microphotographs. It is implied that the texture forming the concentric bands is the heterogeneous character.

The concentric wide and narrow bands in the agates are easily recognized under the electron microscope as well as under the polarizing microscope.

" The concentric wide bands " seen in different colors or shades of the same color can be specified under the polarizing microscope (fig.6.30 and 6.31), it is seen that the band boundaries were completely formed from the textural disposition. Zones which separated the bands are clearly shown as magnified gradually in fig.6.32. The biggest cavities at the band boundaries become visible in microphotograph numbered as 25 in fig.6.32. Overporousness of the band boundary makes possible to the new nucleation of the spherulite. The difference of the porosity between the centre of the bands and its boundaries attracts especially in fig.6.32, numbered as 25 and 28. Porosity of the band

boundary causes the foreign materials (pigments) to precipitate, and the bands to contradistinguished from each other.

"The concentric narrow bands" running as perpendicular to longitudinal of the radial fibres are shown under the polarizing microscope as magnified gradually in fig.6.33. It can be thought that the narrow banding originated from the different refraction of the light

rays as a result of rhythmic aligned of infinitesimal particles and hollows in various dimensions. And so, the narrow banding seen as magnified gradually in fig.6.34, under the electron microscope arises as dark hues in the form of zones which were the parallel to each other, as alternating of the fibrous regions with the infinitesimal particles and hollows, and with bigger particles and cavities.

The particles and spaces formed the fibre zones which were the parallel to each other seen as the regions of dark and light hues in microphotographs numbered as 301 and 302 of fig.6.34 become clear in microphotographs numbered as 309 and 306 of the same figure. It is estimated that the narrow banding seen in the agates arose from the periodic variation of the specific gravity, which is caused by the periodic variation of the infinitesimal particles and hollows (Landmesser, 1984).

It is interesting to note that dark colored foreign material was disseminated both at the boundary which separated the wide bands and in the large cavities which existed between the narrow bands. It is estimated as so also known from literature (Frondel, 1978; Landmesser, 1984-95; Sukow, 1987) that the striae seen as magnified gradually in fig.6.34 signified the regions where the pigments such as iron, copper etc. precipitated. But, the kind and site of the pigments, for lack of transmission feature of the used electron microscopes, could not be strictly elucidated. The striae apparently represent internal boundaries of different optical density at which light is in part scattered and totally reflected and across which crystallographic continuity is maintained. What is seen is the optical effect and not the boundary itself. Examination by both polarizing microscopy and scanning electron microscopy does not clearly indicate the nature of the boundaries.

7.2.2 Uruguay-Bands

The agate structure which displayed the Uruguay-banding (horizontal banding) reveals a distinct texture from the concentric banding under both the polarizing microscope (fig.6.35 and 6.36) and the scanning electron microscope (fig.6.37). In fig.6.37, in microphotograph numbered as 01, loosely and closely bands with straight layers are displayed altogether. In fig.6.37, in microphotographs numbered as 02 to 07 the close

Uruguay-banding magnified gradually, in microphotographs numbered as 08 to 10 the loose Uruguay-banding magnified gradually are seen. Particularly in microphotographs numbered as 06 to 10, magnification up to x3620, it is arisen that the Uruguay-bands consisted of approximately homogenous in size, the silica grains and cavities. But, the dimensions of the grains formed the close and loose layers are different from each other. One of the important results is that the Uruguay-bands never included the fibre and consequently of this never the spherulites. So, it can be implied that they were real crystalline because of having the granular texture as seen under the polarizing microscope (fig.6.35). Otherwise, the distinctness of the layers are due to being more or less of the cavities. Because a different texture from those of the fibrous texture seen under the electron microscope are observed under the electron microscope (fig.6.35), it can be noted that the Uruguay-banding seen in the agates have a distinctly mechanism of the formation from the formation of the concentric banding.

7.2.3 Silicified Bars

Petrographic examination shows that the interior of the columnar bars which existed as inclusions in the agates with the barred structure in the andesites was filled with quartz crystals and solid chalcedony whereas their some parts lacked (fig.6.38 and 6.39). The texture seen in fig.6.40 signifies the irregular grown secondary silica grains and cavities. The vesicle seen in microphotograph numbered as 738 in fig.6.41 is the space left between the silica grains cause of growth irregularly. The interior walls of these vesicles are covered with granular silica, grape-like, as seen in microphotographs numbered as 736 and 735 in fig. 6.41.

7.2.4 Single Quartz Crystals

The central opening of the agates is often filled with coarsely crystalline quartzes. The coarse quartz crystals which filled the spaces between the concentric bands are shown under the polarizing microscope in fig.6.42. If the crystals are big and have the consummate shapes, they can be seen fairly clear even if low magnifications by the electron microscopy (fig.6.43). If the quartz crystals are smaller and they grown the

horizontal to the section plane, they are clear in high magnification by the electron microscopy (fig.6.44).

8. GEOCHEMICAL MECHANISM OF THE AGATE GENESIS

8.1 CRITICISM OF THE THEORIES RELATING TO THE ORIGIN OF AGATES

Although the agates and their occurrences have been known for thousands of years, essential hypothesises have only proposed for the last two centuries. Until the end of 1700's years, the proposed hypothesises were given in 'chapter three'. They can be coarsely arrayed as follows:

-Agate formation depending on rhythmic external events; infilled cavity theory, that depend on the rise and fall of the ground water table in the rocks.

-Agate formation depending on rhythmic internal events; that rhythmic precipitations of iron-pigments spontaneously produce banded structures in silica gel in cavities.

-Agate formation by transformation of solid silica.

-Agate formation as products of volcanic or post-volcanic processes; role of the critical temperature of water or aqueous solutions.

-Agate formations as intramagmatic product; syngenetic connected colloidal silica theory.

-Agate formation depending on internal rhythms in polydispersed colloidal system.

There are many theories about the formation of agates. These theories are not quite as diverse as the kinds of agate, and probably there is some truth to most of them. Most scientists have theorised that agates formed slowly, layer-by-layer, filling existing cavities such as the amygdaloidal cavities in volcanic rock (rhythmic external events). Some scientists say that the silica in solution must have come from surrounding rock. The

Liesegang theory supports the idea that the silica solution left a jelly-like mass in the cavity (rhythmic internal events). Some scientists explain that rhythmic flows of silica were deposited hydrothermal and that the silica did not come from the surrounding rock. Another group of scientists note that chalcedony can form at low temperatures from a liquid or a gel and that silica-rich water can seep in through the walls of cavities formed of porous rock. For the explanation of rhythmic structures in agates two concepts introduced by LIESEGANG; 'external and internal rhythm' are of fundamental importance (Landmesser, 1984). One of the new theories about the formation of agate is put forth by Shaub (1979). While earlier explanations accounted for the origin of agates as epigenetic, or formed in cavities after the solidification of surrounding rock, Shaub assumes that the agates are syngenetic, or were formed contemporaneously with the other rock in a deposit (intramagmatic). One of the enigmas for agate investigators has always been the prominent entrance and exit channels in many Brazilian agates.

Most studies involve banded agate or fortification agate and the agates distinguished by sagenitic, dendritic etc. A few ones have paid much attention to such strange agates as barred agate, tube agate. Scientist do agree that the many colors of agate are due to the infiltration of trace amounts of iron, and sometimes other minerals or elements, among them copper or nickel.

There seems to be no theory that explains all types of agates, since there are so many kinds of agate. Recently, careful, modern, scientific study, that included nearly all of previous theories, was expressed by Landmesser (1984) to elucidate agate genesis. The investigator examined all the important theories proposed since the middle of the 1800's years, and put forward why most of these theories do not hold up. In this and in

subsequent studies until 1995, Landmesser has been gradually enlarging on his ideas about the origin of agate and some of their phenomena.

8.2 THE MECHANISM OF AGATE GENESIS IN ÇUBUK (ANKARA) AREA

8.2.1 Hydrothermal Alteration and Solubility of Silica

When the settling position of the agates, their inclusions, and geological data obtained from the field observations are taken into consideration, we can say that the agates in Çubuk (Ankara) area were likely formed in a colloidal system at the stage following the hydrothermal alteration. The evolution of agate genesis can be elucidate with following explanations:

After andesitic (partially basaltic) lava flows in Çubuk (Ankara) area had spread in lacustrine basin, they became solid. Tension joints with NWW-SEE trend, and shear joints with NE-SW and NNW-SSE trends developed in these rocks due to stresses formed by the rhyolitic stocks. This cracked zone acted as a receiver to the stratiform agate aggregates with the characteristically barred inclusions.

Vesicles and cavities with various dimensions, some of them connectedly, in the contact zone of the rhyolitic stock with the andesite acted as a receiver to the nodular agate aggregates with rounded or irregular shapes, including moss-like or sagenitic inclusions, and crystal-lining cavity aggregates (agate geode).

Various hypothesises about the formation of agate specimens which were found in different region of the world conduced to elucidate the origin of the agates of Ankara region.

It is noted in some theories of agate genesis that the wall rocks including agates of igneous origin should become rhyolite and similar rocks which contain upwards of 75% or more of silica. One of the first requirements of the theories was to find a process that could yield a suitable cavity that was naturally produced in rhyolite and of a generally spherical shape, and the other was the richness of silica. In the other words, as the most important

factors that rhyolite took the most important place, the richness of silica and porousness (cavitation). Nevertheless, considering the geological history of the Ankara region during agate formation, main function of the rhyolite, in addition those of mentioned above, is due to hydrothermal alteration with the affect of water found in the environment and occurrence of some hydrothermal formed minerals. In the cracked zone of the andesites,

tremolite-actinolite $\rightarrow$ chlorite $\rightarrow$ silicified zeolite $\rightarrow$ chalcedony

zoning from the wall to the inwards was observed macroscopically and microscopically.

In the light of the geological observations, agate formation is the subject in mainly two different groups in Çubuk (Ankara) area. But, the difference mentioned here is not in relation to agate genesis, only is of the being found type depending on the surrounding rock of agates and of their structural varieties. Before the first group agates with the barred structure were formed in the cracked zone of the andesites, the secondary minerals such as tremolite-actinolite, chlorite and zeolite formed by hydrothermal alteration, were deposited in this zone. However, it is clearly understood from field observations that the hydrothermal alteration was an important factor at the beginning of agate formation, especially during the dissolving of silicates and transportation of silica.

We can array the evidences of hydrothermal alteration as follows:

The first one, hydrothermal alteration which yielded the zeolite, prepared the site of the characteristic barred agate structure of Ankara region. The second one, hydrothermal alteration helped us to obtain the data of environmental physico-chemical conditions (P, T, concentration etc.) of agate genesis. The third one, hydrothermal circulation made easy to specify the freely movement of compounds and ions which are important to arrange the environmental pH, or requisites during the dissolving, transportation, and accumulation of silica in agate genesis. The fourth one, hydrothermal alteration conduced to the weathering of stable silicates and alteration of them to be set free the required silica for agate formation. The fifth one, because of being found as vein-filling together agate and hydrothermal alteration products, the hypothesis concerning intramagmatic origin is disapproved. The sixth one, concentration of the colloidal silica was higher in hot aqueous solutions; so, hydrothermal circulation helped to both formation of colloidal silica and its transportation in colloidal form. The seventh one, external rhythmic event contended by

different investigators, was hydrothermal diffusive circulation for Ankara region; because the hydrothermal alteration and circulation were a beginning cause for agate formation in the area.

In construction of mechanism of agate formation: dissolving, transportation, and accumulation of SiO_2 are the subject. Principles of colloidal chemistry give a basis to investigate the complex behaviour of silica and can be applied to agate formation.

The weathering of silicate minerals in the rocks is formed in the result of a hydrolysis reaction; so, the weathering solution become alkaline or light acid. The silicate minerals such as amphiboles, feldspars, and pyroxenes were dissolved by both water (H_2O) and carbonic acid (H_2CO_3). The silica set free in the result of the hydrolysis of silicate minerals is represented in silicic acid (H_4SiO_4), but if silica was set free in high concentrations, some of silica could separate in colloidal form or as amorphous silica in solution. The pH of silicic acid-rich solutions is generally above 7, but below 10; because of the first dissociation reaction and constant of silicic acid like following:

$$SiO_2 + 2H_2O \rightleftarrows H_4SiO_4$$

$$H_4SiO_4 \rightleftarrows H^+ + H_3SiO_4^- \quad K = 10^{-9.9} \qquad \text{(Krauskopf, 1982)}$$

In the light of the graphics in fig.6.45, the solubility of silica at the whole pH range is very high in concentrated alkali region. In addition, crystalline silica, quartz, gives a solubility which nearly 6-7 ppm (fig.6.45); opal-CT, chalcedony etc. give a solubility which is between 6-130 ppm (fig.6.46); and silica gel also gives a solubility which is nearly 120-130 ppm (fig.6.45), at ordinary conditions (Barrer, 1982; Krauskopf, 1982). In other words, the solubilities at ordinary conditions imply differences in solubility between quartz and silica gel as extremes (fig.6.45-6.47).

The solution with silicic acid and a few colloidal silica is transported, finding itself ways in the cracked zone in the surrounding rocks by hydrothermal circulation, or diffuses into the closed cavities. If vein or vesicle cavities, and the environmental conditions become convenient to accumulate, the silicic acid dissolves as colloidal silica, that is;

$$H_4SiO_4 \rightleftarrows SiO_2 + 2H_2O\ ,$$

and then the colloidal silica precipitates as silica gel, on some places aiding by electrolytes. It is important note that "only the silica in colloidal form coagulates, the part in true solution remaining unaffected" (Krauskopf, 1982).

A colloidal system consists of two phases, of which one, the dispersed phase, is diffused in the other, the dispersion medium. Colloidal particles range in size between ions in true solution and particles in coarse suspension, the general limits being defined at 10^{-7} and 10^{-3} cm. The colloidal material may be solid, liquid, or gas, and can be dispersed in a medium of any of these same states. But, we are concerned essentially with solids dispersed in a liquid is called a "sol". In addition, a translucent solid formed the gelatine sol is called a "gel". Colloidal silica particles adsorb anions and become negatively charged, that is sign of charge on colloidal silica particles is negative. Since the silica particles of the sol all have the same charge, they repel each other and prevent coagulation. If an electrolyte is added to the silica sol, the colloidal particles become neutralized and flocculate or deposit. A striking characteristic of silica colloids in the form of a gel is the developed of colored diffusion bands when an electrolyte is allowed to diffuse into the silica gel.

In conclusion, the water is a agent which can not be given up for dissolving, transportation, and accumulation of silica. Because the water is a very important factor to be arranged the environmental conditions such as P-T, pH, concentration in the agate forming systems. However, it was noted that the critical-point of water (374°C) was not essentially important in agate formation (Landmesser, 1988 b). Another note, the concentration of colloidal silica in the original hot water is high than the cold surface water (up to about 350 ppm at 90°C; Krauskopf, 1982); therefore, the environment where hydrothermal solution circulated plays an important role during agate genesis; because the silica formed the agates is colloidal silica scattered into solution by dissection of silicic acid. We can strongly specified that the materials that are cryptocrystalline, that commonly occur with botryoidal or reniform or mamillary outer surfaces, that display indistinct color banding are often assigned a colloidal origin.

Figure 6.47 Graphics shown solubility of SiO_2 in water. Lower line signifies the solubility along the three-phase line (vapour, liquid water, quartz) under autogenous pressure whereas one is at 1000 atm. (from Barer, 1982).

8.2.2 Formation Mechanism of the Studied Agates

Hydrothermal activity occurred in two different periods in Çubuk (Ankara) area. During the first activity, tremolite-actinolite, chlorite and radial grown zeolite (scolecite) which are the hydrothermal alteration products were formed in the cracked and vein zone in the andesite and basalt. The second hydrothermal activity composed after the rhyolitic dyke had pushed out conduced to the agate formation in the zone in which the preformed hydrothermal alteration products existed in the andesites, in cooling crevices and gas cavities in the rhyolites. Likewise hydrothermal circulation continued during agate formation. During the first circulation, the radial barred crystals (scolecite) were fully replaced by silica (fig.6.1 and 6.2) and covered over with tiny chalcedony layers (fig.5.5).

During the second and so continue others, chalcedony were deposited as compact masses coating cavity walls in banded layers, from a fraction to several millimetres or more in thickness, until all space was filled with it (fig.5.6). Close examinations show that the seemingly solid layers are composed of multitudes of tiny fibres, all growing away from the walls. It is not possible that the silica-bearing solution formed the agate at one time.

Because it is impossible that quantity of silica transportation in a siliceous solution existed in concentration or content sufficiently to fill the interior of cavity or fissure vein. And so, it should not be thought that the agate as a whole was formed in the result of only

one circulation. The outstanding evidences which show that the siliceous solutions were transported in hydrothermal circulation, are the silicified zeolite (scolecite) crystals in the cracked zone of the andesites, and the formation of sagenitic or moss-like silicate structures in the cavities of the rhyolite. Other important point is also that this circulation was not intermittent, but was continuous until the end of agate formation. In conclusion, it can be connoted that the hydrothermal circulation provides the transportation of siliceous and electrolyte required for the agate formation, and for the formation of different agate structures in adjacent cavities, changing the parameters of the solution in the cavities which acted as a receiver.

Agate-forming silica was set free in consequence of the hydrothermal alteration of the silicate minerals in the surrounding rocks (andesite, basalt, tuff etc.). Most of the dissolving silica are represented as silicic acid in the solution, a few of it also as colloidal silica, and transported. In the region, these siliceous solutions percolate into the tension and shearing zone with the specified directions in the andesites, and into the cooling crevices and gas cavities in the rhyolite, to form the agates.

The most plausible as the medium in agate formation is the colloidal silica system in existence of hydrothermal circulation. It is possible that the colloidal silica has in different sizes. But, infinitesimal and bigger colloids can not stable together in the same pH gap in the same solution. When the alkalinity and concentration of the sol are higher, infinitesimal colloids coagulate, whereas bigger ones coagulate when the alkalinity is lower (or slight acid) and the concentration of the solution decreases. But, this separation validates for the colloids with certain dimensions differences. Otherwise, it is possible to be in different sizes with each other even in both groups. Therefore, every colloid system has an exceptional character and produces various structures even under the same conditions. Because of this character of colloid systems, both it is impossible that agates produce as synthetic and also every agate block or nodule shows the various patterns. In conclusion, agates reflect the characters of the colloid systems. The agates of Çubuk (Ankara) area 118

were also transported and deposited as colloidal that aggregated and crystallized shortly after deposition.

Beside of the hydrothermal activity, the temperature, pressure, pH and concentration are the important agents in agate genesis. In general, agates are formed at the values of temperature between 100-200°C. Lower values such as at the values below 100°C, the growth of agate or quartz is not possible generally. The material formed at the values of 100° C is opal. If at above 200°C, quartz filling the spaces in the agates crystallised as drusy crystals. During agate formation, diffusion of silicic acid molecules in the sol is very important for transportation and precipitation of silica. The amount of concentration of silicic acid required for this kind of diffusion is destroyed in temperatures above 200°C, and quartz crystallises rapidly (Landmesser, 1992). Therefore, the formation of cryptocrystalline silica (agate) is not possible above 200°C. Extrapolating from this hint, the theories that assumed that critical value of the water was effective during formation of agate bands can be repudiated (Landmesser, 1988 b). Pressure is not an essential factor in agate genesis.

Pressure value near surface conditions is enough. The formation at low pressure of secondary products such as chlorite, zeolite, which associated with agate may be a reference for agate genesis. But, it is already impossible to give definitely pressure values for agate genesis. Infinitesimal silica colloids (smaller than 1 micron) coagulate generally when concentration is supersaturated. The concentration should decrease so that bigger particles (granules) or crystals can be formed. With decreasing of the concentration, the stability boundary required for infinitesimal particles becomes to be passed over, and by re-dissolving of a few particles, the others compose the bigger particles or crystals. The concentration or solidification temperature being enough to be formed a large crystals is not enough to be formed the smaller particles than 1 micron . If the concentration rises or temperature reduces, infinitesimal particles will be formed. Because dissolution temperature of the infinitesimal particles is lower than those of bigger ones. In conclusion, the type of crystallization depends on the temperature and concentration. With the most probability, in the case of the crystallization of a supersaturated solution, cryptocrystalline or tiny crystallises are formed. In the case of formation of agate's bands, values below pH of 10 are the subject, generally between 6 and 9.

In the light of geological and optical findings and also geochemical principles, formation of various structures (banding and inclusions) can be specified as follows:

Concentric banding: When the silicic acid-rich-solutions (together with a few colloidal silica) reached to the suitable environments (fissure vein cavity by percolating, gas cavity by diffusion) for agate formation, and when silicic acid riched in concentration, they set free the silica in colloidal form until the equilibrium solubility is reached, according to the following reaction;

$$H_4SiO_4 \rightleftarrows SiO_2 + 2H_2O$$

From a supersaturated solution silica does not crystallise, but forms a sol. The concentration of dissolved silicic acid comes to the equilibrium value. The concentrated sol precipitates a uniform gel and the remainder of silica stays suspended as colloidal particles. The gel which consists of colloidal particles becomes light and solidifies on the wall of cavity to make room for the newly supersaturated sol. These particles grow up as radial fibres during the parameters of the sol remained firm. These fibres microscopically form the spherulites of chalcedony or quartzine, or in the some cases the parallel-fibre zones. Infinitesimal particles which formed the fibres and hollows which remained between them are heterogeneous in size, that is, they have not the same dimensions. This feature refers the spongy-porous texture seen with the scanning electron microscope. These hollows come equivalent to cavities left which a few of the precipitated silica went back into the solution on standing.

As the array at perpendicular direction to the fibre elongation formed from alternating of infinitesimal particles and hollows, and bigger grains and cavities will refract and reflect of light in different ratio, this phenomena reveal contingently the banding with the shades of the same color (fig.6.33). Sometimes deeply striations form at the zones which separated the narrow bands (fig.6.34) and the pigments which diffused into the gel may constellate in these zones. At interface which the fibre sectors terminated (fig.6.32), nucleations which will form the newly spherulites are form. But, in this nucleation region, microscopically large cavities arise due to becoming at a distance from each other of the

nuclei (fig.6.32). Thus, disparity between dimensions of the cavities in interfaces and in fibrous aggregates arise macroscopically the wide banding in the agate (fig.6.30).

Various pigments, chiefly iron may diffuse into both cavities in the interfaces and striae running at the perpendicular direction to the spherulitic aggregate (fig.6.34). These pigments are cause that both the narrow and wide bands are seen clearly, and also different colored bands arise.

In early studies, the role of Fe, Sb, Zr, Na and K elements was determined in coloration of quartz and chalcedony (Hatipoğlu, 1988). Next, Na and K elements were determined even in both natural and synthetic colorless rock crystal (Hatipoğlu,1988). Frondel (1978) specified that foreign elements running at the right direction to the chalcedony fibres existed. Landmesser (1984) demonstrated the sites where Fe elements was present between agate bands. Sukow (1987) proved that in the Lake Superior agates, Cu compounds existed and they were affective in the formation of colored bands.

In conclusion, we can express that the concentric banding of Çubuk agates consist of spherulitic or, on same places, parallel arranged radial fibres, and these fibres were formed in a gel-stage. We can imply that the fibres are not single crystal because of their inclined appearances.

Uruguay-banding (horizontal-banding) : This banding in the agates display the different appearances as macroscopically, polarizing and scanning electron microscopically than the concentric banding. This phenomenon can be shortly explained with the precipitation of relatively coarse silica grains as horizontal by gravitation.

The electron optical morphology of the Uruguay-bands resembles a colloform texture which might form from both true solutions and sols (fig.6.37). It may be proposed the term “hemicolloids” for solution that are intermediate between true and colloidal ones. The cryptocrystalline, whitish, clay-like form of the Uruguay-band was almost certainly deposited as a colloid.

In Çubuk area, the coarse silica grains grew directly as minute druses of continuously euhedral crystals that projected into the true solution. These silica grains set free, then, were horizontally precipitated at the bottom of cavity by gravitation. We can say that this banding was formed in dilute watery silica solution under near-surface conditions.

Crystalline quartzes: The cryptocrystals that form along the walls of an open vein or cavity are usually fine-grained, probably because of heat loss to the wall rocks and consequent rapid crystallization. Conversely, crystals that form in the centres of such spaces are inclined to be coarse and probably form from more dilute.

If the temperature of the sol rises above 200°C and the concentration of dissolved silica in the sol falls below the level necessary to sustain a colloid of sufficient viscosity to promote spherulitic aggregate, quartz crystals begin to occur.

Inclusions with radiating structure: These are radial grown bars with two different origins in the agates in Çubuk (Ankara) area; the bars of zeolite (scolecite) which was radially grown and then completely replaced by silica, in the agates found in andesites, the silicate growths stalactite-like signifying moss-agate in the agates found in the rhyolites. Subsequent their formation mechanism are also different.

The first one: The individual inclusions in the barred agates found in the fissure zone of the andesites are doubtless of replacement origin, formed after the andesite solidified by silica-rich solutions circulating through it. While the silica-rich solutions are circulating along the fissure zone of the andesites, they meet to pre-existing radial zeolite (scolecite) crystals in this zone. Siliceous precipitate which left on them begins to replace the zeolite, often preserving original framework of it with marvellous fidelity. As similar to natural geologic samples like that wood is petrified by silica or chert replaces other rock, minerals preserving original textures and structures; also here the zeolite is replaced. Details of the replacement process are obscure. In addition, on the surface of replaced zeolite crystal with radiating structure, there are the adjacent surfaces (visinal) which grown parallel to its long axis. These visinal surfaces become clear as generally parallel cords (fig. 5.5).

The second one: The tubiform inclusions in the agates found in the cavities of the rhyolite are of particular growth origin. Moss-like or sagenitic growths are formed from SiO_2 gel including alkali-silicate, if the metal-saline solutions reach to the alkali-silicate solutions, these tubiform silicate growths develop (fig.5.42). In Ankara agates, whereas

these silicate growths can be formed alone, they can develop around of the zeolite bars. After the growth forming the moss-agate structure, the interior of the cavity is filled with chalcedony as solid, concentric or Uruguay-banded, if the silica-rich solution presents in appreciable amounts, completely; if not, partially.

CHAPTER SEVEN

CONCLUSIONS

Agates were the first in the world found in India and Anatolia according to agate object which were found in the archaeological excavations made in these places although some people have claimed that the first gravels of agate were found in the river Achates in Sicily, given its name to agate.

There are many theories about formation of agates. Nineteen numbers of those proposed until the last two centuries were summarised. These theories are not quite as diverse as kinds of agate, and probably there is some truth to most of them. But, there seems to be no theory that explains all types of agates since there are so many kinds of agate.

The northern part of the town Çubuk in Ankara where agates have widely obtained was investigated as geologically. Generalised stratigraphic columnar section of the investigated area without scale, geological map and its cross-sections, in 1 /25000 scale were made and named without any discipline. In the study area, the oldest unit consists mainly of schists and meta-greywackes of Palaeozoic age, called “basement rocks”. These are unconformably followed by sedimentary rocks of Mesozoic age, with melange feature, called “mixed series”. Upon these units are the Miocene (Neogene) aged “volcanic sequence” available its unconformable tuffs, pyroclastic materials, intermediate and basic lava flows (andesite, basalt) and acidic stocks (rhyolite, dasite) which cut those rocks. Next sequence upon these with an unconformity is the “sedimentary sequence”. Pliocene aged, consisted of slightly consolidated conglomerate with lava, limestone and sandstone gravels, and limestone, sandstone. Finally an alluvial cover of Quaternary age takes unconformably place upon these.

The agates in Çubuk (Ankara) area were mainly found in two types of surrounding rocks : 1) Andesite (basalt), and 2) rhyolite. After andesitic and basaltic lava flows had become solid, tension joints with NWW-SEE trend, and shear joints with NE-SW and NNW-SSE trends developed in these rocks because of stresses formed by the acidic dykes arose by the igneous activity. This fissure zone acted as a receiver to the stratiform agate

aggregates with radial, pseudomorph, crystalline bars, and other siliceous occurrences. These agates have been particularly and first called “barred agate”. The agates with these individual inclusions have been only found in Ankara region in the world. Cavities and cooling crevices that had various dimensions in the contact zone of the rhyolites acted as a receiver to the nodular agates with rounded or irregular shapes, moss-agates and crystal-lined cavity aggregates.

In Çubuk (Ankara) area there happened alterations and replacement. By hydrothermal activity in the fissure zone of the andesites, tremolite-actinolite, chlorite, and zeolite mineralization developed from the wall to the centre. The mineral zeolite grew in the vein as radiating bars. But, during agate formation, these crystals were replaced by silica, preserving their original framework. As a result of the examinations done to identify the zeolite, it was concluded that this mineral was most probably “scolecite”.

During this study, the textural characters of two main bandings (concentric and Uruguay) and inclusions found in the agates were denoted, and the results of macroscopic, petrographic and electron microscopic observations were compared. It is understood that explanation of the formation of the banding according to macroscopic, and even to polarizing microscopic observations gives often rise to wrong results. The most correct result was obtained with electron optical observations.

When the geological formation types of the agates in Ankara region were taken into consideration, theoretical morphological characters predicted by various hypothesises of agate formation for the specimens found in different regions of the world conduced to elucidate the origin of the agates of Çubuk (Ankara) area. When the structures in agates, such as various bandings and inclusions in this area are considered, we can assume that the agates were likely formed in colloidal silica system at the stage following the hydrothermal alteration. By the agate formation, dissolving, transportation and accumulation of silica

and principles of the colloidal chemistry had played a fundamental role.

Hydrothermal circulation provides the transportation of siliceous solutions and electrolytes required for the agate formation. Beside of hydrothermal activity, the temperature, pressure, concentration and pH are the important agents in agate genesis. The

agates of Çubuk (Ankara) area were formed at the values of temperature between 100-200°C and of pressure near surface conditions. The pH was also for agates generally between 6-9. The concentric banding in the agates consists of spherulitic or parallel arranged radial fibres, and these fibres were formed in a gel-stage. The fibres are not single crystals because of their inclined appearances. The Uruguay-banding can be shortly explained with the precipitation of relatively coarse silica grains as horizontal by gravitation. The individual inclusions in the barred agates found in the fissure zone of the andesites in Çubuk (Ankara) area are doubtless of replacement origin. The tubiform inclusions in the agates found in the cavities of the rhyolite are of particular growth origin. These moss-like or sagenitic growths are formed from silica-gel including alkali-silicate.

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