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# PYRITE OCCURRENCES NEXT TO THE ATTEPE IRON DEPOSITS, FEKE-ADANA, TURKEY

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ABSTRACT. _ The pyrite occurrences described in this paper are located in the lowest section of Infracambrian sequences situated along the eastern border of the Attepe iron ore deposit in the Mansurlu District of Adana. The pyritic formations represent two different mineral parageneses. The dominant group is represented by thin pyrite layers and pyrite-bearing carbonate layers alternating with dark gray to black colored carbonaceous shales and phyllites, whereas the second group is found in siderite veins associated with fahlore. Sedimentary pyrites occurring mostly as small massive layers, lenses, isolated single crystals, diagenetic injection drops, defined in this study, and veins exhibit typical sedimentary and some distinctive geochemical features compared with the other. Their depositional and diagenetic features indicate a mode of sedimentary formation of pyrites under reducing conditions during the Infracambrian. On the contrary, pyrites in siderite veins having quite varying amounts of minor elements such as Cu, As, Sb, Co, Se and Hg when compared to the sedimentary pyrites, must have formed as a younger generation by an epigenetic process between post Cretaceous and Paleocene.

Key words: Pyrite occurrences, sedimentary and hydrothermal origin, geochemistry, Eastern Taurus, Turkey.

## INTRODUCTION

The Attepe iron ore deposit, situated in the northern part of Mansurlu Village near Feke, Adana, is the second biggest mineable iron deposit in Turkey (Fig. 1). The pyritic rocks of Infracambrian age occurring along the eastern boundary of this deposit have been studied in detail.

The aim of this study is to examine the pyritic formations appearing either stratiform or as veins and to elucidate the occurrence of sedimentary pyrites. For this purpose, first of all, a geological map of the Attepe District was prepared, and later hand specimens taken from the pyrite-bearing rocks and their hostrocks were analysed geochemically and studied mineralogically.

## GEOLOGICAL SETTING

The Attepe District, situated in the western part of the Eastern Taurus belt, is represented by rocks of the lower section of the autochtonous Geyikdağı tectonic unit. The exposed rocks of this unit ranging from Infracambrian to Middle Cambrian in age have been subdivided into three lithostratigraphic units, the Kandilcikdere, Attepe and Çaltepe formations (Fig. 1).

Horst and graben structures along two main faults striking in a NW-SE direction were developed in a tensional regime, most likely during Mesozoic time. On the other hand, all rocks were subjected to the low grade metamorphism of the greenschist fades.

The Kandilcikdere Formation has been described here, as the pyritic levels are confined only to this formation. It is composed mainly of dark gray and black shales and phyllites. It is now almost entirely exposed due to a mining operation carried out in the eastern section of the Attepe iron deposit, and the best exposures lie along the edge of the northern horst block (Fig. 1). Because of faulting, its base is unknown. It displays a limited lateral extension with a thickness of 80 m., and is overlain conformably by the Attepe Formation.

Shales and phyllites were partly folded and, in places, faulted and fractured. In these pelitic rocks, typical samples of synsedimentary and diagenetic structures such as lamination, loadcast and geopetal structures are common. Some of the lenses, boudinage and flow structures are related to the late diagerretic and subsequent metamorphic processes. Pelitic rocks composed of mainly sericite, quartz, feldspar, chlorite and opaque minerals have been described as shale, phyllite, quartz phyllite and sericite-quartz phyllite.

No fossils have been found in Kandilcikdere and Attepe formations yet. Consequently, a relative age of Infracambrian is given for these formations, which are unconformably overlain by the Lower-Middle Cambrian Çaltepe Formation.

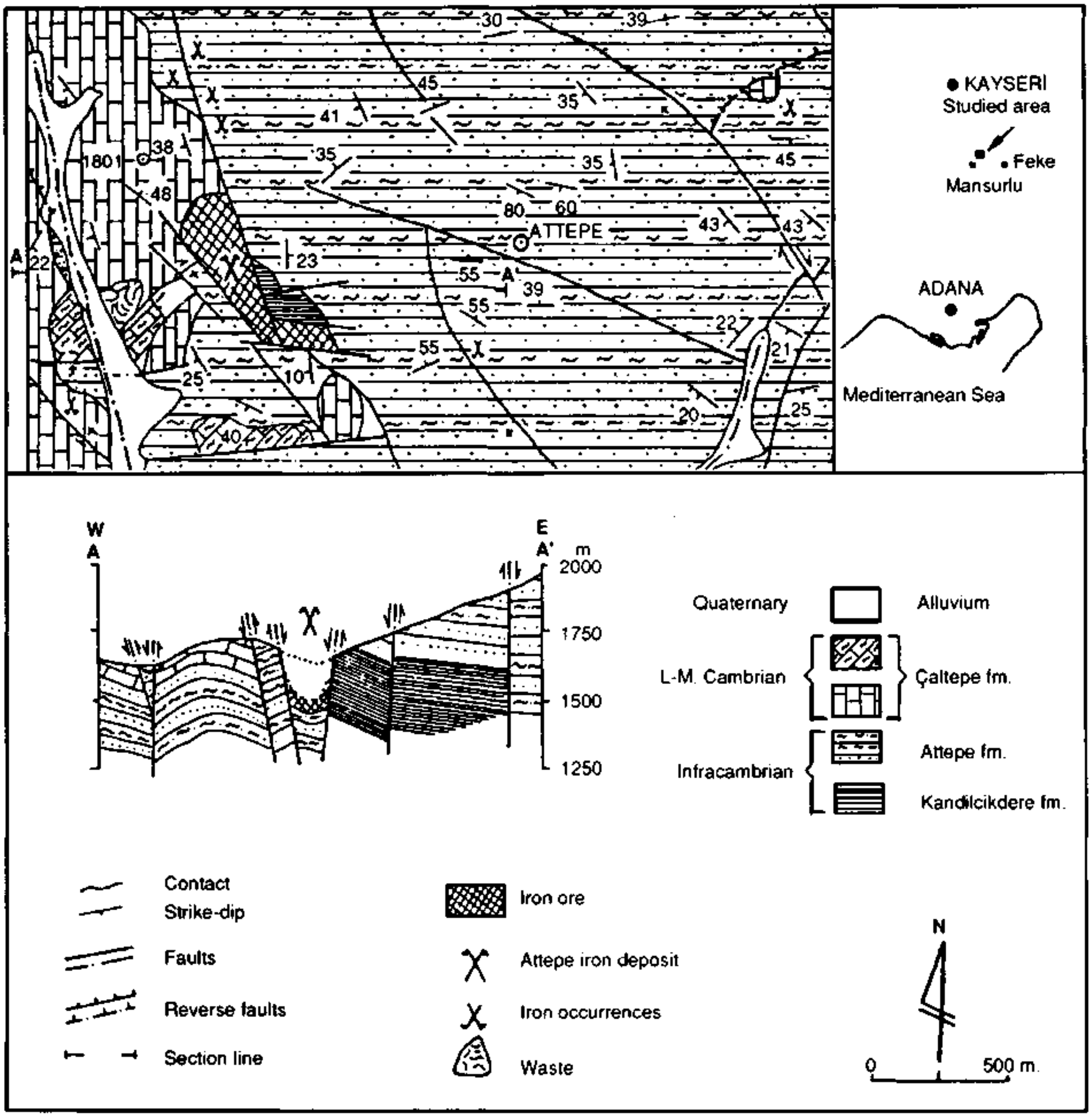


Fig. 1 - Geological map and cross-section of the study area. Scale is the same for both.

## FIELD OBSERVATIONS

In the study area, there are two groups of pyrite occurrences in the shales and phyllites of the Kandilcikdere formation: Sedimentary pyrites, and pyrites in the siderite veins. These are differentiated on the basis of ore geometry, relationship to hostrock, mineral paragenesis and some synsedimentary features.

Sedimentary pyrites occur mostly as layers, groups of laminae, lenses, diagenetic injection drops and veins, individual grains in "disseminated" patterns (Fig. 2). Almost all pyrite-bearing layers and laminae of a few mm to 5 cm. in thickness alternate with the hostrocks. Black layers with high amounts of organic material contain, in most cases, fine-grained, disseminated pyrite crystals. On the other hand, light gray layers composed of mostly calcite have more coarse-grained pyrite.

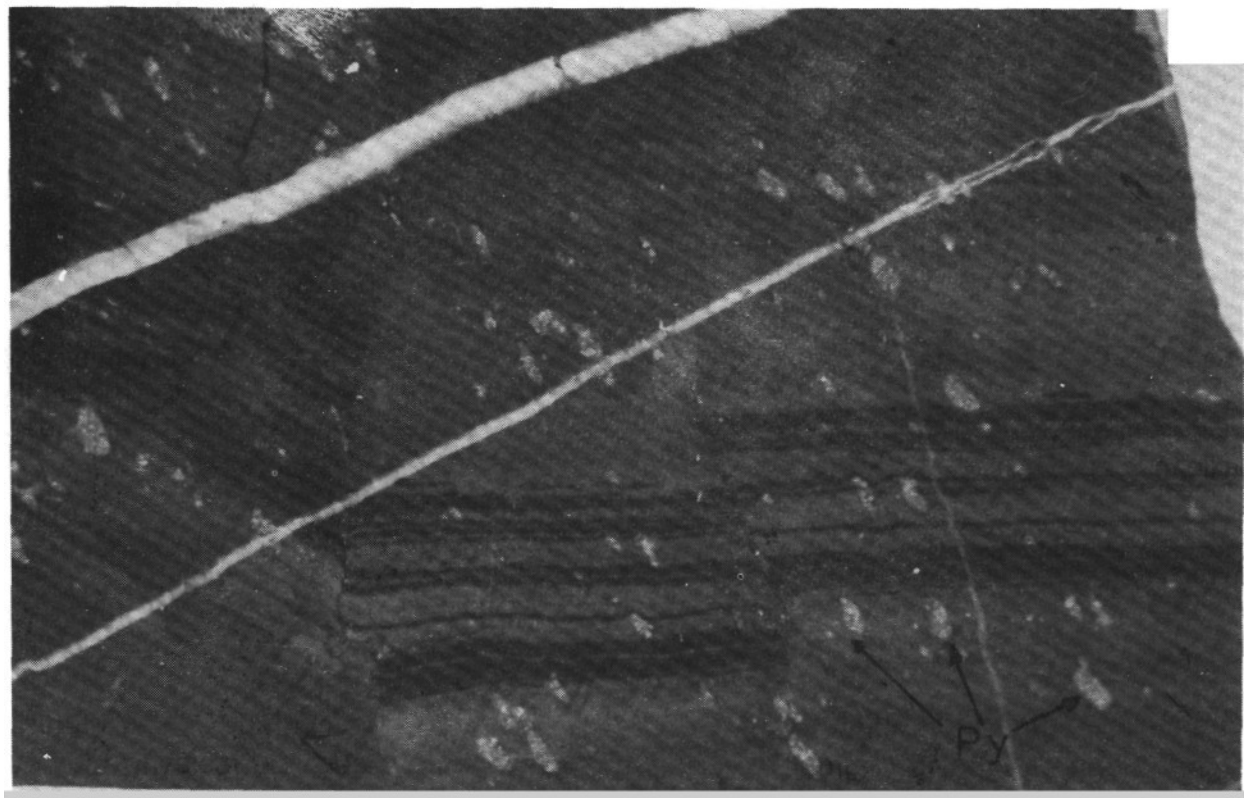


Fig. 2 - Relations between pyrite-bearing laminae and injection drops in shale.

Although some of the pyrite-bearing layers or groups of laminae show bedding, others appear disturbed so that the bedding is partly obliterated by the syndepositional and syndiagenetic deformation processes. In addition, all of the rocks have undergone low grade metamorphism and tectonism.

The pyrite-bearing rocks display many sedimentary features such as bottom to top features, rhythmicity, microcross-lamination, slump folding, diagenetic load casts, lenticular bedding, various other geopetal fabrics, plastic deformation fabric and diagenetic fissure fillings.

A typical feature of all pyrite-bearing layers is their distinctively shaped lower and upper surfaces. Most of the lower surfaces of most layers or groups of laminae are irregular. These are the result of submarine currents and load cast formation. Continuous or occasional submarine currents and compaction periods must have caused mechanical and partly chemical errosion on the yet hydroplastic mud like beds and laminae. This may be the reason of the irregular nature of their lower surfaces. Such curved surfaces were progressively deepened through the loading effects of the overlying sediments such as intensive pyrite accumulations. The overlying laminae were placed both unconformably and conformably on the underlying pelitic constituents, where some pyrite assemblages have a lateral and vertical graded bedding through carbonaceous pelitic and carbonate materials.

Laminated portions of pelitic rocks containing pyrite grains of variable size show differently shaped microfolds. These microfolded laminae imply a deformation stage connected with lateral gravity vectors and horizontal compression (Zimmermann and Amstutz, 1964). All primary depositional structures have undergone, to a certain degree, some diagenetic-tectonic processes.

Late calcite veins crosscutting the earlier structures indicate two stages of tectonic activities and calcite fillings. Diagenetic vein fillings are easly distinguishable from post diagenetic cracks and fillings, which cut earlier structures and layers over considerable distances.

## PETROGRAPHICAL STUDIES

### Sedimentary pyrites

Individual euhedral pyrite grains are widespread especially, in black shales, but in most cases they form coarse-grained crystals in calcite-rich portions of shales, diagenetic injection drops and vein fillings. Most of the pyrites are euhedral to subhedral. They appear dominantly as cubes and, to a lesser degree as pyritohedral and octahedral forms illustrated by Love and Amstutz (1966), and, Zimmermann and Amstutz (1973). Their grain size ranges from 20 m to 2 mm. Some of the large euhedral pyrite grains were replaced by calcite along crystal surfaces and show a remarkable zonation. The etching tests and different reflectivity values of pyrites reveal such zonation, being a result of overgrowth on the previously formed pyrite grains (Fig. 3). Their central parts contain numerous inclusions and replacement products of gangue materials and opaque minerals such as pyrrhotite, chalcopyrite and sphalerite, whereas most of their zoned peripheral portions are quite pure. This case indicates the presence of different stages taking place during diagenesis. These are more likely diagenetical overgrowths. However, they could also form by the gradual transformation of depositional pyrites to euhedral pyrite grains. A similar formation mechanism of pyrites was described by Udubasa (1984) for the iron sulfides in the black shales from Romania.

Framboidal or ring-like pyrites were observed either in the voids of massive pyrite populations or in very few laminae including populations of carbonate intraclasts, tiny individual pyrite grains, detritic quartz, zircon and tourmaline grains. The nuclei of these spheres are represented mainly by fragments of quartz and pelitic rocks as well as by leucoxene. Pyrite rings are composed of tiny, euhedral pyrite crystals with a grain size of 0.1 mm. Their crystal habit is more frequently cubic. Since the aforementioned-spherical forms occur in the same horizon with detritic minerals such as quartz and zircon, they could be related to the submarine currents caused to develop an envelope of pyrites around nonpyritic materials by rotational movements. The pyritic portions have undergone subsequently a diagenetic recrystallization which is connected with the burial grade varying from shallow to deep.

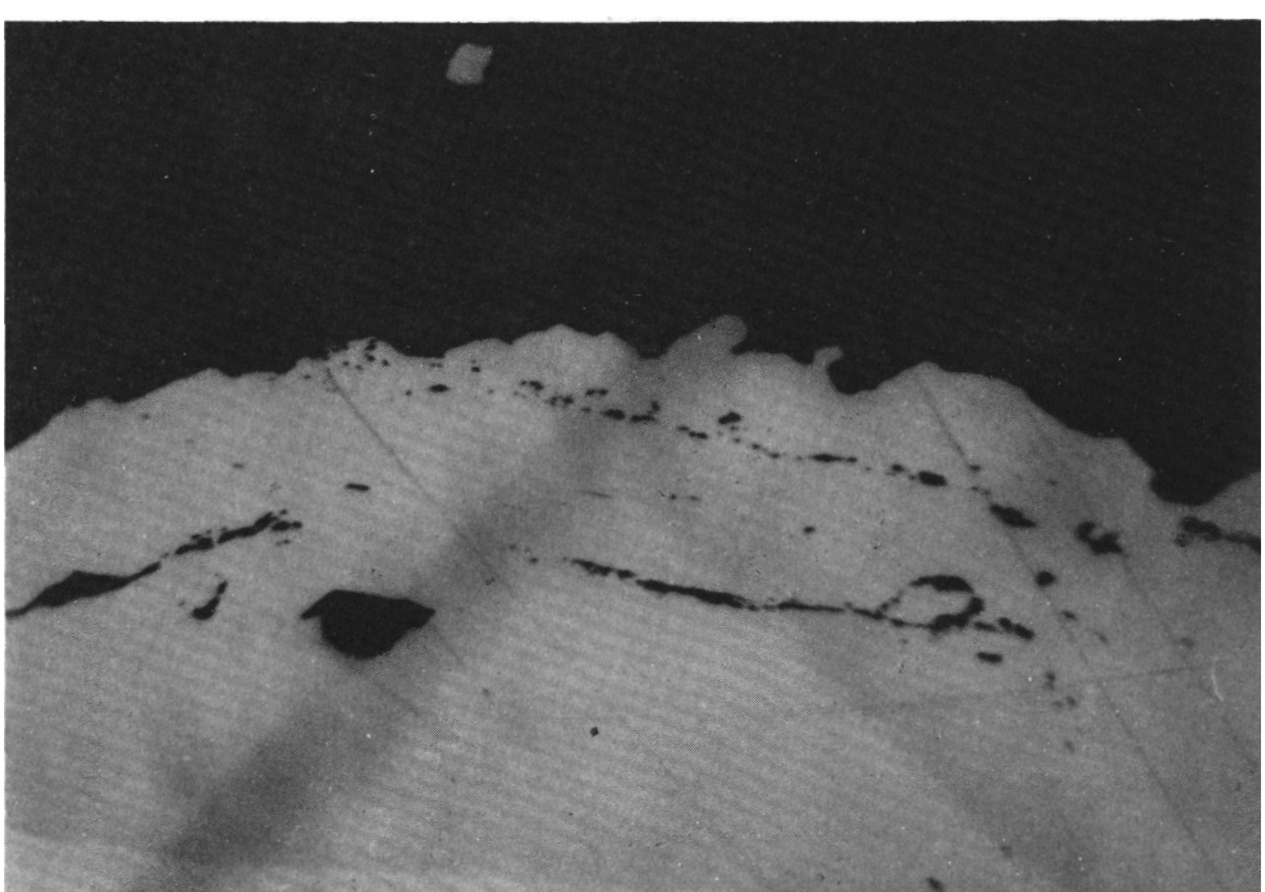

Fig. 3 - Zonation of pyrite crystals. Polished Section, //N, 32 X, in immersion oil.

The great amounts of framboidal pyrites formed between densely packed large euhedral pyrite grains, which grew during diagenetic recrystallization (Fig. 4). Pyrite spheres range from 50 to 200 m m. Their external outlines are relatively even. Microcrysts of pyrite spheres are euhedral to subhedral in habit. They are mostly loosely packed and originated through progressive modification of a colloid of iron monosulphide associated with an organic component into a sized sphere (Kalliokoski, 1965; Love and Amstutz, 1966; Chauhan, 1974).

Pyrite veins and diagenetic injection drops associated with calcite exhibit some explicit characteristics. Pyrites found near the wallrock occur not only as large single euhedral crystals, (Fig. 5) but also as twins and polycrystals packed closely in the sense of Love and Amstutz (1966). They are oriented partly parallel to the long axes of veins. But some euhedral pyrites are irregularly grown on the wallrocks.

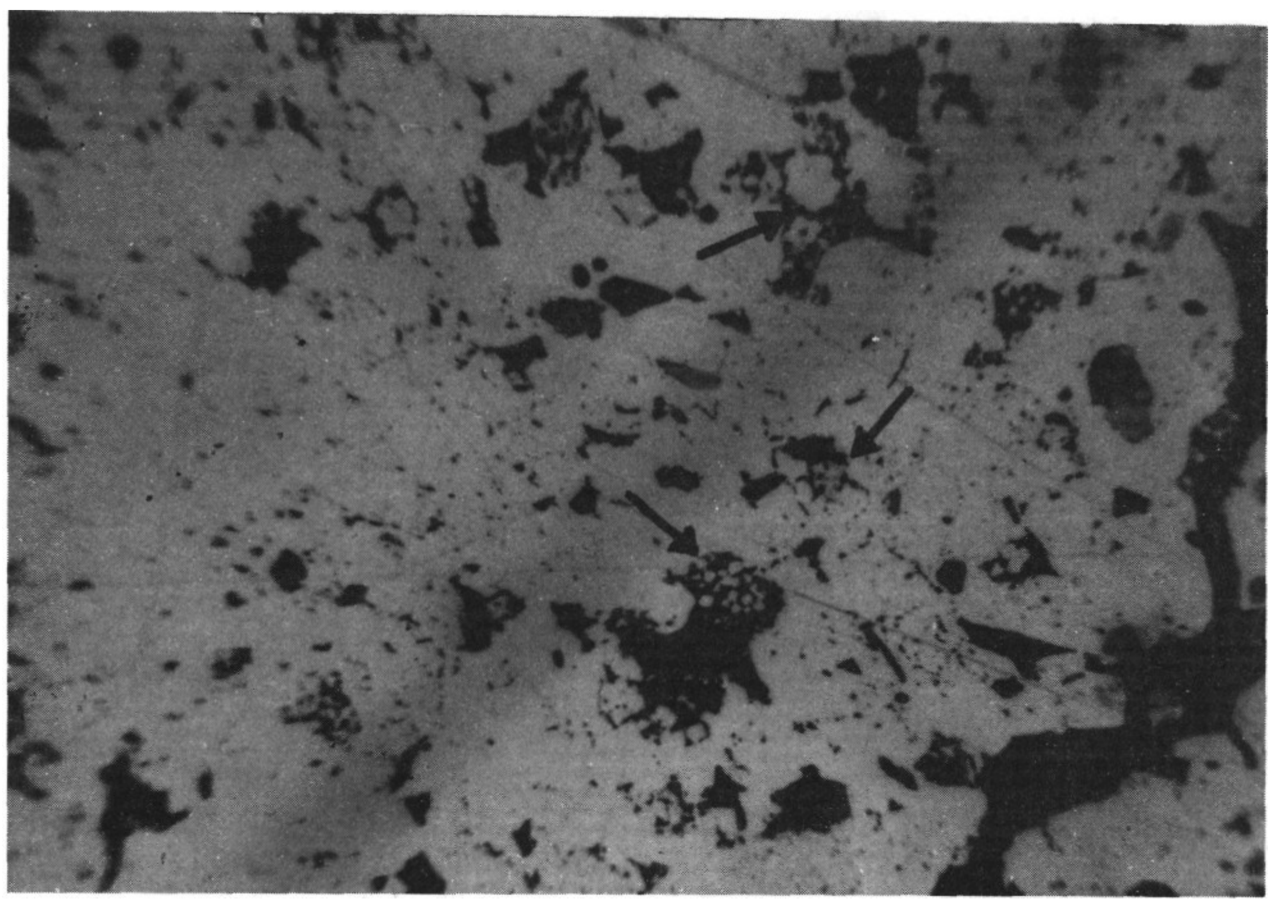

Fig. 4 - Framboidal pyrites (mostly at the center) in the gangue minerals between euhedral pyrite crystals. Polished section, //N, 32 X, in immersion oil.

Drop-like forms defined for the first time in this study are essentially precompactional features, because they do not cut cross shale laminae, and laminated carbonaceous shales found above or below these injection drops give rise to a geopetal fabric. Thus, it is considered that iron-bearing solutions migrated into syntectonically formed deformation places during an early stage of compaction. In contrast to these, pyrite veins cut across all laminae during the postcompactional stage.

Although this region has undergone low grade metamorphism, possibly during the Mesozoic (Küpeli, 1991), numerous examples of depositional or early micro-structures were preserved in the pyrite occurrences. According to McClay and Ellis (1983), such structures can be preserved during metamorphic grades up to the mid-upper greenschist facies.

Carbonaceous laminae contain very frequently tiny dispersed pyrite grains arranged conformably to the general strike direction of laminations and foldings. There is a close relation between the above-mentioned laminae and overlying large individual pyrite crystals creating load cast structures (Fig. 6). According to Chauhan (1974), these are diagenetic load casts in which the underlying still hydro-plastic laminations are pressed down due to the force of growing crystals and their higher specific gravity. Fine pyrite crystals in the shales are thought to have formed post depositionally during early diagenesis (Schieber, 1985).

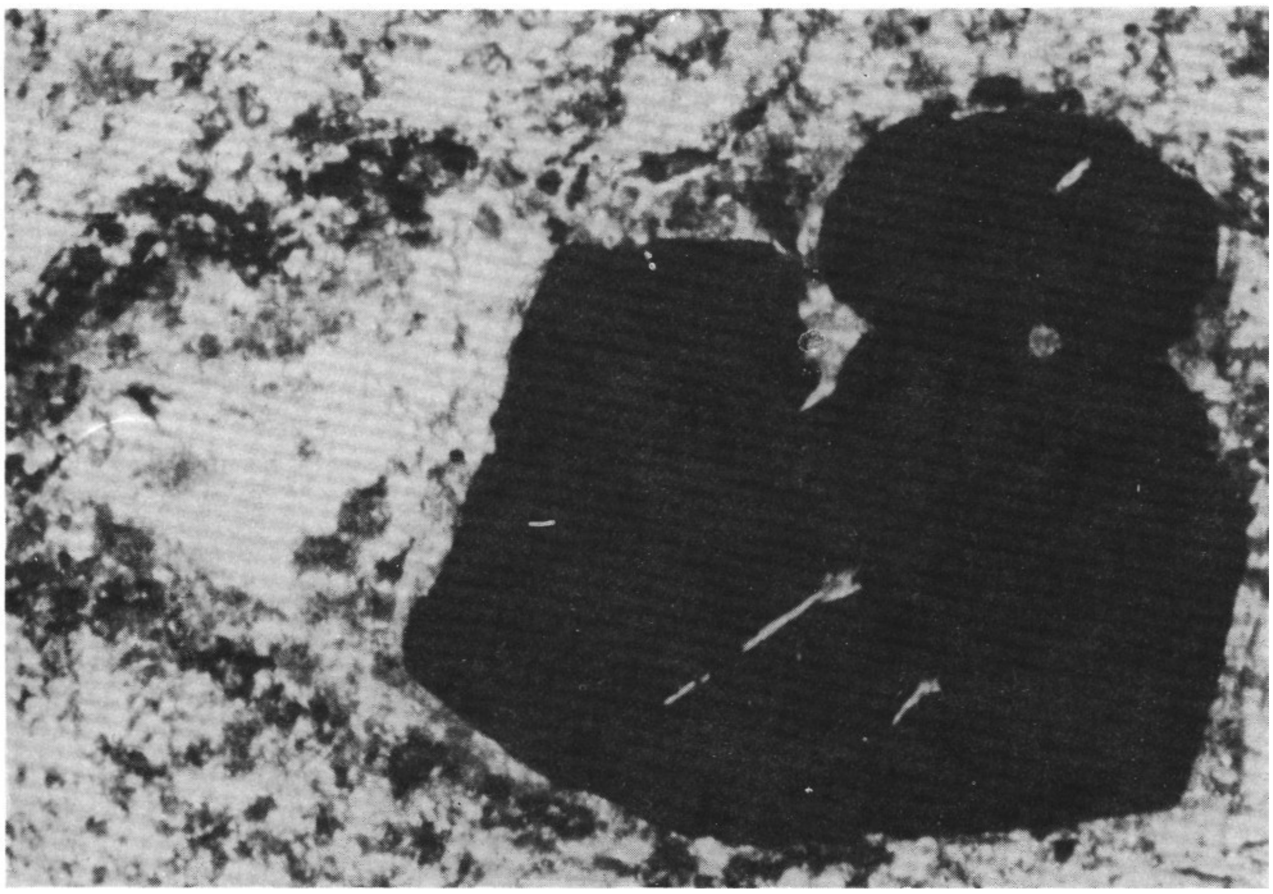

Fig. 5 - A view of a diagenetic injection drop, Pyrites (Black, at the right half) and calcite in fillings (White, in the left half). Thin Section, //N, 6 X.

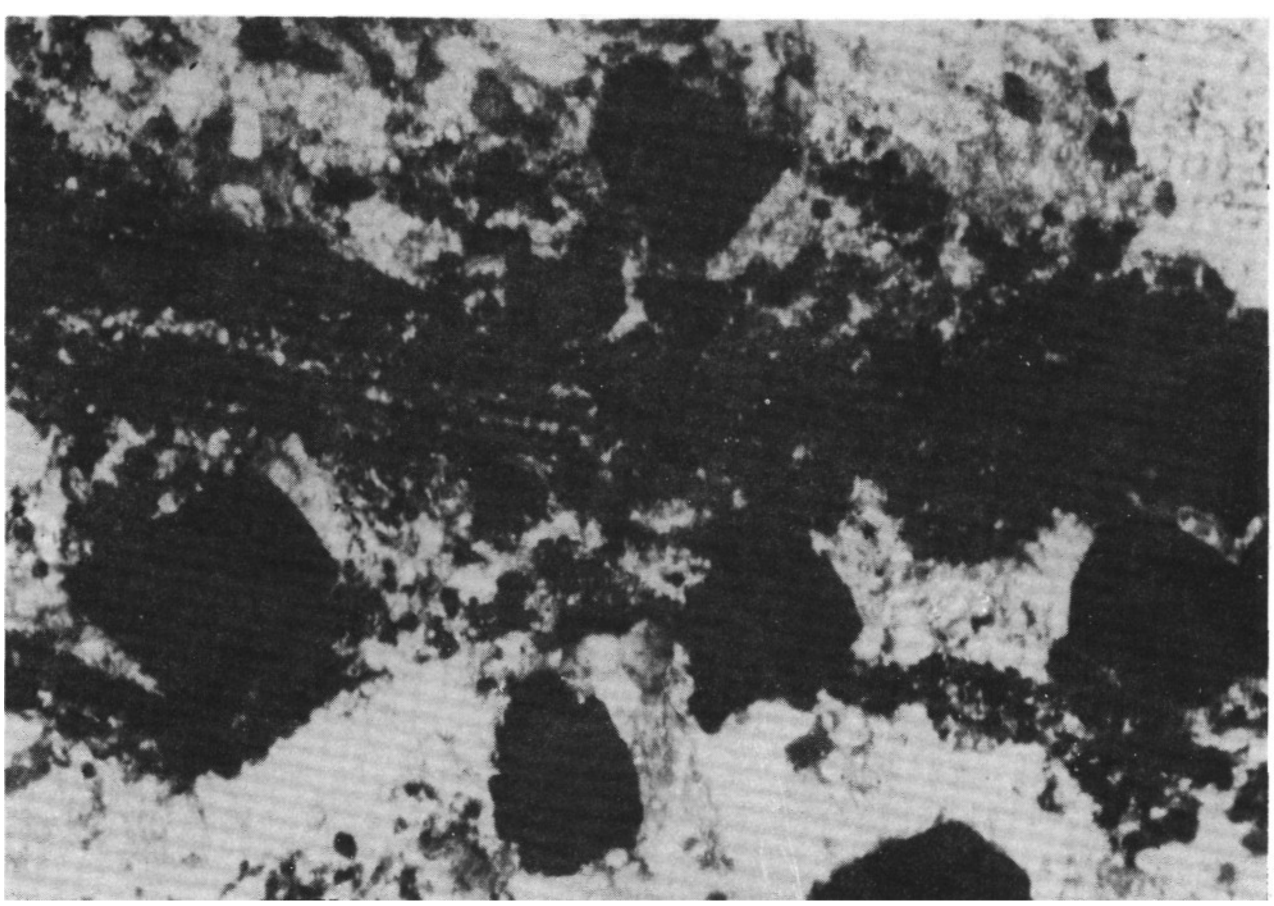

Fig. 6 - Load cast structure between a large pyrite crystal (Black) and an underlying pyrite-bearing lamina (Black, near left cornor). Thin section, //N, 32 X, in immension oil.

Some lenses are composed of rhythmic pyrite and calcite bands. Calcite and, in part, quartz crystals, have grown vertically to the pyrite bands. This rhythmicity resembles that of diagenetic crystallization rhythmites described by Amstutz (1977), Fontbote et al. (1981), Fontbote and Amstutz (1983).

Some large euhedral pyrites appear to be broken partly by intraformational brecciation, and partly to the compaction pressure. The latter were cemented with fibrous calcite.

**Pyrites in siderite veins**

Siderite veins contain massive pyrite and tetrahedrite bands fractured to varying degrees. Massive pyrite bands show perfectly grown euhedral crystals facing hostrocks and tetrahedrite bands (Fig. 7). Besides these,

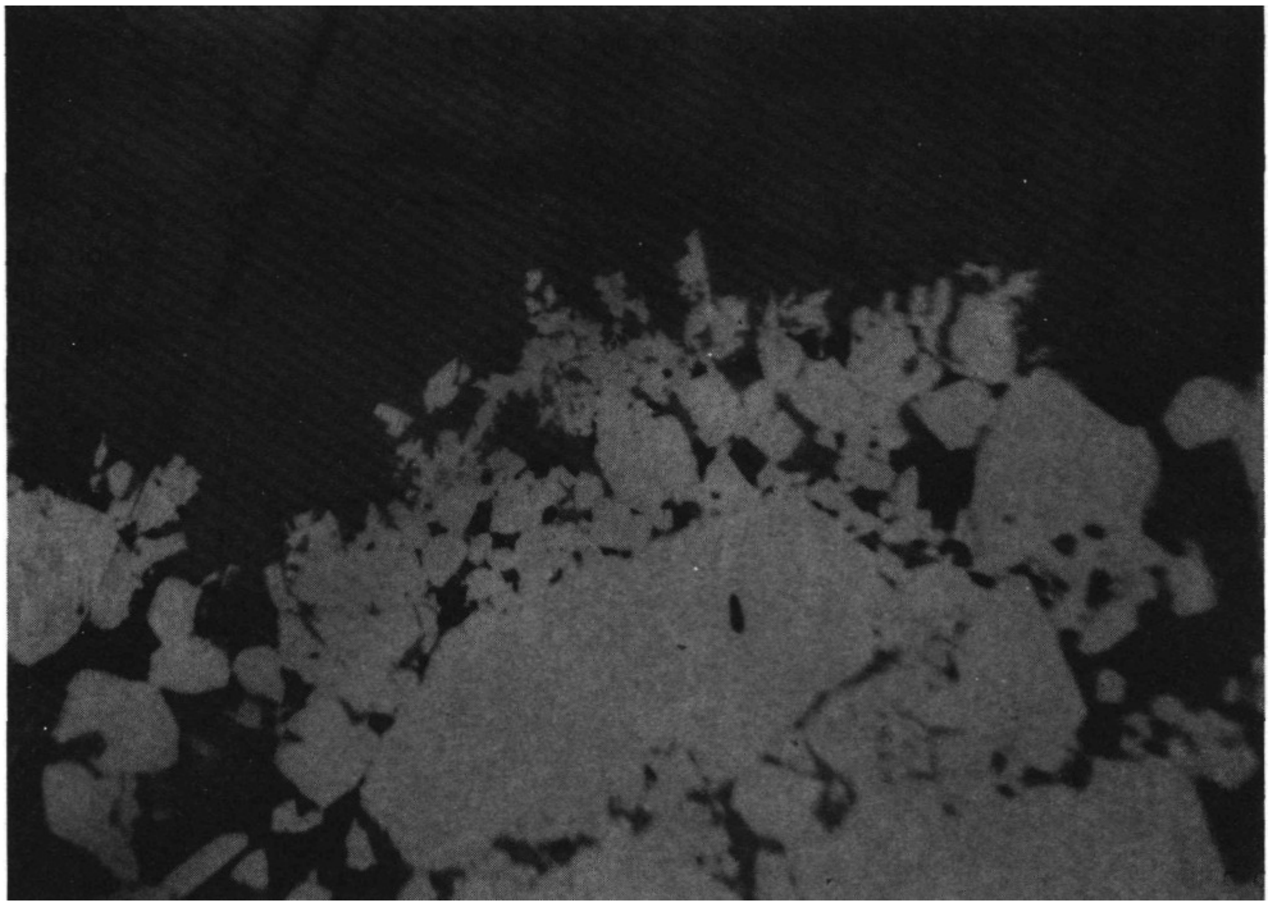

Fig. 7 - Some euhedral crystals of a massive pyrite band (Lower part) grown toward a tetrahedrite band (Upper part). Polished Section, //N. 32 X, in immersion oil.

single euhedral pyrites were observed in the gangue minerals found in the massive pyrite bands. Tetrahedrite, being of a younger generation than pyrite, is formed as bands and infillings between pyrite grains (Fig. 8).

Massive pyrites as well as siderites were fractured due to the brittle behavior of both minerals. This led in part to replacements by other constituents.

Chalcopyrite is very common among pyrite grains, along the boundaries of siderite and opaque minerals, and in the fissures of pyrite and tetrahedrite assemblages.

The second generation of pyrite was formed in the fractured portions of tetrahedrite as fine grains and in the colloform texture.

All siderites which exhibit coarse grains filled entire cavities and fractures. As a latest generation of deposition in siderite veins, small veins contain quartz, and the second generation of siderite cuts across previously formed minerals and features.

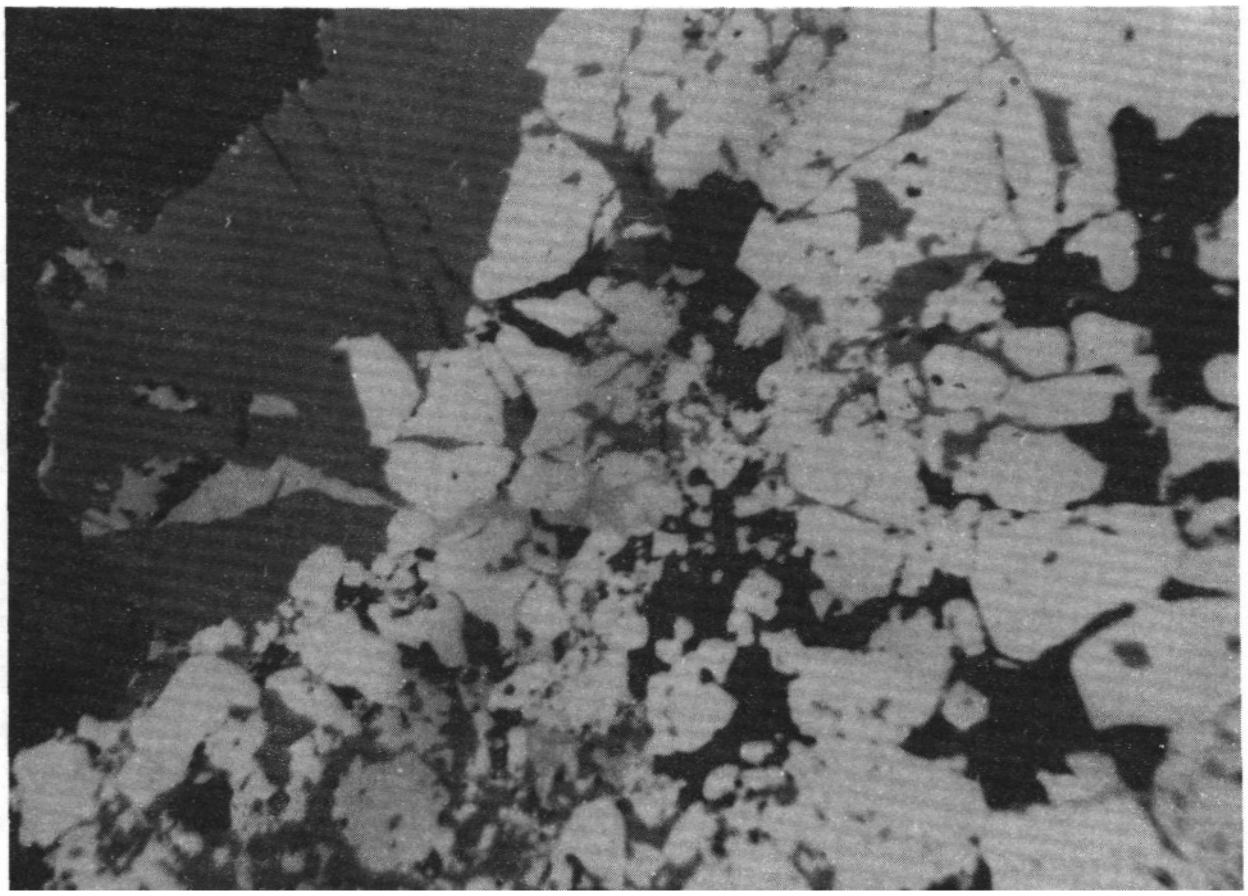

Fig. 8 - Infillings of tetrahedrite (dark gray) between pyrite grains (white). Siderite (black). Polished Section, //N, 32 X, in immersion oil.

## GEOCHEMISTRY

Pyrite samples taken from massive pyrite layers, individual pyrites, pyrite populations and diagenetic injection drops of sedimentary pyrite occurrences and siderite veins were analyzed by a model ARL Sema-semq. Molybden microprobe in the Mineralogical-Petrographical Institute at the University of Heidelberg in Germany. The results of the minimum and maximum values of major and minor elements of pyrites are given in Table 1.

**Table 1 - Microprobe results measured on different pyrites** **(%)**

| | | *Fe* | *S* | *Cu* | *As* | *Sb* | *Co* | *Ni* | *Se* | *Hg* |
|---|---|---|---|---|---|---|---|---|---|---|
| 1. Pyrites in siderite | max. | 43.474 | 51.806 | 0.679 | 2.523 | 0.407 | 0.020 | 0.038 | 0.136 | 0.241 |
| veins | min. | 42.250 | 50.016 | 0.033 | 0.333 | Tr | Tr | Tr | Tr | Tr |
| 2. Massive pyrite | max. | 46.382 | 54.051 | 0.123 | 0.157 | Tr | Tr | 0.060 | 0.040 | Tr |
| layers | min. | 45.537 | 52.355 | Tr | Tr | Tr | Tr | Tr | Tr | Tr |
| 3. Single euhedral | max. | 45.172 | 53.578 | 0.074 | 0.094 | Tr | 0.465 | 0.079 | 0.067 | - |
| pyrites | min. | 43.881 | 51.108 | Tr | Tr | Tr | Tr | Tr | Tr | - |
| 4. Diagenetic injection | max. | 44.299 | 53.304 | 0.049 | 0.115 | Tr | Tr | 0.121 | 0.043 | 0.138 |
| drops | min. | 41.160 | 51.845 | Tr | Tr | Tr | Tr | 0.022 | Tr | Tr |

1. Hydrothermal pyrites

2, 3, 4. Sedimentary pyrites

The results of pyrite analyses were evaluated within each group and were compared. As shown in Table 1, pyrites of siderite veins contain higher Cu, As, Sb, Hg and Se values, but lower Fe and Ni values than the sedimentary pyrite. However, Cu, As, Sb, Co, Se and Hg contents of most of the latter group samples were below detection limits.

High values of As, Sb and Cu in pyrites from siderite veins show a similar trend as the major element contents of associated tetrahedrite minerals. Therefore, it is proposed that pyrites and tetrahedrites in siderite veins may have been originated from similar sources.

The individual pyrite grains have distinctive As contents. Although this content increases up to 2.52 % around the pyrite cores, it decreases toward peripherical zones. This can be related to the character of ore-bearing solutions or a gradual change of physico-chemical conditions. On the other hand, there is a negative correlation between Fe and As. In these pyrites, As, Ni, Se values increase from the centre to the crystal edge; however, Fe and S contents decrease in the same direction. As and Ni contents of four sedimentary pyrite members have distinctive geochemical features. Massive pyrite layers among them contain a relatively high Fe value. But, they have low Se values.

Pyrites in diagenetic injection drops have a higher Ni content. This fact may indicate a mobilization and concentration of material, perhaps, derived from pelitic rocks and related to the zonation as described above.

The chemical composition of fahlore is shown in Table 2. This mineral has 8.8-11.5 %. As and 14.6-15 % Sb. Based on the amounts present of both elements, it can be defined as tetrahedrite. This mineral, also includes considerable amounts of Bi, Se and Hg.

**Table 2 - Chemical Composition of the tetrahedrite from siderite veins (%)**

| | S | Fe | As | Sb | Cu | Bi | Se | Hg |
|---|---|---|---|---|---|---|---|---|
| mm. | 24.212 | 6.064 | 8.841 | 14.621 | 43.543 | Tr | 0.236 | Tr |
| max. | 26.925 | 7.207 | 11.571 | 15.026 | 38.728 | 0.481 | 0.269 | 0.301 |

The other main type of pyrite is represented by the occurrences in siderite veins. From the poind of mineral paragenesis ore geometry, minor and trace element contents the origin of the pyrites associated with tetrahedrite may perhaps be called hydrothermal. But no magmatic activity is known in this area. The nearest volcanic center is found in the Erciyes Mountain, 80 km. from Attepe, and its volcanism began in late Miocene (Baş, 1986). The young Erciyes volcanism cannot have given rise to these sulfides and siderites. The conglomerates of the Zebil Formation in early Miocene contain some pebbles of sideritic formations in the neigboring area (Küpeli, 1991). Therefore, the ore-forming minerals may perhaps be deposited by other hydrothermal processes, between post Cretaceous and pre Miocene time.

After uplifting of the study area At the beginning of Miocene time, siderite veins were altered to the secondary iron minerals by the effects of multikarstification processes (Ayhan and Küpeli, 1991).

## CONCLUSIONS

The present study of the pyrite occurrences showed that two basic genetic groups of pyrites can be distinguished; they are, the sedimentary pyrites, and the pyrite-bearing siderite veins.

Sedimentary pyrite occurrences formed syngenetically in shales and phyllites associated with carbonaceous matter, exhibiting various depositional and diagenetic features. Pyrites having different crystal habits are related to the various stages of sedimentary processes. Small isolated euhedral to subhedral pyrite grains must have occurred during precipitation and early diagenetic stage. However, the largest crystals found, "in most cases, in calcite-rich portions have undergone diagenetic recrystallization. Diagenetic injection drops and small veins were created during the compaction stage by the migration of iron sulfide-bearing solutions upwards into syntectonically formed deformation places. Those can be termed diagenetic remobilization deposits. Subsequently the pyrites were cemented by sparry calcites. Calcium carbonate was derived primarily from dissolution of marine organisms.

In most cases, pyrite layers and laminae occur for the most part, conformably in pelitic rocks; however, they sometimes show discontinuity. In addition, there are some layers containing ring-shaped pyrites and detritic constituents. All these data imply the effects of subaqueous currents and mechanical erosion.

All field and laboratory investigations showed that alldepositional features were produced by the repetitive precipitation under calm, but occasionally active regimes With the availability of reactive iron minerals, dissolved sulphate, organic matter and $H_2S$ (Berner, 1970; 1979; 1984).

The sedimentary pyrites discussed in this paper are Precambrian in age. With this age, it is the oldest sedimentary ore deposit of Turkey.

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