

## Geochemical Constraints on the Origin of Karacaali (Kirikkale) Hydrothermal Iron Mineralization, Turkey

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**Abstract:** Karacaali iron mineralization located about 5 kms north of the city of Kirikkale, is mostly occurring as veins and to a lesser degree as impregnations within fractures and joints in rocks such as diabase, basalt and micro-gabbros. Furthermore, in one location it has been observed as magmatic brecciation. These host rocks to mineralization are affected by hydrothermal alterations. Mineral paragenesis consists mostly of magnetite and pyrite as major constituents as well as lesser amounts of hematite, musketofit, chalcopyrite, bornite, pyrrhotite, fahlore (tetrahedrite-tennantite), marcasite, covellite, goethite, chromite and thuringite. Diagrams showing the distribution of major, trace and also REE in the studied samples, indicated possible hydrothermal origin of mineralization. As a conclusion, the mode of deposition (as veins), wall-rock alterations, mineral paragenesis and the geochemical characteristics of major, trace and REE shows hydrothermal type of mineralization.

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**Key words:** Hydrothermal iron, geochemistry, Kirikkale, Turkey.

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### INTRODUCTION

The study area comprises a region of approximately 20 km<sup>2</sup> in the vicinity of Karacaali village, which is located in i31-a1 map section of Kirsehir and 5 km to Kirikkale province. Microgabbro, diabase and basalt-like rocks crop out in the area. The iron formations in Karacaali consist of mineralizations which are exposed at the surface to a very limited extent and whose signs are observed in diabase pebbles and blocks, partly in the form of debris. Their presence was first detected through geophysical anomalies and was later ascertained through drilling by the General Directorate of Mineral Research and Exploration Institute (MTA). Several studies have been conducted in Karacaali region so far. In his study on the lithostratigraphy of the Upper Cretaceous and Lower Tertiary sequence in the region, Norman (1972) reported that Yahsihan formation, which consists of basic volcanic rocks, green tuff, agglomerates, and tuffites, as well as of a small amount of white semi-crystalline biomicritic limestone layers towards the top, was cut by the Paleocene-aged Karacaali pluton. Studying on the Karacaali granitoids, Kayakiran (1999) demonstrated that the outcropping rocks in the region are post-collision granites and derived from a hybrid magma. Kaya (2002) examined the mineral geology and geochemistry of Karacaali iron deposit. Koc and Kaya (2002) examined the basaltic rocks of the same region, which they reported to have the toleitic character of Ankara Mélange, to be of MORB origin, and to have derived from the same magma through differentiation. The same study demonstrated that the iron formations around Karacaali village were related to microgabbro, diabase and basalt-like rocks. In their studies, Delibas (2002) and Delibas and Genc (2004) asserted that the basic rocks containing iron enrichments did not belong to Ankara Mélange; instead, they represented a magmatism younger than Cretaceous which intrudes into a granitic magma. Furthermore, the authors attributed the Fe, Cu-Mo, and Pb-Zn enrichments in the region to the interaction, mixture, and differentiation processes of the granitic and basic magma. However, it has been demonstrated that the basalts are of MORB (Mid Ocean Ridge Basalt) origin according to their geochemical properties (Koc ve Kaya 2002) and that the granites derived from a post-collision hybrid magma (Kayakiran 1999). The co-presence of pillow lava

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and pelagic sediments sheds doubt on the idea of young basalts intruding into granitic rocks.

In addition to these, the petrographic and petrologic characteristic of the plutonic rocks of the studied area were studied by Bayhan (1988 and 1989), Erler *et al.*, (1991) and Kayakiran (1999). There are also studies about the regional geology of the area such as Norman (1972 and 1973), Capan and Buket (1975), Seymen (1981 and 1982), Oktay (1981) and Ketin (1963).

The geochemical characteristics of the Karacaali iron mineralization is for the first time dealt with in this study. Here, the the geological and mineralogical results obtained by the authors in their previous studies (Koc *et al.*, 2008) were also used. As a conclusion, by evaluating the geological, mineralogical and geochemical characteristics together it was possible to outline the type of mineralization.

## MATERIALS AND METHOD

Research material of this study which consisted of core samples taken from various depths were obtained from the Institute of Mining, Investigation and Exploration (MTA). Eleven mineralized specimens taken from these cores were analyzed for their major, trace and REE geochemistries by ACME Analytical Laboratories (Canada). The major and trace elements were analyzed by Inductively Coupled Plasma- Emission Spectroscopy (ICP-ES), while the REE were analyzed by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS) methods.

### **Geological Conditions of Mineralization:**

The oldest exposed rocks in the study area are ophiolitic sequences of Upper Cretaceous age. This rock unit which is comprised of micro-gabbros at the bottom, overlain by diabase and then basalt at the top, were named as Ankara Melange in the previous studies (Bailey and McCallien, 1950 ) and as Karakaya Ultramafites (Seymen, 1981). All these rocks were later included into the Karakaya Ultramafites ( Bayhan and Tolluoglu, 1987 and Onen and Unan, 1988).

The age of the granitoid magmatic rocks cutting this basic rock unit was estimated to be 54my (Ayan, 1963) and 71my (Ataman,1972) which corresponds to Paleocene according to stratigraphic data. Furthermore, the age of the pluton was estimated to be Paleocene by many authors (Norman, 1972; Buchardt, 1958 and Ketin, 1955). There are dacite dykes in the area which has cross-cutting relation to the ophiolitic rocks. The youngest rocks of the area are the Quaternary alluvium which can be seen along the valleys (Fig.1).

More details about the stratigraphy of the area, and the petrography and petrology of the basic rocks, forming the wall-rocks to mineralization are given in Koc and Kaya (2002).

The Karacaali iron mineralization is related to the micro-gabbro, diabase and basaltic rocks exposed in the region. The mineralization is mostly occurring as veins along the fractures and joints in these rocks and to a lesser degree as impregnations within these rocks. In addition to that, there is another type of mineralization within the basaltic rocks associated with the magmatic brecciation (solution breccia) exposed near Kara river.

Common hydrothermal alterations can be observed in micro-gabbro, diabase and basaltic rocks forming wall rocks to mineralization in Karacaali area. The mineralizing hydrothermal solution which circulated through these rocks had resulted in changes in the mineral structures. Alterations which are common in these rocks are uralitization, albitization, chloritization, actinolitization, tremolitization, epidotization, saussuritization, carbonitization, clayitization and silicification (Koc *et al.*, 2008).

### **Mineralogy:**

The paragenesis and the structural-textural characteristics of Karacaali iron mineralization is summarized from the previous work of the authors (Koc *et al.*, 2008). Accordingly, based on the microscopic properties and XRD analysis, magnetite and pyrite form the main mineral phases of the paragenesis. In addition to these, little amounts of hematite, musketofit, chalcopyrite, bornite, pyrrhotite, fahllore (tetrahedrite-tennantite), marcasite, covellite, goethite, chromite, and thuringite are also present. Lath shaped hematite formed by martitization and later its musketofitization, reflect the changes of physico-chemical conditions during mineralization stages. Changes in the oxygen pressure or the lack of increase in the temperature due to reducing effect of solutions, results in the pseudomorphic formation of magnetite from hematite as mentioned by Ramdohr (1977).

Lath-shaped martitized crystals is an indication that the mineralization had started at higher temperature and on the other hand, it shows high rate of hematitization (Ramdohr, 1977 and Genc, 1998). It was mentioned that the magnetite grains were rarely changing to chromite from their edges. The chromites are mostly homogeneous and show little growth as is the case with the other associated minerals. In contrast to this, they show changes at their edges due to weathering or by the effect of hydrothermal alterations. This clearly proves that they are chromospinel rich in iron, and sometimes its gradual outward transformation into magnetite as mentioned by Ramdohr (1977). The presence of thuringite mineral which was detected by XRD analysis, can be seen in hot hydrothermal veins within iron and manganese deposits (Erkan, 1994).

### **Geochemistry:**

#### **Major Elements Geochemistry:**

Major and some trace elements content as well as Fe/Mn ratios of the Karacaali mineralization are given in Table 1. Fe/Mn ratios can help in the evaluation of the type of mineralization. Crerar *et al.* (1982) indicated that deposits formed from early and quickly deposited hydrothermal solutions show high Fe/Mn ratios (>10) and have wide range of variations. It is known that the Fe/Mn ratio in sedimentary deposits is about 1 and show narrow range of variation (Bonatti *et al.*, 1972). Rona (1978) and later Nicholson (1992) also indicated that the Fe/Mn ratio in the exhalative deposits show wide range of variation.

The Fe/Mn ratio in the samples of Karacaali deposit varies between 221.68 and 6321.92 (Table 1). According to these results, it can be said that the manganese-very poor, iron-very rich mineralization has been formed from early and quickly deposited hydrothermal solutions. As is the case with the content of Fe and Mn in the deposit, the content of Al and Ti can also be used in the interpretation of origin of mineralization. The distribution of Al and Ti in the Karacaali mineralization is given in Table 1, while the  $TiO_2 - Al_2O_3$  diagram (Crerar *et al.*, 1982) which was drawn by using these data is shown in Fig.2. As can be noticed from this table, the range of Al values is 0.54-15.16%, while that of Ti is 0.14-0.86%. The average value of Al is 7.12% and that of Ti is 0.40%. Comparing these values with those of iron-bearing manganese deposits shown in Table 2, it can be said that Ti is approximately similar to those of hydrothermal, but Al show similarity with sedimentary deposits. Taking the comments of Sugisaki (1984) that Ti generally exist as immobile element and indeed as a measure of the clastic energy in the hydrothermal solutions, and the contrasting view of Crerar *et al.* (1982) that Al is probably derived from the clay minerals of sedimentary rocks, into consideration, the excess of Al in the Karacaali ore should be explained. Mineralization being formed as vein type and having geochemical characteristic indicating to possible hydrothermal origin, exclude the idea that the excess Al is related to the clay minerals. It was indicated that the wall-rocks of Karacaali mineralization are of diabasic and basaltic composition which generally showed alterations. In that case, the hydrothermal solutions while circulating through these rocks have derived Al from Al-bearing silicate minerals (e.g. feldspars). Fig.2 shows the positive correlation between Ti-Al pair.

Fig.3 shows the distribution of Karacaali samples dropped on Bonatti *et al.* (1972)'s and Crerar *et al.* (1982)'s Fe-Mn- $10x(Ni+Co+Cu)$  ternary diagram. In this diagram, the curves distinguishing hydrothermal deposits from various sedimentary deposits were given. Accordingly, the studied mineralized samples were fallen in the field pointing to hydrothermal conditions.

For differentiating between hydrothermal mineralizations and sedimentary deposits, Si-Al diagram can also be used (Crerar *et al.*, 1982). Fig.4 shows the variation diagram of Si-Al, prepared from the data published by various authors. In addition to that, the Si and Al values of Karacaali deposit specimens were also plotted. Here, the majority of samples fall within the hydrothermal field and some of them near the border of hydrothermal-sedimentary field. As mentioned earlier, in addition to the primary content of the hydrothermal solutions, Al has also been derived from the wall-rocks as a result of their hydrothermal alterations during the mineralization stages of Karacaali deposit; this has resulted in the increase of Al and sliding of some the specimens towards the field of sedimentary rocks in some diagrams.

Formation of Fe, Mn, Al and Ti metals in the Noblehouse hydrothermal cherts of Scotland, were revealed by Adachi *et al.* (1986) by using some diagrams. For example, the studied specimens representing Karacaali mineralization had fallen within the hydrothermal field in both Fe-Al-Mn ternary diagram (Fig.5) and  $MnO/TiO_2 - Fe_2O_3/TiO_2$  (Fig.6).

In addition to this, Adachi *et al.* (1986) in their study, used data from the work of some other writers (e.g. Corliss and Dymond, 1975 and Eklund, 1974) whom have conducted research on various depositional environments to prepare Fe-Six<sub>2</sub>-Mn ternary diagram. Applying this diagram, they showed that the Fe, Mn, Al and Ti content of the Noblehouse cherts are of hydrothermal origin. In this diagram, the Karacaali ore samples were also fallen in the Fe-rich hydrothermal field as is also shown in Fig.7.

#### **Trace Elements Geochemistry:**

Using Zn, Ni and Co trace elements triangular diagram, it is possible to differentiate between deposits of sedimentary and hydrothermal origins (Crerar *et al.*, 1980). Among trace elements, Cu, Ni and Zn indicates hydrothermal origin of mineralization, while Co generally is indicative of sedimentary deposits (Crerar *et al.*, 1980). Fig.8 shows the distribution of Karacaali ore samples in the Zn-Ni-Co ternary diagram. According to this, the localization of specimens far from the Co end and their accumulation within the Ni-rich field is indicative of the hydrothermal character of mineralization. As is also shown in the ternary Zn, Ni and Co diagram, with the exception of two specimens, the majority did not show much variation in distribution and were concentrated in the same pile.

These characteristics show that mineralization was not derived from much different sources. It can also be seen from Table 3 that the rest of trace elements are generally showing the same characteristics. For example, with the exception of the two samples mentioned above, many elements like Cu, Pb, Mn, As, U, Th, Sr, Ba, V, Cr and many others show close similarity in their values.

#### **Rare Earth Elements (REE) Geochemistry:**

The REE content of Karacaali iron ore is shown in Table 4. For revealing the conditions of deposition of ores, diagrams obtained from REE values normalized to those in chondrites are used. In this respect many researchers can be named. For example, Haskin *et al.* (1966) and Bender *et al.* (1971) have made comparisons between the REE concentrations of Fe-bearing manganese nodules and the recent submarine hydrothermal deposits. While Goldberg *et al.* (1963), Glasby (1972) and Piper (1974 a,b) have investigated their distribution in sea water and in deep marine manganese nodules. Fig.9 shows the diagrams of REE in various environments. These studies showed strong negative Ce anomaly in the submarine hydrothermal deposits, and positive anomaly in manganese nodules. In similar studies, Crerar *et al.* (1982) indicated strong negative anomaly in the South Thomas and Blue Jay deposits which are of hydrothermal origin. Based on the strong positive Ce anomalies observed by Corliss *et al.* (1978) in their study of Galapagos rift mineralizations, and by Choi and Hariya (1992) in their study of mineralizations at Tokyo belt, they have indicated sedimentary origin of these deposits.

It can be seen that the specimens of Karacaali ore are showing negative Ce anomalies in their REE distribution diagrams (Fig.10). This indicates hydrothermal origin of mineralization (Graf 1977, Fryer 1977, Kato 1999, Jiangli 1999 a, b, Huawen *et al.*, 2002, Canet *et al.*, 2004, Fitzgerald and Gills 2006). Strong positive Eu anomaly is observed in the samples, which indicates the hydrothermal character of the formation (Danielson 1992, Jiang *et al.*, 2004). In addition to that, specimens showing negative Ce anomalies and positive Eu anomalies indicates that the hydrothermal solutions had high oxygen fugacity (Möller *et al.*, 1976, Möller and Morteani, 1983 and Constantopoulos, 1988).

#### **Discussion and Conclusion:**

Major, trace and REE content of the Karacaali iron ore shows hydrothermal origin of deposition. Some elemental ratios and distribution diagrams used for differentiating between the types of deposits helped in coming to such conclusion.

Fe/Mn ratios of more than 10 and the wide range of variations in ore specimens, indicates that the hydrothermal solutions were deposited early and in a quick manner (Crerar *et al.*, 1982). Fe-Mn-10(Ni+Co+Cu), Si-Al, Fe-Al-Mn, MnO/TiO<sub>2</sub> – Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> and Fe-Six<sub>2</sub>-Mn diagrams prepared by using major elements content of specimens (Bonatti *et al.*, 1972; Crerar *et al.*, 1982 and Adachi *et al.*, 1986) showed hydrothermal origin of element distributions. Trace element diagram of Zn-Ni-Co (Choi and Hariya, 1992) also showed hydrothermal characteristics of mineralization.

Negative Ce anomalies experienced by REE distribution diagrams (Fig. 10) of Karacaali ore and as it is the case mentioned by many other researchers in their own studies (Goldberg *et al.*, 1963 and Choi and Hariya, 1992) also indicate hydrothermal origin of deposits (Graf 1977, Fryer 1977, Kato 1999, Jiangli 1999 a, b, Huawen *et al.*, 2002, Canet *et al.*, 2004, Fitzgerald and Gills 2006). Strong

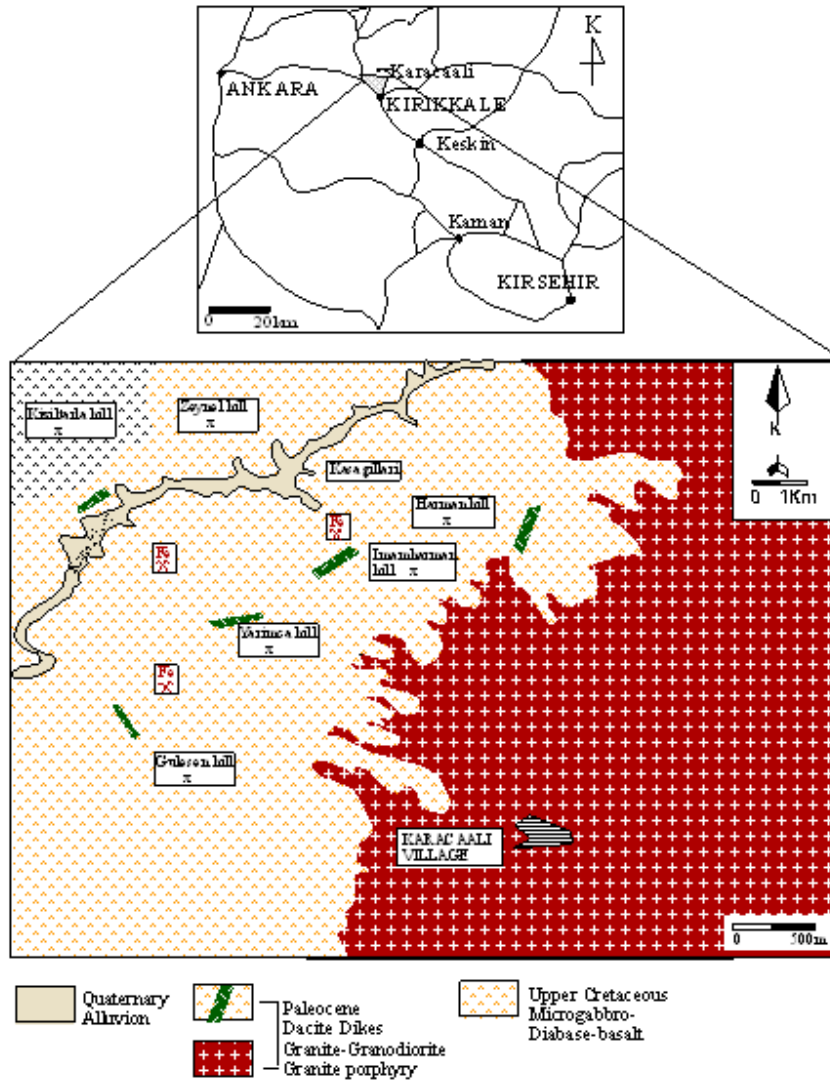


Fig. 1: Location and geology map of study area.

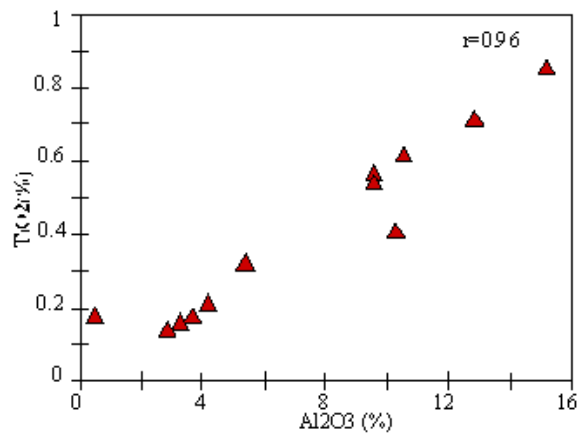
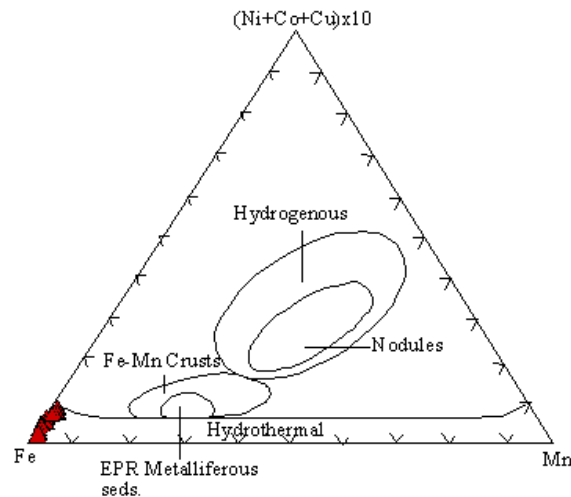


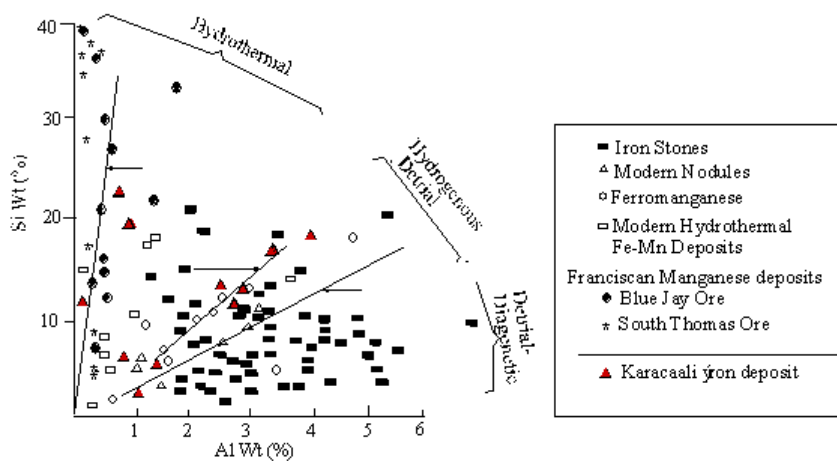
Fig. 2: TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> variation diagram (Crerar 1982) of Karacaali ore specimens.

positive Eu anomaly is observed in the samples, which indicates the hydrothermal character of the formation (Danielson 1992, Jiang *et al.*, 2004). Furthermore, negative Ce anomaly and positive Eu anomaly shown by the specimens, indicates that the hydrothermal solutions had high oxygen fugacity (Moller *et al.*, 1976, Moller and Morteani, 1983 and Constantopoulos, 1988).

According to the previous detailed studies by the authors (Koc *et al.*, 2008) whose data were also benefited of in this study, showed that the paragenesis, structural-textural properties of minerals and the wall-rock alterations are characteristics of hydrothermal deposits. Furthermore, formation of mineralization within rock fractures and joints as veins, locally impregnations and as magmatic breccia (solution breccia) are clear indications of hydrothermal origin. So all geological, mineralogical and geochemical characteristics shows that the Karacaali iron ore is of hydrothermal origin.



**Fig. 3:** Fe-(Ni+Co+Cu)x10-Mn ternary diagram (Bonatti *et al.*, 1972, Crerar 1982) of Karacaali ore specimens.



**Fig. 4:** Si-Al analysis in comparison to the sediments of ore lenses in Franciscan Masif Manganese nodules data, Hydrothermal Fe- Mn deposits data and Ferromanganese crusts data; Toth, 1980, Marine sediments data; Turekian and Wedelohl, 1961, Iron stones data; Kimberly, 1979.

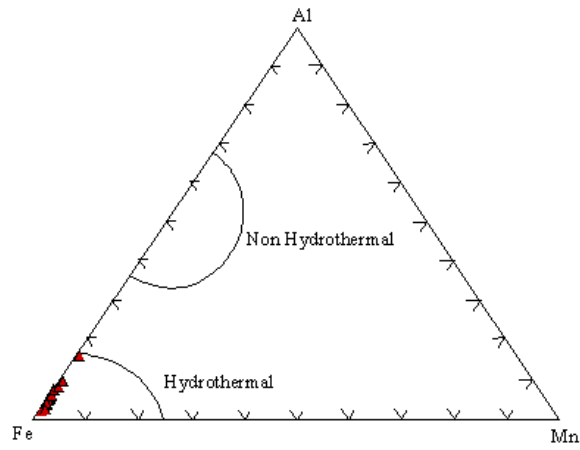


Fig. 5: Al-Fe-Mn ternary diagram (Adachi et al., 1986) of Karacaali ore specimens.

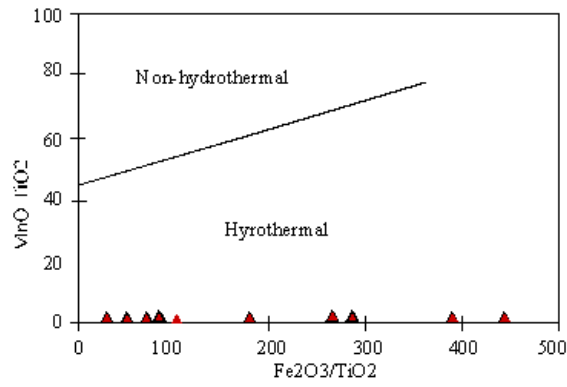


Fig. 6: MnO/TiO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> diagram (Adachi et al., 1986) of Karacaali ore specimens.

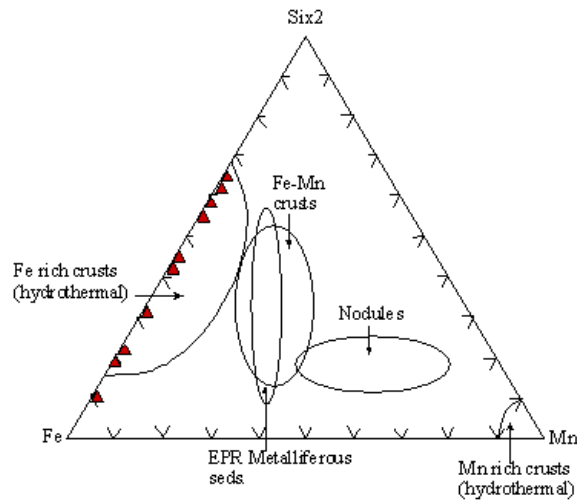
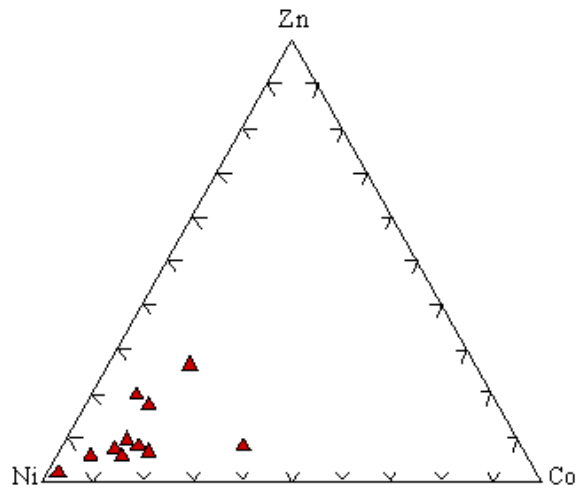
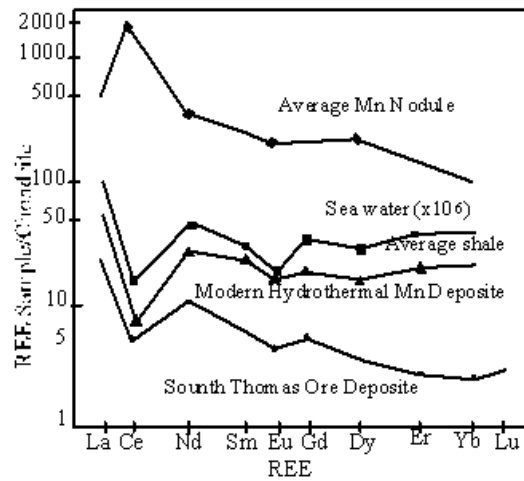


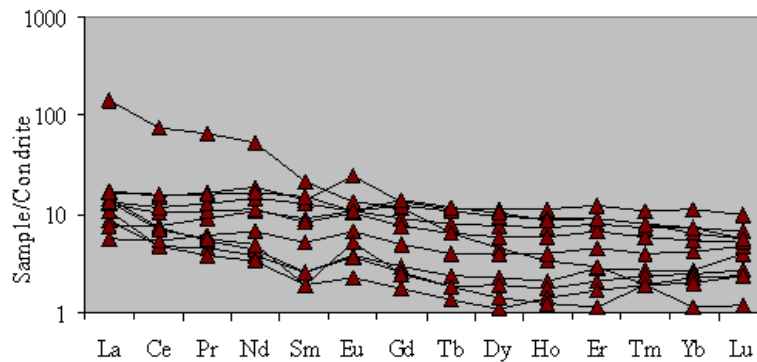
Fig. 7: Fe-Six<sub>2</sub>-Mn ternary diagram (Corliss and Dymond 1975) of Karacaali ore specimens.



**Fig. 8:** Zn-Ni-Co ternary diagram (Choi and Hariya 1992) of Karacaali ore specimens.



**Fig. 9:** Chondrite normalized REE diagram (Normalization values are from Evensen, 1978).



**Fig. 10:** Chondrite normalized REE diagram (Haksin and Haksin 1966) of Karacaali ore specimens.



Table 1: Major elements (%) and some trace elements (ppm) content of ore specimens.

|      | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | MnO  | Cr <sub>2</sub> O <sub>3</sub> | Ba    | Ni      | Sr     | Zr    | Y     | Nb    | Sc    | LOI   | TOT/C | TOT/S | Total  | Fe/Mn   |
|------|------------------|--------------------------------|--------------------------------|------|------|-------------------|------------------|------------------|-------------------------------|------|--------------------------------|-------|---------|--------|-------|-------|-------|-------|-------|-------|-------|--------|---------|
| CK37 | 42.46            | 3.6                            | 44.94                          | 1.97 | 2.90 | 0.33              | 0.04             | 0.17             | 0.13                          | 0.08 | 0.02                           | 5.00  | 443.00  | 23.00  | 23.00 | 10.00 | 10.00 | 8.00  | 3.20  | 0.40  | 3.00  | 99.90  | 507.33  |
| CK38 | 49.29            | 2.86                           | 39.75                          | 1.16 | 2.50 | 0.14              | 0.04             | 0.14             | 0.07                          | 0.08 | 0.02                           | 9.00  | 433.00  | 15.00  | 11.00 | 10.00 | 10.00 | 3.00  | 3.90  | 0.46  | 3.69  | 100.00 | 448.74  |
| CK40 | 25.03            | 0.54                           | 70.00                          | 0.18 | 0.34 | 0.06              | 0.04             | 0.18             | 0.07                          | 0.01 | 0.07                           | 9.00  | 1037.00 | 10.00  | 10.00 | 10.00 | 10.00 | 1.00  | 3.20  | 0.05  | 7.03  | 99.84  | 6321.92 |
| CK41 | 13.87            | 3.29                           | 70.98                          | 2.10 | 5.58 | 0.15              | 0.05             | 0.16             | 0.17                          | 0.12 | 0.00                           | 7.00  | 90.00   | 14.00  | 13.00 | 10.00 | 10.00 | 8.00  | 3.30  | 0.90  | 2.94  | 99.79  | 534.20  |
| CK44 | 36.38            | 12.82                          | 35.70                          | 2.57 | 5.89 | 3.24              | 0.10             | 0.72             | 0.19                          | 0.10 | 0.00                           | 13.00 | 136.00  | 118.00 | 20.00 | 12.00 | 10.00 | 22.00 | 2.20  | 0.12  | 0.73  | 99.95  | 322.42  |
| CK45 | 28.99            | 9.58                           | 47.42                          | 3.73 | 5.12 | 2.08              | 0.13             | 0.56             | 0.16                          | 0.11 | 0.01                           | 17.00 | 285.00  | 75.00  | 13.00 | 10.00 | 10.00 | 23.00 | 1.90  | 0.12  | 1.65  | 99.84  | 389.33  |
| CK47 | 6.95             | 4.25                           | 82.00                          | 1.05 | 3.21 | 0.40              | 0.04             | 0.21             | 0.19                          | 0.09 | 0.02                           | 13.00 | 446.00  | 52.00  | 10.00 | 10.00 | 10.00 | 6.00  | 1.40  | 0.20  | 3.24  | 99.86  | 822.85  |
| CK48 | 27.35            | 10.55                          | 48.02                          | 2.90 | 4.95 | 1.97              | 0.20             | 0.62             | 0.10                          | 0.12 | 0.01                           | 21.00 | 186.00  | 127.00 | 23.00 | 10.00 | 10.00 | 20.00 | 3.00  | 0.05  | 4.05  | 99.83  | 361.40  |
| CK49 | 39.65            | 15.16                          | 27.00                          | 4.12 | 8.62 | 2.63              | 0.14             | 0.86             | 0.37                          | 0.11 | 0.01                           | 26.00 | 120.00  | 151.00 | 22.00 | 14.00 | 10.00 | 29.00 | 1.20  | 0.05  | 0.56  | 99.91  | 221.68  |
| CK54 | 25.40            | 10.26                          | 41.87                          | 3.57 | 5.29 | 1.17              | 1.07             | 0.41             | 0.13                          | 0.11 | 0.03                           | 97.00 | 170.00  | 165.00 | 10.00 | 12.00 | 10.00 | 18.00 | 10.40 | 0.16  | 12.64 | 99.77  | 343.76  |
| CK59 | 12.77            | 5.43                           | 58.82                          | 3.69 | 5.23 | 0.04              | 0.04             | 0.33             | 0.06                          | 0.19 | 0.03                           | 8.00  | 60.00   | 57.00  | 18.00 | 14.00 | 10.00 | 4.00  | 13.20 | 0.72  | 13.96 | 99.84  | 279.59  |
| Max. | 49.29            | 15.16                          | 82.00                          | 4.12 | 8.62 | 3.24              | 1.07             | 0.86             | 0.37                          | 0.19 | 0.07                           | 97.00 | 1037.00 | 165.00 | 23.00 | 14.00 | 10.00 | 29.00 | 13.20 | 0.90  | 13.96 | 100.00 | 6321.92 |
| Min. | 6.95             | 0.54                           | 27.00                          | 0.18 | 0.34 | 0.04              | 0.04             | 0.14             | 0.06                          | 0.01 | 0.00                           | 5.00  | 60.00   | 10.00  | 10.00 | 10.00 | 10.00 | 1.00  | 1.20  | 0.05  | 0.56  | 99.77  | 221.68  |
| Ave. | 26.57            | 7.12                           | 51.50                          | 2.46 | 4.51 | 1.11              | 0.17             | 0.40             | 0.15                          | 0.10 | 0.02                           | 20.45 | 309.64  | 73.36  | 15.73 | 11.09 | 10.00 | 12.91 | 4.26  | 0.29  | 4.86  | 99.87  | 959.38  |

Table 2: Major and trace element content in various types of Mn-Fe deposits.

| Sample numbers                     | 14           | 4            | 3            | 3           | 7           | 28                   | 22           | 7           | 13          | 10                   |              |              |
|------------------------------------|--------------|--------------|--------------|-------------|-------------|----------------------|--------------|-------------|-------------|----------------------|--------------|--------------|
|                                    | Japan        |              |              |             | China       | Pakistan             |              | Türkiye     |             |                      |              |              |
|                                    | Wakasa       | Hokkaido     | Koryu        | Hinode      | Guichi      | Waziristan           | Hazara       | Ulusent     | Binkilic    | Kasimaga             | Gulocağı     | This study   |
|                                    | hydrothermal | hydrothermal | hydrothermal | sedimentary | sedimentary | volcanic-sedimentary | Hydrothermal | sedimentary | sedimentary | volcanic-sedimentary | hydrothermal | hydrothermal |
| SiO <sub>2</sub> (%)               | 58.16        | 32.28        | 40.56        | 12.62       | (-)         | 43.69                | 9.41         | 13.68       | 10.65       | 13.43                | 9.94         | 28.01        |
| TiO <sub>2</sub> (%)               | 0.04         | 0.01         | 0.05         | 0.04        | (-)         | 0.32                 | 0.84         | 0.10        | 0.02        | 0.10                 | 0.02         | 0.40         |
| Al <sub>2</sub> O <sub>3</sub> (%) | 0.55         | 0.05         | 0.63         | 1.27        | (-)         | 0.73                 | 12.53        | 2.49        | 2.85        | 2.95                 | 0.79         | 7.12         |
| Fe <sub>2</sub> O <sub>3</sub> (%) | 0.92         | 0.20         | 0.55         | 0.59        | (-)         | 2.96                 | 20.33        | 3.72        | 2.46        | 14.33                | 62.33        | 51.50        |
| MnO (%)                            | 32.65        | 51.91        | 42.06        | 67.21       | (-)         | 45.88                | 33.78        | 63.78       | 33.39       | 40.43                | 1.67         | 0.10         |
| Mn <sub>2</sub> O (%)              | 0.19         | 0.05         | 0.02         | 0.59        | (-)         | 0.60                 | 0.59         | 1.99        | 1.27        | 12.72                | 3.47         | 2.46         |
| CaO (%)                            | 4.15         | 0.27         | 1.65         | 67.21       | (-)         | 1.28                 | 6.43         | 4.05        | 18.96       | 6.82                 | 5.45         | 4.51         |
| Na <sub>2</sub> O (%)              | 0.04         | 0.07         | 0.11         | 0.08        | (-)         | 0.29                 | 0.07         | 0.24        | 0.39        | 0.06                 | 0.01         | 1.11         |
| K <sub>2</sub> O (%)               | 0.10         | 0.96         | 0.27         | 1.67        | (-)         | 0.22                 | 0.88         | 0.05        | 0.56        | 0.19                 | 0.06         | 0.17         |
| P <sub>2</sub> O <sub>5</sub> (%)  | 0.10         | 0.10         | 0.02         | 0.07        | (-)         | 0.25                 | 3.73         | 0.18        | 0.31        | 0.08                 | 0.32         | 0.15         |
| Ba (ppm)                           | 13.79        | 1.40         | 22.13        | 0.46        | 212.56      | 415.00               | 6304.00      | 427.00      | 6892.00     | 2719.40              | 1028.80      | 11.55        |
| V (ppm)                            | 258.00       | 251.00       | 211.00       | 0.12        | 167.86      | 144.00               | 573.00       |             | 106.00      | 106.10               | 279.80       | 275.09       |
| Cr (ppm)                           | 10.00        | 14.00        | 7.00         | 16.00       | 107.21      | 46.00                | 247.00       |             | 26.00       | 10.00                | 27.20        | 74.88        |
| Co (ppm)                           | 2.00         | 10.00        | 118.00       | 222.00      | 4.77        | 11.00                | 404.00       | 13.00       | 59.00       | 49.50                | 726.80       | 79.40        |
| Ni (ppm)                           | 28.00        | 38.00        | 352.00       | 341.00      | 89.39       | 36.00                | 305.00       | 10.00       | 167.00      | 23.00                | 1399.80      | 571.35       |
| Cu (ppm)                           | 50.00        | 24.00        | 1.17         | 691.00      | 31.03       | 72.00                | 375.00       | 56.00       | 26.00       | 126.80               | 27.20        | 242.79       |
| Zn (ppm)                           | 26.00        | 21.00        | 129.00       | 147.00      | 137.36      | 64.00                | 580.00       | 70.00       | 49.00       | 63.50                | 9617.40      | 50.97        |
| Pb (ppm)                           | 112.00       | 39.00        | 14.00        | 18.00       | 16.49       | 49.00                | 2357.00      | 65.00       |             | 53.50                | 127.40       | 26.76        |
| Th (ppm)                           | 2.00         | 4.00         | 2.00         | 98.00       | (-)         | 2.00                 | 31.00        |             |             | 433.20               | 0.68         | 0.29         |
| Rb (ppm)                           | 2.00         | 4.00         | 3.00         | 4.00        | 37.89       | 2.00                 | 24.00        |             |             | 5.00                 | 0.68         | 5.40         |
| Sr (ppm)                           | 85.00        | 120.00       | 483.00       | 260.00      | 741.34      | (-)                  | (-)          | 185.00      | 2100.00     | 255.00               | 147.40       | 29.85        |
| Y (ppm)                            | 5.00         | 2.00         |              |             | 21.75       | (-)                  | (-)          |             | 15.00       | 22.20                | 141.68       | 11.09        |
| Nb (ppm)                           | 3.00         | 3.00         | 8.00         | 4.00        | 6.70        | (-)                  | (-)          |             |             | 11.10                | 2.64         | 10.00        |
| Zr (ppm)                           | 12.00        | 9.00         | 62.00        | 48.00       | (-)         | (-)                  | (-)          |             |             | 32.00                | 26.90        | 15.73        |

**Table 3:** Trace elements content of Karacaali ore specimens.

| Sample no | V (ppm) | La (ppm) | Cr (ppm) | Ba (ppm) | W (ppm) | Se (ppm) | Te (ppm) | Ga (ppm) | B (ppm) | Sc (ppm) | Tl (ppm) | Ag (ppb) | Au (ppb) | Hg (ppb) |
|-----------|---------|----------|----------|----------|---------|----------|----------|----------|---------|----------|----------|----------|----------|----------|
| CK37      | 90.00   | 1.00     | 99.80    | 6.30     | 0.90    | 0.90     | 0.20     | 10.90    | 31.00   | 2.60     | 0.24     | 3393.00  | 7.20     | 6.00     |
| CK38      | 84.00   | 1.20     | 81.40    | 7.80     | 4.70    | 1.00     | 0.36     | 12.50    | 32.00   | 2.80     | 0.51     | 2417.00  | 12.70    | 5.00     |
| CK40      | 100.00  | 10.00    | 246.80   | 10.70    | 3.10    | 2.00     | 0.60     | 26.20    | 36.00   | 0.40     | 3.38     | 16558.00 | 20.70    | 5.00     |
| CK41      | 142.00  | 2.30     | 14.30    | 8.50     | 0.40    | 1.00     | 0.21     | 20.40    | 1.00    | 3.70     | 0.12     | 308.00   | 4.60     | 11.00    |
| CK44      | 354.00  | 0.80     | 22.70    | 7.30     | 9.30    | 0.50     | 0.08     | 11.00    | 23.00   | 4.40     | 0.02     | 1030.00  | 9.70     | 5.00     |
| CK45      | 386.00  | 0.60     | 33.00    | 11.50    | 0.50    | 0.80     | 0.10     | 9.70     | 23.00   | 3.70     | 0.03     | 5390.00  | 3.30     | 11.00    |
| CK47      | 531.00  | 1.50     | 103.40   | 16.90    | 1.40    | 1.50     | 0.18     | 21.10    | 3.00    | 2.80     | 0.02     | 2053.00  | 23.80    | 10.00    |
| CK48      | 496.00  | 1.20     | 22.00    | 13.90    | 1.00    | 1.80     | 0.35     | 13.90    | 10.00   | 2.70     | 0.06     | 1386.00  | 12.70    | 13.00    |
| CK49      | 475.00  | 2.70     | 22.50    | 19.90    | 0.20    | 0.50     | 0.07     | 15.90    | 14.00   | 2.90     | 0.04     | 967.00   | 4.20     | 5.00     |
| CK54      | 242.00  | 0.90     | 96.90    | 16.40    | 1.30    | 3.70     | 0.83     | 9.80     | 31.00   | 2.60     | 0.07     | 7224.00  | 16.70    | 10.00    |
| CK59      | 126.00  | 1.70     | 80.90    | 7.80     | 0.40    | 2.00     | 0.56     | 15.90    | 18.00   | 2.60     | 0.02     | 4507.00  | 17.20    | 5.00     |
| Max       | 531.00  | 10.00    | 246.80   | 19.90    | 9.30    | 3.70     | 0.83     | 26.20    | 36.00   | 4.40     | 3.38     | 16558.00 | 23.80    | 13.00    |
| Min       | 84.00   | 0.60     | 14.30    | 6.30     | 0.20    | 0.50     | 0.07     | 9.70     | 1.00    | 0.40     | 0.02     | 308.00   | 3.30     | 5.00     |
| Ort       | 275.09  | 2.17     | 74.88    | 11.55    | 2.11    | 1.43     | 0.32     | 15.21    | 20.18   | 2.84     | 0.41     | 4112.09  | 12.07    | 7.82     |

**Table 3:** Continue.

| Sample no | V (ppm) | La (ppm) | Cr (ppm) | Ba (ppm) | W (ppm) | Se (ppm) | Te (ppm) | Ga (ppm) | B (ppm) | Sc (ppm) | Tl (ppm) | Ag (ppb) | Au (ppb) | Hg (ppb) |
|-----------|---------|----------|----------|----------|---------|----------|----------|----------|---------|----------|----------|----------|----------|----------|
| CK37      | 90.00   | 1.00     | 99.80    | 6.30     | 0.90    | 0.90     | 0.20     | 10.90    | 31.00   | 2.60     | 0.24     | 3393.00  | 7.20     | 6.00     |
| CK38      | 84.00   | 1.20     | 81.40    | 7.80     | 4.70    | 1.00     | 0.36     | 12.50    | 32.00   | 2.80     | 0.51     | 2417.00  | 12.70    | 5.00     |
| CK40      | 100.00  | 10.00    | 246.80   | 10.70    | 3.10    | 2.00     | 0.60     | 26.20    | 36.00   | 0.40     | 3.38     | 16558.00 | 20.70    | 5.00     |
| CK41      | 142.00  | 2.30     | 14.30    | 8.50     | 0.40    | 1.00     | 0.21     | 20.40    | 1.00    | 3.70     | 0.12     | 308.00   | 4.60     | 11.00    |
| CK44      | 354.00  | 0.80     | 22.70    | 7.30     | 9.30    | 0.50     | 0.08     | 11.00    | 23.00   | 4.40     | 0.02     | 1030.00  | 9.70     | 5.00     |
| CK45      | 386.00  | 0.60     | 33.00    | 11.50    | 0.50    | 0.80     | 0.10     | 9.70     | 23.00   | 3.70     | 0.03     | 5390.00  | 3.30     | 11.00    |
| CK47      | 531.00  | 1.50     | 103.40   | 16.90    | 1.40    | 1.50     | 0.18     | 21.10    | 3.00    | 2.80     | 0.02     | 2053.00  | 23.80    | 10.00    |
| CK48      | 496.00  | 1.20     | 22.00    | 13.90    | 1.00    | 1.80     | 0.35     | 13.90    | 10.00   | 2.70     | 0.06     | 1386.00  | 12.70    | 13.00    |
| CK49      | 475.00  | 2.70     | 22.50    | 19.90    | 0.20    | 0.50     | 0.07     | 15.90    | 14.00   | 2.90     | 0.04     | 967.00   | 4.20     | 5.00     |
| CK54      | 242.00  | 0.90     | 96.90    | 16.40    | 1.30    | 3.70     | 0.83     | 9.80     | 31.00   | 2.60     | 0.07     | 7224.00  | 16.70    | 10.00    |
| CK59      | 126.00  | 1.70     | 80.90    | 7.80     | 0.40    | 2.00     | 0.56     | 15.90    | 18.00   | 2.60     | 0.02     | 4507.00  | 17.20    | 5.00     |
| Max       | 531.00  | 10.00    | 246.80   | 19.90    | 9.30    | 3.70     | 0.83     | 26.20    | 36.00   | 4.40     | 3.38     | 16558.00 | 23.80    | 13.00    |
| Min       | 84.00   | 0.60     | 14.30    | 6.30     | 0.20    | 0.50     | 0.07     | 9.70     | 1.00    | 0.40     | 0.02     | 308.00   | 3.30     | 5.00     |
| Ort       | 275.09  | 2.17     | 74.88    | 11.55    | 2.11    | 1.43     | 0.32     | 15.21    | 20.18   | 2.84     | 0.41     | 4112.09  | 12.07    | 7.82     |

**Table 4:** REE content (ppm) of Karacaali ore specimens.

| Sample no | La (ppm) | Ce (ppm) | Pr (ppm) | Nd (ppm) | Sm (ppm) | Eu (ppm) | Gd (ppm) | Tb (ppm) | Dy (ppm) | Ho (ppm) | Er (ppm) | Tm (ppm) | Yb (ppm) | Lu (ppm) |
|-----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| CK37      | 2.10     | 3.00     | 0.43     | 1.80     | 0.40     | 0.22     | 0.59     | 0.09     | 0.58     | 0.12     | 0.46     | 0.07     | 0.45     | 0.10     |
| CK38      | 3.50     | 4.60     | 0.53     | 2.10     | 0.40     | 0.21     | 0.53     | 0.07     | 0.49     | 0.10     | 0.35     | 0.06     | 0.41     | 0.07     |
| CK40      | 34.70    | 48.60    | 6.40     | 25.50    | 3.30     | 0.76     | 2.44     | 0.24     | 1.16     | 0.19     | 0.49     | 0.05     | 0.37     | 0.06     |
| CK41      | 2.60     | 3.00     | 0.37     | 1.60     | 0.30     | 0.13     | 0.36     | 0.05     | 0.28     | 0.08     | 0.28     | 0.05     | 0.33     | 0.06     |
| CK44      | 1.90     | 4.90     | 0.87     | 5.00     | 1.40     | 0.62     | 1.81     | 0.30     | 1.95     | 0.42     | 1.34     | 0.19     | 1.19     | 0.17     |
| CK45      | 1.40     | 3.50     | 0.60     | 3.20     | 0.80     | 0.38     | 1.02     | 0.15     | 1.03     | 0.23     | 0.74     | 0.10     | 0.69     | 0.12     |
| CK47      | 3.30     | 4.40     | 0.54     | 2.30     | 0.30     | 0.30     | 0.51     | 0.07     | 0.36     | 0.07     | 0.19     | 0.05     | 0.19     | 0.03     |
| CK48      | 3.10     | 6.50     | 1.03     | 5.30     | 1.30     | 0.59     | 1.55     | 0.24     | 1.50     | 0.34     | 1.10     | 0.15     | 0.88     | 0.13     |
| CK49      | 4.20     | 9.70     | 1.57     | 8.80     | 2.10     | 1.41     | 2.67     | 0.42     | 2.84     | 0.63     | 1.99     | 0.27     | 1.84     | 0.25     |
| CK54      | 3.20     | 7.40     | 1.21     | 6.80     | 2.00     | 0.62     | 2.50     | 0.40     | 2.44     | 0.51     | 1.48     | 0.20     | 1.07     | 0.14     |
| CK59      | 4.10     | 10.00    | 1.53     | 7.70     | 2.30     | 0.62     | 2.80     | 0.43     | 2.63     | 0.50     | 1.53     | 0.20     | 1.18     | 0.14     |

**ACKNOWLEDGEMENTS**

This study was conducted as part of the “Kirikkale iron prospection project” sponsored by the Institute of Mining, Investigation and Exploration (MTA). Due to the help offered by MTA General Directorate especially during the field work and sample preparations, the authors are thankful to the officials and personal of this organization whom have helped.

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