Geochemistry of the Oxide Mn-Fe ores of the Ore Deposit District Keban, Elazığ Province, Turkey

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Abstract: The subject of the present study is the geochemical survey of the oxide Mn-Fe ores of the Ore Deposit District Keban. The ores occur in the calc-schists as stratabound or as stockwork and breccia mineralization. They mainly consist of pyrolusite, psilomelan, polianite and limonite. Their main sulphide minerals are pyrite, galena, sphalerite, chalcopyrite, tetrahedrite and arsenopyrite. 21 Ag-bearing oxide samples of these ores were mineralogically, geochemically and statistically analyzed. The evaluations showed that Ag is enriched with an average of 475 times compared to the Clarke value most. He is followed by the enrichment factors of Pb with 311, Sb 290, As 182, Mn 54 and Fe 1.6. The mean Fe / Mn ratio of 1.6 corresponds to that of exhalative-sedimentary deposits. Relative Frequency distributions of the investigated elements MnO, CaO and Zn are corresponding to the log-normal distribution, which is due to their magmatic origin. Correlation analysis indicates a close relationship between the element pairs MnO-FeO, Al2O3-K2O, Hg-Sb, and a reverse flow from FeO-MgO, will contend for the hydrothermal processes. The metallogenetic interpretation of the Ore Deposit District Keban compared current and similar deposits equivalent to those of sedimentary exhalative deposits.

Keywords: Keban, Mn-Fe-ores, Geochemistry, statistical analysis and sedimentary exhalative.

INTRODUCTION

The deposit Keban district is located in East Anatolia, approx. 45 km west the provincial town Elazığ, at the upper reaches the Euphrates (Figure 1). The actual deposit area covers a surface of approx. 10 km2 and from the Euphrates flowing southward in an east and a west Euphrates half is divided (Figure 2). Old galleries, outlet and cinder waste dumps testify intensive industrial mining activities in Keban, which go back into the early bronze age (more Seeliger, et al. 1985). Deposit Keban represented as one of the most important deposits of Anatolia (Tızlak, 1991). For economic reasons, the mine enterprise had to be stopped 1983.

About the deposit Keban comprehensive and systematic investigations originated only from 1964. These concentrates upon east Euphrates half of the deposit district and treat above all the geologic construction of the surroundings, the mineralogical composition of the ores and the genesis of the deposit. On this occasion, is on Kumbasar (1964), Ziserman (1969), Kineş (1969a, b), Kipman (1976, 1982), Asutay (1988), Hanelçi (1991), Çelebi (1997), Çelebi and Hanelçi (1998) to refer. Newer investigations treat, in addition, intensely the flat-tectonic development of the surroundings of the deposit district (Bozkaya et al., in 2007, Dilek et al., in 2010 and Kuşçu et al., in 2013), isotope-geochemical relations (Kalender and Hanelçi, in 2004; Yiğit, in 2009; Kalender, in 2011 and Kürum, in 2011) and genetic interpretations (Hanelçi, in 1991; Çelebi in 1997; Çelebi and Hanelçi in 1998; Kalender, in 2011; Hanelçi and Çelebi, in 2013 and 2014). Now on account of the exhausted supplies on east Euphrates half of the districts, the research projects concentrate increasingly on west Euphrates half (see Çelebi, in 1997; Çelebi and Şaşmaz, in 1998; Çelebi and Hanelçi, in 1998 and Kürum in 2012).. With this article an attempt is made by microscopic, geochemical investigations, geological interpretations and metallogenetical comparisons gain new insights into the geological deposit ratios of Mn-Fe ores from the west Euphrates-half of the deposit Keban district.
GEOLOGY

The geological structure of the vicinity of the deposit consists of Kebo metamorphic Paleozoic age, transitions from syenit porphyry to the Upper Cretaceous, terraces and alluvial sediments of the Quaternary (Figure 2). The most widespread rock series of the deposit area, the metamorphic unit Perm-Carboniferous age after Kipman (1976). It is divided by Hanelçi (1991) in shales and sericite-chlorite. The oldest and most widespread shale occur in the study area to everywhere. They emphasize northeast-southwesterly direction and a fall to the southeast. Their thickness reaches 1200 m (Figure 2). In places, it shows a clear stratification and foliation parallel thereto. Mineralogically, it consists mainly of calcite. Incidentally, also, albite, epidote, chlorite and quartz are common. With the increase ends chlorite content, this series goes from bright to dark shales over.

Hanelçi (1991) divided the Shale in layered dolomite brick and recrystallized limestones that pass gradually into each other. The unit consist of recrystallized micritic and very brittle limestone, layered limestones are generally characterized by thin layer thicknesses (at most a few meters). Where cracks and fissures are almost always filled with secondary calcite and occasionally displays solution structures. Nearly parallel to this unit come before grey and thick bands of recrystallized dolomitic limestones occurring. The occurrence of Amadiscus and Glomospira fossils refers after Kipman (1976) to Perm-Carboniferous age. They are filled with secondary calcite cracks and crevices systems penetrated and run locally bitumens horizons not exceeding 10 cm in thickness.

The greenish sericite-chlorite schists are widespread east of the shales and lead, especially in lower regions of massive recrystallized bitumens horizons and recrystallized limestones metaturbidites. They arise with shales and are strongly continuous. The cleavage of the corresponding parent, predominantly xenomorphic or hypidiomorphic trained chlorite and Fe-minerals form their mineralogical main constituents. Subordinated calcite and quartz occur. In the affected areas of the metamorphism also, biotite, muscovite and epidote occur (Hanelçi, 1991). With the increase of the Fe-oxides their color changes from yellow to brown. The igneous rocks occurring as transitions and sills are predominantly on the East Euphrates half spread (Figure 2). They are colored pink, emphasize how metamorphic north-south direction and have some places to a thickness of a few 100 m. They show a porphyritic texture with a slight regulation in the direction of flow and are hydrothermally altered greatly. Normally they are trachytes and/or trachyanodesites of the syenites Subvolcanic (Hanelçi, 1991). Asutay (1988) puts it with an absolute age of 76 ± 2 Ma in Upper Cretaceous. Accordingly, they should be regarded as a sequence of alpidic orogeny. Findings of Kuşçu et al. (2013) support this information.

The mineralogical composition of the Kebo-igneous rocks composed mainly of potassium feldspar idiomorphic (sandine and orthoclase), hypidiomorph plagioclase and hornblende. Rarely occur biotite, quartz, zircon, apatite, titanite, pyrite and magnetite.

Metamorphism

For the area of Kebo, the geological interpretation and microscopic examinations give at least one regional and contact metamorphism. The regional metamorphism taken place after the primary mineralisation led to the formation of wrinkles. Hanelçi (1991) assigns it to the quartz-albite-muscovite subfacies and the greenschist facies by Bucher and Grapes (2011). The contact metamorphism has arisen during syenitic or trachytic intrusion in the recrystallized limestones. It corresponds to the hornfels facies.

Tectonics

The deposit Kebo district is characterized by a complicated folding and faulting (Figure 2). After Hanelçi (1991), the northsouth pressure forces acting led to folding in Northeast süwesterlicher direction, while the northwest southeastern tension and tension forces have caused the nearly east-west trending fault systems. Finally, the district formed today’s horst-graben system from north to south. The main tectonic element of the study area is the fold with a NE-SW axis extending to the West Euphrates half. Almost perpendicular to it is a younger faulting developed (Kines 1969a, b and Hanelçi 1991). Accordingly dominate more, preferably NW-SE running fault the tectonic image of the deposit area. They assign the folding tectonics of the Hercynian, and the tectonics of alpidic orogeny (from Jura). It is clear that the folding took place after the primary mineralisation, which is affected by it. The younger fracture systems are not mineralized.
Mineralization

In addition to the deposit District Keban occur until 1983 economically mined sulphide Pb, Ag and Zn ores and a number of oxide Mn, Fe, V, Cu, F and Mo deposits on (Figure 2). Still in this investigation down West Euphrates half, successive stratabound oxide Mn-Fe ores occur (Yiğit, 1989; Hanelçi, 1991; Çelebi, 1997, Çelebi and Hanelçi, 1998). Another important occurrence here is the porphyry-F-Mo mineralization (Yiğit, 2009) of Karamagara (Çelebi et al., 1997), about 3 km the mapping range, as well as the secondary vanadinite and desclozite occurrences of mystic cave in the south (s. also Kines, 1971). On the eastern Euphrates half are exhausted Anaocak (Figure 2) in the north and the Cu-Pb mineralization of Kuroko-type of Zeryan Dere (Hanelçi, 1991) to call in the south.

In contrast to the mineralization of West Euphrates half here occur mainly sulphide Pb-Ag-Cu mineralization. They occasionally show massive ore lenses lower horizontal expansion, but up to 2 m thick. The mineralization of the deposit area Keban occurs in shales and in the contact area to the recrystallized limestones. They are concentrated in folds saddles, emphasize the fold axes and foliation parallel northeast southwest direction. There are open-mined in the lower areas of sulphide, Ag-leading Pb-Zn mineralization (under Gümüş Galeri, Figure 2) and disseminated in the upper regions of oxide Mn-Fe mineralization (above the Gümüş Galeri) to differentiate (Figure 3). These are subjected to a clear primary depth difference, with those after the depth Pb and Ag off, and Zn and Cu increase (Çelebi and Hanelçi, 1998). The sulphide mineralization containing no oxide ore minerals, while oxide mineralization may have high concentrations of sulphide minerals.

The sulphide mineralization is very diverse. It occurs in the exchange of bearings and recrystallized limestones in the form of Kalkschiefern lenses and disseminated on. The appearance of this primary mineralisation reaches 15 m. The predominant sulphide minerals here are idiomorphic, medium grain pyrite and galena, which exhibit high concentrations in parts in the often lens-like high-grade ore zones. Besides step sphalerite, chalcopyrite, tetrahedrite, pyrargyrite, polybasite and arsenic minerals such as arsenopyrite and saflofrite (Figure 4). Increasingly secondary minerals come upward such as Cerussite, anglesite, smithsonite and limonite (s. Also Yiğit, 1989). The oxides mineralisation is separated by the shales impregnated with sulphide ores. The porous Mn-Fe-ores, which are good in the investigation distances GG, BF-1 and BF-2 to tremble eighth, are accompanied within the lower ranges locally by thin baryte horizons. They turn into upward to the secondary Fe-ores, so that in BF-4 and BF-5 no considerable mineralisations are to be found. The oxide mineralization occurs in the Kalkschiefern and form 2 Erzhorizonte that are structurally divided into different styles of mineralization. Hanelçi (1991) distinguishes a stratabound (to 40 mn) and a five stories or breccia mineralization.
The stratabound mineralization occurs in the shales and in their contact area to the recrystallized limestones. The influence of this type of mineralisation reaches at the most 15 m, while its length is 400 m. The mineralization is relatively controlled, occurring in layers or lenticular and Ag-poor. It consists of the most radiating pyrolusite (Figure 5), cryptocrystalline or collomorphic psilomelan, polianite, limonite and siderite. The Ag-rich stockwork mineralization occurs in metamorphic rocks in the form of gears, bags, wires, crevice and crack fillings with small dimensions. We should also mention the mineralization in the karst caves and a gap layer of metamorphic rocks, consisting of local ore concentrations and has not led to any change in the surrounding rocks. Accessory sulphide minerals, dignified and dendritic Ag (Hanelçi, 1991) are characteristic for both oxide and sulphide for product types that indicate their cogenetic origin. Secondary Pb minerals like cerussite and anglesit and smithsonite are widespread, with calcite as the most common secondary mineral. As both types of ore gangue ankerite, barite, garnet, marcasite and quartz are mentioned. Rarely grossular, andradite, epidote and fluorite are found to indicate metasomatic changes.

![Figure 3](image3.png)

*Figure 3:* In addition to rock-ore contact in the Gümüş Gallery: 1 Calc schist, 2 Mn-Fe hydroxides (s. also Figure 2).

![Figure 4](image4.png)

*Figure 4:* Sulfidic ore: 1 Galena, 2 Safflorit (CoAs₂), 3 Tetrahedrite, 4 Sphalerite and 5 Gangues or holes. Nicols crossed in oil immersion.
Genesis

The controversial genesis of deposit District Keban is partly controversial. (Ziserman, 1969; Kumbasar 1964 Kines, 1969a, b and Kipman, 1976). The studies raise before 1986 the Spätmagmatismus forth while Hanelci (1991) a primary sedimentary emergence and subsequent remobilization of ore by subvolcanic activities and meteoric waters (metasomatism) and assumes the deposit assigns the Kuroko-type. Yilmaz et al. (1992), however, Keban bring them with sediment-bound massif-sulphite-deposits (sediment hosted massive sulphides - SHMS / SEDEX) in the context while Yigit (2009) due to the F-Mo mineralization of Karamagara as metasomatic (skarn) deposits with porphyry –copper called features.

In the eighties of the last century conducted by Etibank prospecting and exploration work resulted in a total stock of about 10 million tonnes (proven and probable) with an average copper content of 1 %, 2 % Pb and 50 ppm Ag (Hanelci, 1991). In addition, 430.000 t proven and probable and Proven and 300.000 t possible Mn-Fe-ore reserves with an average content of 15 Mn, 31 ppm Ag and 0.25 ppm Au. Considerations include about 400 surrounding old leaving heaps of approximately 50,000 tons at an average grade of 2.1 ppm Au and 91 ppm Ag (Hanelci, 1989 and Yigit, 1989).

MATERIALS AND METHODS

Sample Material and Methods of Investigation

21 Mn-Fe-ore samples form the basis of geochemical investigations. They originate from the cores of underground drilling GYS-9, GYS-10, GYS-13 and GYS-18, have been drilled in different directions from the Etibank 1983-1989 in the investigation route Gümüş Galeri (s. Figure 2). The nuclear yield of these drillingse averaged 70% (Yigit, 1989). The samples were taken from a distance visually in approx. 3m as piece samples, approx. 0.50 kg. The determination of the element distributions was carried out using the scanning electron microscope and the element contents of an X-ray fluorescence analysis of powder tablets at the TU-Berlin. Experience has shown that the relative error of this analysis method, on the dot of element between ± 3 (Cr, Ni) and 10 (Na, Mg). In the study included 21 samples were analyzed for 40 elements, of which some representative samples are shown in Table 1. Of the analyzed elements Ga and Mo were not detected in any sample. Br, Ti and U were determined only in some samples and at a low concentration. For these reasons, these elements in the geochemical interpretation could not be considered.

RESULTS AND DISCUSSION

Electron Microscopy

From the samples selected after chemical analysis for the electron microscopic investigations the sample has Keb-7 (Table 1) regarding the element distribution the best results supplied. Here the distribution of 14 elements was examined by a micro probe in a surface of approx. 4 mm2 and analyzed half quantitatively (Figure 6), whereby Pb and Ag-distributions could not be represented because of the matrix effect. The intensity of certain elements is a significant predominance of Ca, which reflects the recrystallized limestone. This is followed by Mn and Fe concentrations, which indicate its oxide ore minerals (s. also Çelebi, 2014). Ba and rush-tears means the occurrence of baryte, while of mg as dolomite is to be understood (Figure 7). The low Si, Al and K-intensities indicate low silicate content, which are confirmed by chemical analysis (Table 1).

The specific element distributions show a common occurrence of carbonate (1, calcite, dolomite) oxide / hydroxide (2, hematite, pyrolusite) / (limonite, manganite) and sulfate (3, barite) -main mineral phases (Figure 7). Silicate (kaolins, quartz, feldspar) and chlorite phases are rare (not shown). The carbonate phase represents dolomit recrystallized limestones, while the oxide or hydroxide phases signify the Mn-Fe ores. The individual phases are well differentiated. The sulphate phase consists mainly of baryte, such as the agreement between the distributions of Ba and Sr show that, which accompany also plentifully of Sr (Table 1). The baryte inclusions in the Mn-Fe-ore point to that, it is older than the ore, which encloses the carbonates and its corrodes edges (Figure 7). Hence it follows that the carbonate is older than the ores, which is also consistent with the geological Interpretation in the agreement (s. below).

In analysis, an irregular grid C- and regular Cl distribution is observed. The latter is to be understood as reference to submarines environment which affirms the submarine-
exhalative emergence thesis on Keban districts (s. Hanelçi, 1991 and Yilmaz et al.,

**Geochemistry**

Mineralogical examination methods are not sufficient by Nicholson (1992a), to distinguish Mn ores of different origins from each other clearly. Therefore, the use of geochemical methods of investigation is required. These are mainly the chemical composition of the ore, the relationship of various elements Mn and Fe and the chemistry of the minerals are of great importance. The analytical values of the investigated Mn-Fe ores of the deposit Keban district show a z. T. very varying mineralisation degree and trace element content. The valuable material contents of the main components MnO, FeO, BaO and SO3 as well as those of the trace elements As and Ag spread very strongly. They contain low levels of the main components SiO2, TiO2, Al2O3, K2O and Na2O. By contrast, they lead Ag, As, Ba, Sb and Sn in relatively high concentrations. The Table 1 shows a comparison of the analytical values of the studied ore samples.

High As, Ba and Sr-contents of the Mn-ores refer after Nicholson (1992b) indicate its hydrothermal origin. The As-levels reached in the treated Mn-Fe ores 0.11, so it comes to the formation of safflorit (Figure 4), which excludes a Migration from exogenous sources (Boyle and Jonasson, 1973) and the transition from temperate to medium temperate minerals represents (Pohl, 2005). This is evidenced by the low Fe / Mn ratio of 1.60, the said submarine-hydrothermal deposits (0,1>Fe/Mn>10) corresponds to (Bonatti et al, 1972; Choi and Hariya, 1992 and Nicholson, 1992a), supported by the high Pb contents that cannot be explained by continental weathering, and by the low Cu, Ni and Co contents. In this connection, Maynard (1983) refers to the common occurrence of Mn and Ba, which are characteristic of hydrothermal deposits. This is occupied in Keban by the company of the Mn-Fe-ores by baryte horizons (Hanelçi, 1991 and Yiğit, 1989 and Çelebi, 1997).

![Figure 6](image-url)

**Figure 6:** Intensity of the semi-quantitatively certain elements in the Figure 7 the investigated range.

![Figure 7](image-url)

**Figure 7:** Figure 7. Scanning electron micrographs show the distribution of the major elements (left) and corresponding mineral phases (right). SE: Secondary electron, RE: Backscattered electrons. 1 Carbonates, 2 Mn-Fe oxides / hydroxides, 3 Sulfate and 4 Bitumens.
In addition to the absolute element contents also enrichment factors of the elements towards their Clarke values and their ratios can provide another important clues about the geological events and the genesis and facilitate their recovery. In Keban three element groups, one up to 475 times stronger, and to distinguish up to 50 times moderately enriched member of a group of up to 10 times impoverished element group. The highly enriched element group consists almost exclusively of chalcopyrite elements such as Ag, Pb, Sb, As, Se, Hg and Mn etc. This has led to the ore formation. The moderately enriched element group comprises mainly the elements Sn, Ba, S, Zn, Ca, Mg and Fe, while the predominantly impoverished elements consist lithophile elements such as Si, Al, K, Na, etc..

The joint enrichment of As-Ba-Cu-Li-Mo-Pb-Sb-Sr-V and Zn geochemical Mn Ace bandage is characterised by Nicholson (1992a) for hydrothermal deposits, leading to the enrichment factors of the first two groups of elements as seen. The correlation of the enrichment factors chalcopyrite elements together puts her hydrothermal origin close to what can be observed in many hydrothermal Mn and Pb-Ag-Zn deposits (see Barnes, 1997;; Nicholson, 1992b; Choi and Han, 1992, Flohr, 1992). After Hodkinson et al. (1994) have the high enrichment factors of Ag (475 times), include Pb (310 times) and As (182 times) in their endogenous origin. This view is endorsed by Keban in a significantly primary depth difference and Proportionality (Celebi and Hanelçi, 1998).

**Frequency Distribution**

According to statistical measures, the data series to be examined must be homogeneous, ie they must be normally distributed and represent a population. The frequency distribution of a data series used to determine this quality of data rows by their modal parameters, median and mean. For the investigation, the purpose of the analyse values is, for example, MnO values satisfying this condition (modal value = 3.00< median=3.23< average = 6.71 in %, n = 21). However, the data strew strongly (x = 6.71 ± 7.33). While from a statistic balance a normal distribution follows, a dynamic balance, as diffusion, shows a logarithmic normal distribution of the elements (Schroll, 1976). Rodionov (1964) provides for example. The logarythmic distribution of elements in the igneous rocks as a basic rule. After Ahrens (1954) this is a geochemical principle in rocks. It also depends on whether an element is installed primarily in a mineral or evenly in several minerals, which is reflected in the frequency distribution.

The frequency distribution of the oxide MnO and sulfidic Zn mineral communities in Keban show frequency distributions positive Leaning. This is the example of the Figure 8a and b MnO represented and Zn distributions clearly expressed (stem and leaf method). These are known as 'Arnerztyp' to denote, as in images this type of distributions low values predominate (modal <median <mean values). The skewness of a data distribution is an indication of their logarythmic normal distribution. That's from the Figure 8d and e of the logarythmic normal distributions (Modal=Median=Mean values) can be seen of the investigated elements, indicating their magmatic origin (Rodionov, 1964). In contrast, the frequency distribution of the carbonate rocks CaO shows a negative skewness (mean-median-modal values) (Figure 8c) and is not distributed logarithmically (similar picture of Figure 8c and 8f). These results are also valid for analog distribution of FeO, PbO and MgO (not shown).

In addition to the skewness of the frequency distribution of a data series, also its curvature (kurtosis), with regard to the width or distribution in the data, is of great importance. Here are the curvatures (W) of the frequency distributions of MnO (W = 3.19) oxidic ores, and the Zn (W = 6.40) sulphide ore, positive (Figure 8a, b). This means that they are higher than a standard normal distribution and therefore predominantly each is of a mineral, such as pyrolusite and sphalerite are attached. CaO (W = 0.97), however, has a negative curvature, making it flatter than a standard normal distribution (Figure 8c). This indicates that they are greatly received in different Nebengesteis minerals such. B. plagioclase and mica. were received strongly. Similarly also these results on distributions of FeO, PbO and MgO can do extended warden (not shown). The curvature of the logarithmic distributions (Figure 8d-f) same contrast, with -0.32 (MnO), 0.32 (Zn) and 1.2 (CaO) almost a log normal distribution.

**CORRELATION ANALYSIS**

In the studied ore samples between SiO2 and Al2O3, TiO2, K2O and Rb contents a strong parallelism (Table 1), which for supergene influences such as might be deposits of sand and clay minerals, important (s. also Precejus and Bolton, 1992). Their CaO and MgO contents correlated significantly positive, while MnO, FeO, PbO, Zn, Cu and Ag to run significant. This suggests alternation of lower rock and ore as well as dominance of the country rock by ore, which manifests itself as a metasomatic changes, crack and fissure fillings. The MnO and FeO concentrations correlate significantly positive. This is to be interpreted as an indication of their common origin. They have no significant correlation with the chalcopyrite elements Pb, Zn, Cu and Ag, which can be explained by the separation of the oxide sulphide of the ore. The strong dependence of Ag Pb, SO3 and As is the replacement of Pb2 + by Ag + in PbS and dissemination of arsenopyrite, which has also been detected microscopically. Ag may be mainly bound to Ag complex sulphides such as the presence of tetrahedrite, pyargyrit and polybasit shows. (Hanelci, 1991 and Hanelci and Celebi, 2014).

In order to determine the correlation between the element pairs and the degree of their relationship, the correlation analysis provides important clues that are of geochemical, mineralogical and genetic significance. It shows, for example, a significant negative correlation of FeO and MgO (Figure 9a, r = -0.90) and MnO and CaO (not shown) responsive to changes metasomatic and the recrystallized limes by Mn-Fe-ore (Table 1). An inverse relationship exists between MnO and FeO (Figure 9b, r = 0.91). Its saturation and good separation of MnO and FeO means statistically significant positive correlations. This also exist between SiO2, Na2O and TiO2, and Al2O3 and K2O (Figure 9c, r = 0.92). This reflects the behavior of the elements carbonate (Ca-Mg), siliceous (Si-Al), and oxidic or hydroxidic (Mn-Fe) Mineral communities. This means for example that the lithophile K2O, Na2O, Rb and TiO2 follow the Al2O3 (z. B. in mica), while the siderophile elements Cr, Co, Ni and V in the FeO-MnO-minerals (such as hematite, goethite, pyrolusite and manganese) accumulate.

It also comes to concentration of other trace elements such lithophile Th4 + and W4 + high ionic charges (rMn-Th = 0.92) and chalcopyrite Bi and Se large ionic radii (Bi3 +: 1.17, Se2-: 1.84 pm, to Shannon, 1976). Ag, Cd, Hg and Sb be installed because of their chalcopyritic character in sulphides (z. B. in PbS and ZnS), so that all 4 elements together puts her hydrothermal origin close to what can be seen of the investigated elements, indicating their magmatic origin (Rodionov, 1964). In contrast, the frequency distribution of the carbonate rocks CaO shows a negative skewness (mean-median-modal values) (Figure 8c) and is not distributed logarythmically (similar picture of Figure 8c and 8f). These results are also valid for analog distribution of FeO, PbO and MgO (not shown).
deposits can be used in Keban as a scout. These elements and Sr also correlate partially with BaO as well, which means their enrichment in barite.

The PbO and MnO correlation with Ag (Table. 1, r = 0.54 for n = 21) suggest their cogenetic development. Due to its strong affinity for the S comes Pb, Ag and Zn together in many hydrothermal areas before. Their geochemical Relatives such. B. chalcophoric character and the similar ionic radii of Pb 2+ (133 pm) and of Ag1+ (129 pm) favor the replacement (interception) of Pb2+ by Ag1+. In the joint enrichment of Mn and Zn isomorphic can between their minerals as Alabandin (MnS), sphalerite and similar ionic radii of Mn 2+ (81 pm) and Zn 2+ (88 pm) play an essential role (Berger, 1967, Varentsov and Grassely 1980). Pb2+ ions to the negatively charged sol adsorbs MnO2 (Berger, 1967). Hence it is for Pb concentration in the Mn-minerals such Psilomelan and cryptomelan that occur widely in Keban. Öztunali (1989) has the presence of coronadit (Pb<2Mn8O16) out (quoted by Yiğit, 1989), which can contribute to the Mn-Pb or Mn-Ag-relationship. The field geological and microscopic observations confirm the relationship between Mn and Pb or Mn and Ag, which is why the Mn ores are known as ‘Ag-Mn ores leading’ in the field (Etibank, 1989 and Hanelçi, 1991).

**Genetic Interpretation**

For metallogenetic interpretation, further diagnostic charts were created, based on comparisons with similar deposits. To this end, numerous major and trace elements were related, that are relevant to the genetic interpretation in the literature. Thus the representing points in the Fe-10 (Co + Cu + Ni)-Mn Triangle (Figure 10a) Crera et al. (1982) exactly in the hydrothermal field. Thus, the oxide ores come from Keban to East Pacific Rise (EPR). In the diagram Al / (Al + Fe + Mn) Fe / Ti Chart (Figure 10b) corresponding to the representative points of the Keban area of hydrothermal sediments after Meylan et al. (1981).

They run the line of material terrigenous. Pictured 10c after Adachi et al. (1986), the analysis data of Keban in Fe-Al-Mn-delta only partially in hydrothermal field. Here the oxide Mn ores of Keban are rich in Mn. By contrast, given the low Al content hardly terrigenous influences. This is also from the distribution of trace elements (As + Cu + Mo + Pb + Se) which can be seen in the Figure 10d after Nicholson (1992a), suggesting clearly hydrothermal on marine origin of metals. These comparative results stand with the above geochemical results in good agreement and support an exhalative sedimentary origin thesis. For similar occurrences in Turkey by Şaşmaz et al (2014) and Öksüz et al. (2014) is emphasized.

**CONCLUSION**

The chemical composition of the Mn-Fe ores in Keban district suggest that these usually originate from hydrothermal exhalation. This is supported by numerous findings of the electron microscope, geochemical and statistic investigations. As an example, the structurally and geochemically similar distribution of ore grades, the high concentration of closely occurring elements As, Ba, Pb, Sb, Se as well as the low concentration of Cu primarily to perform Co, K and Na. The low Fe / Mn ratio, the log-normal frequency distribution of the elements, the significant positive correlation between the MnO-FeO, Hg-Sb contents and with its representative hydrothermal deposits and occurrences (s. Şaşmaz et al., 2014; Öksüz et al., 2014 and Heshmatbezhadi and Shahabpour, 2010) confirm this view. The mineralization may have been developed on a seafloor spreading center of the Alpine ophiolites system and then moved as a part of it.

In consequence of the Paleocene syenite intrusions, this recrystallized into the weak zones of limestones Paleozoic age, displaced and deformed. This was followed by tectonic stress and secondary influences that characterize the current appearance of the deposit. Profound research, such as single mineral analysis, study of fluid inclusions, rare earth elements and the isotope geochemistry are still necessary for the presentation of the overall image of the deposit Keban district, involving the deposit as a whole. Only by clarifying the relationship between the sulphide (Ag, Pb, Zn) and the oxide ore (Mn, Fe) could be a realistic economic evaluation of the deposit is possible, requires targeted aboveground deep drilling and a systematic sampling.

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Table 1: Analysis of selected Mn-Fe ore samples.

Drilling   GYS-9   GYS-10   GYS-18   GYS-13
Sample-Nr.: Keb-3    Keb-6    Keb-7    Keb-11    Keb-14    Keb-15    Keb-17    Keb-20

Oxides in wt %
SO₂   3.04    3.83    2.34    2.33    14.10    2.26    3.36    4.22
TiO₂   0.06    0.03    0.03    0.03    0.22    0.04    0.04    0.02
Al₂O₃   1.30    0.97    0.51    0.53    3.79    0.91    1.31    1.20
FeO¹    1.97    4.87    9.79    7.81    42.01    1.71    43.10    5.38
MnO   0.47    3.75    8.06    5.93    12.87    1.37    29.05    5.01
MgO   16.85    17.87    11.70    17.01    5.85    20.10    2.53    16.78
CaO   30.12    26.93    12.73    30.25    16.28    29.01    6.94    25.85
Na₂O   0.05    0.06    0.08    0.04    Na²   0.05    0.09    0.06
K₂O   0.28    0.18    0.05    0.13    0.61    0.24    0.21    0.12
P₂O₅   0.03    0.02    0.02    0.02    0.09    0.01    0.05    0.01
BaO   0.25    0.22    18.60    0.06    0.16    0.12    0.29    0.80
SrO   0.03    0.03    0.13    0.02    0.10    0.03    0.08    0.05
P₂O₅   0.16    0.24    5.16    0.09    0.02    0.16    0.11    0.17
SO₃   0.16    0.79    5.25    1.28    0.45    0.07    0.42    0.65
H₂O   0.04    0.03    0.23    0.01    0.09    0.08    1.25    0.10
LOI   43.08    38.71    24.56    32.65    1.83    43.84    13.04    38.62

Sum   97.99    98.51    99.24    98.19    98.47    100.00    101.87    99.04

Trace elements in ppm

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¹ Total iron oxide as Fe₂O₃
² Below the detection limit

Figure 8: Frequency distribution of selected major elements.

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Figure 9: Correlation between the main element pairs of the investigated Mn-Fe ore samples. Variations attributable to the installation possibilities of the elements in various Mn, Zn and Fe minerals.

Figure 10: Some important element contents and ratios of the ore deposit district Keban compared the deposits of various origins. a, Crerar et al. (1982); b, Meylan et al. (1981); c, Adachi et al. (1986) and d, Nicholson (1992). EPR: East Pacific Rise, TM: Terrigene material and BM: Biogenic material.

REFERENCES


