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Preliminary Findings for A New Iron Mineralization in the Central Anatolian Iron Province (Turkiye) and An Approach to the Genesis

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Abstract
In this study, we present preliminary findings from geological field investigation that may indicate the presence of a new iron deposit in the Central Anatolian Iron Province (Turkiye). The geological field investigation identified massive iron ore outcrops, indicating significant iron mineralization. According to the analysis results of the samples taken from the iron ore outcrops, the outcrops contain 35.87-81.75% Fe. Silica ratios are 10.85 - 48.40%. Fe/Mn ratios, Si-Al values, Si/Al ratios, Fe/Ti and Al/(Al+Fe+Mn) ratios, Fe-Six2-Mn ratios, Fe-Al-Mn ratios, (Ca+Al+Mn) - (Ti+V) and (Ti+V) - (Al+Mn) ratios of the mineralization were evaluated. The positions of the samples taken on all distinction diagrams indicate that the mineralization in the study area was formed by hydrothermal activity (under relatively high-temperature conditions at 300-500 °C). The fact that the iron ores contain small amounts of transition metals such as Ni and V suggests that they are not related to volcanic rocks but are similar to the Lake Superior iron formation type. Ore deposition probably occurred through transgression-regression at the continental passive margin or the arc-back basin. Therefore, a model can be proposed where the iron ores in the study area were deposited by combining two stages in a continental margin or arc-back basin due to transgression-regression processes. These two stages are (1) hydrothermal fluid and fluvial activity (terrestrial dendritic sedimentation) that precipitates Fe and Si, and (2) oxidation and iron formation. Therefore, the primary source of the mineralization may have been volcanosedimentary or exhalative sedimentary type (synsedimentary), and later metamorphism and tectonic events may have led to the present position of the mineralization.

Keywords
iron mineralization, iron ore, volcanosedimentary type iron deposit, exhalative sedimentary type iron deposit, Central Anatolian Iron Province

Introduction

Iron oxides in ophiolitic systems predominantly originate in gabbroic and ultramafic lithologies, typically via magmatic cumulates or hydrothermal alteration, and are concentrated in tectonic zones where mantle dynamics and magmatic processes converge (Khedr et al., 2024; Rollinson, 2008). Iron ore reserves of Turkiye are concentrated in the Sivas, Malatya, Bingöl, Adana, and Kayseri regions. In addition to these ores, there are iron ore reserves of different sizes in Ankara, Balıkesir, and Adapazarı regions, and the ore produced is used in cement plants (Fig. 1). Known iron reserves are used in integrated iron and steel plants with the current consumption level. It is not in a position to meet the needs of its factories for a long time (Tuncel et al., 2017). When the regional distributions of iron deposits, ophiolitic and granitic rocks in Turkiye are compared with each other, it is determined that iron deposits and ophiolitic rocks are closely related (Öztürk ve diğ., 2016; Tuncel et al., 2017; Ünlü et al., 2019) (Fig. 1). The critical studies on iron mineralization in the vicinity of the study area located in the Central Anatolian Iron Ore Province (Kırşehir Massif, see Fig. 1). The Kesikköprü (Ankara) deposit is the most important deposit of the Central Anatolian Iron Ore Province. Around the deposit, the recrystallized limestone and ultramafic-mafic rocks of the Upper Cretaceous ophiolite complex are exposed. Upper Cretaceous sedimentary and volcanic-volcanoclastic rocks overlie the complex. This whole sequence is intruded by Upper Cretaceous-Paleocene granitoids. Skarn formations are also common at the contact between granitic rocks and crystallized limestone blocks of the complex (Doğan et al., 1998; Ünlü et al., 2019). The deposit is recognized as a granite-related skarn type by Brennich (1960), Kraeff (1962a,b), Boroviczeny (1964a, b, c, d), Sözen (1970), Öztürk and Öztürk (1983), Öztürk et al. (1983), Wondemagegnehu (1990), Doğan (1996), Kuşcu et al. (2002), İşbaşarır ve diğ. (2002, 2004). Doğan et al. (1998) suggested that the deposit should be classified as associated with "magmatic-metamorphic" processes. The reserve of Kesikköprü deposit is rated at 3.8 Mt with a grade of 44-60% Fe (Sözen, 1970; Ünlü et al., 2019).

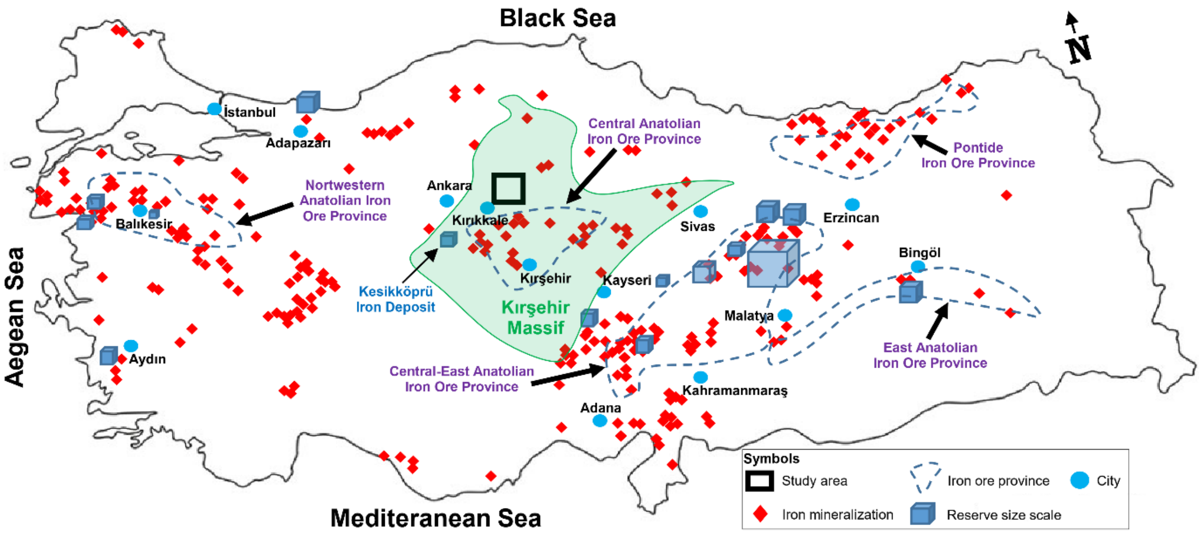

Fig. 1. Distribution of iron ore occurrences and deposits in Turkiye (compiled from the General Directorate of Mineral Research and Exploration of Turkiye-MTA archive, Öztürk et al., 2016 and Ünlü et al., 2019)

Some studies have also been carried out on other iron mineralizations and their origins in the province (Fig. 1). Öztürk (1977), in his research in Kaman (Kırşehir), revealed the presence of hydrothermal iron mineralization located in the faults within granite aplites. Kuşcu et al. (2002) noted that the iron mineralization in the region was linked to the Çelebi granitoid. Kaya (2002) stated that the Karacaali (Center/Kırıkkale) pyrite iron mineralization is located in Cretaceous ophiolitic basement rocks known as Ankara Melange (tholeiitic character, formed by differentiation from the same magma of MORB (mid-ocean ridge basalts) origin, microgabbro at the bottom, diabase on this unit and basalt at the top). Iron mineralization was determined to be hydrothermal due to the host rock's crack and fracture system. Delibaş and Genç (2004) reported that the Karacaali igneous complex consists of granitoid, rhyolite/rhyodacite, and basaltic rocks in the Karacaali (Kırıkkale). They have attributed the iron mineralization in the region to basaltic rocks. Acar (2018) and Ozdemir and Sahinoglu (2019) reported that the Büğüz iron mineralization in Kırıkkale is a skarn mineralization formed in the quartz monzonite-crystallized limestone intersection, transitioning to the hydrothermal phase and that elements of basic origin are also mixed with acid solutions, which are the main factor in mineralization. In conclusion, they stated that the Büğüz iron deposit is a mineralization associated with contact metasomatic and metamorphic processes.

The study area is located between Büyükyağlı and Taşyazı villages within the borders of Delice (Kırıkkale) in Kırşehir Massif (Central Anatolian Iron Ore Province, see Figs. 1 and 3). In this study, we present preliminary findings from geological field investigations that may indicate the presence of a new iron deposit in Central Anatolia (Turkiye). During the geological field surveys, massif iron ore outcrops were identified, which indicated the presence of significant iron mineralization in the study area (Figs. 2 and 3). According to the evaluations and interpretations of the analysis results of the samples taken from these outcrops, preliminary findings are determined for the possibility of a volcanic sedimentary or exhalative sedimentary type mineralization in the study area.

Fig. 2. A view from massive iron ore outcrops in the study area

Geology of the Study Area

The oldest unit of the study area, the volcanosedimentary assemblage consisting of diabase, basalt, spilitic basalt, spilite, basic tuff, lava, pelagic limestone, mudstone, radiolarite, cherts, and volcanic sandstones was named as Çiçekdağı Formation by Kara and Dönmez (1990) (Fig. 3). Black, dark green coloured gabbro and micro gabbro are located in the lower bed of the Çiçekdağ Formation. The unit starts with diabase dykes, basalt, syphilitic basalt, spilite and pelagic limestone, mudstone, radiolarite, and chert bands and ends with yellowish-brownish sandstones and siltstones. It is dated as Late Santonian-Campanian (Upper Cretaceous). Cretaceous granitoids cut the unit in the eastern and northeastern areas of the study area (Dönmez et al., 2005a).

The regressive, evaporitic, red, brown, grey, parallel and cross-bedded, less angular and non-angular grained, moderately to well and sometimes loosely consolidated terrestrial pebbles, sandstones, and mudstones were named the Incik Formation by Birgili et al. (1975). The lower parts of the Incik Formation consist of moderately to well consolidated, thin-medium-thick parallel layered sandstones alternated with gypsum, anhydrite, and mudstones. The middle-upper levels comprised of pebbles and sandstones alternating with mudstones and increasingly cross-bedded towards the top. The unit, which contains no fossils to give age, is stated to be Upper Eocene-Middle Miocene aged according to the formations above and below it. Upper Miocene-Pliocene terrestrial facies in Central Anatolia, such as rivers, fans, lakes, etc., are grouped under the Central Anatolia Group. The sections of the unit deposited under terrestrial conditions, represented by the sloping rubble, consist of red-coloured, unsupported pebbles, a few sandstones, and the mudstones in which they are found. The sections forming the channel facies are red, brown-coloured, cross-layered, pebble, sandstone, and mudstone bands and lenses. The relatively upper parts of the unit, represented by mid-basin lacustrine facies, are composed of unconsolidated sandstones, mudstones, gypsum, and anhydrite in some places, and intermediate levels of pebbles, sandstones, mudstones, limestones, and ignimbrites in other places. The sediments belonging to the Central Anatolian group unconformably cover the pre-Miocene rocks. Quaternary sediments are unconformably overlying it (Dönmez et al., 2005b).

Material and Method

Iron ore outcrops and some alteration zones were identified in the study area, indicating that there may be significant iron mineralization (Figs, 1 and 2). As it can be understood from the literature, significant iron mining operations in the region have been explored and operating in terms of iron ores. However, although 11 iron ore outcrops in different locations have been identified in this study in the study area, indicating that there may be significant iron mineralization, no preliminary geological investigations have been carried out for iron ore exploration. The samples from the iron ore outcrops identified during the geological field studies were collected and analyzed. Analysis results of the samples taken, with diagrams of Fe/Mn ratios, Si-Al values, Si/Al ratios, Fe/Ti and Al/(Al+Fe+Mn) ratios, Fe-Six2-Mn ratios, Fe-Al-Mn ratios, (Ca+Al+Mn) - (Ti+V) and (Ti+V) - (Al+Mn) ratios of the mineralization were evaluated and interpretations.

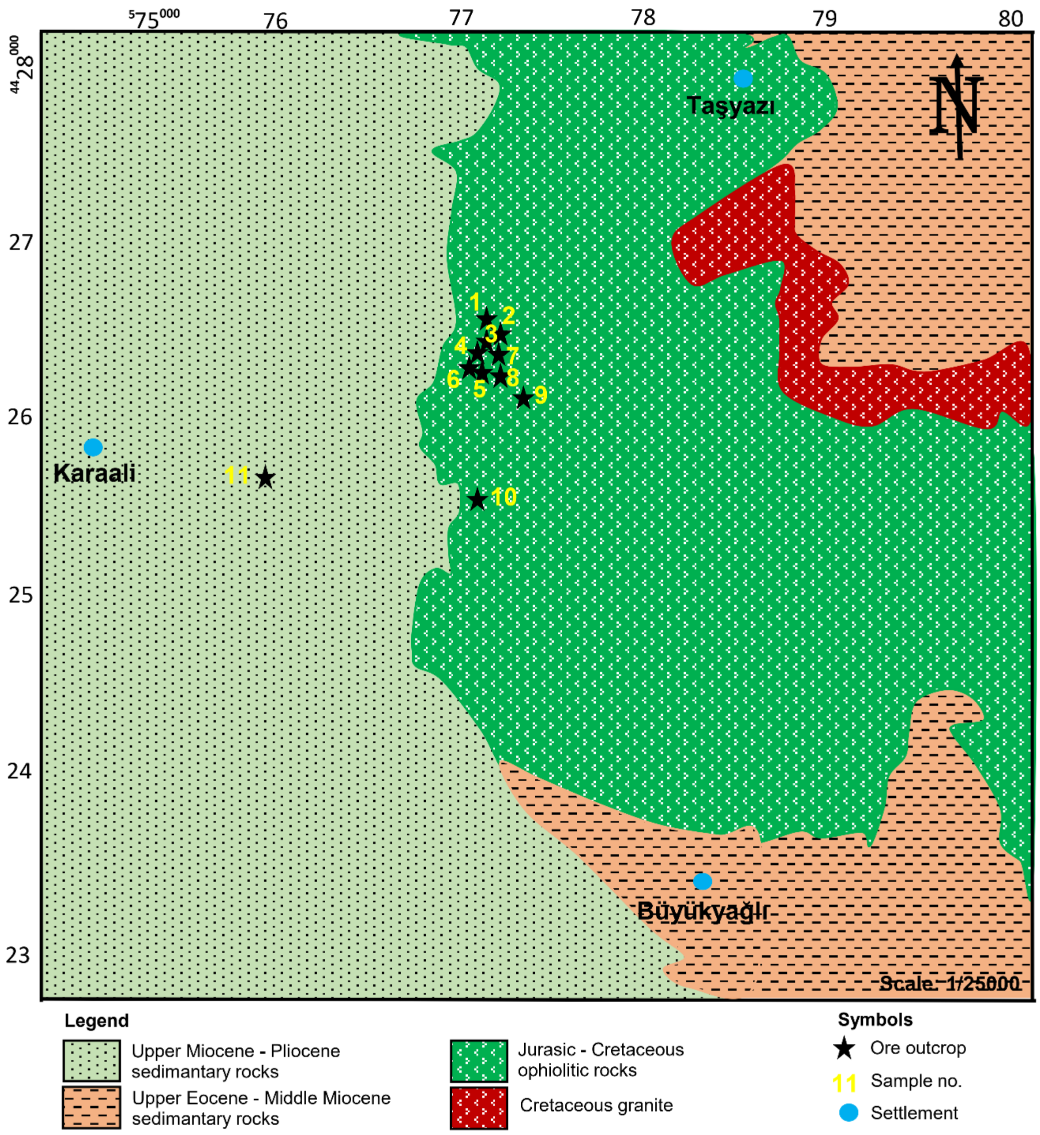

Fig. 3. Geology map (redrawn from Kırsehir I31-b2 of MTA according to field survey) and locations of iron ore outcrops (black stars) of the study area

Results and Discussion

Samples were taken from iron outcrops in the study area for X-ray fluorescence (XRF) analysis. According to the analysis results of the samples taken, the outcrops in the study area contain 35.87-81.75% Fe (Fig. 3 and Tab. 1). Silica ratios are 10.85-48.40%. Fe/Mn ratios of the mineralizations in the study area were determined to be 327.09-4087.50 (Tab. 1). Generally, very high values were observed. High Fe/Mn ratios (Fe/Mn >10) explain that the mineralizations are Fe-rich deposits (Crerar et al., 1982). Early and rapid precipitation from hydrothermal solutions forms deposits with high Fe/Mn ratios varying widely. In contrast, in sedimentary deposits, the Fe/Mn ratio varies over a narrow range (around 1) (Bonatti et al., 1972). However, some researchers argue that the variation of this ratio in a wide range and very small or very large values may indicate exalative sedimentary-type deposits (Rona, 1978; Nicholson, 1992). Accordingly, the Fe/Mn ratios of the mineralizations in the study area indicate that the deposit may be hydrothermal or volcanosedimentary (Tab. 1).

Tab. 1. *X-ray fluorescence analysis results of the samples taken from iron ore outcrops in the study area*

Outcrop No. (see Fig. 3)	Coordinates		Sample Description	Fe (%)	Si (%)	Al (%)	Mn (%)	Ti (%)	V (%)	Ca (%)	Ni (%)	Fe/Mn
	X	Y										
Outcrop 1	39.984439°	33.903611°	Massive ore sample	68,93	24,02	3,93	0,15	0,13	0,02	0,53	0,01	459,53
Outcrop 2	39.983885°	33.904165°	Massive ore sample	71,96	11,66	3,63	0,22	0,06	0,01	6,61	0,01	327,09
Outcrop 3	39.983605°	33.904162°	Massive ore sample	57,13	36,78	1,73	0,15	0,12	0,06	1,08	0,02	380,87
Outcrop 4	39.983326°	33.904158°	Massive ore sample	81,75	10,85	3,58	0,02	0,06	0,02	0,32	0,02	4087,50
Outcrop 5	39.982776°	33.903050°	Massive ore sample	70,75	17,89	5,61	0,08	0,07	0,09	0,54	0,03	884,38
Outcrop 6	39.982774°	33.903331°	Massive ore sample	69,10	22,22	4,64	0,08	0,08	0,02	0,28	0,04	863,75
Outcrop 7	39.982497°	33.904159°	Massive ore sample	78,25	12,96	3,89	0,17	0,09	0,01	1,15	0,02	460,29
Outcrop 8	39.983054°	33.904436°	Massive ore sample	62,91	24,09	6,24	0,10	0,08	0,04	0,44	0,02	629,10
Outcrop 9	39.981662°	33.906104°	Massive ore sample	66,96	19,22	5,49	0,13	0,15	0,02	1,67	0,03	515,08
Outcrop 10	39.976386°	33.903329°	limonite dominant sample	35,87	40,68	11,91	0,04	0,15	0,02	1,06	0,01	896,75
Outcrop 11	39.977776°	33.890278°	host rock dominant sample	44,06	48,40	3,86	0,17	0,14	0,01	0,62	0,03	259,18

The Si-Al diagram (Crerar et al., 1982) distinguishes hydrothermal mineralizations and sedimentary formations. The Si-Al values of the samples taken from the outcrops in the study area are plotted on this diagram in Fig. 4. In this diagram, it is seen that some of the samples are located in the hydrothermal area, and a significant part of the samples are located as near of the hydrothermal-sedimentary boundary (volcanosedimentary). The hydrothermal alteration during the mineralization process, in addition to the initial composition, also added Al from the side rocks, and this shows an excess of this element content, which is reflected in the diagram.

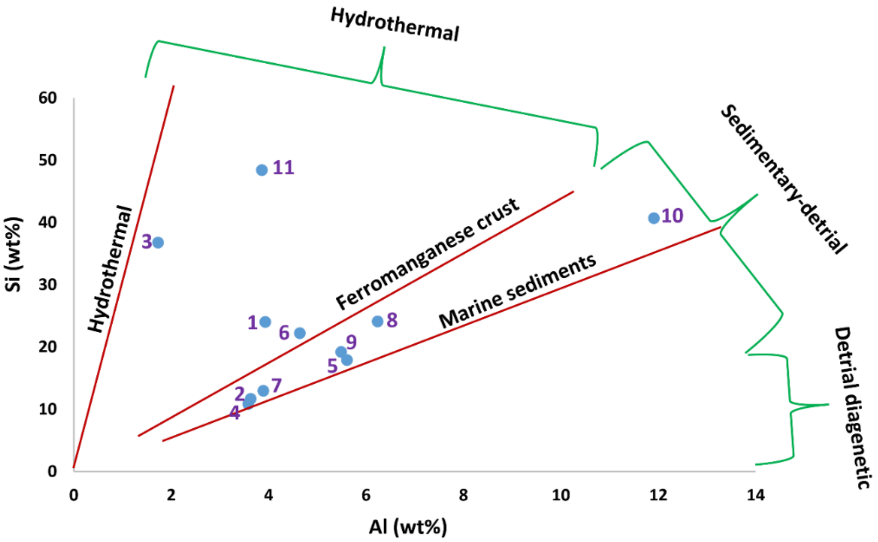

Fig. 4. Positions of the ore samples in the study area on the Si-Al diagram (diagram: from Crerar et al., 1982)

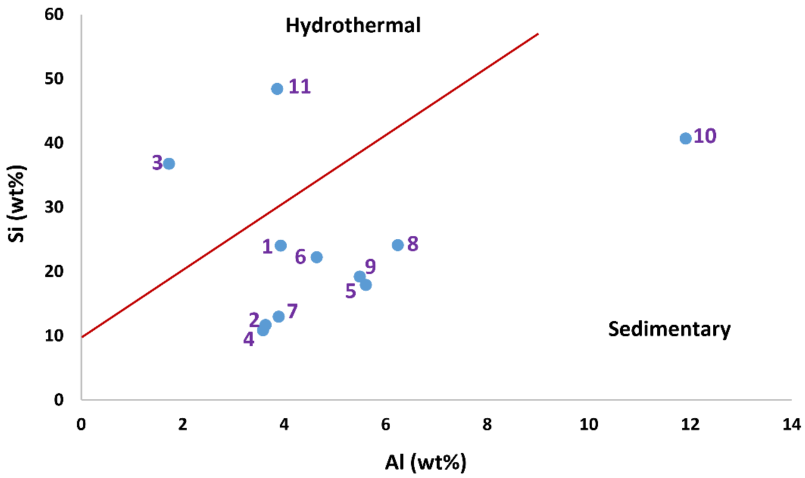

Fig. 5. Si-Al diagram of the outcrop samples in the study area according to hydrothermal tendency *(diagram: from Choi and Hariya, 1992)*

Fe- and Si-rich sediments are thought to be derived from a combination of erosion of continental crustal material and submarine hydrothermal vent fluids (Belevtsev, 1982; Hamade et al., 2003). The methods proposed to distinguish between seawater, hydrothermal, biogenic, and clastic sources are based on mineralogical, chemical, and isotopic composition differences. The Si/Al ratio determines the hydrothermal tendency of mineralization. According to Choi and Hariya's (1992) Si-Al discriminant diagram, the mineralization in the study area is of volcanosedimentary origin (Fig. 5).

Undoped hydrothermal deposits contain very little Al and have high Al/Ti ratios (Marchig et al., 1982). Contamination of such deposits by pelagic and terrestrial deep-sea sediments enriches them in components such as Ti and Al, leading to a drastic decrease in Fe/Ti ratios and an increase in the Al/(Al+Fe+Mn) ratio. In the Fe/Ti and Al/(Al+Fe+Mn) diagram, most of the samples in the study area are clustered near the hydrothermal Red Sea deposits and the East Pacific Rise deposits (Fig. 6). This indicates that the main components (>80%) of the ore in the study area are predominantly hydrothermal in origin. This suggests that the mineralization in the study area initially formed in sediments through hydrothermal systems, which then underwent metamorphism.

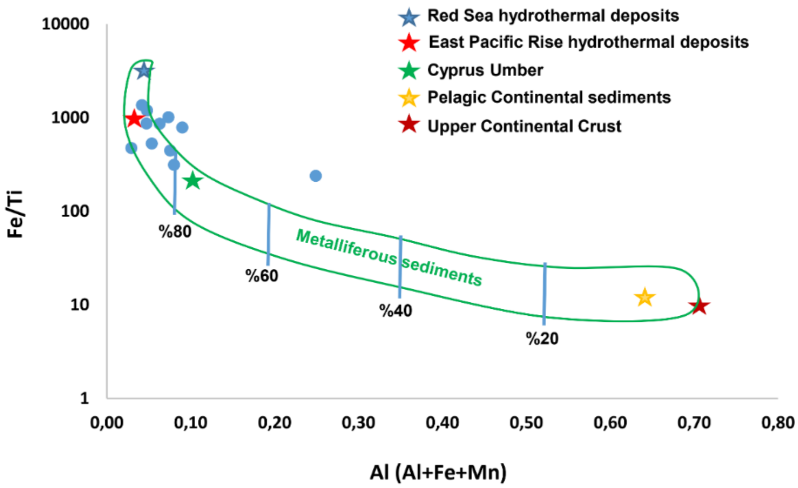

Fig. 6. Fe/Ti - Al/(Al+Fe+Mn) diagram of the outcrop samples in the study area (diagram: from Barret, 1981)

Another diagram utilizes Fe-Six2-Mn ratios (Corliss and Dymond, 1975). This diagram differentiates Fe-rich environments (hydrothermal), Fe-Mn environments, nodule formation, or Mn-rich environments (hydrothermal). Application of the ore samples in the study area to this diagram shows that all samples are located in the Fe-rich environment (hydrothermal) (Fig. 7). In the Fe-Al-Mn diagram (Adachi et al., 1986) (Fig. 8), hydrothermal - non-hydrothermal discriminant of the study area outcrop samples was made. Accordingly, all samples were located in the hydrothermal zone.

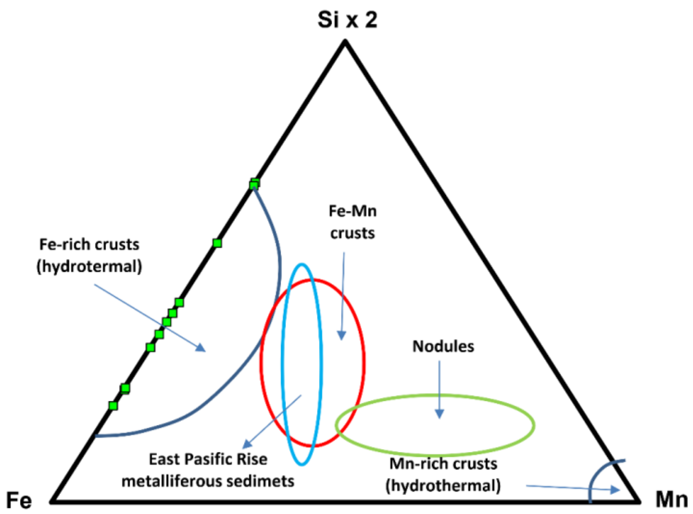

Fig. 7. Positions of the outcrop samples of the study area on the Fe-Six2-Mn triangle diagram (diagram: from Corliss and Dymond, 1975)

The high amounts of Al, V, Ti, and Mn in the iron ore suggest that the mineralization is associated with volcanic rocks (Zhen-Ju et al., 2017). The (Ca+Al+Mn) - (Ti+V) discriminant diagram has been proposed to distinguish iron ore from IOCG, Kiruna, porphyry Cu, BIF, skarn, and Fe+Ti+V deposits (Dupuis and Beaudoin, 2011; Nadoll et al., 2014; Huang et al., 2015, 2016). In the diagram, all samples are in the 300-500 °C temperature range (Fig. 9). This indicates that the ore was precipitated from medium to high-temperature fluids slightly enriched in Al and Ti. The slight enrichment in Al+Mn and Ti+V also suggests that the mineralization is not volcanic. According to the (Ca+Al+Mn) - (Ti+V) and (Ti+V) - (Al+Mn) discriminant diagrams, the iron ore may be of magmatic origin and may have undergone metasomatism and formed under relatively high temperature (300-500 °C) conditions. Also, the mineralization is a skarn mineralization because all samples are located entirely in the skarn area (Fig. 9).

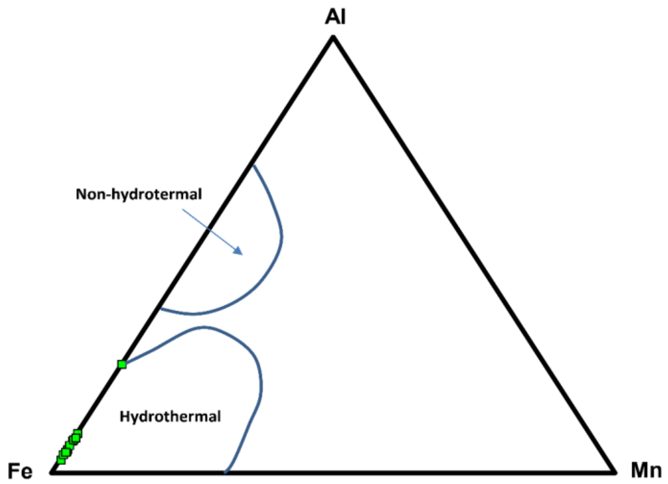

Fig. 8. Positions of the outcrop samples of the study area on the Al-Fe-Mn diagram (diagram: from Adachi et al., 1986)

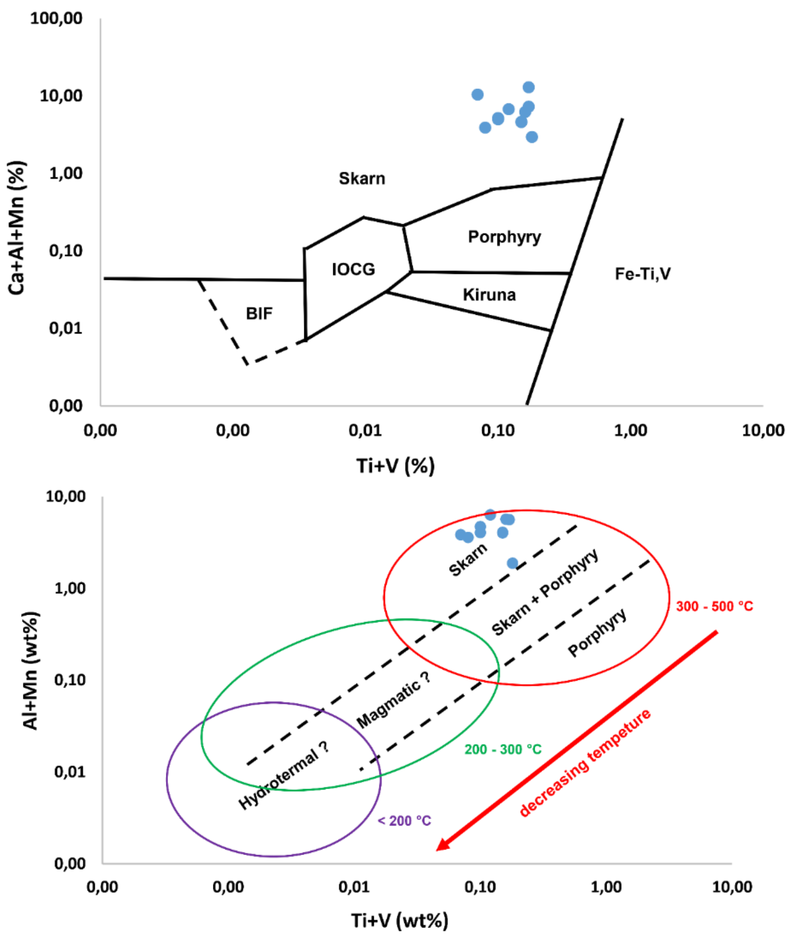

Fig. 9. Positions of the outcrop samples in the study area on the (Ca+Al+Mn) - (Ti+V) and (Al+Mn) - (Ti+V) diagrams (diagrams: compiled from Dupuis and Beaudoin, 2011; Nadoll et al., 2014; Huang et al., 2015, 2016; Bonda et al., 2022)

The positions of the samples taken on all discriminant diagrams indicate that the mineralization in the study area was formed by hydrothermal activity (under relatively high-temperature conditions at 300-500 °C) (Figs, 4-9). The fact that the iron ores contain small amounts of transition metals such as Ni and V (Tab. 1) suggests that they are not related to volcanic rocks but are similar to the Lake Superior iron formation type. Ore deposition probably occurred through transgression-regression at the continental passive margin or the arc-back basin. Therefore, a model can be proposed in which the iron ores in the study area were deposited by a combination of two processes in a continental margin or arc-back basin like the Lake Superior-type iron formations as a result of transgression-regression processes (Fig. 10). These two stages are; Stage 1: hydrothermal fluid and fluvial activity (terrestrial dendritic sedimentation) that precipitates Fe and Si; Stage 2: oxidation and iron formation. Therefore, the primary source of the mineralization may have been volcanic sedimentary or exhalative sedimentary type (synsedimentary), and then metamorphism and tectonic events may have led to the present situation of the mineralization.

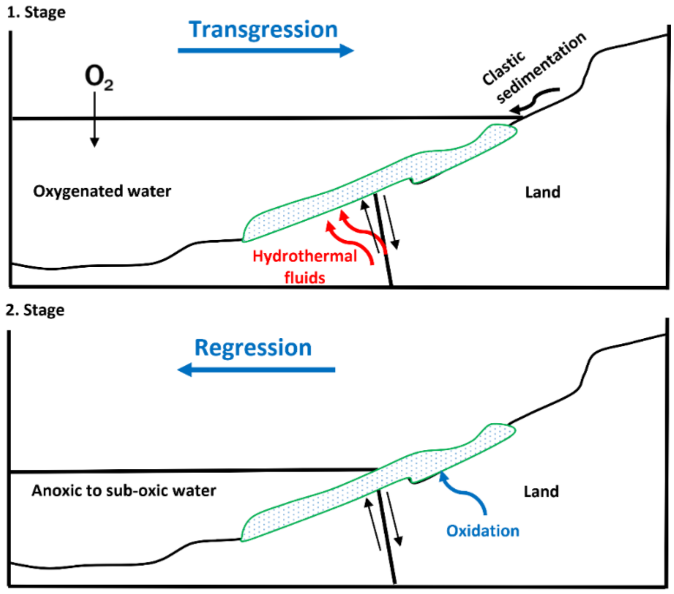

Fig. 10. Schematic model for iron ore formation in the study area

Conclusion

According to the results of the analysis of the samples, the outcrops contained 35.87-81.75% Fe in the study. According to the discriminant diagrams, the mineralization in the study area is of volcanosedimentary origin. This suggests that the mineralization in the study area initially formed in sediments through hydrothermal systems, which then underwent metamorphism. The ore was deposited from medium to high-temperature fluids, and the mineralization is not volcanic.

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