

Article

Geochemical Characteristics of Aluminum-Bearing Iron Ores: A Case Study from the Kolijan Karst-Type Bauxite Deposit, Northwestern Iran

Ali Abedini ^{1,*}  and Maryam Khosravi ² ¹ Department of Geology, Faculty of Sciences, Urmia University, Urmia 57561-51818, Iran² Department of Mining Engineering, Isfahan University of Technology, Isfahan 84156-83111, Iran; maryamkhosravi@iut.ac.ir

* Correspondence: a.abedini@urmia.ac.ir

Abstract: The Kolijan bauxite deposit (southeast Mahabad, northwestern Iran) mainly contains aluminum-bearing iron ores and was deposited in karstic depressions and sinkholes of the middle Permian carbonate rocks of the Ruteh Formation. Based on microscopic observations, the aluminum-bearing iron ores were allogenic in origin. According to XRD and SEM-EDS analyses, hematite and goethite are their main constituents, accompanied by lesser amounts of kaolinite, illite, amesite, boehmite, rutile, anatase, calcite, pyrolusite, crandallite, and parisite-(Ce). Chondrite-normalized REE patterns are indicative of fractionation and enrichment of LREE (La–Eu) compared to HREE (Gd–Lu), along with positive Eu and Ce anomalies ($\text{Eu}/\text{Eu}^* = 2.29\text{--}5.65$; $\text{Ce}/\text{Ce}^* = 3.63\text{--}5.22$). Positive Ce anomalies can be attributed to the role of carbonate bedrock as a geochemical barrier and the precipitation of parisite-(Ce). A strong positive correlation between Eu/Eu^* and Ce/Ce^* ($r = 0.84$) indicates that Eu anomalies, similar to Ce anomalies, are closely dependent on an alkaline pH. The distribution and fractionation of elements in the iron ores were controlled by a number of factors, including the pH of the environment in which they formed, wet climatic conditions, adsorption, isomorphic substitution, scavenging, co-precipitation, fluctuations of the groundwater table level, and the role of carbonate bedrock as a geochemical barrier. This research indicates that the aluminum-bearing iron ores were probably generated from the weathering of basaltic protolith.



Citation: Abedini, A.; Khosravi, M. Geochemical Characteristics of Aluminum-Bearing Iron Ores: A Case Study from the Kolijan Karst-Type Bauxite Deposit, Northwestern Iran. *Minerals* **2024**, *14*, 151. <https://doi.org/10.3390/min14020151>

Academic Editors: Alireza Somarin and Santanu Banerjee

Received: 23 November 2023

Revised: 18 January 2024

Accepted: 28 January 2024

Published: 30 January 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Keywords: aluminum-bearing iron ores; positive Ce and Eu anomalies; parisite-(Ce); alkaline pH; northwestern Iran

1. Introduction

The term bauxite was first used by Berthier in 1821 referring to alumina-rich sediments in the Les Baux region of France. Bauxite deposits are formed by the weathering of aluminosilicate-rich rocks such as granite, basalt, diabase, andesite, nepheline syenite, marl, tuff, clayey limestone, shale, slate, etc., in tropical and subtropical regions under warm and humid climatic conditions [1]. Al (oxyhydr)oxides are the dominant mineral components of bauxite ore [1], together with variable amounts of Fe and Ti (oxyhydr)oxides. Bauxite deposits are classified into two main categories: (1) bauxite deposits on aluminosilicate bedrocks, and (2) those on carbonate bedrocks, known as karst-type bauxite deposits [1,2]. Studies conducted over the past two decades have shown that some karst bauxite deposits show a characteristic structure called “iron-bauxite”. This structure has been reported from the Nurra bauxite deposit in Italy [3], bauxite deposits in northwestern Iran [4,5], and most bauxite deposits in China [6–10]. In these deposits, the “bauxite” part of the structure includes bauxite ores, bauxitic clays, and clay-rich bauxites. The “iron-rich” part of the structure includes iron-rich clays, bauxitic iron ores, and aluminum-bearing iron ores [3–10].

In recent years, there have been studies of the distribution and fractionation of trace elements and rare earth elements (REE), and factors controlling their distribution and mobility in bauxite deposits worldwide. These studies show that the distribution and fractionation of trace elements and REE in bauxite deposits is controlled by a number of factors, including the chemical composition of the protolith and bedrocks [11–13], physico-chemical conditions in the weathering environment (Eh–pH) [14–16], fluctuations of the water table [17,18], the presence of organic and inorganic ligands in the soil [19,20], bacterial activity, mineral species in bedrocks [21–25], adsorption, scavenging [3,26,27], climatic conditions [28–31], stability of REE-bearing primary and secondary minerals [6,32–34], chemical properties of elements during weathering [35,36], complexation with different ligands, and diagenetic and epigenetic processes [37–39].

Similarly, in recent years, comprehensive studies have been carried out on geodynamic evolution and geochemical characteristics of the Iranian karst-type bauxite deposits [5,6,40–49]. The Iranian bauxite deposits are a part of the Irano-Himalayan karst bauxite belt [5,41–49]. The sedimentary hiatus during the Permian caused the generation and development of bauxite deposits in Iran. In northwestern Iran, bauxite deposits dominantly occur in karstic sinkholes and depressions of middle–late Permian shallow carbonate bedrocks of the Ruteh and Nessen Formations. Based on geochemical investigations, these deposits probably related to the weathering of igneous rocks, mainly of a mafic composition [48,49]. Studies show that the middle–late Permian bauxite deposits in northwestern Iran mainly consist of bauxitic clays, bauxites, and Fe-rich bauxites [41–49]. Mineralogical and geochemical features of these categories of the northwestern Iran bauxite deposits were presented by Abedini and Khosravi [43] and Abedini et al. [5,45–47]. In addition, Al-bearing iron ores are developed in some bauxite deposits of the northwestern Iran, but mechanisms of the generation and development of the ores have not been considered.

The Kolijan bauxite deposit is one of the typical karst-type bauxite deposits in southeast Mahabad, northwestern Iran. The development of “iron-bauxite” structure is one of the most important geological features of this deposit. The Al-bearing iron ores were taken from the lowermost parts of the selected profile in the Kolijan area. The mineralogy and geochemistry of the Kolijan Al-bearing iron ores from the perspective signatures will clarify the mechanism of formation and development of this ore type and also help to explore potential resources of this ore type in the Irano-Himalayan karst-type bauxite belt. The main aims of this paper are to determine the factors controlling the distribution and fractionation of trace elements and REE, the reasons of Ce and Eu anomalies, the formation environment, and the protolith of the Kolijan Al-bearing iron ores.

2. Geological Setting of the Deposit

According to structural divisions of Iran proposed by Nabavi [50], the Kolijan area is a part of the Khoy–Mahabad structural zone (Figure 1). From the oldest to youngest, rock units in the Kolijan area include shale and phyllite of the Kahar Formation (Precambrian), shale and dolomite of the Soltanieh Formation (Cambrian), sandstone of the Lalun Formation (Cambrian), dolomite and limestone of the Mila Formation, dolomitic limestone of the Ruteh Formation (Permian), volcanic rocks, carbonates, along with phyllite and sandstone of Cretaceous age, limestone of the Qom Formation (Miocene), Plio-Quaternary alkaline volcanic lavas, and recent alluvial sediments (Figure 2).

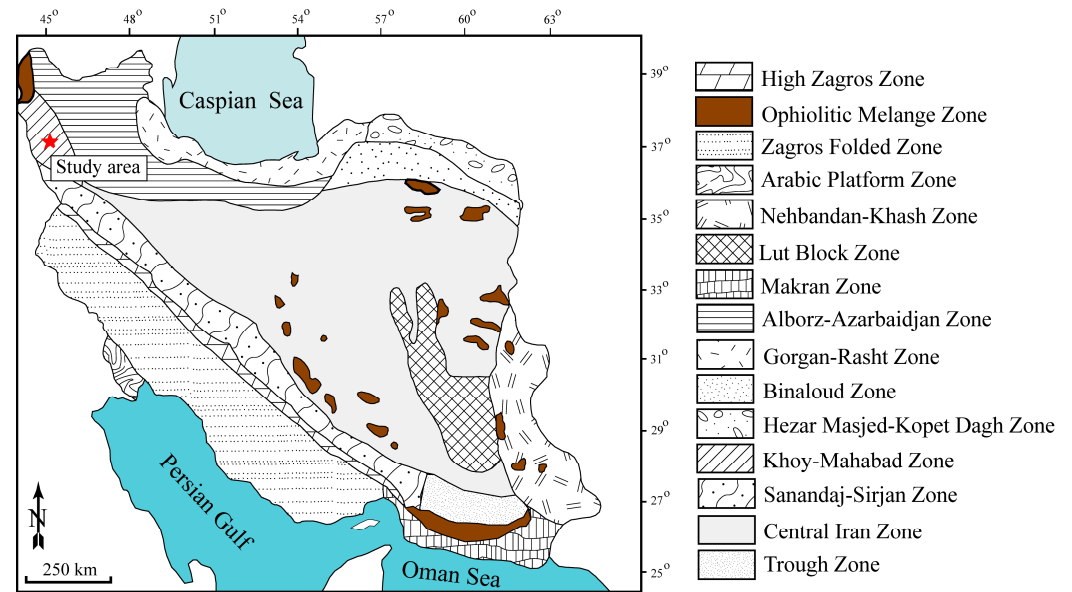


Figure 1. Map of structural zones of Iran [50] showing the location of the Kolijan area, southeast Mahabad, northwestern Iran.



Legend

- Recent alluvium (Quaternary)
- Basic lava flows (Plio-Quaternary)
- Qom Formation (Miocene): limestone
- Volcanic and carbonate rocks, phyllite, and sandstone (Cretaceous)
- Bauxite layers and lenses (Thickness exaggerated)
- Ruteh Formation (middle Permian): dolomitic limestone
- Mila Formation (Cambro-Ordovician): dolomite and limestone
- Lalun Formation (Cambrian): sandstone
- Soltanieh Formation (Cambrian): dolomite and shale
- Kahar Formation (Precambrian): phyllite and shale
- Kolijan village
- Fault

Figure 2. Geological map of the study area showing the local geological setting and lithological units of the Kolijan deposit.

The bauxite deposit in the Kolijan area is present in five discrete outcrops as stratiform layers and lenses in karstic sinkholes and depressions of the middle Permian dolomitic limestones of the Ruteh Formation (Figure 2). They have a length of 1.4 km and a variable thickness from 8 to 18 m with an overall trend of NE–SW and NW–SE. According to field observations, ores of these five layers and lenses have various colors, ranging from red, brownish red, brick red, through gray, to green, greenish cream, and white. The white, gray, green, and greenish cream ores are clay-rich bauxites (Figure 3a) and bauxitic clays (Figure 3b), and mainly occur in the upper parts of layers and lenses. Whereas, red, brownish red, and brick-red ores are Al-bearing iron ores and mainly occur in the lower parts of layers and lenses (Figures 3a,b and 4a,b). Only the Al-bearing iron ores are considered in this study; they are massive with high specific gravity and hardness. The supergene oxidation on the surface, the presence of macropisoids, ooids, pisoids, and nodular forms, and traces of manganese dendrites are the significant mesoscopic characteristics of the Al-bearing iron ores.

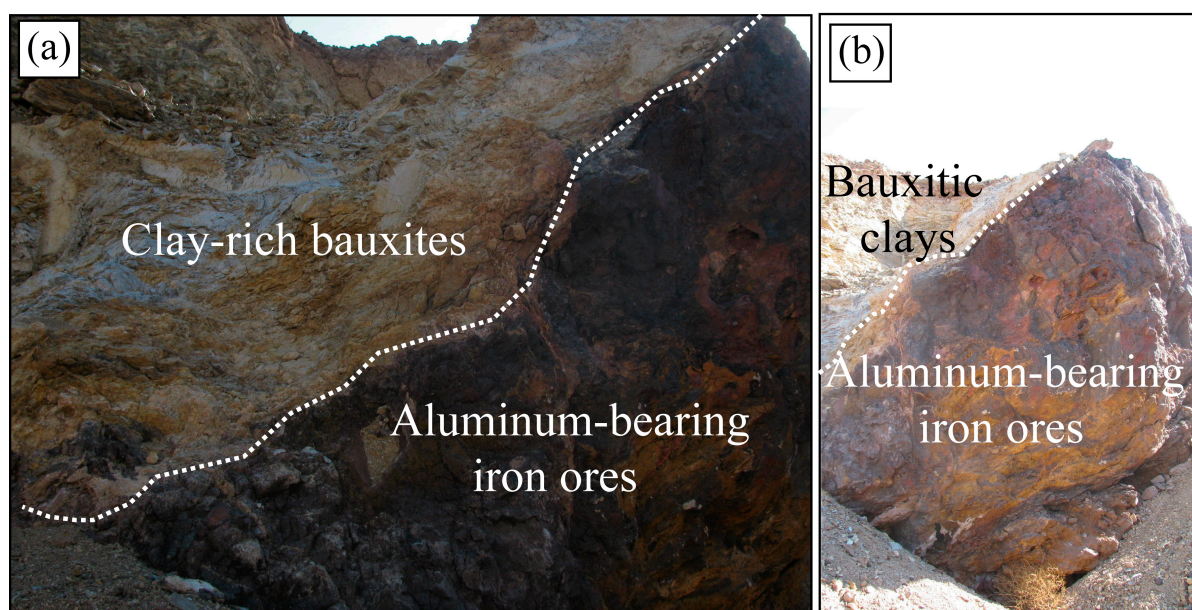


Figure 3. Photographs representing outcrops of the Al-bearing iron ores and their relationships with clay-rich bauxites (a) and bauxitic clays (b) in the Kolijan deposit, northwestern Iran.

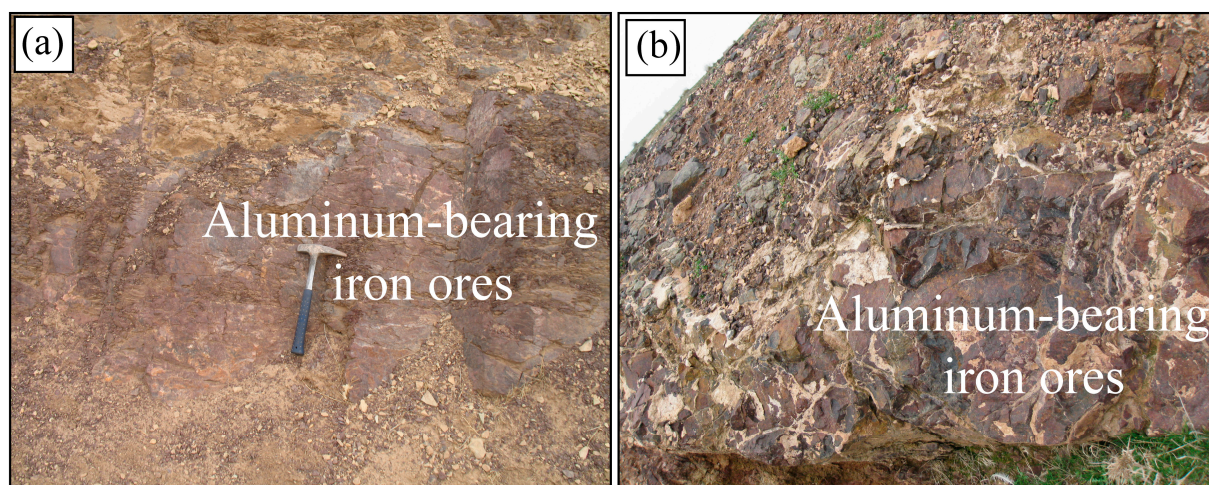


Figure 4. Photographs showing outcrops of the Al-bearing iron ores (a,b) in the Kolijan deposit, northwestern Iran.

3. Method of Investigation

Following field works, 11 whole-rock samples of the Al-bearing iron ores from the lower parts of the Kolijan deposit were taken. Petrographical and mineralogical studies of the collected samples were examined by Olympus (Tokyo, Japan) BX60F5 Transmitted and Reflected Light Microscope at the Department of Geology of Urmia University, Iran and X-ray diffraction (XRD) with a D-5000 (Munich, Germany) SIMENS diffractometer at the Kansaran Binaloud Co., Tehran, Iran. Mineralogical results of the Kolijan Al-bearing iron ores are presented in Table 1. Microscale mineralogical analysis of the samples was performed at the Razi Metallurgical Research Center, Iran by scanning electron microscope coupled with energy-dispersive X-ray spectrometry (SEM–EDS) using a Hitachi (Tokyo, Japan) S-3400 N SEM equipped with a Link Analytical Oxford IE 350 energy dispersive X-ray spectrometer (EDS) under the following conditions: 15 kV, 1 nA-beam current, and 1 μm-beam diameter.

Major oxides and trace elements, including REE, contents of 11 samples from the Kolijan Al-bearing iron ores were measured at the ALS Chemex Laboratory, Canada by inductively coupled plasma–atomic emission spectrometry (ICP–AES) and inductively coupled plasma–mass spectrometry (ICP–MS), respectively. Results of geochemical analyses of major oxides and trace elements of the studied ores, southeast Mahabad, northwestern Iran are presented in Table 2. About 0.2 g of the powdered samples were mixed with lithium tetraborate–lithium metaborate flux, fused in a furnace at 1000 °C, and then cooled, digested with nitric acid, and finally diluted to 100 mL. Values of loss-on-ignition (LOI) were obtained by weight difference after ignition at 1000 °C in a muffle furnace. The detection limit for major oxides was 0.01 wt%, for trace elements from 0.05 to 10 ppm, and for REE from 0.01 to 0.5 ppm. In this paper, Pearson correlation coefficients among the elements were calculated by the SPSS statistics software (version 16).

Table 1. Results of mineralogical analysis of the Al-bearing iron ores.

	Kj-01	Kj-02	Kj-03	Kj-04	Kj-05	Kj-06	Kj-07	Kj-08	Kj-09	Kj-10	Kj-11
Hematite	×××××	×××××	××××	×××××	×××××	×××××	×××××	××××	××××	××××	××××
Goethite	×	×	×	×	×	×	×	×	×	×	×
Kaolinite	ac	ac	ac	ac	ac	ac	×	×	×	×	ac
Calcite	ac				ac	ac					ac
Pyrolusite	ac					ac		ac	ac	ac	ac
Anatase		ac				ac					
Rutile						ac		ac	ac	ac	ac
Crandallite						ac		ac	ac	ac	ac
Illite								ac			ac
Amesite		ac		ac		ac				ac	
Boehmite									ac		ac

ac: accessory; ×: the relative abundance of mineral.

4. Results and Discussion

4.1. Texture and Mineralogy of the Al-Bearing Iron Ores

Textural components in the Kolijan Al-bearing iron ores include concentric shapes, such as micro-ooids, ooids, pisoids, and macropisoids, secondary films and coatings, nodules, concretions, clasts (clastic fragments), and fissure fillings (Figure 5a–c). In polished sections, hematite is the only mineral identified in the core of ooids, pisoids (Figure 5b), spastoids, and macropisoids. The concentric forms are sometimes elliptical, due to effects of tectonic pressures (Figure 5d). Hematite in the studied ores occurs in the form of nodule, granule, sphere, oval, and veinlet. The nodules, ranging from 3 to 9 mm in size, are almost spherical to oval-shaped and sometimes show weak orientations in the matrix of the Al-bearing iron ores. Ooidic, pisoidic, nodular, pelitomorphic, collomorphic, clastic, and round-grained textures are the most dominant textures identified in the Kolijan Al-bearing iron ores. Micro-ooids and ooids are sometimes observed in the core of pisoids (Figure 5a), indicating a

multi-cyclic nature of the formation environment for the Al-bearing iron ores [51]. Moreover, irregular or radial fractures in hematite cores of concretionary forms (Figure 3b) are probably related to gel shrinkage during the formation and development of the ores [1]. According to Bárdossy [1], the presence of a round-grained texture (Figure 5c) is indicative of an allogenic origin for the Kolijan Al-bearing iron ores. Elongation of texture-forming components and elongated ooids with a hematite core are related to the function of tectonic processes and the effect of overburden pressures on the ores (Figure 5d). The secondary coatings around the hematite are possibly formed during diagenetic or epigenetic processes (Figure 5e) [2]. In any case, the presence of fractured pisoids and clastic fragments mainly of hematite suggests an allogenic origin for the Kolijan Al-bearing iron ores (Figure 5f).

The presence of Fe-bearing nodules in the studied samples suggests that fluctuations of the groundwater table level played a role in the development and evolution of the Kolijan Al-bearing iron ores. According to Valetton [52], fluctuations of the water-table level produce Fe-bearing nodules in weathered deposits. As a whole, it can be deduced that the development and evolution of the studied ores is related to the chemistry of the groundwater. In other words, the dissolution of carbonate bedrocks, promoting a higher pH of weathering solutions, can cause precipitation of Fe in the Kolijan area [33,41].

XRD analyses show that hematite and goethite are the main constituents of the Kolijan iron ores, accompanied by lesser amounts of kaolinite, illite, boehmite, calcite, rutile, anatase, amesite, pyrolusite, and crandallite (Table 1, Figure 6). Hematite and goethite as the main mineral phases, with kaolinite as an accessory mineral, are present in all the studied samples. Pyrolusite in six samples, rutile and crandallite in five samples, calcite and amesite in four samples, and boehmite, anatase, and illite in two samples were identified as accessory minerals (Table 1). According to SEM–EDS analyses, parisite-(Ce) occurs as individual subhedral crystals on hematite and kaolinite (Figure 7a,b). This mineral has been reported from other karst-type bauxite deposits, such as Wuchuan–Zheng’an–Daozhen, Quyang, Taiping, Guangxi, and Wulong–Nanchuan bauxite deposits in China [27,29,53–55], Abruzzi and Apulian bauxite deposits in Italy [30,32,35], Parnassos–Ghiona bauxite deposit in Greece [25], and Soleiman Kandi, Baghoushi, Bidgol, and Tang-e-Pirzal bauxite deposits in Iran [41,46].

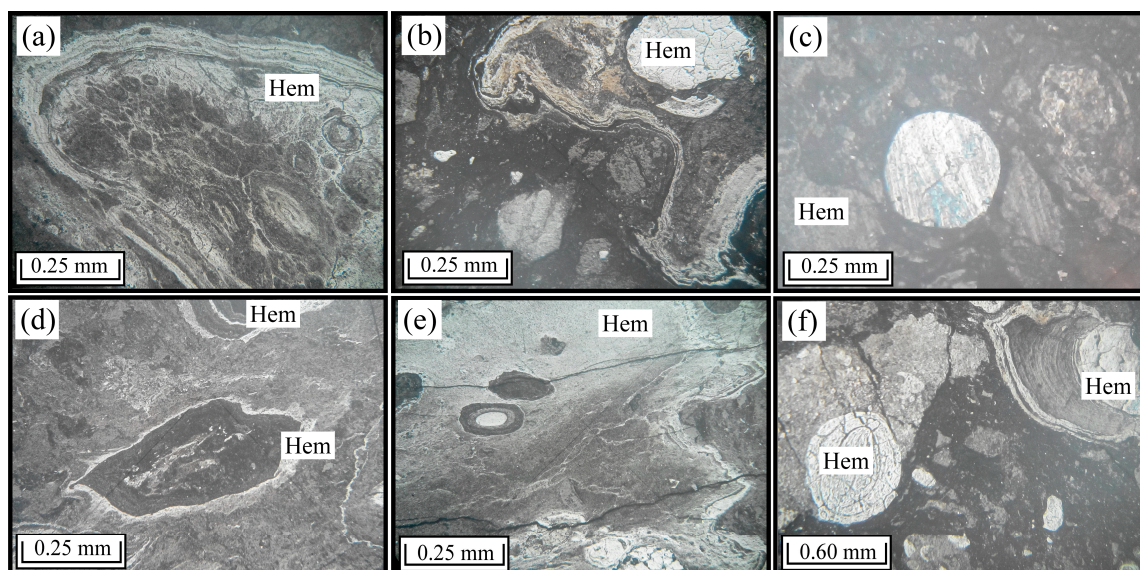


Figure 5. Photomicrographs showing textural and mineralogical features of the Kolijan Al-bearing iron ores. (a) Micro-ooids and ooids in the core of a pisoid, indicating the multi-cyclic nature of the formation environment. (b) Concretion forms with a hematite core, which have irregular fractures, due to gel shrinkage. (c) Round-grained texture. (d) Elongation and orientation in concretion forms. (e) Oval-shaped ooids with a hematite core. (f) Fractured clasts and pisoids. All figures are in reflected light/cross polarized light (XPL). Hem = hematite [56].

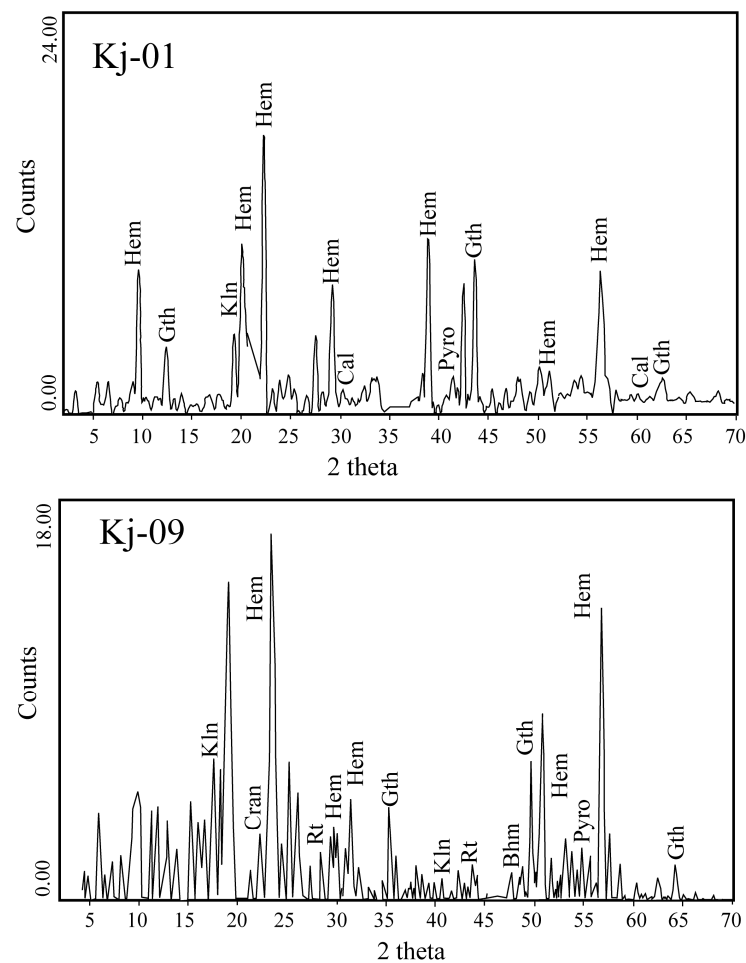


Figure 6. XRD patterns of the Kolijan Al-bearing iron ores. Abbreviations: Bhm = boehmite, Cal = calcite, Cran = crandallite, Gth = goethite, Hem = hematite, Kln = kaolinite, Pyro = pyrolusite, Rt = rutile [56].

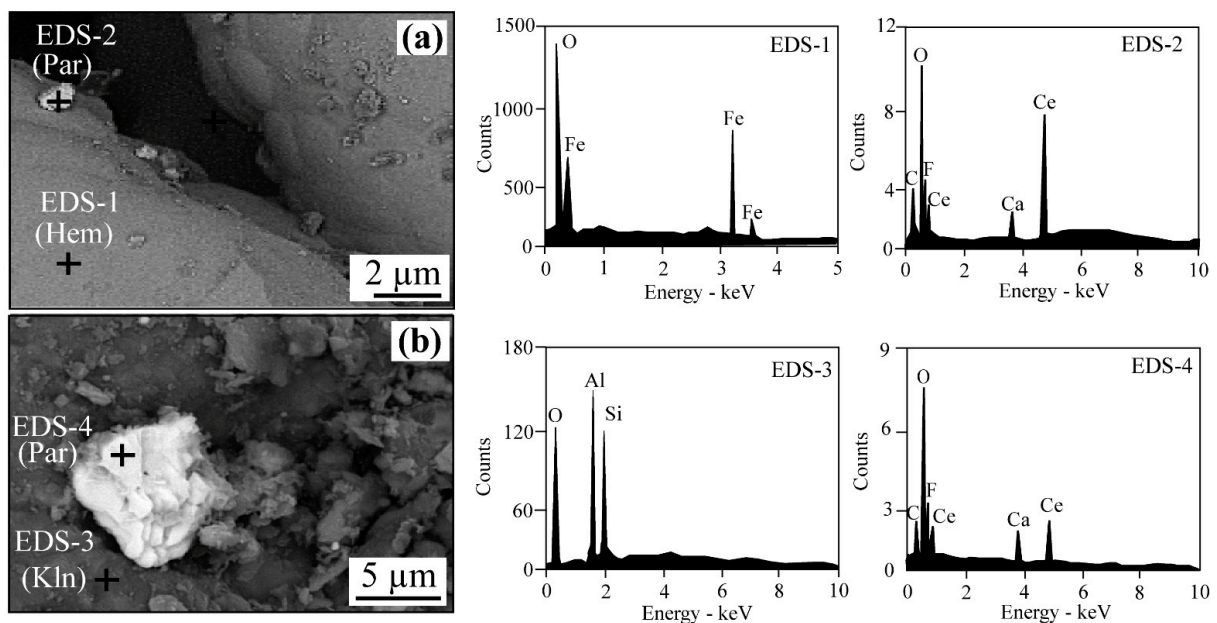


Figure 7. SEM-EDS analyses of the Kolijan Al-bearing iron ores. (a) Parisite-(Ce) on hematite (a) and kaolinite (b) in sample Kj-09. Abbreviations: Hem = hematite, Kln = kaolinite, Par = parisite [56].

4.2. Distribution of Major Elements in Kolijan Iron Ore

Among major oxides, Fe_2O_3 is the main constituent of the Kolijan iron ores, and occurs in the range 60.90–91.12 wt% (average = 82.88 wt%). The next most abundant components of the studied ores are SiO_2 (1.47–14.42 wt%, average 4.08 wt%) and Al_2O_3 (0.27–8.12 wt%, average 1.97 wt%) (Table 2). Major oxides TiO_2 (0.08–2.65 wt%, average 0.71 wt%), P_2O_5 (0.21–1.35 wt%, average 0.71 wt%), and MnO (0.41–1.09 wt%, average 0.75 wt%) occur at significantly lower levels. Alkaline and alkaline earth oxides (Na_2O , K_2O , MgO , and CaO) are in the range 0.01 to 1.97 wt%.

There is a strong negative correlation between Al_2O_3 and Fe_2O_3 in the Kolijan iron ores ($r = -0.99$, $p < 0.01$; Figure 8a). This strong negative correlation is indicative of the different geochemical behavior of Al and Fe during weathering processes related to Eh–pH changes of groundwater during weathering [11,57]. Recent studies indicate that the competition between Al and Fe in the generation of Al and Fe (oxyhydr)oxides during weathering depends on climatic changes. Iron concentration occurs under wetter climatic conditions than Al concentration, which is favored under arid climatic conditions [33]. The significant concentration of Fe_2O_3 compared to Al_2O_3 in the studied ores suggests that climatic conditions were probably wet during the formation of the iron ores. Moderate-to-strong negative correlations between Fe_2O_3 and SiO_2 ($r = -0.98$, $p < 0.01$; Figure 8b), MgO ($r = -0.95$, $p < 0.01$; Figure 8c), TiO_2 ($r = -0.97$, $p < 0.01$; Figure 8d), MnO ($r = -0.83$, $p < 0.01$; Figure 8e), and P_2O_5 ($r = -0.74$, $p < 0.01$; Figure 8f) are also observed, indicating that the amount of kaolinite, boehmite, crandallite, pyrolusite, rutile, anatase, and amesite decreases with increasing amounts of hematite and goethite. A strong positive correlation between Al_2O_3 and TiO_2 ($r = 0.96$, $p < 0.01$) indicates the similar behavior of these elements during weathering [58,59]. The Al_2O_3 – SiO_2 – Fe_2O_3 ternary diagram of Schellmann [60] indicates that the Kolijan iron ores formed during strong laterization (Figure 9). This diagram also shows that during the formation and development of the studied ores, the content of Fe increased and the content of Si and Al decreased.

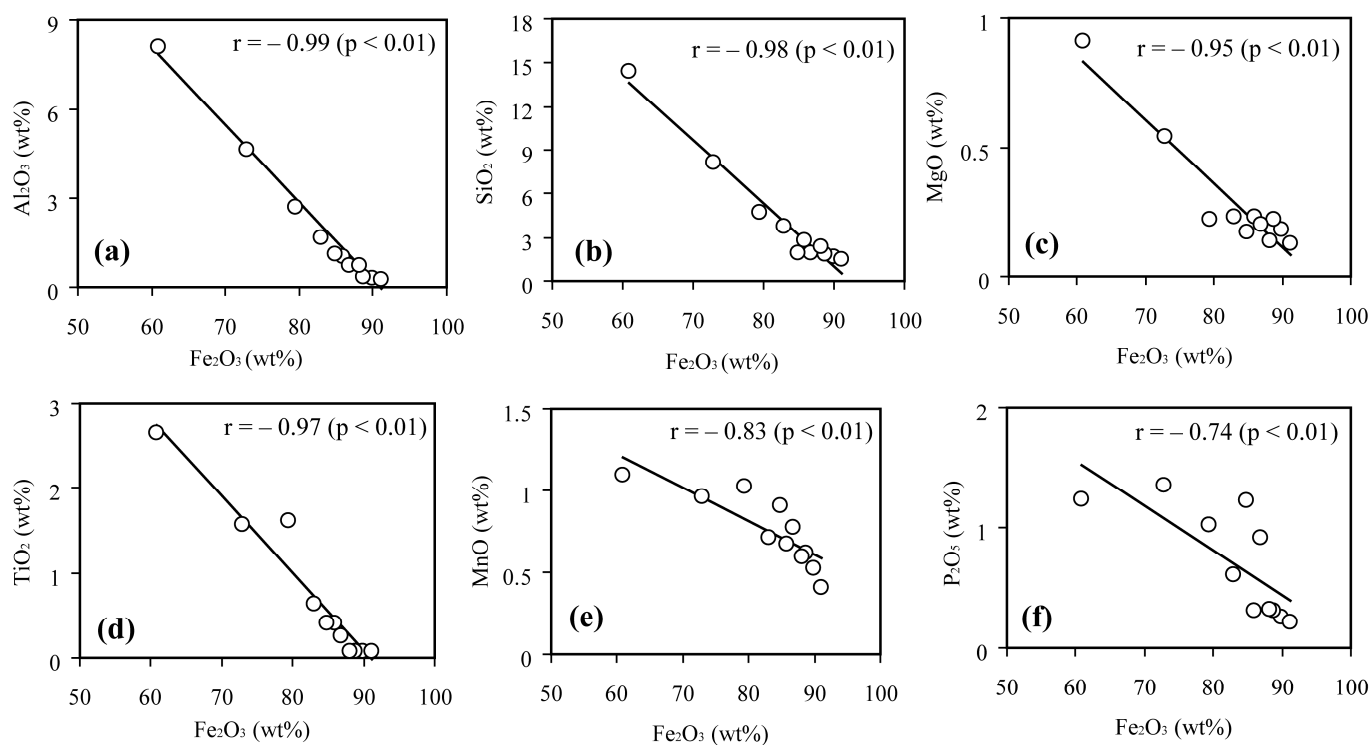


Figure 8. Bivariate plots of (a) Fe_2O_3 – Al_2O_3 , (b) Fe_2O_3 – SiO_2 , (c) Fe_2O_3 – MgO , (d) Fe_2O_3 – TiO_2 , (e) Fe_2O_3 – MnO , and (f) Fe_2O_3 – P_2O_5 for the Kolijan iron ores, showing negative correlations between Fe_2O_3 and major oxides.

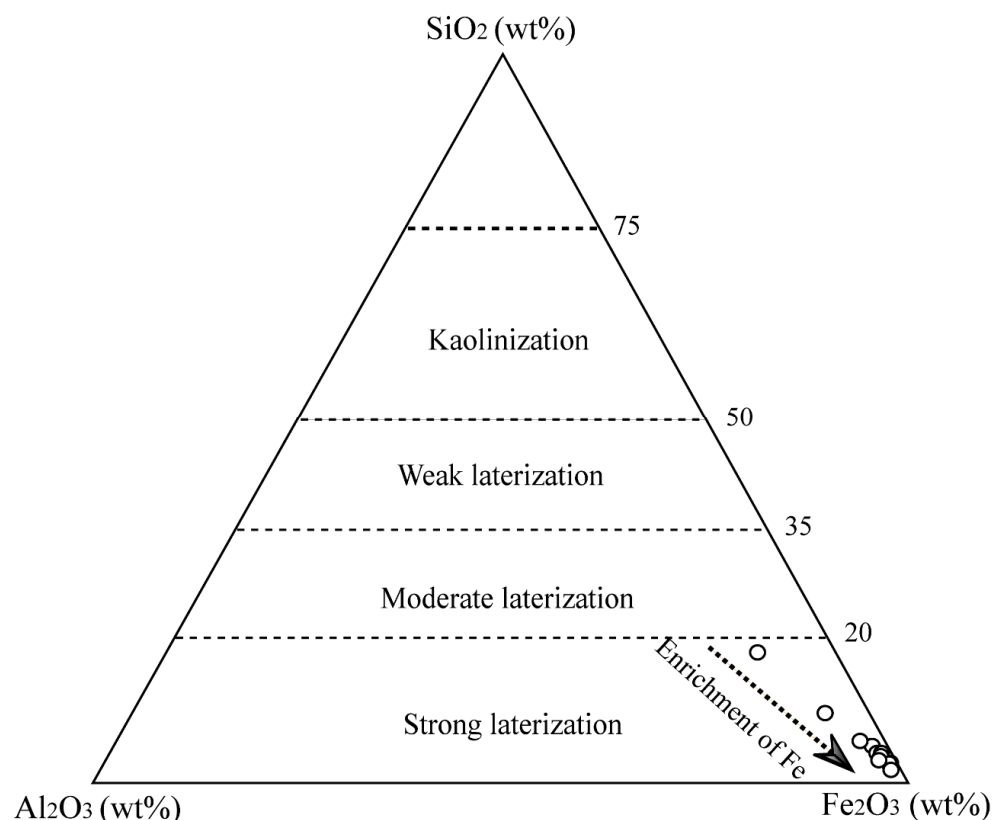


Figure 9. Plot of the Kolijan iron ores on a SiO_2 – Al_2O_3 – Fe_2O_3 ternary diagram [60].

4.3. Distribution of Trace Elements in Kolijan Iron Ore

Cr is the most abundant trace elements, ranging from 470 to 1010 ppm, average 851.8 ppm. Barium (63–286.1 ppm, average 160.4 ppm), V (80–312 ppm, average 133.8 ppm), Sr (76.3–265.4 ppm, average 156.8 ppm), Pb (46–152 ppm, average 91.1 ppm), Ni (42–109 ppm, average 82.6 ppm), Co (14.6–32.1 ppm, average 27.8 ppm), Zr (4–71 ppm, average 17.4 ppm), and U (5.6–18.2 ppm, average 9.1 ppm) are the next most abundant trace elements of the studied ores. Average values for Th, Hf, Nb, Cs, Rb, Ga, Y, and Ta are less than 4 ppm.

Strong positive correlations between Fe_2O_3 and Cr ($r = 0.89$, $p < 0.01$), Co ($r = 0.87$, $p < 0.01$), and Ni ($r = 0.91$, $p < 0.01$) indicate that trace elements Cr, Co, and Ni were incorporated into Fe (oxyhydr)oxides by scavenging and/or co-precipitation [61–66]. Moderate-to-strong positive correlations between K_2O and Ba ($r = 0.72$, $p < 0.01$), Cs ($r = 0.93$, $p < 0.01$), and Rb ($r = 0.96$, $p < 0.01$) indicate that trace elements Ba, Cs, and Rb are easily incorporated into the mineral structure of clay minerals, such as illite, as interlayer cations [67–70]. Moreover, a strong positive correlation between CaO and Sr ($r = 0.92$, $p < 0.01$) suggests that Sr in the iron ore is probably controlled by calcite.

Strong positive correlations between Pb and MnO ($r = 0.95$, $p < 0.01$) and Al_2O_3 ($r = 0.80$, $p < 0.01$) indicate that scavenging of Pb by Mn oxides, along with the substitution of Pb for Al in boehmite and/or the adsorption onto surfaces of this mineral probably were responsible for the distribution and concentration of Pb in the ores, as outlined by Mordberg [21]. Similarly, a strong positive correlation between Al_2O_3 and Zr ($r = 0.99$, $p < 0.01$) indicates the distribution and concentration of Zr in the mineral structure of boehmite as adsorption and/or isomorphic admixture [21]. Strong positive correlations between Al_2O_3 , SiO_2 , and TiO_2 , and trace elements U, Th, Hf, Nb, Ga, Y, and Ta ($r \geq 0.91$, $p < 0.01$) indicate the role of clays, boehmite, and rutile/anatase in the distribution of these trace elements.

Table 2. Major, trace, and rare earth elements contents of the Kolijan iron ore. $(La/Yb)_N = (La/La_N)/(Yb/Yb_N)$; $(\Sigma LREE/\Sigma HREE)_N = (\Sigma LREE/\Sigma LREE_N)/(\Sigma HREE/\Sigma HREE_N)$; $Eu/Eu^* = (Eu/Eu_N)/\sqrt{[(Sm/Sm_N) \times (Gd/Gd_N)]}$; $Ce/Ce^* = (Ce/Ce_N)/\sqrt{[(La/La_N) \times (Pr/Pr_N)]}$. The subscript “N” refers to chondrite normalized values [71].

	Detection Limit	Kj-01	Kj-02	Kj-03	Kj-04	Kj-05	Kj-06	Kj-07	Kj-08	Kj-09	Kj-10	Kj-11
SiO ₂ (wt%)	0.01	3.72	1.67	1.85	2.81	1.47	1.88	2.33	4.68	8.15	14.42	1.88
Al ₂ O ₃	0.01	1.68	0.32	0.36	1.02	0.27	0.74	0.75	2.71	4.62	8.12	1.11
Fe ₂ O ₃	0.01	82.99	89.93	88.74	85.87	91.12	86.81	88.14	79.45	72.89	60.9	84.87
CaO	0.01	1.97	0.22	0.26	1.12	0.18	1.07	0.33	0.66	1.12	0.36	1.88
Na ₂ O	0.01	0.03	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.01
MgO	0.01	0.23	0.18	0.22	0.23	0.13	0.2	0.14	0.22	0.54	0.91	0.17
K ₂ O	0.01	0.05	0.01	0.01	0.03	0.01	0.09	0.06	0.19	0.09	0.19	0.32
TiO ₂	0.01	0.64	0.08	0.08	0.41	0.08	0.25	0.08	1.61	1.57	2.65	0.41
MnO	0.01	0.71	0.52	0.62	0.67	0.41	0.77	0.59	1.02	0.96	1.09	0.91
P ₂ O ₅	0.01	0.61	0.26	0.31	0.31	0.21	0.92	0.32	1.02	1.35	1.23	1.22
L.O.I	0.01	7.35	6.77	7.52	7.45	6.03	7.21	7.21	8.35	8.65	10.02	7.16
Sum	–	99.98	99.97	99.98	99.94	99.92	99.95	99.96	99.93	99.96	99.91	99.94
U (ppm)	0.05	8.24	6.69	6.11	5.67	6.28	8.75	7.05	9.6	13.82	18.26	10.39
Th	0.05	0.78	0.10	0.12	0.44	0.11	0.34	0.19	1.07	2.43	4.27	0.58
Ba	0.5	214.4	79.5	96.1	155.2	63	191.1	140.6	215.3	203.2	120.3	286.1
Hf	0.2	2.1	0.5	0.8	1.4	0.2	0.8	1.2	3.1	3.7	6.6	0.8
Cr	10	1010	940	920	980	910	880	960	870	580	470	850
Co	0.5	26.3	29.4	28.6	27.3	30.3	31.6	32.1	27.1	24.5	14.6	34.5
Nb	0.2	1.6	0.7	0.7	1.1	0.7	0.9	0.7	3.9	3.6	6.2	1.1
Cs	0.01	0.29	0.13	0.05	0.17	0.05	0.18	0.16	0.68	0.51	0.51	0.82
Rb	0.2	1.3	0.3	0.2	1.0	0.6	0.9	0.6	2.4	1.6	2.6	3.6
V	5	149	99	105	127	93	80	102	138	183	312	84
Ga	0.1	5.0	3.2	3.3	4.1	3.2	3.2	2.6	3.4	5.2	7.5	3.0
Sr	0.1	227.9	102.1	124.8	176.4	79.3	195.1	133.1	173.8	170.8	76.3	265.4
Y	0.5	1.6	0.6	0.7	1.1	0.6	2.1	2.3	1.2	3.8	9.7	1.8
Ta	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.3	0.6	0.1
Zr	2	11	4	4	8	4	7	7	24	41	71	10
Pb	5	71	74	74	70	46	109	65	124	116	152	110
Ni	5	71	102	95	78	109	92	83	79	70	42	88
La (ppm)	0.5	6.1	1.7	2.6	4.4	0.9	4.9	2.3	12.5	10.9	14.6	7.3
Ce	0.5	42.3	16.5	19.6	32.5	7.1	49.8	21.3	94.3	94.2	99.6	74.2
Pr	0.03	1.25	0.33	0.49	0.87	0.17	1.61	0.84	2.47	2.75	2.78	2.72
Nd	0.1	4.1	1.3	1.5	2.8	1.1	7.3	5.6	10.7	12.5	11.8	13.1
Sm	0.03	1.18	0.24	0.33	0.76	0.15	2.54	1.81	1.86	3.37	1.98	4.75
Eu	0.03	1.62	0.45	1.28	1.95	0.26	7.48	2.75	2.02	7.67	3.00	7.77
Gd	0.05	1.57	0.45	0.60	1.09	0.29	4.81	2.37	1.14	5.96	2.9	9.01
Tb	0.01	0.20	0.05	0.07	0.14	0.04	0.73	0.32	0.29	0.93	0.47	1.39
Dy	0.05	1.32	0.47	0.57	0.95	0.36	4.20	1.98	1.56	5.65	3.45	7.84
Ho	0.01	0.20	0.11	0.15	0.17	0.07	0.80	0.31	0.34	1.02	0.58	1.46
Er	0.03	0.44	0.24	0.35	0.39	0.13	1.51	0.99	0.90	2.23	1.79	2.67
Tm	0.01	0.09	0.02	0.02	0.05	0.03	0.16	0.10	0.14	0.28	0.24	0.31
Yb	0.03	0.43	0.19	0.24	0.33	0.15	0.84	0.57	0.73	1.39	1.34	1.45
Lu	0.01	0.11	0.02	0.02	0.06	0.02	0.12	0.12	0.12	0.24	0.26	0.22
$\Sigma LREE$ (La–Eu) (ppm)	–	56.55	20.52	25.80	43.28	9.68	73.63	34.6	123.85	131.39	133.76	109.84
$\Sigma HREE$ (Gd–Lu) (ppm)	–	4.36	1.55	2.02	3.18	1.09	13.17	6.76	5.22	17.70	11.03	24.35
ΣREE (La–Lu) (ppm)	–	60.91	22.07	27.82	46.46	10.77	86.8	41.36	129.07	149.09	144.79	134.19
$(La/Yb)_N$	–	1.05	0.66	0.80	0.99	0.44	0.43	0.30	1.27	0.58	0.81	0.37
$(\Sigma LREE/\Sigma HREE)_N$	–	7.29	7.45	7.18	7.65	4.99	3.14	2.88	13.34	4.18	6.82	2.54
Eu/Eu*	–	3.64	4.25	8.87	6.55	3.82	6.53	4.06	4.24	5.23	3.83	3.63
Ce/Ce*	–	0.93	3.49	5.02	3.96	3.79	4.14	4.04	3.49	3.87	3.92	3.57
La/Y	–	3.81	2.83	3.71	4.00	1.50	2.33	1.00	10.42	2.87	1.51	4.06

4.4. Distribution Patterns of REE in Kolijan Al-Bearing Iron Ores

Contents of $\Sigma LREE$ (La–Eu), $\Sigma HREE$ (Gd–Lu), and ΣREE (La–Lu) in the Kolijan iron ores are in the range 9.68–133.76 ppm $\Sigma LREE$ (average 69.35 ppm), 1.09–24.35 ppm $\Sigma HREE$ (average 8.22 ppm), and 10.77–149.09 ppm ΣREE (average 77.57 ppm; Table 2). The $(La/Yb)_N$ and $(\Sigma LREE/\Sigma HREE)_N$ ratios indicate fractionation of LREE from HREE and have been used both in metallic and non-metallic deposits, and especially in karst bauxite

deposits [33,48]. The fractionation of LREE from HREE depends on the pH of the depositional environment and mainly occurs as pH increases [33]. Under these circumstances, the HREE dissolve more readily in acid conditions, and so deposit as pH rises [33]. The $(La/Yb)_N$ and $(\sum LREE/\sum HREE)_N$ ratios in the Kolijan iron ore are in the range 0.30–1.27, average 0.70, and 2.54–13.34, average 6.13, respectively. Therefore, it suggests that changes in the pH of solutions responsible for weathering was the main agent of fractionation of LREE from HREE in the Kolijan iron ores.

The chondrite-normalized REE distribution diagram has been used to investigate fractionation of LREE from HREE in bauxites [33]. During weathering processes, mobility and concentration of REE is mainly controlled by the Eh and pH of the depositional environment [34,44]. Among REE, Ce behaves differently, due to its low ionization potential and atypical redox chemistry. As a result, the distribution of Ce anomaly has been widely used to track paleo-redox changes during generation of bauxite ores [33,41,44]. In the chondrite-normalized REE distribution diagram, the Kolijan iron ores are characterized by weak enrichment of LREE compared to HREE, together with significant positive Ce and Eu anomalies (Figure 10). The chondrite-normalized REE distribution in the ores indicates that changes in the oxidation potential and pH of the deposition environment were the dominant controls on the distribution and fractionation of REE [42].

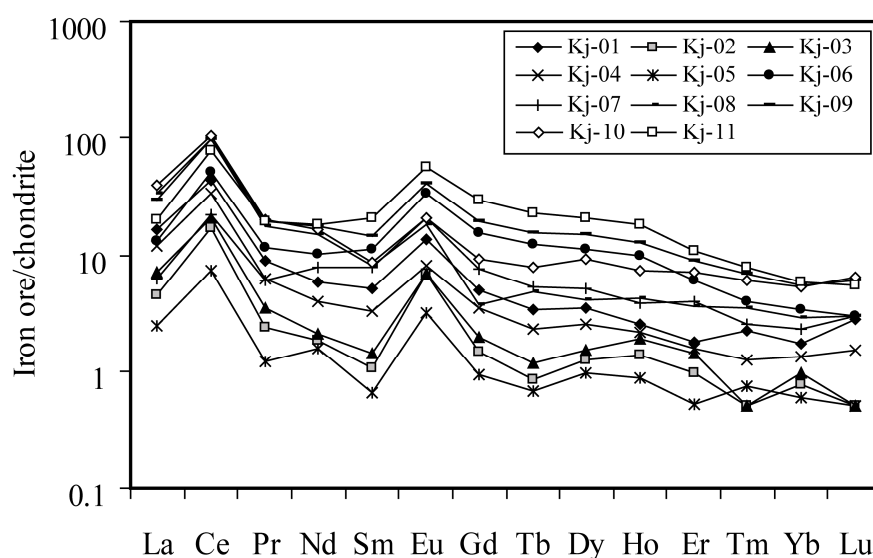


Figure 10. Chondrite-normalized REE patterns for the Kolijan iron ores. Data for the chondrite are from Taylor and McLennan [71].

4.5. Mineralogical Controls on REE Distribution in the Kolijan Al-Bearing Iron Ores

Correlation coefficients between REE and major oxides provide insights into the role of minerals in the distribution and concentration of lanthanides in the Kolijan Al-bearing iron ores. Moderate positive correlations of SiO_2 –LREE ($r = 0.71$, $p < 0.01$; Figure 11a) and Al_2O_3 –LREE ($r = 0.77$, $p < 0.01$; Figure 11b) probably indicate the role of kaolinite and boehmite in the distribution and concentration of LREE through preferential adsorption and isomorphic substitution processes. In contrast, a weak positive correlation between Al_2O_3 and HREE ($r = 0.33$, $p < 0.01$; Figure 11c) indicates that kaolinite and boehmite did not exert a strong control on the distribution and concentration of HREE in the ores.

Weak-to-strong negative correlations between Fe_2O_3 and LREE ($r = -0.82$, $p < 0.01$; Figure 11d) and HREE ($r = -0.38$, $p < 0.01$; Figure 11e) show that hematite and goethite, as the main constituents of the Kolijan ores, probably did not exert a strong control on the distribution and concentration of both LREE and HREE in the ores. A strong positive correlation between K_2O and LREE ($r = 0.80$, $p < 0.01$; Figure 11f) suggests that illite as an accessory mineral of the ores probably played an important role in the distribution and concentration of LREE in the ores. Similarly, a strong positive correlation between TiO_2

and LREE ($r = 0.85$, $p < 0.01$; Figure 11g) suggests a pronounced role for rutile and anatase in the distribution and concentration of LREE in the ores. Moreover, moderate-to-strong positive correlations of MnO–LREE ($r = 0.98$, $p < 0.01$; Figure 11h), MnO–HREE ($r = 0.63$, $p < 0.01$; Figure 11i), P_2O_5 –LREE ($r = 0.96$, $p < 0.01$; Figure 11j), and P_2O_5 –HREE ($r = 0.82$, $p < 0.01$; Figure 11k) suggest that pyrolusite and crandallite probably acted as host minerals for both LREE and HREE in the Kolijan Al-bearing iron ores, respectively, possibly through adsorption and substitution processes.

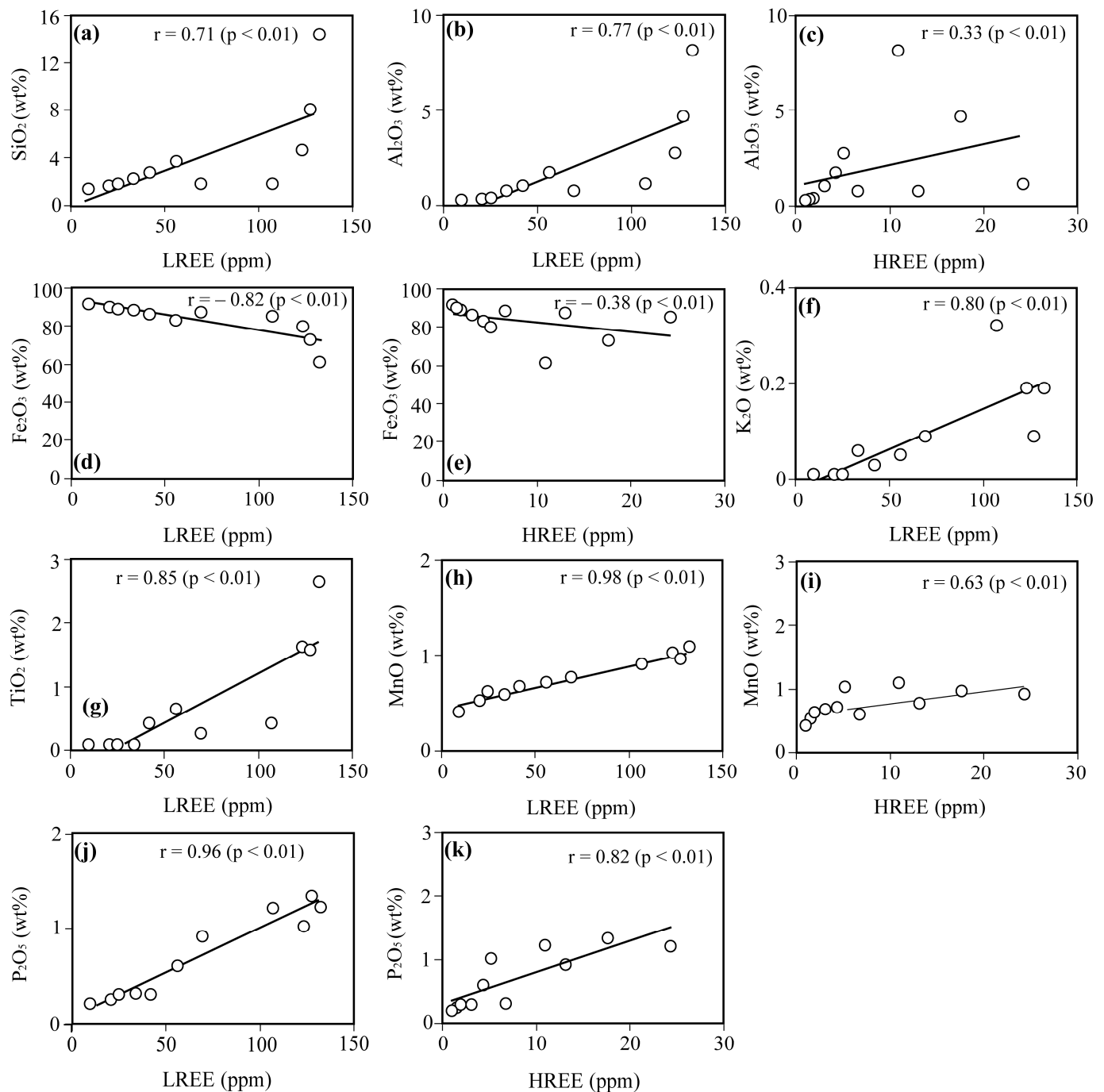


Figure 11. Bivariate diagrams (a) SiO_2 –LREE, (b) Al_2O_3 –LREE, (c) Al_2O_3 –HREE, (d) Fe_2O_3 –LREE, (e) Fe_2O_3 –HREE, (f) K_2O –LREE, (g) TiO_2 –LREE, (h) MnO –LREE, (i) MnO –HREE, (j) P_2O_5 –LREE, and (k) P_2O_5 –HREE for the Kolijan iron ores.

On the whole, pyrolusite and crandallite were host minerals of both LREE and HREE in the ores, whereas boehmite, illite, kaolinite, rutile, and anatase only acted as host minerals for LREE. Indeed, fractionation and concentration of LREE from HREE in the ores can be attributed to mineral control. Adsorption by clay minerals, together with isomorphic substitution in boehmite and fixation in rutile and anatase play fundamental roles in the concentration of LREE, whereas fixation by phosphate minerals and scavenging by Mn oxides influenced the distribution and concentration of both LREE and HREE.

4.6. Ce and Eu Anomalies in the Kolijan Al-Bearing Iron Ores

In this study, Ce and Eu anomalies in the iron ores were calculated by the following formula:

$$\text{Ce/Ce}^* = \text{Ce}_N / [(\text{La}_N \times \text{Pr}_N)]^{0.5} \quad (1)$$

$$\text{Eu/Eu}^* = \text{Eu}_N / [(\text{Sm}_N \times \text{Gd}_N)]^{0.5} \quad (2)$$

The subscript “N” refers to values normalized to chondrite [71]. The Ce and Eu anomalies in the Kolijan iron ores are in the range 3.63–5.22 and 2.29–5.65, respectively. Various reasons for positive Ce anomalies in bauxite deposits have been presented in the literature. In general, positive Ce anomalies in ores in the upper parts of the weathered profile are attributed to oxidation of Ce^{3+} to less mobile Ce^{4+} and the precipitation of cerianite (CeO_2) [25,27,30,72–75] and/or the precipitation of monazite-(Ce) during early diagenesis processes [44]. In contrast, positive Ce anomalies in ores in the lower parts of the weathered profiles result from the mobilization of Ce and the precipitation of Ce-rich fluorocarbonates, such as parisite-(Ce) [30]. Precipitation of parisite-(Ce) occurs as a result of the deposition of Ce^{3+} in an alkaline pH [26,76,77]. Wang et al. [27] stated that the reaction between fluoride complexes (CeF^{2+} or CeCO_3F^0) and Ca^{2+} and HCO_3^- causes the precipitation of parisite-(Ce) in bauxite ores. Therefore, positive Ce anomalies in the Kolijan Al-bearing iron ores can be attributed to the precipitation of parisite-(Ce), as identified by SEM–EDS analyses (Figure 7). This mechanism has been proposed for positive Ce anomalies in the lower parts of studied profiles from Wuchuan–Zhengan–Daozhen bauxite deposits, northern Guizhou, China) [27]. Because under alkaline conditions solutions rich in Ce^{3+} precipitate parisite in bauxite ores, it suggests that the pH of fluids involved in weathering had an important role in producing the strong positive Ce anomalies in Kolijan iron ores.

The behavior of REE in lateritic iron ores depends on the physicochemical conditions (Eh and pH) of the environment during the weathering processes that produced them [78]. In general, the leaching and precipitation of REE occurs in low and high pH environments, respectively [72,79]. In this study, alkaline conditions during the development of the aluminum-bearing iron ores is confirmed by the La/Y ratio and bivariate plot of La/Y versus REE (Figure 12). According to Crnički and Jurković [80], La/Y ratios more than 1 and less than 1 represent alkaline and acidic conditions, respectively. The La/Y ratio in the Kolijan Al-bearing iron ores is in the range of 1.00 to 10.42 (average 3.46), indicating buffering of weathering solutions by carbonate bedrocks during development of the ores. Strong positive Eu anomalies in the ores indicate alkaline conditions during ore formation. This is supported by the plot of the studied ore samples on the Eu/Eu* vs. Ce/Ce* diagram. A strong positive correlation between Eu/Eu* and Ce/Ce* ($r = 0.84$, $p < 0.01$; Figure 13) suggests that, similar to positive Ce anomalies, strong positive Eu anomalies are produced by environmental conditions related to the role of carbonate bedrock as a geochemical barrier, as stated by Li et al. [53] and Wang et al. [55].

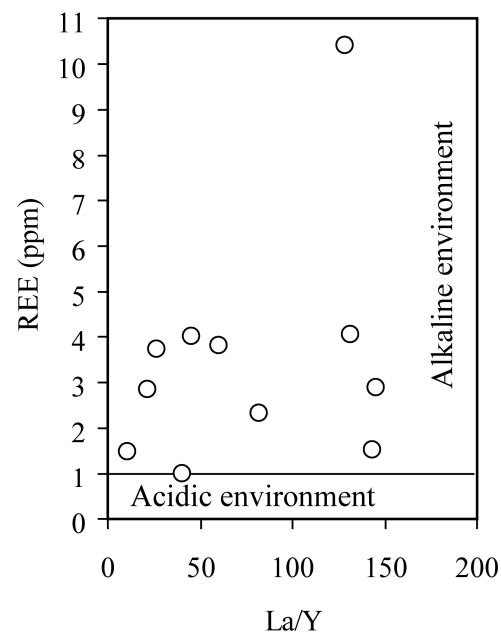


Figure 12. Bivariate plot of La/Y versus REE for the Kolijan Al-bearing iron ores, indicating an alkaline environment during formation of the ores.

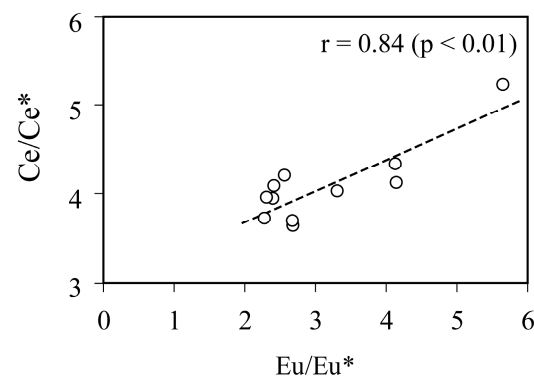


Figure 13. Bivariate plot of Eu/Eu* versus Ce/Ce* for the Kolijan Al-bearing iron ores.

4.7. Protolith of the Kolijan Al-Bearing Iron Ores

In this study, various geochemical techniques such as accumulation coefficients of trace elements and contents of elements Cr and Ni, were used to determine the protolith(s) of the Kolijan Al-bearing iron ores. The following equation was utilized to calculate the accumulation coefficient of elements Mn, Th, Ba, Cr, Nb, V, Pb, and Ni [81]:

$$R = \sum_{i=1}^n K_i / K_l \quad (3)$$

where R is the accumulation coefficient of the element, i = the given element, n = the number of used elements, K_i = the average concentration of element i in the ores, and K_l = the average concentration of element i in the lithosphere [82].

The R values alone cannot determine the lithology of the protolith(s), so they are normalized to element Cr [83]. The bivariate plot of R versus Cr [83] reveals that the Kolijan iron ores plot in the area of influence of mafic precursor rocks (Figure 14). The bivariate plot of Log Cr versus Log Ni [84] also shows that the ores plot close to basaltic protolith (Figure 15). These findings are consistent with results from other karst-type bauxite deposits of different ages in northwestern Iran [41–49,85].

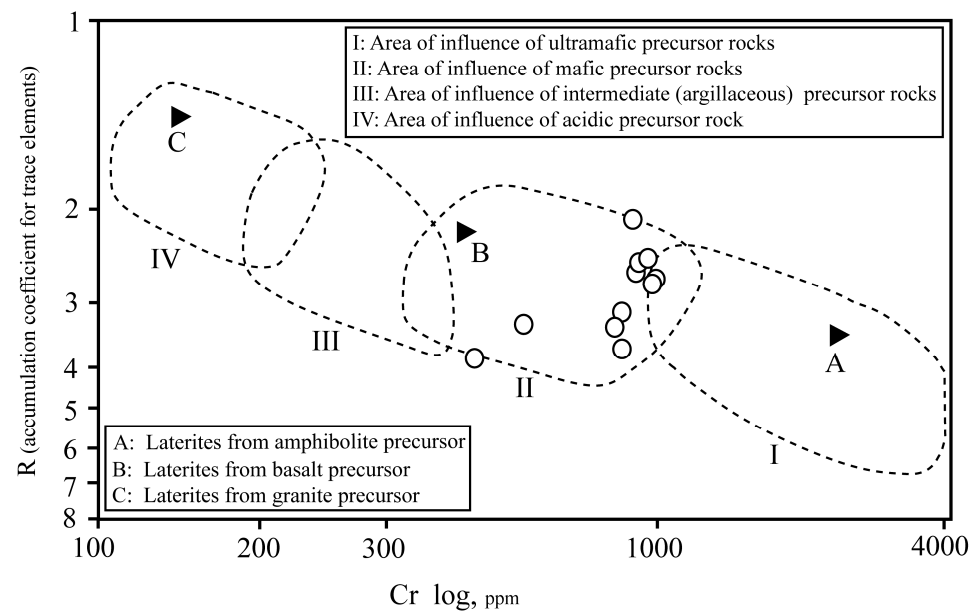


Figure 14. Log Cr versus R along with the influence area of various precursor rocks [83]. A, B, and C represent laterites from amphibolite, basalt, and granite precursor rocks, respectively. The numbers I, II, III, and IV denote the area of influence of ultramafic, mafic, intermediate (or argillaceous), and acidic precursor rocks, respectively. The Kolijan Al-bearing iron ores plot in the area of influence of mafic precursor rocks.

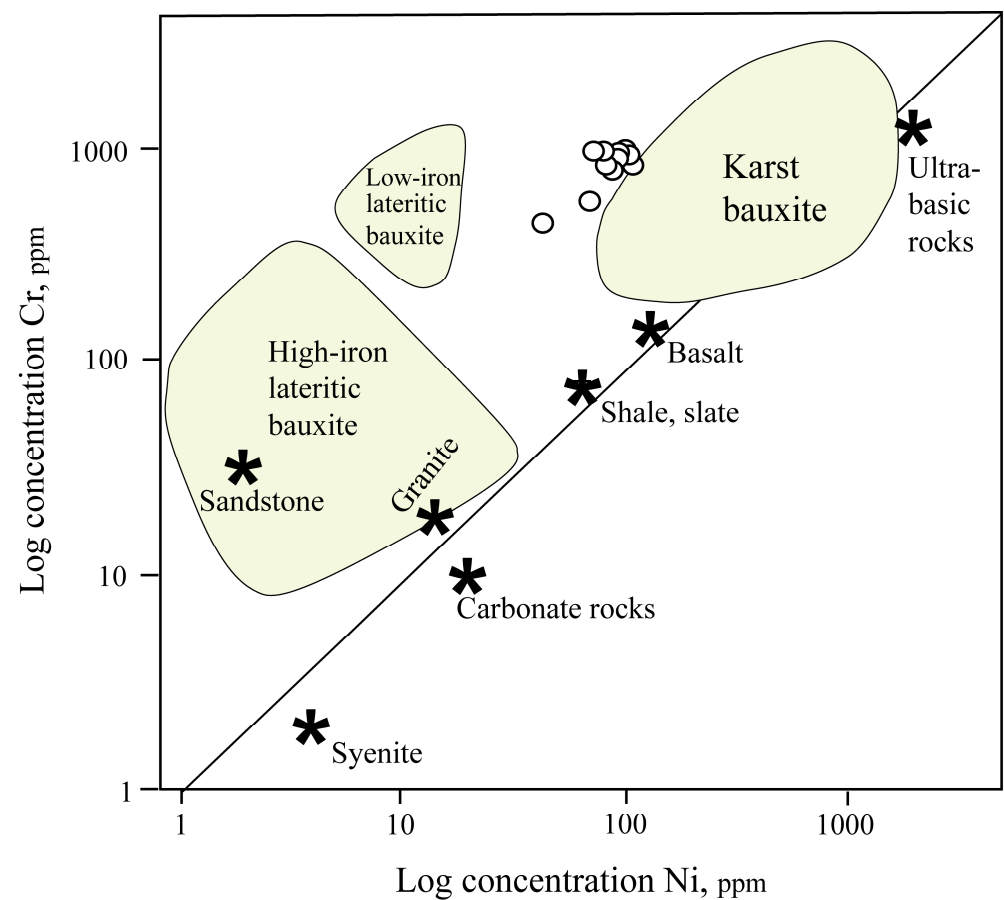


Figure 15. Bivariate plot showing concentration of Cr versus Ni in laterite- and karst-type bauxite deposits with different protoliths [84]. Circles show data from the Kolijan iron ores.

5. Conclusions

The most important results of the mineralogical and geochemical studies of the Kolijan Al-bearing iron ores, southeast Mahabad, northwestern Iran, are:

1. Microscopic observations show that the ores developed in multiple stages, and diagenetic and epigenetic processes were important during their formation.
2. Hematite and goethite are the main constituents of the Kolijan iron ores, accompanied by lesser amounts of kaolinite, illite, amesite, boehmite, rutile, anatase, calcite, pyrolusite, crandallite, and parisite-(Ce).
3. The distribution of trace elements in the Al-bearing iron ores developed by scavenging, co-precipitation, isomorphic substitution, adsorption, and fixation in new mineral phases, such as parisite-(Ce).
4. Preferential adsorption of LREE by kaolinite, illite, boehmite, rutile, and anatase resulted in their separation from HREE in the ores; pyrolusite and crandallite host both LREE and HREE in the ores.
5. Geochemical ratios, such as La/Y, indicate that fluctuations in the level of the water-table, and the function of carbonate bedrocks as a geochemical barrier caused fractionation and the concentration of REE during formation of the iron ores.
6. Strong positive Ce anomalies in the Kolijan iron ores result from alkalinity produced by carbonate bedrocks resulting in precipitation of parisite-(Ce).
7. Strong positive Eu anomalies in the ores are closely dependent on alkaline pH.
8. Based on geochemical data (Ni and Cr contents and accumulation coefficients of elements), basaltic rocks are the probable protolith of the Kolijan iron ores.

Author Contributions: Conceptualization, A.A.; methodology, A.A. and M.K.; software, A.A. and M.K.; validation, A.A. and M.K.; formal analysis, M.K.; investigation, M.K.; resources, A.A.; data curation, A.A.; writing—original draft preparation, A.A. and M.K.; writing—review and editing, A.A. and M.K.; visualization, A.A. and M.K.; supervision, A.A.; project administration, A.A.; funding acquisition, A.A. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially fully supported by the Bureau of Deputy of Research and Complementary Education of Urmia University.

Data Availability Statement: Data are contained within the article.

Acknowledgments: We extend our gratitude to Academic Editor of the Journal of Minerals for his editorial handling and four anonymous reviewers for reviewing and making critical comments on this manuscript. The authors thank Noel White of the University of Tasmania, Australia for English editing of the final version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Bárdossy, G. *Karst Bauxites: Bauxite Deposits on Carbonate Rocks*; Elsevier Scientific Publication: Amsterdam, The Netherlands, 1982; p. 441.
2. Bárdossy, G.; Aleva, G.J.J. *Lateritic Bauxites. Developments in Economic Geology*; Elsevier Scientific Publication: Amsterdam, The Netherlands, 1990; Volume 27, p. 624.
3. Mameli, P.; Mongelli, G.; Oggiano, G.; Dinelli, E. Geological, geochemical and mineralogical features of some bauxite deposits from Nurra (Western Sardinia, Italy): Insights on conditions of formation and parental affinity. *Int. J. Earth Sci.* **2007**, *96*, 887–902. [[CrossRef](#)]
4. Abedini, A.; Mongelli, G.; Khosravi, M.; Sinisi, R. Geochemistry and secular trends in the middle–late Permian karst bauxite deposits, northwestern Iran. *Ore Geol. Rev.* **2020**, *124*, 103660. [[CrossRef](#)]
5. Abedini, A.; Khosravi, M.; Mongelli, G. The middle Permian pyrophyllite-rich ferruginous bauxite, northwestern Iran, Irano-Himalayan karst belt: Constraints on elemental fractionation and provenance. *J. Geochem. Explor.* **2022**, *233*, 106905. [[CrossRef](#)]
6. Ling, K.Y.; Zhu, X.Q.; Tang, H.S.; Li, S.X. Importance of hydrogeological conditions during formation of the karstic bauxite deposits, Central Guizhou Province, Southwest China: A case study at Lindai deposit. *Ore Geol. Rev.* **2017**, *82*, 198–216. [[CrossRef](#)]
7. Liu, X.; Wang, Q.; Zhang, Q.; Yang, S.; Liang, Y.; Zhang, Y. Genesis of the Permian karstic Pingguo bauxite deposit, western Guangxi, China. *Miner. Depos.* **2017**, *52*, 1031–1048. [[CrossRef](#)]

8. Yu, W.; Algeo, T.J.; Yan, J.; Yang, J.; Du, Y.; Huang, X.; Weng, S. Climatic and hydrologic controls on upper Paleozoic bauxite deposits in South China. *Earth-Sci. Rev.* **2019**, *189*, 159–176. [\[CrossRef\]](#)
9. Zhang, Z.; Zhou, L.; Li, Y.; Wu, C.; Zheng, C. The “coal-bauxite-iron” structure in the ore-bearing rock series as a prospecting indicator for southeastern Guizhou bauxite mines. *Ore Geol. Rev.* **2013**, *53*, 145–158. [\[CrossRef\]](#)
10. Ling, K.; Wen, H.; Fan, H.; Zhu, X.; Li, Z.; Zhang, Z.; Grasby, S.E. Iron loss during continental weathering in the early Carboniferous period recorded by karst bauxites. *JGR Earth Surf.* **2023**, *128*, e2022JF006906. [\[CrossRef\]](#)
11. Mondillo, N.; Di Nuzzo, M.; Kalaitzidis, S.; Boni, M.; Santoro, L.; Balassone, G. Petrographic and geochemical features of the B3 bauxite horizon (Cenomanian–Turonian) in the Parnassos-Ghiona area: A contribution towards the genesis of the Greek karst bauxites. *Ore Geol. Rev.* **2022**, *143*, 104759. [\[CrossRef\]](#)
12. Öztürk, H.; Haniç, N.; Cansu, Z.; Kasapci, C. Formation of Ti-rich bauxite from alkali basalt in continental margin carbonates, Payas region, SE Turkey: Implications for sea level change in the upper cretaceous. *Turk. J. Earth Sci.* **2021**, *30*, 116–141. [\[CrossRef\]](#)
13. Yang, S.; Qingfei, W.; Xuefei, L.; Kan, Z.; Santosh, M.; Deng, J. Global spatio-temporal variations and metallogenic diversity of karst bauxites and their tectonic, paleogeographic and paleoclimatic relationship with the Tethyan realm evolution. *Earth Sci. Rev.* **2022**, *233*, 104184. [\[CrossRef\]](#)
14. Yang, S.J.; Wang, Q.F.; Deng, J.; Wang, Y.Z.; Kang, W.; Liu, X.F.; Li, Z.M. Genesis of karst bauxite-bearing sequences in Baofeng, Henan (China), and the distribution of critical metals. *Ore Geol. Rev.* **2019**, *115*, 103–161. [\[CrossRef\]](#)
15. Sinisi, R. Mineralogical and geochemical features of Cretaceous bauxite from San Giovanni Rotondo (Apulia, Southern Italy): A provenance tool. *Minerals* **2018**, *8*, 567. [\[CrossRef\]](#)
16. Reinhardt, N.; Proenza, J.; Villanova-de-Benavent, C.; Aiglsperger, T.; Bover-Arnal, T.; Torró, L. Geochemistry and mineralogy of rare earth elements (REE) in bauxitic ores of the Catalan Coastal Range, NE Spain. *Minerals* **2018**, *8*, 562. [\[CrossRef\]](#)
17. Torró, L.; Proenza, J.A.; Aiglsperger, T.; Bover-Arnal, T.; Villanova-de-Benavent, C.; Rodriguez, D.; Ramírez, A.; Rodriguez, J.; Mosquea, L.A.; Salas, R. Geological, geochemical and mineralogical characteristics of REE-bearing Las Mercedes bauxite deposit, Dominican Republic. *Ore Geol. Rev.* **2017**, *89*, 114–131. [\[CrossRef\]](#)
18. Radusinović, S.; Jelenković, R.; Pačevski, A.; Simić, V.; Božović, D.; Holclajtner-Antunović, I.; Životić, D. Content and mode of occurrences of rare earth elements in the Zagrad karstic bauxite deposit (Nikšić area, Montenegro). *Ore Geol. Rev.* **2017**, *80*, 406–428. [\[CrossRef\]](#)
19. Luo, C.; Yang, R.; Chen, J.; Gao, L.; Zu, H.; Ni, X. Genesis of the Carboniferous karstic bauxites in Qingzhen region, Central Guizhou, Southwest China. *J. Geochem. Explor.* **2022**, *235*, 106955. [\[CrossRef\]](#)
20. Liu, X.; Wang, Q.; Zhao, L.; Peng, Y.; Ma, Y.; Zhou, Z. Metallogeny of the large-scale Carboniferous karstic bauxite in the Sanmenxia area, southern part of the North China Craton China. *Chem. Geol.* **2020**, *556*, 119851. [\[CrossRef\]](#)
21. Mordberg, L.E. Geochemical evolution of a Devonian diaspore-crandallite-svanbergite-bearing weathering profile in the Middle Timan, Russia. *J. Geochem. Explor.* **1999**, *66*, 35–361. [\[CrossRef\]](#)
22. Yuste, A.; Bauluz, B.; Mayayo, M.J. Genesis and mineral transformations in lower cretaceous karst bauxites (NE Spain): Climatic influence and superimposed processes. *Geol. J.* **2015**, *50*, 839–857. [\[CrossRef\]](#)
23. Yuste, A.; Bauluz, B.; Mayayo, M.J. Origin and geochemical evolution from ferrallitized clays to karst bauxite: An example from the Lower Cretaceous of NE Spain. *Ore Geol. Rev.* **2017**, *84*, 67–79. [\[CrossRef\]](#)
24. Gamaletsos, P.N.; Godelitsas, A.; Filippidis, A.; Pontikes, Y. The rare earth elements potential of Greek bauxite active mines in the light of a sustainable REE demand. *J. Sustain. Metall.* **2019**, *5*, 20–47. [\[CrossRef\]](#)
25. Gamaletsos, P.N.; Godelitsas, A.; Kasama, T.; Church, N.S.; Douvalis, A.P.; Göttlicher, J.; Steininger, R.; Boubnov, A.; Pontikes, Y.; Tzamos, E.; et al. Nano-mineralogy and -geochemistry of high-grade diasporic karst-type bauxite from Parnassos-Ghiona mines Greece. *Ore Geol. Rev.* **2017**, *84*, 228–244. [\[CrossRef\]](#)
26. Karadağ, M.M.; Küpeli, S.; Arýk, F.; Ayhan, A.; Zedef, V.; Döyen, A. Rare earth element (REE) geochemistry and genetic implications of the Mortas bauxite deposit (Seydişehir/Konya-Southern Turkey). *Chem. Erde Geochem.* **2009**, *69*, 143–159. [\[CrossRef\]](#)
27. Wang, X.; Jiao, Y.; Du, Y.; Ling, W.; Wu, L.; Cui, T.; Zhou, Q.; Jin, Z.; Lei, Z.; Weng, S. REE mobility and Ce anomaly in bauxite deposit of WZD area, Northern Guizhou, China. *J. Geochem. Explor.* **2013**, *133*, 103–117. [\[CrossRef\]](#)
28. Haniç, N. Geological and geochemical evolution of the Bolkardagi bauxite deposits, Karaman, Turkey: Transformation from shale to bauxite. *J. Geochem. Explor.* **2013**, *133*, 118–137. [\[CrossRef\]](#)
29. Liu, X.; Wang, Q.; Zhang, Q.; Zhang, Y.; Li, Y. Genesis of REE minerals in the karstic bauxite in western Guangxi, China, and its constraints on the deposit formation conditions. *Ore Geol. Rev.* **2016**, *75*, 100–115. [\[CrossRef\]](#)
30. Mongelli, G. Ce-anomalies in the textural components of Upper Cretaceous karst bauxites from the Apulian carbonate platform (southern Italy). *Chem. Geol.* **1997**, *140*, 69–79. [\[CrossRef\]](#)
31. Gu, J.; Huang, Z.; Fan, H.; Jin, Z.; Yan, Z.; Zhang, J. Mineralogy, geochemistry, and genesis of lateritic bauxite deposits in the Wuchuan–Zheng’an–Daozhen area, Northern Guizhou Province, China. *J. Geochem. Explor.* **2013**, *130*, 44–59. [\[CrossRef\]](#)
32. Zhu, K.Y.; Su, H.M.; Jiang, S.Y. Mineralogical control and characteristics of rare earth elements occurrence in Carboniferous bauxites from western Henan Province, north China: A XRD, SEM-EDS and LA-ICP-MS analysis. *Ore Geol. Rev.* **2019**, *114*, 103144. [\[CrossRef\]](#)
33. Mongelli, G.; Boni, M.; Buccione, R.; Sinisi, R. Geochemistry of the Apulian karst bauxites (southern Italy): Chemical fractionation and parental affinities. *Ore Geol. Rev.* **2014**, *63*, 9–21. [\[CrossRef\]](#)

34. Mongelli, G.; Buccione, R.; Gueguen, R.; Langone, A.; Sinisi, R. Geochemistry of the Apulian allochthonous karst bauxite, Southern Italy: Distribution of critical elements and constraints on Late Cretaceous Peri-Tethyan palaeogeography. *Ore Geol. Rev.* **2016**, *77*, 246–259. [\[CrossRef\]](#)
35. Putzolu, F.; Piccolo Papa, A.; Mondillo, N.; Boni, M.; Balassone, G.; Mormone, A. Geochemical characterization of bauxite deposits from the Abruzzi Mining District (Italy). *Minerals* **2018**, *8*, 298. [\[CrossRef\]](#)
36. Lei, Z.; Ling, W.; Wu, H.; Zhang, Y.; Zhang, Y. Geochemistry and mineralization of the Permian bauxites with contrast bedrocks in northern Guizhou, South China. *J. Earth Sci.* **2023**, *34*, 487503. [\[CrossRef\]](#)
37. Mongelli, G.; Boni, M.; Oggiano, G.; Mameli, P.; Sinisi, R.; Buccione, R.; Mondillo, N. Critical metals distribution in Tethyan karst bauxite: The cretaceous Italian ores. *Ore Geol. Rev.* **2017**, *86*, 526–536. [\[CrossRef\]](#)
38. Mongelli, G.; Mameli, P.; Sinisi, R.; Roberto, B.; Oggiano, G. REEs and other critical raw materials in Cretaceous Mediterranean-type bauxite: The case of the Sardinian ore (Italy). *Ore Geol. Rev.* **2021**, *139*, 104559. [\[CrossRef\]](#)
39. Radusinović, S.; Papadopoulos, A. The potential for REE and associated critical metals in karstic bauxites and bauxite residue of Montenegro. *Minerals* **2021**, *11*, 975. [\[CrossRef\]](#)
40. Ahmadnejad, F.; Zamanian, H.; Taghipour, B.; Zarasvandi, A.; Buccione, R.; Ellahi, S.S. Mineralogical and geochemical evolution of the Bidgol bauxite deposit, Zagros Mountain Belt, Iran: Implications for ore genesis, rare earth elements fractionation and parental affinity. *Ore Geol. Rev.* **2017**, *86*, 755–783. [\[CrossRef\]](#)
41. Ahmadnejad, F.; Mongelli, G. Geology, geochemistry, and genesis of REY minerals of the late Cretaceous karst bauxite deposits, Zagros Simply Folded Belt, SW Iran: Constraints on the ore-forming process. *J. Geochem. Explor.* **2022**, *240*, 107030. [\[CrossRef\]](#)
42. Abedini, A.; Rezaei Azizi, M.; Dill, H.G. Formation mechanisms of lanthanide tetrad effect in limestones: An example from Arbanos district, NW Iran. *Carbonates Evaporites* **2020**, *35*, 1–18. [\[CrossRef\]](#)
43. Abedini, A.; Khosravi, M. Geochemical constraints on the Triassic–Jurassic Amir-Abad karst-type bauxite deposit, NW Iran. *J. Geochem. Explor.* **2020**, *211*, 106489. [\[CrossRef\]](#)
44. Abedini, A.; Khosravi, M. REE geochemical characteristics of the Huri karst-type bauxite Deposit, Irano–Himalayan Belt, Northwestern Iran. *Minerals* **2023**, *13*, 926. [\[CrossRef\]](#)
45. Abedini, A.; Mongelli, G.; Khosravi, M. Geochemical constraints on the middle Triassic Kani Zarrineh karst bauxite deposit, Irano–Himalayan belt, NW Iran: Implications for elemental fractionation and parental affinity. *Ore Geol. Rev.* **2021**, *133*, 104099. [\[CrossRef\]](#)
46. Abedini, A.; Mongelli, G.; Khosravi, M. Geochemistry of the early Jurassic Soleiman Kandi karst bauxite deposit, Irano–Himalayan belt, NW Iran: Constraints on bauxite genesis and the distribution of critical raw materials. *J. Geochem. Explor.* **2022**, *241*, 107056. [\[CrossRef\]](#)
47. Abedini, A.; Khosravi, M.; Mongelli, G. Critical metals distribution in the late Triassic–early Jurassic Nasr-Abad bauxite deposit, Irano–Himalayan karst bauxite belt, NW Iran. *Geochemistry* **2024**, *84*, 126039. [\[CrossRef\]](#)
48. Khosravi, M.; Abedini, A.; Alipour, S.; Mongelli, G. The Darzi-Vali bauxite deposit, West-Azarbaidjan Province, Iran: Critical metals distribution and parental affinities. *J. Afr. Earth Sci.* **2017**, *129*, 960–972. [\[CrossRef\]](#)
49. Khosravi, M.; V  rard, C.; Abedini, A. Palaeogeographic and geodynamic control on the Iranian karst-type bauxite deposits. *Ore Geol. Rev.* **2021**, *139*, 104589. [\[CrossRef\]](#)
50. Nabavi, M.H. *An Introduction to the Geology of Iran*; Geological Survey of Tehran, Iran: Tehran, Iran, 1976; 105p.
51. Mutakyahwa, M.K.D.; Ikingura, J.R.; Mruma, A.H. Geology and geochemistry of bauxite deposits in Lushoto district, Usambara Mountains, Tanzania. *J. Afr. Earth Sci.* **2003**, *36*, 357–369. [\[CrossRef\]](#)
52. Valet, I. *Bauxites*; Elsevier Scientific: Amsterdam, The Netherlands, 1972; 226p.
53. Li, Z.; Din, J.; Xu, J.; Liao, C.; Yin, F.; Lu, T.; Cheng, L.; Li, J. Discovery of the REE minerals in the Wulong–Nanchuan bauxite deposits, Chongqing, China: Insights on conditions of formation and processes. *J. Geochem. Explor.* **2013**, *133*, 88–102. [\[CrossRef\]](#)
54. Sun, X.; Yang, S.; Liu, X.; Zhao, L.; Lin, L.; Zhang, Q.; Feng, Y.; Wang, W. Metallogenic process of Permian Taiping karstic bauxite deposit in Youjiang Basin, China. *Ore Geol. Rev.* **2022**, *152*, 105258. [\[CrossRef\]](#)
55. Wang, Q.; Deng, J.; Liu, X.; Zhang, Q.; Sun, S.; Jiang, C.; Zhou, F. Discovery of the REE minerals and its geological significance in the Quyang bauxite deposit, West Guangxi, China. *J. Asian Earth Sci.* **2010**, *39*, 701–712. [\[CrossRef\]](#)
56. Whitney, D.L.; Evans, B.W. Abbreviations for names of rock-forming minerals. *Am. Mineral.* **2010**, *95*, 185–187. [\[CrossRef\]](#)
57. Norton, S.A. Laterite and bauxite formation. *Econ. Geol.* **1973**, *68*, 353–361. [\[CrossRef\]](#)
58. MacLean, W.; Bonavia, F.; Sanna, G. Argillite debris converted to bauxite during karst weathering: Evidence from immobile element geochemistry at the Olmedo Deposit, Sardinia. *Miner. Depos.* **1997**, *32*, 607–616. [\[CrossRef\]](#)
59. Mondillo, N.; Balassone, G.; Boni, M.; Rollinson, G. Karst bauxites in the Campania Apennines (southern Italy): A new approach. *Period. Mineral.* **2011**, *80*, 407–432.
60. Schellmann, W. Geochemical differentiation in laterite and bauxite formation. *Catena* **1994**, *21*, 131–143. [\[CrossRef\]](#)
61. Ajouyed, O.; Hurela, C.; Ammarib, M.; Ben Allal, L.; Marmier, N. Sorption of Cr(VI) onto natural iron and aluminum (oxy)hydroxides: Effects of pH, ionic strength and initial concentration. *J. Hazard. Mater.* **2010**, *174*, 616–622. [\[CrossRef\]](#)
62. Fern  ndez-Caliani, J.; Cantano, M. Intensive kaolinization during a lateritic weathering event in southwest Spain mineralogical and geochemical inferences from a relict paleosol. *Catena* **2010**, *80*, 23–33. [\[CrossRef\]](#)
63. Gustafsson, J.P. Vanadium geochemistry in the biogeosphere–speciation, solid-solution interactions, and ecotoxicity. *Appl. Geochem.* **2019**, *102*, 1–25. [\[CrossRef\]](#)

64. Jeon, B.; Dempsey, B.A.; Burgos, W.D.; Royer, R.A. Sorption kinetics of Fe(II), Zn (II), Co(II), Ni(II), Cd(II), and Fe(II)/Me(II) onto hematite. *Water Res.* **2003**, *37*, 4135–4142. [[CrossRef](#)] [[PubMed](#)]
65. Ramos de Oliveira, L.A.; Rosiere, C.A.; Rios, F.J.; Andrade, S.; de Moraes, R. Chemical fingerprint of iron oxides related to iron enrichment of banded iron formation from the Cauê Formation-Esperança Deposit, Quadrilátero Ferrífero, Brazil: A laser ablation ICP-MS study. *Braz. J. Geol.* **2015**, *45*, 193–216. [[CrossRef](#)]
66. Santoro, L.; Putzolu, F.; Mondillo, N.; Boni, M.; Herrington, R. Trace element geochemistry of iron-(oxy)-hydroxides in Ni (Co)-laterites: Review, new data and implications for ore forming processes. *Ore Geol. Rev.* **2022**, *140*, 104501. [[CrossRef](#)]
67. Schwertmann, U.; Pfab, G. Structural vanadium in synthetic goethite. *Geochim. Cosmochim. Acta* **1994**, *58*, 4349–4352. [[CrossRef](#)]
68. Atun, G.; Bascetin, E. Adsorption of barium on kaolinite, illite and montmorillonite at various ionic strengths. *Radiochim. Acta* **2003**, *91*, 223–228. [[CrossRef](#)]
69. Keceli, G. Adsorption kinetics and equilibrium of strontium onto kaolinite. *Sep. Sci. Technol.* **2015**, *50*, 72–80. [[CrossRef](#)]
70. Mahoney, J.; Langmuir, D. Adsorption of Sr on kaolinite, illite and montmorillonite at high ionic strengths. *Radiochim. Acta* **1991**, *54*, 139–144. [[CrossRef](#)]
71. Taylor, Y.; McLennan, S.M. *The Continental Crust: Its Composition and Evolution*, 1st ed.; Blackwell: Oxford, UK, 1985.
72. Braun, J.J.; Pagel, M.; Muller, J.P.; Bilong, P.; Michard, A.; Guillet, B. Cerium anomalies in lateritic profiles. *Geochim. Cosmochim. Acta* **1990**, *54*, 781–795. [[CrossRef](#)]
73. Li, M.Y.H.; Zhou, M.F.; Williams-Jones, A.E. Controls on the dynamics of rare earth elements during subtropical hillslope processes and formation of regolith-hosted deposits. *Econ. Geol.* **2020**, *115*, 1097–1118. [[CrossRef](#)]
74. Ma, J.; Wei, G.; Xu, Y.; Long, W.; Sun, W. Mobilization and re-distribution of major and trace elements during extreme weathering of basalt in Hainan Island, South China. *Geochim. Cosmochim. Acta* **2017**, *71*, 3223–3237. [[CrossRef](#)]
75. Sanematsu, K.; Kon, Y.; Imai, A.; Watanabe, K.; Watanabe, Y. Geochemical and mineralogical characteristics of ion-adsorption type REE mineralization in Phuket, Thailand. *Miner. Depos.* **2013**, *48*, 437–451. [[CrossRef](#)]
76. Johannesson, K.H.; Stetzenbach, J.K.; Hodge, V.F. Speciation of the rare earth element neodymium in groundwaters of the Nevada Test Site and Yucca Mountain and implications for actinide solubility. *Appl. Geochem.* **1995**, *10*, 565–572. [[CrossRef](#)]
77. Johannesson, K.H.; Stetzenbach, J.K.; Hodge, V.F.; Lyons, W.B. Rare earth element complexation behavior in circumneutral pH groundwaters: Assessing the role of carbonate and phosphate ions. *Earth Planet. Sci. Lett.* **1996**, *139*, 305–319. [[CrossRef](#)]
78. Patino, L.C.; Velbel, M.A.; Price, J.R.; Wade, J.A. Trace element mobility during spheroidal weathering of basalts and andesites in Hawaii and Guatemala. *Chem. Geol.* **2003**, *202*, 343–364. [[CrossRef](#)]
79. Nesbit, H.W. Mobility and fractionation of rare earth elements during weathering of a granodiorite. *Nature* **1979**, *279*, 206–210. [[CrossRef](#)]
80. Crnički, J.; Jurković, I. Rare earth elements in Triassic bauxites of Croatia Yugoslavia. *Travaux* **1990**, *19*, 239–248.
81. Shaw, D.M. *Interprétation Géochemique des Éléments en Traces dans les Roches Cristallines*; Masson et Cie: Paris, France, 1964.
82. Rudnick, R.L.; Gao, S. Composition of the continental crust. In *Treatise on Geochemistry*, 2nd ed.; Holland, H., Turekian, K., Eds.; Elsevier: Amsterdam, The Netherlands, 2004; pp. 1–64.
83. Özlü, N. Trace element contents of karst bauxites and their parent rocks in the Mediterranean belt. *Miner. Depos.* **1983**, *18*, 469–476. [[CrossRef](#)]
84. Schroll, E.; Sauer, D. Beitrag zur Geochemie von Titan, Chrom, Nickel, Cobalt, Vanadium und Molibdan in Bauxitischen gestermen und problem der stofflichen herkunft des Aluminiums. *Trav. ICSOBA* **1968**, *5*, 83–96.
85. Abedini, A.; Calagari, A.A. The mineralogy and geochemistry of Permian lateritic ores in east of Shahindezh, West-Azarbaidjan province. *Iran. J. Crystallogr. Mineral.* **2012**, *20*, 59–72.

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.