

Petrography, and mineralogical and geochemical control on distribution of major, minor, and trace elements in bauxitic-lateritic deposit of the NE Malekan, East-Azarbaidjan Province, NW Iran

A. Abedini^{1*}, A. A. Calagari²

1- Department of Geology, Faculty of Sciences, Urmia University, Urmia, Iran.

2- Department of Geology, Faculty of Natural Sciences, University of Tabriz, Tabriz, Iran.

(Received: 22/7/2011, in revised form: 1/11/2011)

Abstract: The bauxitic-lateritic deposit at northeast of Malekan (East-Azarbaidjan Province, NW Iran) occurred as interlayer horizon within the Ruteh carbonate formation (Middle-Upper Permian). Based on compositional values of major elements, this deposit is divided into four discrete lithologic facies including, (1) laterite, (2) ferruginous bauxite, (3) bauxitic clay, and (4) siliceous bauxite. Petrographically, the ores display pelitomorphous, micro-granular, nodular, pseudo-breccia, colloform, spongy, and collomorphous-fluidal textures which are indicative of an authigenic origin. According to field evidence and geochemical data, the basaltic rocks whose remnants still exist in places adjacent to the lower contact within the carbonate bedrocks are most likely to be the protolith of this deposit. Textural and geochemical studies indicate that besides volume reduction of the protolith and physico-chemical variations (e.g., pH and Eh) within depositional environment during weathering processes, factors such as the availability of the complexing ligands, heterogeneity of the protolith, adsorption, function of carbonate bedrock as geochemical barrier, contemporaneous deposition of elements, existing in the resistant mineral phases, indirect bauxitization, morphological and hydro-dynamical conditions, and finally formation in a passive and undisturbed aqueous environment played important roles in the formation of the bauxitic-lateritic ores in northeast of Malekan. Correlation coefficients among the elements indicate that trace elements within the ores were fixed by boehmite, diaspore, rutile, anatase, zircon, muscovite, Mn-oxides, and xenotime.

Keywords: *Malekan; bauxitization; mineralogical control; fixation of elements; petrography.*

Introduction

Based on bedrock lithology, bauxite deposits can be divided into two types, (1) bauxites associated with alumino-silicate bedrocks and (2) bauxites affiliated with carbonate bedrocks (karst bauxite). Most of the nation's known bauxite deposits are chiefly of karstic type. Based upon geographic divisions of karstic bauxites throughout the world [1], the bauxite deposits in Iran are a part of Irano-Himalayan bauxitic belt. The bauxite deposits in Iran occurred temporally within five discrete periods, (1) Permian, (2) Permo-Triassic, (3) Triassic, (4) Triassic-Jurassic, and (5) Middle Cretaceous (Cenomanian-Turonian) [2].

The studied bauxitic-lateritic horizon (Permian) is located in about 30 km northeast of Malekan (East-Azarbaidjan, NW Iran) (Fig.1a) and lies as an interlayer horizon within the Ruteh carbonates. The area extends from 46°, 14', 16" to 46°, 18', 17" east longitude and from 37°, 12', 48" to 37°, 15', 05" north latitude (Fig.1b). Many geological features of the area have been noted by various researchers during the past three decades. Alavi-Naini et al. [3] were the first who worked on the regional geology of the area. Paleontological work was done within the enclosing sedimentary rocks by Entezari [4], and on the basis of identified fossils, stated that the horizon is a portion of

* Corresponding author, Tel: (0441) 2972134, Fax: (0441) 2776704, Email: a.abedini@urmia.ac.ir

Permian bauxitic-lateritic deposit. Abedini [2] assessed the economic potential and industrial applicability of the horizon in more detail and concluded that its mode of formation is highly analogous to that of Mediterranean-type karst bauxite deposits. More detail investigations on mineralogy and distribution patterns of REEs by Abedini and Calagari [5] demonstrated that the ores in this deposit contain principally boehmite, diaspore, kaolinite, montmorillonite, rutile, anatase, chlorite, calcite, and muscovite. They also concluded that minerals such as muscovite, rutile,

anatase, zircon, monazite, rhabdophane, gorceixite, and Mn-oxides are the potential hosts for REEs. So far, comprehensive studies concerning petrographic characteristics and behavior of major, minor and trace elements during evolution of the ores in this area have not been done. In present study, however, it has been endeavored to consider the genetic aspects of this deposit in more detail by applying textural data and considering factors influencing (mineralogical and geochemical control) on mobility, fixation, and distribution of major, minor and trace elements.

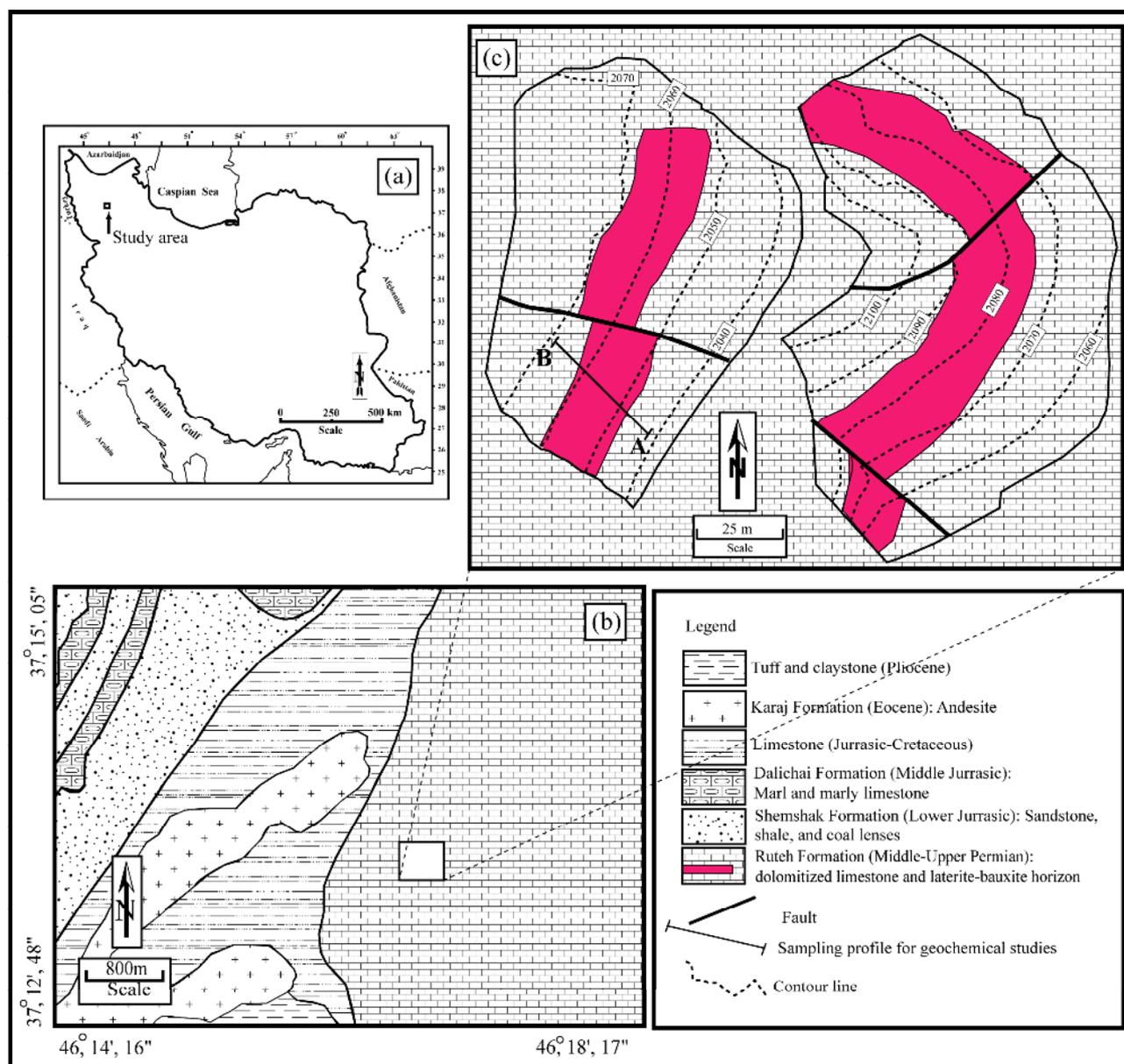


Fig 1. (a) An index map of Iran showing the location of study area. (b) Corrected geologic map of the study area (after [3]). (c) Geologic map of the mining area of the bauxitic-lateritic deposit [4].

Method of investigation

This work has been implemented in three stages. The first stage is field works including traverses along and across the bauxite horizon in order to understand the geologic structures, lithological relation of various rocks in the area, and finally random and systematic sampling of bauxite and related rocks across a selected profile. The second stage includes preparation and examination of 20 thin and polished sections for identification of textures and obtaining data for determination of genesis of the ores by polarized-light microscope. The third stage includes chemical analysis of major, minor, and trace elements of ores and the potential protolith (basalt). Eight samples were analyzed by ICP-AES and ICP-MS methods at laboratories of ALS Chemex in Canada. The obtained results are listed in table 1.

Geology of the area

Field studies show that the study area includes various geologic formations that from the oldest to the youngest are Middle-Upper Permian dolomitized

limestone with cherty bands and nodules (Ruteh Formation); lower Jurassic sandstone, shale, and coal lenses (Shemshak Formation); Middle Jurassic marl and marly limestone (Dalichai Formation); Jurassic-Cretaceous limestone; Eocene andesite (Karaj Formation); and Pliocene tuff and mudstone (Fig.1b). The bauxitic-lateritic horizon lies within the Ruteh carbonate formation and geometrically occurs as two separate interlayer trending NE-SW and NW-SE (Fig.1c) with different thicknesses ranging from 14 to 25 meters. The function of three faults on these two layers caused this horizon to be divided into five blocks (Fig.1c). The boundaries between these blocks are recognizable in the field owing to relatively severe cataclastic textures. The important geologic features in this horizon are the existence of remnants of relatively altered mafic igneous rocks within the carbonate bedrocks near to the lower contact and also of the sharp contact between the residual horizon and the enclosing carbonate rocks.

Table1 Results of chemical analyses obtained from ICP-AES and ICP-MS methods for major, minor, and trace elements in bauxitic-lateritic ores along with a sample of basaltic rock (as protolith) at Malekan.

	T-1 Basalt	MS-1	MS-2	MS-3	MS-4 Residual ores	MS-5	MS-6	MS-7
SiO₂ (Wt%)	51.36	30.00	3.87	16.50	15.85	38.70	37.10	31.80
Al₂O₃	16.80	14.40	39.10	42.10	42.60	33.10	33.90	46.50
Fe₂O₃	9.92	43.30	33.80	21.50	21.50	8.08	10.70	3.30
CaO	6.60	0.44	5.20	0.30	0.25	0.12	0.14	0.12
MgO	3.96	0.78	0.39	0.86	0.87	0.21	0.13	0.08
Na₂O	3.90	0.16	0.19	0.13	0.07	0.05	0.11	0.15
K₂O	2.39	0.59	0.12	0.63	0.34	0.37	0.22	0.01
TiO₂	1.31	2.14	3.75	4.71	4.34	3.34	4.86	3.95
MnO	0.23	0.02	0.13	0.01	0.01	0.08	0.01	0.01
P₂O₅	0.64	0.08	0.04	0.16	0.02	0.16	0.02	0.02
LOI	1.71	8.00	13.45	11.45	11.85	14.6	12.95	14.00
Total	98.82	99.91	100.04	98.35	97.7	98.81	100.14	99.94
Ba (ppm)	665.5	285	57.3	73.4	62.4	236	93.9	27.3
Co	14.5	10.3	3.9	10.3	10.7	106.5	16.5	18.9
Cr	44	70	130	760	820	90	330	380
Cs	2.14	3.24	0.31	0.51	0.36	0.49	1.04	0.49
Cu	23	19	29	18	5	73	19	12
Ga	30.5	18.2	28.5	50.1	52.1	32.9	40.3	73.6
Hf	7.3	8.3	11.8	16.3	15.9	11.3	15	11.7
Nb	22.9	28.4	38.2	108	102	88.6	92.1	66.7
Ni	32	11	5	147	154	106	258	236
Pb	16	56	11	7	5	19	14	10
Rb	57.4	24.5	6	9.8	5.2	10.4	12.2	1.4
Sr	658	142.5	360	158.5	166.5	645	367	294
Ta	0.9	1.6	2.2	6.4	5.9	4.8	5.7	4.2
Th	8.16	17.5	25	28.4	29.1	16.15	21.5	20.1
U	2.29	11.95	20.7	24.7	24.7	24.2	5.81	4.98
V	147	182	411	1130	1040	310	366	452
Y	24.6	32.1	42.3	31.1	29.7	25.3	47.4	29
Zn	88	55	33	87	89	56	97	66
Zr	179	302	493	625	609	436	545	420

Classification of the ores based on their chemistry of major elements and macroscopic characteristics

According to chemistry of major elements, the ores can be divided into four general types (Fig.2). The type 1 ores are mainly present at the base of weathered horizon with the carbonate bedrocks. Macroscopically, these types of ores are layered and reddish brown in color and have earthy aggregates and nodular texture. The major oxides in this type of ores, in order of abundance, are $\text{Fe}_2\text{O}_3 > \text{Al}_2\text{O}_3 > \text{SiO}_2$. The type 2 ores have relatively low hardness, relatively low density, soapy feel, and spheroidal shape. They overlie the type 1 ores and are seen in two colors, reddish brown and green. The order of abundance of major elements in the type 2 ores is $\text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{SiO}_2$. The type 3 ores are white and light gray in color, have tough feeling, and overlie the type 2 ores. The development of nodular texture within these ores is the most conspicuous macroscopic feature. The order of abundance of major elements in this type of ores is $\text{SiO}_2 > \text{Al}_2\text{O}_3 > \text{Fe}_2\text{O}_3$. The type 4 ores are white and have earthy aggregates with low hardness and relatively low density. The type 4 ores lie at the upper part of the studied residual horizon and exhibit massive texture. Based on order of abundance of the major oxides in various

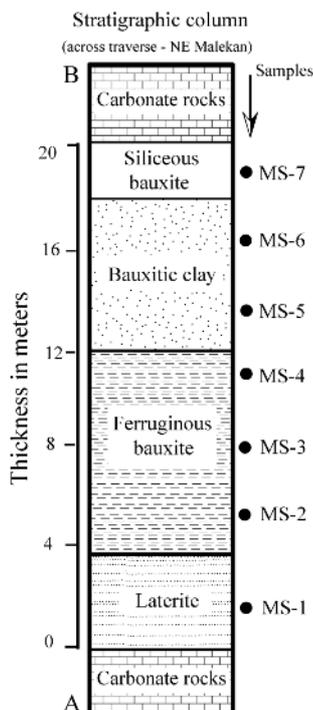


Fig 2. Distribution mode of lithologic facies in the studied profile at NE Malekan. Filled circles are sampling locations for geochemical investigations.

types of ores at Malekan and also pointing to the suggestions of Bardossy and Aleva [6], this bauxite deposit can be considered as residual ores and the above mentioned types (1 to 4) of ores are designated as laterite, ferruginous bauxite, bauxitic clay, and siliceous bauxite, respectively (Fig.2).

Petrographic studies

The discrete texture-forming units within the ores include nodules, ooids (Fig.3a) and flaky-like aggregates (Fig.3b). Texture-forming units in the matrix are peditomorphic (Fig.3c) and micro-granular (Fig.3d). In microscopic sections, hematite is the most important identifiable mineral that forms the nodules, the nucleus of ooids (Fig.3a), and the flaky aggregates (Fig.3b). The number of concentric bands in ooids scarcely exceeds 3 (Fig.3a). According to the distribution mode of texture-forming units, the ores contain peditomorphic (aphanitic) (Fig.3c), micro-granular (Fig.3d), collomorphic-fluidal (Fig.3e), spongy (Fig.3f), colloform (Fig.3g), and pseudo-breccia (Fig.3h), and oriented structure (Fig.3i). Peditomorphic and micro-granular textures along with oriented structures are related to the ores of bauxitic clay and siliceous bauxite units; collomorphic-fluidal textures to the ores of laterite unit; nodular texture to the ores of laterite, ferruginous bauxite, and bauxitic clay units; and finally spongy, colloform and pseudo-breccia textures to the ores of laterite and ferruginous bauxite units.

Geochemistry of major, minor, and trace elements in deposit

Chemical analyses demonstrate that the major components of the studied ores are SiO_2 (3.87-38.70 wt%), Al_2O_3 (14.40-46.50 wt%), Fe_2O_3 (3.30-43.30 wt%), and TiO_2 (2.14-4.86 wt%) (table 1). They mark a wide range of variations. Among these components, Fe_2O_3 exhibits a profound variation within the profile. Alkalis and earth alkalis along with P and Mn (in oxide form) are present in very low abundance and their total values range from 0.39 to 6.07 wt%.

Trace elements are present relatively in very low quantity in the studied ores. They are, in order of abundance, mainly V (182-1130 ppm), Cr (70-820 ppm), Zr (302-609 ppm), and Sr (142.5-645 ppm). The rest exist relatively in lower amounts which, in decreasing abundance, are Ba, Nb, Ni, and Hf (in 10s-100s ppm); Ga, Th, Y, and Zn (in 10s ppm); Co, Cu, U, Pb, and Rb (in a few ppm to 10s ppm); and Cs and Ta (in a few ppm).

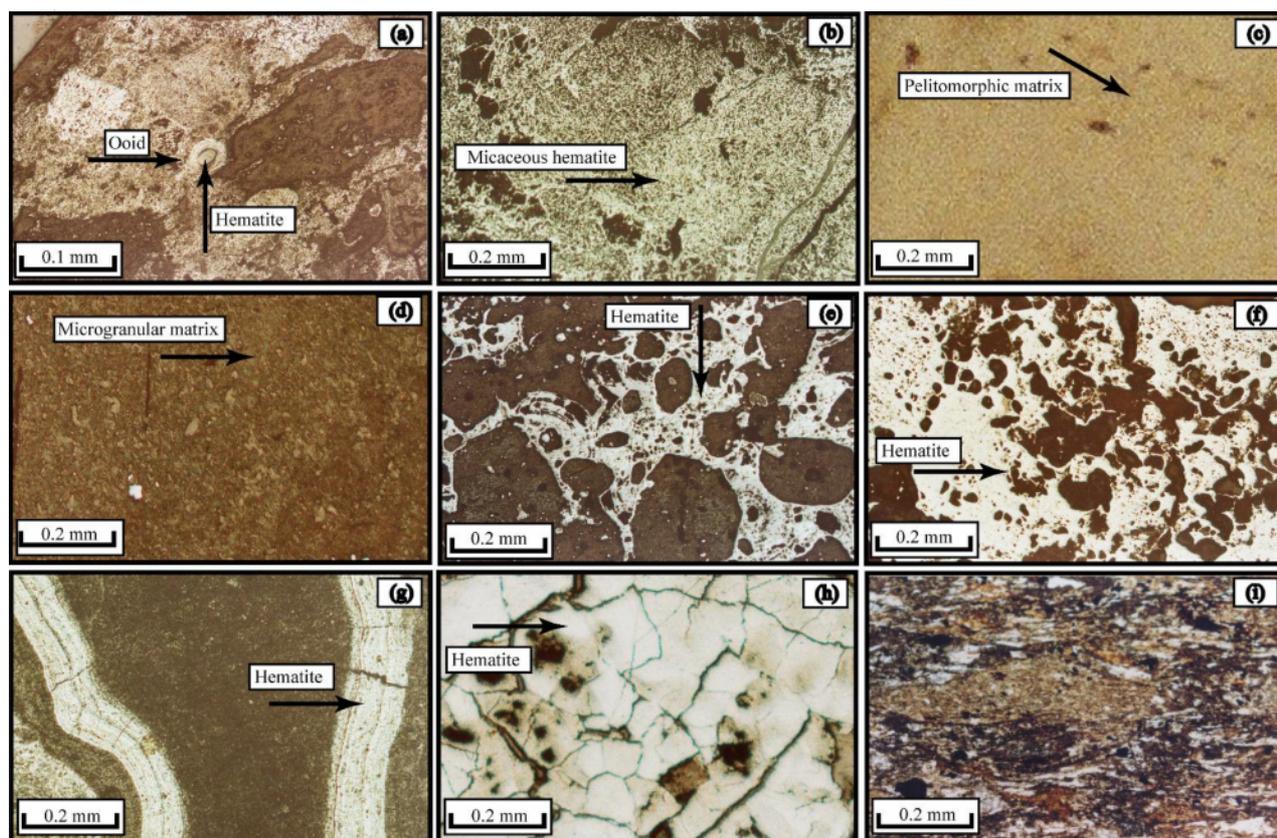


Fig 3. Photomicrographs of the bauxitic-lateritic ores. (a) Distribution of ooids (with hematite nucleus) in ferruginous bauxite unit. (b) Distribution of micaceous hematite in the matrix of the ores in the laterite unit. (c) Pelitomorphous texture in bauxitic clay unit. (d) Microgranular texture in the bauxitic clay unit. (e) Collomorphic-fluidal texture in the laterite unit. (f) Spongy texture in the ferruginous bauxite unit. (g) Colloform texture in the ferruginous bauxite unit. (h) Pseudo-breccia texture in the laterite unit. (i) Oriented structure in the siliceous bauxite unit. All pictures were taken in the crossed polarized light (xpl) condition.

Isocon geochemistry

So far, various methods were suggested for consideration of behavior of elements during weathering processes by many researchers including volume factor [7], isocon [8], and immobile element [9, 10]. In this study, for estimation of degree of mobility and enrichment during weathering processes, isocon method [8] was used which is based on (1) authigenic origin of the deposit, (2) identification of protolith, and (3) drawing isocon line.

Authigenic origin of the deposit: Based on various type of textures (pelitomorphous, microgranular, nodular, pseudo-breccia, colloform, spongy, and collomorphic-fluidal) being accompanied by quite fresh ooids within the matrix, and also comparison of these textures with those presented by Bardossy [1] for authigenic and allochthonous bauxitic-lateritic

ores, it can be conceived that the residual deposit at Malekan has quite authigenic origin.

Identification of protolith: The existence of the relatively altered mafic igneous rocks near the contact of the lateritic ores with carbonate bedrocks and also the presence of quite sharp boundaries between the weathered horizon and the enclosing rocks, advocate the idea that the studied ores are likely related genetically to these mafic igneous rocks. Petrographic examinations, implemented by Abedini, [2] indicate that these rocks have almost basaltic composition and mineralogically consist of plagioclase, alkali-feldspar, hornblende, biotite, olivine, augite, ilmenite, chlorite, sericite, zircon, and calcite. For consideration of genetic relationships between these basaltic rocks and the ores, in addition to the mentioned field evidence, attempts have been made to compare the weathering products at

Malekan with those of some protoliths from different places of the world by using appropriate geochemical diagrams. Comparison of weathering products from different protoliths at different places of the world [11-15] with the studied horizon displays that the deposit at Malekan should have had a protolith with a composition within the range of basaltic rocks. Hayashi et al. [16] concluded that weathered rocks with $Al_2O_3/TiO_2 < 21$ and > 21 are derived from mafic and felsic protolith, respectively. The data points on the $TiO_2 - Al_2O_3$ plot (Fig.4a) demonstrate that the ores at Malekan should have been derived from the alteration and weathering of mafic igneous rocks. Plotting the Malekan's data on the bivariate plot of Ti-Zr [17] (Fig.4b) further supports the derivation of the ores from a protolith of basaltic composition. By taking the above inferences into account, it appears that the basaltic rocks existing adjacent to the lower contact of lateritic ores with the carbonate bedrocks are the logical and rational candidates for being the protolith of the ores.

Drawing isocon line: Utilizing Grant's method [8] for isocon geochemistry (for consideration of the behavior of elements during alteration and weathering processes) requires some immobile elements such as Al, Ti, Zr, Hf, Th, and Nb to delineate the isocon line (on which elements have immobile behavior). In this regard, elements such as Al, Zr, and Hf are used for drawing isocon line. Then the compositional values of elements in the protolith (basaltic rocks) and the residual lithologic facies are plotted on a X-Y diagram (Fig.5) and a tie line covering the data points of the three elements (Al, Zr, and Hf) is drawn as isocon line. The data points of elements lying above and below this line denote enrichment and depletion, respectively during weathering processes. The results obtained from this method (see Fig.5) demonstrated that elements such as Si, Na, K, Mg, Mn, P, Ca, Ba, Rb, Sr, and Zn were leached out (depleted) and elements such as U, V, Th, Cr, Nb, and Ta along with volatiles (LOI) were enriched during the evolution of this residual profile. Nevertheless, elements such as Fe, Ga, Cs, Ni, Y, Co, and Pb were leached out from some lithologic units while were enriched in some others.

Discussion

Consideration of genetic aspects of the ores by using textural data

Detailed microscopic examinations revealed that the lack of separated debris and other texture-forming components caused the formation of pelitomorphic and micro-granular textures from amorphous colloids and/or fine crystals in this deposit. Displacement of colloids derived from the weathering of the protolith during diagenetic and supergene processes brought about colloidomorphic-fluidal texture. Function of dynamic pressures, dehydration of colloids, and recrystallization produced pseudo-breccia texture. The rhythmic separation of hematite from alumino-silicate colloids engendered colloform texture within the ores. It appears that homogeneity of the original colloids and the lack of appropriate nucleus along with the weak energy of the depositional environment (deposition from a quiescent and inactive aqueous environment), and frequent fluctuation of underground water table level impeded the formation and development of concentric textures (both quantitatively and in light of the number of concentric bands around the nucleus) such as ooids, pisoids, and macro-pisoids and hence caused the development of nodular texture instead [18]. The existence of pelitomorphic and colloform textures within the ores may indicate indirect bauxitization [19] and poor draining processes as a morpho-dynamic factor in the evolution of this deposit. In other words, the transformation of the protolith into an intermediate composition (clay minerals) and ultimately to bauxite invokes a longer period of time. With regarding the mode of formation of the above textures and obliteration of the relict textures of the protolith by the effect of supergene processes, it is better to use the term alloteritic bauxite (as coined by [19]) for this type of deposit. The formation of hematitic nodules, especially in the lateritic ores, can be related to the variation of water activity in the pedogenic environment and is likely derived from climatic fluctuations as a hydro-dynamic factor [20]. The presence of oriented structures within the ores is likely owing to the effect of directed structural stress on this deposit.

Total mass change calculations for the protolith in the course of evolution of the residual facies

For calculation of the degree of total mass changes during evolution of the residual units, the slope of the isocon line (see Fig.5) was initially calculated. The results of calculations demonstrated that the isocon slopes are numerically about 1.23, 1.99, 2, and 1.94 for laterite, ferruginous bauxite, bauxitic clay, and siliceous bauxite units, respectively. Then the total values of mass changes were computed by using the following equation:

$$\Delta M = [(1/S)-1] \times 100 \quad [8]$$

S is the numeric degree of isocon slope. By utilizing the obtained results from the above equation, it became evident that the conversion (by alteration processes) of basaltic rocks into residual facies such as laterite, ferruginous bauxite, bauxitic clay, and siliceous bauxite were accompanied by mass reductions of about 18.70%, 49.74%, 50%, and 48.45%, respectively.

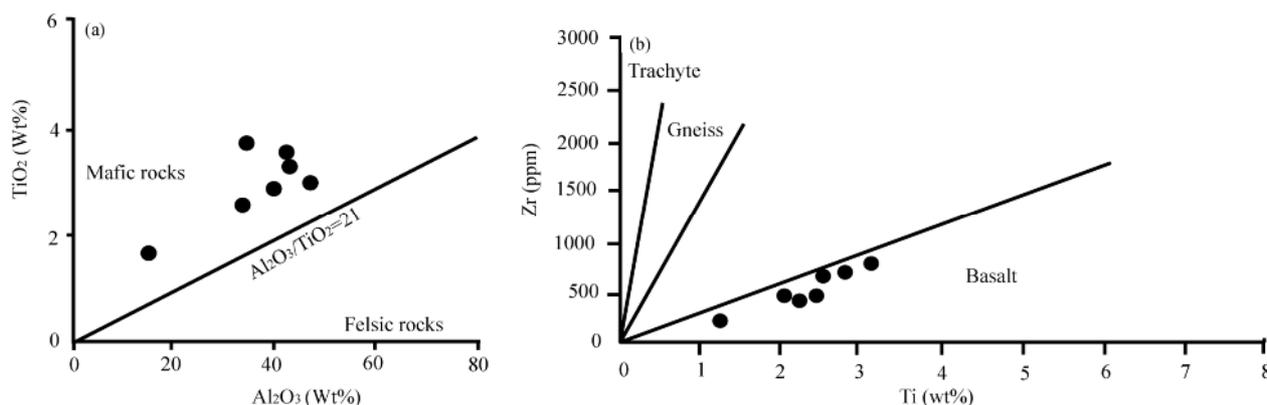


Fig 4. (a) The position of data points of the ores at Malekan on a bivariate plot of $\text{TiO}_2\text{-Al}_2\text{O}_3$. The boundary between mafic and felsic protoliths is from Hayashi et al. [16]. (b) The position of data points of the studied ores on a bivariate plot of Ti-Zr . The boundaries between rock units are determined by Hallberg [17].

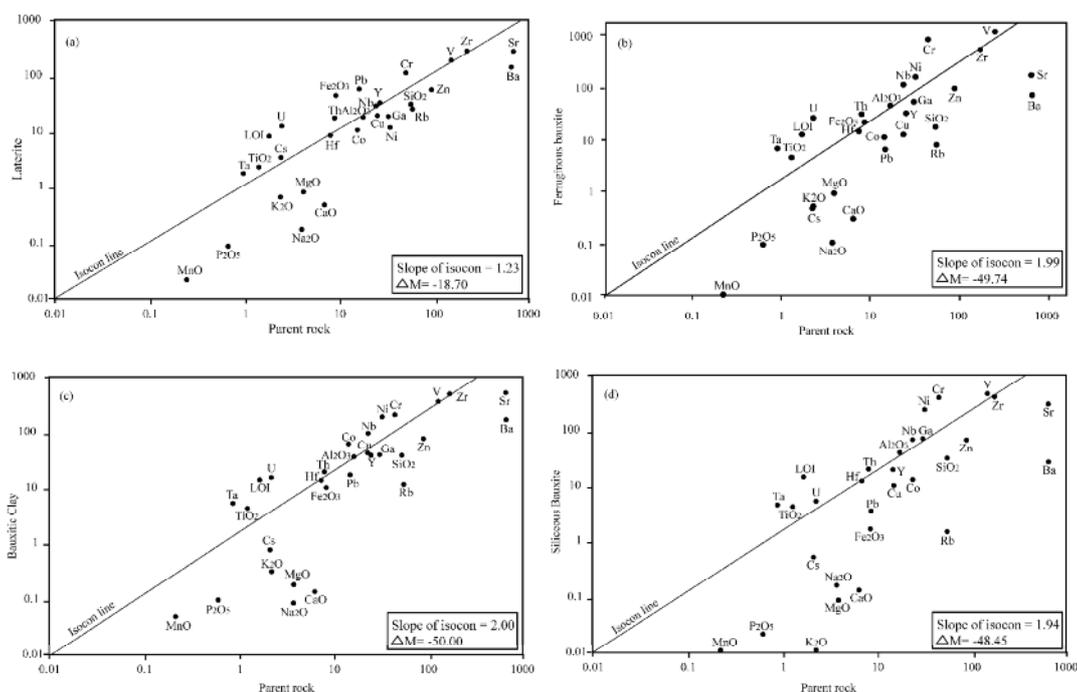


Fig 5. Diagrams of isocon mass equilibrium [8] for major, minor, and trace elements showing the development and evolution of lithologic facies, (a) laterite, (b) ferruginous bauxite, (c) bauxitic clay, and (d) siliceous bauxite in the studied profile.

Mineralogical and geochemical control on mobilization and distribution of major, minor, and trace elements

Leached elements

1- Leached major and minor elements: By considering the mineralogy of the ores examined by Abedini and Calagari [5] and also the mineralogy of the basaltic rocks (as protolith) studied by Abedini [2], the partial depletion of Si from the weathered profile may be as the result of kaolinization and/or sericitization of feldspars in the protolith and its moving into weathering solutions [21]. Depletion of Na, Ca, Mg, and K during the formation of all four residual facies (see Fig.5) is likely due to the reaction between plagioclase, K-feldspar, and mica with acidic solutions and the selective leaching of these elements during the primary stages of weathering. The acidity of the percolating meteoric water (necessary for destruction of these minerals) was probably furnished by dissolved CO₂ [21]. Depletions of Mn and also a proportion of Mg from the profile (see Fig.5) are likely due to the breakdown of ferromagnesian minerals. Partial leaching of phosphorus may be owing to the decomposition of apatite.

2- Leached trace element: The partial departure of Sr, Ba, Zn, Rb, and Cu from the weathered system took place as the result of destruction of feldspars and biotite in the protolith by weathering solutions. Calculation of Pearson's correlation coefficients [22] (table 2) displays that a moderate and positive correlation exists between Sr and Si ($r = 0.55$) and between Cu and Si ($r = 0.53$). These values suggest that the remaining Sr and Cu in the system are likely due to the presence of clay minerals. The high and positive correlation between Rb and K ($r = 0.91$) and between Ba and K (0.85) testify that these elements may be hosted by muscovite in the profile. Furthermore, the moderate and positive correlations between Zn and Al ($r = 0.63$) and between Zn and Mn ($r = 0.65$) attest that the distribution of Zn was chiefly controlled by clay

minerals (due to adsorption) and Mn-oxides.

Enriched elements

1- Enriched major elements: Since Ti commonly behaves as an immobile element during weathering processes [14] therefore, there is every reason to believe that it should have acted in such manner (e.g., immobile) during the formation of this profile as well. The variation trend of this element was closely examined and became evident that it was enriched to some extent during the evolution of this profile. It seems that this enrichment occurred authigenically (due to both its high stability field strength and very low solubility in aqueous solutions) [23] because of volume reduction of protolith during weathering processes. The remarkable increase in LOI is related both to the development of highly hydrous mineral phases during bauxitization-lateritization processes and to the presence of relatively high organic matters within the residual profile [24].

2- 2- Enriched trace elements: Although commonly distribution of elements such as V and Cr in bauxitic-lateritic formation is principally affiliated to Fe-oxides [25], correlation coefficient values (table 2) between V and Fe ($r = -0.36$) and between Cr and Fe ($r = -0.18$) in the studied profile show that hematite does not play any significant role in concentrating V and Cr. The high and positive correlation between Al and V ($r = 0.68$) and between Ti and V ($r = 0.71$) indicate that boehmite, diaspore, rutile, and anatase (due to contemporaneous deposition of Al and Ti oxides) are the principal agents for the fixation of V. Similarly, the high and positive correlation between Al and Cr ($r = 0.82$) and between Ti and Cr ($r = 0.78$), it can be conceived that the clay minerals along with rutile and anatase played crucial roles in concentrating Cr in this deposit. Zircon is commonly an important mineral for hosting Th in severely weathered profile [21]. The good correlation between Th and Zr ($r = 0.82$) provides reasonable inference that zircon may be

Table 2. Pearson's correlation coefficients among elements in the studied ores at Malekan.

	Si	Al	Fe	K	Ti	Mn	P	Ba	Co	Cr	Cs	Cu	Ga	Hf	Nb	Ni	Pb	Rb	Sr	Ta	Th	U	V	Y	Zn	Zr	
Si	1.00																										
Al	-0.24	1.00																									
Fe	-0.35	-0.82	1.00																								
K	-0.20	-0.88	0.93	1.00																							
Ti	-0.22	0.90	-0.78	-0.68	1.00																						
Mn	-0.41	0.10	0.05	0.29	0.49	1.00																					
P	-0.02	-0.61	0.52	0.79	-0.21	0.71	1.00																				
Ba	0.34	-0.99	0.74	0.85	-0.84	-0.05	0.67	1.00																			
Co	0.69	0.07	-0.54	-0.21	0.36	0.33	0.35	0.08	1.00																		
Cr	-0.74	0.82	-0.36	-0.47	0.78	0.38	-0.35	-0.87	-0.30	1.00																	
Cs	0.22	-0.95	0.82	0.77	-0.99	-0.37	0.35	0.91	-0.28	-0.80	1.00																
Cu	0.53	-0.17	-0.23	0.14	0.21	0.55	0.67	0.32	0.93	-0.36	-0.09	1.00															
Ga	-0.01	0.90	-0.82	-0.97	0.64	-0.34	-0.88	-0.91	-0.04	0.59	-0.75	-0.37	1.00														
Hf	-0.44	0.76	-0.54	-0.42	0.95	0.72	0.04	-0.72	0.26	0.82	-0.90	0.24	0.41	1.00													
Nb	-0.11	0.74	-0.71	-0.52	0.96	0.66	0.06	-0.65	0.56	0.62	-0.90	0.48	0.42	0.94	1.00												
Ni	0.34	0.83	-0.99	-0.96	0.75	-0.13	-0.60	-0.76	0.47	0.37	-0.80	0.15	0.86	0.49	0.66	1.00											
Pb	0.26	-0.96	0.80	0.77	-0.98	-0.36	0.37	0.92	-0.23	-0.83	0.99	-0.05	-0.76	-0.9	-0.89	-0.78	1.00										
Rb	0.17	-0.99	0.85	0.91	-0.87	-0.03	0.66	0.98	-0.08	-0.78	0.94	0.18	-0.93	-0.71	-0.71	-0.86	0.94	1.00									
Sr	0.55	0.36	-0.74	-0.44	0.61	0.38	0.17	-0.22	0.95	-0.02	-0.55	0.83	0.22	0.50	0.76	0.68	-0.51	-0.38	1.00								
Ta	-0.09	0.80	-0.77	-0.60	0.98	0.59	-0.04	-0.71	0.54	0.64	-0.94	0.42	0.51	0.93	0.99	0.72	-0.92	-0.77	0.75	1.00							
Th	-0.91	0.56	-0.03	-0.10	0.60	0.58	-0.03	-0.61	-0.39	0.93	-0.59	-0.31	0.25	0.77	0.50	0.02	-0.62	-0.49	-0.17	0.50	1.00						
U	-0.7	-0.02	0.35	0.48	0.29	0.92	0.67	0.01	-0.06	0.44	-0.19	0.22	-0.43	0.59	0.40	-0.41	-0.20	0.10	-0.03	0.32	0.72	1.00					
V	-0.85	0.68	-0.18	-0.25	0.71	0.54	-0.13	-0.72	-0.32	0.97	-0.71	-0.29	0.38	0.83	0.59	0.17	-0.73	-0.62	-0.07	0.59	0.99	0.64	1.00				
Y	-0.05	-0.18	0.11	0.43	0.27	0.91	0.88	0.27	0.58	-0.02	-0.12	0.81	-0.55	0.47	0.52	-0.19	-0.10	0.23	0.51	0.43	0.20	0.75	0.15	1.00			
Zn	0.08	0.63	-0.72	-0.47	0.89	0.65	0.15	-0.51	0.72	0.44	-0.82	0.64	0.33	0.85	0.98	0.66	-0.80	-0.60	0.87	0.97	0.33	0.33	0.42	0.59	1.00		
Zr	-0.52	0.70	-0.43	-0.32	0.90	0.78	0.11	-0.66	0.20	0.83	-0.85	0.22	0.32	0.99	0.90	0.38	-0.85	-0.64	0.42	0.89	0.82	0.68	0.86	0.51	0.81	1.00	

the main fixing agent for Th in the studied profile as well. The moderate and positive correlation between Al and Th ($r = 0.56$) illustrates that in addition to zircon, boehmite and diaspore were also effective in fixing Th. The good and positive correlations between Nb with Al ($r = 0.74$) and between Nb and Ti ($r = 0.96$) furnish sufficient evidence that Nb was likely fixed by boehmite, diaspore, rutile, and anatase. The good positive correlations between Ta and Al ($r = 0.80$) and between Ta and Ti ($r = 0.98$) mark that Ta was probably concentrated by the same minerals hosting Nb in the weathered system. The moderate and positive correlations between U and each individual elements of Zr, Mn and P ($r=0.67$ to 0.92) may testify to the fixation of U by secondary phosphate minerals, zircon, and Mn-oxides.

Considerations of the behavior of immobile elements such as Zr, Th, Ti, and V (see Fig.5) in the residual facies unveiled that these elements suffered mass gain in almost irregular fashion. Possibility exists that a part of these irregularities to be related to heterogeneity of the protolith.

Enriched-leached elements

1- Enriched-leached major elements: Fe was leached out of the upper parts of the profile (bauxitic clay and siliceous bauxite units) and was enriched in the lower parts of the profile (laterite and ferruginous bauxite units). This may indicate that downward moving of the meteoric solutions with low pH along with the existence of local reducing conditions (due to oxidation of organic matters) might have caused the partial leaching of

Fe out of the upper parts of the weathered profile. It appears buffering of downward percolating acidic weathering solutions by the carbonate bedrocks and ensuing increase of pH brought about enrichment for Fe in the lower parts of the profile.

2- Leached-enriched minor elements: The good and positive correlations between Ni and Al ($r = 0.83$) and between Ni and Ti ($r = 0.75$) and moderate and positive correlation between Co and Si ($r = 0.69$) show that distribution of Ni in the studied profile was controlled mainly by boehmite, diasporite, rutile, and anatase and Co by clay minerals (by adsorption). The good and positive correlation between Al and Ga ($r = 0.90$) exhibits that Ga was fixed by boehmite, diasporite and clays. Although much of Cs and Pb were leached from the weathered system (due to the decomposition of feldspars in the protolith) their partial fixation, as noted by the good and positive correlation coefficients between Pb and K ($r = 0.77$) and between Cs and K ($r = 0.77$), might have been done by muscovite. The moderate to good positive correlations between Y and individual elements such as P, Mn, and Zr ($r = 0.51$ to 0.91) unravel the fixation of Y by minerals such as xenotime, Mn-oxides, and weathering-resistant zircon. Similar results have been also reported by Henderson [26] and Mutakyahwa et al. [27].

Conclusion

The important results obtained from field evidence, petrographic examinations, and geochemical investigations of bauxitic-lateritic deposit at Malekan are as follows:

1- The studied deposit was developed as of interlayer horizon within Ruteh carbonate formation (Middle-Upper Permian) and are divided into four distinct lithologic facies, (1) laterite, (2) ferruginous bauxite, (3) bauxitic clay, and (4) siliceous bauxite.

2- Petrographic examinations of the ores indicate that they are alloteritic and have authigenic origin. Various factors such as indirect bauxitization,

dynamic stress, hydrodynamic and morpho-dynamic conditions, and deposition in a quiet and passive aqueous environment played important role in development and evolution of this deposit.

3- Field evidence, comparison of the ores with the products of various weathered protolith, and compositional values of immobile elements such as Al, Ti, and Zr in the ores provide reasonable indications to believe that the studied ores were derived from alteration and weathering of basaltic rocks.

4- Consideration of isocon geochemistry demonstrated that the protolith was suffered volume reduction during weathering processes. Besides the role of carbonate bedrocks in concentrating of elements, factors such as pH variation of weathering solutions, Eh, existence of organic complexes, adsorption, and contemporaneous deposition had significant influence in formation and development of the ores.

5- Correlation coefficients among the elements attest to the fixation of V, Nb, Ni, and Ta by boehmite, diasporite, rutile, and anatase; Co by clay minerals, rutile, and anatase; Zr by zircon; Th by Zircon, boehmite, and diasporite; U by secondary phosphate minerals, Mn-oxides, and Zircon; Ga by boehmite, diasporite, and clays; Cs and Pb by muscovite; Y by xenotime, Mn-oxides, and zircon; and Zn by clay minerals and Mn-oxides.

References

- [1] Bardossy G., *"Karst Bauxites"*, Elsevier Scientific, Amsterdam, (1982) 441p.
- [2] Abedini A., *"Investigations of mineralogy, geochemistry and genesis of the Permian to Triassic bauxitic- lateritic deposits in northwest of Iran"*, unpublished Ph.D. Thesis (in Persian), Geology Department, Tabriz University, (2008) 184p.
- [3] Alavi-Naini M., Shahrabi M., Saidi A., *"1:250000 map of Urmia guardrangle"*, Geological Survey of Iran (1985).

- [4] Entezari A., "Investigation of economic geology of bauxite-laterite deposits in Mendilbesar area, SE Maragheh", unpublished MSc Thesis (in Persian), Geology Department, Tabriz University, (2006) 123p.
- [5] Abedini A., Calagari A.A., "Studies of normative mineralogy and REE geochemistry of Permian residual horizon in northeast of Malekan, East-Azarbaidjan province (in Persian)", Journal of Geosciences (in press).
- [6] Bardossy G.Y., Aleva G.Y.Y., "Lateritic Bauxites", Akademia, Kiado Budapest, (1990) 646p.
- [7] Gresens R.L., "Composition-volume relationships of metasomatism", Chemical Geology 2 (1967) 47-55.
- [8] Grant J.A., "The isocon diagram: A simple solution to Gresens equation for metasomatic alteration", Economic Geology 81 (1986) 1976-1982.
- [9] Brimhall G.H., Chadwick O.A., Lewis C.J., Compson W., Williams I. S., Danty K.J., Dietrich W.E., Power M.E., Hendricks D., Bratt J., "Deformational mass transfer and invasive processes in soil evolution", Science 255 (1991) 695-702.
- [10] Nesbitt H.W., Markovics G., "Weathering of granodioritic crust, long-term storage of elements in weathering profiles, and petrogenesis of siliciclastic sediments", Geochimica et Cosmochimica Acta 61 (1997) 1653-1670.
- [11] Hieronymus B., Kotschoubey B., Boulegue J., "Gallium behaviour in some contrasting lateritic profiles from Cameroon and Brazil", Journal of Geochemical Exploration 72 (2001) 147-163.
- [12] Meyer F.M., Happel U., Hausberg J., Wiechowski G., "The geometry and anatomy of the Pijigaos bauxite deposit, Venezuela", Ore Geology Review 20 (2002) 27-54.
- [13] Ndjigui P., Bilong P., Bitom D., Dia A., "Mobilization and redistribution of major and trace elements in two weathering profiles developed on serpentinites in the Lomie ultramafic complex, southeast Cameroon", Journal of African Earth Sciences 50 (2008) 305-328.
- [14] Beyala V.K.K., Onana V.L., Priso E.N.E., Parisot J., Ekodeck G.E., "Behaviour of REE and mass balance calculations in a lateritic profile over chlorite schists in South Cameroon", Chemie der Erde-Geochemistry 69 (2009) 61-73.
- [15] Karadag M., Kupeli S., Arik F., Ayhan A., Zedef V., Doyen A., "Rare earth element (REE) geochemistry and genetic implications of the Mortas bauxite deposit (Seydisehir/Konya-southern Turkey)", Chemie der Erde-Geochemistry 69 (2009) 143-159.
- [16] Hayashi K., Fujisawa H., Holland H.D., Ohmoto H., "Geochemistry of sedimentary rocks from northeastern Labrador, Canada", Geochimica et Cosmochimica Acta 61 (1997) 4115-4137.
- [17] Hallberg J.A., "A geochemical aid to igneous rocks identification in deeply weathered terrain", Journal of Geochemical Exploration 20 (1984) 1-8.
- [18] Valetton I., "Bauxites", Elsevier, (1972) 226p.
- [19] Boulange B., "Les formation bauxitiques lateriques de Cote d Ivoire", Travaux et Documents ORSTOM, Paris 175 (1984) 341p.
- [20] 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", International Journal of Earth Sciences 96 (2007) 887-902
- [21] Fernandez-Caliani J., Cantano M., "Intensive kaolinization during a lateritic weathering event in southwest Spain mineralogical and geochemical inferences from a relict paleosol", Catena 80 (2010) 23-33.
- [22] Rollinson H., "Using geochemical data: Evaluation, presentation, interpretation", Longman Scientific and Technical, (1993) 352p.
- [23] Etame J., Gerard M., Bilong P., Suh C.E., "Behaviour of elements in soils developed from

nephelinites at Mount Etinde (Cameroon): Impact of hydrothermal versus weathering processes", Journal of African Earth Sciences 54 (2009) 37-45.

[24] Ji H., Wang S., Ouyang Z., Zhang S., Sun C., Liu X., Zhou D., "Geochemistry of red residua underlying dolomites in karst terrains of Yunnan-Guizhou plateau: The formation of the Pinba profile", Chemical Geology 203 (2004) 1-27.

[25] Margues J.J., Schulze D.G., Curi N., Mertzman S.A., "Trace element geochemistry in

Brazilian Cerrado soils", Geoderma 121 (2004) 31-43.

[26] Henderson P., "Rare Earth Element Geochemistry", Elsevier, Amsterdam, (1984) 510p.

[27] Mutakyahwa M.K.D., Ikingura J.R., Mruma A.H., "Geology and geochemistry of bauxite deposits in Lushoto District, Usambara Mountains, Tanzania", Journal of African Earth Sciences 36 (2003) 357-369.