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Geochemical investigations on Permo-Triassic bauxite horizon at Kanisheeteh, east of Bukan, West-Azarbaidjan, Iran

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Abstract

The studied bauxite horizons of Kanisheeteh located \sim 19 km east of Bukan (NW of Iran), are part of the Irano-Himalayan karst bauxite belt lying conformably between Permian carbonates and shales and Triassic limestones. They extend laterally over ~ 8 km and are variable in thickness (8–28 m). Petrographically, the rocks within the horizon show nodular, panidiomorphic-granular, ooidic, pseudo-breccia and pseudo-porphyry textures along with pressure shadow features. These textural features may suggest that the bauxite has an authigenic origin but suffered tectonic deformation. Diaspore, hematite, and clay minerals are the principal constituents accompanied by some minor accessory minerals such as muscovite, plagioclase, quartz, magnesio-sidero-riebeckite, calcite and zircon. Based upon type and quantities of constituent minerals, three distinct mineralogical types can be differentiated within the horizon, namely (1) bauxitic clayey iron ore, (2) clayey bauxite, and (3) bauxitic clay. Based upon field evidence, calculation of accumulation coefficients of trace elements, concentration of elements such as Cr, Ni, Zr and Ga and the ratios of immobile elements, the diabasic rocks which occur in the study area are the most plausible and probable source rock for the bauxite deposits of Kanisheeteh. The mass changes of elements were calculated on the basis of Ti (as immobile element). These calculations demonstrate that elements such as Mg, Na, Ca, Si, Fe, Y, Rb, Ba, P, K and Mn were leached out of the weathered system whereas elements such as Nb, Hf, Cr, Ce, V, Zr, Al, La, Co, Th, U and Ni became concentrated in the residual system. The variability in obtained data is explained by factors such as stability of host minerals, fixation of elements in neomorphic phases, preferential sorption, and the chemistry of solutions involved in weathering (e.g. pH of percolating waters). © 2007 Elsevier B.V. All rights reserved.

Keywords: Bauxite; Immobile elements; Mass changes; Karst bauxite; Bukan; West-Azarbaidjan

1. Introduction

Bauxites are an important source of many metal ores particularly for Al and Ga (Evans, 1993). Important known bauxite deposits in Iran which occur in the so called Irano-Himalayan belt are spatially distributed in four regions, namely (1) the northwest of Iran (e.g. Bukan, Shahindezh), (2) the Zagros heights, (3) the Alborz mountain chain and (4) the central plateau of Iran. They are restricted to Permo-Triassic, Triassic and middle Cretaceous (Cenomanian-Turonian) ages (Fig. 1a).

This study focused on the deposits situated in northwest of Iran (e.g. Bukan) where Permo-Triassic and late

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Fig. 1. (a) Index map of Iran showing the distribution of some high aluminum (bauxites and clays) prospect areas. (b) A geologic map illustrating the position of bauxite horizons at Kanisheeteh.

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Fig. 2. Stratigraphic columns along two profiles across Permo-Triassic bauxite horizon at Kanisheeteh (for position see Fig. 1) with indication of analyzed samples. The distance between two profiles is about 2.5 km.

Triassic deposits occur. The former, however, are more important and data reported mainly address these occurrences.

Geochemical aspects of bauxite deposits have been reported by many workers including Boulange et al. (1996), Mongelli (1997), Hill et al. (2000), Mordberg et al. (2001), Meyer et al. (2002), Öztürk et al. (2002), Zhang and Lalor (2003), and Laskou and Economou-Eliopoulos (2007). Mobility and enrichment of elements during bauxitization processes have been discussed by MacLean et al. (1997), Valeton et al. (1997) and Francheschelli et al. (1998).

Various methods for mass balance calculation of weathered and altered systems were developed including the volume factor method (Gresens, 1967), the isocon method (Grant, 1986) and the immobile element method (Millot and Bonifas, 1955; Nesbitt, 1979; Nesbitt et al., 1980; MacLean and Kranidiotis, 1987; Brimhall and Dietrich, 1987; Brimhall et al., 1988; MacLean, 1990; Chadwick et al., 1990; Brimhall et al., 1991; Nesbitt and Wilson, 1992; Brimhall et al., 1992; Colin et al., 1992; Bestland et al., 1996; Nahon and Merino, 1997; Nesbitt and Markovics, 1997). The first studies on geochemistry of immobile elements on bauxite horizons in northwestern Iran (west of Miandoab, ~ 60 km northwest of Kanisheeteh) have been carried out by the authors (unpublished reports). But, geochemical studies on the bauxites at Kanisheeteh are lacking. The aim of the present study is to report on the comprehensive petrographical and geochemical database. Based on the latter the appropriate methods were used to identify the type of bauxite, its precursor rock(s), the important factors involved during bauxitization processes, the influence of mobilization and segregation processes in concentrating the elements, and the paleoweathering mechanisms.

2. Geology

The bauxite horizons at Kanisheeteh are located \sim 19 km east of Bukan (south of West-Azarbaidjan, NW of Iran; Fig. 1a). The important rock units from oldest to

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Fig. 3. Photograph and microphotographs of bauxitic and diabasic samples: (a) microgranular texture in diabase. Cross-polarized light; (b) panidiomorphicgranular texture in BRB unit. Polarized reflective light; (c) pseudo-breccia texture in RB unit. Polarized reflective light; (d) pseudo-porphyry texture in GCB unit. Cross-polarized light; (e) pressure shadow structure in YB unit. Cross-polarized light; (f) photograph showing flattened nodules; (g) ooid with hematite core in RB unit. Polarized reflective light; (h) flattened diaspore crystals in GCB unit. Cross-polarized light. Py=pyrite, Ilm=ilmenite, Plg=plagioclase, Hem=hematite, Dsp=diaspore, Amp=amphibole, Ndu=nodule.

Sample #	Bauxitic unit	Minerals identified	
Sample #	Bauxite unit	Major	Minor
Rs-2	Dark red bauxite (DRB)	Diaspore, hematite, chlorite	Rutile, muscovite
V1-2	Dark red bauxite (DRB)	Diaspore, hematite, chlorite	Magnesio-sidero-riebeckite, kaolinite
R _s -5	Red bauxite (RB)	Hematite, pyrophyllite, diaspore	Muscovite, rutile, kaolinite
V1-5	Red bauxite (RB)	Hematite, diapore, pyrophyllite	Rutile
V1-6	Brownish red bauxite (BRB)	Hematite, pyrophyllite, diaspore	Rutile, kaolinite
V1-8	Brownish red bauxite (BRB)	Hematite, diaspore, pyrophyllite	Rutile
V1-10	Greenish cream bauxite (GCB)	Pyrophyllite, chlorite, diaspore	Rutile, quartz
V1-12	Greenish cream bauxite (GCB)	Chlorite, pyrophyllite, muscovite	Quartz
R ₈ -16	Yellow bauxite (YB)	Diaspore, pyrophyllite	Nacrite, kaolinite, rutile, hematite, calcite
Rs-17	Yellow bauxite (YB)	Diaspore, pyrophyllite	Nacrite, kaolinite, rutile, feldspar, hematite

Table 1	
Constituent minerals (identified by XRD method) in various	bauxitic units at Kanisheeteh

youngest include Precambrian volcanic and metamorphic (phyllite and gneiss) rocks, Infracambrian dolomite, Cambrian shale and sandstone, Cambro-Ordovician shale and carbonates, lower Permian sandstone, middle to late Permian carbonates and shale, Triassic carbonates, Jurassic shale and sandstone, Cretaceous limestone, Miocene limestone and clastic rocks, and Quaternary sediments (Fig. 1b). There are also a series of diabasic rocks occurring as sills and irregular patches within lower Permian sandstone and the upper part of late Permian carbonates. The bauxites occur as a semi-continuous layer along the boundary of

late Permian units (carbonates and shales) with Triassic carbonates and of Triassic carbonates with Jurassic units (shale and sandstone). The bauxite horizon of Permo-Triassic age at Kanisheeteh is stratiform trending NE– SW over a length of 8 km (Fig. 1b) and dips 35–90°NW. The bauxites in this horizon vary in thickness from 8 to 28 m (average 10 m) and have various colors such as greenish cream, red, brownish red and dark red. The bauxites along with enclosing rocks suffered severe tectonic stresses and have been intensely folded and deformed. The contact between the horizon and the underlying late Permian carbonate bedrock is sharp. The



Fig. 4. Ternary plot for the system of Fe, (Al+Ti), and clay minerals (after Bardossy, 1982) showing the position of Kanisheeteh data points.

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Table 2 Major, minor, and trace element compositions of 33 bauxite samples from Kanisheeteh analyzed by XRF

	D 1	D 0	D 0	D (D (D 7	D 0	D 0	D 10
	Rs-1	Rs-2	Rs-3	Rs-4	Rs-5	Rs-6	Rs-7	Rs-8	Rs-9	Rs-10
SiO ₂ %	28.21	40.34	25.42	23.57	39.20	31.34	35.27	37.44	38.39	43.61
Al_2O_3	21.80	29.22	33.36	32.26	20.84	22.18	27.02	21.87	20.24	24.59
Fe ₂ O ₃	34.20	17.18	26.96	29.56	28.07	33.97	22.40	29.45	29.71	20.56
CaO	0.14	0.11	0.11	0.10	0.35	0.26	0.36	0.16	0.26	0.26
Na ₂ O	0.01	0.16	0.01	0.01	0.40	0.23	0.90	0.26	0.25	0.08
MgO	0.67	0.16	0.43	0.57	0.08	0.28	0.33	0.06	0.09	0.01
K ₂ O	0.02	0.81	0.47	0.45	0.89	0.56	1.34	0.48	0.53	0.16
TiO ₂	4.80	3.76	3.76	3.90	3.33	3.09	4.12	3.527	3.63	4.17
MnO	0.02	0.01	0.01	0.01	0.01	0.02	b.d	0.01	0.01	b.d
P_2O_5	0.06	0.04	0.04	0.04	0.16	0.12	0.33	0.18	0.22	0.03
L.O.I	9.67	7.82	9.09	9.04	6.37	7.38	7.40	6.03	6.07	6.02
Sum	99.6	99.61	99.66	99.51	99.7	99.43	99.47	99.46	99.40	99.49
U ppm	21	17	20	9	6	6	1	1	1	1
Th	21	24	23	30	15	7	2	6	3	2
Ba	683	79	259	316	564	548	5	526	681	19
Ce	540	315	246	181	547	517	295	354	701	699
La	245	156	125	168	255	259	145	203	405	295
Ga	14	14	10	14	18	15	13	15	19	12
Hf	20	21	19	20	19	13	20	28	15	19
Co	54	50	81	79	34	66	1	49	51	23
Cr	982	476	514	612	309	556	685	456	481	357
Cu	1	3	5	1	34	1	32	12	11	3
Nb	75	65	65	65	47	45	51	44	50	48
Pb	27	4	9	10	16	29	15	22	27	11
Rb	1	15	14	11	20	16	1	12	13	88
Mo	1	1	1	1	1	1	1	1	1	1
V	1108	680	865	980	642	743	1125	859	886	564
W	1	14	12	1	1	1	1	1	1	1
Y	13	18	18	20	18	20	18	1	15	17
Zr	465	446	428	430	418	323	850	325	349	334
Zn	110	48	53	52	57	82	42	26	22	19
Ni	53	183	238	264	296	304	101	153	157	57
Sr	85	86	86	1299	236	1050	1060	1208	533	37

B.d. = Below detection limit.

bauxite horizon has been offset (<50 m) by small-scale strike–slip faults. Based upon color and textural features five distinct bauxitic facies are distinguished, (1) dark red bauxite (DRB), (2) red bauxite (RB), (3) brownish red bauxite (BRB), (4) greenish cream bauxite (GCB) and (5) yellow bauxite (YB) (Fig. 2). The three lower units (i.e. DRB, RB and BRB) contain ferruginous nodules while the upper two units (i.e. GCB and YB) display massive structures.

3. Methods of investigation

Field work was carried out in Spring 2005. About 100 representative samples from various bauxite units, bedrocks, and diabasic sills were systematically collected along two traverses separated by 2.5 km from each other across the Permo-Triassic bauxite horizon (Fig. 1b). The mineralogy of the ores was thoroughly studied by

petrographical examinations of thin-polished sections (20 samples) and by X-ray Diffraction (XRD) method (10 samples). The latter analysis was carried out at Geological Survey of Iran (GSI) using a SIMENS Model D-5000 diffractometer with Cu k α radiation, fixed graphite monochromators, voltage 40 kV, current 40 mA, scanning speed 2° per minute, scan range 2–70°, drive axis 2 θ .

Bulk chemical analysis on 34 pulverized samples was carried out by X-ray Fluorescence (XRF) method using a Philips Model 1480 spectrometer at the Geological Survey of Iran. Major and trace elements were analyzed using sample powders fused with a Li-tetraborate flux. Detection limit is 0.01 wt.% for major elements (as oxides), and 2 ppm for trace elements (except for Y, Mo, Rb, Cu, Co, V and W that is 1 ppm). Accuracy is $\pm 0.5\%$ of the amount of each major element present, and $\pm 2\%$ of each trace element. Analysis error for major and trace elements is $\pm 2\%$ and $\pm 10\%$, respectively. Loss on

Rs-11	Rs-12	Rs-13	Rs-14	Rs-15	Rs-16	Rs-17	Rs-18	V1-1	V1-2	V1-3
55.63	54.45	52.35	46.63	56.60	45.95	50.30	57.79	24.65	22.88	37.38
28.43	26.35	27.22	29.32	27.58	29.58	30.74	26.83	22.55	24.30	21.30
5.02	7.30	6.65	10.14	3.99	8.50	4.80	3.21	38.44	40.01	28.06
0.09	0.13	0.09	0.16	0.06	0.22	0.14	0.07	0.11	0.16	0.29
0.01	0.01	0.01	0.02	0.01	0.02	0.03	0.01	0.01	0.01	0.38
0.12	0.26	0.12	0.42	0.08	0.10	0.03	0.01	0.97	0.87	0.17
0.08	0.15	0.12	1.00	0.07	0.20	0.27	0.16	0.16	0.16	0.78
2.95	2.44	2.58	3.08	3.29	4.44	4.21	3.03	3.42	3.00	2.94
b.d	b.d	b.d	0.01	b.d	0.01	b.d	b.d	0.03	0.03	0.01
0.33	0.03	0.04	0.03	0.02	0.05	0.05	0.03	0.04	0.03	0.10
7.19	8.50	10.36	8.69	7.68	10.62	8.96	8.40	9.02	8.27	8.14
99.85	99.62	99.54	99.5	99.38	99.69	99.53	99.54	99.40	99.72	99.55
4	8	13	10	17	22	19	17	15	1	1
5	13	3	4	10	15	16	10	20	24	6
54	69	10	153	95	71	82	54	394	228	537
54	99	95	42	12	112	94	28	357	265	381
32	45	20	15	10	35	41	19	159	158	225
14	17	10	15	18	13	16	10	16	17	16
24	26	23	18	15	16	28	21	19	25	17
12	21	21	86	12	25	8	6	111	122	39
403	327	421	403	380	368	339	376	731	741	313
72	54	32	28	94	27	3	22	1	2	8
38	35	33	42	45	60	67	45	63	46	47
12	2	6	16	7	58	90	12	2	6	20
10	10	26	8	12	12	9	15	7	9	22
1	1	1	1	1	1	1	1	1	1	1
242	306	255	276	219	399	312	404	1080	1117	479
10	2	9	1	1	6	1	1	1	1	1
17	15	13	14	16	16	14	15	15	15	18
328	296	280	288	360	466	468	353	365	304	328
32	35	31	54	24	107	54	15	58	54	39
104	160	114	271	69	215	146	182	203	222	312
69	46	84	33	151	168	85	187	102	73	540

(continued on next page)

ignition (LOI) was measured by weighing the samples before and after 1 h of heating at 1000 °C.

4. Petrography

Under microscope, the diabasic rocks show typically microgranular texture (Fig. 3a), containing feldspars (55–60%), ferromagnesians (~30%), opaques (~10%) and accessory minerals (apatite and zircon). The rocks have suffered slight saussuritization alteration. Feldspars are principally plagioclase (50–55%) with lesser amounts (~5%) of K-feldspars. Plagioclase was partially altered to fine-grained aggregates of sericite and calcite. Ferromagnesians are chiefly augite (18–20%) and olivine (10–12%) which were partially altered to chlorite and epidote. The opaques are mainly pyrite (5–7%) and ilmenite (3–5%).

The very fine-grained constituent minerals in the bauxite rocks can hardly be identified under microscope.

Therefore, petrographic examinations were mainly focused on textural features. The rocks within the various units of the bauxite horizon mainly display panidiomorphic-granular (Fig. 3b), pseudo-breccia (Fig. 3c), nodular, pseudo-porphyritic (Fig. 3d), and ooidic textures along with pressure shadow structure (Fig. 3e). The presence of these textures points towards an authigenic development during the bauxitization processes followed by later tectonic deformation.

Pressure shadow structures mainly developed in GCB and YB units, while nodular, panidiomorphic-granular, ooidic and pseudo-breccia textures are most frequently observed in BRB, RB and DRB units. Hematite in three lower units (BRB, RB, and DRB) occurs in the form of nodules, granules, and veinlets. Nodules are more or less spherical and/or elliptical with varying diameters (3– 10 mm) decreasing in size upwardly. Occasionally, in some samples the nodules are flattened that may be as a

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Table 2 (continued)

	V1-4	V1-5	V1-6	V1-7	V1-8	V1-9	V1-10	V1-11	V1-12	V1-13	V1-14	V1-15
SiO ₂ %	37.83	41.65	40.62	36.35	42.55	57.72	46.69	49.68	51.47	56.15	57.13	58.79
Al_2O_3	20.81	24.04	24.99	22.00	24.99	27.24	26.20	24.47	27.04	27.35	25.90	27.21
Fe ₂ O ₃	28.69	21.35	21.81	28.38	21.66	3.40	14.25	13.33	9.43	4.96	5.89	2.52
CaO	0.35	0.32	0.12	0.14	0.35	0.06	0.16	0.17	0.13	0.23	0.34	0.09
Na ₂ O	0.40	0.64	0.34	0.22	0.06	0.01	0.01	0.04	0.01	0.01	0.01	0.01
MgO	0.09	0.01	0.02	0.06	0.01	0.08	0.46	0.50	0.30	0.01	0.01	0.01
K ₂ O	0.81	1.09	0.53	0.40	0.15	0.05	0.31	0.33	0.69	0.08	0.03	0.04
TiO ₂	3.97	3.58	4.07	3.51	3.76	3.15	2.32	2.32	2.56	2.56	2.75	2.66
MnO	0.01	0.01	0.01	0.01	b.d	0.01	b.d	b.d	b.d	b.d	0.01	b.d
P_2O_5	0.15	0.14	0.17	0.19	0.28	0.02	0.04	0.02	0.03	0.03	0.02	0.02
L.O.I	6.31	6.62	6.85	8.45	5.91	7.70	9.26	8.78	8.09	8.11	7.36	8.04
Sum	99.42	99.45	99.53	99.71	99.72	99.44	99.70	99.64	99.75	99.49	99.45	99.39
U ppm	1	1	2	1	1	14	20	12	3	9	14	7
Th	4	6	8	3	10	9	7	3	3	3	4	6
Ва	532	163	130	612	99	114	122	144	150	125	115	44
Ce	331	502	376	457	763	357	19	81	69	11	15	12
La	216	258	254	215	358	12	45	32	10	12	7	16
Ga	10	15	15	18	14	13	14	14	18	12	15	14
Hf	14	19	26	24	20	18	22	29	13	18	14	16
Со	43	36	34	43	30	7	49	42	60	6	12	4
Cr	370	302	341	340	426	370	363	312	398	445	336	307
Cu	33	28	28	16	7	110	91	32	44	60	36	16
Nb	71	58	46	42	48	46	24	25	34	33	33	41
Pb	21	5	22	22	19	7	17	5	2	8	1	7
Rb	22	24	16	13	7	6	12	14	19	6	8	8
Мо	1	1	1	1	1	1	1	1	1	1	1	1
V	742	565	826	861	548	209	518	401	247	284	231	200
W	3	34	12	1	18	1	1	1	1	6	11	9
Y	19	20	15	17	16	15	14	13	14	13	13	13
Zr	457	370	309	329	332	350	236	269	259	290	271	314
Zn	52	53	25	16	13	26	54	50	56	28	28	19
Ni	288	254	136	123	69	59	225	294	231	105	80	88
Sr	1235	1383	1062	1112	549	32	88	74	68	59	35	34

result of deviatoric stress (Fig. 3f). Veinlets of micaceous hematite particularly in lower units are common that suggest redistribution of Fe in the weathered profile. The cores of the ooids mainly consist of hematite (Fig. 3g). Elliptical zircon is also present in the GCB unit. Diaspore occurs as flattened crystals accompanied by clays mainly in GCB unit (Fig. 3h). Relict minerals are principally altered amphibole and plagioclase. Among the relict minerals only amphibole constitutes the pressure shadow structures (Fig. 3e).

5. Mineralogy

Mineralogical and chemical aspects of bauxite deposits are decisively controlled by environment of formation (Tardy et al., 1990, 1991; D'Argenio and Mindszenty, 1995; Tardy and Roquin, 1998). Generally, chemical variations in lateralization processes are manifested by variations in constituent bauxite minerals. Fine crystalline nature and its intense weathering unfortunately did not allow to quantify the modal composition of the rocks under investigation. Therefore, the mineral assemblages were principally identified by XRD. Identified minerals include diaspore, hematite, kaolinite, nacrite, chlorite, pyrophyllite, quartz, muscovite, rutile, calcite, and amphibole (magnesio-sidero-riebeckite) (Table 1). Normative values of constituent minerals were calculated using both XRD and XRF data. The types and semiquantified values of constituent minerals of bauxite samples were determined by XRD. Since the amorphous and very low abundance mineral phases cannot be identified by XRD, the obtained semi-quantified values do not represent the real values of constituent minerals. This problem was resolved by applying the method presented by Bardossy and Aleva (1990). In these calculations it was assumed that muscovite is formed by K, Al, and Si; rutile by Ti; chlorite by Fe, Al, Si; kaolinite, pyrophyllite and nacrite by Al and Si; magnesio-sidero-

riebeckite by Na, Mg, Fe and Si; calcite by Ca; and plagioclase by Ca, Al and Si. The excess Fe was converted into hematite, and excess Al and Si into diaspore and quartz, respectively. In light of mineralogical composition, the bauxite samples at Kanisheeteh can be grouped into three mineralogical types, (1) bauxitic clayey iron ore, (2) clayey bauxite, and (3) bauxitic clay (Fig. 4).

6. Geochemistry

6.1. Geochemistry of weathered bauxite profile

The bauxite samples were analyzed for the major, minor and trace elements (Table 2). Al_2O_3 (20.81– 33.36%), Fe₂O₃ (2.52–40.01%), SiO₂ (22.88–58.79%) and TiO₂ (2.32–4.80%) demonstrate a wide range in values, while alkalis and alkali earth elements display low values and define a narrow range (0.15–2.93%). Among the major elements, Fe₂O₃ and SiO₂ show the largest concentration variations. Based on the geochemical dataset (see Table 2) and on the behavior of elements during weathering, the different elements can be grouped in seven categories:

- Si shows a continuous enrichment upward within the bauxite profiles.
- (2) Al displays moderate concentration variations, and is concentrated mainly in the middle and upper parts of the weathered profiles.
- (3) Elements such as K, Mg, Na, Ca, Mn, P, Zn, Zr, Y, Rb, Pb, Nb, Hf, Ga and Ti show the least concentration variations across the weathered profiles.
- (4) U displays the lowest concentration in the middle parts of the weathered profiles.
- (5) Th possesses the highest concentration in the lower parts of the weathered profiles.
- (6) Elements such as Ba, Ce, La, Cr, V and Fe show gradual increase upwardly.
- (7) Sr and Cu display higher values in the middle of the weathered profiles.

6.2. Determination of the possible parent rock type

Bivariate plots of Cr and Ni concentration values were employed for determining the precursor rock(s) of the bauxite at Kanisheeteh (Fig. 5). The majority of data points plot within the area of basalt and ultrabasic rocks. The comparison of concentration values of Cr, Zr and Ga in various bauxitic units in our study area with those of Mediterranean karst bauxites and Arkansas lateritic bauxite (Fig. 6; Table 3) indicates that the parent rock(s) for the bauxites at Kanisheeteh lie within the area of basic rocks. Another method for determining the parent rock(s) is by employing the accumulation coefficients (R) of trace elements such as Zr, V, Cr, Ni, Cu, Pb, Zn and Ga. The accumulation coefficients were calculated by applying Shaw's formula (Shaw, 1964):

- $R \qquad \sum_{i=1}^{n} K_i / K_I$
- *R* Accumulation coefficient
- *n* Number of trace elements
- *K* Mean concentration value of given trace elements in sample
- K_I Average concentration value of a given trace element in the lithosphere

The calculated *R* value by itself cannot determine the lithologic characteristics of the parent rock(s) of karst bauxites. Thus, they were normalized relative to Cr which is regarded more or less as a stable element (Özlü, 1983). The Kanisheeteh data point (#15) plots in the area of mafic parent rocks (II) (Fig. 7). Comparing the mean values of *R* at Kanisheeteh with those of other bauxite deposits throughout the world (Table 3) indicates that the bauxite analyzed in this study is genetically analogous to the Mediterranean bauxite deposits in SE of France.

Elements such as Ti, Hf, Zr, Th, Nb and Cr are considered to be immobile during weathering and hydrothermal alteration processes (MacLean and Kranidiotis, 1987; MacLean and Barrett, 1993; Panahi et al., 2000; Kurtz et al., 2000). The ratios of immobile elements (e.g. Ti/Zr) in bauxite are therefore similar to those of parent rock (Valeton et al., 1987), and can be used for determination of



Fig. 5. Plot of Ni versus Cr concentration values for various types of bauxites in relation to various precursor rocks (indicated by*) (after Schroll and Sauer, 1968). The Kanisheeteh data plot mainly in the karst bauxite domain between basalt and ultrabasic precursors.

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Fig. 6. Ternary plot for the concentration of Ga, Zr and Cr in samples of Mediterranean karst bauxites and Arkansas lateritic bauxite deposits (after Özlü, 1983). A, B, C and D (the asterisked) stand for the concentration values of Zr, Cr and Ga in ultrabasic, basic, intermediate, and acidic igneous rocks, respectively. The numbers I, II, III and IV represent the area of influence of ultramafic, mafic, intermediate (or argillaceous), and acidic precursor rocks, respectively. Numbers 1–14 (filled circles) belong to data from various bauxite deposits from different parts of the world (see Table 3). The Kanisheeth data (#15) plots close to the position of point C within the domain of basic precursor rocks.

various source rocks. These ratios when plotted in cross plots create linear arrays with high correlation that pass through the data point belonging to parent rock(s) (MacLean, 1990). The positive correlation between V, Zr, Nb and Ti (0.6 to 0.85) may indicate the effect of substitution of V and Zr for Ti in anatase during weathering (Angelica and Da Costa, 1993; Costa and Araujo, 1996). Anatase is commonly converted into rutile during diagenesis. The ratios of Ti/Zr, Ti/V and Ti/Nb in diabase at Kanisheeteh are approximately similar to those of bauxite samples and their data points lie almost on or close to the weathering line delineated by interpolation of bauxite data points (Fig. 8). This points to an intimate correlation between the diabasic sills and the bauxite horizon at Kanisheeteh. The previous works by authors (unpublished) on Permo-Triassic bauxite deposits in northwest of Iran (i.e. west of Miandoab ~60 km NW of Kanisheeteh; east of Shahindejh ~40 km east of Kanisheeteh; and northeast of Shahindejh ~ 80 km of NE of Kanisheeteh) also indicated that the diabasic sills present within the base of Permian sandstones and the upper parts of Permian limestones are the most likely potential parent rocks for the bauxite deposits in these areas.

6.3. Mass change calculation

The mass change calculations have been carried out for the bauxites and the diabasic sills (as the accepted precursor) in order to constrain the geochemical processes involved in the development of bauxitic units at Kanisheeteh. The mass changes were calculated by applying equations presented by MacLean (1990) which is based on three parameters, namely:

(1) Monitor immobile element: Ti is regarded as immobile element under common weathering condi-

tion (Chesworth et al., 1981; Colman, 1982; Middleburg et al., 1988). Based on its abundance, and its uniform behavior during weathering processes (Driese et al., 2000; Hill et al., 2000; Ashley

Table 3

Overview table of mean values of Zr, Ga, Cr and R (accumulation coefficient) values of the Kanisheeteh bauxite with those of Mediterranean karst bauxite and Arkansas lateritic bauxite deposits

Location	R	Zr	Ga	Cr	References
		ppm	ppm	ppm	
Ariege (France)	2.32	367	63	530	Caillere et al.
					(1976)
SE France	2.50	389	61	485	Caillere et al.
					(1976)
Herzegovine	10.00	380	40	740	Maksimovic
					(1968)
Obrovac (Yugoslavia)	2.55	140	20	900	Maric (1969)
Bosnie	1.73	714	46	280	Catovic et al.
					(1976)
Kosova	4.54	285	20	3500	Paplovic and
					Nikolic (1973)
Parnasse I (Jurassic)	2.27	314	40	323	Maksimovic and
(Greece)					Papastamatiou
					(1973)
Parnasse II	3.58	276	32	991	Maksimovic and
(Cretaceous)					Papastamatiou
(Greece)					(1973)
Mandra II	5.72	590	30	2000	Papastamatiou
(Greece)					and Maksimovic
					(1970)
Tran (Bulgaria)	-	200	15	75	Karanov (1965)
Padura Graiului	3.63	820	43	430	Papiou et al.
(Romania)					(1967)
Gant, Halimbia	3.00	400	40	250	Dudich and S
(Hungary)					iklosi (1970)
Arkansas (USA)	1.91	1300	86	110	Gordon and
					Murata (1952)
Aksoki-seydisehir	2.44	520	68	365	Özlü (1978)
(Mortas and Dog¢					
ankuzu) (Turkey)					
Kanisheeteh (Iran)	2.07	364	15	449	

and Driese, 2000), this element was chosen as monitor element in the calculations.

- (2) Enrichment factor (E.F.): After normalizing of the analytical data for LOI and calculation of standard deviation of elements in the bauxitic units (Table 4), the enrichment factor was calculated on the basis of Ti values in samples of bauxites and diabasic rocks using the equation: E.F.= Ti_{(diabase})/Ti_(bauxite).
- (3) Reconstructed composition (R.C.): This parameter reflects the actual mass of the weathered rock that commonly becomes enriched or depleted in a mobile constituent element, and was calculated using the equation: R.C.=E.F. × (abundance of an element).

By taking the above parameters into account, the mass changes were finally calculated as follows: Mass change (M.C.)=R.C.-precursor.

The mass change calculations of elements in the bauxitic units (Figs. 9 and 11) demonstrated that the geochemical behavior of elements during bauxitization processes can be grouped into three distinct categories.

- (a) Enriched elements: Cr, Nb, Th, U, Hf, Ni, Ce and Zr gained mass in all bauxitic units.
- (b) Depleted elements: Y, Rb, Ba, Na, K, Ca, Mn, Mg, Fe, P and Si underwent mass loss in all bauxitic units.
- (c) Leached-fixed elements: elements such as V, Co, Al and La underwent leaching-fixation processes within the bauxitic units.

7. Discussion

7.1. Depleted elements

Depleted major elements: Silicon in all bauxitic units shows substantial mass loss (Fig. 9a) which may be the result of kaolinization of feldspars and subsequent breakdown of kaolinite. However, large quantities of Si were fixed by clay minerals, muscovite, and amphibole and remained within the bauxite system. Fe is present in the form of hematite in the bauxite system and may have been originated from pyrite oxidation and/or weathering of ilmenite and ferromagnesian minerals. Mineralogical studies indicate that any increase in Al2O3 and clay minerals (e.g. chlorite, pyrophyllite, kaolinite and nacrite) correlates to a decrease in hematite (Fig. 10). This may be due to the dissolution of Fe under reducing conditions, and to the simultaneous precipitation of clay minerals from silicic acid solution (Bardossy, 1982). By accepting this premise, it can be inferred that a relatively lower pH condition prevailed during bauxitization processes in the upper units (GCB and YB) at Kanisheeteh (see Fig. 9b).

Depleted minor elements: Based on the constituent minerals present in the diabasic sills (which are considered to form the parent rocks), it can be inferred that Na, K and Ca entered into solution as a result of plagioclase breakdown. They show considerable mass loss in the water–rock reaction system during weathering (Fig. 9c, d, e). In other words, the uniform decrease in ratios of Na₂O/TiO₂, K₂O/TiO₂, and CaO/TiO₂,



Fig. 7. Log Cr versus accumulation coefficient values (R: for calculation see text) with indication of the area of influence of various precursor rocks (e.g. amphibolite, basalt and granite) (after Özlü, 1983). A, B and C correspond to laterites from amphibolite, basalt and granite precursors, respectively. Numbers 1–14 (filled circles) correspond to data points for various Mediterranean karst bauxites and Arkansas lateritic bauxite deposits from different parts of the world (see Table 3). The numbers I, II, III and IV represent the area of influence of ultramafic, mafic, intermediate (or argillaceous), and acidic precursor rocks, respectively. The Kanisheeth data plots adjacent to B (basalt) within the domain of basic precursor rocks.

across the bauxite profile indicates their high mobility during weathering processes. Potassium relative to sodium underwent less mass loss. This may be due to its fixation as muscovite and larger ionic radius. Cation exchange capacity theory (e.g. Wilson, 1994) implies that larger cations (e.g. K) are preferentially retained on clay minerals. Mn and Mg are probably released from breakdown of ferromagnesian minerals (e.g. olivine and augite) (Fig. 9f and g). The relatively low amounts of Mg and Na left in bauxite samples are likely due to their substitution in chlorite and magnesio-sidero-riebeckite, respectively. The consistent mass loss of phosphorus (Fig. 9h) in the bauxite system may be due to weathering of apatite in parent rock. Rb and Ba display a similar behavior as the alkali and alkali earth and were leached out of the system during the bauxitization processes (Fig. 11a and b). It seems that the lack of minerals such as montmorilonite and vermiculite in the bauxite profile that could act as fixing agents for these elements explains their depletion.

Y that normally acts as an immobile element during weathering processes (MacLean et al., 1997) behaves as a mobile element at Kanisheeteh (Fig. 11c). Y is commonly enriched in boehmite or diaspore (because of their high sorption capacity), but is depleted where gibbsite is dominant (Mordberg, 1993). Therefore, it can be deduced that the mobility of Y in the bauxitic units at Kanisheeteh was primarily controlled by the precipitation of gibbsite (rather than diaspore) from aluminosiderogels. Investigations done by authors (unpublished) showed that the values of Σ LREE (La, Ce, Nd, Sm, Eu) and Σ HREE (Tb, Ho, Tm, Yb, Lu) in bauxite samples at Kanisheeteh vary from ~ 121 to ~ 874 ppm and from ~ 5 to ~ 9 ppm, respectively. The mass balance calculations demonstrated that Σ LREE increases (particularly in the lower units of the horizon) relative to the parent rock (diabase) whereas Σ HREE shows a minor mass decrease. It seems that the Y mobility in the bauxite system at Kanisheeteh is somehow related to the mobility of HREE.

7.2. Enriched elements

Ni shows mass increase mainly in the bauxite profile (Fig. 11d). This may be due to the presence of carbonate bedrock that acted as a geochemical barrier (Maksimovic, 1976). The slight mass increase of Ce in the upper units (i.e. GCB and YB, see Fig. 11e) is due likely to its preferential sorption by metallic oxides (i.e. hematite) (Koppenkastrop and De Carlo, 1993) and clay minerals (Coppin et al., 2002; Bradbury and Baeyens, 2002). The buffering of percolating waters by carbonate bedrocks also brings about deposition of Ce (Braun et al., 1990). This may further account for the substantial enrichment of Ce in the lower units (i.e. DRB, RB and BRB) (Fig. 11e). Zr and Hf show an enrichment relative to Ti, and are chiefly related to zircon (Fig. 11f and g). The mass change patterns of U and Th (Fig. 11h and i) are almost similar to one another. However, the U gained relatively more mass than Th in the upper units (i.e.



Fig. 8. Diagrams featuring the positive correlation between (a) $Zr-TiO_2$, (b) Nb $-TiO_2$ and (c) $V-TiO_2$ for bauxite and diabase samples. The diabase data point lies on and close to the so called weathering line (WL).

Table 4						
Number of analyses (n), standard deviation	(S.D.) and the maximum	(Max), minimum	(Min), and mean	values of elements	of bauxitic units in	Kanisheeteh

	Da	rk red ba	uxite			Re	d bauxite				Brownish red bauxite					Greenish cream bauxite					Yellow bauxite				
	п	Mean	S.D.	Minimum	Maximum	1 <i>n</i>	Mean	S.D.	Minimum	Maximum	п	Mean	S.D.	Minimum	Maximum	n	Mean	S.D.	Minimum	Maximum	n	Mean	S.D.	Minimum	Maximun
iO ₂ %	6	29.81	7.27	22.88	40.34	6	35.70	6.96	23.57	41.65	5	38.00	2.80	35.27	42.55	10	51.48	4.76	43.61	57.72	6	54.35	5.09	45.95	58.79
l_2O_3	6	25.42	4.83	21.30	33.36	6	24.19	4.30	20.81	32.26	5	23.22	2.73	20.24	27.02	10	26.85	1.52	24.47	29.32	6	27.94	1.83	25.90	30.74
e_2O_3	6	30.81	8.51	17.18	40.01	6	27.24	4.85	21.35	33.97	5	26.32	3.96	21.66	29.71	10	9.41	6.07	3.40	20.56	6	4.98	2.12	2.52	8.50
aO	6	0.15	0.07	0.11	0.29	6	0.25	0.11	0.10	0.35	5	0.25	0.10	0.14	0.36	10	0.13	0.06	0.06	0.26	6	0.18	0.10	0.07	0.34
a ₂ O	6	0.10	0.15	0.01	0.38	6	0.34	0.21	0.01	0.64	5	0.34	0.32	0.06	0.90	10	0.02	0.02	0.01	0.08	6	0.02	0.01	0.01	0.03
1gO	6	0.55	0.34	0.16	0.97	6	0.18	0.22	0.01	0.57	5	0.11	0.13	0.01	0.33	10	0.24	0.18	0.01	0.50	6	0.03	0.04	0.01	0.10
20	6	0.40	0.34	0.02	0.81	6	0.72	0.25	0.45	1.09	5	0.58	0.45	0.15	1.34	10	0.30	0.31	0.05	1.00	6	0.13	0.10	0.03	0.27
iO ₂	6	3.61	0.68	2.94	4.80	6	3.66	0.39	3.09	4.07	5	3.71	0.25	3.51	4.12	10	2.89	0.57	2.32	4.17	6	3.28	0.83	2.56	4.44
1nO	6	0.02	0.01	0.01	0.03	6	0.01	0.00	0.01	0.02	5	0.01	0.01	0.00	0.01	10	0.01	0.01	0.00	0.01	6	0.00	0.01	0.00	0.01
₂ O ₅	6	0.05	0.02	0.03	0.10	6	0.13	0.05	0.04	0.17	5	0.24	0.06	0.18	0.33	10	0.06	0.10	0.02	0.33	6	0.03	0.01	0.02	0.05
.0.I	6	8.67	0.70	7.82	9.67	6	7.10	1.03	6.31	9.04	5	6.77	1.12	5.91	8.45	10	8.23	1.19	6.02	10.36	6	8.58	1.13	7.36	10.62
otal	6	99.59	0.11	99.40	99.72	6	99.52	0.10	99.42	99.70	5	99.55	0.15	99.40	99.72	10	99.62	0.15	99.38	99.85	6	99.52	0.14	99.39	99.69
ppm	6	13	9.16	1	21	6	4	3.31	1	9	5	1	0.00	1	1	10	10	6.21	1	20	6	15	5.82	7	22
h	6	20	6.88	6	24	6	12	9.73	4	30	5	5	3.27	2	10	10	6	3.70	2	13	6	9	5.59	3	16
a	6	363	220.60	79	683	6	376	199.37	130	564	5	385	310.33	5	681	10	93	52.91	10	150	6	82	32.52	44	125
e	6	351	106.18	246	540	6	409	140.37	181	547	5	514	208.43	295	763	10	153	215.56	12	699	6	45	45.44	11	112
a	6	178	46.37	125	245	6	235	36.65	168	259	5	265	110.67	145	405	10	52	86.58	10	295	6	22	13.41	7	35
ia	6	15	2.51	10	17	6	15	2.59	10	18	5	16	2.59	13	19	10	15	2.59	10	18	6	13	2.16	10	16
ſ	6	20	2.71	17	25	6	19	4.68	13	26	5	21	4.88	15	28	10	21	4.99	13	29	6	19	5.08	14	28
0	6	76	34.33	39	122	6	49	19.20	34	79	5	35	20.60	1	51	10	33	25.43	7	86	6	10	7.76	4	25
r	6	626	238.32	313	982	6	415	134.31	302	612	5	478	127.56	340	685	10	373	34.93	312	421	6	362	47.65	307	445
u	6	3	2.73	1	8	6	21	15.56	1	34	5	16	9.71	7	32	10	56	34.54	3	110	6	27	19.45	3	60
lb	6	60	11.39	46	75	6	55	11.04	45	71	5	47	3.87	42	51	10	37	8.39	24	48	6	46	14.14	33	67
b	6	11	9.95	2	27	6	17	8.70	5	22	5	21	4.42	15	27	10	9	5.32	2	17	6	29	36.22	I	90
.b	6	1	7.28	1	22	6	18	4.75	11	24	5	9	5.22	1	15	10	21	24.41	0	88	6	10	5.27	6	15
10	6	12	0.00	1	1	6	1	0.00	1	1	5	1	0.00	1	1125	10	1	0.00	1	1	6	1	0.00	1	1
7	6	888	264.11	4/9	111/	6	450	144.69	565	980	5	856	205.04	548	1125	10	524	127.13	209	564	6	305	84.41	200	404
	6	5	6.23	1	14	6	9	15.13	1	34	5	4	/.60	1	18	10	5	3.55	1	10	0	0	4.08	12	11
	0	10	2.136	15	18	6	19	1.97	15	20	5	13	7.02	1	18	10	15	1.48	13	1/	6	14	1.26	15	10
r	6	389	66.43	304	465	6	584	60.24	309	45/	5	43/	231.06	325	850	10	300	41.28	236	560	6	360	87.05	2/1	468
n	6	60	25.19	39	110	6	54	18.12	25	82	5	24	11.37	13	42	10	38	14.04	19	50	6	42	54.70	15	10/
i	6	202	85.27	53	312	6	257	62.27	136	304	5	121	36.83	69	157	10	158	90.59	57	294	6	136	54.51	80	215



Fig. 9. Diagrams of mass changes for major and minor elements on the basis of Ti (as immobile element) during bauxitization processes at Kanisheeteh for different lithologic units recognized.

GCB and YB). This may be the result of their differentiation during superficial weathering processes. Nb (Fig. 11j) displays an enrichment that may be the result of their substitution for Ti in Ti-bearing minerals.

Cr was enriched in the weathered profile (Fig. 11k). The comparison of its pattern with that of Fe across the bauxite profile shows that the mass increase of Cr in the DRB unit of the profile is accompanied by the least mass loss of Fe, whereas in upper parts of the profile where Cr shows relatively less abundance, Fe is highly depleted. The positive correlation (0.59) between Fe and Cr may suggest that Cr geochemically behaved in a similar way as Fe in bauxite system.

7.3. Leached-fixed elements

Aluminum remarkably gained mass in the two upper units (i.e. GCB and YB, Fig. 9i) which may be due largely to intense Fe leaching out of these units. Furthermore, its slight mass gain in the two lower units (i.e. DRB and RB) and even its slight depletion in the middle unit may be the result of slight mass loss of Fe in these units.

La was depleted in the upper units (i.e. GCB and YB) and gained mass in the lower units (i.e. DRB, RB and BRB) (Fig. 111). The mobility of La seems to be somehow related to pH. It was leached out of the upper units at relatively low pH and was fixed in the lower units where it was absorbed at higher pH condition (buffering by carbonates) by hematite and clay minerals.



Fig. 10. Bivariate plots of (a) Al_2O_3 versus hematite and (b) clay minerals versus hematite. Significance is drawn at the p=0.05 level for N=10.

Despite being leached from the YB unit, V and Co were fixed in the rest of the units (Fig. 11m and n). The V mass gain may be the result of its substitution for titanium in Ti-bearing minerals. The relatively more Co mass increase in the lower units may be due to the pH increase (buffering by carbonates) of percolating solutions (Maksimovic, 1976). Furthermore, V and Co can be scavenged by hematite (Wehrli and Stumm, 1989; Aiuppa et al., 2000). The substantial depletion of hematite in the YB unit may justifiably account for the slight V and Co mass decrease (see Fig. 11m and n).

7.4. Comparison of mass change of Al, Fe and Si

According to the geochemical diagrams (Fig. 9a, b, i), the bauxitic units that show severe mass loss of Fe are



Fig. 11. Diagrams of mass changes for trace elements (Ni, Co, Ce, La, Rb, Ba, Zr, Hf, U, Th, Nb, V, Y and Cr) on the basis of Ti (as immobile element) during bauxitization processes at Kanisheeth for different lithologic units recognized.

favored by overall enrichment of Al, whereas those samples that underwent relatively lower Fe mass loss display a higher mass decrease in Si and slight mass change in Al. This may suggest that the mobility of Fe may have played a crucial role in the formation of the bauxitic units at Kanisheeteh. Since the rate of mass loss of Fe decreases continuously from top to the bottom of the profile, it may be thought that the pH increase in percolating waters (due to buffering of the underlying carbonate bedrock) played a key role in the evolution of bauxitization at Kanisheeteh. The overall mass loss of Fe across the profile may be suggestive of a persistent wet climate during bauxitization processes (Hill et al., 2000). Mongelli (2002) believes that the formation of the concretions (nodules and ooids) in the karst bauxite deposits is a two-stage process likely resulting from climatic changes, stage (1) a relatively long period of dominantly wet tropical climate, and stage (2) timelimited drier conditions alternating with a time-limited wetter climate. The presence of nodules and ooids observed in the three lower units (i.e. DRB, RB and BRB) indicates that these climatic conditions likely prevailed during bauxitization processes at Kanisheeteh.

8. Summary and conclusion

The stratigraphical gap emerged during the upper Permian to lower Triassic is manifested by the development of a bauxite horizon at Kanisheeteh (NW-Iran).

The presence of panidiomorphic-granular, pseudoporphyry, pseudo-breccia, nodular and ooidic textures along with pressure shadow structures within the bauxitic units indicate that Al–Fe oxides were accumulated authigenically and then underwent tectonic deformation.

Diaspore, hematite, chlorite, and pyrophyllite along with lesser amounts of muscovite, kaolinite, quartz, nacrite, calcite, zircon, magnesio-sidero-riebeckite, rutile, and plagioclase are the major mineralogical constituents in the bauxite horizon. Mineralogically three bauxitic facies were recognized at Kanisheeteh, (1) bauxitic clayey iron ore, (2) clayey bauxite, and (3) bauxitic clay.

Based upon field evidence, calculations of accumulation coefficients of trace elements, the concentration rate of elements such as Cr, Ni, Zr, and Ga in bauxite samples, and the ratios of immobile elements and their distribution, it may be conceived that the bauxitic units at Kanisheeteh probably originated from diabasic sills in the area.

Mass change calculations for elements in bauxitic units indicate that bauxitization at Kanisheeteh occurred as a result of desilicification, hydration, segregation of Al from Fe, and leaching of alkali and alkali earth from the weathered horizon.

The combination of data from geochemistry of immobile elements and the mineralogy of diabasic parent rock show that the formation of bauxitic minerals at Kanisheeteh most likely resulted from oxidation of pyrite and decomposition of minerals such as olivine, augite, feldspar, ilmenite, and apatite. By taking the behavior of major, minor and trace elements into account during weathering processes, it seems that factors such as stability of host minerals, fixation in neomorphic phases, preferential sorption and increase in pH of percolating waters as a result of carbonate bedrock buffering played a crucial role in the formation of the various bauxitic units at Kanisheeteh. By considering the geochemical data an overall prolonged period of wet climate can be postulated for the development of bauxites at Kanisheeteh.

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