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PETROGRAPHY AND GEOCHEMISTRY OF EARLY PALAEOZOIC CLASTIC ROCKS FROM THE SOUTHEAST ANATOLIAN AUTOCHTHONE ROCKS IN MARDIN AREA (DERIK-KIZILTEPE), TURKEY

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Abstract: Petrography and geochemistry (major, trace and rare earth elements) of clastic rocks from the Early Paleozoic age in the Southeast Anatolian Autochthon (SEAA) units of the Arabian Plate in southeastern Turkey have been investigated to understand their provenance. The Precambrian-Early Paleozoic units in the Mardin-Derik-Kızıltepe region consist of sandstone (red and cross-bedded siliceous sandstone, green sandstone), shale, siltstone, and sandstones intercalated with limestone with red Fe-nodule and dolomite. The sedimentary units contain mainly in order of abundance as siliceous (quartz, moganite), feldspar (plagioclase, microcline), phyllosilicate (illite, chlorite, kaolinite, I-S, C-V, smectite), carbonate (calcite, dolomite) and associating with rarely goethite minerals. According to chemical compositions, siliceous amount decrease from older to younger units in the siliciclastics rocks called as litharenite, wacke and arkose. In addition, CIA, CIW, PIA and ICV index values, element contents and their ratios (Th, U, Sc Z, La, Yb, Eu, Gd and Yb) indicate that weathering and/or alteration degrees of silicates increase and sedimentary sorting developed well. On the other hand, chondrite-normalized trace (+REE) element pattern, element contents and ratios of sandstones suggest that they transported from magmatic and partly a silicic/felsic source and also deposited in mostly passive and active continental margins.

Keywords: Arabian Plate, Siliciclastic Rocks, Petrography, Provenance, Geotectonic setting

1. INTRODUCTION

Although not as common as in magmatic rocks, petrologic and geochemical examinations have been used for 30 years in order to understand sedimentary and metamorphic periods, and provenance and geotechnical environments especially in clastic rocks (i.e. Dickinson & Suczek, 1979; Dickinson et al., 1983; Taylor & McLennan, 1985; Bhatia & Crook, 1986; Roser & Korch, 1986, 1988; Winchester & Max, 1982. Shale is the most abundant types of sediments in sedimentary basins worldwide (Pettijohn, 1975) and represents the mean crustal composition of the provenance much better than other detrital sedimentary rocks (McCulloch & Wasserburg, 1978). Researchers have thus proposed that the major element geochemistry of sedimentary rocks is more useful for distinguishing the tectonic setting (Bhatia, 1983; Roser & Korsch, 1986). However, trace elements such as La, Y, Sc, Cr, Th, Zr, Hf and Nb, especially in combination with TiO_2 among other major elements, are appropriate for provenance and tectonic setting studies because of their relatively low mobility during sedimentary processes (McLennan et al., 1993, 2006).

In addition, the relative distribution of immobile elements, which differs in terms of concentration in felsic and basic rocks such as La and Th (enriched in felsic rocks) compared with Sc, Cr and Co (enriched in basic rocks), has been used to infer the relative contributions of felsic and basic sources in shales from different tectonic environments (Wronkiewicz & Condie, 1990). The same geochemical factors have alsobeen used to understand the paleo-oxygenation condition of older sediments (Calvert & Pedersen, 1993; Jones & Manning, 1994; Nath et al., 1997; Cullers, 2002; Armstrong-Altrin et al., 2003; Dobrzinski et al., 2004). This study examines Early Paleozoic units that have a sedimentary origin of Mardin-Derik-Kızıltepe in the Southeastern Anatolian Authoucton (SEAA).

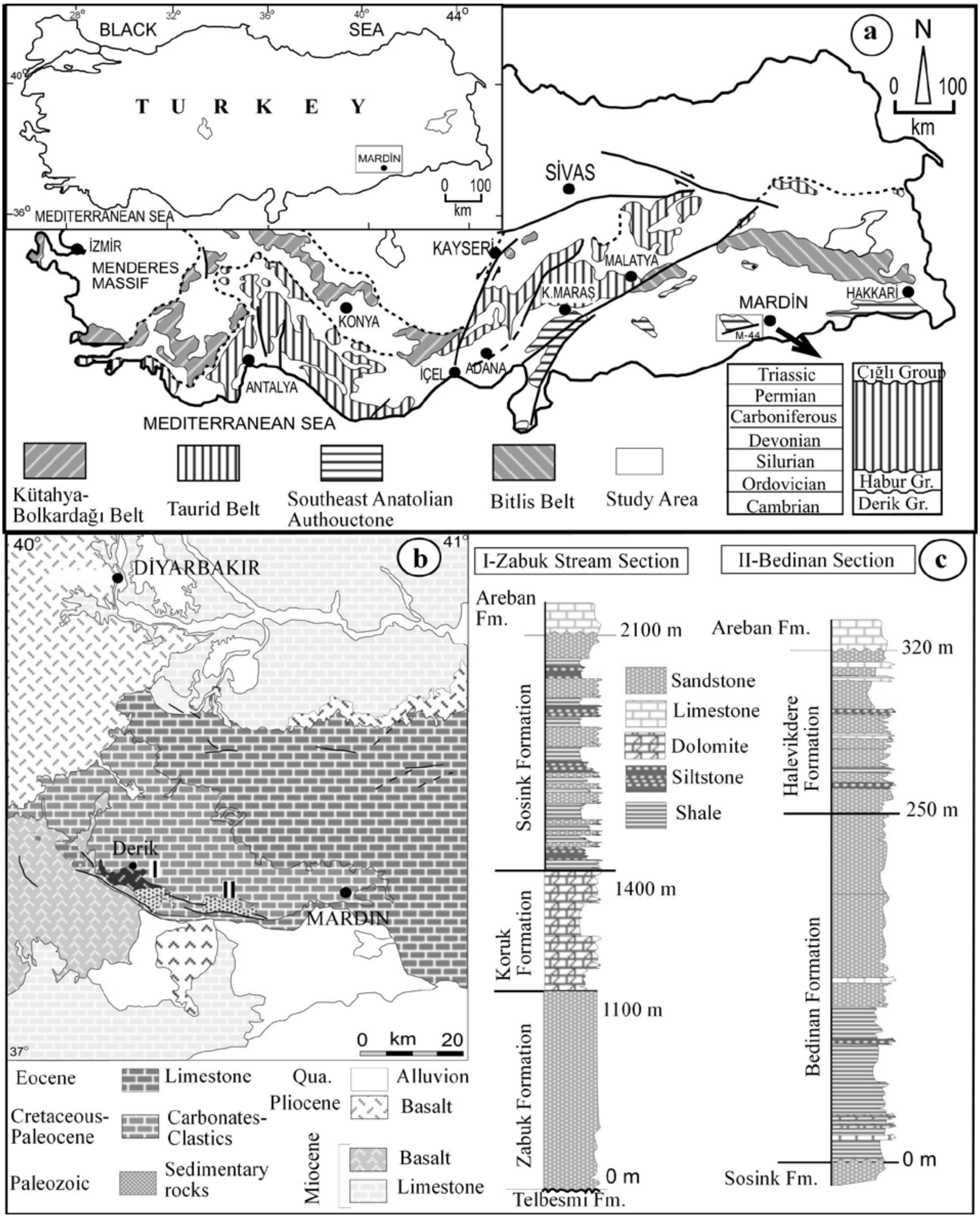

Figure 1. Geological map and section location of investigation areas from the SEAA a) Location of study area, b) Generalized geological map of the study area (modified from MTA, 2002), c) lithologic column showing the location area of the Early Paleozoic sedimentary units from the Zabuk stream and Bedinan sections.

It evaluates the mineral associations in fine–coarse-grained clastic rocks in the units, the relationships between feeding regime resources, zone resources, the rock environment and/or facies minerals and the tectonic setting and paleoweathering conditions during deposition.

2. GEOLOGICAL SETTING

Arabian plate units surfacing along the Southeastern Anatolia geographic belt are one of the tectono-stratigraphic Alpine unions that form the orogenic frame of Turkey. This particular platform mostly contains Bitlis-Pütürge Crystalline Mélange (BPCM) and SEAA rocks. SEAA units consist of a Precambrian-dated base and coverage of Early Paleozoic-Tertiary-dated sedimentary rocks (Fig. 1a). In the investigation area of Arabian plates containing SEAA rocks, the north-northeastern sections were found to contain units from the Bitlis and Southeastern Anatolia Ophiolite Belts (SAOB), whereas the north-northwestern sections were found to contain units from the Toros Belt (Fig. 1). Stated to have a similar Paleozoic stratigraphy as that of SEAA, the Bitlis Belt is claimed to be a deformed and metamorphosed part of the Arabian plate that experienced variations during Neotethyan closure (Göncüoğlu & Turhan, 1984). SAOB, which represents several tectonic periods and extends through the Southeastern Anatolia suture zone, is formed of rocks from oceanic and subduction prisms aggregated during the submerging of the southern Neotethyan branch. According to the allocation of the tectonic belt (from south to north; Arabian Platform, Ekay Zone and Nap Region) by Yılmaz (1993), SEAA is in Arabian Platform, while SAOB and BPCM are Nap Region rocks. SEAA rocks are examined around the Derik and Kızıltepe regions (Fig. 1b) and they are divided into Precambrian- and Lower Paleozoic-dated units compared with their stratigraphic distributions (from bottom to top: Derik Group (Cambrian and Precambrian) and Mardin Group (Ordovician) (Perinçek, 1978). Early Paleozoic units from SEAA are investigated in two section areas, namely the Zabuk stream and Bedinan section (Fig. 1c).

In the study area, the Zabuk Formation mainly consists of a 1 km thick succession of dominantly red siliciclastic rocks. The Zabuk Formation is in fault contact with older formations or it unconformably overlies the Koruk Formation (pink and white dolomite). The Sosink Formation, which surfaces along the Koruk stream, in general presents intercalations of 50–100 cm thick, green shale-type clay rocks and 10–20 cm thick, thin-layered, pink-red sandstones together with siltstones. There are also 20 m thick gray-black shale-type clayey rocks in the base levels of the leveled cross-section of the Bedinan Formation in the Bedinan section. Yellowish and reddish sandstones with high silica content have local siltstone and shale intercalations as well as sandy limestone levels. The Halevikdere Formation, observed in leveled cross-sections between Yurteri and Bedinan villages, and that is represented by the intercalation of yellow-white sandstone and shale in upper sections. At some levels, dolomitic rocks and brown-red tile-shaped, nodular-Fe limestone bands exist. The red and yellow colors of sandstones are correlated with their iron oxide-hydroxide contents (i.e. goethite and limonite contents) and this indicates that the unit experienced lateritic decomposition under surface environmental conditions; in other words, it was affected by equatorial-tropical climate conditions.

3. MATERIAL AND METHODS

A total of 84 rock samples were selected from measured sections in Early Paleozoic formations, representing the Mardin-Derik and Mardin-Kızıltepe areas of SEAA rocks. All samples were analyzed by methods such as optical microscopy, in order to define the textural properties, and X-ray diffractometry (XRD), in order to identify the submicroscopic minerals, at the Laboratories of Mineralogy-Petrography and Geochemistry, Department of Geological Engineering, Cumhuriyet University, Sivas. Some sandstone samples were examined by scanning electron microscopy by using a JEOL JSM-6490 instrument at the Turkish Petroleum Corporation in Ankara, Turkey.

The XRD whole-rock analyses were conducted by using a Rigaku DMAX IIIC diffractometer with the setting conditions of Cu-Kα, 35 kV, 15 mA, slits (divergence 1º, scatter=1º, receiving=0.15 mm, receiving-monochromator = 0.30 mm). The semi-quantitative percentages of whole rock and clays in fine-grained metasedimentary rocks were obtained by using the external standard method of Brindley (1980). Clay-size fractions (< 2 mm) separated by the classic sedimentation method were analyzed under various conditions such as air-dried, glycolated (in a desiccator at 60°C for 16 h) and heated (490°C for 4 h).

Geochemical investigations were used to carry out a chemical analysis of 17 sandstone samples at Canada Activation Laboratories. The major element analysis is lithium metaborate / tetraborate fusion ICP, trace and REE analysis is used in ICP-MS.

4. RESULTS

4.1. Petrography of Sandstones

The compositions in quartz sandstones belonging to the Zabuk Formation are mainly composed of quartz, feldspar (plagioclase), mica (sericite, muscovite and biotite) and minor secondary minerals (apatite, zircon and tourmaline). The rocks are observed as having a micro-orientation that is mineralogically maturated with psammitic - textured and fine-grained rocks. The groundmass material is mostly formed by the phyllosilicate matrix together with lesser amounts of calcite cement. Quartz minerals are mostly monocrystalline, whereas locally polycrystalline forms are also found (Fig. 2a, b). Biotite minerals were chloritized and bent.

The psammitic rocks (siltstone and sandstone) belonging to the Sosink Formation are mostly composed of quartz, feldspar (plagioclase), mica (muscovite, serizite, biotite), chlorite and, rarely, minor minerals (apatite, zircon and tourmaline). The micro-orientation is observed in the mica minerals (biotite and muscovite) in these rocks, which are fine-grained and mineralogically matured. Microcline minerals typically have cross-hatched twinning. The groundmass material is by a majority formed by the phyllosilicate matrix together with lesser amounts of calcite cement. Biotite minerals were transformed into chloritized and muscovite minerals that experienced bending.

The major components of the sandstones belonging to the Bedinan Formation are formed by quartz, feldspar (plagioclase), sericite, mica (minor muscovite), chlorite, carbonate (dolomite) and opaque minerals. The matrix was observed in the micro-orientation of plate-like minerals in these psammitic-textured, fine-grained and mineralogically matured rocks. The groundmass material is mostly generated by the phyllosilicate matrix. Fine-grained pelitic-textured siltstones contain quartz, feldspar (plagioclase), mica (muscovite, sericite and biotite), chlorite and opaque minerals (Fe-oxides) as the major constituents. Owing to having a high clay matrix content, these siltstones provide a more significant orientation compared with sandstones. Fe-oxide minerals with a pelletized and round form are typical of these siltstones. Additionally, plastering by Fe-oxide minerals can be locally observable. Plagioclase minerals exhibit polysynthetic twinning. Very fine-grained, mineralogically matured shales with a semi-mature texture contain quartz, feldspar (plagioclase), mica (sericite, minor muscovite), chlorite, opaque minerals and, rarely, calcite. Argillization and serizitization are common in the matrix, while orientation with obvious plastering by yellow Fe-oxides is commonly observed.

The psammitic (siltstone and sandstone) and carbonate (sandy limestone) rocks belonging to the Halevikdere Formation are mostly composed of quartz, feldspar (plagioclase), mica (biotite, sericite, muscovite) and chlorite as well as secondary (apatite, zircon) and opaque minerals (Fe-oxides). For medium–fine-grained, mineralogically matured sandstones with a semi-mature texture, the micro-orientation in the plate-like minerals within the matrix is observable. As groundmass material, there is a phyllosilicate matrix. Fe-oxide minerals as plasterings are in abundance.

4.2. Scaning Electron Microscopy

Silica minerals are surrounded by clay minerals in the sandstone sample of the Zabuk Formation (ZDG-11: quartz+moganite+calcite). Quartz and feldspar minerals are euhedral and coarse-grained (Fig. 2c). Moganite crystals that are monoclinic silica minerals are short rod-like shaped (2–4 µm) and partly radiating and they occupy interspacing in the euhedral quartz (10–15 µm). The kaolinites observed in the siltstones of the Bedinan Formation (BDG-81: kaolinite + illite + chlorite + quartz + feldspar) are formed by pseudo-hexagonal sheets parallelly piled like typical booklets. Kaolinite sheets are also typically arranged as accordion. Euhedral, prismatic feldspar minerals are also observed in the unit rocks (Fig. 2d).

4.3. X-ray Mineralogy

The chemical minerals in Zabuk Formation sandstones are observed such as quartz, moganite and calcite. A minor amount of calcite minerals was associated with the most commonly observed quartz+moganite paragenesis. Volcanogenic (feldspar), weathering/alteration (phyllosilicates) and diagenetic (quartz, moganite) minerals are observed in clastic rocks (sandstone, siltstone, shale), representing the Sosink Formation. The most common paragenesis in sandstones is quartz+ feldspar+phyllosilicate, which are accompanied with calcite, dolomite and moganite minerals.

Phyllosilicate minerals include illite, chlorite, smectite and I-S minerals. Volcanogenic (feldspar), weathering/alteration (phyllosilicates) and (quartz, moganite) minerals are found in the Bedinan Formation. For sandstones, the most commonly observed paragenesis was detected to be quartz+feldspar+phyllosilicate with contributions from calcite, dolomite and moganite minerals. Phyllosilicates are represented by illite, chlorite, smectite, kaolinite, C-V and I-S minerals. The Bedinan Formation show differences by containing chlorite and kaolinite assemblage compared with the Sosink Formation. Determination minerals in clastic (sandstone, siltstone, shale) and carbonate (nodular-Fe limestone and dolomite) rocks from the Halevikdere Formation are volcanogenic (feldspar), weathering/alteration (phyllosilicates) and chemical (quartz and goethite) minerals. The most commonly observed paragenesis in sandstones is quartz+feldspar, while phyllosilicates are involved in this paragenesis in places. The same paragenesis is also observed in fine-grained clastic rocks. In minor amounts, calcite and dolomite also accompany this paragenesis. Phyllosilicate minerals are represented by kaolinite, illite and I-S minerals. For all clastic rocks, kaolinite+illite paragenesis is widely observed. The absence of chlorite and a higher amount of kaolinite in the samples provide differences compared with the Bedinan Formation.

4.4. Geochemistry

In the following subsection, the geochemical data obtained from sandstones, which represent different units of SEAA rocks, are compared with the average combinations of varying aged rocks including Enriched-Mid-Ocean Ridge Basalts (E-MORB), Lower Continental Crust (LCC), Upper Continental Crust (UCC), Archean-Proterozoic-Paleozoic-MesoCenozoic Basalts (B), Archean-Proterozoic-Phanerozoic Granites (G), Archean-Proterozoic-Paleozoic-MesoCenozoic Felsic Volcanics (FV), Northern American Shales-Combined (NASC) and Archean-Proterozoic-Phanerozoic Cratonic Sandstones (CS). The chemical analyses and alteration index values for sandstones of different units are given in tables 1 and 2.

4.4.1. Classification and nomenclature

According to the Log (SiO_2/Al_2O_3) – Log (Na_2O/K_2O) binary variation diagram by Pettijohn et al., (1973), the samples from the Sosink Formation originate from the literanite region, whereas the sample from the Bedinan Formation comes from the arkose region (Fig. 3a). These partially occurring differences are caused by the abundance of white serizite K-mica minerals in the matrix. In the Log (SiO_2/Al_2O_3) – Log (Fe_2O_3/K_2O) binary variation diagram by Herron (1988), the sandstones are spread over the wacke and arkose ranges (Fig. 3b). In the wacke region, the samples (clay-containing and silt-containing sandstones with petrographic 50–90 % clay-silt size components) are related to the abundance of chlorites in the matrix, which creates a high Fe_2O_3 content.

4.4.2. Sedimentary processes

Weathering/alteration is one of the sedimentary processes that most affects the geochemistry of terrigene sedimentary rocks. The alteration of feldspars (partly volcanic glasses) determines the typical weathering of the upper continental crust.

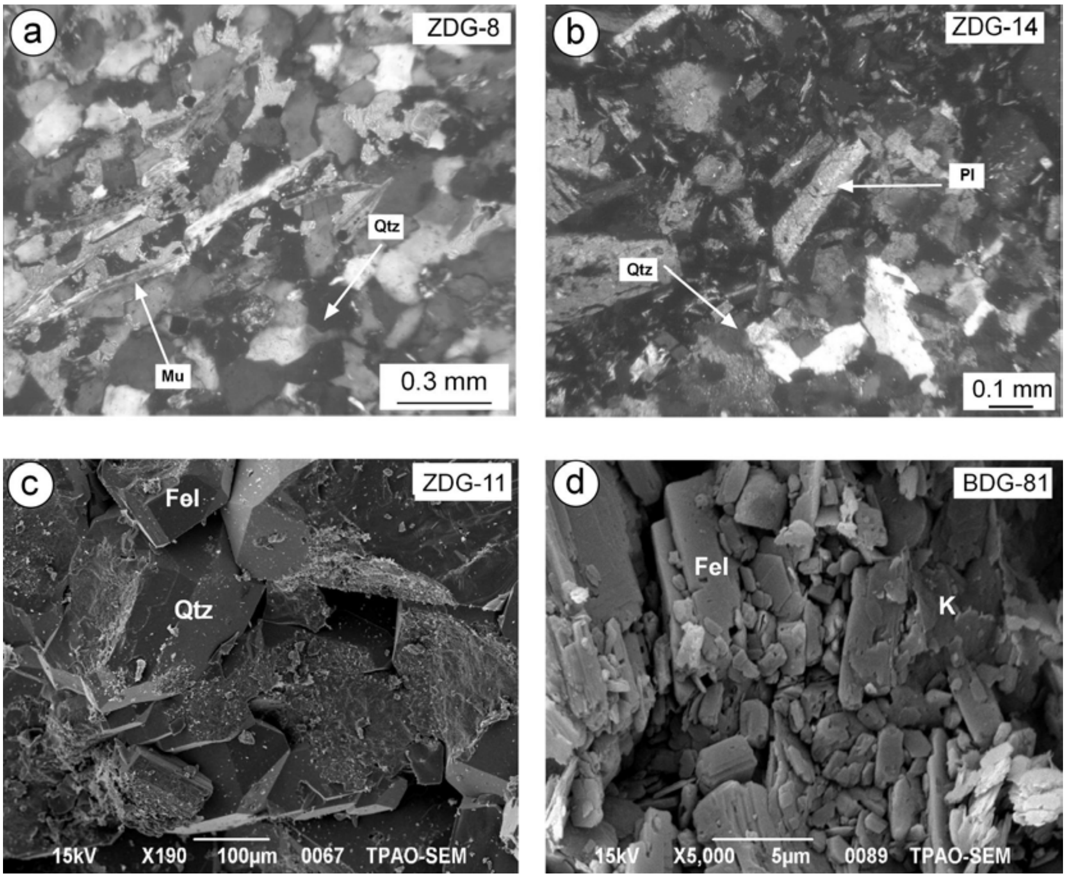

Figure 2. Optical microphotography and SEM images of SEAA sandstones a) orientated and bended muscovite and quartz minerals in Zabuk formation sandstone (crossed nicol) b) Angular quartz and plagioclase minerals from Zabuk formation, c) Euhedral quartz, feldspar and illite minerals in Zabuk Formation), d) Prismatic feldspar and kaolinite minerals in Bedinan formation ((Mu= Muscovite, Qtz=Quartz, Pl=Plagioclase, Fel=Feldspar, K=Kaolinite).

Table 1. Major element chemical composition of SEAA sandstone.

Formation	Zabuk		Sosink					Bedinan						Halevikdere			
Lithology	Sandstone					Silt-stone	Sand-stone	Siltstone			Sand-stone	Siltstone					Sand-stone
Sample/ Oxide %	ZDG -8	ZDG-11	SDG-20	SDG-24	SDG-30	SDG-36	SDG-40	BDG-42	BDG-44	BDG-47	BDG-75a	BDG-79	BDG-81	MKH-56	MKH-63	MKH-67	MKH-69
SiO_2	94.47	97.97	68.09	72.66	62.09	68.67	74.14	94.69	96.72	87.59	54.84	76.82	71.36	73.75	65.61	68.25	83.54
TiO_2	0.077	0.099	0.748	0.609	0.746	0.645	0.652	0.139	0.083	0.325	0.773	0.962	1.096	0.757	0.832	0.952	0.564
Al_2O_3	1.88	0.62	13.84	11.39	16.02	13.33	12.3	1.85	1.10	3.77	11.19	10.47	14.46	11.86	14.87	14.16	7.34
Fe_2O_3	0.32	0.27	4.99	5.19	6.31	6.20	2.71	0.80	0.62	0.25	14.97	0.72	1.04	1.29	6.06	4.98	0.89
MnO	0.012	0.012	0.039	0.025	0.04	0.037	0.021	0.005	0.004	0.003	0.097	0.004	0.004	0.004	0.009	0.007	0.003
MgO	0.10	0.01	1.88	1.73	2.60	1.88	1.11	0.07	0.05	0.08	1.90	0.28	0.38	0.30	0.59	0.50	0.16
CaO	0.15	0.40	0.62	0.38	0.40	0.38	0.40	0.27	0.09	2.00	1.31	1.19	0.38	0.87	0.23	0.22	0.15
Na_2O	0.05	0.02	2.00	1.84	1.58	2.00	2.18	0.03	0.03	0.07	0.81	0.10	0.08	0.09	0.10	0.09	0.10
K_2O	1.16	0.40	3.18	2.47	3.98	2.67	2.96	0.72	0.55	2.39	3.57	5.16	5.30	7.00	4.75	5.28	4.36
P_2O_5	0.03	0.05	0.17	0.09	0.12	0.12	0.13	0.02	0.01	0.03	0.23	0.03	0.05	0.03	0.06	0.04	0.02
LOI	0.95	0.57	4.16	3.23	5.04	3.30	2.87	0.98	0.52	2.31	9.10	3.35	4.59	2.72	5.89	4.64	1.75
Total	99.20	100.50	99.72	99.61	98.92	99.22	99.48	99.57	99.78	98.82	98.79	99.08	98.74	98.68	99.00	99.12	98.89

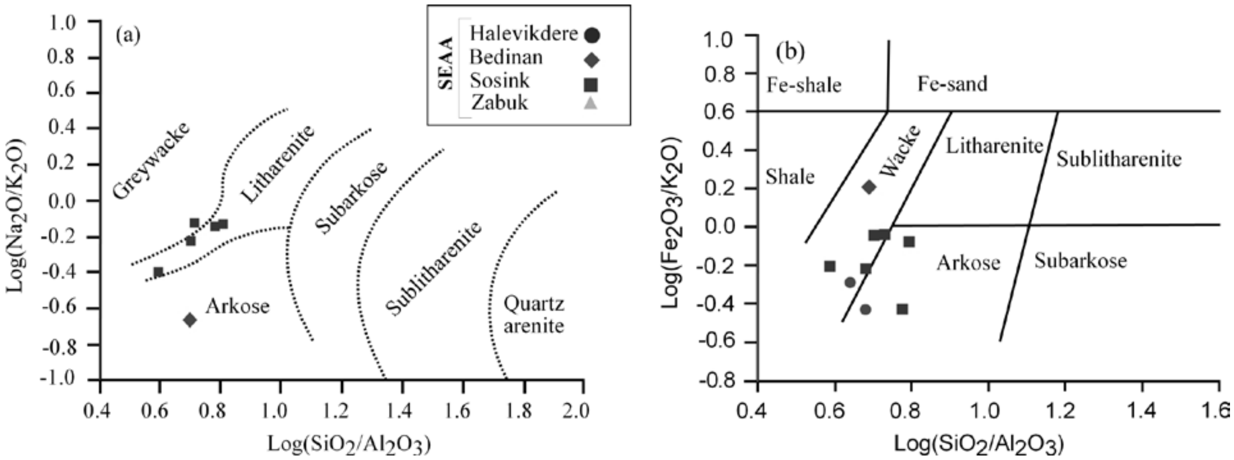

Figure 3. The nomenclature in binary variation diagrams of sandstones, a) $Log(SiO_2(Al_2O_3)$ – $Log(Na_2O/K_2O)$ (Pettijohn et al., 1973); b) $Log(SiO_2(Al_2O_3)$ – $Log(Fe_2O_3/K_2O)$ (Herron, 1988)

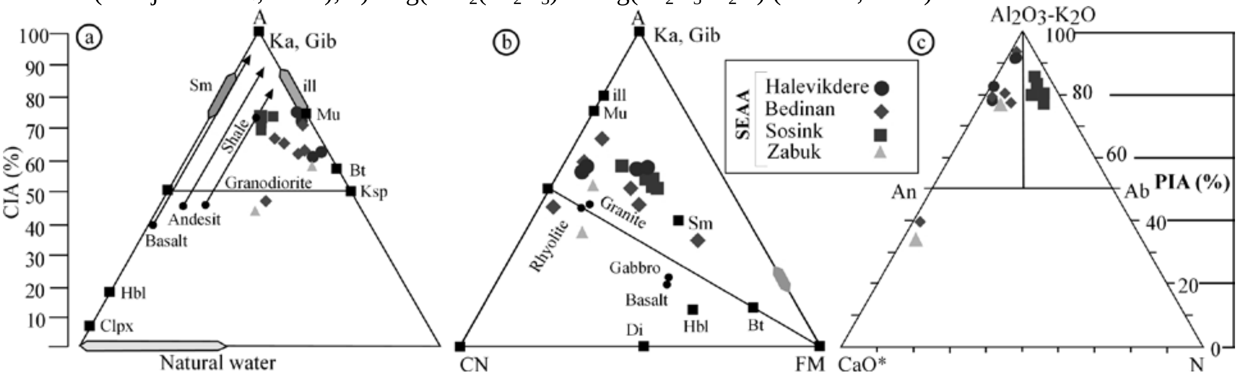

Figure 4. Distribution in triangular diagrams of molecular ratios of some oxides with CIA values of the sandstones (McLennan & Murray, 1999) a) Felsic diagram (weathering tendency of some rock species from the upper crust with ideal compositions of some magmatic and sedimentary minerals: McLennan et al., 2006), b) Mafic diagram, c) Distribution in triangular diagrams of molecular ratios of some oxides with PIA values of the sandstones(Ab=Albite, An=Anortite) (Avarage magmatic rock compositions: Nockolds, 1954)($A=Al_2O_3$; $C= CaO^*+Na_2O$, $N= Na_2O$, $CNK=CaO^*+Na_2O+K_2O$, $FM= \Sigma Fe_2O_3+MgO$, Bt=Biotite, Cal=Calcite, Chl=Chlorite, Clpx=Clinopyroxene, ill=Illite, Prx=Pyroxene, F=Feldspar, Mu=Muscovite, Pl=Plagioclase, Sm=Smectite)

For that reason, most of the effect on the composition of the major elements occurs within the Al_2O_3–$(CaO+Na_2O)$–K_2O geochemical system (Nesbitt & Young, 1984), thus allowing the Chemical Index of Alteration (CIA) to be formulized (i.e. Nesbitt & Young, 1984; Nesbitt et al., 1996). As can be seen in the Al_2O_3–(CaO+Na_2O)–K_2O diagram (Fig.4a), the sandstones from the investigation field have the following range of CIA values with respect to their formations: 34–54 (mean of 44) for Zabuk, 62–68 (mean of 65) for Sosink, 37–69 (mean of 56) for Bedinan and 56–75 (mean of 64) for Halevikdere.

Table 2. Trace element chemical composition of SEAA sandstones

Formation	Zabuk		Sosink					Bedinan						Halevikdere			
Lithology	Sandstone					Silt-stone	Sand-stone	Siltstone			Sand-stone	Siltstone					Sand-stone
Sample/ Element (ppm)	ZDG-8	ZDG-11	SDG-20	SDG-24	SDG-30	SDG-36	SDG-40	BDG-42	BDG-44	BDG-47	BDG-75a	BDG-79	BDG-81	MKH-56	MKH-63	MKH-67	MKH-69
Cr	30	<20	60	40	70	40	40	<20	<20	<20	40	40	60	40	60	60	<20
Ni	20	<20	40	30	50	50	30	<20	<20	<20	40	20	30	20	30	30	<20
Co	27	434	260	83	149	120	53	262	448	345	50	7	14	7	11	4	24
Sc	24	1	11	8	13	8	8	2	2	3	12	7	10	7	11	10	3
V	128	6	76	53	94	59	56	14	12	22	58	64	90	66	124	85	35
Cu	<10	<10	60	20	60	30	<10	20	<10	<10	10	<10	20	10	<10	<10	<10
Pb	8	<5	28	10	12	10	10	9	6	14	19	15	25	25	21	17	16
Zn	<30	<30	70	60	100	90	50	110	<30	<30	100	<30	<30	<30	50	<30	<30
Bi	0.4	<0.1	0.2	0.2	0.5	0.3	0.3	<0.1	<0.1	<0.1	0.3	0.2	0.302	0.2	0.3	0.3	<0.1
In	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Sn	2	<1	4	3	5	3	3	<1	<1	1	2	2	3	2	3	3	1
W	140	2660	1780	458	1000	676	268	1660	2720	1990	72.7	9.9	7.2	7	9.4	6.8	85.5
Mo	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2	<2
As	26	<5	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	6	6	7	<5	<5
Sb	18.4	<0.2	0.6	0.3	0.4	0.7	0.5	<0.2	<0.2	<0.2	0.5	0.4	0.6	0.7	0.5	0.6	<0.2
Ge	1.7	0.9	2	2	2.5	3	3	0.9	0.9	1.2	1.6	1.3	1.6	1.5	1.7	1.7	8
Be	1	<1	2	2	3	2	2	<1	<1	<1	2	1	2	1	5	3	<1
Ag	0.7	<0.5	0.8	0.9	0.6	0.8	1	0.7	<0.5	2	1	2.1	1.4	1.4	0.9	1.4	2.7
Rb	58	6	113	94	169	103	106	12	12	40	80	85	101	100	106	121	77
Cs	0.2	0.2	4.9	4.3	10.8	5.7	4.9	0.7	0.5	1.1	4.2	4.6	6.8	4.6	11	9.3	3.5
Ba	379	71	1610	765	442	331	391	140	119	364	846	569	593	605	507	608	635
Sr	55	11	102	73	81	83	78	76	39	91	93	101	201	129	143	129	118
Tl	0.18	<0.05	0.61	0.52	0.91	0.67	0.66	0.07	0.05	0.28	0.41	0.54	0.59	0.62	0.48	0.57	0.38
Ga	15	2	20	15	23	15	14	2	2	5	12	13	18	15	19	19	8
Ta	0.67	1.07	20.8	1.19	1.9	1.36	1.17	0.64	0.99	1.04	1.24	1.59	1.48	1.18	1.17	1.39	1.37
Nb	7.7	1.6	13.9	10.8	15.3	12.1	11.5	2.5	1.1	5.4	14.9	17.1	15.3	13.4	15.8	15.6	11.3
Hf	4.5	1.4	6.3	6.3	4.5	6.2	7.3	4.8	2.1	13.7	7.7	15.5	9.7	9.7	7.5	9.5	18.4
Zr	159	51	219	222	154	204	248	184	78	534	258	567	363	347	313	348	690
Y	28.8	5.1	24.9	21.1	24.2	25.9	24.2	7.2	3.6	11.8	38.5	25.6	26.3	16.7	23.7	17.3	20.3
Th	4.56	2.3	11.2	10.1	12.1	11.7	11.1	2.39	1.62	5.64	10.8	12.8	12.7	9.45	11.7	12.7	8.19
U	2.08	0.71	2.68	2.15	2.69	2.58	3.03	0.68	0.53	1.94	2.28	3.17	3.35	2.35	1.94	2.51	2.25
La	15.1	5.99	32.2	26.8	36.1	31	29.6	16.5	8.04	21.3	32.8	31.2	37.6	26.8	38.6	30.9	28.7
Ce	29.9	15.9	65.2	54.1	72.1	61.9	59.8	36.9	16.5	43.5	72.7	60.5	76.4	50.8	84.1	57.7	57.2
Pr	4.03	2.18	8.45	6.91	9.33	7.96	7.69	3.99	1.94	5.15	10.3	7.4	9.69	6.03	10.3	7.01	6.97
Nd	16.5	9.37	33.5	26.1	34.8	30.1	29	17	6.97	18.2	43.1	26.1	37	20.6	42	26	25.2
Sm	4.21	2.04	7.73	5.72	7.25	6.65	6.42	3.72	1.3	3.04	10.7	5.03	8.13	3.8	8.16	4.79	5.08
Eu	1.27	0.392	1.51	1.04	1.45	1.31	1.22	0.738	0.271	0.551	3.32	0.903	1.62	0.758	1.54	0.871	0.957
Gd	4.34	1.47	6.64	4.71	6.02	5.49	5.45	2.52	0.91	2.36	9.97	4.35	6.29	3.26	6.63	3.813	4.28
Tb	0.81	0.21	1.01	0.77	0.92	0.93	0.87	0.33	0.14	0.39	1.66	0.76	0.97	0.54	0.79	0.626	0.69
Dy	5.34	1.09	5.48	4.48	5.27	5.46	5.05	1.73	0.81	2.37	9.04	5.01	5.6	3.35	4.51	3.58	4.04
Ho	1.19	0.22	1.02	0.89	1.03	1.11	1.02	0.33	0.16	0.49	1.73	1.08	1.13	0.7	0.88	0.76	0.83
Er	3.68	0.64	2.8	2.54	2.93	3.15	2.88	0.87	0.47	1.47	4.53	3.2	3.21	2.11	2.54	2.21	2.36
Tm	0.582	0.097	0.405	0.387	0.433	0.489	0.423	0.131	0.069	0.231	0.648	0.529	0.514	0.332	0.399	0.37	0.387
Yb	4.03	0.68	2.5	2.51	2.85	3.15	2.67	0.85	0.43	1.69	3.89	3.63	3.5	2.38	2.69	2.51	2.76
Lu	0.673	0.107	0.394	0.391	0.449	0.511	0.427	0.142	0.067	0.282	0.608	0.616	0.542	0.382	0.451	0.42	0.474

The sandstones lie close to the Al_2O_3–K_2O curve, extending parallel to the alteration tendency of magmatic rocks (basalt-andesite-granite) and accumulating above the plagioclase-K-feldspar curve around the shale point of the plagioclase-smectite-shale triangle. The samples belonging to the Sosink Formation accumulate on the shale point altogether.

In figure 4b, which contains the Al_2O_3–(CaO^*+Na_2O+K_2O) – (ΣFe_2O_3 + MgO) diagram, it can be seen that the CIA values of sandstones from the investigation field range between 31 and 64 and that they are concentrated on the granite-smectite-muscovite triangle right above the feldspar-pyroxene curve. The data presented in both these figures can be explained by the abundance of diagenetic/metamorphic and/or detritic phyllosilicates and feldspar. Simultaneously, this also points out the well-developed sedimentary sorting.

The Chemical Index of Weathering (CIW) values proposed by Harnois (1988) range from 31 to 46 (mean of 25) for Zabuk samples, whereas they are 69–72 (mean of 70), 33–58 (mean of 51) and 48–64 (mean of 56) for the samples from Sosink, Bedinan and Halevikdere, respectively. The values of another alteration index (Plagioclase Index of Alteration - PIA) proposed by Fedo et al., (1995) range as follows: 68–72 (mean of 72) for Sosink, 24–91 (mean of 64) for Bedinan and 86–94 (mean of 86) for Halevikdere. These values indicate that the plagioclases of sandstones were significantly altered. The chemical weathering/alteration relations of the sandstones from the study area are presented in PIA (Fedo et al., 1995), CIA (McLennan & Murray, 1999) and CIW (Harnois, 1988) diagrams (Fig. 5a and 5b). The weathering of silicates in the Halevikdere and Zabuk Formations are observed to be low compared to medium for those in the other units in accordance with both diagrams. Furthermore, it can be seen that these relations have positive and important correlation coefficients.

The examined samples are given in figure 6a by means of Al_2O_3 (final product of weathering/alteration) versus other oxides in order to introduce the detritic tendency. Apart from silica (SiO_2), all other element oxides have a positive correlation with Al_2O_3. The weakest correlation of Al_2O_3 is observed with CaO for which r^2=0.001, and the strongest correlations are observed with SiO_2 and TiO_2 for which r^2=0.84 and r^2=0.83, respectively.

With respect to their content, sandstones with high Al_2O_3 and low SiO_2 content accumulate on the right side of the diagram, whereas those with low Al_2O_3 and high SiO_2 content accumulate on the left. This situation is related to the increase in K-micas and/or feldspars despite the decrease in quartz. Similar relations can be seen between Al_2O_3 and K_2O. The relatively stable behavior of CaO and Na_2O in spite of an increase in Al_2O_3 is controlled by plagioclase.

Likewise, the following controllers are found for the following relations: for the Al_2O_3—TiO_2 relation, the controller is/are Ti- and/or Ti-Fe-oxides; for the Al_2O_3–tFe_2O_3 relation, the controllers are in the order of Fe-oxide and biotite; for the Al_2O_3–MgO relation, the controllers are amphibole and biotite; and for Al_2O_3-P_2O_5, the controller is apatite content

The correlation of Al_2O_3 with some of the trace elements is reported in figure 6b. The Al_2O_3 trace element correlation is more distinct compared with the major elements and ranges between r^2=0.35 and 0.87 (V and Rb). The increases in Rb and Ga, which are Low Field Strength Elements against Al_2O_3, are related with K-micas, whereas the increases in transition metal V in Th, Nd and Sm are related to the terrigene components that refer to the source region from where these elements were derived.

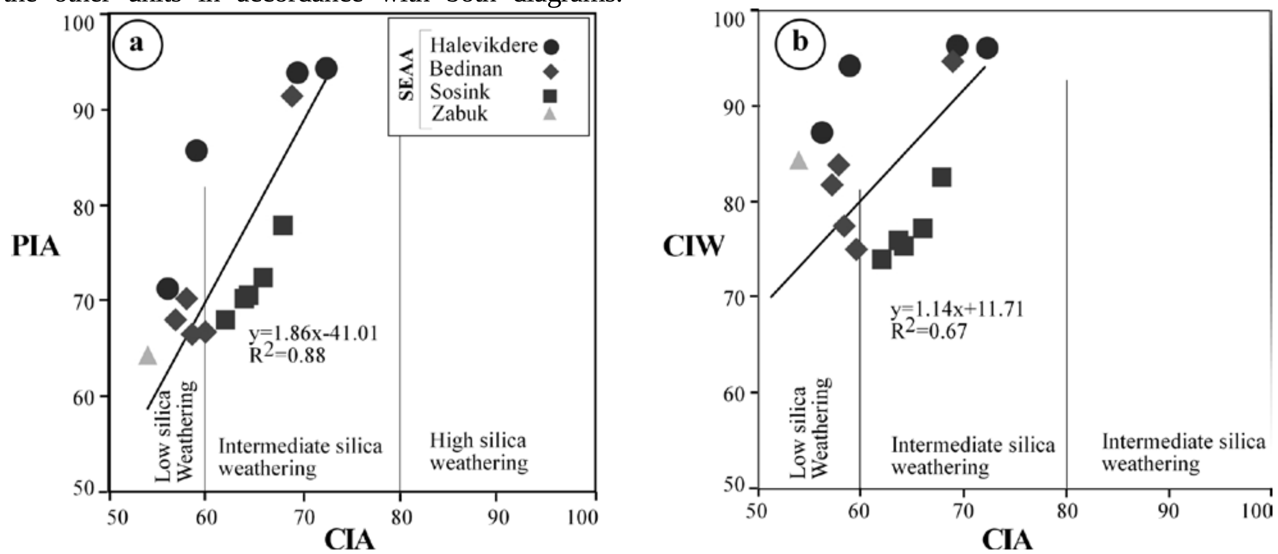

Figure 5. Diagrams showing chemical weathering/alteration correlation of the SEAA sandstones a) PIA (Fedo et al., 1995)-CIA (McLennan & Murray, 1999), b) CIW (Harnois, 1988) -CIA (McLennan & Murray, 1999)

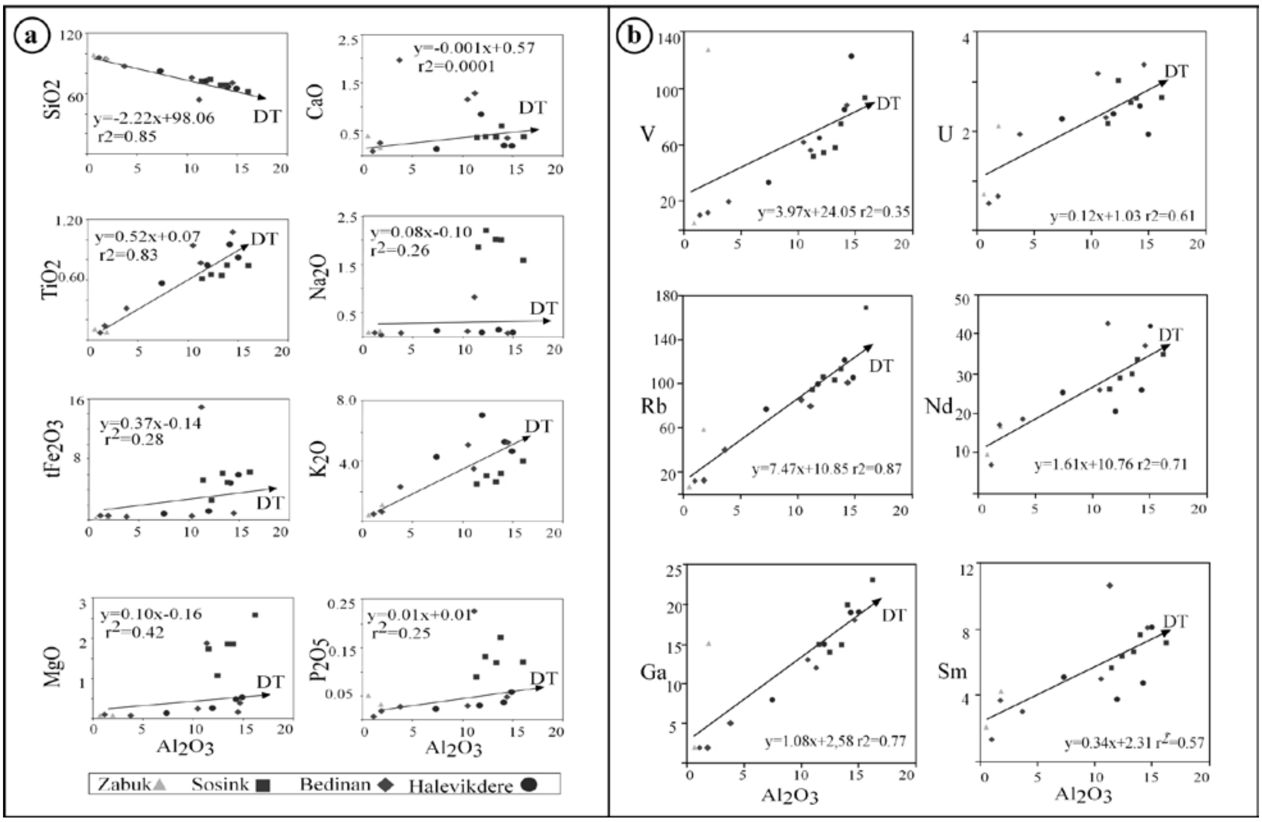

Figure 6. a) Variation diagrams of major oxides versus Al_2O_3 from sandstones, b) Variation diagrams of trace element versus Al_2O_3 from sandstones (DT=Detritic Tendency)

The average compositions of some elements in sandstones compared with the units and of the chondrite-normalized trace element plot, (Sun & McDonough, 1989), distributions are given in Fig. 7a. Additionally, for comparison purposes, LCC, UCC, NASC, CS, G and FV are also included in the same figure. The textures of sandstones are similar to those in NASC, CS, LCC, G and FV, while the units differ from each other and imply distinctive differentiation. Sandstones have strong enrichment (Ta, Zr and Hf) except for P, which shows depletion (approximately four times) compared with the chondrite values.

Depletion in the P element indicates the absence or low appearance of P-containing heavy minerals such as apatite, while enrichment in the Hf element indicates contributions from Hf-containing heavy minerals, especially from zircon, monazite and/or titanite. The sandstones have positive anomaly for and in the order of the Th, Ta, La, Nd and Tb elements and negative anomaly for the K, Nb, Sr, P, Y and Ti elements. Total REE concentrations are between 38 and 205 ppm in all formations. The concentration values in accordance with the units are as follows: 40–92 ppm (average of 66 ppm) for the Zabuk Formation, 137–181 ppm (average of 160 ppm) for the Sosink Formation, 38–205 ppm (average of 129 ppm) for Bedinan and 122–204 ppm (average of 152 ppm) for the Halevikdere Formation.

The REE element content of sandstones is compared with the abundance of elements in the chondrite-normalized plots (Sun & McDonough, 1989) (Fig. 7b). The REE content in sandstones declines from LREE to HREE, while the textures of sandstones from the investigation field partially differ from each other, too. There are significant enrichments in all elements within sandstones that range from 132 to 12 times (La-Ho) and show negative Eu anomaly. The REE content is quite similar to those for NASC, G and FV, whereas it remains distinctively higher than those for LCC, UCC and CS. These data derived from the investigated sandstones area have been mostly fed from a magmatic source rather than a sedimentary source. Roser & Korch (1988) suggested discrimination diagrams for the detection of evidence of sandstone–mudstone associations.

Sandstones that are examined in the discrimination diagram mostly appear in the quartz sedimentary provenance region (Fig. 8a). A single sample from the Bedinan Formation is found in the mafic magmatic source region. Petrographic and geochemical data indicate sedimentary and partly magmatic provenance. These results, as well as the height of the K content of the serizition matrix, are caused by the growth in diagenetic secondary silica.

Figure 8b is a transformation diagram based on the primary and secondary discriminant functions proposed by Bhatia (1983) for Paleozoic sandstones, which are used for the determination of the tectonic medium of major elements and clastic sediments. SEAA sandstones mainly represent the active and passive continental margins. Sandstones from the Zabuk Formation are at the passive continental margin and those from the Halevikdere Formation are at the active continental margin. Two of the samples from the Sosink Formation are found at the active continental margin, whereas another two are at the passive continental margin and one at the continental arc.

Bhatia & Crook (1986) developed diagrams for the graywackes belonging to different tectonic environments. The samples in the La-Th-Sc ternary diagram are close to the La corner and mostly represent the continental arc (Fig. 9a), whereas in the Ti/Zr-La/Sc variation diagram, many samples represent the active continental margin environment. Two of the samples from the Bedinan Formation and one sample from the Halevikdere Formation are representatives of the passive margin environment (Fig. 9b) in the same variation diagram.

In the La/Y-Sc/Cr variation diagram, these mainly represent the passive continental margin environment (Fig. 9c). In the Th-Sc-Zr/10 ternary diagram, once again most of the samples are found to concentrate on the continental arc environment, while only one sample from the Halevikdere Formation focuses on the island arc region (Fig. 9d).

5. DISCUSSIONS AND CONCLUSIONS

Concentrations of elements in sediments are controlled by weathering, diagenesis and sediment sorting, provenance and fluid geochemistry effects. The highest concentrations are found in clay-containing sediments, and most geochemical studies focus on these lithologies. From this aspect, the most important elements are Fe, Th, Al, Co, Mn, Pb, REE, Y, Sc, Zr, Ti, Hf, Cr, Ni, Si and V. These elements have very low solubility in natural water and similar concentrations during their transportation into sediments as a result of which important information about the provenance nature can be ascertained (i.e. Fleet, 1984; McLennan, 1989; Rollinson, 1993).

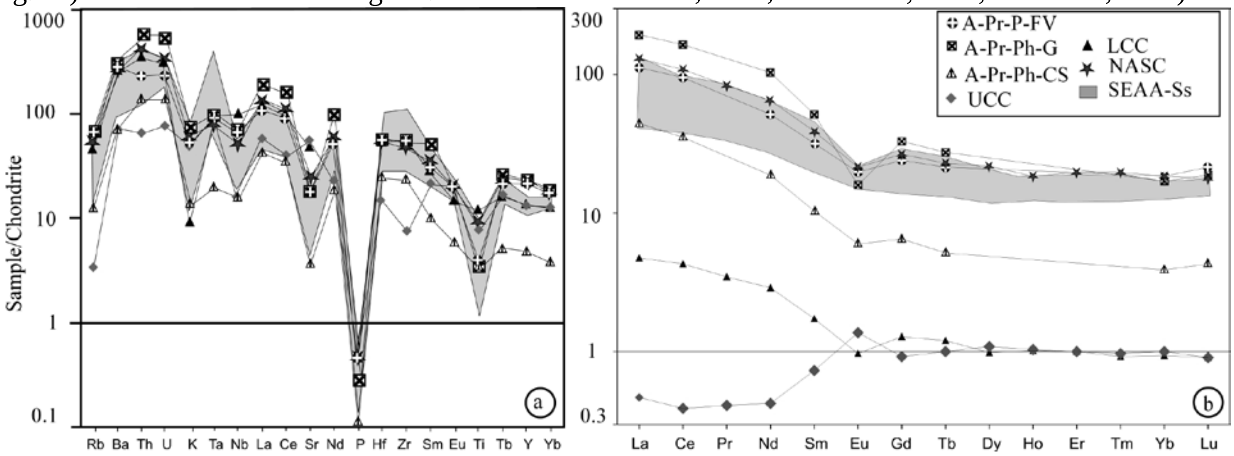

Figure 7. Chondrite-normalized element patterns of the sandstones, (a) trace elements, (b) rare elements (SEAA-Ss: SEAA-sandstones; Chondrite: Sun & McDonough, 1989; A-Pr-Ph-CS, A-Pr-Ph-FV, A-Pr-Ph-G: Condie, 1993; Nb and Y for NASC: Condie, 1993; LCC and UCC: Taylor and McLennan, 1981; other elements: Gromet et al., 1984).

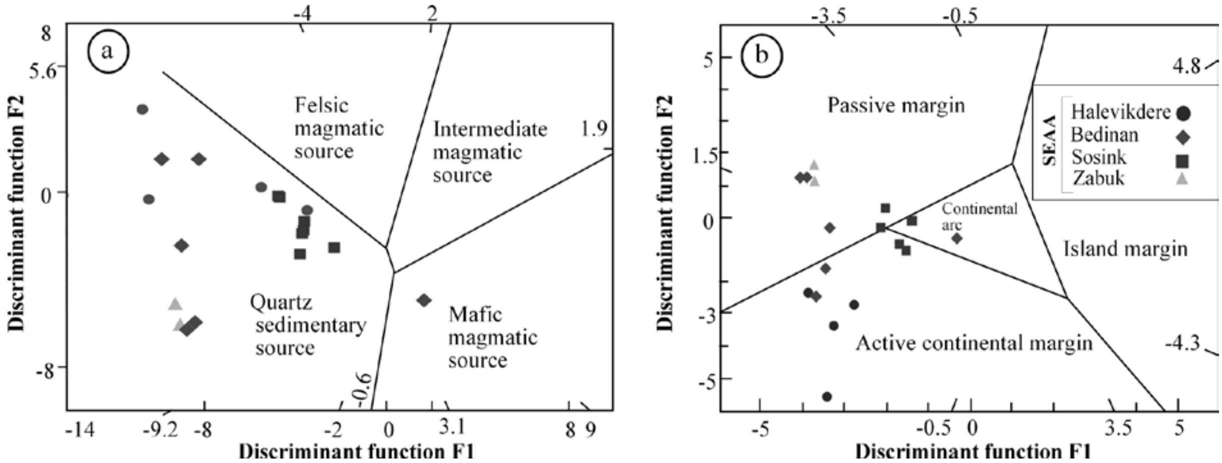

Figure 8. Provence discrimination diagrams for studied sandstones (Roser & Korsch, 1988), a) Major oxide contents, b) Major element ratios (Bhatia, 1983)

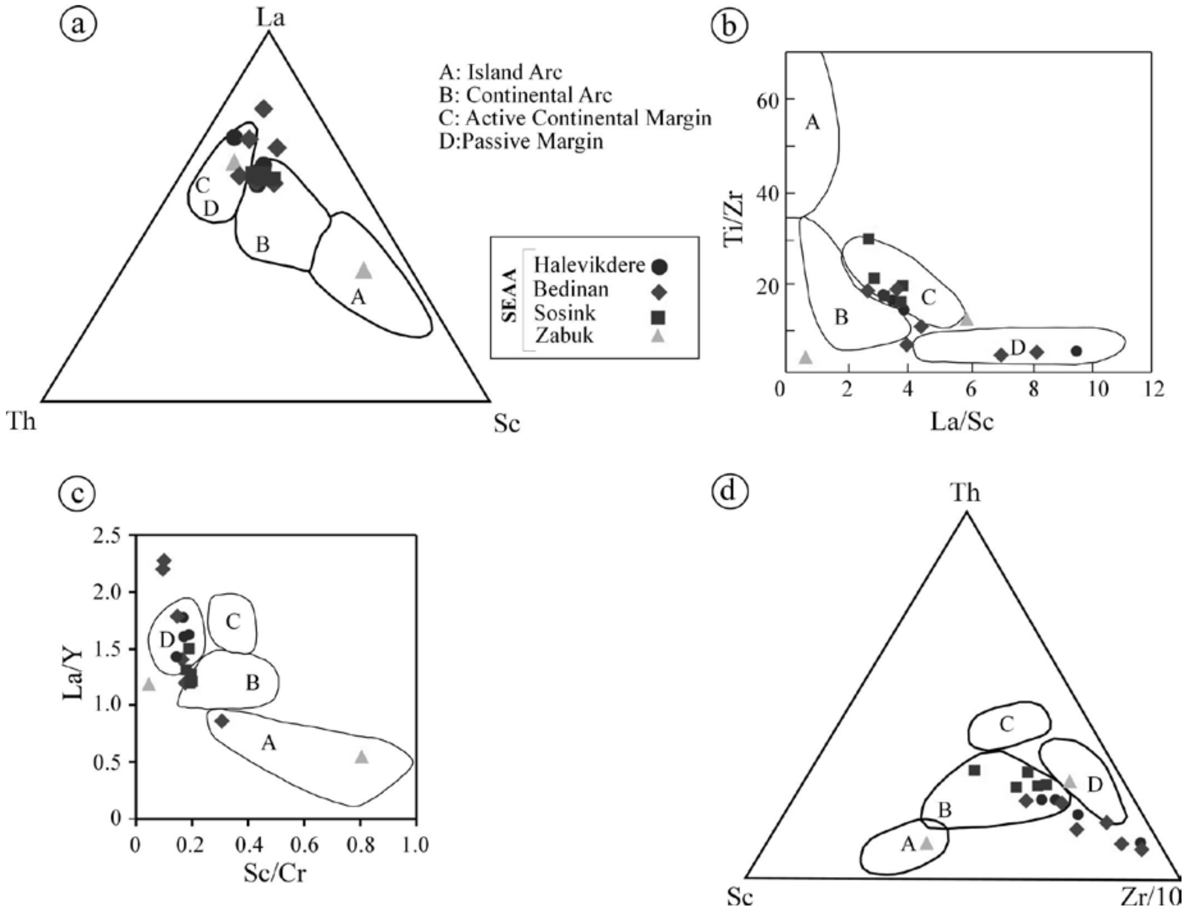

Figure 9. The geotectonic variation and ternary discrimination diagrams for greywacke (Bhatia & Crook, 1986); a) La–Th–Sc, b) Ti/Zr-La/Sc, c) La/Y-Sc/Cr, d) Th–Sc–Zr/10

Consequently, their elemental ratios are not affected by diagenesis and metamorphism. Those elements not mentioned in the group above have higher solubility. For instance, elements such as Na, Mg, K, Sr, Ca, U, Rb, Cs and Ba that strongly dissolve in seawater are limitedly used for understanding the provenance because they are mobile during sedimentary processes. Fe, Mn, Pb and sometimes Cr are also mobile during diagenesis. Rb and Ba stabilize and remain in the medium during weathering, but the Sr element is rather washed away from the environment. Immobile elements such as Zr, Hf and Sn may show mechanical distributions with respect to grain size and these can be controlled by heavy mineral concentrations. Petrographic, petrologic and geochemical investigations as well as several studies have aimed to determine the source region, source rock, origin and/or tectonic environments for clastic rocks, which are useful for older units without more orogenesis (Dickinson & Suczek, 1979; Bhatia, 1983; Condie & Martell, 1983; Bhatia & Crook, 1986; Roser & Korsch, 1986; Wronkiewicz & Condie, 1987; Eriksson et al., 1994; La Fléche & Camiré, 1996; Fralich & Kronenberg, 1997; Bock et al., 1998; Holail & Moghazi, 1998; Bauluz et al., 2000; Shao et al., 2001; Lee, 2002; Cingolani, 2003; Zhiming et al., 2003; Zimmermann & Bahlburg, 2003; Goodge et al., 2004; Mader & Neubauer, 2004; Yoshida & Machiyama, 2004; Joo et al., 2005).

The differences compared with the units in sandstones, which are defined based on their chemical compositions as literanite, wacke and arkose, are generally related to the types of phyllosilicates that sandstones contain. Samples belonging to Zabuk Formation are relatively poor in all major oxides excluding SiO_2. In general, the quartz ratio (feldspar+phyllosilicate) is highest for Zabuk and lowest for Halevikdere. In other words, the silica content declines from older to younger units. While the average trace element abundances may differ from unit to unit and sample to sample, Cr, Ni, Rb, Cs, Ba and Tl are the most abundant are the most abundant elements for the Bedinan elements for the Sosink Formation; Co, W, Sr, Nb, Th, U, Sm and Eu as well as the Zn and As elements Formation; Sc, V, W and Y are the most abundant elements for Zabuk; and Hf and Zr are most abundant for Halevikdere.

The CIA and CIW values of sandstones are somewhat close to each other and range between 31 and 72, implying they are generally clustered in plagioclase-smectite-shale or granite-smectite-muscovite triangles. The PIA values exhibit differences from unit to unit, ranging from 20 to 94. In Parker (1970) and Hamdan & Burnham (1996), WIP was used in order to evaluate the weathering intensity of silicate rocks based upon the proportions of alkali and alkaline earth elements in weathered products. In this study, the WIP values are between 5 and 63, namely lower than the PIA and CIW index values. Moreover, the upper levels of the Ordovician-aged Bedinan Formation and the Halevikdere Formation are observed to be most affected by the weathering and alteration processes in SEAA rocks (Fig. 10). Similarly, phyllosilicate paragenesis (I+Chl+K) belongs to the formations featured with the weathering and alteration processes.

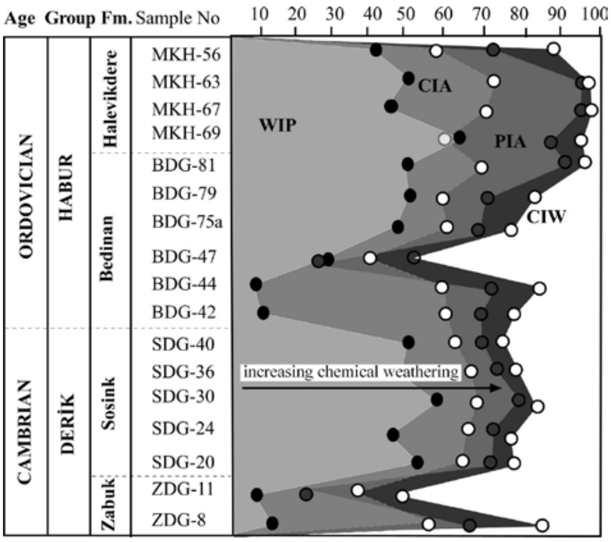

Figure 10. The variations of chemical weathering and alteration index of the SEAA units

The Th/U (2–6), Th/Sc (0.2–2.7), Zr/Sc (7–230), $(La/Yb)_N$ (2.7–13.9), Eu_N/Eu^* (0.6–1.0) and $(Gd/Yb)_N$ (0.9–2.5) ratios generally increase in the order of the Zabuk, Sosink, Bedinan and Halevikdere Formations. When all weathering/alteration indexes are considered together, it can be seen that the results concur with the petrographic results. It is found that silicates in the Zabuk Formation experience low weathering, whereas silicates from other formations experience medium weathering. In other words, these data indicate two results: (i) the detritic components as well as significant amounts of weathering/alteration and new minerals are formed and (ii) sedimentary sorting is well developed. The ICV values (ICV-Index of Compositional Variability; Cox et al., 1995) of sandstones differ in a wide range (5–31) and diagenetic evolution seems to affect Sosink sandstones at the highest amount and Bedinan sandstones at the lowest amount.

The textures of the sandstones based on chondrite are similar to those found in NASC, cratonic sandstones, LCC, Granites and Felsic Volcanics, while the units differ from each other distinctively. Except for P, which has depletion/consumption compared with chondrite values, there is strong enrichment (Ta, Zr and Hf). The depletion in P indicates the absence or a low amount of P-containing heavy minerals such as apatite, while enrichment in Hf indicates Hf-containing heavy minerals, especially zircon, monazite and titanite. Examined sandstones have positive anomalies for Th, Ta, La, Nd and Tb (in that order) and negative anomalies for K, Nb, Sr, P, Y and Ti. The REE content of sandstones is similar to that in NASC, Granites and FV but higher than that in LCC, UCC and CS. There are also significant enrichments in all elements within sandstones that range from 132 to 12 (La-Ho) and show a negative Eu anomaly. According to the field data, this finding implies that sandstones have mostly been fed from a magmatic source rather than a sedimentary source.

The examined sandstones represent a range of magmatic provenance regions, mostly from quartz sedimentary to partially felsic and mafic composition. Furthermore, the very low Cr/V ratios of sandstones that range between 0.3 and 0.7 show that they have not been fed from an ophiolitic or ultramafic source. Similarly, the ratio vales of Y/Ni (0.2–1.4) and Cr/Ni (0.8–2.0) indicate a silicic/felsic provenance.

The abundance of major and trace elements in Paleozoic-dated SEAA clastics is controlled by sedimentary processes (e.g. weathering/alteration degree, sorting, diagenesis and source rock/provenance), types and ratios of clastics and/or diagenetic components. The sandstones from the investigation area have experienced low-to-medium weathering and alteration and they are well arranged. They have also been affected by diagenetic processes, especially neoformation and/or transformation mechanisms.

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