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PETROGRAPHY AND GEOCHEMICAL CHARACTERIZATION OF THE LOWER CRETACEOUS DEPOSITS OF THE VANDAM ZONE (SOUTHERN SLOPE OF THE GREATER CAUCASUS, AZERBAIJAN): IMPLICATIONS FOR MATURITY, PALEOCLIMATE AND PALEOWEATHERING

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Summary. This study presents a detailed petrographic and geochemical analysis of Lower Cretaceous deposits of the southern slope of the Greater Caucasus (Vandam zone). By analysing the siliciclastic rocks of the Kepuch and Gyrkhbulag formations, this research aims to assess the compositional maturity of the sediments and to reconstruct the paleoenvironmental conditions, including paleoclimate paleoweathering processes. Petrographic analysis reveals that the sediments were poorly sorted and made of angular to subangular grains, implying deposition relatively close to the source area. The mineralogical maturity of the sediments was assessed through the Index of Compositional Variability (ICV), while weathering intensities were evaluated using the Chemical Index of Alteration (CIA), Chemical Index of weathering (CIW), and the Plagioclase Index of Alteration (PIA). Based on geochemical classification, the sediments were classified as litharenites and wackes. The Al_2O_3-(CaO^*+Na_2O)-K_2O (A-CN-K) diagram, along with weathering indices, suggest low to moderate weathering in the source area, consisted with the arid-to-semi-arid climate of the studied area. On the other hand, the Index of Compositional Variability (ICV), ranging from 0.9 to 1.59, indicates low compositional and mineralogical maturity. In addition, the discriminant diagrams of Zr/Sc-Th/Sc and Al_2O_3-Zr-TiO_2 suggest that the sediments were primarily first-cycle deposits derived from igneous rocks, with minimal evidence of obvious recycling and hydraulic sorting.

Keywords: *maturity, paleoclimate, paleoweathering, ICV, CIA, PIA, CIW, recycling, sorting*

Introduction

During the processes of transportation and deposition, sediments undergo alterations in their mineral content, leading to changes in their major element composition compared to their source rocks. The geochemical signatures of siliciclastic sedimentary rocks are controlled by a complex interplay of various factors, like chemical weathering, the distance of transportation, the conditions of sedimentation, sorting processes occurring during transport and post-depositional diagenetic reactions (McLennan, 1989).

Quartz, as well as iron (Fe) and titanium (Ti) oxides, are known for their resistance to weathering. In contrast, minerals such as plagioclase, potash feldspar, and volcanic glass, which comprise 75% of the exposed mineral content, are highly vulnerable to chemical weathering and are classified as labile minerals (Nesbitt and Young, 1984; 1989). Consequently, the primary process during chemical weathering, transportation, deposition and soil formation involves the degradation of unstable feldspars from source rocks into corresponding clay minerals. The intensity of degradation can infer its maturity, distance from the source. These chemical transformations are recorded in the sedimentary deposits, providing a reliable signature for assessing the original compositional maturity and the following weathering conditions (Oni, Olatunji, 2017).

For this reason, geochemical and petrographic studies have been confined to Neocomian deposits of the Kepuch and Gyrkhbulag Formations well exposed in the Vandam zone. The purpose of the present study is to evaluate major and trace element geochemistry of Neocomian deposits of the Vandam zone in relation to their mineral composition, in order to classify the sediments on their degree of maturity and to unravel source area paleo-weathering and paleoclimatic conditions. The mineralogical maturity of the sediments was determined through the Index of Compositional Variability (ICV), while weathering intensities were evaluated using the Chemical Index of Alteration (CIA), Chemical Index of weathering (CIW), and the Plagioclase Index of Alteration (PIA).

Geological setting

The Kakheti-Vandam-Gobustan megazone corresponds to the northern flank of the South-Caucasian microplate, with an Alpine cover composed of sedimentary and magmatogenic formations. From west to east, the Girdiman-chay-Velvelechay flexure divides the megazone into two tectonically distinct zones. In the west it corresponds to Vandam tectonic zone represented by geoanticlinal uplift, where predominantly Cretaceous flysch deposits and volcanogenic formations are exposed. Structurally, this zone is characterized by several anticlines and synclines, along with multiple south-directed thrusts. The southern border is in tectonic contact with Ganikh-Ayrichay zone (Fig. 1). Most part of arch and southern slope of uplift is covered by Pleistocene-Holocene continental formations of Ganih-Ayrichay depression.

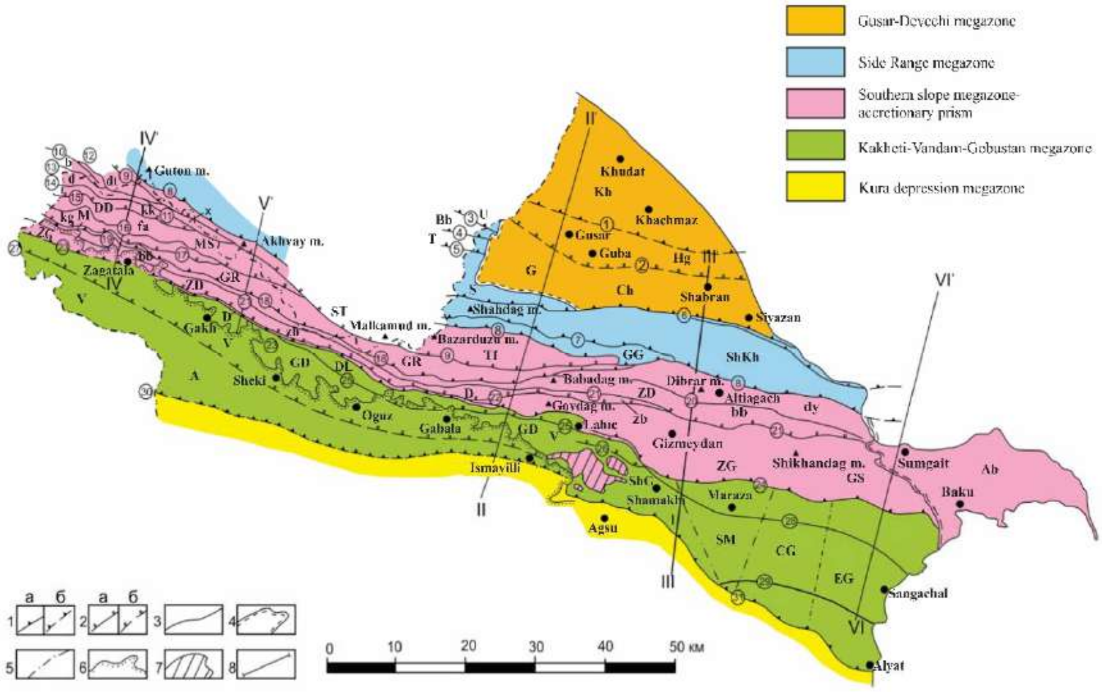

Fig. 1. Tectonic scheme of the Azerbaijani part of Greater Caucasus (Kangarli, 2012)

Boundary of strucrure: 1 – interzone tectonic boundaries (**a** – traced on surface; **b** – buried); **2** – tectonic boundaries between subzones (**a** – traced on surface; **b** – buried); **3** – boundaries of tectonic schuppens; **4** – stratigraphic boundaries; **5** – conventional boundaries; **6** – distribution boundary of modern sediements on Ganikh-Ayrichay superposed depression; **7** – Basgal nappe; **8** – lines of synthesized geological-geophisical sections (fig. 3, 6, 7, 11)

Structures: Gusar-Devechi megazone: zones: **Kh** – Xachmaz; **G** – Quba; subzones: **Hg** – Hasangala; **Ch** – Chilagir. Side Range megazone: zones: **U**– Ulluchay; **Bb**– Beybulag; **T** – Tairdjal; **S** – Sudur; **ShKh** – Shakhdag-Khizi; **GG** – Guton-Gonagkend. Southern Slope megazone: zones: **ST** – Speroz-Tufan; **ZG** – Zagatala-Govdag; **Ab** – Absheron; subzones: **Tf** – Tufan; **DD** – Djikhikh-Dindidag; **MS** – Mazim-Saribash; **M** – Megikan; **GR** – Galal-Rustambaz; **ZD** – Zagatala-Dibrar; **D** – Durudja; **GS** – Govdag-Sumqait; schuppens (nappe plates): **dt** – Djurmut-Tunsaribor; **kh** – Khalakhel; **p** – Rokhnor; **b** – Boskal; **d** – Djikhikh; **кк** – Kasdag-Kasmala; **fa** – Filizchay-Attagay; **kg** – Katekh-Gumbulchay; **dy** – Dibrar-Yashma; **bb** – Balakan-Babadag; **zb** – Zagatala-Burovdal. Kakheti-Vandam-Gobustan megazone: zones: **V** – Vandam; **ShamG** – Shamakhi-Gobustan; subzonesr: **DL** – Dashagil-Lahidj; **GD** – Gulluk-Dadagunash; **A** – Ayrichay; segments: **Sh** – Shamakhi; **SM** – Sundi-Maraza; **CG** – Central-Gobustan; **EG** – East-Gobustan

Fractures: 1 – İmamgulukend-Khachmaz; **2** – Khazra-Guba-Kuchay; **3** – Ashagimaki; **4** – Tendi-Keyda; **5** – Tairdjal; **6** – Siyazan; **7** – Shakhdag-Gonagkend; **8** – Major Caucasus; **9** – Khuray-Malkamud; **10** – Djoakhor-Gudurdag; **11** – Khalakhel; **12** – Kasmaldag; **13** – Machkhalor; **14** – Djikhikh-Chugak; **15** – Kokhnamadan; **16** – Hamzagor-Saribash; **17** – Suvagil; **18** – Gamarvan; **19** – Megikan; **20** – Altiagach; **21** – İlisu-Aladash; **22** – Gaynar-Gozluchay; **23** – Mamrux-Galadjig; **24** – Zangi-Garadjuzlu; **25** – Dashagil-Madrasa; **26** – Mudji; **27** – Shambul-İsmailli; **28** – Ganikh-Ayrichay; **29** – Adjichay-Alat

In the east (interfluve of the Girdimanchay and Agsuchay rivers) the Mesozoic core of the Vandam uplift is flexurally downwarped along the Girdimanchay-Velvelechay flexure and its southeastern continuation opens up into the wide Shamakhi-Gobustan depression, which is primarily composed of Paleocene-Pliocene terrigenous-clayey deposits. These deposits are folded into small, often overturned to the south sharp and isoclinal folds (Alizadeh et al., 2005a).

The Lower Cretaceous deposits of the Vandam tectonic zone are characterized by slope facies sediments primarily composed of carbonate and siliciclastic turbidites (Fig. 2). The Berriasian–Valanginian succession (Kepuch Formation) cropping out in the Vandam zone is composed of massive layers of conglomerates, separated by packages of limestones, marls, and tuffaceous sandstones (50 m), above which lies a sequence of light-gray carbonate-terrigenous flysch. In some places, pelitomorphic limestones alternate with marly clays and grey non-carbonate clays. The Hauterivian succession is comprised of terrigenous-carbonate flysch series and corresponds to the Gyrkhbulag Formation. The thickness of these deposits reaches 300 m. These sediments are sharply different from the marly Kepuch Formation in their almost exclusively terrigenous character. The Hauterivian stage is dominated by argillites with interlayers of siltstones and sandstones. There are also individual interbeds of pelitomorphic limestone with a schistose structure (Alizadeh et al., 2005b).

Samples and methodology

For this study, ten samples were collected from the Kepuch and Gyrkhbulag Formations that crop out in the Vandam zone on the southern slope of the Greater Caucasus. These units were examined in five representative outcrops: four riverside ops along the Behmezchay (BC), Kishchay (KC), Damiraparanchay (DC, and Galachay (FL) rivers, and one, SQ, along the road from Sheki to Gakh (Fig. 3). The samples were initially crushed for 20 minutes in a planetary ball mill to create a well-mixed powder. This powder was then further pulverized in a pulverizing machine. The finely ground powder (<100 μm) was placed in a porcelain crucible and dried at 1000°C overnight to remove moisture. The dried powder was mixed with a binder (citric acid and powder in a 1:10 ratio) and pulverized for two minutes. The mixture was then spooned into a 30 mm aluminum cap and sandwiched between two tungsten carbide pellets. Using a manual hydraulic press, the cap was pressed with a pressure of 10-15 tons per square inch for two minutes, after which the pressure was slowly released. The resulting pressed powder pellet was then ready for analysis. The major and trace element contents were measured using inductively coupled plasma mass spectrometry (ICP-MS) at the Laboratory of Geochemistry, Geochronology, and Isotope Geology of the Department of Earth Sciences "Ardito Desio" at the Università degli Studi di Milano Statale in Milan, Italy.

Thin-section petrography was conducted on ten representative samples at the geological laboratories of the University of Milano-Bicocca to determine their mineral composition and mineral structure under microscope. The unconsolidated samples were initially impregnated with epoxy resin, then cut and mounted on glass slides using Canada balsam. Slide preparation involved three stages of grinding, with careful inspection between each stage to ensure uniform reduction of interference colors. Once prepared, the slides were labeled and examined using transmitted light under a petrographic microscope with a flat stage. Photomicrographs were taken to document the features of the mineral grains, which were observed based on their optical properties.

Results and discussion

Petrography

Petrological studies revealed that studied samples are rich in lithic grains, followed by quartz, feldspar and mica. Lithic grains are dominated by volcanic (felsic volcanics) and low-grade metamorphic rocks (mainly fine-grained mica schist and quartz-mica schist (Fig. 4A, B)), along with a few sedimentary rock fragments (carbonate rock fragments). Among the quartz grains, monocrystalline quartz dominates over polycrystalline quartz. Both plagioclase and K-feldspar varieties are reported; plagioclase feldspar presence is higher than the potash feldspar (Fig. 4C). Calcite and dolomite are found both as detrital grains and as cements. Majority of the samples contain varying proportions of mica, and muscovite (Fig. 4D) is more abundant than biotite since it is more resistant to weathering.

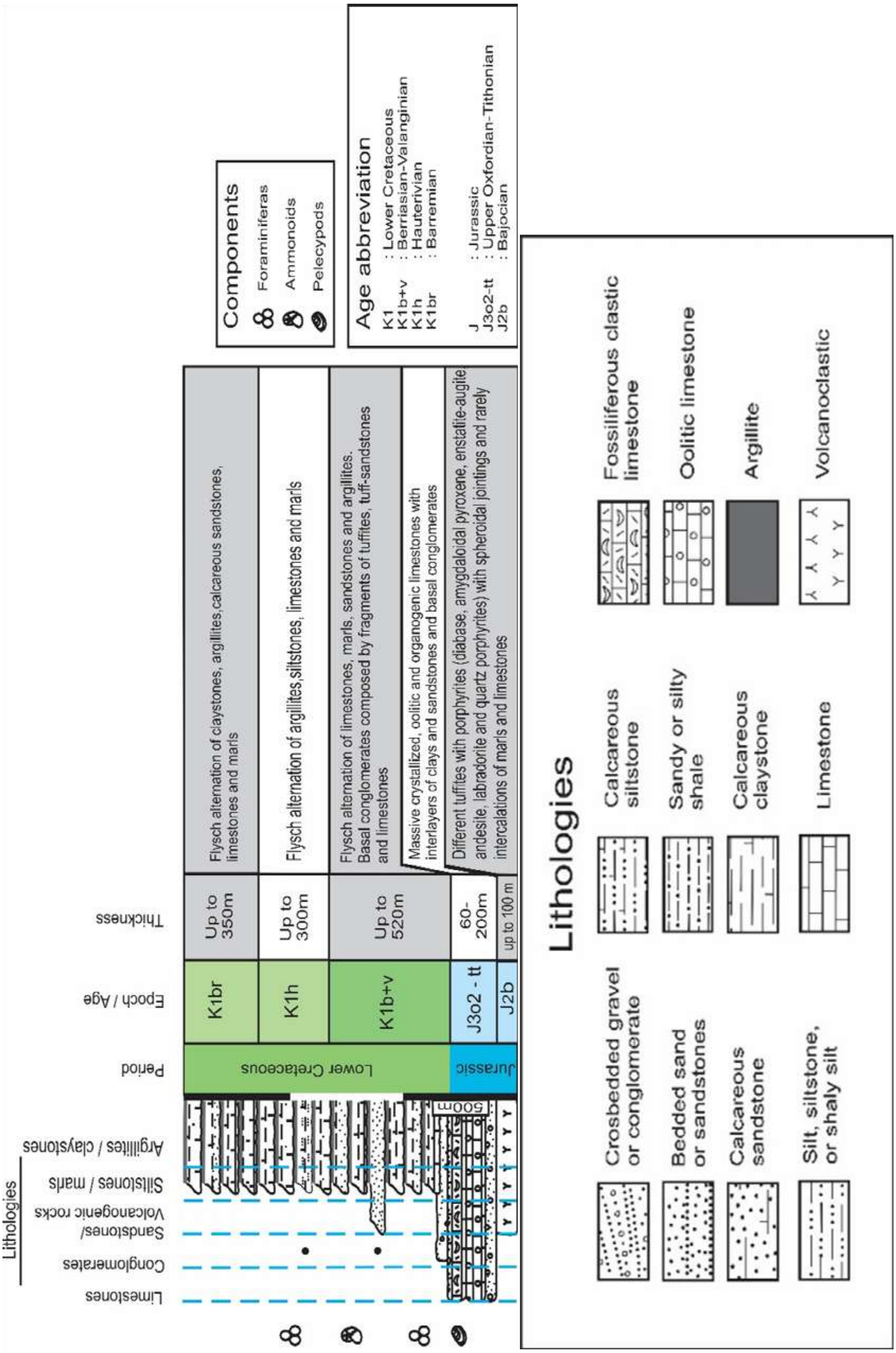

Fig. 2. Lithostratigraphic column of the Lower Cretaceous deposits of the Vandam zone (Alizadeh et al., 2005b)

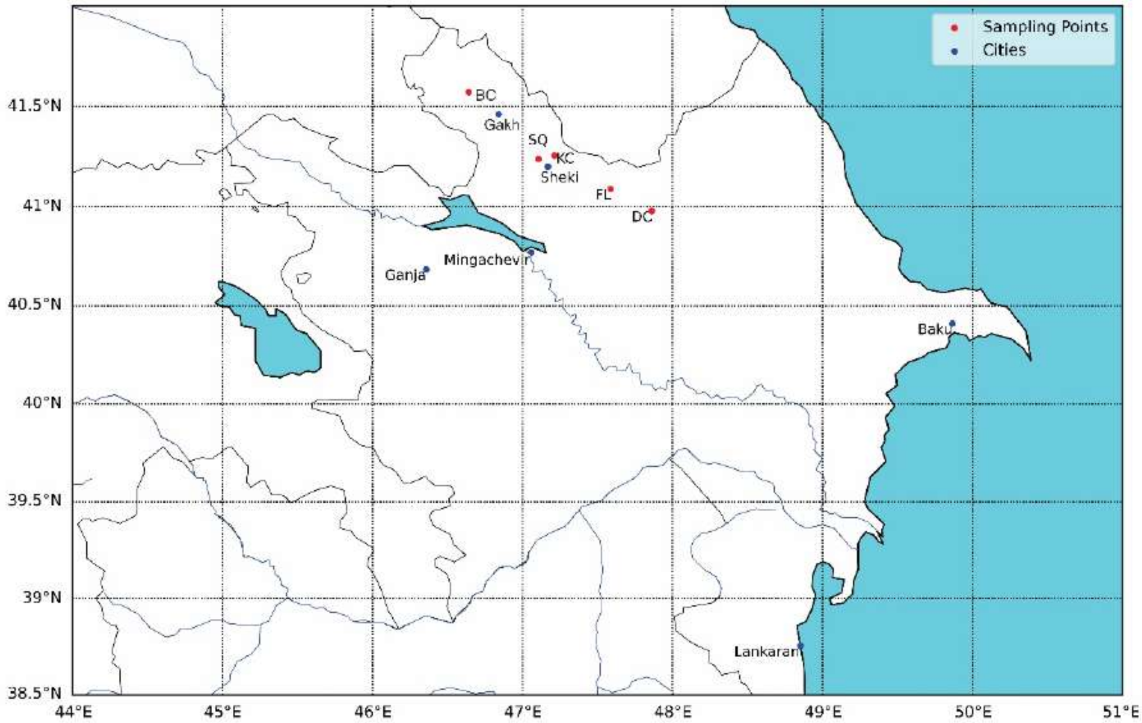

Fig. 3. Location map showing sampling points for the datasets used in the present work

The presence of matrix material, both detrital and pseudo matrix, is quite evident in the samples. Consequently, the classification system proposed by Crook (1974) was employed. Given that the matrix content exceeds 15%, the samples are classified as greywacke.

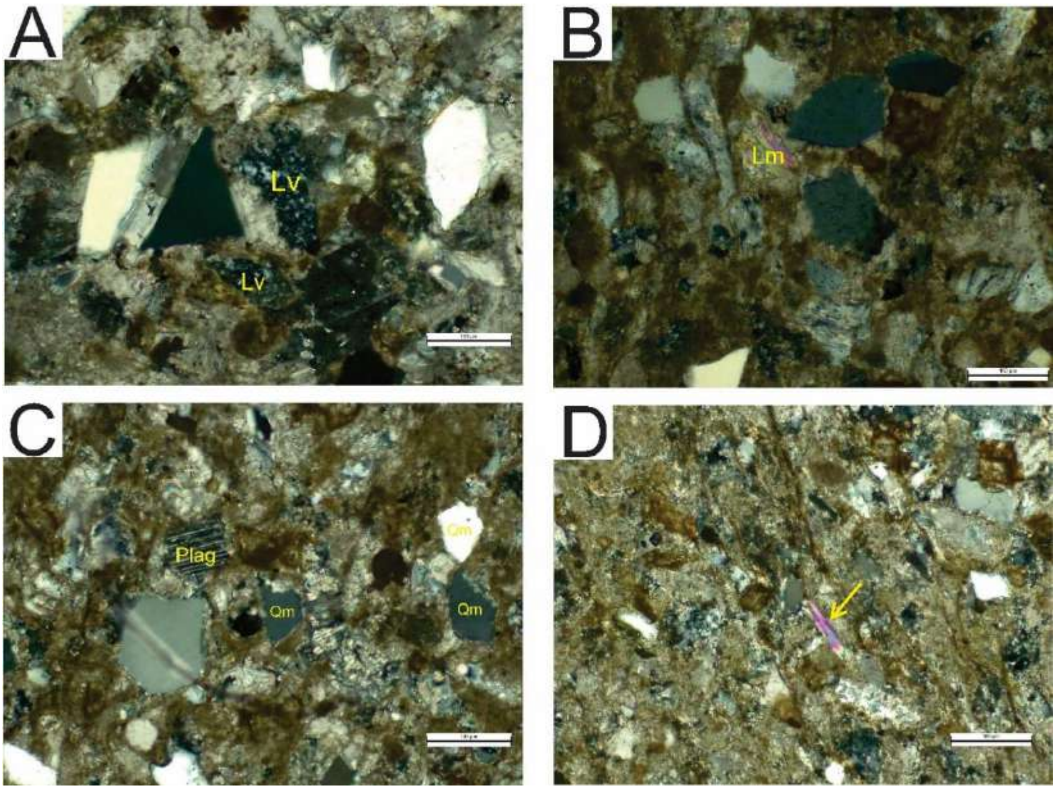

Fig. 4. Photomicrographs (in XPL) of thin-sectioned sandstones of the Kepuch and Gyrkhbulag formations showing: (**A**) angular to subangular monocrystalline quartz grains (Qm) and plagioclase (Plag); (**B**) metamorphic lithic fragment (Lm); **(C)** felsic volcanic lithic fragment (Lv); (**D**) detrital muscovite (yellow arrow)

Whole-rock geochemistry

The major oxide- and trace-element concentrations of the analysed rocks are given in the Table.

Kepuch Formation. The content of SiO_2 ranges from 55.61 to 79.27 wt.% with an average of 65.51 wt.% similar to that of UCC (Upper Continental Crust) (Taylor, McLennan, 1985). The average content of Al_2O_3 is moderately high (about 9.09 wt%) ranging from (6.41 to 10.36 wt%). K_2O and Na_2O contents range from 1.21wt% to 2.08 wt% and 0.55 wt% to 2.06 wt%, with average values of 1.58% and 1.09%, respectively. These clastic rocks are also characterized by variable amounts of CaO (2.63-13.64 wt%), MgO (1.39-1.96 wt%), and Fe_2O_3 (3.34-4.39 wt%). The positive correlation of Al_2O_3 with Fe_2O_3 (R=0.54) and TiO_2 (R=0.72) (Fig. 5A, B) indicates that these elements are present in clay minerals resulting from weathering processes. Concentrations of trace elements in sandstones of Kepuch Formation (Table) are generally lower than the average upper continental crust (UCC) concentrations. The average concentrations of Sc (13.59 ppm), Ba (534 ppm) and Cs (4.69 ppm) are close to the average values of UCC.

Major (wt %) and trace (ppm) elements concentration of the samples of Kepuch and Gyrkhbulag Formations

Formation	Kepuch Formation						Gyrkhbulag Formation					
Sample no.	SQ-1	KC-1	KC-3	DC-1	DC-3	DC-4	BC-1	FL-1	FL-2	FL-3	UCC*	PAAS*
SiO_2	67.70	55.61	63.82	66.33	79.27	60.33	61.41	68.69	70.14	69.98	65.89	62.9
TiO_2	0.45	0.45	0.45	0.36	0.28	0.46	0.66	0.69	0.58	0.66	0.50	0.99
Al_2O_3	9.52	9.24	10.36	9.97	6.41	9.02	17.55	14.02	10.71	12.91	15.17	18.9
Fe_2O_3	3.55	3.71	4.39	3.53	3.34	4.22	6.56	5.40	6.65	4.50	4.49	7.22
MnO	0.03	0.08	0.05	0.10	0.12	0.13	0.05	0.01	0.06	0.06	0.07	0.11
MgO	1.79	1.69	1.96	1.39	1.49	1.61	2.90	1.35	1.73	1.71	2.20	2.20
CaO	5.86	13.64	7.38	6.78	2.63	10.04	0.43	0.17	1.10	1.08	4.19	1.29
Na_2O	0.76	1.79	2.06	0.81	0.55	0.58	1.28	1.24	1.28	1.42	3.89	1.18
K_2O	2.08	1.24	1.28	1.71	1.21	1.96	3.66	2.42	1.57	2.19	3.39	3.70
P_2O_5	0.08	0.12	0.13	0.07	0.05	0.09	0.11	0.12	0.12	0.11	0.20	0.16
LOI	8.17	12.42	8.12	8.95	4.66	11.58	5.38	5.88	6.06	5.37	-	-
Sc	13.90	11.87	11.60	14.79	14.19	15.20	21.63	18.40	16.89	16.63	13.6	16
V	89.09	62.90	63.03	103.56	77.02	86.99	165.83	165.13	110.82	139.50	107	130
Cr	47.05	39.74	34.60	41.36	32.05	41.25	87.16	83.44	75.89	72.27	85	110
Co	16.56	11.06	11.30	13.20	13.38	15.36	19.03	4.39	17.87	16.65	17	23
Ni	37.08	32.32	41.16	26.19	27.06	32.95	62.53	23.87	57.53	51.74	44	55
Cu	14.54	15.02	17.01	61.98	34.78	64.19	47.25	48.51	44.84	45.35	25	50
Zn	55.56	60.61	75.53	65.52	53.22	57.47	134.38	63.80	138.38	90.05	71	85
Rb	94.07	53.26	52.23	76.49	54.70	84.83	166.17	117.91	76.75	107.27	112	160
Sr	143.40	488.02	335.03	609.42	79.39	129.09	59.02	70.28	74.54	84.57	350	200
Zr	106.00	131.73	104.84	73.50	55.78	84.60	141.06	171.22	272.17	184.02	190	210
Cs	5.66	4.35	4.46	5.36	3.57	4.75	8.25	8.92	4.62	7.74	4.6	9.3
Ba	211.74	328.01	242.46	1208.43	619.72	596.55	418.54	426.20	234.42	315.47	550	650
Pb	15.14	12.13	14.36	13.69	8.33	25.46	28.66	19.26	15.63	20.34	17	20
Th	7.23	6.12	6.16	5.64	3.86	4.10	10.40	8.72	7.94	9.73	10.7	14.6
U	1.59	1.60	1.32	1.21	0.98	0.78	1.90	3.75	3.15	3.40	2.8	3.1

*Taylor and McLennan (1985, 1995)
PAAS (Post-Archean Australian Shale)
UCC (Upper Continental Crust)

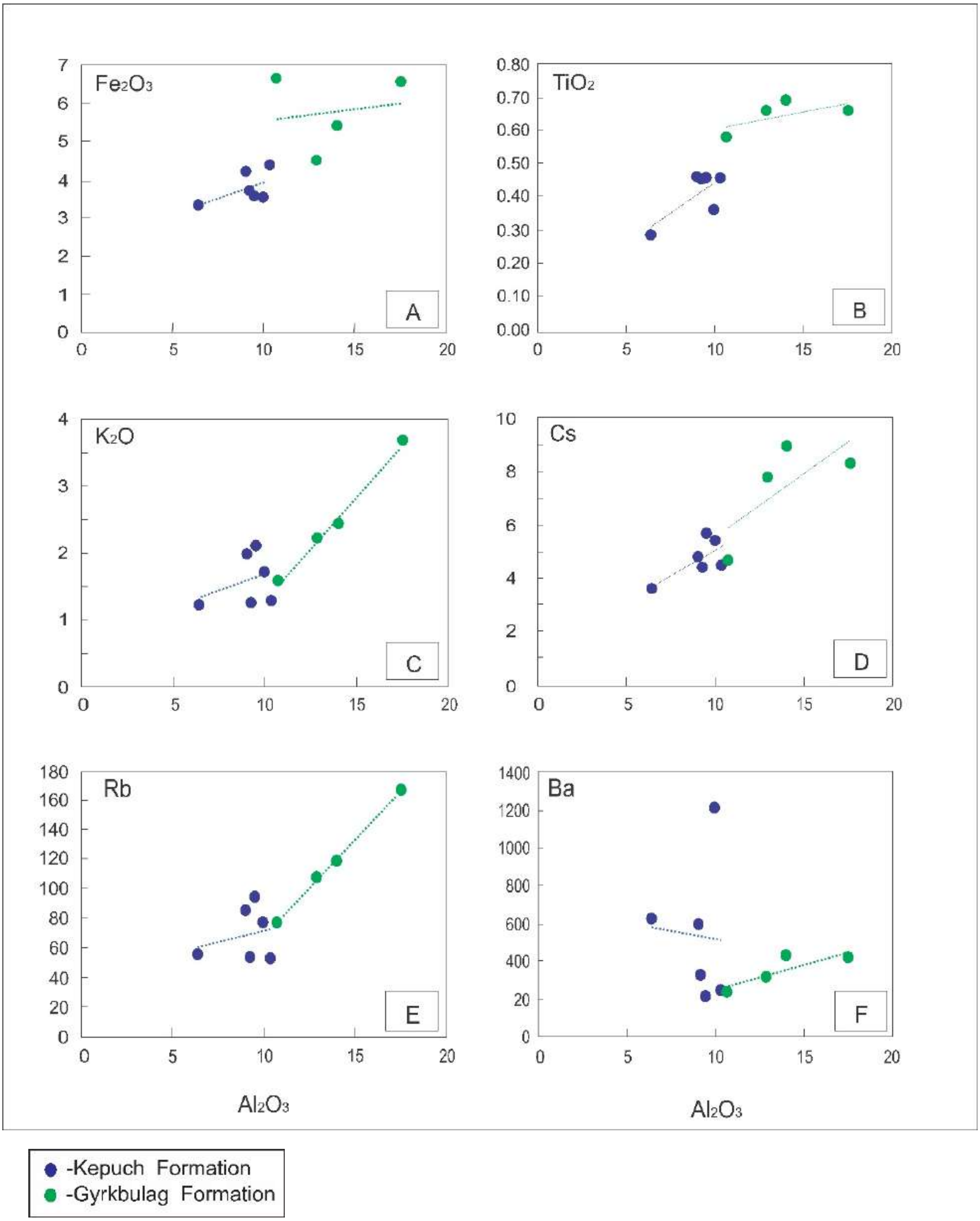

Fig. 5. Al_2O_3 vs. major oxides covariation diagrams (**A-C**); Al_2O_3 vs. trace elements covariation diagrams (**D-F**)

Gyrkhbulag Formation. SiO_2, Al_2O_3, and Fe_2O_3 are the predominant oxides, with their contents varying from 61.41% to 70.14%, 10.71% to 17.55%, and 5.40% to 6.65%, respectively. The concentrations of MgO, Na_2O and K_2O are mostly similar, with ranges of 1.35-2.90 wt.% (average 1.92 wt.%), 1.24-1.42 wt.% (average 1.31 wt.%), and 1.57-3.66 wt.% (average 2.46 wt.%), respectively. Meanwhile, the levels of TiO_2, CaO and P_2O_5 are generally low, ranging from 0.58 to 0.69%, 0.17 to 1.10%, 0.11 to 0.12%, respectively. The positive correlation

(R=0.99) between Al_2O_3 and K_2O (Fig. 5C) suggests that potassium serves as a significant trace component in clay minerals. Compared to the Upper Continental Crust (UCC), the samples of Gyrkhbulag Formation are moderately enriched in Sc, V, Cs, and show a moderate to extreme depletion in Ba and Sr respectively. Al_2O_3 shows a strong positive correlation with Cs (R=0.72), Rb (R=0.99) and Ba (R=0.84) (Fig. 5 D-F). This suggests that phyllosilicates play a key role in determining the concentrations of Large Ion Lithophile Elements (LILE).

Geochemical classification

Pettijohn et al. (1972) and Herron (1988) developed classification schemes based on geochemical characteristics to categorize sedimentary rocks. By employing classification diagram after Herron (1988) (Fig. 6A), it was concluded that the majority of analysed samples fall within the wacke classification field, suggesting immaturity. According to the classification scheme by Pettijohn et al. (1972) depicted in Figure 6B, the studied samples are primarily categorized within the litharenite field, with a few samples falling into the arkose field.

Maturity and paleoclimate

The compositional maturity primarily reflects the weathering process occurring in the source area and the extent of reworking/recycling, and transportation. Sediments classified as compositionally immature are typically located close to their source area or have undergone rapid transportation and deposition with minimal reworking from the source area characterized by limited physical and chemical weathering (Oni, Olatunji, 2017).

Sediment maturity is assessed through two distinct aspects: textural and mineralogical maturity, each characterized by different properties (Boggs, 2009; Nichols, 2015). Textural maturity focuses on the characteristics of the grains and their degree of sorting, while mineralogical maturity is determined by the presence of resistant minerals like quartz and zircon and the relative scarcity of more easily weathered minerals such as feldspars and ferromagnesian phases (Eric et al., 2021). Mature sediments present a uniform appearance with minimal compositional variability, contrasting with immature sediments, which are characterized by angular grains, various grain sizes, and significant compositional diversity (Boggs, 2006). The petrographic analyses show that the studied samples are immature mineralogically because of high content of rock fragments and scarcity of well-rounded quartz minerals, suggesting limited weathering and transportation processes.

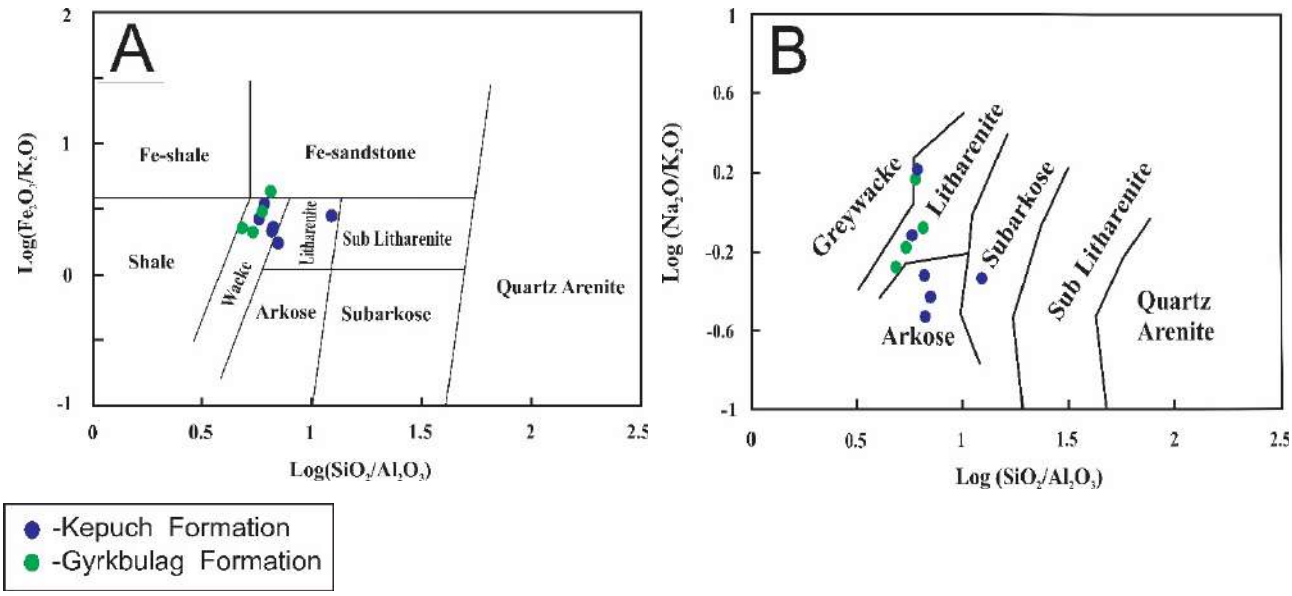

Fig. 6. Geochemical classification of samples (**A**) log ratios of SiO_2/Al_2O_3 – Fe_2O_3/K_2O (Herron, 1988); (**B**) log ratios of SiO_2/Al_2O_3 – Na_2O/K_2O (Pettijohn et al., 1972)

The petrographic results are further supported by various geochemical indicators, including the SiO_2/Al_2O_3 ratio and the Index of Chemical Variability (ICV). The SiO_2/Al_2O_3 ratios in clastic rocks are highly affected by processes such as sediment recycling and weathering, thus serving as reliable indicator of sediment maturity. Higher SiO_2/Al_2O_3 ratios in sandstone suggest the presence of mineralogically mature, quartz-rich sediments, while lower ratios indicate chemically immature sediments (Potter, 1978). In average volcanic rocks, the SiO_2/Al_2O_3 values typically lie in the narrow range, from around 3 in basic rocks (gabbros and basalts) to around 5 in acidic end members such as granites and rhyolites. Values more than 5 or 6 indicate that sedimentary rocks underwent recycling and became more mature (Roser and Korsch, 1986; Roser et al., 1996). The SiO_2/Al_2O_3 ratios of the sandstones vary from 3.49 to 12.36 (average 6.53). Low values of SiO_2/Al_2O_3 indicate that sandstones are mineralogically immature.

The Index of Compositional Variability (ICV) suggested by Cox et al. (1995), is a geochemical tool used to evaluate the compositional maturity of clastic sedimentary rocks. Since clay minerals and nonclay minerals are characterized by very different proportions of alumina, Cox et al. (1995) defined a ratio to measure the abundance of alumina relative to the other major cations in a rock or mineral. The ICV calculation involves the molar amounts of major oxides present in a rock or mineral.

$$ICV=(Fe_2O_3+TiO_2+K_2O+Na_2O+CaO^*+MgO+MnO)/Al_2O_3$$

CaO* is the amount in silicates

Sandstones which are more mature and predominantly composed of clay minerals exhibit lower ICV values, typically less than 1. This is because clay minerals are products of extensive weathering and thus indicate a higher degree of sediment maturity. In contrast, immature sandstones with a higher proportion of feldspars and other unstable minerals will have higher ICV values, indicating mild to moderate degree of weathering and lower sediment maturity. The ICV decreases further in the montmorillonite group clay minerals and lowest in the kaolinite group minerals (Baiyegunhi et al., 2017). The higher ICV values (more than 1) for most samples indicate poor maturity, which is also supported by their weak chemical weathering. In a plot of ICV versus CIA (Chemical Index of Alteration) as shown in Fig. 7A (after Long et al., 2012) the studied samples (except for DC-4) are plotted in immature and weak weathering fields, suggesting that recycling has a negligible impact on CIA values and these values can effectively reflect the paleoweathering conditions.

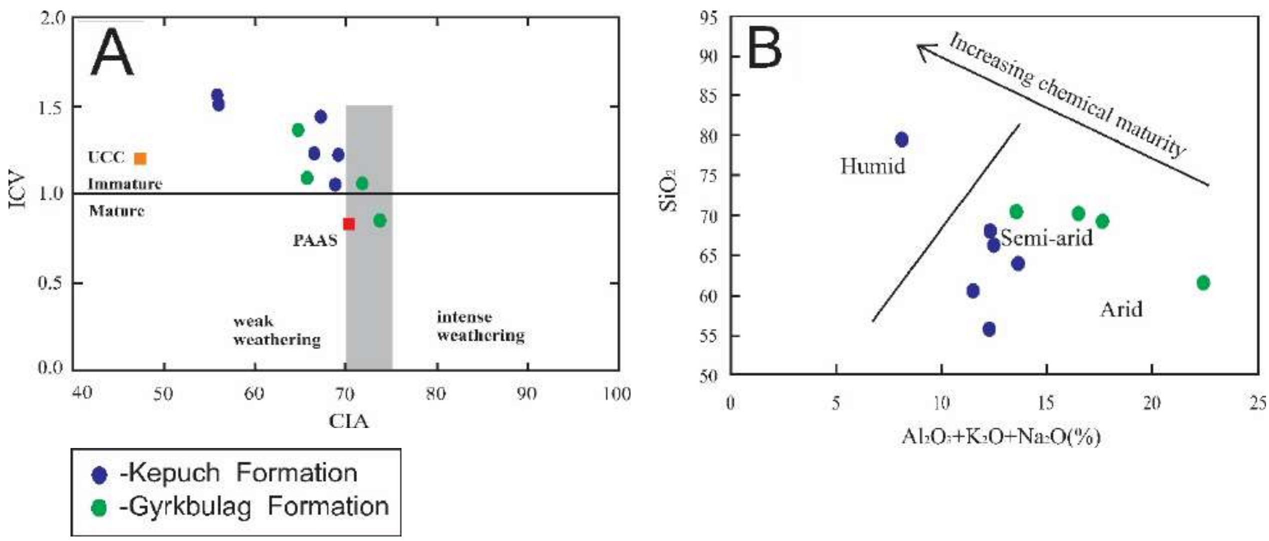

Fig. 7. (**A**) CIA (Chemical Index of Alteration) versus ICV (Index of Compositional Variability) plot displays the intensity of weathering and maturity of the sandstones of both the Kepuch and Gyrkhbulag Formations (after Long et al., 2012); (PAAS-Post-Archean Australian Shale; UCC-Upper Continental Crust) (**B**) Paleoclimate discriminant diagram, after Suttner and Dutta (1986)

The degree of weathering and composition of detritus are also affected by climatic conditions (Suttner and Dutta, 1986). Accordingly, the relationship between SiO_2 and $Al_2O_3+K_2O+Na_2O$ indicates that the studied rock formations have experienced arid and semi-arid climatic conditions with a low-medium chemical maturity (Fig. 7B).

Source area weathering, recycling and sorting

Chemical weathering plays a crucial role in driving interelemental fractionation, resulting in elemental ratios that differ from those of the source rocks. The intensity and degree of chemical weathering in clastic rocks can be obtained by the calculation of various indices including chemical index of alteration (CIA), plagioclase index of alteration (PIA) and chemical index of weathering (CIW) (Nesbitt and Young, 1982, 1984; Fedo et al., 1995; Harnois, 1988).

The Chemical Index of Alteration (CIA) introduced by Nesbitt and Young (1982) is the most accepted among weathering indices. The CIA value increases in response to more intense chemical weathering and a greater abundance of residual clays, including illite, chlorite, kaolinite, and gibbsite. Elevated CIA values indicate strong weathering or recycling under warm and humid paleoclimatic conditions, characterized by the depletion of readily soluble cations such as Ca^{2+}, Na^{+}, K^{+} in favor of less soluble cations like Al^{3+} and Ti^{4+}. Conversely, low CIA values suggest minimal or almost no chemical weathering, typically indicative of cool and/or arid environmental conditions. The CIA is expressed as CIA= $[Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O)]x100$, where Al_2O_3, CaO, Na_2O, and K_2O are in molar proportions, and CaO* is the amount in silicates. The effect of carbonate minerals has been ruled out in CIA, which mainly reflects the weathering intensity of silicate minerals, so it can well reflect the chemical weathering of the source area. The CIA values of Lower Cretaceous deposits ranging from 55.9 to 73.7 indicate a range from weak to moderate degrees of chemical weathering at the source.

CIA values can also be plotted graphically on a Al_2O_3-($CaO+Na_2O$)-K_2O (A-CN-K) diagram to evaluate weathering trends and the effects of K-metamorphism more effectively. In addition, the A-CN-K diagram allows for the constraining of the primary composition of the source rocks (Nesbitt and Young, 1982, 1984; Fedo et al., 1995). The studied samples plot along the ideal weathering line for granodiorite towards the illite composition, and do not indicate any evidence of K-metasomatism (Fig. 8).

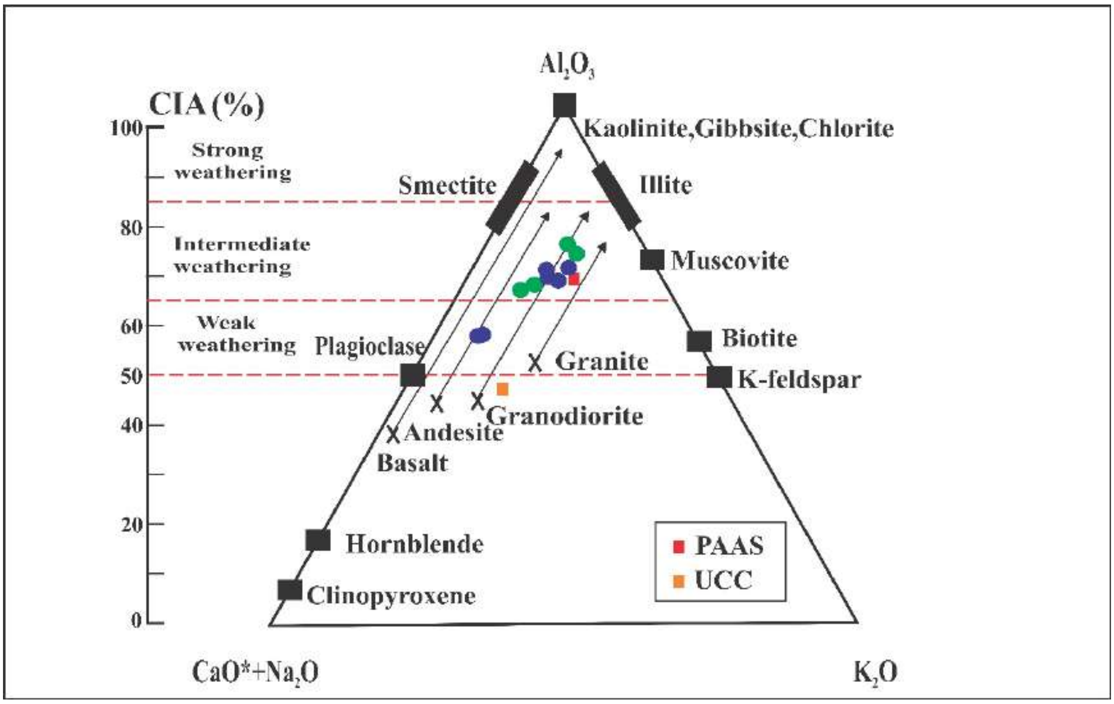

Fig. 8. The A-CN-K ternary plot of the samples; Al, Al_2O_3; CN, $CaO^* + Na_2O$; K, K_2O (oxides are plotted as molar); (PAAS-Post-Archean Australian Shale; UCC-Upper Continental Crust)

The impact of weathering can also be evaluated by examining the molecular percentages of oxide components through the Chemical Index of Weathering (CIW) proposed by Harnois (1988). Similar to CIA, the CIW also measures the degree of chemical weathering and conversion of feldspar into clays (Nesbitt and Young, 1984, 1989; Fedo et al., 1995; Maynard et. al., 1995). It is defined as: CIW=[Al_2O_3/(Al_2O_3+CaO*+Na_2O]x100, where Al_2O_3, CaO, and Na_2O are in molar proportions and CaO* is restricted to the amount of CaO in the silicate fraction only. This index is alike CIA except to the elimination of K_2O. This exclusion accounts for the leaching of potassium or its gathering within the weathering products during sedimentation processes. Due to its higher ion exchange capacity, it is more readily accommodated by clay minerals compared to Na^+ and Ca^+ (Kroonenberg, 1994). The CIW precludes the issues related to the remobilization of K during diagenesis or metamorphism. Both CIA and CIW values are similarly interpreted, with the values ~50 representing unweathered upper continental crust and values close to 100 for highly weathered materials (i.e. kaolinite and gibbsite). The CIW values of samples, varying between 60 and 85 with an average of 75, suggest low to moderate levels of weathering of the source materials, consistent with the CIA.

The Plagioclase Index of Alteration (PIA), introduced by Fedo et al. (1995), serves as an alternative to the Chemical Index of Weathering (CIW). PIA specifically focuses on the destruction of plagioclase feldspar, a common mineral in silicate rocks, and is used when plagioclase weathering alone needs to be monitored. Unweathered plagioclase has a PIA value of 50 and the maximum of PIA is 100 for completely altered materials. The PIA is calculated using the relationship: PIA=[(Al_2O_3-K_2O)/(Al_2O_3+CaO*+ Na_2O-K_2O)]x100, where CaO* is limited to the amount of CaO incorporated in silicate fraction only while the oxide amounts are expressed in moles. The PIA values for the studied samples ranged between 56.9 and 82.8, with an average of 72.1, suggesting low to moderate degrees of chemical weathering.

In addition to weathering in the source area, recycling of previously deposited sediments can significantly alter their geochemical signature, complicating the interpretation of their original source and depositional history. (Weltje and von Eynatten, 2004). The Zr/Sc ratio is employed to identify zircon enrichment resulting from sedimentary recycling, given that Zr is significantly enriched in zircon mineral, while Sc tends to be retained by clay particles during the recycling process. On the other hand, the Th/Sc ratio is a reliable chemical indicator of igneous differentiation, as Th is regarded as an incompatible element in most igneous processes, whereas Sc typically behaves compatibly. The Th/Sc vs. Zr/Sc diagram is an effective tool for distinguishing between samples with compositional variability and those enriched in Zr due to sedimentary recycling. During the sedimentary recycling, Zr/Sc and Th/Sc ratios of the first-order sediments form a simple positive correlation along the composition evolution line. In contrast, recycled sediments demonstrate Zr/Sc increasing substantially, with Th/Sc increasing far less, consistent with zircon enrichment (McLennan et al., 1993). In this regard, all the analysed samples follow a general trend consistent with their direct derivation from igneous rocks. The Th/Sc ratio values of the samples (0.26-0.58, average 0.44) are relatively low, indicating that the source rocks were not altered by obvious sedimentary recycling.

McLennan et al. (1993) employed the Rb/Sr and Th/U ratios as a tool to trace the weathering conditions and recycling processes experienced by sedimentary rocks. Due to its similar ion radius to K^+, Rb^+ tends to be homogeneously distributed within minerals that contain potassium, such as biotite, muscovite, and K-feldspar, in various rock formations. During the process of supergene weathering, these potassium-rich minerals are decomposed, releasing Rb. The released Rb tends to be adsorbed by clay minerals rich in potassium, with only a small part being transported or leached away. These characteristics limit the extent of Rb's leaching and migration into soil during weathering processes (Fei et al., 2017). Sr is another example of a typically dispersed element. Its ionic radius of 112 picometers (PM) positions it between that of Ca^{2+} (99 PM) and K^+ (123PM). As a result, Sr^{2+} is often found as a trace element in minerals such as calcite, plagioclase, K-feldspar, and mica. Due to Sr^{2+}'s geochemical behaviour being more closely aligned with that of Ca^{2+} in the supergene environment, Sr^{2+} tends to migrate more readily with soil solutions or surface water, primarily in its carbonate form. Consequently, a considerable amount of Sr in the formation can be leached away as a result. The high values (1.02-2.81), characteristic of the Gyrkhbulag Formation, presumably reflect moderate weathering, supported by similar variation in the CIA proxy. The rest show Rb/Sr values ranging from 0.10 to 0.68, indicating lesser degree of weathering in the source area. A positive correlation (R=0.87) between Rb/Sr and 1/Sr ratios suggests that variations in the Rb/Sr ratios are primarily influenced by the activity of Sr during the weathering process (Jin et al., 2006).

Sedimentary recycling under oxidizing conditions typically leads to the fractionation of thorium (Th) and uranium (U), as U^{4+} is easily oxidized to the more soluble U^{6+} during the weathering process. The dissolution and loss of uranium (U) can lead to increased thorium to uranium (Th/U) ratios in sediments. Typically, upper continental crust (UCC) Th/U values range from 3.5 to 4. Therefore, Th/U ratios greater than 4.0 indicate that the source rocks have undergone sedimentary recycling. The Th/U ratios in Neocomian rocks, which range from 2.32 to 5.48 with an average of 4.0, suggest that these sediments have started to experience sedimentary recycling (McLennan, 1993). Hence, it can be deduced from Fig. 9 (A) and (B) that the Neocomian sediments derived directly from igneous rocks, which had experienced low to moderate degrees of weathering and no significant sediment recycling.

The Al_2O_3-TiO_2-Zr plot is used to monitor the effects of sorting processes and zircon concentration in sediments. Interpretation of compositional variation for these three elements assumes that sedimentation involves weathering, transport, mixing from different sources and sorting. In the first three processes, the contents of less soluble elements such as Al, Ti and Zr may vary in response to the degree of leaching of the soluble elements. However, their relative proportions are preserved from the source area to bulk sediment without, or with little, modification. This material is then sorted according to the hydraulic properties of its constituent minerals, leading to a chemical differentiation between shales and sandstones. In fact, the ternary diagram eliminates the impact of weathering and focuses on highlighting the effects of sorting processes. On this diagram, sediments exhibiting a wide range of TiO_2/Zr variations are indicative of high compositional maturity, while immature clastic rocks, on the contrary, have a more limited range of TiO_2/Zr variations (Garcia, 1994). The limited range of TiO_2/Zr variations observed in the samples suggests that they likely originate from ill-sorted, rapidly deposited sediments derived from a less weathered source (Fig. 10).

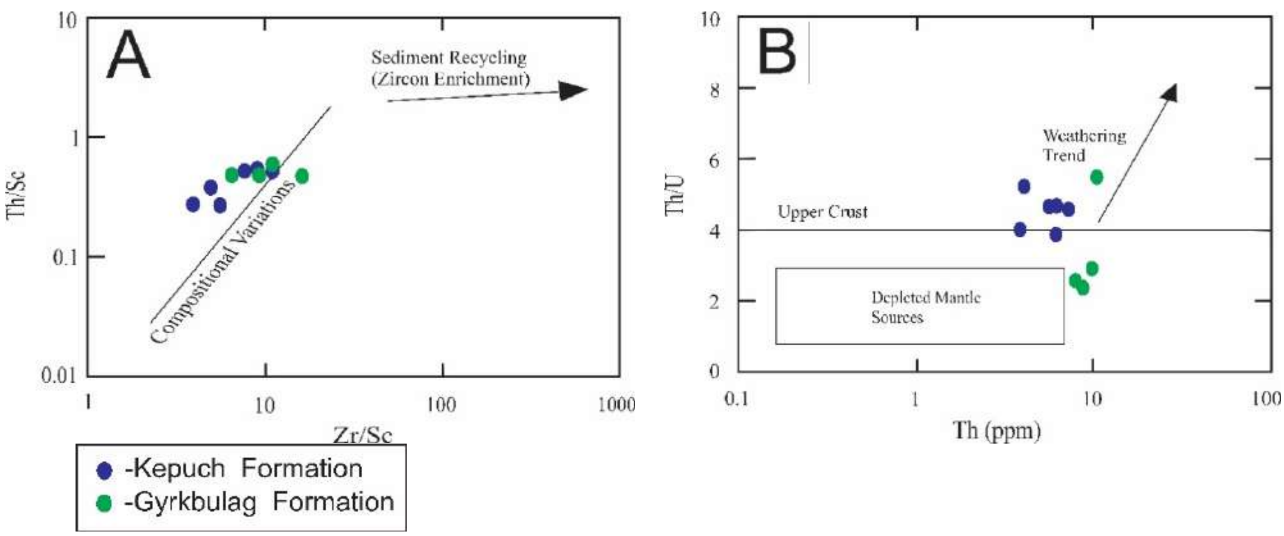

Fig. 9. Discrimination diagrams illustrating the influence of weathering and sediment recycling. (**A**) Th/ Sc versus Zr/Sc; (**B**) Th/U versus Th; Diagrams after McLennan (1993).

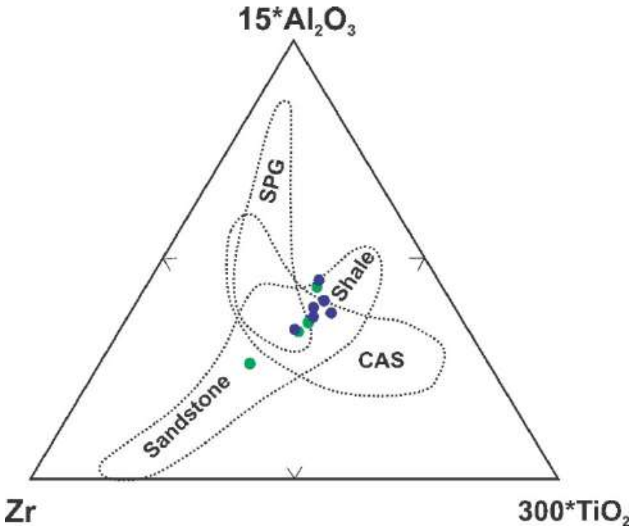

Fig. 10. Al_2O_3-TiO_2-Zr 'immobile element' diagram showing typical fields for some rock types (SPG and CAS are fields for strongly peraluminous granite and calc-alkaline igneous suites respectively; from Garcia et al., 1994)

Conclusion

Based on petrographic and geochemical composition of the Lower Cretaceous (Neocomian) deposits of the Vandam zone the following conclusions can be drawn. The sandstones are fine to medium grained, angular to sub-rounded, and moderately sorted. They show a low textural and mineral maturity. According to geochemical classification diagrams, the studied samples are identified as wackes and litharenites. However, considering the matrix content exceeds 15%, they are more accurately classified as greywackes. Chemical Index of Alteration (CIA) values for the analyzed sandstones range from 55.9 to 73.7, indicating a low to moderate level of chemical weathering in their source areas. Furthermore, the Chemical Index of Weathering (CIW) and the Plagioclase Index of Alteration (PIA) ratios support the interpretation that the sediments from the source areas experienced low to moderate degrees of weathering before deposition in the basin. The SiO_2/Al_2O_3 ratio, along with the Th/U, Zr/Sc, Th/Sc, and Al_2O_3-TiO_2-Zr plots, reveal that the samples have low compositional and mineralogical maturity, and minerals did not undergo obvious fractionation and sedimentation recycling, representing the first sedimentation of tectonic active zones. This conclusion is further supported by Index of Compositional Variability (ICV) values exceeding 1. Based on paleoweathering proxies and the SiO_2 vs. Al_2O_3+Na_2O+K_2O paleoclimate discriminant diagram, it can be inferred that the studied area was influenced by arid to semi-arid climatic conditions.

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ПЕТРОГРАФИЯ И ГЕОХИМИЧЕСКАЯ ХАРАКТЕРИСТИКА НИЖНЕМЕЛОВЫХ ОТЛОЖЕНИЙ ВАНДАМСКОЙ ЗОНЫ (ЮЖНЫЙ СКЛОН БОЛЬШОГО КАВКАЗА, АЗЕРБАЙДЖАН): ЗРЕЛОСТЬ, ПАЛЕОКЛИМАТ И ПАЛЕОВЫВЕТРИВАНИЕ

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Резюме. В данной статье приводится подробный петрографический и геохимический анализ нижнемеловых отложений южного склона Большого Кавказа (Вандамская зона). Цель данной работы – оценить зрелость вещественного состава пород путем исследования кремнисто-обломочных пород кепучской и гырхбулагской свит и реконструировать палеоусловия, включая палеоклимат и палеовыветривание. Петрографический анализ выявил, что эти отложения характеризуются плохой сортировкой обломочного материала и состоят из угловатых и полуугловатых зерен, что свидетельствует об их формировании вблизи источника сноса. Минералогическая зрелость осадков оценивалась с помощью индекса зрелости осадков (ICV), а интенсивность выветривания – по индексу химической изменчивости (CIA), химическому индексу выветривания (CIW) и индексу изменения плагиоклазов (PIA). Установлено, что согласно геохимической классификации отложения соответствуют лититовым аренитам и грауваккам. Диаграмма Al_2O_3–(CaO* + Na_2O)–K_2O (A–CN–K) наряду с индексами химического выветривания указывают на низко-умеренное выветривание в районе источника, что соответствует аридным и полуаридным климатическим условиям исследуемого района. С другой стороны, значения индекса зрелости осадка (ICV), варьирующиеся в пределах от 0.9 до 1.59, свидетельствуют и низкой зрелости вещественного и минералогического состава терригенных отложений. Кроме того, дискриминационные диаграммы Zr/Sc-Th/Sc и Al_2O_3-Zr-TiO_2 показывают, что осадки не подвергались рециклингу и гидравлической сортировке.
Ключевые слова: *зрелость, палеоклимат, палеовегетация, ICV, CIA, PIA, CIW, рециклинг, сортировка*

VƏNDAM ZONASININ (BÖYÜK QAFQAZ, AZƏRBAYCANIN CƏNUB YAMACI) ALT TƏBAŞİR ÇÖKÜNTÜLƏRİNİN PETROQRAFİKASI VƏ GEOKİMYƏVİ XÜSUSİYYƏTLƏRİ: YETKİNLİK, PALEOİQLİM VƏ PALEOAŞINMA

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Xülasə. Məqalədə Böyük Qafqazın cənub yamacının (Vəndam tektonik zonası) Alt Təbaşir çöküntülərinin petroqrafik və geokimyəvi göstəriciləri əsasında Kepuç və Qırxbulaq formasiyalarının terrigen süxurlarının yetkinliyi, paleoiqlim və paleoaşınma şəraitləri öyrənilir. Petroqrafik təhlil zamanı müəyyən olunmuşdur ki, bu çöküntülər qırıntı materialın zəif çeşidlənməsi ilə xarakterizə olunur. Qırıntıların bucaqlı və yarımbucaqlı olması onların yaxın terreynlərdən gətirildiyini göstərir. Çöküntülərin mineraloji yetkinliyi tərkibcə dəyişkənlik indeksidən (ICV), aşınma xüsusiyyətləri isə kimyəvi dəyişkənlik indeksi (CIA), kimyəvi aşınma indeksi (CIW) və plagioklaz dəyişkənlik indeksindən (PIA) istifadə etməklə qiymətləndirilmişdir. Aparılmış geokimyəvi təsnifata görə çöküntülərin litarenitlərə və qrauvaklara uyğun olduğu müəyyən edilmişdir. Al_2O_3-(CaO+Na_2O)-K_2O (A-CN-K) diaqramı kimyəvi aşınma indeksləri ilə birlikdə mənbə sahəsindəki quraqlıq və yarımquraqlıq iqlim şəraitinə uyğun olaraq zəif və mülayim aşınmanı göstərir. Digər tərəfdən, “ICV”nin 0,9-1,59 diapazonunda dəyişməsi çöküntülərin maddi və mineraloji tərkibinin zəif yetkinliyinin indikatorudur. Bundan başqa, Zr/Sc-Th/Sc və Al_2O_3-Zr-TiO_2 kimi diskriminant diaqramlar çöküntülərin təkrar çökmədiyini və hidravlik çeşidlənməyə məruz qalmadığını ifadə edir.
Açar sözlər: *yetkinlik, paleoiqlim, paleoaşınma, ICV, CIA, PIA, CIW, təkrar sedimentasiya, çeşidlənmə*