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RESEARCH ARTICLE

**GEOCHEMISTRY OF TRIASSIC SANDSTONES (HIGH ATLAS OF MARRAKECH, MOROCCO):
IMPLICATIONS FOR PROVENANCE, WEATHERING, AND TECTONIC SETTING.**

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The geochemical composition of fifteen fresh Triassic sandstone samples from two localities (Oukaimeden and Ourika Valley, Morocco) was carried out, in order to assess their provenance, weathering and tectonic setting. These sandstones are classified as litharenites and wackestones. The CIA (Chemical Index of Alteration; mean value GK= 57.6 and GI = 71.77) values and Al_2O_3 - CaO +Na₂O-K₂O suggest that the source materials for these sandstones must have been subjected to low and moderate degree of weathering and reworking. Sandstones from studied areas had a high SiO₂ content in the range of 62-82% due to their mineralogical maturation. However, the negative correlation between SiO₂ content and the other major elements proposes another contribution of silica. AIT KEJOU sandstones show the presence of a small amount of clay minerals than IGHHERMANE sandstones. The Upper Continental Crust (UCC) and North American Shales (NAS) normalization showed depletion in light rare earth elements (LREE) and enrichment in HREE. The negative europium (Eu/Eu*) anomaly support a felsic rocks provenance of the studied sandstones. The cerium (Ce/Ce*) anomaly indicated an oxidizing depositional environment. The depletion in LREE in relation to the HREE and low La/Lu ratio values suggest that the sandstones are as a result of fluvial/river channel system with a slight sea contribution. According to the provenance discrimination diagram, the sandstones were derived from the adjacent Cambrian basement units of Tifnout granitic massif, associated andesites and the granodiorites of the Precambrian basement units of Central High Atlas, located to the south of the studied areas. Discrimination diagrams suggested a passive margin tectonic setting for AIT KEJOU sandstones and an active continental margin tectonic setting for the IGHHERMANE sandstones.

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Introduction:-

The Triassic formation of Marrakech High Atlas including structural evolution (Petit and Beauchamp, 1986; Manspeizer, 2015), sedimentology, the architectural style and a detailed stratigraphy of their specific formation (Benaouiss et al., 1996; Kayser, 2005; Fabuel-Perez et al., 2010) have been studied by many authors. These outcrops provided in the valley of Ourika-Oukaimeden have an excellent exposures to investigate the respective roles played by the tectonic and climate on the filing of continental sediments (Baudon et al., 2009).

The geochemical composition of the sedimentary rocks is controlled by several parameters. The study of this composition reveals very important information as provenance, weathering and tectonic setting (Bhatia, 1983). The meaning of the geochemical composition of these rocks have been studied by various authors like Schwab (1975); McLennan and al (1983); Taylor and McLennan (1985); Wronkiewicz, and Condie (1987); Roser and Korsch (1988); Condie and al 1991; McLennan and al (1993); Condie (1993); cullers (1994); Nesbitt and al (1997); cullers (2000); Yan and al (2007). In particular, the use of major and trace elements, supposed immobile to be transported in the load of particles (Taylor and McLennan, 1985; Cullers, 2000; Roser and Korsch, 1988). Currently, no geochemical study has been made on sandstones of this region. However, the contribution of the geochemistry of these Triassic sandstones has a benefit in the clarification of geodynamic context.

The aim of the study is to determine the variation of the levels of the major and rare earth elements in Oukaimeden sandstones, their provenance, weathering and tectonic setting. So, we have achieved a geochemical study of those sandstones based on 15 samples taken in two locations: AIT KEJOU (GK) and IGHERMANE (GI) (Fig. 1).

Geographical and geological contexts:-

The study area is located in the High Atlas of Morocco, 40 km south Marrakesh (Figure 1). The High Atlas is a mountain range oriented ENE consisting mainly of Mesozoic rocks, and is found between Precambrian and Paleozoic of the Anti-Atlas to the south and the ancient massif to the East. The Permo-Triassic succession of the central High Atlas basin of Morocco shows exceptional exhibition in Ourika-valley, dominated by fluvial sediments deposited in a continental Rift basin (Fabuel-Perez et al., 2010). These rift basins formed in response to extensional tectonics associated with the break-up of Pangea, attributed to the opening of the Atlantic Ocean and Neo-Tethys Sea (Houten, 1977; Petit and Beauchamp, 1986). These formations have been divided into six formations, based on their lithology and the identification of their major discontinuities (Mattis, 1977; Biron and Courtinat, 1982; Benaouiss et al., 1996)(Fig 2A).

Two formations have been the subject of this study: 1) The Ramutcho Siltstone Formation (Mattis, 1977)(F4) ,200 m thick, begins with coarse levels to small pebbles, and continues with mainly silty sediment except two sandstone levels (Biron, 1982). 2) The Oukaimeden Sandstone Formation (Mattis, 1977)(F5) materialized by thick sandstone unit (Biron, 1982), and overlies F4 with a sharp contact in the north and a more gradational contact to the south (Fabuel-Perez et al., 2010).

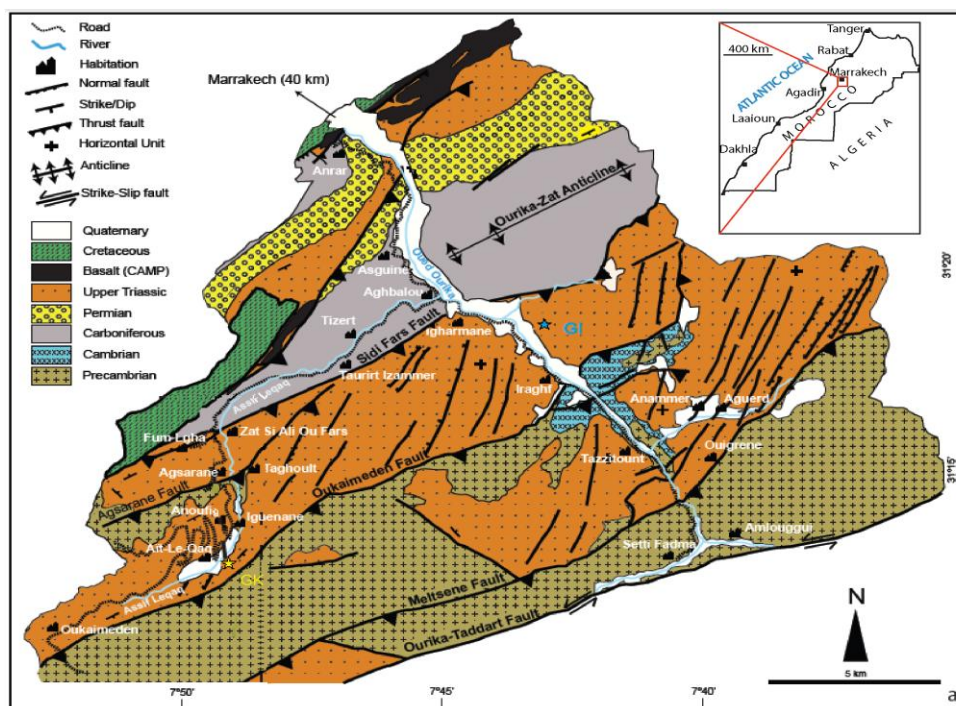


Figure 1 : Studied area location in the geological map of the central High Atlas basin (Taj-Eddine Pignone, 2005, modified); GK: AIT Kejou, GI: Ighermame.

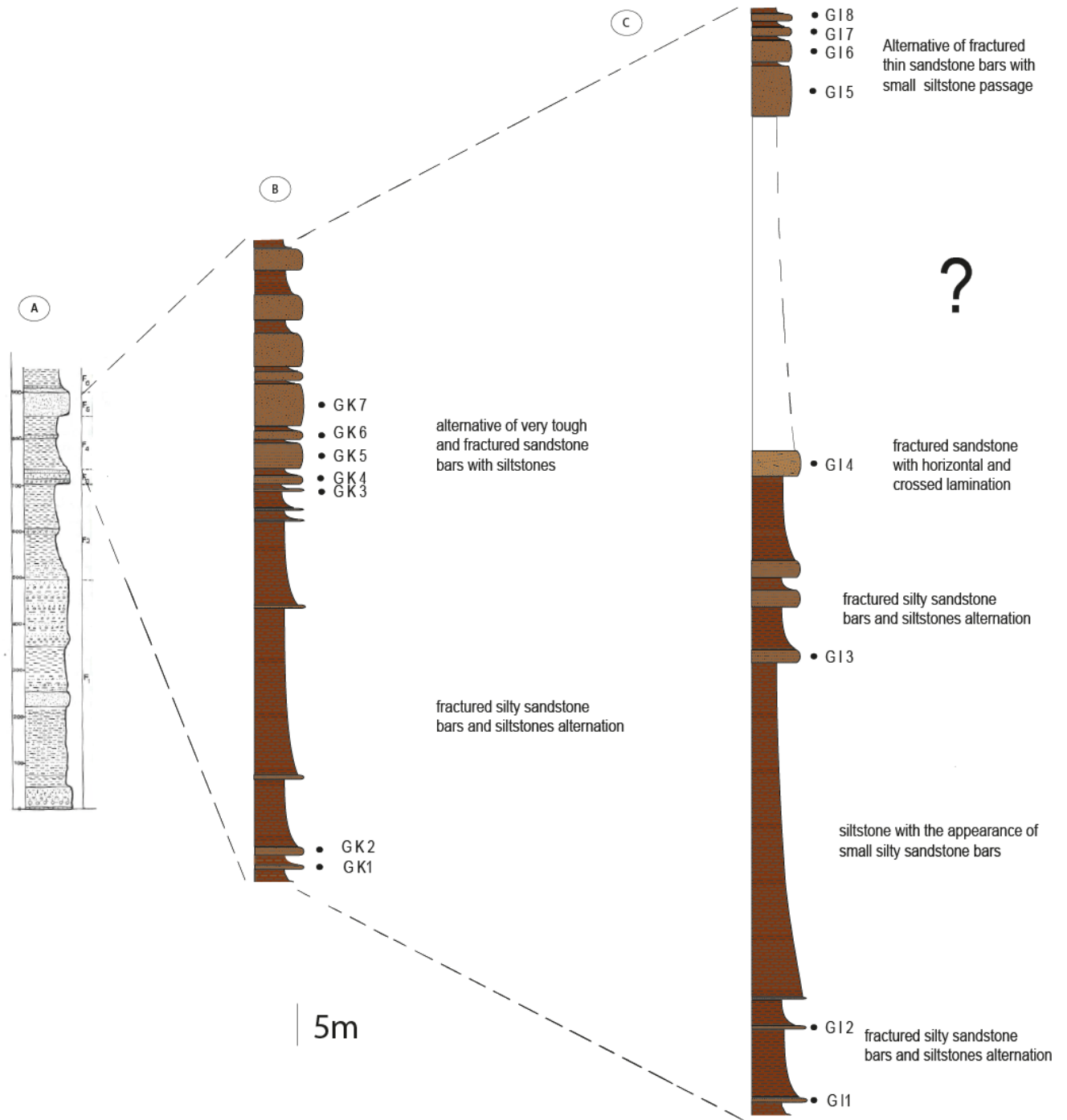


Figure 2 : Stratigraphic columns of the study areas. A: After Biron 1982; B: AIT KEJOU (GK) column, this work; C: IGHERMANE (GI) column, this work.

Material and Methods:-

Seven representative samples were collected in AIT KEJOU region (Fig. 1 and 2B) and eight in Ighermene (Fig. 1 and 2C). These samples were crushing and grinding in the Geology laboratory of Ben M'SIK Sciences Faculty, Hassan II University of Casablanca. Chemical analysis were conducted in National Center of Scientific and Technical Research (CNRST) of Rabat. The composition of major elements was determined by X-ray fluorescence spectrometry technique and rare earth elements by ICP AES technique (Table1).

Result and Discussion:-

Major elements:-

The sandstones from the two studied areas reported an enrichment of SiO_2 content (62 to 82%), TiO_2 , with an average of 0.49 %, Al_2O_3 approximately 9.27 % in AIT KEJOU sandstones , 12.07 % in IGHERMANE , $\text{Fe}_2\text{O}_3 + \text{MgO}$ with an average of 3.31 % in AIT KEJOU sandstones and 4.38 % in those of IGHERMANE. The comparison between major elements content in studied areas shows enrichment in Al_2O_3 , Fe_2O_3 , Na_2O and MnO_2 in IGHERMANE sandstones and enrichment in CaO in AIT KEJOU sandstones. The high content of Al_2O_3 was due to the presence of clay minerals and micas subordinates (Banerjee, 2010). Most of AIT KEJOU sandstone samples show lower Al_2O_3 and high CaO content than that of IGHERMANE sandstones. These results indicate that sandstone from two areas can be derived from different provenance, as well give an idea on grain size fractionation during transport and sedimentation.

According to the chemical classification scheme of Herron (1988) (Fig. 3), IGHERMANE sandstones are classified as wacke to litharenite and litharenites for those of AIT KEJOU except for three samples that fall in the wacke and sublitharenite field.

Harker diagram was used to compare the abundances of the major element oxides with silica abundance (Fig. 4). SiO_2 content showed a linear relationship with Al_2O_3 , Fe_2O_3 , MgO , and K_2O in both AIT KEJOU and IGHERMANE sandstones. The negative correlation between SiO_2 content with most of the elements is due to the significant amount of silica trapped in quartz, as reported by Osman (1996), as well Silica contribution. Generally, SiO_2 abundance increase as TiO_2 , Al_2O_3 , Fe_2O_3 , MnO_2 , MgO , CaO , K_2O and Na_2O decrease in the studied areas; suggesting a cratonic and recycled sediments associated with passive margins provenances. The high rate of quartz is due to the mineralogical maturation (Bhatia, 1983). There was a dispersion in CaO , MgO , Na_2O and MnO_2 content in the samples analyzed and this can be related to their mobility. Therefore, TiO_2 , Al_2O_3 , Fe_2O_3 and K_2O content exhibit a regular correlation with SiO_2 . The titanium oxide in the IGHERMANE sandstones shows a low variation in function of the silica.

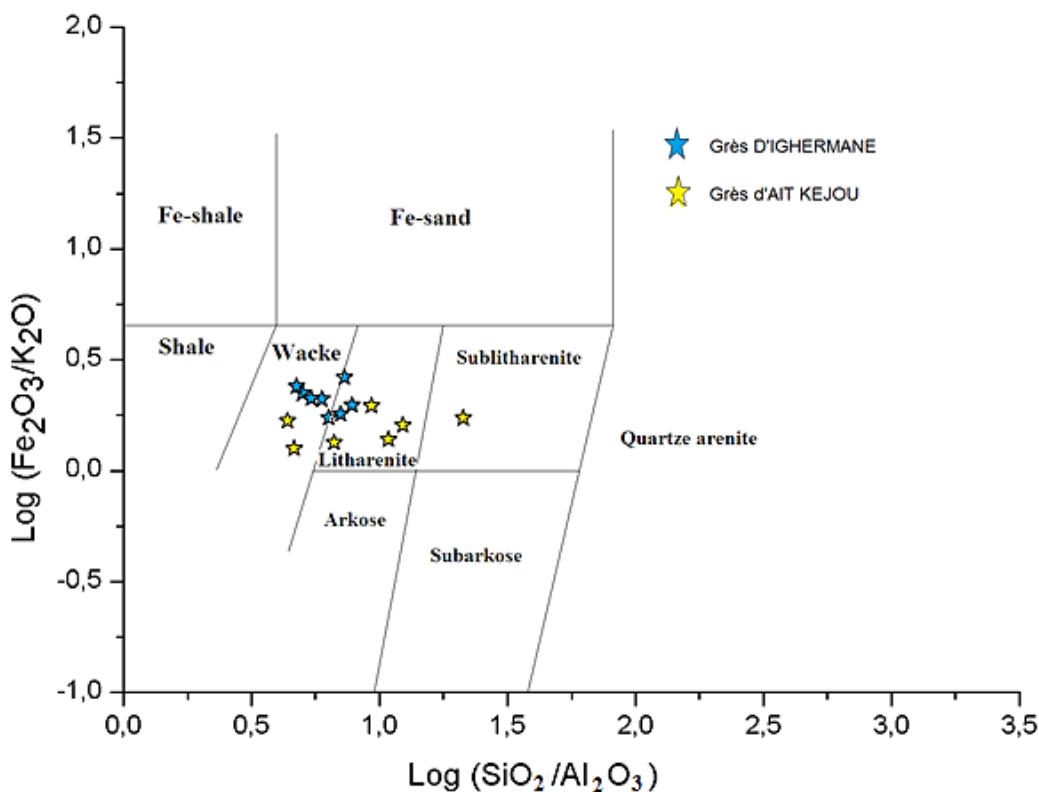


Figure 3 : Chemical classification scheme of Oukaimeden and Ourika-valley sandstones based on major elements (Herron 1988).

Table 1 : Major and rare earth elements analyze of studied areas GK and GI.

$Eu/Eu^* = \log[2 * Eu_{NASC} / (Sm_{NASC} + Gd_{NASC})]$; $This/EC^* = Ce_{NASC} / (0.5 * (La_{NASC} + Pr_{NASC}))$; $\sum REE$ (La-Lu); LREE (La-Gd); HREE (Dy-Lu); n = normalize by report to the NASC (Haskin and Haskin 1966)

Sampls	GK1	GK2	GK3	GK4	GK5	GK6	Gk7	GI1	GI2	GI3	GI4	GI5	GI6	GI7	GI8
In wt%															
SiO ₂	76,5	62,6	73,2	63,4	82,8	74,6	88,5	70,4	69,2	79,8	80,2	68,3	72,5	73,5	73,4
Al ₂ O ₃	7,06	13,5	11	14,5	6,71	8,01	4,16	11,8	13,8	10,2	11	14,4	13,4	11,6	10,4
CaO	1,25	6,42	4,75	10,4	3,42	7,02	2,3	1,98	1,75	0,16	0,49	3,83	2,3	4	5,46
Fe ₂ O ₃	1,51	2,87	2,25	3,67	1,46	2,53	1,03	2,58	3,41	2,04	2,29	3,31	2,53	2,27	2,25
K ₂ O	1,09	2,27	1,68	2,19	0,91	1,29	0,6	1,23	1,53	1,03	0,87	1,38	1,19	1,31	1,25
MgO	0,81	1,65	1,36	1,86	0,77	0,88	0,51	2,1	2,38	0,98	1,48	2,72	2,05	1,56	1,14
TiO ₂	0,33	0,55	0,37	0,74	0,21	0,64	0,14	0,58	0,57	0,65	0,55	0,57	0,38	0,4	0,37
Na ₂ O	0,52	1,05	0,65	0,83	0,47	0,63	0,42	1,39	1,05	1,37	0,72	1,08	1,74	1,31	1,18
MnO ₂	0,09	0,18	0,14	0,19	0,06	0,19	0,25	0,72	0,59	0,03		0,62	0,06	0,1	0,06
P ₂ O ₅	0,09	0,24	0,11	0,18	0,09	0,15	0,1	0,06	0,08	0,07	0,11	0,16	0,13	0,12	0,15
CIA	71,18	58,09	60,84	51,93	58,27	47,27	55,61	71,95	76,12	79,96	84,05	69,6	71,93	63,67	56,86
In ppm															
La	22,76		4,84		2,93		2,2	15,96		2,04		3,15		2,23	
Ce	16,26		52,77		34,64		46,29	39,91		59,29		44,14		28,95	
Pr	3,25		4,4		2,66		2,2	3,33		2,27		3,15		2,23	
Nd	28,29		4,4		2,66		2,2	130,69		2,27		22,39		2,23	
Sm	0,3		0,32		0,23		0,15	0,34		0,36		0,35		0,04	
Eu	0,74		0,84		0,39		0,19	0,74		0,71		0,7		0,41	
Gd	5,53		14,95		23,72		8,38	18,62		13,63		27,12		1,78	
Dy	31,86		46,61		2,4		21,6	108,08		21,58		80,72		7,13	
Ho	12,68		27,7		9,06		7,05	18,29		5,22		16,4		2,67	
Er	3,25		5,28		2,66		2,2	3,33		2,27		3,15		2,23	
Tm	0,33		0,47		0,26		0,16	0,37		0,45		0,44		0,42	
Yb	3,25		4,4		2,66		2,2	3,33		2,27		3,15		2,23	
Lu	3,25		4,4		2,66		2,2	3,33		2,27		3,15		2,23	
$\sum REE$	131,76		171,38		86,92		97,02	346,32		114,63		208,01		54,77	
LREE/HREE	1,41		0,93		3,41		1,74	1,53		2,37		0,94		2,24	
Ce/Ce*	0,41		2,13		2,31		3,81	1,24		4,82		2,54		2,35	
Eu/Eu*	1,33		0,92		0,54		0,87	0,75		0,84		0,54		2,46	
La/Sc	2,92		0,69		1,1		1,25	2,29		0,36		0,48		0,56	
(La/Lu)n	0,71		0,11		0,11		0,10	0,49		0,09		0,10		0,10	

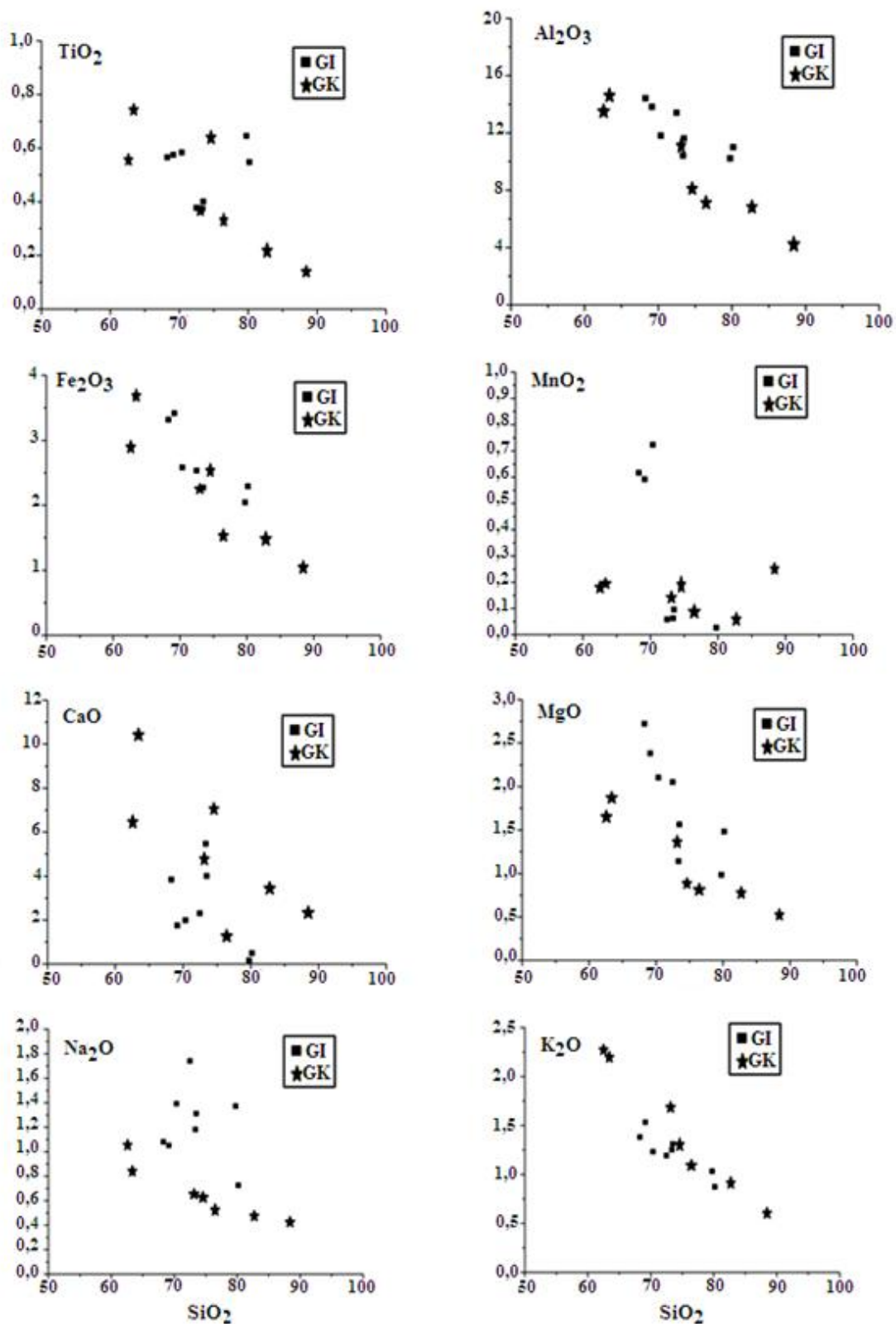


Figure 4 :Harker variation diagram for sandstones samples from two areas, AIT KEJOU (GK) & IGHERMANE (GI).

Rare earth elements:-

The rare earths elements are known to be strong resistance to the weathering conditions, which make them good indicators of sediments provenance and tectonic setting. In IGHERMANE sandstones, Σ REE concentration vary widely from 54.77 to 346.31 ppm (average 180.93 ppm), and from 86.92 to 171.38 ppm (with an average of 121.77 ppm) in AIT KEJOU sandstones. All samples of the analyzed sandstones show less Σ REE abundances compared to the upper continental crust (UCC) (≈ 143 ppm; Taylor and McLennan 1985), except for GI1, GI5 and GK3 samples (Table 1). The upper continental crust normalized REE distribution (Taylor and McLennan, 1985) shows depletion in light rare earth element (LREE) in relation to the heavy REE (HREE) except for Nd in GI1 sample (Fig. 5). The NASC normalized REE distribution (Haskin and Haskin, 1966) shows a similar trend of the UCC in both studied areas, with variables concentrations in Nd, Gd, Tm, Yb, and Lu (Fig. 5). The parallel appearances of the normalization patterns suggest that these sandstones have the same provenance. The negative europium (Eu/Eu*) anomaly support a felsic rocks provenance of the studied sandstones, except for GK1 and GK7. The cerium (Ce/Ce*) anomaly can be used as indicator of the depositional environment conditions (McDaniel et al., 1994), in our study, the cerium (Ce/Ce*) anomaly indicated an oxidizing depositional environment. The observed Sm anomaly is probably related to the samples preparation as indicated by Rousseau (2013). The depletion in light rare earth elements (LREE) in relation to the HREE and the low La/Lu ratio values are similar to that of the rivers waters (Rousseau et al., 2013). These results suggest that sediments are products of fluvial/river channel system with a slight sea contribution, confirming the results of Biron (1982).

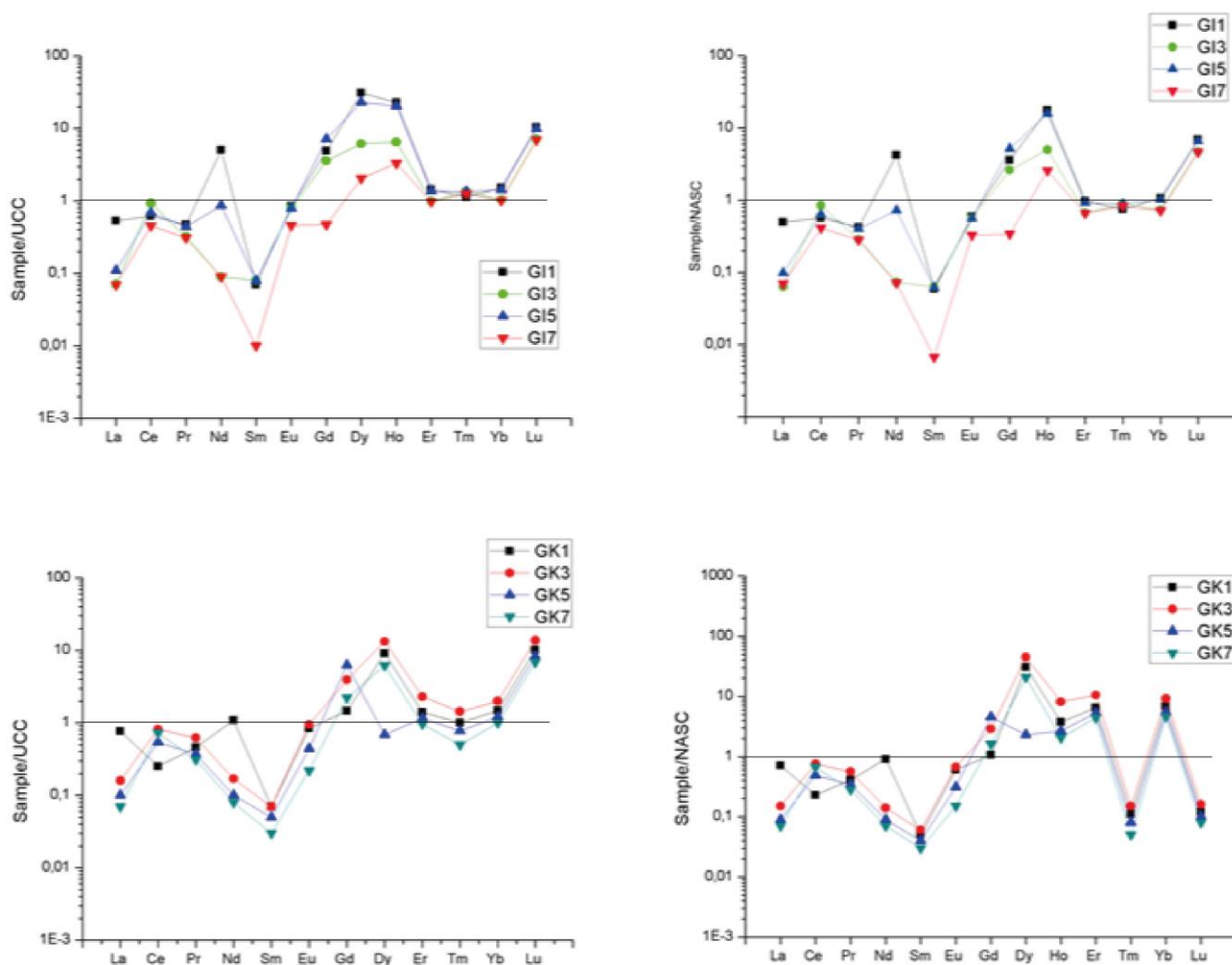


Figure 5 : REE distribution patterns of Triassic Oukaimeden sandstone from Ighermane station. REE data of UCC-normalization are from Taylor and MCLENNAN (1985) and NASC-normalization is from Haskin & Haskin (1966). GK: AIT KEJOU sandstone; GI: IGHERMANE sandstone.

Weathering:-

Sandstones from different tectonic setting have different geochemical characteristics (Bhatia, 1983; Roser and Korsch, 1986). The major element composition of clastic sedimentary rocks which have not been affected strongly by weathering process have a great value in the determination of their depositional environment (McLennan et al., 1993). However, some alkalis and alkaline earth elements (for example, Ca^{2+} , Na^+ and K^+) in terrigenous rocks can be sensitive to weathering conditions in the provenance (Wronkiewicz and Condie, 1987). Therefore, it is necessary to know the weathering degree of these rocks. The low to medium values of the chemical index of alteration (CIA) of these rocks indicate that they are not subject to several weathering, and thus will allow the use of these elements to differentiate between samples. The degree of chemical weathering is mainly linked to the climate and the rate of tectonic uplift (Wronkiewicz and Condie, 1987), the increase in the intensity of chemical weathering may reflect the decrease of the tectonic activity and/or the change in climate toward warm and wet conditions, which are more favorable for the chemical weathering of the source rocks (Jacobson et al., 2003). Consequently, the indices of alteration of the sedimentary rocks can provide useful information of the tectonic activity and the climatic conditions of the source area. The chemical index most commonly used in the quantification of alteration degree of the source rock is the chemical index alteration (CIA) (Nesbitt and Young, 1982). This index is defined by molecular proportions, where $\text{CIA} = [\text{Al}_2\text{O}_3 / (\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})] \times 100$. For this study, CIA ranged from 56.86 to 84.05 in IGHERMANE sandstones samples, with an average of 71.77, suggesting a moderate weathering. In AIT KEJOU sandstones, CIA vary in a range of 47.27 to 71.18, with an average of 57.60 suggesting that these sandstones have been submitted to a low alteration degree. These results suggest an abundance of igneous rocks fragments in our samples materialized by the low rates of alteration. In Al_2O_3 - $\text{CaO}+\text{Na}_2\text{O}$ - K_2O diagram (Fig.6), all IGHERMANE and AIT KEJOU sandstones samples fall above the line plagioclase-K-feldspar and biotite with a composition more near to the plagioclase than potassium feldspar and biotite. The majority of AIT KEJOU sandstones are located at some percentage of the feldspar seal which indicated the low quantity of alumina-bearing minerals (clay minerals), unlike IGHERMANE sandstones samples. This conclusion confirms the results obtained by the chemical index alteration (CIA).

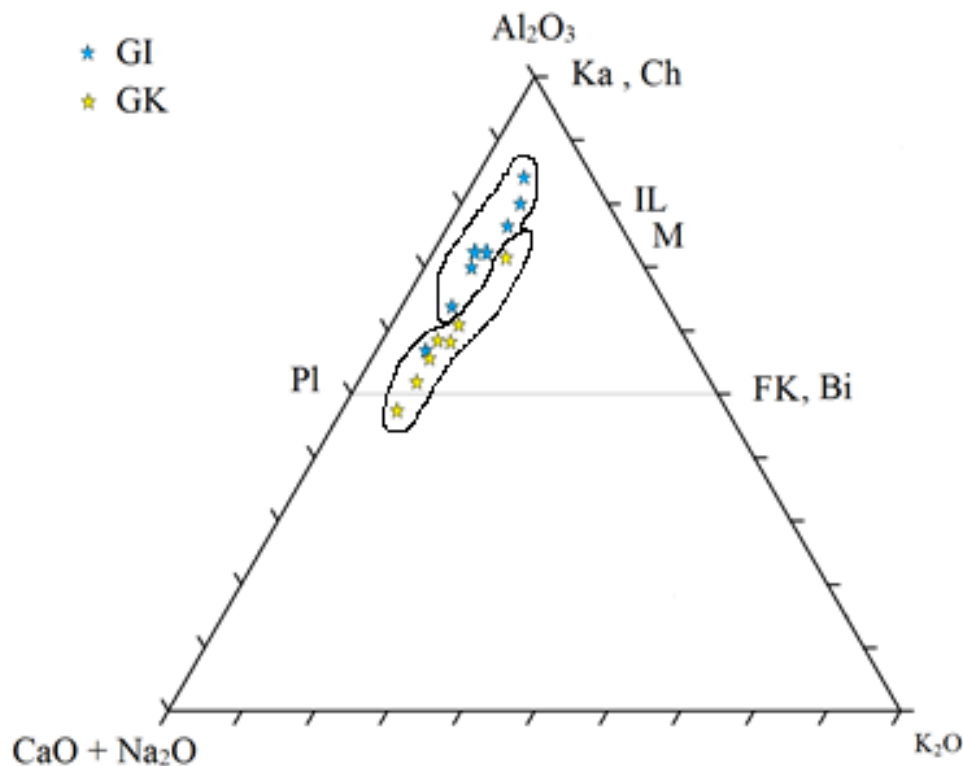


Figure 6 : Al_2O_3 - $\text{CaO} + \text{Na}_2\text{O}$ - K_2O ternary diagram (after Nesbitt and Young 1982) showing plots studied sandstones. GI: IGHERMANE sandstones, GK: AIT KEJOU sandstones, Ka: kaolinite, Ch : chlorite, Pl: plagioclase, IL: Illite, M: muscovite, FK: potassium feldspar.

Provenance:-

The provenance of these sedimentary rocks can be approached by CaO-Na₂O-K₂O triangular diagram (Bhatia, 1983). According to a study conducted by Le Maitre (1976) on the chemical variability of 39 igneous rocks group, it proves that this diagram could indicate the provenance of our sandstones samples. Studied and analyzed sandstones samples fall into the field of andesites for AIT KEJOU sandstones and in the field of granite and granodiorite for IGHHERMANE sandstones (Fig. 7). This result suggest that the provenance is constrained to the adjacent Cambrian basement units of Tifnout granitic massif, associated andesites (Baouch, 1984) and the granodiorites of the Precambrian basement units Central High Atlas (Proust, 1961), located to the south of the studied areas. These results confirmed those of major and rare earths elements geochemistry.

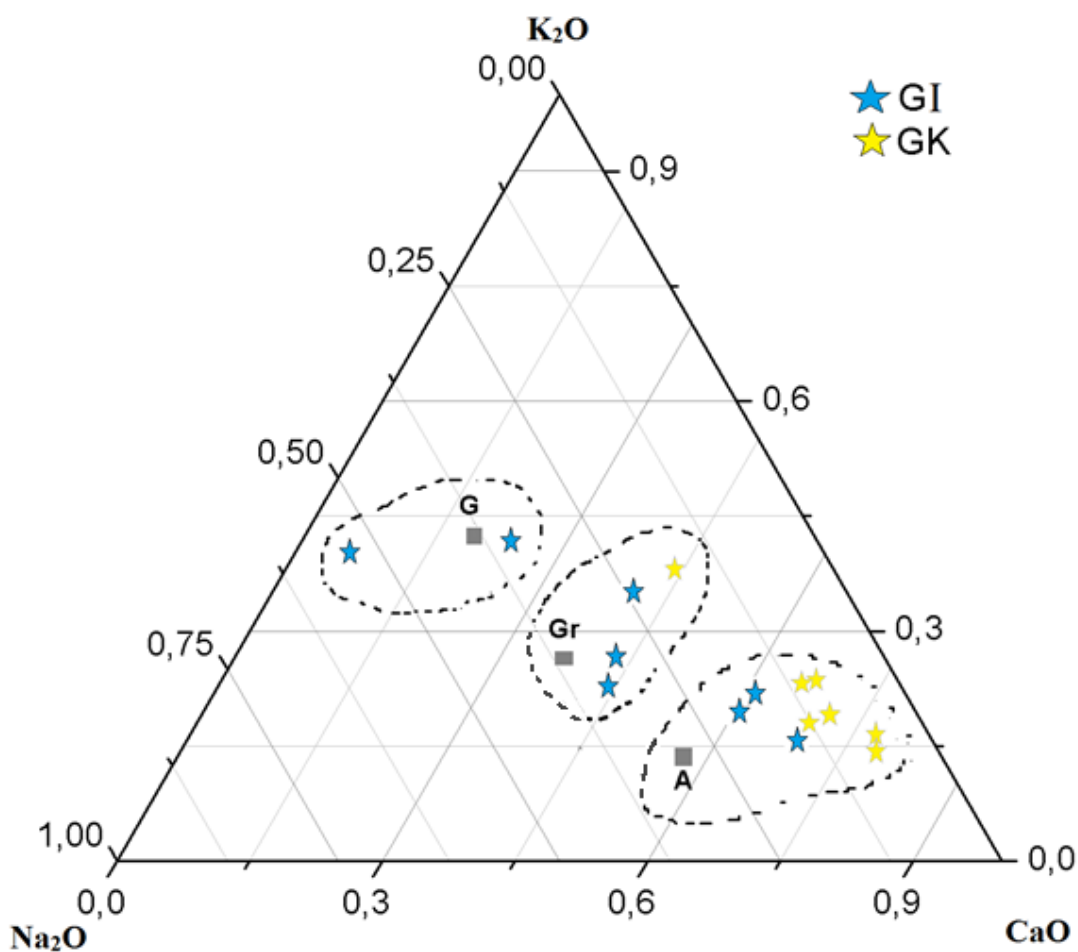


Figure 7: CaO-Na₂O-K₂O plot of Ighermene (GI) and AitKejou (GK) sandstone. G, GR and A are successively the average of granite, granodiorite and andesite after LeMaitre (1976).

Tectonic setting:-

Roser and Korsch (1986) defined three tectonic setting for terrigenous sedimentary rocks using the cross plot of K₂O/Na₂O versus SiO₂, as shown in Fig. 8A which indicates a passive margin for AIT KEJOU sandstones, except for GK2 and GK4 samples and an active continental margin tectonic setting for the IGHHERMANE sandstones except for GI3 and GI4.

Bhatia (1983) defined four tectonic setting using the cross plot of TiO₂ versus Fe₂O₃+MgO, which are oceanic island arc, continental island arc, active continental margin, and the passive continental margin. Sandstones samples from IGHHERMANE area plot in continental island arc and the active continental margin tectonic setting (Fig. 8B). However, AIT KEJOU sandstones samples plot in continental island arc and passive continental margin. Sandstones samples distribution in TiO₂ versus Fe₂O₃+MgO (Fig 8B) suggests the presence of an orogenic signature.

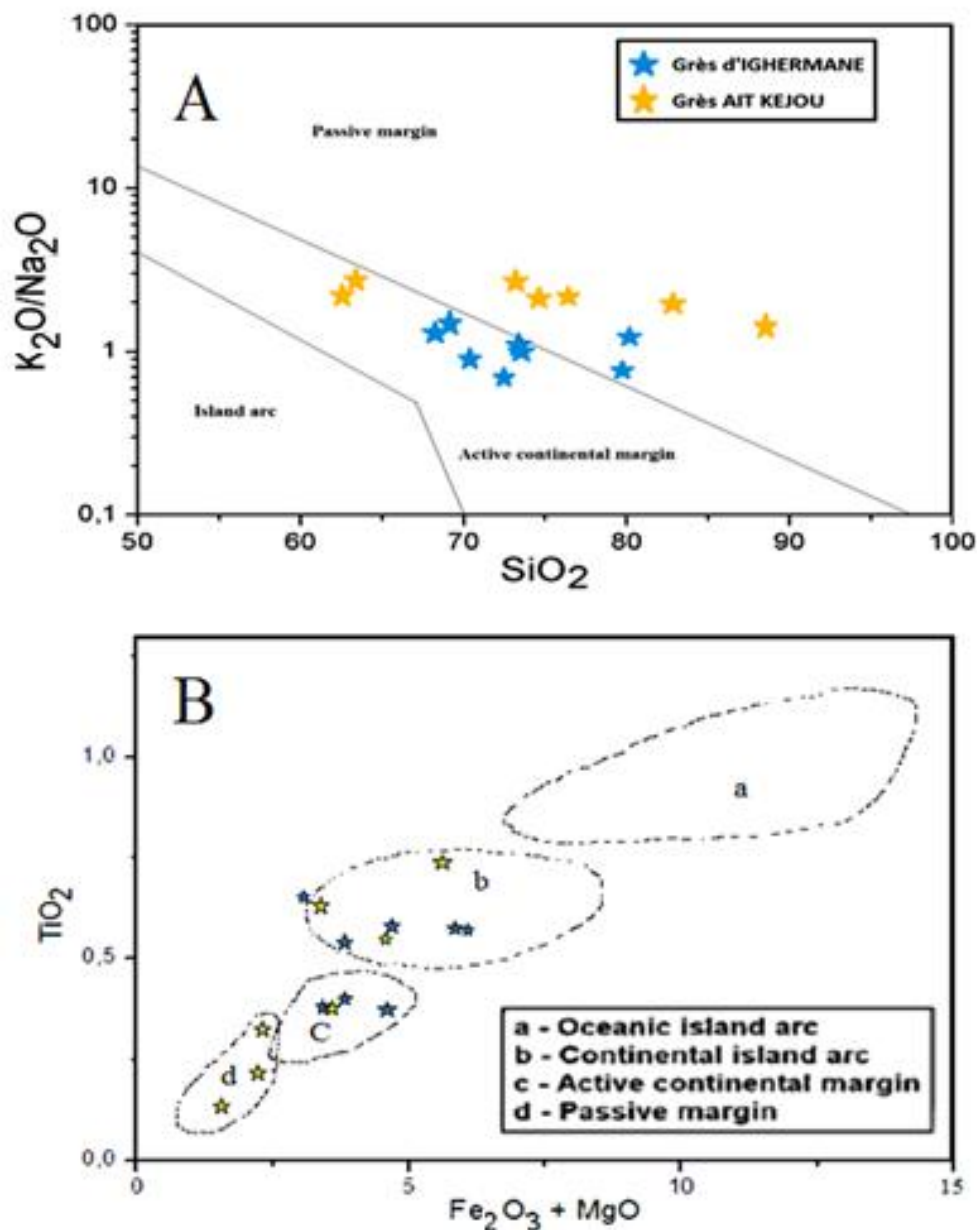


Figure 8 : Tectonic-setting discrimination diagrams of IGHERMANE and AIT KEJOU sandstones. The tectonic settings are named in each plot. A) SiO_2 -(K_2O/Na_2O) After Roser and Korsch (1986); (B) Fe_2O_3+MgO - TiO_2 after Bhatia (1983).

Conclusion:-

A geochemical study has been carried out on Triassic sandstones from two areas of the Marrakech High Atlas, Morocco. The conclusion was to define their geochemical characterization, weathering, provenance and their tectonic setting. The results indicate that Oukaimeden sandstones are characterized by a high SiO_2 content. According to Herron diagram, IGHERMANE sandstones are classified as wackes to litharenite whereas the AIT KEJOU sandstones are litharenites for the majority of samples. The low to medium CIA values and Al_2O_3 - $Na_2O+CaO-K_2O$ ternary diagram shows the presence of clay minerals in sandstones from the two studied areas, with a low amount suggesting the abundance of igneous rocks fragments in our sandstones samples. The positive correlation between K_2O and Al_2O_3 has a significant influence on the distribution of the aluminum and suggests that this element is mainly controlled by the amount of clay minerals. The negative linear relationship between SiO_2 content and TiO_2 , Al_2O_3 , Fe_2O_3 , MgO and K_2O content in the sandstones of the two areas suggest a mineralogical

maturation with the presence of another SiO₂ provenance. CIA values suggest low to moderate weathering in AIT KEJOU sandstones and moderate in IGHHERMANE sandstones samples. The spectres patterns parallel appearances suggest that these sandstones have the same provenance. The negative europium (Eu/Eu*) anomaly (La/Lu)_n, La/Sc ratios support a felsic provenance of the studied sandstones, except for GK1 and GK7 samples. Cerium (Ce/Ce*) anomaly suggest an oxidizing depositional environment. LREE/HREE and (La/Lu) ratios suggest a fluvial sedimentation with a slight sea contribution. Discrimination diagrams support passive margin tectonic setting for AIT KEJOU sandstones and an active margin tectonic setting for IGHHERMANE sandstones. Sandstones samples distribution in TiO₂ versus Fe₂O₃+MgO (Fig 8B) suggests the presence of an orogenic signature. The present study suggest that the provenance is constrained to the adjacent Cambrian basement units of Tifnout granitic massif, associated andesites (Baouch 1984) and the granodiorites of the Precambrian basement units Central High Atlas (Proust, 1961), located to the south of the studied areas.

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