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# The Relationship Between Chemical Index of Alteration and Some Major and Trace Elements Content in Rocks of Injana Formation of Northern Iraq

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## ABSTRACT

The average CIA value for the Injana Formation (Late Miocene) sampled across a section consisting of alternating mudstones, siltstones and sandstones deposited mainly in fresh water environment is rather low value (45.6) indicating the very low level of chemical alteration which the source rocks have suffered which is mainly due to semi-arid to arid climate of weathering and also due to nearby position of the basin of deposition. No overall variation in climatic condition was observed along the section from bottom to top .The variation of major and trace elements involved in this study with mean values of CIA for the sandstone, siltstone and mudstone lithologies was attributed to either mobility of the element concerned (Na, K and Rb) or to gravity fractionation of minerals that host the element or to climate of weathering and deposition ($P_2O_5$, Ni, Co & $TiO_2$). Major contribution of recycled argillaceous or clay rich sediments to the Injana Formation do not agree with the results reached in the present study.
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# العلاقة بين معامل التغير الكيميائي ومحتوى البعض من العناصر الرئيسية والأثرية في صخور تكوين إنجانة في شمال العراق

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**الملخص**

إن معدل قيمة CIA لتكوين إنجانة (المايوسين المتأخر) التي تم نمذجتها على امتداد مقطع مكون من صخور طينية وغرينية ورملية متناوبة والتي ترسبت أساسا في بيئة مياه عذبة هي نوعا ما قيمة واطئة (45.6) والتي تؤشر المستوى الواطئ جدا للتغيرات الكيميائية التي تعرضت لها صخور المصدر والتي كانت بشكل رئيسي بسبب المناخ شبه الجاف والجاف لبيئة التجوية وكذلك قرب الحوض الترسيبي. لم يلاحظ تغير شامل في الظروف المناخية على امتداد المقطع من الأسفل نحو الأعلى.

لقد أُعزي التغاير في محتوى العناصر الرئيسية والأثرية المعنية بهذه الدراسة مع تغاير قيم CIA للأنواع الصخرية الثلاث،الحجر الرملي،الحجر الغريني والحجر الطيني إلى إما حركية العنصر المعني(Rb,K,Na) أو التجزئة بسبب الجاذبية للمعادن التي تضيف العنصر أو إلى مناخ التجوية والترسيب ( $TiO_2$, Co, Ni, $P_2O_5$ ). ومساهمة رئيسية لصخور طينية أو رواسب غنية بالطين معادة في تكوين الإنجانة لا تتوافق مع النتائج التي تم التوصل إليها في هذه الدراسة.


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## INTRODUCTION

Sediments and sedimentary rocks are the products of disintegration and solution of source rocks which are subjected to various degrees of weathering and chemical alteration usually reflected in the chemical composition of the lithoclasts and the alteration products. Resisting minerals e.g. zircon, chromite, ilmenite etc. are the least altered while olivine, pyroxene and feldspars suffer most. The alteration of the latter group of minerals may finally lead to the formation of secondary mineral phases such as various iron oxides, hydroxides and clay minerals. Feldspars differ in their relative resistance to chemical weathering, calcium rich plagioclase being the least resistant while k-feldspars are more resistant.The survival of any of these minerals depend largely on the intensity of the chemical weathering at the provenance sites which is undoubdtly related to climatic conditions.

Alteration may also takes place during transport of mineral phases and also during later diagentic-processes. During hydrolysis of aluminium silicates one product of their weathering is practically always a clay mineral where some of the original aluminium and silicon remain combined. The alkali elements Ca, Mg, K, Na released during hydrolysis are highly soluble and little of them remain with the alteration product.

From the foregoing discussion it is obvious that as the intensity of chemical weathering increases the content of highly mobile elements relatively decreases while the immobile elements e.g. Al, Ti increases. For this reason Nesbitt and Young (1982) derived an index which can be used to express the degree of intensity of weathering that sediments have suffered at provenance sites. The index named Chemical Index of Alteration (CIA) is calculated using the formula:

$$CIA = [ Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O) ] \times 100$$

In this formula the oxides represent molar fractions and the CaO* represent calcium oxide combined with silicates only and therefore excess CaO combined with carbonate minerals should be subtracted from total CaO in the analyses of rock samples.

It should be pointed out that different fresh rock types and constituent minerals have different initial CIA values, for example basalts have initial value ranging between 30 to 45 while granite and granodiorite have values between 45 to 55. On the other hand fresh feldspars have CIA value around 50, biotite about 55, hornblende between 10 to 30 and pyroxene between 0 to 10. Secondary minerals e.g. chlorite have CIA value may reach 100, clay minerals for example illite and smectite have CIA values ranging between 70 to 85(Nesbitt and Young, 1982).

It is apparent now that CIA values of clastic sedimentary rocks depends in addition to intensity of weathering, the nature and proportion of source rocks from which the composition of the sedimentary rocks were derived. Large proportion of argillaceous rocks supplying lithoclasts to the basin of deposition will increase the CIA value of the sediments despite that the intensity of the weathering may not be effective. On the contrary, ultramafic rocks supplying products of mafic minerals constituents will depress CIA values even if weathering was intense. Nesbitt and Young (1982) and many others including Price and Velbel (2003); Osae *et al* . (2006); Rahman and Suzuki (2007). Roser and Korsch (1988) used CIA values in reconstructing paleoclimate of sedimentary rocks of different ages. However little attention been paid to the relationship between elements and element ratios particularly trace elements in sediments and sedimentary rocks and their CIA values. Selvaraj and Chen (2006) have correlated CIA values of sediments and sedimentary rocks of Taiwan with molar (K/Na) and (Rb/Sr) ratios and found that there is an increase in the latter ratios with increasing CIA values. Nhleko (2003) in studying paleosols of 2.97 Ga indicated that Th, Sc and Nb are retained on the basis of constant Al and Ti in the chlorite zone but are leached from the sericite zone. The former zone represent the incipient stage of chemical weathering and the Th, Sc and Nb have been considered immobile at this stage of weathering (Nhleko, 2003). The quantitative retention of V and Hf and constant ratio of V/Ti, V/Al, Hf/Al and Hf/Ti suggest that V and Hf remained nearly immobile during weathering and any subsequent alteration.

Because the three size fractions of the Injana Formation (Late Miocene) of north Iraq are cogenetic and because these represent various stages of weathering which the source rocks have suffered, this allows an evaluation of the behaviour of elements in source rocks in response to increasing effect of chemical weathering.

## LOCATION AND GEOLOGY

The Injana Formation which was sampled in the present study crops out in Wadi Pastora on the road side between Erbil and Salahdin cities (Fig. 1).

The section from which the samples were collected lies on the northeast border of the Butmah-Chemchemal Subzone which belong to the Foothill Zone, one of the Unstable Shelf Units of the tectonic divisions of northern Iraq (Jassim and Buday, 2006).

Injana Formation is regarded as one of the Formations that were deposited during the Late Miocene - Pliocene Sequence of the Fluvial Systems. The age is Tortonian (Jassim and Buday, 2006). The lower contact is gradual and conformable with the Fatha Formation. The upper contact is also gradual and conformable with the Mukdadiya Formation recognized by the first appearance of gravely sandstone. In the studied section the Injana Formation consists of terrigenous sediments (Molasse) of cyclic alternation of fining upward sequence of sandstones, siltstones and mudstones (Basi, 1973; Buday, 1980).

The colour varies from red to grey while the grain size increases from the lower beds towards the top reflecting increase in the uplift of the source rocks due to collision of the Arabian plate with the Iranian one which reached its climax in the Pliocene. Environment of deposition of the Injana Formation is on the whole continental. However the lower part is regarded as being transitional from littoral to brackish and to continental of fluviatile nature.

Petrographic and mineralogic studies of rocks of Injana Formation by many researchers summarized by Othman (1990) and later by Al-Juboury (1994, 2001) and Aghwan *et al.*,(2008) indicated that the Injana sediments were derived from acid, basic and metamorphic rocks as well as sedimentary lithoclasts. These were located to the north and northeastern borders of the basin of deposition which are parts of the Zakros-Touros Belts. It is also assumed that parts of the lithoclasts were derived from sources located towards the southwest of the depositional basin which belong to the Arabian Shield.

The major mineral constituents include quartz, feldspars, carbonate (calcite) and clay minerals consisting of smectite, illite, kaolinite and chlorite. Igneous, metamorphic and sedimentary rock fragments are present conspicuously. The rocks are classified as calclithic arenite (Al-Rawi, 1982). Heavy minerals composed of opaque, chromite, magnetite and ilmenite and coloured including pyroxene, olivine, hornblende, zircon, tourmaline etc. The presence of mafic silicate minerals and alkali feldspars indicate that the source rocks were subjected to immature probably under semi-arid environment weathering which inhibited the formation of mature soil profile. It is also apparent that physical weathering was probably more effective than chemical alteration of the non resistant minerals.

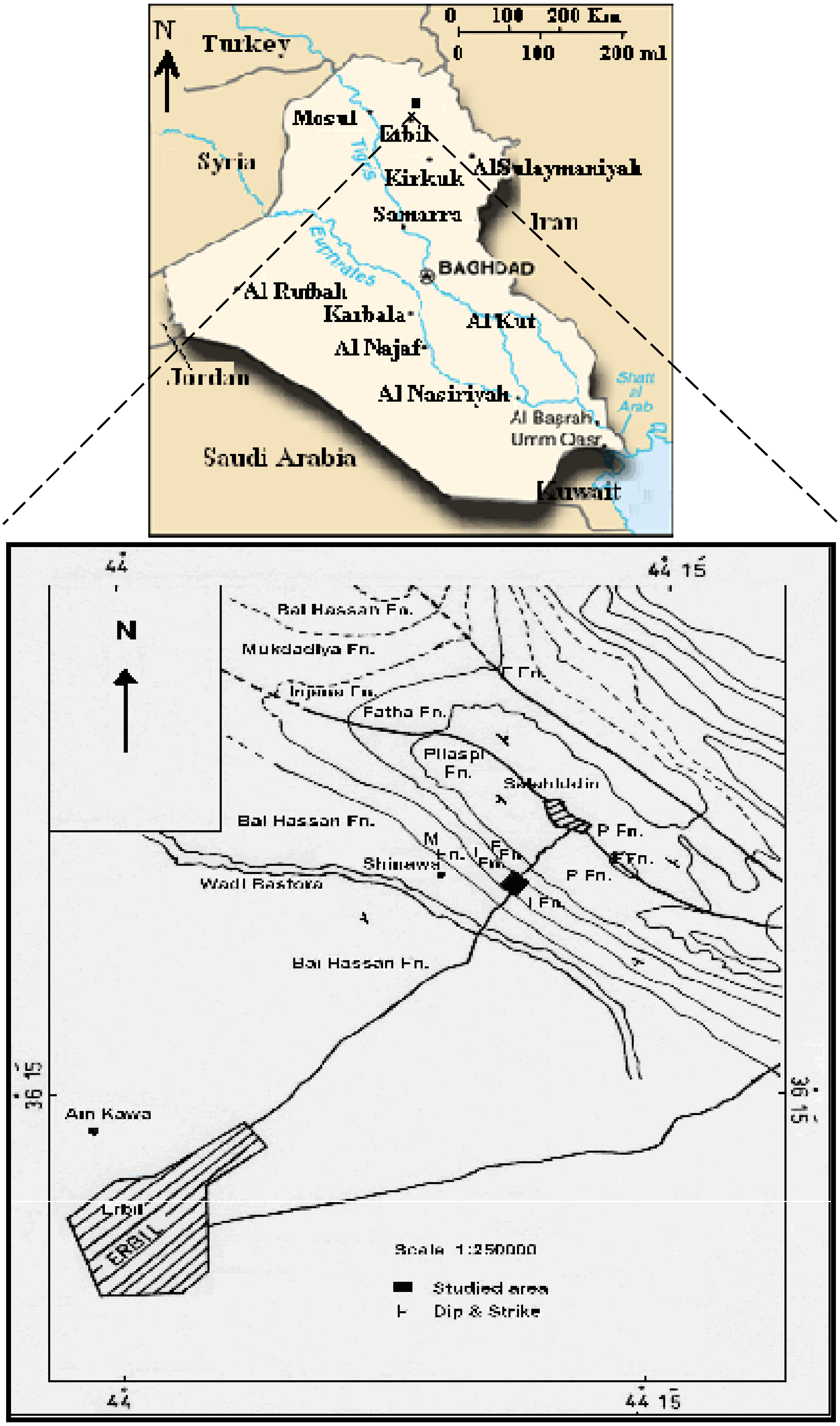



Fig. 1: Location of Section of the Injana Formation.

## SAMPLING AND ANALYSIS

A total of 33 samples were collected from the outcrop of Injana Formation exposed in Wadi Pastora. The locations of the samples are shown on a lithological section in (Fig. 2) of these 16 were of sandstones, 7 of siltstones and 10 of mudstones. All samples were analysed (Othman, 1990) for major and trace elements by XRF spectrometer (Phillips pw 1450/10) at the Geology Department of science college in Mosul University / Iraq, using the procedure described by Norrish and Hutton (1964) for major elements while trace elements analysed following the procedure of calculating the mass absorption coefficient for the elements concerned and employing international and other standards for comparison using the equation of Norrish and Chappell outlined in Zussman (1977). $CO_2$ content was determined by weight lose after treatment of samples with dilute HCl under controlled conditions. $H_2O^+$ was determined by calculating the difference between L.O.I and $CO_2$, $SO_3$ and Cl content of dry samples.

## RESULTS

The analytical results of the major and trace elements are shown in (Table 1). Also shown the range and mean of the elements contents and CIA values of the three lithological groups.

## DISCUSSION

The variation of CIA values of each of the lithological groups of the Injana Formation (Table.1) undoubtedly reflects secular variation in the intensity of chemical weathering of the source rocks. However the range of variation is rather small and almost symmetrically positioned about the mean (Fig. 3). This indicates that there was no overall positive or negative (increase or decrease) trend in the nature of weathering along the whole time span of the lithological section under study. The average CIA value of mudstone (54.3), siltstone (49.2) and sandstone (38.5) are obviously very low indicating the very low chemical weathering intensity of the source rocks possibly aided by fast washing of the weathered products due to high elevation of provenance areas. The weighted mean of the CIA values across the section is 45.6, a value much lower than average shale for example ~ 70 for PAAS (Dokuz and Tanyolu, 2006) which is normally correlated with intermediate to high weathering intensity. It should be mentioned that sorting was probably not the major contributor for the slightly higher CIA value of the mudstone in comparison with siltstone and sandstone. This is because fresh feldspars and other weakly resistant minerals are found in the mudstone.

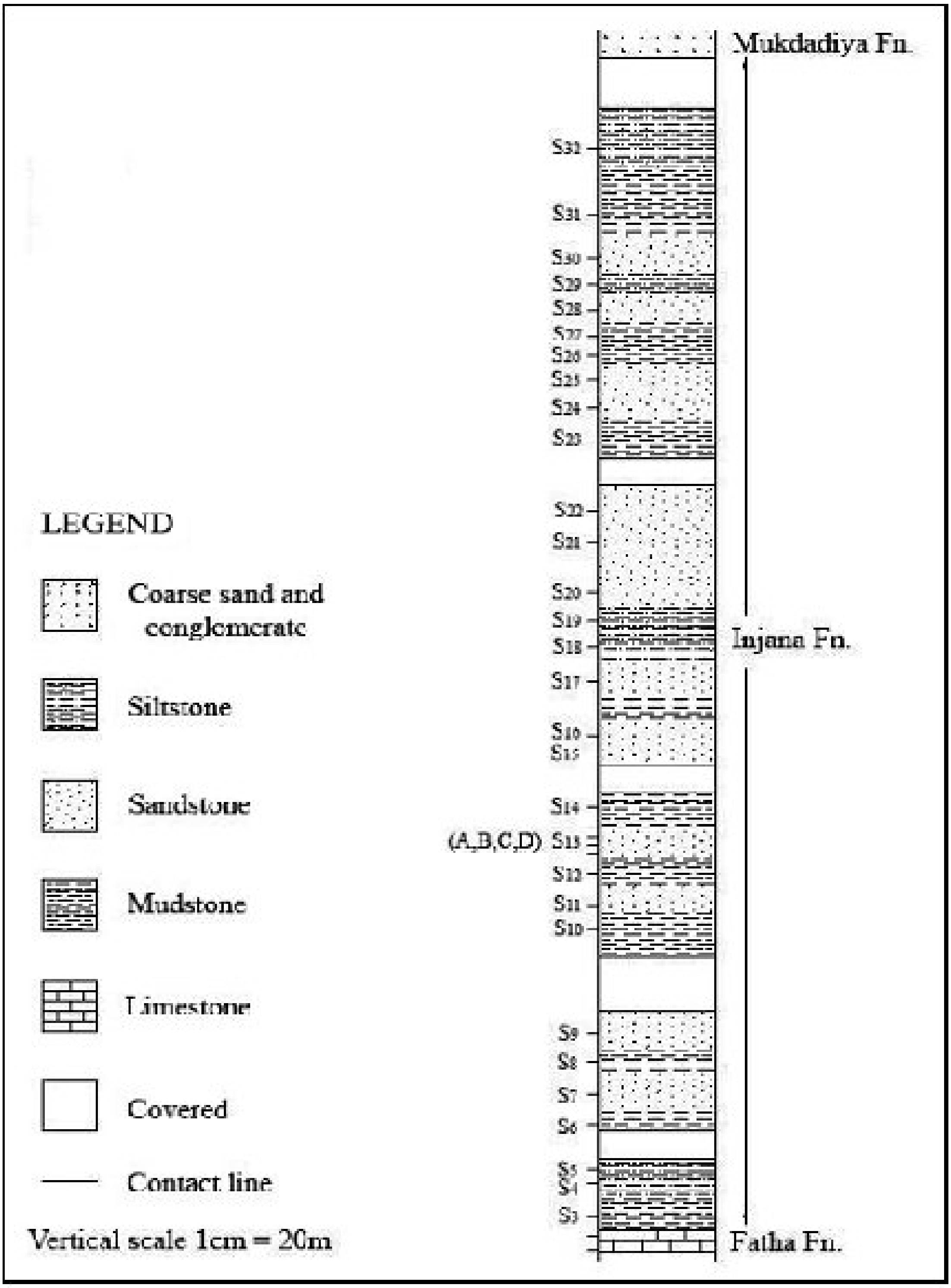



Fig. 2: Lithological Section of Injana Formation in Study Area.

Table 1: Major and Trace Element Contents and the CIA Values of Sandstone Siltstone and Mudstone Samples of the Injana Formation in Study Area.

| Const. / Sample no. | $SiO_2$ % | $Al_2O_3$ % | $CaO_T$ % | MgO % | $K_2O$ % | $Na_2O$ % | $Fe_2O_{3T}$ % | $TiO_2$ % | $P_2O_5$ % | $CO_2$ % | $H_2O^+$ % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sandstone** | | | | | | | | | | | |
| $S_7$ | 42.45 | 7.41 | 18.10 | 4.95 | 1.29 | 3.24 | 2.88 | 0.69 | 0.21 | 12.00 | 5.42 |
| $S_9$ | 37.00 | 6.72 | 23.61 | 4.25 | 1.10 | 2.37 | 2.12 | 0.67 | 0.25 | 14.50 | 5.28 |
| $S_{11}$ | 41.32 | 7.01 | 19.73 | 3.92 | 1.27 | 2.91 | 2.84 | 0.64 | 0.24 | 13.30 | 5.20 |
| $S_{13A}$ | 40.49 | 7.17 | 20.84 | 3.93 | 1.21 | 3.06 | 2.99 | 0.58 | 0.24 | 12.90 | 5.87 |
| $S_{13B}$ | 35.79 | 6.88 | 24.65 | 3.59 | 1.05 | 3.23 | 1.70 | 0.43 | 0.25 | 19.80 | 3.40 |
| $S_{13C}$ | 44.08 | 7.21 | 18.42 | 3.61 | 1.32 | 3.27 | 3.08 | 0.60 | 0.24 | 13.60 | 3.82 |
| $S_{15}$ | 51.41 | 6.98 | 15.04 | 3.90 | 1.38 | 4.08 | 2.25 | 0.63 | 0.20 | 9.40 | 4.38 |
| $S_{16}$ | 45.29 | 6.98 | 15.56 | 6.21 | 1.33 | 3.21 | 2.96 | 0.91 | 0.22 | 11.70 | 2.61 |
| $S_{17}$ | 55.06 | 7.30 | 12.83 | 3.42 | 1.58 | 5.60 | 2.44 | 0.69 | 0.19 | 9.70 | 2.41 |
| $S_{20}$ | 40.89 | 6.66 | 23.92 | 2.29 | 1.36 | 3.20 | 1.43 | 0.36 | 0.22 | 15.40 | 3.11 |
| $S_{21}$ | 38.54 | 6.64 | 25.13 | 2.19 | 1.27 | 3.29 | 1.39 | 0.43 | 0.22 | 15.20 | 4.85 |
| $S_{22}$ | 42.53 | 6.78 | 22.09 | 2.34 | 1.39 | 3.23 | 1.46 | 0.34 | 0.21 | 15.00 | 2.34 |
| $S_{24}$ | 35.23 | 6.50 | 27.53 | 1.93 | 1.29 | 2.40 | 1.30 | 0.26 | 0.25 | 17.10 | 4.99 |
| $S_{25}$ | 41.45 | 6.75 | 21.95 | 2.88 | 1.17 | 2.34 | 1.90 | 0.39 | 0.26 | 15.90 | 2.10 |
| $S_{28}$ | 39.40 | 7.24 | 21.29 | 4.58 | 1.03 | 2.91 | 3.15 | 0.66 | 0.28 | 15.70 | 3.61 |
| $S_{30}$ | 34.02 | 6.26 | 27.73 | 3.04 | 0.86 | 1.31 | 2.16 | 0.41 | 0.27 | 17.50 | 5.46 |
| **Range** | **34.02 -55.06** | **6.26 - 7.41** | **12.83 - 27.73** | **1.93 -6.21** | **0.86 -1.58** | **1.31 - 5.60** | **1.30 - 3.15** | **0.26- 0.91** | **0.19- 0.28** | **9.40- 19.80** | **2.10 -5.87** |
| **Mean** | **41.56** | **6.91** | **21.15** | **3.56** | **1.24** | **3.10** | **2.25** | **0.54** | **0.23** | **14.29** | **4.05** |

| Const. / Sample no. | CIA % | Ni ppm | Co ppm | Cr ppm | Mn ppm | V ppm | Rb Ppm | Y ppm | Th ppm | La ppm | Nd ppm | Ce ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Sandstone** | | | | | | | | | | | | |
| $S_7$ | 38.90 | 77 | 23 | 170 | 837 | 71 | 65 | 19 | 7 | 29 | 24 | 38 |
| $S_9$ | 33.30 | 160 | 30 | 2645 | 1109 | 52 | 43 | 16 | 6 | 9 | 46 | 22 |
| $S_{11}$ | 38.90 | 74 | 24 | 271 | 794 | 67 | 58 | 19 | 9 | 16 | 0 | 43 |
| $S_{13A}$ | 33.30 | 52 | 25 | 206 | 703 | 72 | 55 | 17 | 8 | 17 | 0 | 39 |
| $S_{13B}$ | 53.80 | 43 | 24 | 126 | 921 | 54 | 43 | 15 | 8 | 20 | 28 | 26 |
| $S_{13C}$ | 46.70 | 64 | 28 | 140 | 695 | 70 | 63 | 19 | 9 | 21 | 38 | 38 |
| $S_{15}$ | 31.80 | 71 | 22 | 959 | 621 | 52 | 61 | 20 | 8 | 12 | 54 | 31 |
| $S_{16}$ | 50.00 | 109 | 26 | 554 | 671 | 63 | 62 | 22 | 7 | 5 | 64 | 34 |
| $S_{17}$ | 36.80 | 91 | 24 | 654 | 574 | 56 | 75 | 22 | 11 | 16 | 97 | 26 |
| $S_{20}$ | 31.80 | 34 | 14 | 236 | 758 | 34 | 63 | 19 | 3 | 13 | 37 | 27 |
| $S_{21}$ | 30.40 | 32 | 13 | 486 | 664 | 34 | 53 | 17 | 5 | 13 | 13 | 28 |
| $S_{22}$ | 36.80 | 24 | 21 | 158 | 703 | 33 | 60 | 19 | 7 | 11 | 33 | 25 |
| $S_{24}$ | 28.60 | 33 | 15 | 156 | 904 | 30 | 53 | 17 | 4 | 17 | 13 | 18 |
| $S_{25}$ | 46.70 | 75 | 25 | 106 | 638 | 38 | 49 | 16 | 9 | 23 | 20 | 28 |
| $S_{28}$ | 46.70 | 112 | 31 | 332 | 886 | 83 | 43 | 19 | 8 | 23 | 10 | 35 |
| $S_{30}$ | 31.60 | 55 | 19 | 343 | 538 | 49 | 33 | 13 | 3 | 11 | 22 | 23 |
| **Range** | **28.6- 53.8** | **24 - 160** | **13 - 31** | **106 - 2645** | **538 - 1109** | **30 - 83** | **33 - 75** | **13 - 22** | **3 - 11** | **5 - 29** | **0 - 97** | **18 - 43** |
| **Mean** | **38.51** | **69** | **23** | **471** | **751** | **54** | **55** | **18** | **7** | **16** | **31** | **30** |

## CONTIN. TABLE : 1

| Const. / Sample no. | $SiO_2$ % | $Al_2O_3$ % | $CaO_T$ % | MgO % | $K_2O$ % | $Na_2O$ % | $Fe_2O_{3T}$ % | $TiO_2$ % | $P_2O_5$ % | $CO_2$ % | $H_2O^+$ % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Siltstone** | | | | | | | | | | | |
| $S_4$ | 37.63 | 7.25 | 23.22 | 3.75 | 1.13 | 2.78 | 2.20 | 0.53 | 0.18 | 18.70 | 1.48 |
| $S_5$ | 43.81 | 7.86 | 16.15 | 7.33 | 1.36 | 2.64 | 3.48 | 0.81 | 0.19 | 10.50 | 5.11 |
| $S_{13D}$ | 44.66 | 7.75 | 15.09 | 4.60 | 1.47 | 2.56 | 3.77 | 0.87 | 0.21 | 10.00 | 5.71 |
| $S_{18}$ | 38.06 | 7.32 | 21.24 | 5.46 | 1.26 | 2.43 | 2.57 | 0.83 | 0.26 | 14.50 | 2.94 |
| $S_{19}$ | 40.52 | 7.61 | 19.74 | 4.64 | 1.31 | 2.72 | 2.58 | 0.76 | 0.24 | 12.00 | 4.65 |
| $S_{29}$ | 41.26 | 7.70 | 18.71 | 5.26 | 1.18 | 2.07 | 3.54 | 0.77 | 0.25 | 14.10 | 3.28 |
| $S_{32}$ | 39.86 | 7.37 | 24.22 | 3.00 | 1.27 | 0.59 | 1.86 | 0.47 | 0.23 | 18.10 | 2.31 |
| **Range** | **37.6-44.66** | **7.25 - 7.86** | **15.09 - 24.22** | **3.00 -7.33** | **1.13 -1.47** | **0.59 - 2.78** | **1.86 - 3.77** | **0.47-0.87** | **0.18-0.26** | **10.0-18.70** | **1.48 - 5.71** |
| **Mean** | **40.83** | **7.55** | **19.77** | **4.86** | **1.28** | **2.26** | **2.86** | **0.72** | **0.22** | **13.99** | **3.64** |

| Const. / Sample no. | CIA % | Ni ppm | Co ppm | Cr ppm | Mn ppm | V ppm | Rb Ppm | Y ppm | Th ppm | La ppm | Nd ppm | Ce ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Siltstone** | | | | | | | | | | | | |
| $S_4$ | 53.80 | 83 | 48 | 577 | 900 | 54 | 42 | 15 | 5 | 7 | 47 | 31 |
| $S_5$ | 42.10 | 118 | 33 | 437 | 842 | 84 | 63 | 20 | 9 | 17 | 0 | 40 |
| $S_{13D}$ | 44.40 | 77 | 43 | 381 | 720 | 98 | 73 | 21 | 7 | 12 | 7 | 48 |
| $S_{18}$ | 41.20 | 124 | 33 | 392 | 802 | 55 | 57 | 0 | 6 | 22 | 8 | 45 |
| $S_{19}$ | 38.10 | 87 | 28 | 355 | 660 | 57 | 59 | 21 | 4 | 7 | 0 | 41 |
| $S_{29}$ | 61.50 | 124 | 33 | 309 | 763 | 79 | 54 | 21 | 7 | 21 | 0 | 43 |
| $S_{32}$ | 63.60 | 59 | 30 | 165 | 387 | 40 | 56 | 18 | 7 | 10 | 11 | 28 |
| **Range** | **38.1-63.6** | **59 - 124** | **28 - 48** | **165 - 577** | **387 - 900** | **40 - 98** | **42 - 73** | **0 – 21** | **4 – 9** | **7 – 22** | **0 - 47** | **28 - 48** |
| **Mean** | **49.24** | **96** | **35** | **374** | **725** | **67** | **58** | **17** | **6** | **14** | **10** | **39** |

## CONTIN. TABLE : 1

| Const. / Sample no. | $SiO_2$ % | $Al_2O_3$ % | $CaO_T$ % | MgO % | $K_2O$ % | $Na_2O$ % | $Fe_2O_{3T}$ % | $TiO_2$ % | $P_2O_5$ % | $CO_2$ % | $H_2O^+$ % |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Mudstone** | | | | | | | | | | | |
| $S_3$ | 44.20 | 9.37 | 11.88 | 7.66 | 1.82 | 2.21 | 4.75 | 0.93 | 0.21 | 8.90 | 4.45 |
| $S_6$ | 47.39 | 9.52 | 9.29 | 6.29 | 1.93 | 2.86 | 5.37 | 1.11 | 0.20 | 7.20 | 5.03 |
| $S_8$ | 45.03 | 9.07 | 11.95 | 6.02 | 1.83 | 2.32 | 5.70 | 0.98 | 0.24 | 10.50 | 3.92 |
| $S_{10}$ | 41.60 | 9.24 | 13.92 | 6.53 | 1.65 | 1.88 | 4.82 | 0.88 | 0.21 | 9.50 | 5.96 |
| $S_{12}$ | 42.28 | 8.87 | 16.02 | 4.80 | 1.47 | 2.51 | 3.64 | 0.87 | 0.22 | 10.30 | 6.06 |
| $S_{14}$ | 44.82 | 8.79 | 12.23 | 7.78 | 1.60 | 2.36 | 4.79 | 1.05 | 0.22 | 7.80 | 3.90 |
| $S_{23}$ | 45.88 | 9.09 | 7.03 | 8.74 | 1.70 | 0.33 | 7.47 | 1.63 | 0.20 | 4.80 | 5.74 |
| $S_{26}$ | 41.90 | 9.19 | 15.74 | 4.68 | 1.63 | 1.07 | 4.53 | 0.75 | 0.23 | 12.10 | 4.66 |
| $S_{27}$ | 44.11 | 9.49 | 12.1 | 7.26 | 1.55 | 0.98 | 5.29 | 1.02 | 0.22 | 7.00 | 7.14 |
| $S_{31}$ | 44.28 | 9.23 | 14.59 | 5.82 | 1.28 | 0.35 | 4.20 | 1.05 | 0.24 | 8.60 | 6.48 |
| **Range** | **41.6-47.39** | **8.79 - 9.52** | **7.03 - 16.02** | **4.68-8.74** | **1.28-1.93** | **0.33 - 2.86** | **3.64 - 7.47** | **0.75-1.63** | **0.20-0.24** | **4.80-12.10** | **3.9 - 7.14** |
| **Mean** | **44.15** | **9.19** | **12.48** | **6.56** | **1.65** | **1.69** | **5.06** | **1.03** | **0.22** | **8.67** | **5.33** |

| Const. / Sample no. | CIA % | Ni ppm | Co ppm | Cr ppm | Mn ppm | V ppm | Rb Ppm | Y Ppm | Th ppm | La ppm | Nd ppm | Ce ppm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Mudstone** | | | | | | | | | | | | |
| $S_3$ | 56.30 | 138 | 40 | 308 | 739 | 103 | 90 | 23 | 7 | 21 | 17 | 42 |
| $S_6$ | 55.60 | 100 | 48 | 251 | 715 | 104 | 103 | 26 | 11 | 23 | 34 | 50 |
| $S_8$ | 60.00 | 136 | 38 | 253 | 726 | 105 | 98 | 23 | 11 | 33 | 39 | 46 |
| $S_{10}$ | 52.90 | 136 | 33 | 383 | 571 | 97 | 75 | 20 | 9 | 10 | 0 | 36 |
| $S_{12}$ | 45.00 | 81 | 32 | 210 | 649 | 70 | 72 | 21 | 11 | 18 | 5 | 40 |
| $S_{14}$ | 47.40 | 195 | 43 | 411 | 665 | 90 | 77 | 23 | 9 | 17 | 0 | 42 |
| $S_{23}$ | 64.30 | 236 | 57 | 386 | 683 | 148 | 90 | 27 | 9 | 21 | 40 | 54 |
| $S_{26}$ | 64.30 | 72 | 35 | 131 | 875 | 97 | 84 | 23 | 9 | 20 | 5 | 32 |
| $S_{27}$ | 47.40 | 154 | 40 | 352 | 727 | 100 | 77 | 23 | 11 | 17 | 0 | 49 |
| $S_{31}$ | 50.00 | 142 | 38 | 320 | 654 | 78 | 66 | 25 | 7 | 25 | 36 | 41 |
| **Range** | **45.0-64.30** | **72 - 236** | **32 - 57** | **131 - 411** | **571 - 875** | **70 - 148** | **66 - 103** | **20 - 27** | **7 - 11** | **10 - 33** | **0 - 40** | **32 - 54** |
| **Mean** | **54.32** | **139** | **40** | **301** | **700** | **99** | **83** | **23** | **9** | **21** | **18** | **43** |

**T** mean Total

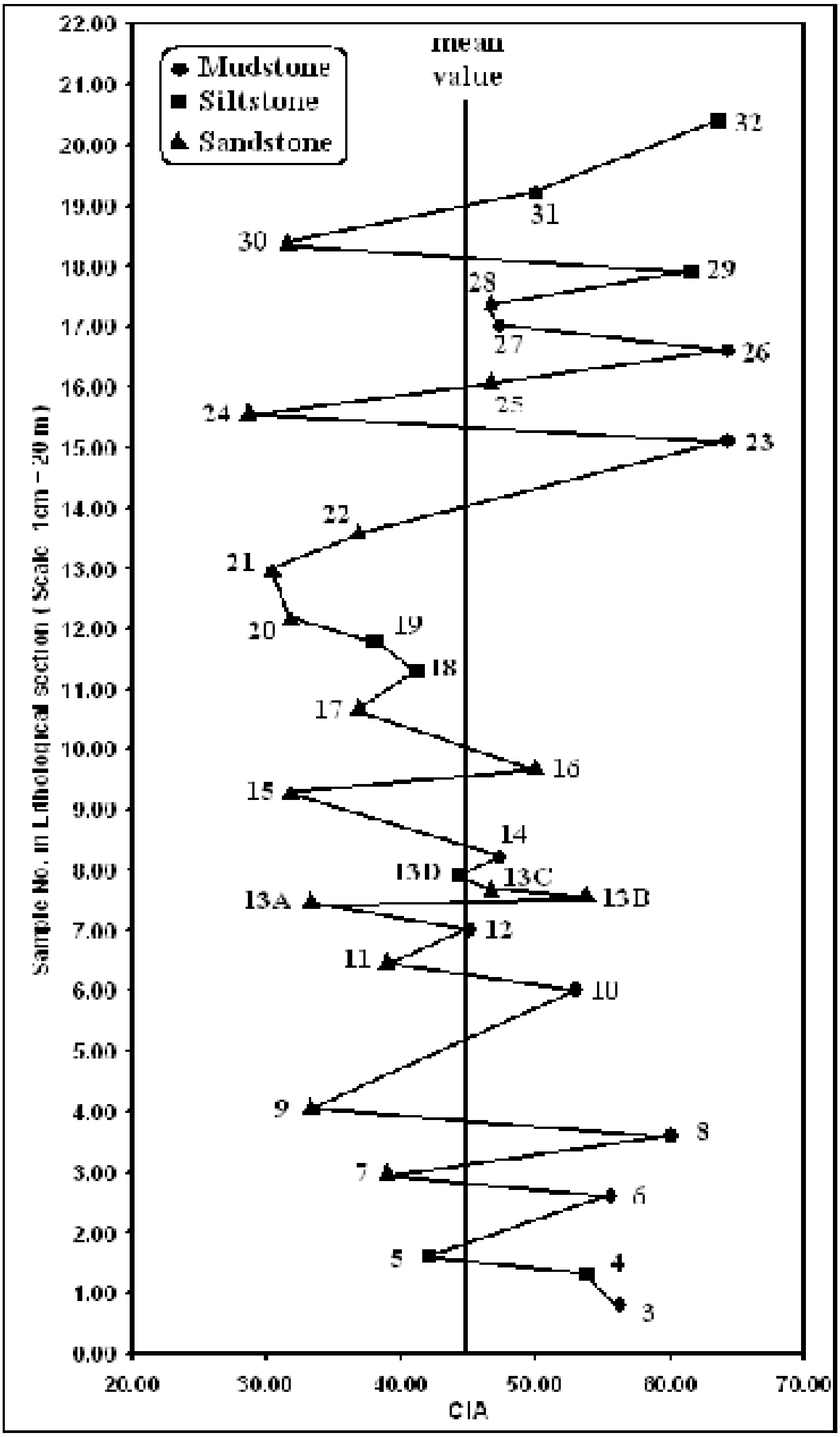



Fig. 3: Variation of CIA Values about the Mean in the Lithological Section in Study Area.

Furthermore the quartz content of mudstone do not differ much from its content in the siltstone and sandstone (Othman, 1990). Also the total $SiO_2$ content in the three size fractions do not differ greatly (Table 1). Therefore the three size fractions making the Injana section represent three weathering stages in the development of highly immature and poorly differentiated soil mantle at provenance sites. Such profiles were ultimately subjected to mass wasting, the material being transported and deposited in sedimentary basin as sands, silts and muds. Mass wasting of profiles in which chemical weathering is minimal such as those of the Injana Formation may result in fine grained detrital sediments contain high proportion of unaltered feldspars and rock fragments which lower the CIA values to low levels.

Although size sorting may not have been very effective in the fractionation of the major mineral constituents of the Injana rocks, however, gravity sorting i.e., fractionation of the highly heavy minerals may have been active especially in the sandstone, an observation which, as will be seen later, may explain the anomalous content of some elements particularly some of the rare earth in the sandstone.

Because weathering lead to a change in the volume of the products as compared with fresh rocks, it was found necessarily to normalize the element content in the lithological groups to an immobile element before comparing variation of element content with CIA values. This is because change of density of the weathering products will introduce erroneous picture in element content changes if one use absolute element content values. $Al_2O_3$ and $TiO_2$ are normally used as normalizing elements on the assumption that these are among the least mobile elements. Such assumption is highly valid especially in the case of weathered products subjected to low level chemical weathering as the case of source rocks of the Injana sediments.

The use of immobile trace elements such as Zr, Nb and Ta in normalization usually faces some difficulties among which their low content and the low accuracy of the analytical results of such elements.

Table (2) contains ratios of some major and trace elements normalized to $Al_2O_3$ and $TiO_2$ contents in the three groups of the Injana Formation. Also shown other ratios of particular interest in following the fate of elements that are normally closely associated in primary crystalline rocks. (Fig. 4) Show plots of the ratios versus CIA values of the sandstone, siltstone and mudstone. (Table 2) and (Fig. 4) Shows that elements may be grouped into three groups according to their behaviour through increasing chemical index of alteration. Group(1) include $SiO_2$, $P_2O_5$, $Na_2O$, $K_2O$, Cr and Mn. These elements, with the exception of the ratio $K_2O/Al_2O_3$, when normalized to both $Al_2O_3$ and $TiO_2$ show obvious negative correlation with CIA value. The decrease in the ratios of $Na_2O/Al_2O_3$ and $Na_2O/TiO_2$ is easily explained on the bases of the high mobility of Na during weathering of the plagioclase feldspars, and it also indicate that little Na is retained in the clay minerals.

Table 2: Ratio of Elements to $Al_2O_3$ and $TiO_2$ in the Sandstone, Siltstone and Mudstone of the Injana Formation also Shown other Ratios of Interest.

| **Ratio** | **Sandstone** | **Siltstone** | **Mudstone** |
|---|---|---|---|
| $SiO_2$ / $Al_2O_3$ | 6.02 | 5.41 | 4.81 |
| $SiO_2$ / $TiO_2$ | 76.52 | 56.71 | 42.99 |
| $TiO_2$ / $Al_2O_3$ | 0.08 | 0.10 | 0.11 |
| $P_2O_5$ / $Al_2O_3$ | 0.034 | 0.03 | 0.024 |
| $P_2O_5$ / $TiO_2$ | 0.43 | 0.31 | 0.21 |
| $K_2O$ / $Al_2O_3$ | 0.180 | 0.170 | 0.179 |
| $K_2O$ / $TiO_2$ | 2.29 | 1.78 | 1.60 |
| $Na_2O$ / $Al_2O_3$ | 0.45 | 0.30 | 0.18 |
| $Na_2O$ / $TiO_2$ | 5.71 | 3.13 | 1.64 |
| $Na_2O$ / $K_2O$ | 2.49 | 1.76 | 1.02 |
| V / $Al_2O_3$ * $10^4$ | 7.77 | 8.83 | 10.8 |
| V / $TiO_2$ * $10^4$ | 98.73 | 92.66 | 96.59 |
| Mn / $Fe_2O_3$ * $10^4$ | 333.31 | 253.7 | 138.53 |
| Mn / $TiO_2$ * $10^4$ | 1382.74 | 1006.75 | 681.99 |
| Mn / $Al_2O_3$ * $10^4$ | 108.75 | 95.99 | 76.25 |
| Ni / $Al_2O_3$ * $10^4$ | 10.01 | 12.71 | 15.13 |
| Ni / $TiO_2$ * $10^4$ | 127.27 | 133.33 | 135.35 |
| Co / $Al_2O_3$ * $10^4$ | 3.29 | 4.69 | 4.40 |
| Co / $TiO_2$ * $10^4$ | 41.89 | 49.21 | 39.34 |
| Cr / $Al_2O_3$ * $10^4$ | 68.26 | 49.49 | 32.71 |
| Cr / $TiO_2$ * $10^4$ | 867.89 | 519.05 | 292.60 |
| Rb / $K_2O$ * $10^4$ | 44.17 | 44.99 | 50.55 |
| Th / $Al_2O_3$ * $10^4$ | 1.01 | 0.85 | 1.02 |
| Th / $TiO_2$ * $10^4$ | 12.89 | 8.93 | 9.15 |
| Ce / $Al_2O_3$ * $10^4$ | 4.35 | 5.22 | 4.7 |
| Ce / $TiO_2$ * $10^4$ | 55.35 | 54.76 | 42.06 |
| La / $Al_2O_3$ * $10^4$ | 2.32 | 1.82 | 2.23 |
| La / $TiO_2$ * $10^4$ | 29.46 | 19.05 | 19.96 |
| Y / $Al_2O_3$ * $10^4$ | 2.62 | 2.19 | 2.55 |
| Y / $TiO_2$ * $10^4$ | 33.26 | 23.02 | 22.78 |
| Nd / $Al_2O_3$ * $10^4$ | 4.52 | 1.38 | 1.92 |
| Nd / $TiO_2$ * $10^4$ | 57.42 | 14.48 | 17.14 |

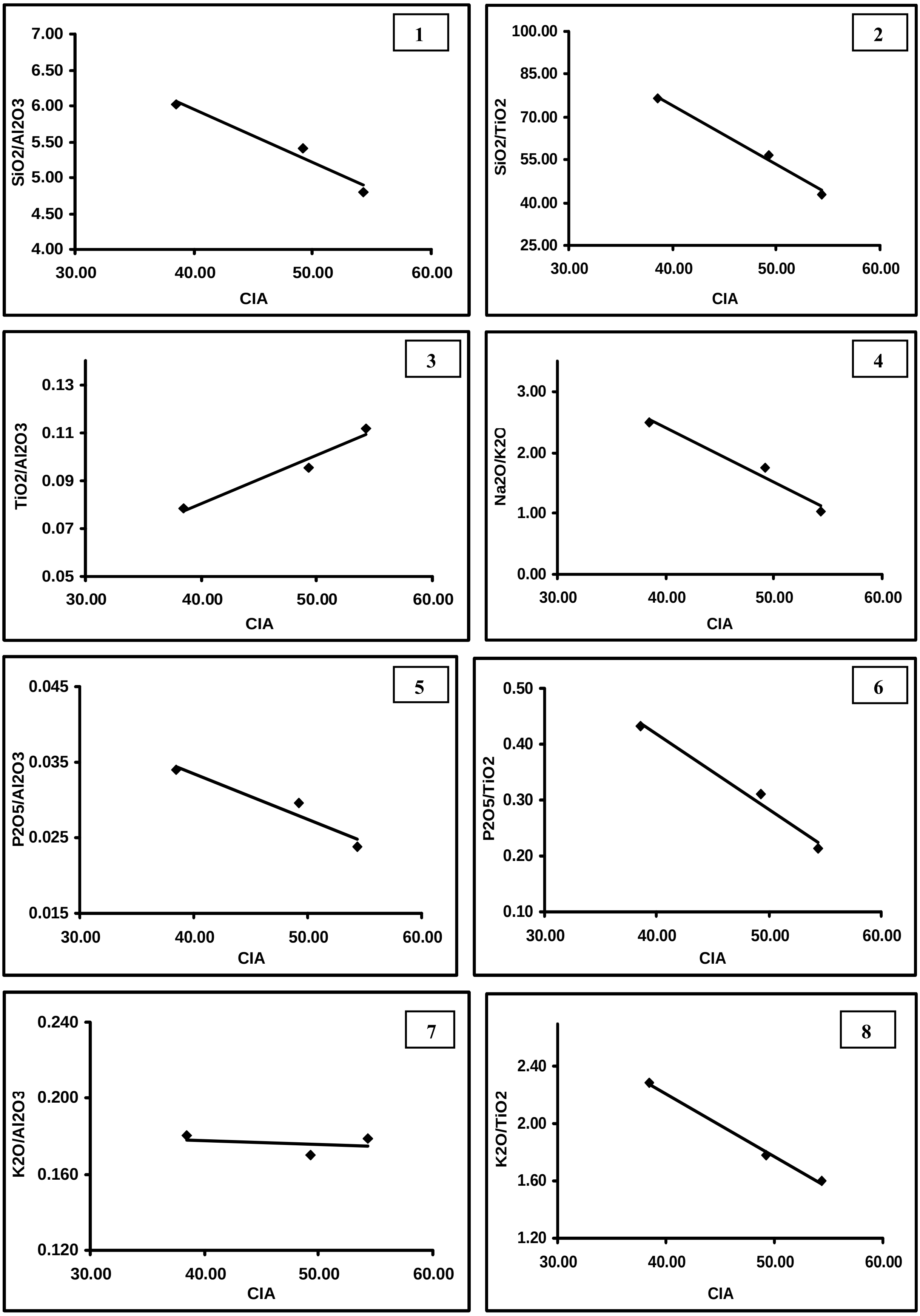
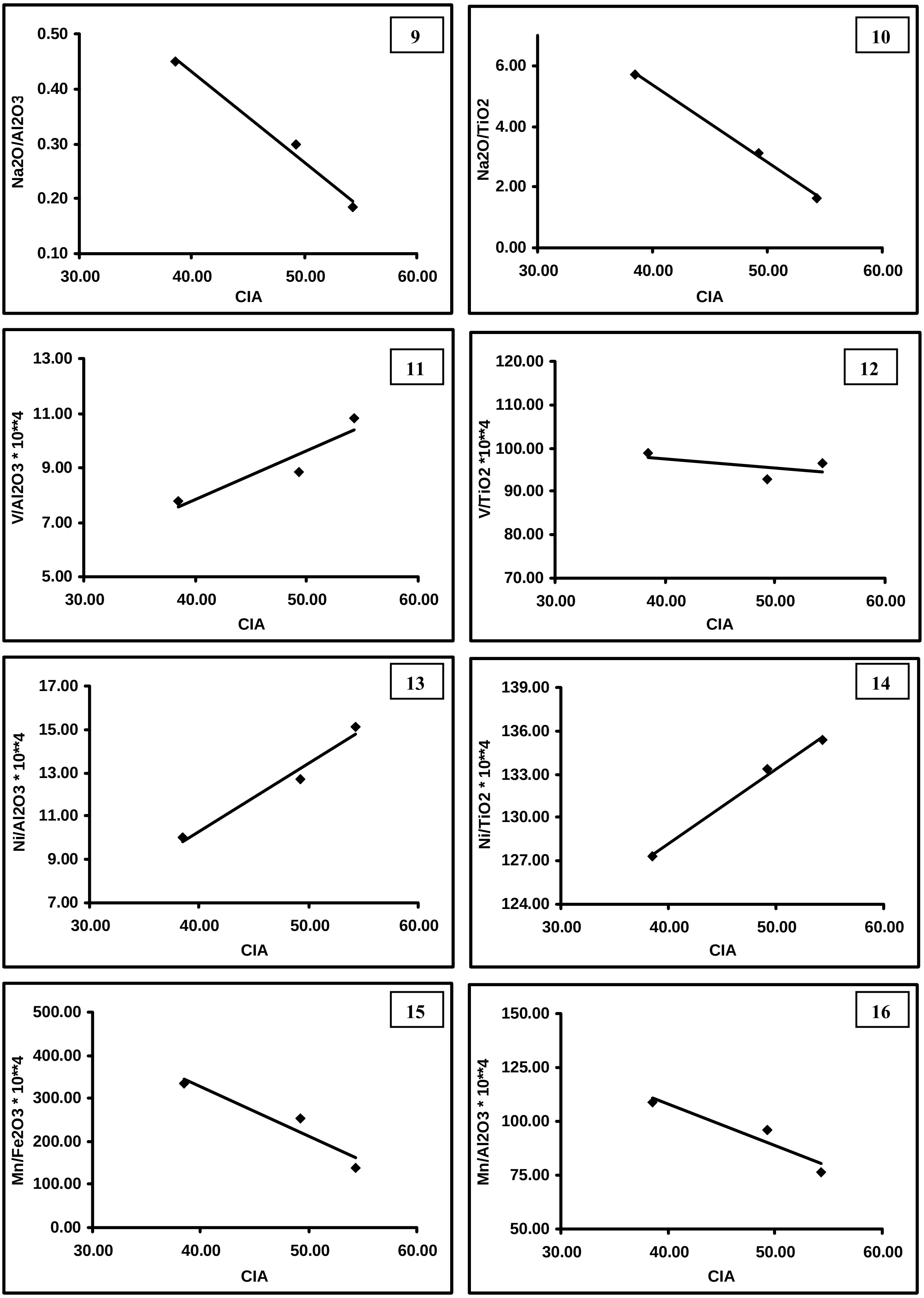
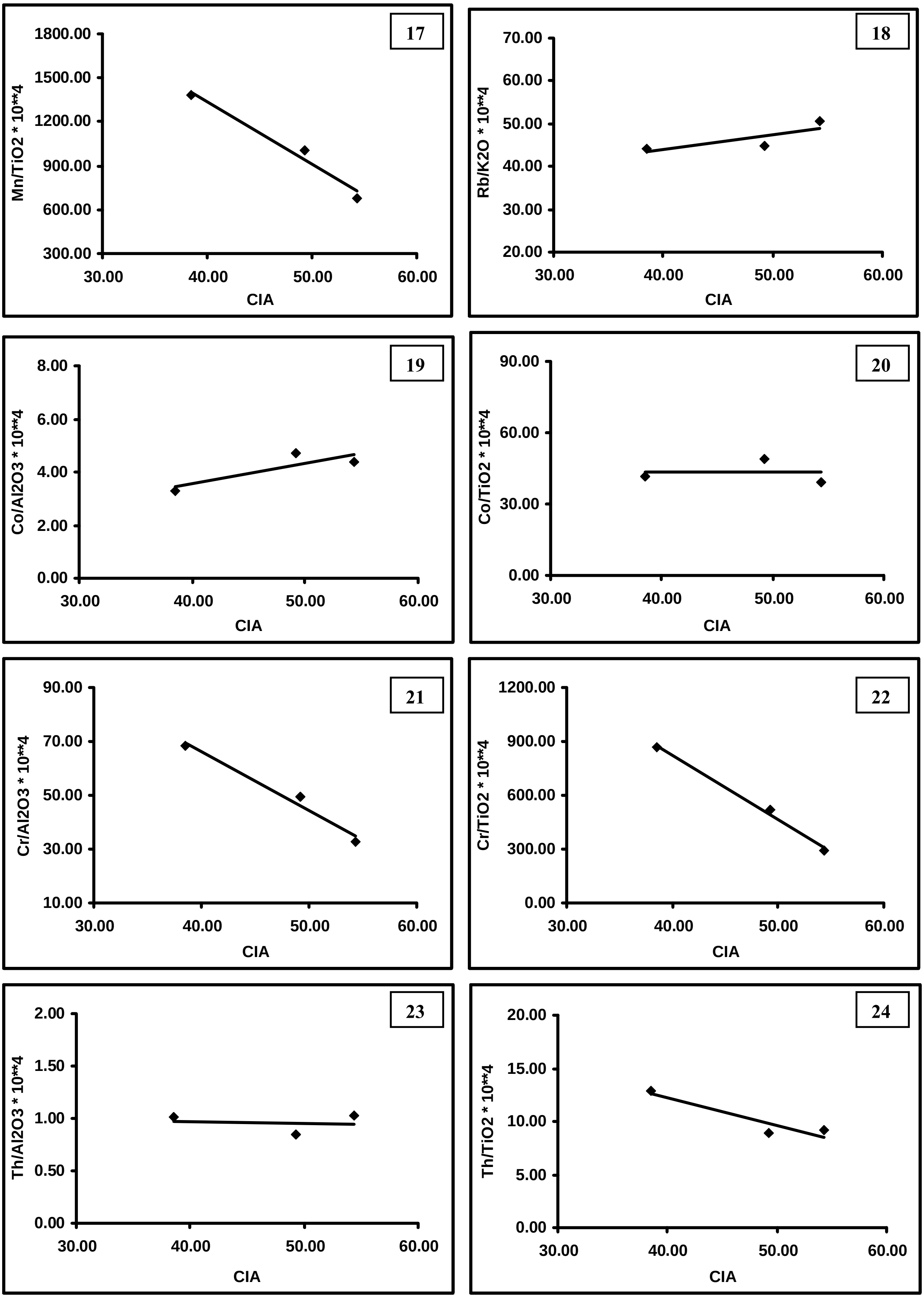



Fig. 4: The Relationship Between the Mean CIA Value of the Three lithologies of

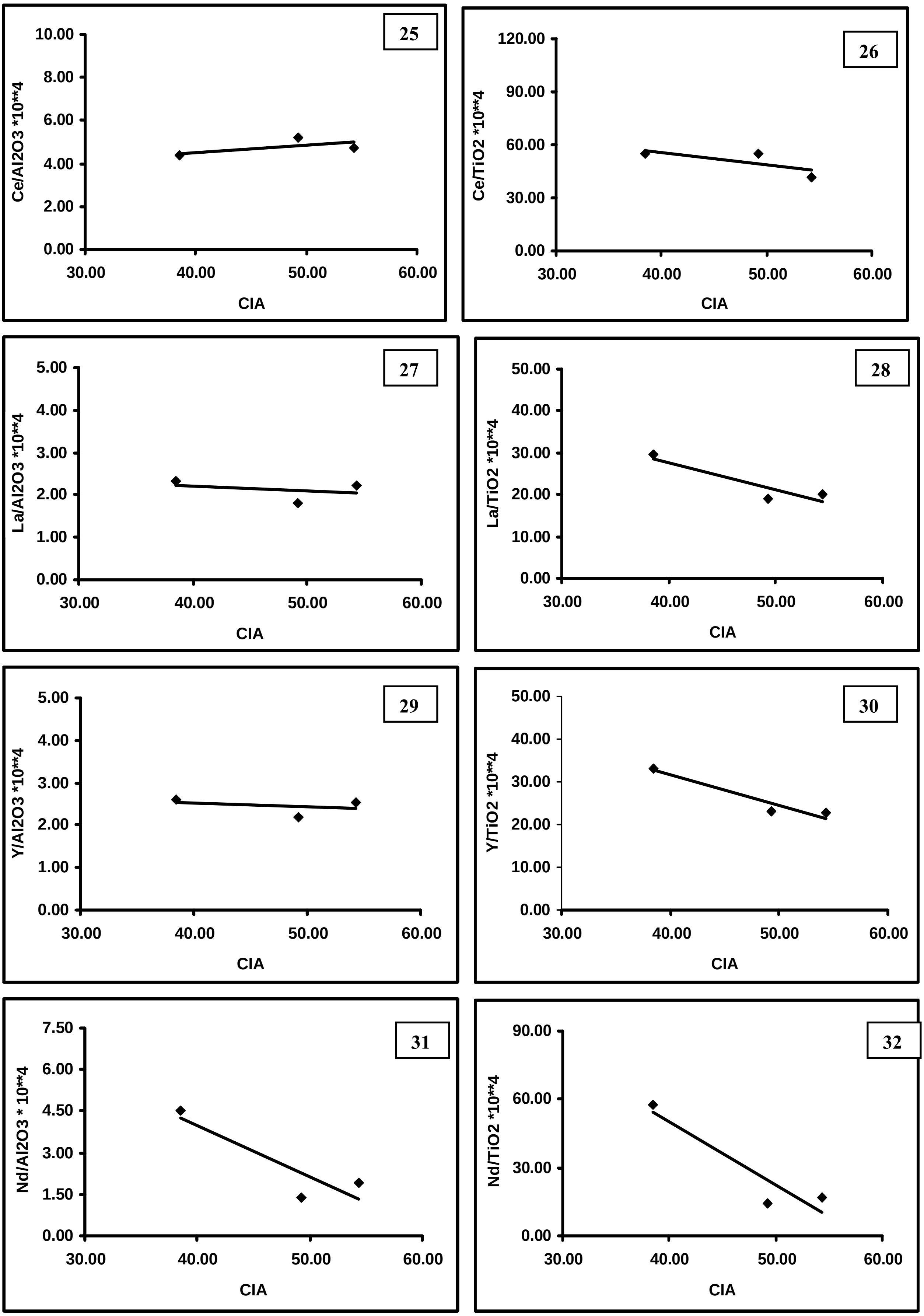
the Injana Formation and Ratios of Elements.



Cont. Fig. 4:




Cont. Fig. 4:


25
Ce/Al2O3 *10**4
10.00
8.00
6.00
4.00
2.00
0.00
30.00
40.00
50.00
60.00
CIA
26
Ce/TiO2 *10**4
120.00
90.00
60.00
30.00
0.00
30.00
40.00
50.00
60.00
CIA
27
La/Al2O3 *10**4
5.00
4.00
3.00
2.00
1.00
0.00
30.00
40.00
50.00
60.00
CIA
28
La/TiO2 *10**4
50.00
40.00
30.00
20.00
10.00
0.00
30.00
40.00
50.00
60.00
CIA
29
Y/Al2O3 *10**4
5.00
4.00
3.00
2.00
1.00
0.00
30.00
40.00
50.00
60.00
CIA
30
Y/TiO2 *10**4
50.00
40.00
30.00
20.00
10.00
0.00
30.00
40.00
50.00
60.00
CIA
31
Nd/Al2O3 * 10**4
7.50
6.00
4.50
3.00
1.50
0.00
30.00
40.00
50.00
60.00
CIA
32
Nd/TiO2 *10**4
90.00
60.00
30.00
0.00
30.00
40.00
50.00
60.00
CIA

Cont. Fig. 4:

On the other hand the decrease in $K_2O/TiO_2$ ratio and the almost constant ratio of $K_2O/Al_2O_3$ indicate that what remained of $K_2O$ in the weathered product is totally associated with the Al bearing minerals(K feldspar and clay minerals).
The differential mobilities of Na and K has led to obvious, as expected, decrease in the ratio $Na_2O/K_2O$ with increasing CIA value. The increase of $Rb/K_2O$ with increasing CIA value agrees well with the geochemical characteristics of Rb during weathering processes. For Rb ions being larger than K can be held more firmly in clay minerals than the smaller K ions.

The decrease in $SiO_2/Al_2O_3$ and $SiO_2/TiO_2$ with increasing CIA value could follow more than one explanation; it could mean slight mobility of $SiO_2$ during weathering, this is probably aided by relatively high pH (≈8) due to the presence of carbonate clasts in the source area or it could mean a slight fractionation of quartz in the sand and silt fractions due to sorting, but this is unlikely since as mentioned earlier the clay size fraction (mudstone) do not contain much less quartz than the sandstone and the siltstone. It also could be explained as being due to precipitation of amorphous $SiO_2$ as cementing material in the porous sandstone and to a lesser degree in the siltstone during lithification of the sediments. The latter may explain the slightly higher $SiO_2$ content of sandstone as compared with mudstone.

The decrease of Mn relative to $Al_2O_3$, $TiO_2$ and $Fe_2O_3$ with increasing CIA value indicates the mobile nature of Mn in the weathering process even in the low degree of chemical weathering of the Injana source rocks. This is due to relatively higher Eh value required to oxidize the soluble $Mn^{2+}$ to the insoluble $Mn^{4+}$ at the pH (≈8) of weathering environment as compared with Eh value required to oxidize $Fe^{2+}$ to $Fe^{3+}$.

The trend shown by Cr is obviously due to fractionation of chromite by gravity action. Such fractionation is well documented by Othman (1990) where chromite rich thin laminae are observed in the Injana sandstone. Such gravity action is best developed at shorelines and in river sediments.

The decreasing $P_2O_5$ content relative to constant $Al_2O_3$ and $TiO_2$ with increasing CIA value can be explained as being due to the predominantly arid conditions of the weathering sites and also due to the mostly fresh water depositional environment of
the Injana rocks. Under arid conditions little phosphate are released from phosphate bearing minerals and most of these are gravity concentrated in the sandstone fraction as heavy and highly insoluble minerals including monazite, xenotime etc. while fresh water environment does not contribute much phosphate to hydrolysate sediments particularly clay minerals due to lower concentration of P in fresh water as compared with marine water (Goldschmidt, 1958) in fact Dhannoun and Al-Delaime (in preparation) found that the ratio of $P_2O_5/Al_2O_3$ in argillaceous sediments can be used to distinguish marine from fresh water sediments.

Group (2) elements include Ni, Co and V. (Fig. 4) Show that there is an enrichment of Ni relative to $Al_2O_3$ and $TiO_2$ in the mudstone, indicating that little lose of Ni is encountered during development of weathered mantle over source of Injana Formation. Here Ni released from Ni bearing silicates is reprecepitated with Al and Ti bearing secondary phases (clay minerals and possibly colloidal $Ti(OH)_4$). The almost constant ratios of $Co/TiO_2$ and $V/TiO_2$ with CIA variation and the increase in the ratios of $V/Al_2O_3$ and $Co/Al_2O_3$ indicate that both Co and V are mainly hosted in the clay minerals, it also indicate that these elements were highly immobile during the development of the Injana rocks beginning with weathering of source rocks and ending with deposition of products. As mentioned earlier this is due to the arid to semi-arid condition of the weathering sites. A similar behaviour of Ni and Co is also exhibited by the Gercus Formation of Eocene age (Dhannoun *et.al* ., 1988).

Although the variation of $TiO_2/Al_2O_3$ with CIA values is rather small, however an explanation is required for the slightly higher $TiO_2/Al_2O_3$ in the mudstone. The contrasted behaviour of $TiO_2$ when compared with Cr in the sandstone undoubtedly rules out a gravity enrichment of $TiO_2$ in the sandstone. This is because Ti bearing minerals e.g. rutile, ilmenite would be expected to fractionate in a similar manner to Cr, for these constitute members of the heavy minerals group such minerals do not constitute significant proportion of the bulk Ti content in the Injana rocks. Therefore other Ti bearing phases are likely to be present in the mudstone. These include $Ti(OH)_4$ which is cooprecipitated with clay minerals. Migdisov (1960) have indicated that the epochs of impoverishment in titanium in sandstone coincides with times of dominantly arid climate and a deposition of polymict sands rich in primary aluminosilicate. The fact that the mineral constituents of the sandstones of the Injana Formation are not affected to high degree of chemical alteration support this conclusion.

Group(3) elements include Th, La, Ce, Y and Nd. All these elements relative to $TiO_2$ content are enriched in sandstones and relatively depleted in siltstones and mudstones. Only Nd follow a similar pattern when normalized to $Al_2O_3$ content while the others(Th, Ce, La and Y) do not show fractionation when normalized to $Al_2O_3$. Because these elements are known to be associated in many accessory minerals which have rather high specific gravity e.g. allanite$(Ca, Ce, La, Y)_2$ $(Al, Fe)_3(SiO_4)_3OH$ and monazite$(Ce, La, Th, Nd, Y)PO_4$. probably explain why these elements are enriched relative to $TiO_2$ in the sandstones and depleted in the siltstones and mudstones. For because of the high specific gravity they are hydraulically concentrated in the sandstones. The almost constant ratio of La, Y, Ce and Th when normalized to $Al_2O_3$ indicate that the minerals containing these elements are of clay size or that the greater part of these elements in the siltstones and mudstones are associated with clay minerals.

## CONCLUSIONS

The following conclusions are drawn from the present study:

1- The three size fractions of the Injana Formation represent mainly fractions that have suffered various degrees of chemical and physical weathering. Size sorting associated with transportation and deposition of the sediments, however, was of minimum effect on the fractionation of elements. Gravity fractionation of some elements could have been effective during deposition.

2- Chemical weathering was of minimum level which reflected the semi-arid to arid conditions of source rocks weathering which produced undifferentiated and highly immature mantle over source rocks. This was mass washed probably during short wet seasons to a near by basin of deposition. Under such conditions even the highly irresisting minerals (olivine, pyroxene etc.) have survived intensive alteration.

3- The degree of chemical weathering as expressed by CIA values across the vertical section of the Injana Formation indicated that there was no obvious overall change in the climate during the period of deposition of the Injana Formation. However slight fluctuation may have occurred during this period.

4- The relationship between alkali elements K, Na and Rb content and CIA values agrees well with their known behaviour during weathering of minerals that host these elements. It also shows that high degree of selective leaching of Na compared with K, a phenomenon expected when source rocks are subjected to chemical weathering of low intensity.

5- The relationship between some elements included in this study and variation in CIA values was explained on the basis of the semi-arid to arid nature of the weathering climate or on reason of gravity fractionation of heavy minerals that host such elements.

6- The abnormally low value of CIA of the Injana rocks denies any major contribution of argillaceous rocks in the lithoclasts of the sediments of the Formation.

## REFERENCES


Aghwan, T.A., Al-Banna, N. Y., and Al-Rashedi, M.A., 2008. Diagenesis and Factor Analysis of Sandstones of Injana Formation in Selected Sections Northern Iraq. Iraqi Journal of Earth Sciences, Vol. 8, No. 1, pp. 11-23.

Al-Juboury, A.I., 1994. Petrology and Provenance of the Upper Fars Formation, Northern Iraq. Acta Geologica Universitatis Commenianae (Slovakia), Vol. 50, pp. 45-53.

Al-Juboury, A.I., 2001. Provenance and Paleogeography of Injana Formation in Iraq based on Petrography and Heavy Minerals Distribution. Iraqi Jour. of Earth Sci., Vol. 1, No. 2, pp. 36 - 51.

Al-Rawi, Y., 1982. Carbonate - Rich Sandstone: Occurrence, Classification and Significance. Iraqi Jour. Sci., Vol. 23, No. 3, pp. 371- 419.

Basi, M. A., 1973. Geology of Injana Area, Hemrin South. Unpub. M.Sc. thesis, University of Baghdad, Iraq, 124 p.

Buday, T., 1980. The Regional Geology of Iraq: Stratigraphy and Paleogeography. Dar Al- Kutib pub. House, Mosul, Iraq, 445 p.

Dhannoun, H.Y., Al-Dabbagh, S. M.A., and Hasso, A.A., 1988. The Geochemistry of the Gercus red bed Formation of Northeast Iraq. Chem. Geol., Vol. 69, pp. 87 - 93.

Dokuz, A., and Tanyolu, E., 2006. Geochemical Constraints on the Provenance, Mineral Sorting and Subaerial Weathering of Lower Jurassic and Upper Cretaceous Clastic Rocks of Eastern Pontides Yusufeli (Attvin), NE Turkey. Turkish. Jour. of Earth Scie., Vol. 15, pp. 181-209.

Goldschmidt, V. M., 1958. Geochemistry. Oxford University Press, Edited by Alex Muir, 730 p.

Jassim, S.Z. and Buday, T., 2006. Units of the Unstable Shelf and the Zagros Suture. (CH.6) In: Jassim, S. Z. and Goff, J.C., 2006. Geology of Iraq. Published by Dolin, Prague and Moravian, Museum Brno Czech Republic, 341p.

Migdisov, A.A., 1960. On the Titanium - Aluminum Ratio in Sedimentary Rocks. Geochemistry, No. 2.

Nesbitt, H.W. and Young, G.M., 1982. Early Proterozoic Climate and Plate Motion Inferred from Major Element Chemistry of lutites. Nature, Vol. 299, pp. 715 -717.

Nhleko, N., 2003. The Pongola Super Group in Swaziland. Ph.D. thesis in Rand Afrikaans University, 310 p.

Norrish, K. and Chappell, B.W., 1977. X-Ray Fluorescence Spectrometry. In: Zussman, J., 1977. Physical Methods in Determinative Mineralogy. 2nd Edition, Academic Press Inc.( London) LTD, 720 p.

Norrish, K. and Hutton, J.T., 1964. In: Zussman, J., 1977. Physical Methods in Determinative Mineralogy. 2nd Edition, Academic Press Inc.( London) LTD, 720 p.

Osae, S., Asiedu, D.K., Yakubo, B. B., Koeberl, C., and Dampane, S.B., 2006. Provenance and Tectonic Setting of Late Proterozoic Buem Sandstones of Southeastern Ghana: Evidence from Geochemistry and Detrital Modes. Jour.of African. Earth Scie., Vol. 44, pp. 85 - 96.

Othman, S.M., 1990. Distribution of Major, Minor and Trace Elements in the Mineral Cconstituents of the Sediments of the Upper Fars Formation at Permam Dagh- Erbil. (In Arabic), Unpub.M.Sc.thesis, University of Mosul, 132 p.

Price, J.R., and Velbel, M.A., 2003. Chemical Weathering Indices Aapplied to Weathering Profiles Developed on Heterogeneous Felsic Metamorphic Parent Rocks. Chem. Geol., Vol. 202, pp. 397- 416.

Rahman, M.J.J., and Suzuki, S., 2007. Geochemistry of Sandstones from the Miocene Surma Group, Bengal Basin, Bangladesh: Implication for Provenance Tectonic Setting and Weathering. Geoch. Jour., Vol. 41, No. 6, pp. 415 - 428.

Roser, B.P., and Korsch, R.J., 1988. Provenance Signature of Ssandstone-Mudstone Suites Determined Using Discriminant Function Analysis of Major Element Data. Chem. Geol., Vol. 67, pp. 119 - 139.

Selvaraj, K., and Chen, C.T.A., 2006. Moderate Chemical Weathering of Subtropical Taiwan: Constraints from Solid-Phase Geochemistry of Sediments and Sedimentary Rocks. The Jour. of Geol., Vol. 114, pp. 101-116.

Zussman, J., 1977. Physical Methods in Determinative Mineralogy. 2$^{nd}$ Edition, Academic Press Inc.( London) LTD, 720 p.