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THE WEATHERING INTENSITY SCALE (WIS): AN ALTERNATIVE APPROACH OF THE CHEMICAL INDEX OF ALTERATION (CIA)

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ABSTRACT. The chemical index of alteration (CIA) is a tool to calculate the weathering intensity (Nesbitt and Young, 1982). It has been largely used to reconstitute the past climates on Earth at different epochs and to determine the sediment source rocks from shale and graywacke stratigraphical series. However, because it induces some uncertainties, we propose a new approach based on the M^+-4Si-R^{2+} system ($M^+ = Na^+ + K^+ + 2Ca^{2+}$; 4Si = Si/4; $R^{2+} = Fe^{2+} + Mg^{2+}$) that takes silica into account. In these coordinates, the chemical compositions of the weathered granitic, mafic and ultramafic rocks determine clearly separated trends which all converge toward the 4Si pole, namely the kaolinite composition (chlorites plot near the R^{2+} pole). Consequently, the alteration intensity for a given parent rock can be measured by the migration of its chemical composition toward the kaolinite pole: $\Delta 4Si\% = [(4Si_{\text{altered sample}} - 4Si_{\text{unaltered parent rock}}) \times 100]/(100 - 4Si_{\text{unaltered parent rock}})$. The ultimate stage of weathering leads to the progressive accumulation of the insoluble R^{3+} components ($R^{3+} = Al^{3+} + Fe^{3+}$). It is attained in bauxite deposits where kaolinite is replaced by gibbsite. This ratio varies from 0 to 1 with increasing weathering degree, namely the leaching of soluble components (M^+ and R^{2+}), the oxidation of Fe^{2+} and the concentration of the residual ones (Al^{3+}, Fe^{3+}). Because hydroxides cannot be represented in the M^+-4Si-R^{2+} system, the Weathering Intensity Scale (WIS) including the ultimate bauxite stage must be based on the co-variation of the Δ4Si% parameter and the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratio.

The effects of the diagenetic illitization on the composition of sediments (so-called K-metasomatism) are difficult to measure since the K_2O amount of sediments may be highly variable due to the inheritance of detrital potassic minerals. In spite of this variability, if the compositions of the shales in a given series are aligned toward the diagenetic illite pole ($[Si_{3.30}Al_{0.70}]O_{10}(Al_{1.78}Fe^{3+}{}_{0.05}Mg_{0.17})(OH)_2K_{0.87}$) in the M^+-4Si-R^{2+} coordinates, a correction is required. The illite amount has been calculated for the Gulf Coast shale series assuming that the K_2O percent of the original sediment (K_2O_{sediment}) is equal to that of the shale sample having the lowest K_2O%: ($K_2O_{\text{shale}} - K_2O_{\text{sediment}}$) × 100/9.9. The correction modifies the amounts of all the elements and not only that of potassium. Consequently, the normalized values of the M^+, 4Si, and R^{2+} parameters for the corrected composition are changed and the Δ4Si% parameter modified.

The WIS has been tested on a Neoproterozoic shale-graywacke series (Mirbat Group, Oman) in which the sediments have been deposited in contrasted climatic conditions (glacial and interglacial). The variation of the Δ4Si% parameter along the stratigraphic pile exhibits large and low magnitude oscillations. The former are coherent with that given by the CIA and could correspond to changes in global conditions (temperature, latitude) while the second could indicate changes in more local ones (precipitation, elevation, denudation, runoff).

Key words: Weathering intensity, alteration index, paleo-climates

INTRODUCTION

Sediments record the supergene transformations that have reworked the Earth's crust throughout its history. They are the final products of a chain of dynamic phenomena that operated from Proterozoic to present day: weathering, ablation, transport, deposition and diagenesis. Because ancient undisturbed weathered rocks are rare (paleosols), most of the climate markers are considered to be archived in sediments. However, the physical and chemical modifications experienced by the alteration products from their origin (undisturbed weathered rocks) to the final state in which they are presently observed (mudstones, shales and graywackes) may obscure the climatic message recorded in their chemical and mineral composition.

Since Nesbitt's pioneer work defining a Chemical Index of Alteration (CIA) (Nesbitt and Young, 1982; Nesbitt, 1992), several other indexes have been proposed based on mineralogical or chemical data to evaluate the intensity of alteration. Nevertheless, the CIA remains, by far, the most widely used one. It has been refined using the kinetics and thermodynamics of the dissolution reactions commonly encountered in weathering processes (Nesbitt and Young, 1984; Nesbitt, 1992) and completed by the addition of another chemiographic space including the Fe and Mg components: the Al_2O_3-CaO, Na_2O, K_2O-FeO, MgO (A-CNK-FM) system (Nesbitt and Young, 1989). Considering that the major chemical effects of the weathering processes are the leaching of the most soluble components (Ca, Na) and the concentration of the residual aluminium, the CIA is based on the $Al_2O_3/(Al_2O_3 + Na_2O + CaO^*)$ molar ratio (CaO* is the CaO associated to the silicates).

The CIA is commonly used to evaluate the alteration intensity and to determine the sediment source rocks. High values indicate an intense alteration comparable to that operating today in the inter-tropical area; low values reflect limited chemical transformations typical of colder countries. However, because both the A-CN-K or the A-CNK-FM systems do not take into account the SiO_2 content, the index suffers of unavoidable limitations. This is why it is associated sometimes with a Mineralogical Index of Alteration or MIA (Johnsson, 1993; Rieu and others, 2007). Ohta and Arai (2007) used another method based on the principal component analysis (PCA) in which the compositions of the sediments are represented in a mafic-felsic-weathering diagram (M-F-W). They obtained a clear separation of the weathering chemical trends for the major rock types. However, the M, F and W parameters are complex combinations of chemical component amounts that make the method difficult to use currently for diagenetic shale series. Besides, the effects of illitization (K-metasomatism) and the oxidation state of iron are not taken into account.

The temperature dependence of the CIA has been confirmed by the chemical composition of the suspended matter in 44 rivers worldwide (Li and Yang, 2010 and references therein). However, sediments are not directly comparable to suspended matter since they are progressively transformed during diagenesis. Particularly, the illitization of the clay fraction leads to a potassium enrichment (K-metasomatism). Thus, the CIA is not directly measurable from the composition of shales or graywackes; a correction of the K-metasomatism effects is necessary to recover the original composition of the sediment (Nesbitt and Young, 1989). Fedo and others (1995) show that the correction can be easily performed using a chemiographic projection in the Al_2O_3-$CaO+Na_2O$-K_2O system (A-CN-K) by the difference between the sediment composition and a predicted weathering trend. Then, the corrected CIA values can be used to reconstitute the climatic conditions that prevailed during the weathering of the sediment rock sources in the past. For instance, this has been done for Neoproterozoic series (Rieu and others, 2007; Bahlburg and Dobrzinski, 2009, among others).

Knowing the limitations of the CIA and the rebutting complexity of the PCA, we focused our work on the research of another chemiographic method including most of the major chemical components of silicate rocks. We aim to define another index of alteration which does not have the CIA-A-CN-K limitations. The first step is the research of a chemiographic representation including silica, divalent, trivalent and alkali-alkaline earth cations and adapted to describe the chemical modifications experienced by silicate rocks under weathering as well as diagenetic conditions. The

Table 1

Composition parameters of major rock types in the M^+-4Si-R^{2+} system

	average parameters			
	4Si%	**M^+%**	**R^{2+}%**	**$R^{3+}/(R^{3+}+R^{2+}+M^+)$**
Average upper crust 1.8-1.6 Ga	39.8	42.7	17.4	0.42
TTG	45.6	48.5	5.9	0.51
granite	53.7	44.6	1.7	0.53
fels volc rocks	53.6	43.6	2.8	0.54
** diorite	31.4	50.6	18.0	0.42
andesite	35.4	50.9	13.7	0.42
**granodiorite	40.9	47.0	12.1	0.50
basalt	25.2	53.8	21.0	0.40
*gabbro	22.3	43.6	34.1	0.30
komatiites	18.4	22.1	59.5	0.23
**peridotites	13.0	6.0	81.0	0.03

See text and appendix 1 for calculation details. The chemical compositions are taken from Condie (1993) except for gabbros (* Ildefonse, 1978) and diorite, granodiorite, peridotites (** Best, 2011). Data from Condie (1993) are given with Fe_{total} = FeO.

second step is the application of this new method to shale-graywacke series in order to examine its potentialities as a tracer of the sediment source rocks and the intensity of weathering. The climatic significance will be tested using a contrasted climatic sedimentary sequence: the Neoproterozoic glacial-interglacial diamectite-shale series described by Rieu and others (2007) in south Oman. Then, in a third step, the new method will be compared to the CIA calculation procedure.

METHODS

The M^+-4Si-R^{2+} system is currently used to represent the composition of clay mineral assemblages formed in different water-rock interaction systems as are soils, weathered rocks, diagenetic or hydrothermal series (Meunier, 2005). In that system, because the alkaline and alkaline earth elements (M^+ pole: $Na^+ + K^+ + 2Ca^{2+}$) and divalent metallic elements (R^{2+} pole: $Mg^{2+} + Fe^{2+} + Mn^{2+}$) are taken into account with silica, the major rock types composition domains are clearly separated. The 4Si amount corresponds to the number of Si^{4+} cations divided by 4 to refer to the general formula unit of phyllosilicates. The M^+, 4Si and R^{2+} amounts are normalized to 100 percent and subsequently plotted in a ternary diagram. The residual trivalent components ($R^{3+} = Al^{3+} + Fe^{3+}$) are not taken into account here. The M^+%, 4Si% and R^{2+}% calculation procedure is the following (see Appendices 1 and 2 for detailed calculation):

1) calculation of the number of monocationic millimoles (equivalent to number of cations) from the oxide amount;
2) calculation of the 4Si, R^{3+}, R^{2+}, M^+ parameters (4Si = mMol Si/4, M^+ = mMol Na^+ + mMol K^+ + 2 × mMol Ca^{2+}; R^{2+} = mMol Fe^{2+} + mMol Mg^{2+} + mMol Mn^{2+}, R^{3+} = mMol Fe^{3+} + mMol Al^{3+});
3) plot of compositions in the M^+-4Si-R^{2+} ternary system after normalisation to 100%; (see table 1).

The chemical compositions of the major rock types forming the continental crust are taken from Condie (1993) except for gabbro (Ildefonse, ms, 1978) and diorite, granodiorire and peridotite (Best, 2011). They are largely scattered in the M^+-4Si-R^{2+} system according to their relative M^+ and R^{2+} amounts, namely along the M^+%-R^{2+}% side of the diagram (table 1, fig. 1A). The $M^+\%/(M^+\% + R^{2+}\%)$ ratio is discriminant for the felsic, mafic and ultramafic groups. However, because the actual oxidation state of iron is most often undetermined in current bulk rock chemical analyses, the total Fe amount is frequently presented as Fe_2O_3% (except in Condie, 1993 where it is considered as FeO%). Whatever the assumption (Fe_2O_3% or FeO%), the actual R^{2+} amount cannot be precisely calculated. This uncertainty makes the $M^+\%/(M^+\% + R^{2+}\%)$ ratio less discriminative for the mafic and ultramafic rock types than it could theoretically be. The $M^+\%/(M^+\% + R^{2+}\%)$ ratio is overestimated when the total Fe amount given as Fe_2O_3%. If this error is not important for granite, granodiorite, graywackes or shales, it becomes more significative for mafic and ultramafic rocks. The discrimination of the rock types is less accurate and one may not expect more than the separation of three groups in the M^+-4Si-R^{2+} system (fig. 1A). It is to be noticed that, because one of the major weathering effects is the oxidation of Fe^{2+} to Fe^{3+}, the error made on the calculation of the $M^+\%/(M^+\% + R^{2+}\%)$ ratio decreases in the altered facies of these rocks.

Any index aiming to measure the weathering intensity cannot be based only on the decreasing amounts of alkali-alkaline earth and divalent metallic components. It must also take into account the progressive concentration of trivalent chemical components (R^{3+}). By definition, the M^+-4Si-R^{2+} system that ignores the R^{3+} components cannot fully depict the weathering processes. It has to be completed by an additional parameter that associates the M^+ and R^{2+} component loss by lixiviation or oxidation with the progressive accumulation of the insoluble R^{3+} components: the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratio. Fortunately, because the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratio is correlated to the normalized $M^+\%/(M^+\% + R^{2+}\%)$ ratio as shown in figure 1B ($R^2 = 0.94$), it conserves the discrimination property for the three major rock groups (fig. 1C): felsic (granite, volcanic rocks, andesite Tonalite, Trondjhemite, Granodiorite designed as TTG), mafic (gabbro, basalts) and ultramafic (lherzolite, komatiite). A combination of the M^+-4Si-R^{2+} system on one hand with the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratio on the other hand must be researched and tested for altered sample series of different rock types, sediments and shales (see table 2 for references).

RESULTS

Application to Various Data Sets

Undisturbed weathered rocks.—The chemical analyses of weathered granite-granodiorite (Meunier, 1980; White and others, 2002), gabbro (Ildefonse, ms, 1978) and lherzolite (Fontanaud, ms, 1982) determine three distinct chemical trends in the M^+-4Si-R^{2+} ternary plot (fig. 2A). They all converge toward the 4Si pole, namely kaolinite that is the ultimate silicate clayey product of weathering as quartz does not form in supergenic conditions. The weathering trend of basalts (Eggleton and others, 1987; Nesbitt and Wilson, 1992) is less clear since the chemical compositions are more scattered than are the gabbro ones (gray area in fig. 2B). This is probably due to the simultaneous action of two rapid processes (Fe^{2+} oxidation and leaching of soluble elements). Indeed, the basalts are particularly sensitive to alteration because of the presence of highly reactive solid components: glass and microcrystalline minerals.

Kaolinite is the unique stable phyllosilicate species in the extreme hydrolitic weathering environments. It is the dominant secondary mineral phase in highly weathered soils (Dixon and Weed, 1989). It is often associated with goethite [FeO(OH)]

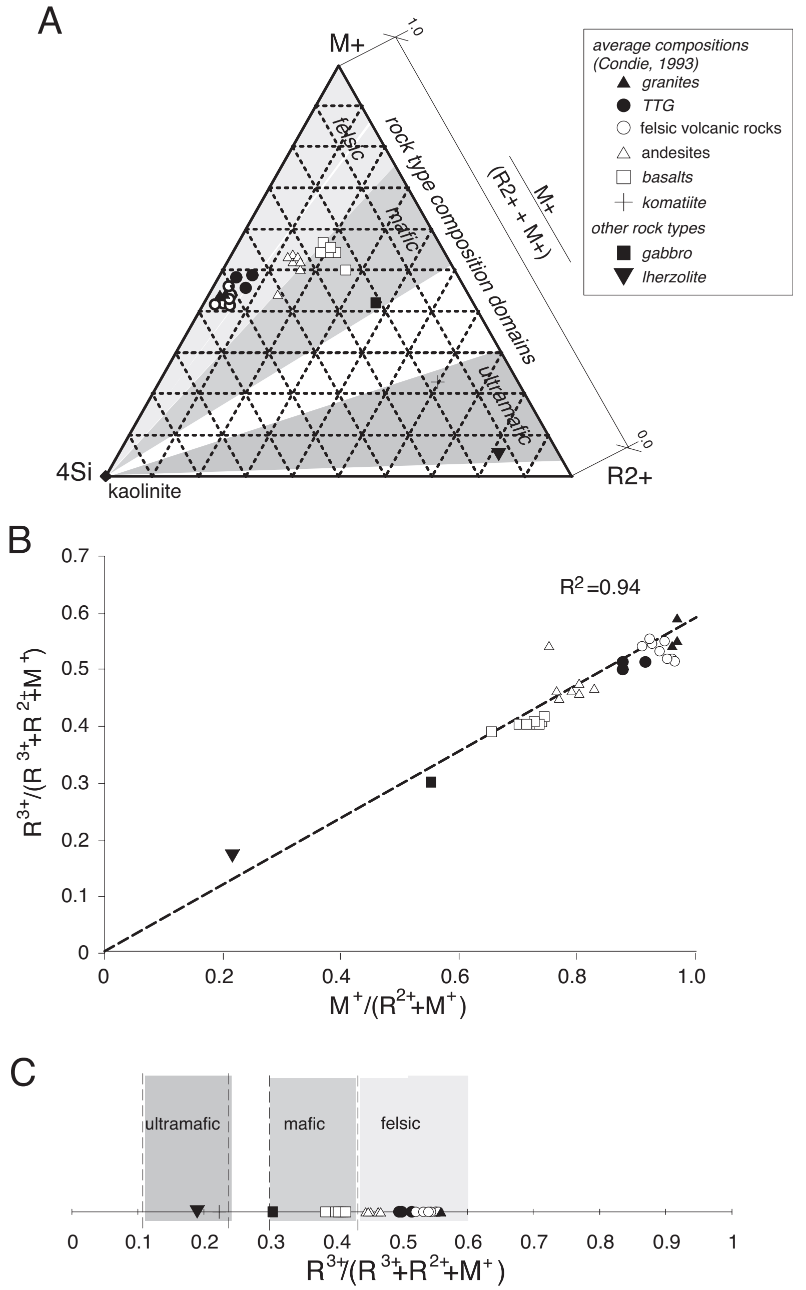

Fig. 1. Chemiographic bases of the Weathering Alteration Scale (WIS). (A) The principal types of rocks forming the continental crust from Archean to Phaneorozoic (Condie, 1993) plotted in the M^+-4Si-R^{2+} system (Fe_{total} = FeO). (B) Correlation between the $M^+/(M^+ + R^{2+})$ and $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratios. (C) The representative domains of the major rock groups as scaled in the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ coordinate. The M^+, $4Si^+$ and R^{2+} parameters are the normalized values of atomic proportions corresponding to $Na^+ + K^+ + 2Ca^{2+}$; number of Si^{4+} cations divided by 4 and $Fe^{2+} + Mg^{2+} + Mn^{2+}$, respectively (see text and Appendix 1 for calculation details). The R^{3+} parameter corresponds to $Fe^{3+} + Al^{3+}$.

Table 2

Data sources for the chemical compositions of rocks and their altered facies, soils, and shales

Rock type	reference	N° tables – page
Archean rocks	Condie (1993)	Annexes A to F pages 32-36
Granite	Meunier (1980)	Tables 28 & 29 page 64
Granodiorite	White and others (2002)	Table 2 page 40
Gabbro	Ildefonse (1978)	Table 2 page 11
Basalts	Eggleton and others (1987)	Table 1 pages 164-165
	Nesbitt & Wilson (1992)	Table 1 page 745
Lherzolite	Fontanaud (1982)	Tables 7 and 8 pages 25 and 28
Mudstones - diamictite	Rieu and others (2007)	Table 1 pages 255-256
Shales	Awwiller (1993)	Table 2 page 504
	Hofmann and others (2003)	Table 1 page 426
	Naqvi and others (1988)	Tables 3a-b pages 203-204
Mg-rich shales	Wense Dos Anjos and others (2010)	Table 2 page 619
Laterites	Tardy (1993)	Table 22 page 193
		Table 34 page 279
Amazon sediments	Kronberg and others (1986)	Table 2 pages 287-286

and/or haematite [Fe_2O_3] in lateritic mantles (Tardy, 1993 and references therein). However, kaolinite becomes unstable in bauxite deposits where it is progressively replaced by aluminum hydroxides (gibbsite $Al(OH)_3$, boehmite AlOOH). This reaction represents the ultimate stage of alumino-silicate hydrolytic weathering. Aluminum and iron oxi-hydroxides cannot be represented in the M^+-4Si-R^{2+} system making it improper to generate alone a complete alteration index. As stated above, it is necessary to combine the reaction progress toward the kaolinite pole (that is silica and base cations leaching) measured in the M^+-4Si-R^{2+} system with the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratio (R^{3+} accumulation) in order to define a complete Weathering Intensity Scale (WIS) from fresh silicate rocks to bauxite deposits.

The reaction progress toward the kaolinite pole is measured by the difference between the compositions of unweathered and weathered samples along the chemical trend corresponding to the rock source (fig. 2C):

$$\Delta 4\mathrm{Si}\% = [(4\mathrm{Si}_{\text{altered sample}} - 4\mathrm{Si}_{\text{unaltered parent rock}}) \times 100)]/(100 - 4\mathrm{Si}_{\text{unaltered parent rock}}).$$

The maximum intensity of alteration is reached when the parent rock, whatever its original composition, is transformed into kaolinite (Δ4Si% = 100%). This is typically the case for laterites which are mainly composed of kaolinite + Fe-oxi-hydroxides (Tardy, 1993). The silica content of bauxite deposits being never null (Tardy, 1993), the accumulation of Al, Fe-oxi-hydroxides coincides with Δ4Si = 100%. Consequently, a full WIS can be correctly depicted from 0 to 100 percent for any rock type in a Δ4Si% versus $R^{3+}/(R^{3+} + R^{2+} + M^+)$ diagram. The co-variation of the Δ4Si% parameter with the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratio determines distinct chemical trends for the altered facies of the felsic, mafic and ultramafic rock types (figs. 3A and 3B). As expected, the discrimination of rock sources disappears progressively with increasing weathering intensity because of the convergence of the different chemical trends toward the composition of laterites or bauxite deposits. The WIS increases along the three curved chemical trends from the composition of fresh rocks (Δ4Si% = 0%) to the ultimate alteration degree (Δ4Si% = 100%).

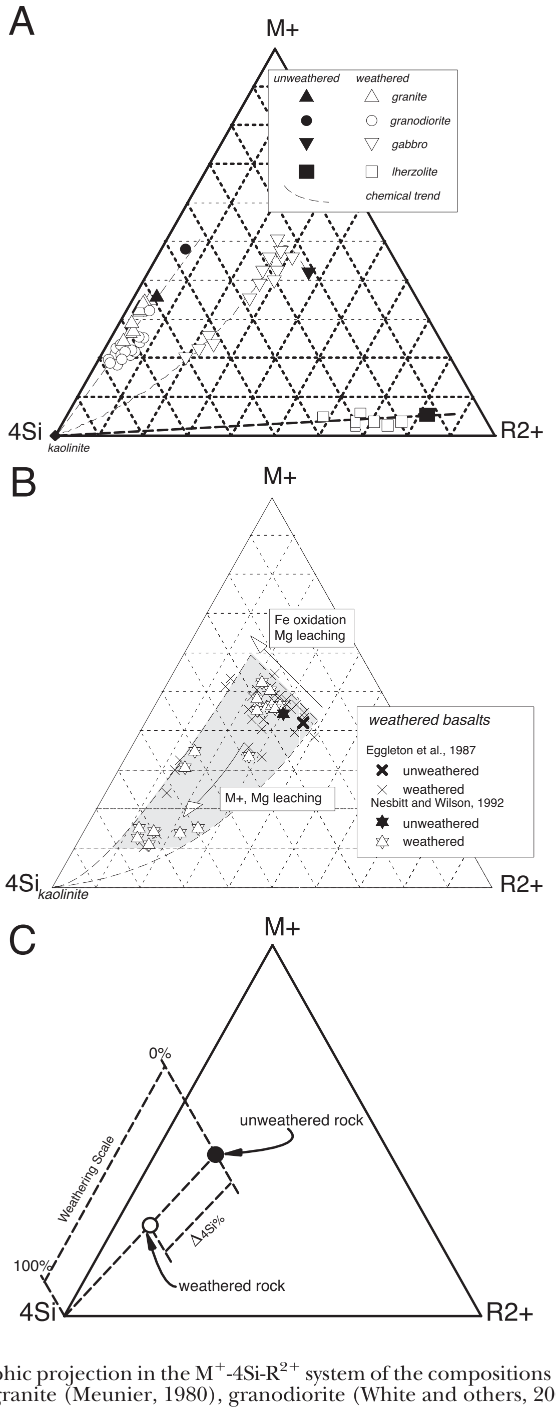

Fig. 2. Chemiographic projection in the M^{+}-4Si-R^{2+} system of the compositions of weathered rocks. (A) Weathering trends for granite (Meunier, 1980), granodiorite (White and others, 2002), gabbro (Ildefonse, ms, 1978) and lherzolite (Fontanaud, ms, 1982). (B) Weathering trend of basalts from the Baynton profiles, Victoria, Australia (Eggleton and others, 1987; Nesbitt and Wilson, 1992). (C) Definitions of the full weathering intensity scale and of the Δ4Si% parameter which corresponds to the degree of alteration of a given sample.

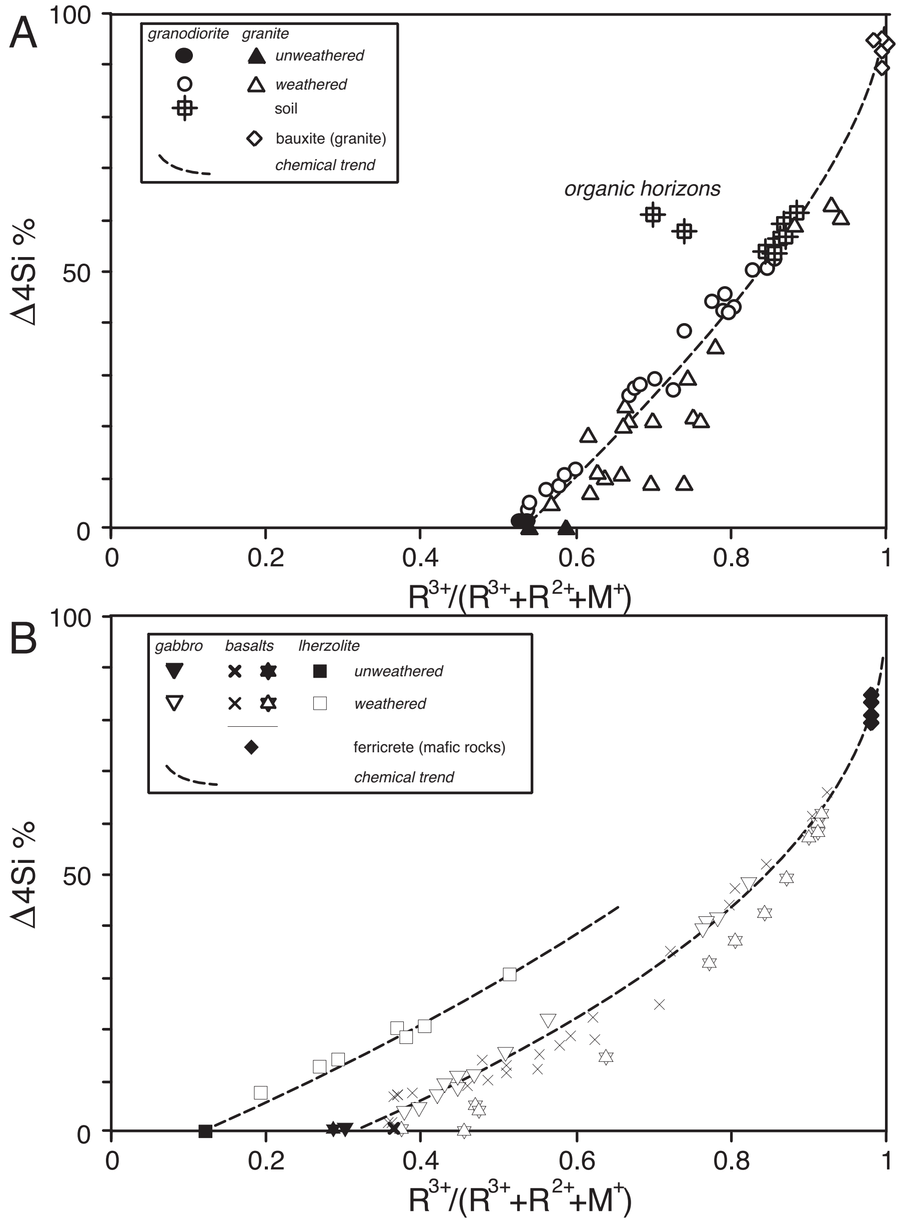

Fig. 3. Composition of altered samples of the different rock groups in the Δ4Si% versus $R^{3+}/(R^{3+} + R^{2+} + M^{+})$ diagram (see text for details). (A) Granites (Meunier, 1980; Tardy, 1993) and granodiorite (White and others, 2002). (B) Mafic and ultramafic rocks (Fontanaud, ms, 1982; Ildefonse, ms, 1978; Eggleton and others, 1987; Nesbitt and Wilson, 1992); bauxite and ferricretes (Tardy, 1993).

Diagenesis of sediments deriving from felsic rocks.—The chemical composition of a sediment is necessarily different from that of its parent rock because of the loss of the most soluble elements into water and the particle hydrodynamic sorting during transport by rivers to sea. Nevertheless, at a global scale, a latitude dependence of the

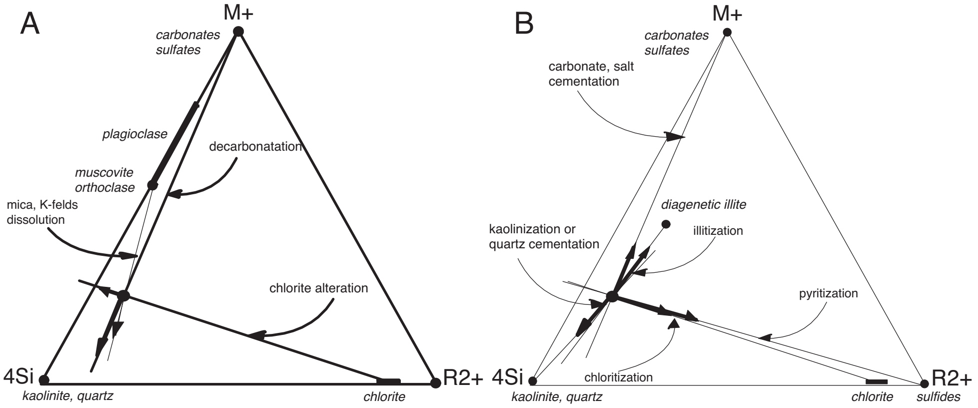

Fig. 4. Theoretical vectorial representation in the M^+-4Si-R^{2+} system of the composition changes experienced by a given sediment during diagenesis. (A) Dissolution of some primary components of the sediment. (B) Effects of the illitization and the crystallization of other secondary minerals.

sediment source has been early evidenced using the kaolinite/chlorite ratio (Biscaye, 1965 in Chamley, 1989) and confirmed recently by Li and Yang (2010) who showed that the CIA values of the suspended matters from 44 rivers worldwide suggest also a latitude dependence (temperature, soil depth) but no direct environmental significance (precipitation, elevation, runoff). After deposition, a sediment may experience several mineral transformations during its burial diagenesis history. These transformations depend on the local physico-chemical conditions that prevail at a given time: some of the primary minerals may be dissolved (feldspars) or re-crystallized (clays) while new ones precipitate in pores (quartz, carbonates, chlorites). Consequently, the composition of the sediments is modified according to the type and intensity of the different possible diagenetic reactions. Plotted in the M^+-4Si-R^{2+} system, the initial sediment composition may be displaced along one of the reaction paths (dominant reaction) or along a combination of different paths (concomitant reactions) according to the physical-chemical conditions imposed during diagenesis: dissolution of primary components (fig. 4A) or precipitation of secondary ones (fig. 4B). For instance, the sediments which are deposited at the mouth of the Amazon river are mainly composed of clays and carbonates in different proportions (Kronberg and others, 1986). As expected, most of their compositions are aligned along a carbonatation trend line in the M^+-4Si-R^{2+} coordinates (fig. 5A).

The Gulf Coast shale series (Texas, USA) offers a good standard to investigate the actual chemical trend triggered by the illitization of sediments. The mineralogical composition of these shales is dominated by a quartz-illite/smectite mixed layers (I/S) − kaolinite assemblage (Awwiller, 1993). The I/S illite content in the shale series varies practically from 0 to 100 percent as indicated by X-ray diffraction. This large variation range allows us to research the chemical trend of increasing illite proportions in the rock that contains also K-feldspars, quartz and small amounts of pyrite and chlorite. As expected, the chemical composition of the bulk rocks plot inside the illite-quartz, kaolinite-pyrite domain in the M^+-4Si-R^{2+} system (gray area in fig. 5A) and are aligned toward the diagenetic illite pole (illitization trend). It has been shown that the loss of expandability for I/S is obtained before the formation of pure diagenetic illite (diag. illite) whose half unit formula is: $[Si_{3.30}\ Al_{0.70}]\ O_{10}\ (Al_{1.78}\ Fe^{3+}{}_{0.05}\ Mg_{0.17})\ (OH)_2\ K_{0.87}$ (Meunier and Velde, 1989). Thus, the chemical effects of

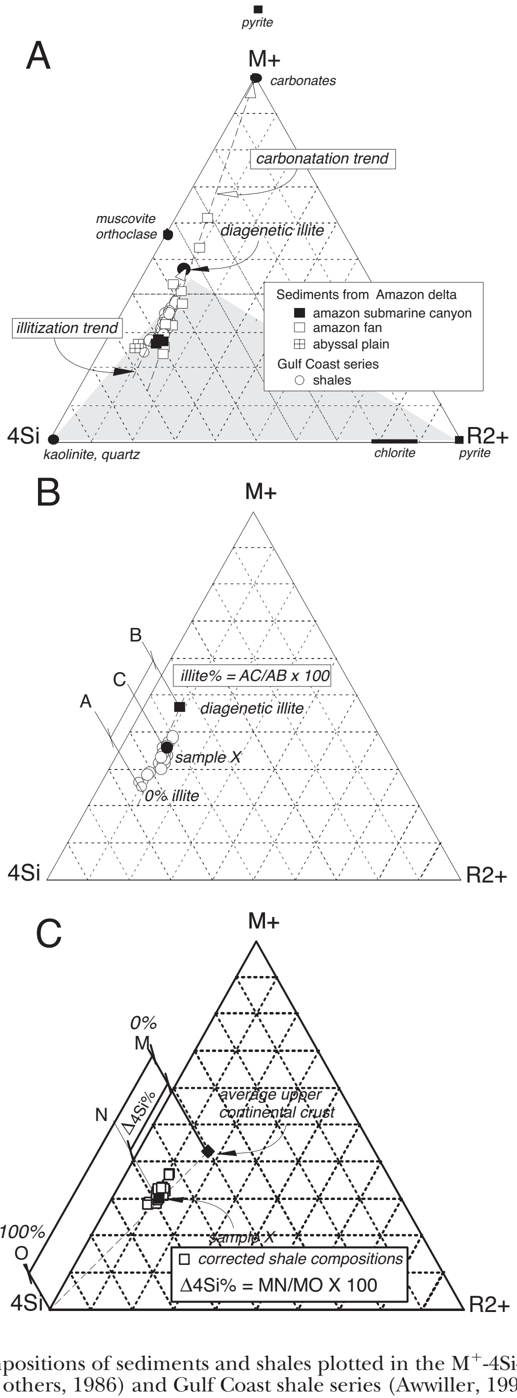

Fig. 5. Chemical compositions of sediments and shales plotted in the M^+-4Si-R^{2+} system. (A) Amazon sediments (Kronberg and others, 1986) and Gulf Coast shale series (Awwiller, 1993). The gray area depicts the composition domain of the kaolinite-illite-pyrite mineral assemblage. (B) Calculation of the illite amount for a given sample (x) in the Gulf Coast shale series. (C) Calculation of the Δ4Si% parameter for a sample x after illite correction (see text and Appendix 2 for details).

TABLE 3

Chemical composition of the diagenetic illite (diag.illite)

Element	Weight %
SiO_2	47.70
Al_2O_3	30.33
Fe_2O_3	0.99
MgO	1.62
K_2O	9.90

End-member have half unit formula: $[Si_{3.30}\ Al_{0.70}]\ O_{10}\ (Al_{1.78}\ Fe^{3+}_{0.05}\ Mg_{0.17})\ (OH)_2\ K_{0.87}$ (Meunier and Velde, 1989).

illitization on the original composition of the sediments cannot be simply reduced to the increase of the K_2O amount (K-metasomatism) because silica and R^{2+} components are also involved in the reaction. Any correction must take into account all the components of the diagenetic illite (table 3).

The first step of the illite correction procedure is based on the calculation of the illite amount in the rock (expressed as illite percent). It is assumed that the composition of the less illitic shale sample in the Gulf coast series can be considered close to that of the original sediment ($K_2O_{sediment}$). This is consistent with the composition of the non-carbonated Amazon sediments (fig. 5A). Then, the illite proportion (illite %) is given by the K_2O amount difference between the original sediment and the shale sample. The K_2O content of the diagenetic illite being about 9.9 percent (table 3), the illite percent is given by $(K_2O_{shale} - K_2O_{sediment}) \times 100/9.9$. The illite percent value is represented in the M^+-4Si-R^{2+} system by the normalized AC/AB ratio (fig. 5B). Finally, the corrected chemical composition of the shales is given by subtracting the illite contribution for each component: for instance, $SiO_{2cor} = SiO_{2shale} - SiO_{2illite}$ with $SiO_{2illite} = SiO_{2diag.ill.} \times$ illite %. The correction modifies the M^+, 4Si, and R^{2+} coordinates of each sample as shown in figure 5C. The detailed procedure is given in Appendix 2.

The second step aims to calculate the chemical difference between the putative rock source and the corrected composition of the shale samples. Because granitoids and metamorphic rocks are dominating in the Mississippi watershed, one may assume that the average 4Si% value is close to that of the average upper continental crust (AUCC) given by Condie (1993): $4Si\% = 39.8\%$ (table 1). Thus the illite corrected $\Delta 4Si\%_{cor}$ parameter is equal to $(4Si\%_{shale} - 4Si\%_{AUCC}) \times 100/(100 - 4Si\%_{AUCC})$. The $\Delta 4Si\%_{cor}$ value corresponds to the normalized MN/MO ratio in the M^+-4Si-R^{2+} system (fig. 5C). As expected, the corrected compositions of the Gulf Coast shales plot between the felsic and mafic chemical trends in the Δ4Si percent versus $R^{3+}/(R^{3+} + R^{2+} + M^+)$ coordinates (fig. 6).

Even if empirical, the illite correction reduces the uncertainty inherent to the calculation of the Δ4Si% values that determine the WIS. The Δ4Si% values for the Gulf Coast shales increases after illite correction. Non-corrected compositions lead to under-estimate the Δ4Si% and, consequently, the alteration intensity. Because important errors can be made when sediments originating from different source rocks are compared in a given stratigraphical series, it is necessary to define the conditions required for an illite correction to be justified. Indeed, the presence of potassium does not automatically indicate that the shale sample has been illitized. This element can be totally or partly inherited from the original sediment (detrital K-feldspars or micas). The correction is pertinent only when evidence of illitization is

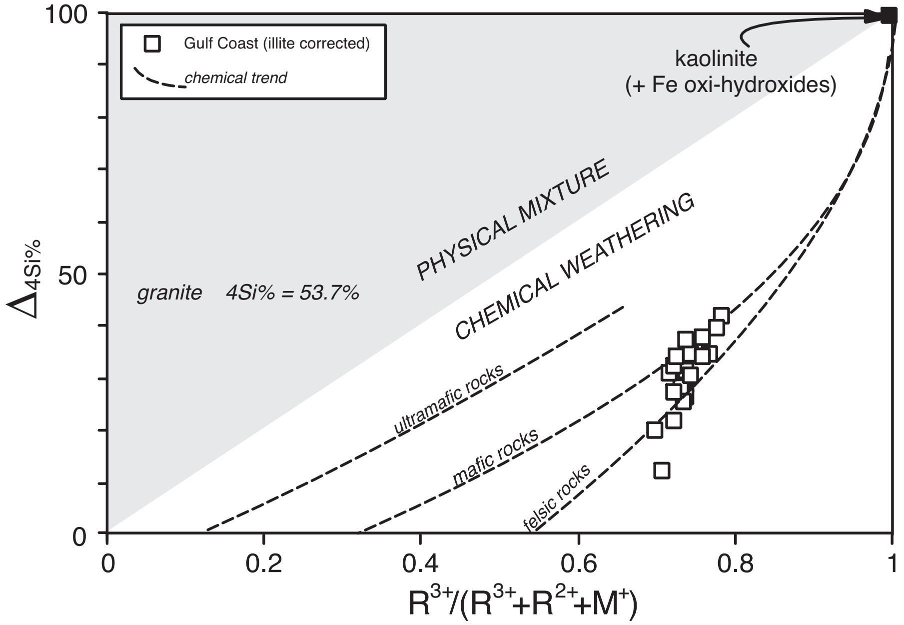

Fig. 6. After illite correction, the compositions of the shale in the Gulf Coast series (Awwiller, 1993) plot between the mafic and felsic rock chemical trends in the Δ4Si% versus $R^{3+}/(R^{3+} + R^{2+} + M^{+})$ coordinates. The gray area represents the theoretically forbidden composition field for weathered rock series. However, it is not forbidden for the composition of multi-source sediments (mixing of fresh rock debris with clays, carbonates or Fe oxi-hydroxides).

provided by the composition trend oriented toward the diagenetic illite pole in the M^{+}-4Si-R^{2+} system as shown by the Gulf Coast shale series (fig. 5B). If not the case, the variability of the original sediment compositions is more important than that induced by the chemical effects of illitization. Consequently, the correction is not justified and may induce large errors. This uncertainty makes it safer to use the Δ4Si% relative variations (Δ4Si% differences between samples in a given shale series) rather than their absolute values. Indeed, the Δ4Si% relative variations are conserved even if their magnitude is modified by the illitization chemical effects. They record the changes of some of the environmental conditions prevailing during the formation of the sediment.

Diagenesis of sediments deriving from mafic-ultramafic rocks.—The shales from the Permian formations of the northern Paranà basin were shown to derive from altered ultramafic rocks (Wense Dias dos Anjos and others, 2010). They are dominantly composed of a trioctahedral Mg-rich smectite (saponite) with chlorite and quartz as minor phases (no illite present). These minerals are associated with carbonates or talc forming two distinct mineral assemblages (dark gray areas in fig. 7A). The Zeederbergs and Cheshire shale series in the Belingwe greenstone belt from Zimbabwe derive from ultramafic and mafic rocks respectively (Hofmann and others, 2003). Their chemical compositions are largely scattered around the basalt alteration domain (fig. 7A) suggesting that multiple sources have contributed to the formation of most of the sediment samples. The illite correction is not justified neither for the shales from the Paranà basin nor for those from the Belingwe greenstone belt since none of their respective composition groups are aligned toward the diagenetic illite pole. The rock sources being identified in both cases, namely ultramafics and basalts,

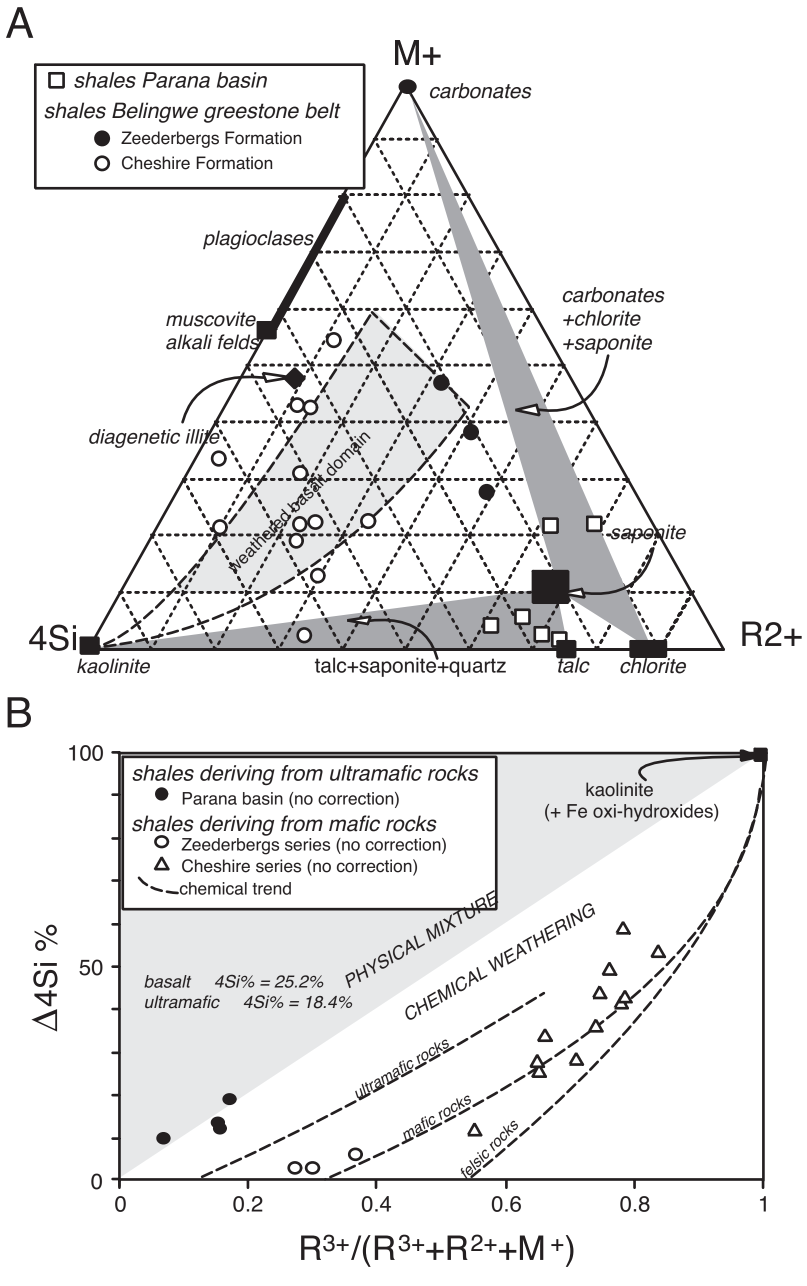

Fig. 7. Shales of the Zeederbergs and Cheshire Formations in the Archean Belingwe greenstone belt (Hofmann and others, 2003) and saponite-rich black shales from Paranà Basin, Brazil (Wense Dias dos Anjos and others, 2010). (A) Composition domains in the M$^+$-4Si-R^{2+} system. The light gray area represents the composition domain of weathered basalt (see fig. 2B). The dark gray areas represent the composition domains of the kaolinite-saponite-talc and saponite-chlorite-calcite mineral assemblages identified in the Paranà shales. (B) The illite correction being not pertinent, the uncorrected shales compositions are used here. The Zeederbergs and Paranà shale compositions plot around the ultramafic rock chemical trend in the Δ4Si% versus R^{3+}/(R^{3+} + R^{2+} + M$^+$) coordinates while those of the Cheshire series plot around the mafic one.

it is possible to use their corresponding 4Si% values (table 1), namely 25.2 percent and 18.4 percent for basalts and ultramafics respectively, to calculate the Δ4Si% parameter directly from the uncorrected shale composition. The shale compositions of the Paranà, Zeederbergs and Cheshire series plot around but not precisely on the ultramafic and mafic trends in the Δ4Si% versus $R^{3+}/(R^{3+} + R^{2+} + M^{+})$ diagram (fig. 7B). This suggests that the original sediments were probably polygenic. For instance, the shales from the Paranà basin contain some quartz indicating a contribution of granitic rocks while the clays (saponite and nontronite) derive from ultrabasics. Nevertheless, in spite of the probable polygenic origin of the sediments, the maximum uncorrected Δ4Si% values of the shales reach 20 percent, <10 percent and ≈60 percent for the Paranà, Zeederberg and Cheshire series respectively which suggest contrasted weathering intensity conditions (fig. 7B). The difference is high enough to consider that the Paranà and Zeederbergs series derive mostly from moderately altered ultrabasic rocks while the Cheshire one derives from intensely weathered mafic rocks.

Evaluation Using the Neoproterozoic Sediments

The shale and diamictite series of the Neoproterozoic Mirbat Group (south Oman) was chosen to test the WIS for sediments that record contrasted climatic conditions (Rieu and others, 2007). Two glacial events separated by an interglacial episode have been identified using the variations of the chemical and mineralogical indexes of alteration (CIA and MIA) of mudstones and fine-grained matrix of diamictites along the stratigraphic pile. Both the Arkahawl mudstones (interglacial) and the fine-grained matrix of Ayn and Shareef diamictites (glacial) are thought to derive in average from granodioritic source rocks. The Th/Sc signature indicates a tonalitic to granitic origin (Taylor and McLennan, 1985). This series offers the possibility to compare the variation of the Δ4Si% values with that of the corresponding CIA ones. Is the illite correction justified here? When plotted in the M^{+}-4Si-R^{2+} coordinates, the compositions of the mudstones and the diamictite clay fractions are not distributed on a line oriented toward the diagenetic illite pole (fig. 8A). This suggests that either the illitization did not occur in the Mirbat Group or the variability of the original sediments overcomes its chemical effects. In both cases, an illite correction is not pertinent. Consequently, the 4Si% parameter must be directly calculated from the uncorrected compositions of the mudstones and the diamictite clay fractions implying that the Δ4Si% absolute values could not be significant. Only, their variation along the sediment pile record environmental modifications with time. The sediment source rocks being granodioritic, the corresponding 4Si% value is 40.9% (table 1). Consequently, the Δ4Si% is given by $(4Si\%_{sample} - 40.9) \times 100/(100 - 40.9)$. However, this calculation gives negative values for the Δ4Si% of two samples in the Ayn diamictites. This indicates that their sediment rock source cannot be granodioritic but rather dioritic or tonalitic. The calculation for these samples has been made using a diorite as the source rock (4Si% = 31.4%; table 1): $\Delta 4Si\% = (4Si\%_{sample} - 31.4) \times 100/(100 - 31.4)$.

Most of the compositions of samples from the three formations plot between the granitic and mafic chemical trends in the $\Delta 4Si\%_{cor}$ versus $R^{3+}/(R^{3+} + R^{2+} + M^{+})$ diagram (fig. 8B). Rieu and others (2007) noted that the Ayn and Marsham series are Ca and Mg richer that the Arkahawl ones and claimed that this difference was due to a less extensive weathering degree. This is roughly consistent with the values of the Δ4Si% parameter that are low (<25%) and high (25-40%) for the Ayn-Marsham and Arkahawl series respectively. However, the Δ4Si% variation along the sedimentary series is more complex that that of the CIA (fig. 9). According to Rieu and others (2007), the warm episode duration has been very long (about 78 Ma). So a long lasting climatic stability is questionable. It seems that if the CIA variation represents the

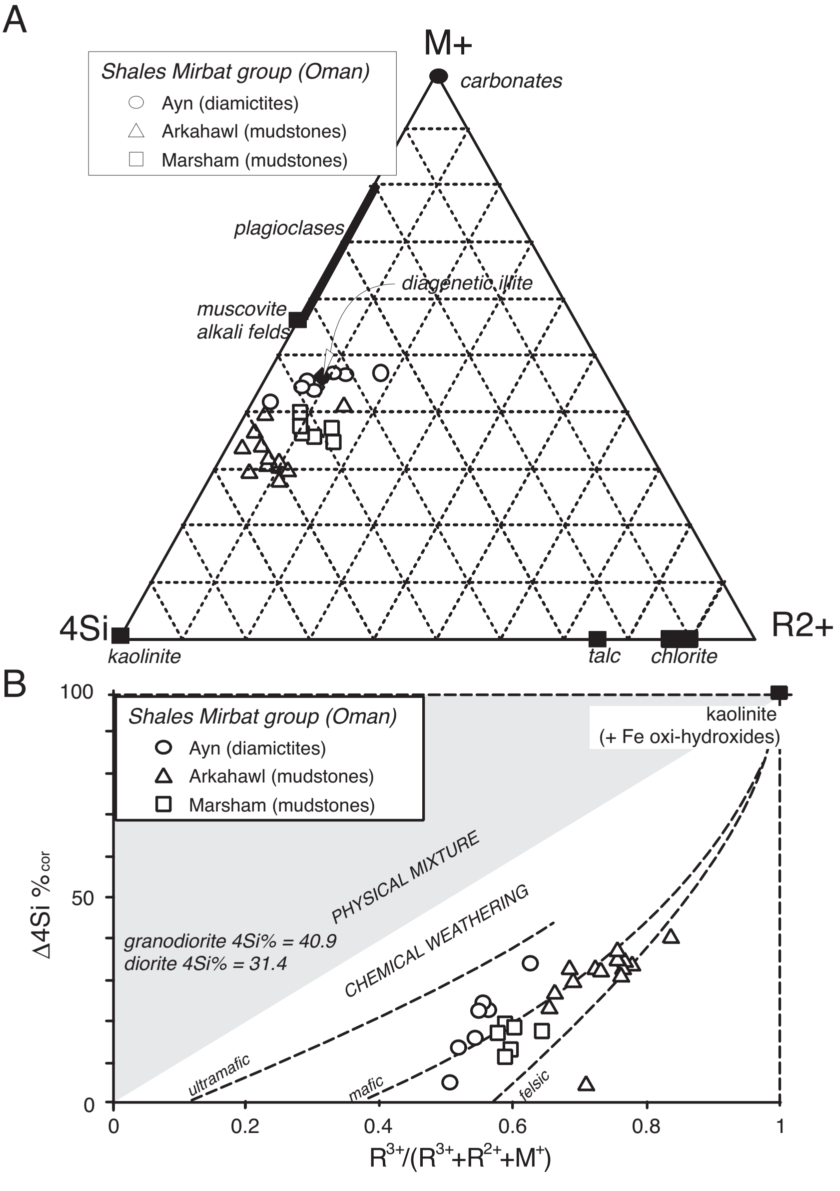

Fig. 8. The Neoproterozoic Mirbat mudstone-diamictite series (Rieu and others, 2007). (A) Plotted in the M^+-4Si-R^{2+} system, the shale compositions are not aligned toward the diagenetic illite pole. Consequently, the illite correction is not pertinent here. (B) The Δ4Si%$_{cor}$ parameter is calculated using the granodiorite compositions for the Arkahawl and Marsham formations (4Si% = 45.6%) and diorite composition (4Si% = 31.4%) for the Ayn one (see text for details). Most of the compositions (no illite correction) plot around the mafic chemical trend in the Δ4Si%$_{cor}$ versus $R^{3+}/(R^{3+} + R^{2+} + M^+)$ coordinates. The Δ4Si% values of the Arkahawl series are globally higher than that of the Ayn and Marsham ones. The gray area represents the theoretically forbidden compositions for weathered rocks.

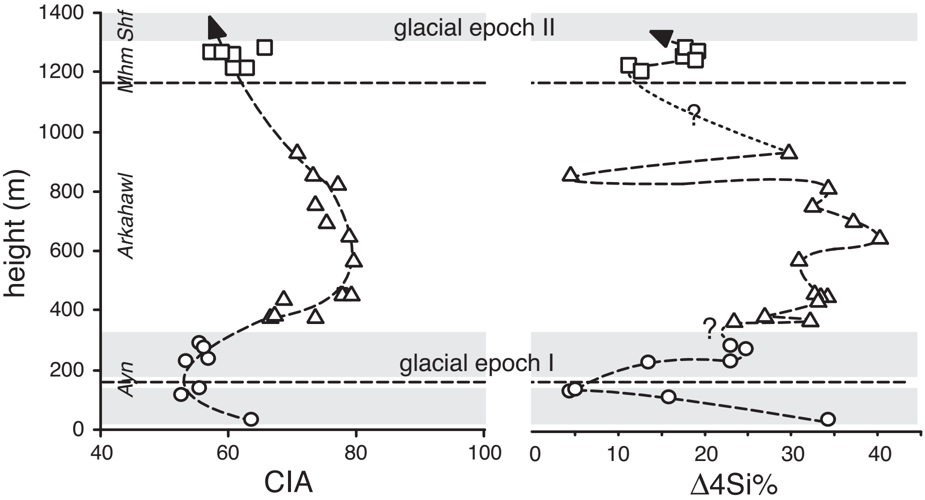

Fig. 9. Variation of the CIA and the $\Delta 4Si\%_{cor}$ parameter along the Mirbat stratigraphic column. The gray areas represent the glacial sediment series.

alternation of glacial and warm climatic conditions, it is insensitive to environmental (climatic?) changes of lower magnitude. In other words, the glacial to interglacial transition is recorded by the large magnitude variation (first order) of both the CIA and the Δ4Si% values (fig. 9) but the low magnitude ones (second order) which do not appear in the CIA curve, are clearly evidenced in the Δ4Si% one. According to Li and Yang (2010), the CIA is not directly related to climate since it is correlated with temperature and latitude but not with precipitation and average elevation. Thus, the second order oscillations of the Δ4Si% parameter may record changes in environmental conditions, including precipitation, modification of the drainage basin, denudation of new lithologies, changes in sea level, and other factors that may alter the apparent extent of alteration. Such changes are highly probable for period of time as long as the interglacial epoch (78 Ma).

Comparison to Original CIA

The CIA and M^+-4Si-R^{2+} definitions.—The calculation of the CIA is focused on the weathering of feldspars that are the dominant silicate minerals in felsic rocks. The fate of the divalent metallic elements (Fe^{2+}, Mg^{2+}, Mn^{2+}) that are concentrated in mafic minerals (biotite, amphibole, pyroxene, olivine) is not considered in the A-CN-K system. This is why a complementary compositional space has been proposed (Nesbitt and Young, 1989): the Al_2O_3-CaO, Na_2O, K_2O-FeO, MgO (A-CNK-FM) system. However, both the A-CN-K and A-CNK-FM systems do not take into account the major component of the silicate minerals: SiO_2. The M^+-4Si-R^{2+} system avoids this drawback because it combines the variations of the alkali and alkaline earth components with that of silica and the divalent ones. Whatever the chemical system considered here, none of them takes directly into account the Fe_2O_3 component. It is ignored in the A-CN-K and A-CNK-FM systems and indirectly integrated into the M^+-4Si-R^{2+} system since the oxidation of Fe^{2+} decreases the R^{2+} amount that, consequently, modifies the 4Si% and M^+% values.

The alteration intensity.—As shown by the chemiographic projections in the Al_2O_3-CaO, Na_2O-K_2O (A-CN-K) system (Fedo and others, 1995), the CIA does not vary from

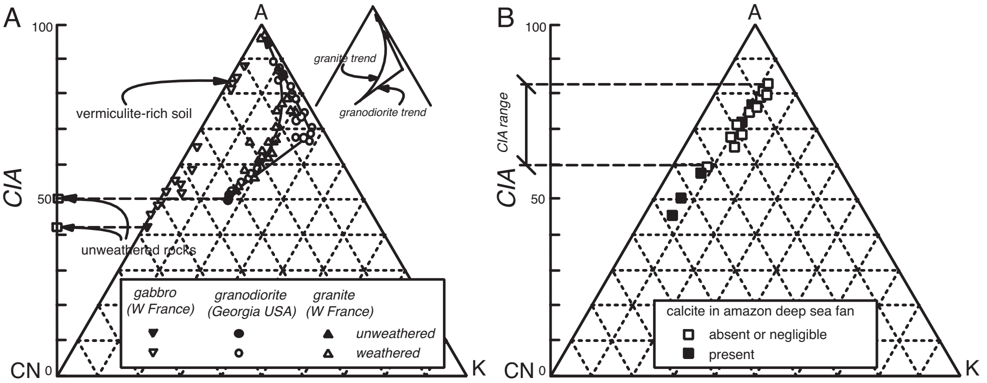

Fig. 10. Weathering trends of different silicate rock types in the Al_2O_3-CaO,Na_2O-K_2O (A-CN-K) system. (A) Granites (Meunier 1980), granodiorite (White and others, 2002) and gabbro (Ildefonse, ms, 1978). The granite and granodiorite trends are schematically represented in the insert top right. (B) Sediments from the Amazon fan (Kronberg and others, 1986).

0 to 100 percent. This is, at least, ambiguous since one expects that un-weathered rocks would be theoretically represented by a CIA value equal to zero. Because this is not the case, the unaltered granitic and mafic-ultramafic rocks have not the same CIA values (fig. 10A). Consequently, the magnitude of the CIA variation does not depend only on the intensity of alteration but also on the chemical composition of the unweathered rock (position in the A-CN-K diagram). Therefore, the magnitude of the CIA variation from the unaltered state to the A pole is not the same for rocks having different compositions even if they have been altered under the same climatic conditions. This is illustrated in figure 10A by the gabbro and granite weathering sequences from the western part of France which climate is temperate and humid (Ildefonse, ms, 1978; Meunier, 1980). The ambiguity comes from the fact that the A pole in the A-CN-K system represents kaolinite as well as chlorite. These two phyllosilicate species are considered to be indicative of intense and weak alteration degrees respectively. Consequently, the weathering sequences of mafic and granite or granodiorite rocks whatever the climatic conditions converge to identical CIA values (fig. 10A). For instance, the vermiculite-rich horizon of the gabbro alteration profile at Le Pallet, France, has the same CIA value than the kaolinite-rich saprolite of the granodiorite from Georgia, USA. Conversely, rocks of similar compositions but altered under different climatic regimes are not discriminated in the diagram: for example the weathering sequence of granites in the western part of France (Meunier, 1980) and granodiorite in Georgia, USA (White and others, 2002) where climatic conditions are temperate and humid subtropical with mild winters and hot summers respectively, are largely superimposed (fig. 10A). Such confusions are not possible using the M^+-4Si-R^{2+} system for two reasons: 1) the different chemical trends are clearly separated (figs. 2A and 2B); 2) the alteration intensity is independently evaluated for each trend through its own Δ4Si% variation from 0 to 100 percent (fig. 2C).

The effect of the original sediment composition variability.—The dismantling of a given weathered rock produces different types of sediments according to the energy and length of transport. The chemical composition of arkoses, graywackes and shales gives different CIA values in spite of their common source (same parent rocks forming the drainage basin, same climatic conditions). To avoid the particle sorting effect on the composition of the sediment, it is safer to consider only the clay-rich mudstones. An illustrative example can be found in the mudstones of the Amazon river delta that are

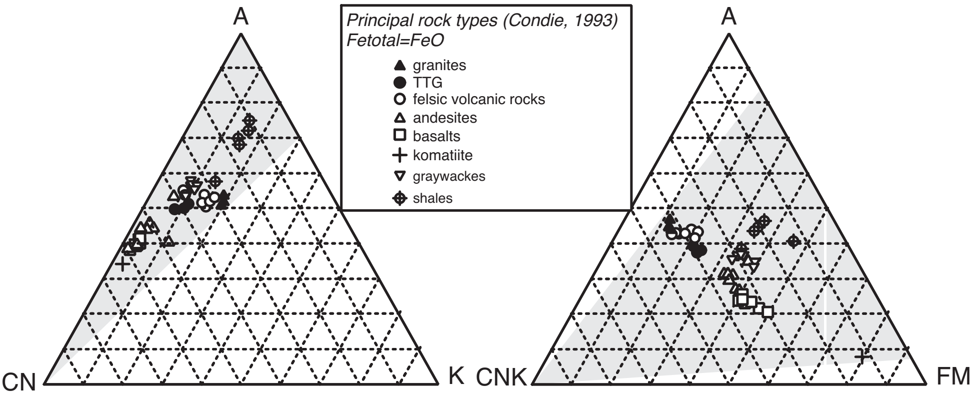

Fig. 11. Chemiographic projection in the A-CN-K and A-CNK-FM systems of the compositions of the principal types of rocks forming the continental crust from Archean to Phaneorozoic (Condie, 1993). Gray areas: composition field of the common igneous rocks and sediments; TTG: Tonalite, Trondjhemite, Granodiorite.

deposited under sea water in different topographic situations: river canyon, fan and abyssal plain (Kronberg and others, 1986). In spite of the fact that the sediments all originate from the same drainage basin, their compositions are scattered in the A-CN-K system. Even in the absence of carbonates, the corresponding CIA varies over a large range of values (fig. 10B). This means that the climatic significance based on the weathering intensity as measured by the CIA is biased even for a given sedimentary facies (mudstones) deriving from the same sediment rock sources.

The research of the sediment parent rock sources.—Because the divalent metallic elements (Fe^{2+}, Mg^{2+}) are not taken into account in the A-CN-K system, the major types of rocks constituting the continental crust plot in a small portion of the diagram even with total Fe as FeO (Condie, 1993). This drawback is eliminated using the A-CNK-FM systems as shown by the size of the gray areas in figure 11. Nevertheless, a comparison between the figures 2A, 2B and 12 shows that the alterations trend for basalts and gabbro are better defined in the M^{+}-4Si-R^{2+} system than in the A-CNK-FM one. This is due to the fact that the latest cannot represent the major chemical effect of weathering that leads to the relative enrichment in silica till kaolinite becomes unstable. The compositions of the weathered samples of felsic, mafic and ultramafic rocks are scattered in the A-CNK-FM diagram making difficult the definition of their respective chemical trends. Consequently, the identification of the sediment rock sources from shale-graywacke series is uncertain.

Evaluation of the diagenetic K-metasomatism intensity.—The CIA has been largely applied to shale and graywacke sedimentary series in order to determine the origin of the sediments and the climatic conditions under which they have been formed. However, both the origin and climatic messages are obscured by the illitization experienced by the original clays during diagenesis. Fedo and others (1995) considered that the illitization corresponds simply to a potassium enrichment that has been assigned as K-metasomatism. They proposed a correction method based on geometrical relations in the A-CN-K system. The aim is to reconstitute the original composition of the sediments that is determined by the intersection of "*the predicted weathering trend*" with the line going from the K pole through the measured shale or graywacke compositions (fig. 13). This method has been applied to Paleoproterozoic shales for which the predicted weathering trend was considered to originate from the average composition of the Upper Archean crust (Nesbitt, 1992). However, because it is based

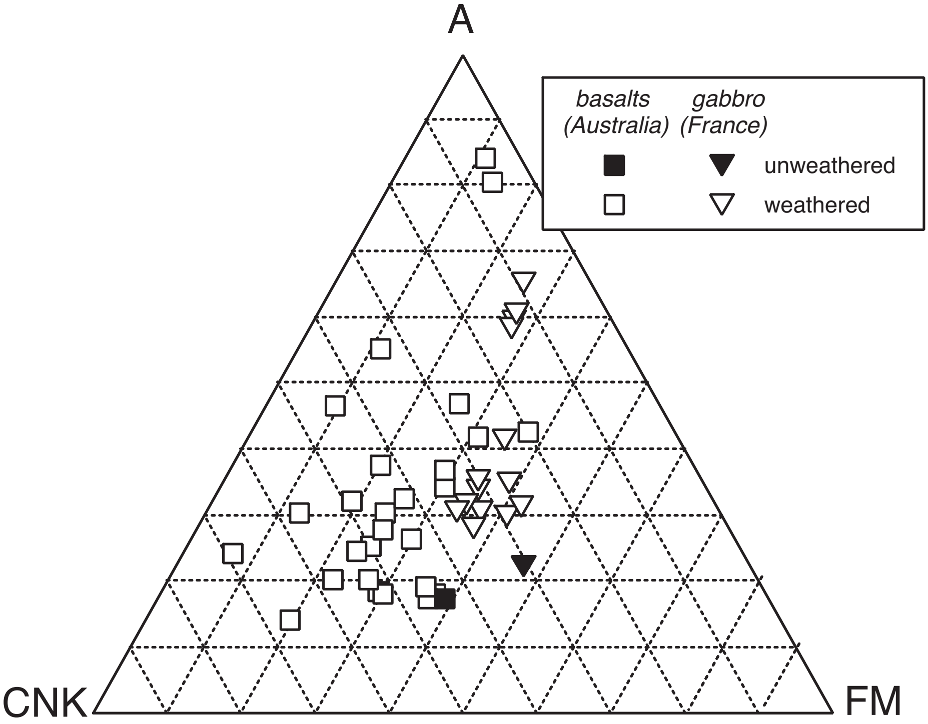

Fig. 12. Plot of the chemical compositions of weathered basalts from Baynton profiles, Victoria, Australia (Eggleton and others, 1987; Nesbitt and Wilson, 1992) and gabbro from western France (Ildefonse, ms, 1978) in the A-CNK-FM system.

on a geometrical extrapolation in the A-CN-K ternary diagram, the extrapolation from the K pole implies that the composition of the shales must be significantly different from that of the original sediment rock source, in other words, significantly K-enriched. This enrichment can be graphically evidenced using the Gulf Coast shale series if the composition of the less illitized shale samples are considered to be a plausible origin for "*a predicted weathering trend*" line. Then, the K-metasomatism intensity is represented by a vector joining the predicted weathering trend to the composition of the shale samples. As expected, the maximum value is attained for the most illitized one (black arrow in fig. 13A).

In other sedimentary series, graywackes represent the less evolved sediments since their chemical compositions are genetically close to that of their parent rocks. They can be considered as a plausible origin for "*a predicted weathering trend.*" When applied to the Archean sediment series of the Chitradurga schist belt, India (Naqvi and others, 1988), the extrapolation from the K pole gives K-metasomatism values comparable to that observed in the mudrocks of the Texas Gulf Coast Paleocene-Eocene deposits (fig. 13B). A counter-example is found in the mudstones and diamictites from a Neoproterozoic sedimentary series of south Oman (Rieu and others, 2007) whose compositions plot near the predicted weathering trend issued from the average upper continental crust at 2.5 Ga (fig. 13C). The geometrical method indicates that the K-metasomatism is very weak or absent as proved by the persistence of kaolinite. Thus, at the spatial resolution of the A-CN-K chemical space, the graphical extrapolation proposed by Fedo and others (1995) seems to be a robust procedure that can be applied to any

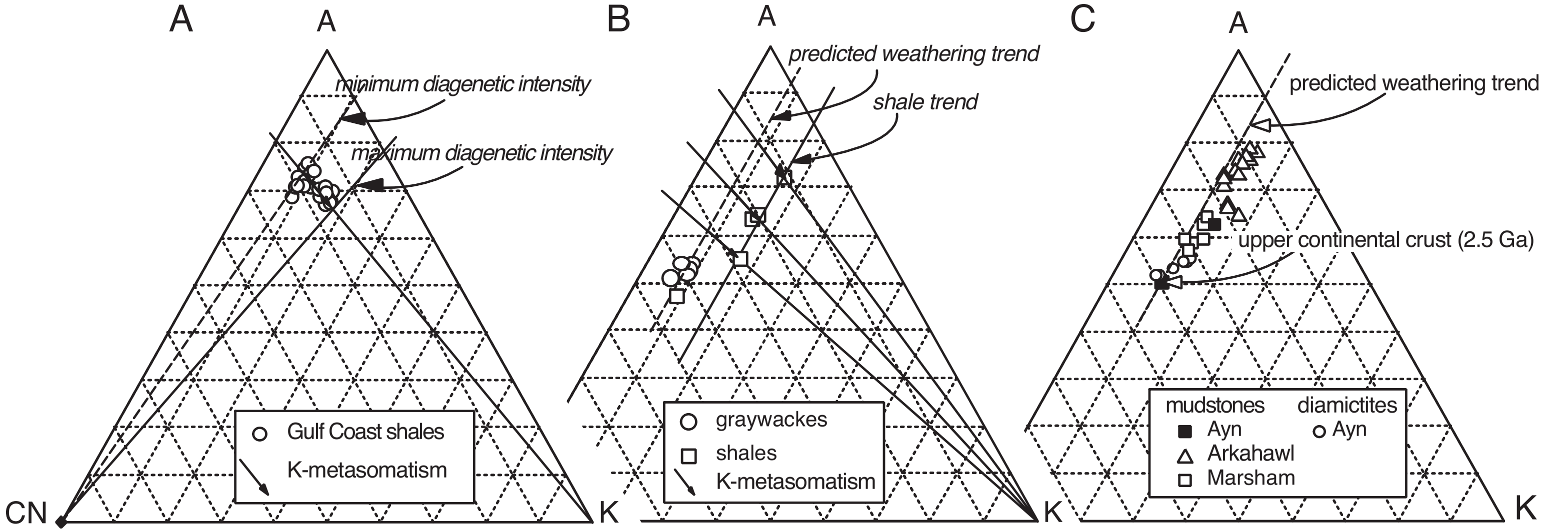

Fig. 13. The effect of the K-metasomatism (diagenesis) on shale composition in the A-CN-K system. (A) Shales from the Texas Gulf Coast (Awwiller, 1993). The black vector represents the effective intensity of the K-metasomatism from nearly 0 to 100% illite. (B) Average chemical compositions of graywackes, wacke and shales from the Archean Chitradurga schist belt, India (Naqvi and others, 1988). (C) Mudstones and diamictites from Neoproterozoic sedimentary series of south Oman (Rieu and others, 2007).

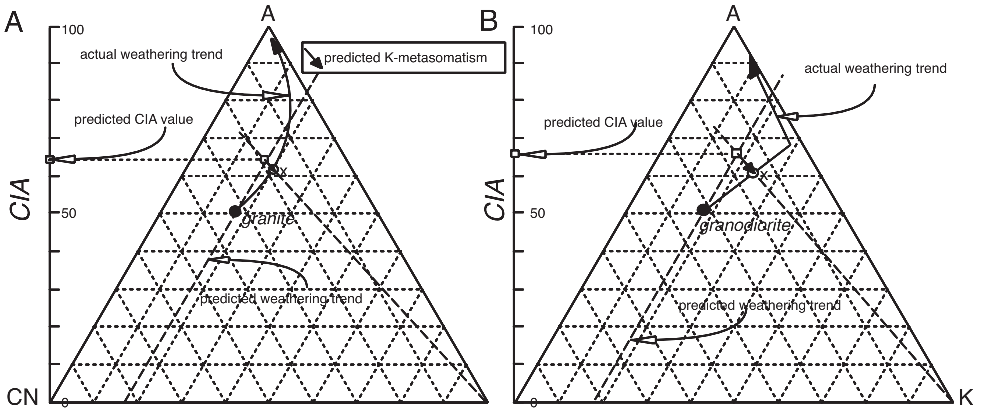

Fig. 14. Comparison of the actual and predicted weathering trends (actual trends are given in fig. 10A). (A) Granite. (B) Granodiorite. In both cases, the actual weathering trends are significantly different from the predicted ones. The predicted CIA values are systematically overestimated for weakly altered rocks (sample x).

sediment series whatever its age. However, to that point, it is necessary to re-examine the validity of "*the predicted weathering trend*" assumption. Indeed, significant differences exist between the predicted and the actual weathering trends of granite and granodiorite since the later are not depicted by straight lines parallel to the A-CN side of the diagram (fig. 14A). Consequently, most of the altered samples are K-richer than predicted for weathering conditions as different as those prevailing in western France (fig. 14A) and Georgia, USA (fig. 14B). Therefore, the K-metasomatism is less intense than given by the method of Fedo and others (1995) and the corresponding CIA values are inevitably overestimated.

CONCLUSIVE REMARKS

Any study of recent or ancient sedimentary basins aims to reconstitute the geological history recorded in sediments. This is why a method helping to identify the source rocks and to estimate their alteration intensity from the chemical composition of the sediments is so strongly needed. The CIA has been largely employed (see the review of Bahlburg and Dobrzinski, 2009). However, its genetic limitations may induce erroneous interpretations of the weathering intensity. Even when based on a more complete chemical space (A-CNK-FM), the fact that silica is not taken into account forbids the definition of comparable scales of the weathering intensity for the different silicate rock types. This drawback is avoided using the M^+-4Si-R^{2+} system that offers a better discrimination of the weathering trends. The co-variation of the Δ4Si% parameter with the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratio integrates the two major phenomena involved in the weathering processes: 1) the relative enrichment in silica (kaolinization); 2) the final enrichment in insoluble components (Al_2O_3 and Fe_2O_3) which accompanies the dissolution of kaolinite. Nevertheless, even if the weight of the assumptions used in the Δ4Si% versus $R^{3+}/(R^{3+} + R^{2+} + M^+)$ coordinates is lower than that supporting the CIA calculation, some unavoidable uncertainties remain. The most important one is due to the fact that ordinary rock chemical analyses do not take into account the actual Fe oxidation state. Considering that the total Fe amount is given either by Fe_2O_3% or FeO% may have important consequences on the determination of the source rocks of the sediments and their alteration degree.

Whatever the procedure used (CIA or WIS), it is clear that the discrimination of the sediment rock sources becomes more and more uncertain with increasing weathering intensity. The chemical trends of the felsic, mafic and ultramafic rock types converge rapidly with increasing $\Delta 4Si\%_{cor}$ values. It is an unavoidable consequence of the Fe oxidation and the leaching of the soluble components in the ultimate weathering stages that lead to the formation of laterites or bauxite deposits whatever the rock type. The value of the $[R^{3+}/(R^{3+} + R^{2+} + M^{+})]$ ratio approaches 1 when $\Delta 4Si\%$ reaches 100 percent. Consequently, it is not reasonable to try to determine the sediment rock source types for $\Delta 4Si\% > 50$ percent. Another limitation comes from the appreciation of the natural chemical variability of the original sediments versus the effects of their illitization during diagenesis. An illite correction is needed only when the sediment compositions are clearly aligned toward the diagenetic illite pole in the M^{+}-4Si-R^{2+} system. If not, the correction is not pertinent.

What is the climatic significance of the WIS? Since "climatic" conditions include parameters as different as are latitudinal location, temperature, precipitation, elevation or runoff, it is quite difficult to determine precisely the actual significance of the WIS. No simple relations can be actually established between WIS variations and one or several of these parameters in the sediments presently deposited at the Amazon river mouth. Nevertheless, it seems that the WIS variations in stratigraphical series deposited during a long period of time could record the changes of one or several of these parameters. The large magnitude variations (tens of million years) could be related to global factors such as average temperature and latitude while the secondary oscillations (million years) could probably record more local conditions such as precipitation, elevation, denudation or runoff. This potentiality has to be tested on various sedimentary series including mudstones, shales or diamectites as well as on paleosols that are considered to be remnants of undisturbed weathered rocks.

ACKNOWLEDGMENTS

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Appendix 1

CALCULATION PROCEDURE FOR THE WIS WITHOUT CORRECTION OF ILLITIZATION EFFECTS

Table A1-1

Example: the Cheshire shale series in the Belingwe greenstone belt, Zimbabwe (Hofmann and others, 2003). Chemical compositions are given in oxide weight %

SiO_2	**Al_2O_3**	**Fe_2O_3**	**MgO**	**CaO**	**Na_2O**	**K_2O**
62.95	21.06	8.06	0.9	0.35	1.58	3.45
60.99	16.01	13.71	3.77	1.12	2.84	1.06
55.08	18.34	15.2	2.76	3.83	0.87	2.6
57.37	17.97	13.29	2.35	3.53	0.83	3.15
53.37	21.07	10.41	2.98	3.75	7.05	0.03
59.89	19.97	11.84	4.04	0.32	0.58	2.37
54.64	20.47	17.3	4.71	0.11	1.11	0.57
54.62	21.41	14.85	4.45	0.94	1.41	0.94
52.15	22.84	13.92	6.01	0.71	0.94	2.2
54.87	23.99	13.18	3.66	0.5	1.3	1.34
67.85	17.83	8.29	1.64	0.15	0.73	2.63
54.14	16.25	23.75	4.5	0.03	0.07	0.27

TABLE A1-2

Calculation of monocationic molar proportions (ex. Si = (62.95 × 1000)/60.09)

mMol SiO_2	mMol $AlO_{3/2}$	mMol $FeO_{3/2}$	mMol MgO	mMol CaO	mMol $NaO_{1/2}$	mMol $KO_{1/2}$
1047.60	413.10	100.94	22.33	6.24	50.98	73.25
1014.98	314.04	171.70	93.53	19.97	91.64	22.51
916.63	359.75	190.36	68.47	68.30	28.07	55.20
954.73	352.49	166.44	58.30	62.95	26.78	66.88
888.17	413.30	130.37	73.93	66.87	227.49	0.64
996.67	391.72	148.28	100.22	5.71	18.72	50.32
909.30	401.53	216.66	116.84	1.96	35.82	12.10
908.97	419.97	185.97	110.39	16.76	45.50	19.96
867.86	448.02	174.33	149.09	12.66	30.33	46.71
913.13	470.58	165.06	90.80	8.92	41.95	28.45
1129.14	349.74	103.82	40.68	2.67	23.56	55.84
900.98	318.75	297.43	111.63	0.53	2.26	5.73

TABLE A1-3

Calculation of the R^{3+}, R^{2+}, and M^+ parameters − calculation of the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ ratio: $R^{3+} = Al^{3+} + Fe^{3+}$; $R^{2+} = Mg^{2+} + Fe^{2+} + Mn^{2+}$; $M^+ = Na^+ + K^+ + 2Ca^{2+}$

$R^{3+}+R^{2+}+M^+$	$R^{3+}/(R^{3+}+R^{2+}+M^+)$
673.08	0.76
733.36	0.66
838.44	0.66
796.78	0.65
979.46	0.56
720.67	0.75
786.87	0.79
815.32	0.74
873.80	0.71
814.66	0.78
578.99	0.78
736.88	0.84

TABLE A1-4

Calculation of the M^+ %, 4Si%, and R^{2+} % normalized parameters. 4Si = Si/4

	Bulk composition			**Normalized parameters**		
4Si	**M^+**	**R^{2+}**	**4Si+M^++R^{2+}**	**4Si%**	**M^+%**	**R^{2+}%**
261.90	136.71	22.33	420.94	62.2	32.5	5.3
253.74	154.09	93.53	501.36	50.6	30.7	18.7
229.16	219.87	68.47	517.49	44.3	42.5	13.2
238.68	219.55	58.30	516.54	46.2	42.5	11.3
222.04	361.87	73.93	657.84	33.8	55.0	11.2
249.17	80.45	100.22	429.84	58.0	18.7	23.3
227.33	51.84	116.84	396.01	57.4	13.1	29.5
227.24	98.98	110.39	436.62	52.0	22.7	25.3
216.97	102.36	149.09	468.42	46.3	21.9	31.8
228.28	88.23	90.80	407.31	56.0	21.7	22.3
282.28	84.74	40.68	407.71	69.2	20.8	10.0
225.25	9.06	111.63	345.94	65.1	2.6	32.3

APPENDIX 2

TABLE A2-1

Example: the Gulf Coast shale series (Awwiller, 1993)

SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	ΔK_2O	*%illite*
58.58	17.65	5.38	1.59	0.98	1.21	1.92	*0*	*0.0*
58.94	17.96	5.47	1.59	0.86	1.23	1.99	*0.07*	*0.7*
58.06	16.82	5.3	1.97	1.18	1.32	2.26	*0.34*	*3.4*
58.19	16.61	5.36	1.95	0.82	1.34	2.15	*0.23*	*2.3*
57.58	17.67	5.67	1.93	1.06	1.15	2.33	*0.41*	*4.1*
54.97	18.45	5.6	1.92	2.54	0.76	2.27	*0.35*	*3.5*
57	17.81	5.18	1.89	2.09	0.73	2.05	*0.13*	*1.3*
57.15	17.78	5.34	1.76	1.94	0.73	2.05	*0.13*	*1.3*
58.03	16.93	5.27	1.75	1.77	0.81	2.15	*0.23*	*2.3*
57.32	17.12	5.45	1.83	1.56	0.95	2.25	*0.33*	*3.3*
58.15	17.55	5.98	2.03	1.43	1.15	2.55	*0.63*	*6.4*
57.12	17.58	6.34	2.09	1.37	1.18	2.7	*0.78*	*7.9*
57.48	17.52	6.45	2.09	1.12	1.15	2.99	*1.07*	*10.8*
58.7	17.75	4.74	1.88	0.91	1.27	3.79	*1.87*	*18.9*
59.58	17.94	4.98	1.86	0.83	1.25	3.82	*1.9*	*19.2*
57.45	17.45	5.82	2.02	1.31	1.07	3.44	*1.52*	*15.4*
59.07	17.61	5.78	1.92	0.98	1.2	3.49	*1.57*	*15.9*
57.26	18.05	5.96	1.98	1.58	1.19	4.04	*2.12*	*21.4*
59.23	17.25	5.66	1.8	1.17	1.12	3.77	*1.85*	*18.7*
59.14	17.88	5.14	1.93	1.09	1.2	4.02	*2.1*	*21.2*
57.67	17.39	7.53	1.96	0.97	1.1	3.09	*1.17*	*11.8*

Chemical compositions are given in oxide weight %. ΔK_2O: difference between the K_2O% of a given sample and 1.92% (the lowest content). The illite % is given by $\Delta K_2O \times 100/9.9$ (the K_2O% of the diagenetic illite is 9.9%, Table 3, Meunier and Velde, 1989).

Table A2-2

The corrected chemical composition of a shale is given after substraction of the illite contribution

SiO_{2cor}	Al_2O_{3cor}	Fe_2O_{3cor}	MgO_{cor}	CaO_{cor}	Na_2O_{cor}	K_2O_{cor}
58.58	17.65	5.38	1.59	0.98	1.21	1.92
58.60	17.75	5.46	1.57	0.86	1.23	1.92
56.42	15.78	5.27	1.85	1.18	1.32	1.92
57.08	15.91	5.34	1.87	0.82	1.34	1.92
55.60	16.41	5.63	1.78	1.06	1.15	1.92
53.28	17.38	5.57	1.79	2.54	0.76	1.92
56.37	17.41	5.17	1.84	2.09	0.73	1.92
56.52	17.38	5.33	1.72	1.94	0.73	1.92
56.92	16.23	5.25	1.67	1.77	0.81	1.92
55.73	16.11	5.42	1.72	1.56	0.95	1.92
55.11	15.62	5.92	1.80	1.43	1.15	1.92
53.36	15.19	6.26	1.80	1.37	1.18	1.92
52.32	14.24	6.34	1.69	1.12	1.15	1.92
49.69	12.02	4.55	1.22	0.91	1.27	1.92
50.43	12.12	4.79	1.19	0.83	1.25	1.92
50.13	12.79	5.67	1.46	1.31	1.07	1.92
51.51	12.80	5.62	1.36	0.98	1.20	1.92
47.05	11.56	5.75	1.21	1.58	1.19	1.92
50.32	11.58	5.48	1.16	1.17	1.12	1.92
49.02	11.45	4.93	1.18	1.09	1.20	1.92
52.03	13.81	7.41	1.54	0.97	1.10	1.92

Ex: $SiO_{2cor} = SiO_2 - (SiO_{2illite} \times \text{illite } \%/100)$.

TABLE A2-3

Calculation of the number of millimoles of each element from the corrected composition

mMolSiO_2	**mM$AlO_{3/2}$**	**mM$FeO_{3/2}$**	**mMMgO**	**mMCaO**	**mM$NaO_{1/2}$**	**mM$KO_{1/2}$**
974.9	346.2	67.4	39.4	17.5	39.0	40.8
973.9	349.8	68.0	39.2	15.2	39.4	42.0
933.0	318.6	64.1	47.2	20.3	41.1	46.3
945.9	318.2	65.6	47.3	14.3	42.2	44.6
918.5	332.3	68.1	45.9	18.1	35.6	47.4
882.5	349.1	67.7	45.9	43.7	23.7	46.5
936.1	344.8	64.0	46.3	36.8	23.2	43.0
938.6	344.2	66.0	43.1	34.1	23.2	43.0
943.3	324.4	64.5	42.4	30.8	25.5	44.6
922.1	324.6	66.0	43.9	26.9	29.6	46.2
906.1	322.3	70.1	47.2	23.9	34.7	50.7
875.7	317.7	73.1	47.8	22.5	35.1	52.8
853.2	306.5	72.0	46.2	17.8	33.1	56.6
792.3	282.4	48.1	37.8	13.2	33.2	65.3
801.2	284.4	50.4	37.3	12.0	32.6	65.5
809.3	289.7	61.7	42.4	19.8	29.2	61.8
827.1	290.6	60.9	40.1	14.7	32.6	62.3
748.8	278.2	58.7	38.6	22.1	30.2	67.4
801.5	275.1	57.6	36.3	17.0	29.4	65.1
775.4	276.3	50.7	37.7	15.3	30.5	67.2
846.3	300.8	83.2	42.9	15.3	31.3	57.9

Table A2-4

Calculation of the M^+ %, 4Si%, and R^{2+} % normalized parameters

M^+	4Si	R^{2+}	sum	M^+%	4Si%	R^{2+}%
73.99	243.72	39.44	357.16	20.7	68.2	11.0
69.86	243.48	39.17	352.51	19.8	69.1	11.1
81.77	233.26	47.19	362.22	22.6	64.4	13.0
70.80	236.47	47.25	354.52	20.0	66.7	13.3
71.81	229.64	45.90	347.34	20.7	66.1	13.2
111.04	220.61	45.95	377.60	29.4	58.4	12.2
96.80	234.03	46.27	377.11	25.7	62.1	12.3
91.53	234.65	43.09	369.26	24.8	63.5	11.7
87.19	235.82	42.40	365.41	23.9	64.5	11.6
83.41	230.53	43.88	357.82	23.3	64.4	12.3
82.50	226.53	47.16	356.19	23.2	63.6	13.2
80.09	218.92	47.76	346.77	23.1	63.1	13.8
68.72	213.29	46.24	328.26	20.9	65.0	14.1
59.56	198.09	37.83	295.48	20.2	67.0	12.8
56.51	200.31	37.29	294.11	19.2	68.1	12.7
68.77	202.32	42.42	313.51	21.9	64.5	13.5
61.99	206.78	40.08	308.85	20.1	67.0	13.0
74.46	187.21	38.60	300.27	24.8	62.3	12.9
63.32	200.37	36.31	300.00	21.1	66.8	12.1
61.14	193.86	37.72	292.71	20.9	66.2	12.9
61.81	211.58	42.88	316.26	19.5	66.9	13.6

Table A2-5

Calculation of the $R^{3+}/(R^{3+} + R^{2+} + M^+)$ and Δ4Si% parameters

$R^{3+}/(R^{3+}+R^{2+}+M^+)$	Δ4Si%
0.73	47.2
0.73	48.6
0.69	40.9
0.70	44.7
0.71	43.7
0.67	30.9
0.69	37.0
0.70	39.4
0.69	41.1
0.69	40.9
0.69	39.5
0.68	38.8
0.69	41.8
0.67	45.2
0.68	47.0
0.67	41.1
0.68	45.1
0.65	37.5
0.67	44.8
0.66	43.9
0.70	45.0

The source rock is considered to be represented by the average upper continental crust (Condie, 1993): 4Si% = 39.8. Δ4Si% = $(4Si\%_{sample} - 39.8) \times 100/(100 - 39.8)$.

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