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Notes

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ABSTRACT

Lutites are commonly metasomatized during diagenesis, but the analysis presented here accounts for most postdepositional change. Potassium metasomatism is particularly common, and typically involves the conversion of kaolin (residual weathering product) to illite by reaction with K^+ -bearing pore waters. Sandstones also undergo K metasomatism, which involves the replacement of plagioclase by potassium feldspar. These changes can be identified petrographically and are quantitatively accounted for by techniques discussed herein. Bulk chemical analyses and ternary diagrams are used to determine the amount of K addition, premetasomatized sediment composition, and composition of provenance areas. The premetasomatized mineralogy of paleosols can be compared with the mineralogy of recent soil profiles and thus, climate and topographic conditions determined for past weathering events. Some weathering indices lead to erroneous conclusions because, by excluding K_2O from consideration, correction cannot be made for metasomatic effects.

INTRODUCTION

Chemical weathering strongly affects the major-element geochemistry and mineralogy of siliciclastic sediments (e.g., Nesbitt and Young, 1982; Johnsson et al., 1988; McLennan, 1993). Quantitative measures, such as the chemical index of alteration (CIA; Nesbitt and Young, 1982), are therefore potentially useful to evaluate the degree of chemical weathering. High CIA values reflect the removal of labile cations (e.g., Ca^{2+} , Na^+ , K^+) relative to stable residual constituents (Al^{3+} , Ti^{4+}) during weathering (Nesbitt and Young, 1982). Conversely, low CIA values indicate the near absence of chemical alteration, and consequently might reflect cool and/or arid conditions.

Geologic systems, however, are not simple, and a single calculated value may not adequately reflect their complexities. Growing concerns regarding potassium metasomatism in shale (Condie, 1993; see below) point to the complex processes involved in chemical weathering in situ (production of clay minerals), mechanical breakdown, and continued chemical alteration during transport, burial, and diagenesis. In this paper, we demonstrate a technique that quantitatively evaluates K enrichment of shales, determines the paleoweathering index prior to enrichment, and provides information on source-area composition. We also compare two commonly employed paleoweathering indices, namely the chemical index of alteration and the chemical index of weathering (Harnois, 1988).

K METASOMATISM OF SEDIMENTARY ROCKS AND PALEOSOLS

Shales

The chemical compositions of sedimentary rocks and paleosols are plotted as molar proportions within Al_2O_3 , $CaO^* + Na_2O$, K_2O (A-CN-K) compositional space, where CaO^* represents Ca in silicate-bearing minerals only (Fig. 1). The A-CN-K system is useful for evaluating fresh rock compositions and examining their weathering trends because the upper crust is dominated by plagioclase- and K-feldspar-rich rocks (Nesbitt and Young, 1984, 1989) and their

weathering products, the clay minerals. Average Paleoproterozoic shale and its probable source composition, average Upper Archean upper crust, are plotted in Figure 1A. The weathering trend for Upper Archean crust, predicted from kinetic leach rates (Nesbitt and Young, 1984; Nesbitt, 1992), is also plotted in Figure 1A (arrow b). The accumulated weathering products of Upper Archean crust, as represented by average Paleoproterozoic shale, should plot on this trend, but instead plot well below it; the average shale contains considerably more K_2O than expected and therefore has undergone K metasomatism (Nesbitt, 1992).

Both the amount of K enrichment and the paleoweathering index prior to such enrichment can be ascertained from the A-CN-K plot. Because this type of K enrichment involves addition of K_2O to aluminous clays, it follows a path toward the K_2O apex of the triangle. A line from the K apex through average shale (Fig. 1A, arrow c) intersects the predicted weathering trend at a point representing its premetasomatized composition. A paleoweathering index corrected for K enrichment can then be determined by reading off the CIA value (Fig. 1A, arrow d). A premetasomatized CIA value of 76 indicates that the average shale has gained about 10% K_2O during metasomatism.

Sandstones

K metasomatism of sandstones can take two different paths, representing (1) conversion of aluminous clay minerals (e.g., kaolinite as matrix) to illite (Fig. 1B, short arrow), and/or (2) conversion of plagioclase to K-feldspar (Fig. 1C, short arrow). Both of these processes result in the sample being enriched in K_2O , and therefore offset from the weathering trend. Conversion of secondary aluminous clay minerals such as kaolinite to illite by K addition (Fig. 1B) results in a CIA value lower than the premetasomatized one. The petrographic expression is the presence of illite, both as matrix material between grains, and as alteration of partially weathered plagioclase grains (Fig. 1B, petrographic example).

For the second possibility (Fig. 1C), where K metasomatism

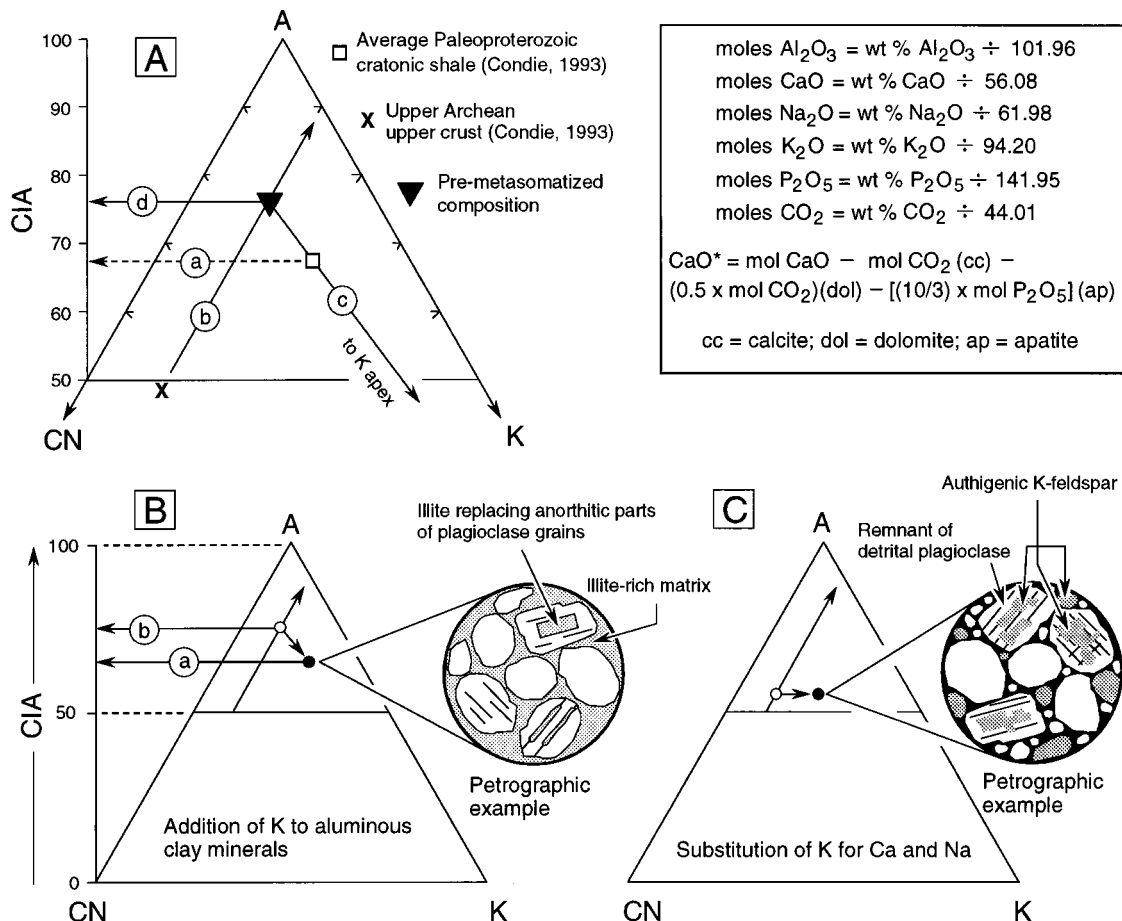


Figure 1. Average shale and continental crust (Condie, 1993) plotted as molar proportions on Al_2O_3 -($\text{CaO}^* + \text{Na}_2\text{O}$)- K_2O (A-CN-K) diagram. A: Effect of K metasomatism on weathered residue of Archean crust to produce average Paleoproterozoic shale. Dashed arrow (a) shows chemical index of alteration (CIA) of shale; arrow b, predicted weathering trend of Archean crust; arrow c, addition of K to weathered residues; arrow d, CIA of weathered residues (before metasomatism). B: K metasomatism of kaolin in weathered residues to illite. C: Replacement of plagioclase grains by K-feldspar. These two processes are illustrated by "petrographic examples" of sandstones. Formulas for calculations are given in upper right.

involves replacement of plagioclase by authigenic K-feldspar, the CIA value does not change because the process involves mole for mole substitution of K_2 for Ca or Na_2 . Glazner (1988) provided an example of this type of K metasomatism in Miocene volcanic rocks (compare his samples 13-21C and 13-21B in his Table 4).

Both metasomatic processes (Fig. 1, B and C) may affect paleosols and sedimentary rocks, and in this regard we have presented the extremes of a continuum. However, the extent to which each process has affected a particular sandstone can be determined petrographically, and the original CIA value prior to K enrichment generally can be determined.

IMPLICATIONS FOR PALEOSOLS: AN EXAMPLE

Evaluation of Weathering Intensity

Rainbird et al. (1990) discussed the geochemistry and K metasomatism of a Paleoproterozoic paleosol developed on the Ville Marie granite near Ville Marie, Quebec, Canada. The majority of samples from this paleosol plots on a trend well removed from the predicted weathering trend for the Ville Marie granite (Fig. 2, solid arrow) and indicates that K metasomatism resulted in conversion of kaolin to illite.

Three analyses from the Ville Marie paleosol (Fig. 2, samples 1, 2, and 3) illustrate the technique to correct for K metasomatism. It is apparent that different amounts of K_2O have been added during metasomatism to the three samples. All three samples have low CIA values (56, 63, and 66), whereas the premetasomatic CIA values are 61 (sample 1), 72 (sample 2), and 82–100 (sample 3). The variable degree of K metasomatism in the Ville Marie paleosol reflects the quantity of secondary kaolin (derived from plagioclase) available for

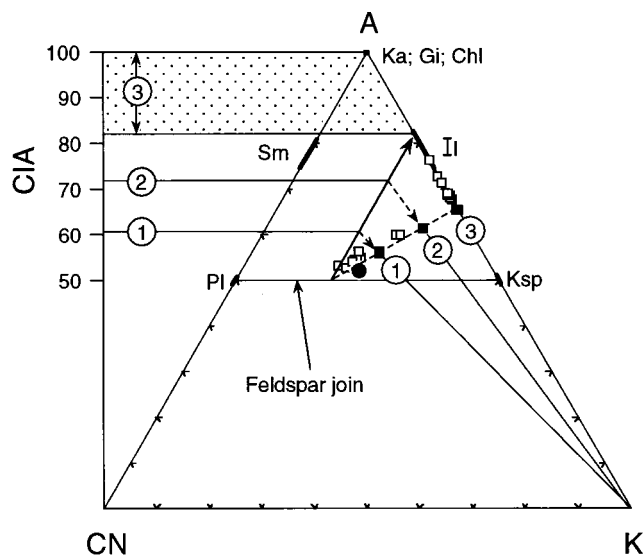


Figure 2. Ville Marie paleosol bulk compositions (Rainbird et al., 1990) plotted in A-CN-K space. Solid-line arrow represents predicted weathering trend for Ville Marie granite; dashed-line arrows show effects of K addition to three samples (black squares 1, 2, and 3). Dashed line connecting samples 1–3 represents metasomatic trend, and its intersection with feldspar join indicates feldspar proportion of unweathered source. Solid circle represents feldspar proportion of fresh Stone Mountain granite. Lines 1 and 2 show premetasomatized chemical index of alteration (CIA) values of samples 1 and 2, and zone 3 illustrates range of CIA values possible for premetasomatized sample 3. Ka = kaolinite; Gi = gibbsite; Chl = chlorite; Sm = smectite; Il = illite; Pl = plagioclase; Ksp = K-feldspar.

conversion to illite. In samples with relatively minor metasomatic alteration (e.g., sample 1 in Fig. 2; ~6% K_2O addition), kaolinite was not abundant and much original plagioclase was preserved, whereas samples that show a high degree of K enrichment contained abundant kaolinite for metasomatism (point 3, >14% K_2O addition), and after weathering, no primary plagioclase.

Samples that plot on the A-K join (e.g., sample 3, Fig. 2) had a CIA value between 82 and 100 prior to metasomatism, based on the predicted weathering trend for the Ville Marie granite (Fig. 2, solid arrow). Although a precise CIA value cannot be ascertained, the presence of partly sericitized microcline in the saprolite zone (Rainbird et al., 1990, Fig. 7, A and B) indicates that the CIA was less than 100 (a value indicative of 100% kaolinite).

Some implications for paleoweathering intensity are now discussed. Fresh Ville Marie granite has plagioclase to K-feldspar proportions similar to those of fresh Stone Mountain granite exposed in Georgia, southeastern United States (Fig. 2, large solid circle, data from Grant, 1963). As a result, the predicted weathering trends for both granites are nearly identical (Nesbitt and Young, 1989), and the only way they could vary from each other in A-CN-K space would be if weathering intensities affecting the Ville Marie and Stone Mountain profiles were different. The premetasomatized mineralogy of the Ville Marie paleosol is identical to the mineralogy of the Stone Mountain profile; in the uppermost zone, both consist of clay minerals, quartz, and K-feldspar, but no plagioclase, which has been converted to aluminous clays. This consistency in primary and secondary mineralogy indicates that the two profiles developed under similar weathering intensities, where the systematic progression in alteration minerals tracks incipient (CIA = 50–60), to intermediate (CIA = 60–80), to extreme (CIA > 80) chemical weathering.

The mineralogy of soils depends on the combined effects of chemical weathering and physical erosion, and achievement of steady-state conditions between both processes yields a constant surface soil mineralogy (Bates, 1962; Nesbitt and Wilson, 1992). That the mineralogy of the weathered zones of the Ville Marie and Stone Mountain profiles is the same suggests that they have achieved the same steady-state conditions, which implies that the balance between physical and chemical processes was similar for both profiles. This balance suggests that the climate and physiography influencing the Stone Mountain and Ville Marie profiles was the same. In this regard, the Stone Mountain granite is located in an area of subdued to moderate topographic relief with a warm, moist climate (Grant, 1963).

Evaluation of Provenance

The A-CN-K triangle also can be used to constrain initial compositions of source rocks. Many weathering profiles show a linear trend subparallel to the A-CN join in the A-CN-K triangle (e.g., Nesbitt and Young, 1984). In the absence of K metasomatism, a line extended through the data points intersects the feldspar join at a point that shows the proportion of plagioclase and K-feldspar of the fresh rock. This proportion yields a good indication of the type of parent rock. A metasomatized sample suite will typically have a linear trend with a less steep slope, but its intersection with the feldspar join indicates the likely source rock composition because the amount of K addition to clays necessarily decreases as the amount of host clay material decreases.

In the Ville Marie paleosol, none of the data points falls on the feldspar join, which suggests that even the freshest samples are somewhat altered. Rainbird et al. (1990) reported that even the least-altered samples have plagioclase grains that are partially replaced by fine-grained sericite and hematite. In Figure 2, the straight

line connecting samples 1, 2, and 3 is extended to the feldspar join at a point representing the unweathered composition of the Ville Marie granite. This point is close to the open squares representing the “fresh” granite samples.

DISCUSSION: UTILITY OF PALEOWEATHERING INDICES

A useful weathering index should yield a unique value, or range of values, for *unweathered* parental rocks; the index should also yield distinctly different values characteristic of different weathered materials. Most attempts to generate an equation to quantify the degree of chemical weathering based on major-element analysis have involved many variables in complex calculations (Harnois, 1988). However, Nesbitt and Young (1982) introduced the relatively simple chemical index of alteration (CIA; Appendix 1), which monitors the progressive alteration of plagioclase and potassium feldspars to clay minerals. The wide applicability of this index stems from the fact that feldspars are the dominant minerals of the upper crust (Nesbitt and Young, 1984). Furthermore, unweathered rocks and minerals ranging in composition from gabbro through K-feldspar have similar CIA values of about 50 (Fig. 3), and thus provide a consistent quantitative framework for examining weathering.

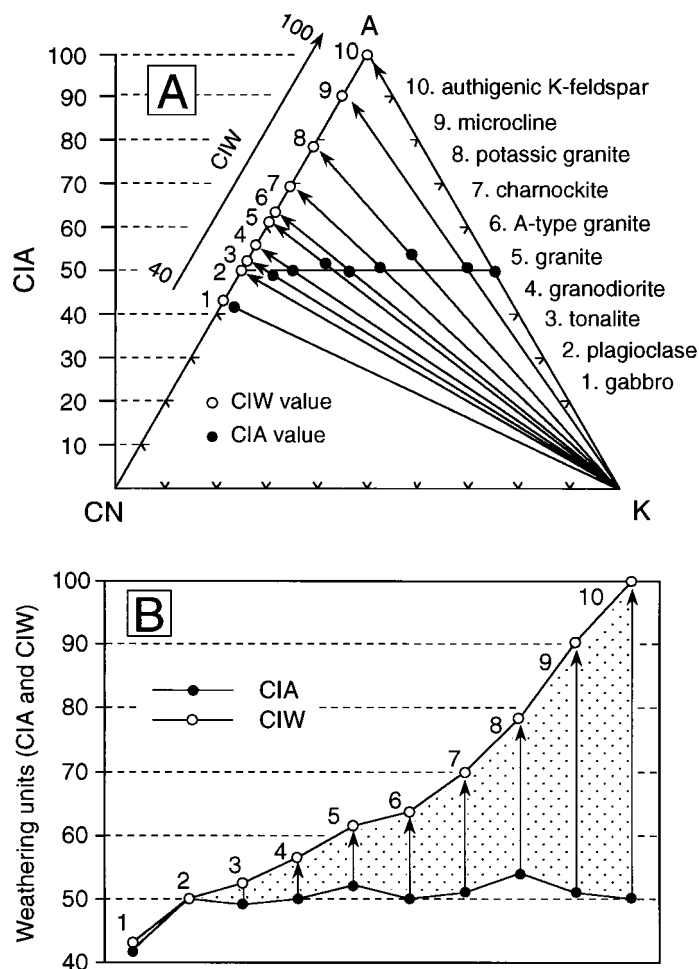


Figure 3. A: Solid circles are chemical index of alteration (CIA) values for variety of fresh rocks and minerals; corresponding open circles show chemical index of weathering (CIW) values for same fresh materials (analyses from Smith, 1974; Anderson and Bender, 1989; Carmichael et al., 1974; Cox et al., 1979; De Ros et al., 1994). B: Plot of corresponding CIA and CIW values shows extreme range of CIW values for unweathered materials. CIA values of varied composition are consistently near 50, as expected for unweathered feldspathic materials.

Several papers on the geochemistry of sedimentary rocks and paleosols have reported that K is typically more abundant than might be predicted by comparison with basement sources (e.g., Retallack, 1986; Nesbitt and Young, 1989; Rainbird et al., 1990). This potassium "problem" led Harnois (1988; also see Maynard, 1992) to propose a new weathering index, the chemical index of weathering (CIW), which is identical to the CIA except that it eliminates K_2O from the equation (Appendix 1). This simple transformation *does not* account for the aluminum associated with the K-feldspar in the studied materials. Because this approach utilizes total aluminum without correction for Al in K-feldspar, calculated CIW values are misleading in that they yield very high values for K-feldspar-rich rocks, whether chemically weathered or not (Fig. 3A). Citing the K enrichment problem, numerous authors have used the CIW in preference to the CIA as weathering index (e.g., Condie et al., 1992; Maynard, 1992; Condie, 1993; Sreenivas and Srinivasan, 1994).

The CIW calculation is the equivalent of projecting the samples represented by the filled circles (Fig. 3A) onto the A-CN join (open circles), from the K apex. The Al_2O_3 percentages shown by the solid circles are identical to CIA values (vertical scale to left of diagram). By contrast, the *apparent* Al_2O_3 percentages of the projected samples (open circles) are equivalent to CIW values. Most strikingly, *unweathered* potassic granite has a CIW of 80 and fresh K-feldspar has a CIW of 100, similar to values for residual products of chemical weathering (smectite CIW = 80; kaolinite, illite, and gibbsite CIW = 100). It is clear that the use of the CIW calculation to quantify chemical weathering intensity is inappropriate.

Where plagioclase weathering alone needs to be monitored the following equation can be used:

$$PIA = 100 \times (Al_2O_3 - K_2O) / (Al_2O_3 + CaO^* + Na_2O - K_2O),$$

where PIA is plagioclase index of alteration. This modification of the CIA equation is equivalent to projecting the solid circles (Fig. 3A) onto the A-CN join from the K-feldspar composition. The equation yields values of 50 for fresh rocks and values close to 100 for clay minerals such as kaolinite, illite, and gibbsite, consistent with values derived from the CIA equation.

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APPENDIX 1.

CIA—chemical index of alteration (Nesbitt and Young, 1982): $[Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)] \times 100$

CIW—chemical index of weathering (Harnois, 1988): $[Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O)] \times 100$

CIA-K— K_2O -free CIA (Maynard, 1992): $[Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O)] \times 100$

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