



# Chemical weathering indices applied to weathering profiles developed on heterogeneous felsic metamorphic parent rocks

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## Abstract

Chemical weathering indices are commonly used for characterizing weathering profiles by incorporating bulk major element oxide chemistry into a single metric for each sample. Generally, on homogeneous parent rocks, weathering indices change systematically with depth. However, the weathering of heterogeneous metamorphic rocks confounds the relationship between weathering index and depth. In this paper, we evaluate previously defined chemical weathering indices for their suitability in characterizing weathering profiles developed on felsic, heterogeneous, metasedimentary bedrock from Coweeta Hydrologic Laboratory, North Carolina, USA.

Among the weathering indices evaluated here, the Weathering Index of Parker (WIP) is the most appropriate for application to weathering profiles on heterogeneous (and homogeneous) parent rock. Because the WIP includes only the highly mobile alkali and alkaline earth elements in its formulation, it yields values that differ greatly from those of the parent rock. In addition, the WIP allows for aluminum mobility, unlike other weathering indices. These characteristics combine to make the Weathering Index of Parker the most applicable index for studying the weathering of heterogeneous metasedimentary rocks. However, the WIP should be applied judiciously, as alkali and alkaline earth metals may be readily depleted during weathering.

In addition to reflecting weathering, the Chemical Index of Alteration (CIA), Chemical Index of Weathering (CIW), Plagioclase Index of Alteration (PIA) and Vogt's Residual Index (V) may be sensitive to subtle geochemical changes such as hydrothermal alteration along a fault and/or alteration at the water table. Weathering indices that include iron in their calculations were not included in this study, because they do not distinguish between ferric and ferrous iron. The oxidation state and distribution of iron in a weathering profile is influenced by the proportion of oxidation states in the pre-weathered metamorphic rock and interaction with groundwater during weathering.

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## 1. Introduction

A weathering profile developed on a heterogeneous (e.g., metamorphic) parent rock is also heterogeneous,

greatly complicating the interpretation of vertical weathering profile trends in major element bulk chemistry. Under such circumstances, differences in the regolith chemistry between samples may simply reflect variation in parent rock bulk chemistry and mineralogy, rather than the degree or extent to which the sample has been geochemically weathered.

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Chemical weathering indices, sometimes referred to as indices of alteration (Table 1), are commonly used for characterizing weathering profiles. Chemical weathering indices incorporate bulk major element oxide chemistry into a single value for each sample. Weathering indices are typically applied by plotting some specific index versus depth in the weathering profile, providing a visual representation of changes in bulk chemistry with presumed increasing (or decreasing) weathering of the parent rock. Changes in the weathering index with depth commonly are gradual or continuous, steady and systematic for homogeneous parent rocks (e.g., granite; Sutton and Maynard, 1992), reflecting continuous leaching of elements as weathering progresses on an initially homogenous parent material. Similar patterns have been reported in at least some instances of saprolitic profiles developed on deformed gneisses and schists (e.g., Gardner and Walsh, 1996). However, weathering of metamorphic felsic silicate rocks does not always produce simple systematic trends in up-profile elemental changes (e.g., Ciampone et al., 1992; Ciampone, 1995; Duzgoren-Aydin et al., 2002). Segregation of micaceous minerals from tectosilicates (e.g., the development of schistosity), and development of foliation during metamorphism pro-

duces layers with different chemical and mineral composition, and thus with different susceptibility to weathering.

Concerns about chemical methods of evaluating weathering profiles on heterogeneous parent rock date to Goldich's (1938) study of regolith developed on the Morton Gneiss of Minnesota, USA. Goldich's bulk chemical major element analyses exhibited consistent trends, except for his analysis #5. Reiche (1943) intentionally omitted this apparently aberrant analysis from his graphical representation of chemical weathering, presuming it to be the result of parent-rock variation. The purpose of this paper is to evaluate chemical weathering indices for their applicability to saprolite developed on felsic, heterogeneous, metamorphic parent rocks.

## 2. Background

Weathering indices are widely used in studies of both modern and ancient in situ weathering profiles. In recent settings, weathering indices are used for evaluating soil fertility and development (e.g., Delvaux et al., 1989), demonstrating the impact of climate on bedrock weathering (e.g., Neall, 1977), character-

Table 1  
Summary of weathering indices (if calculated using molecular proportions of elements oxides) evaluated in this study

| Index | Formula  | Optimum fresh value | Optimum weathered value | Ideal trend of index up-profile (increase in weathering) | Allows Al mobility | Reference  |
|-------|--|---------------------|-------------------------|--|--------------------|--|
| R     | $\text{SiO}_2/\text{Al}_2\text{O}_3$   | > 10                | 0                       | Negative   | No                 | Ruxton (1968)  |
| WIP   | $(100)[(2\text{Na}_2\text{O}/0.35) + (\text{MgO}/0.9) + (2\text{K}_2\text{O}/0.25) + (\text{CaO}/0.7)]$  | > 100               | 0                       | Negative   | Yes                | Parker (1970)<br>(see also Table 1 of Harnois, 1988) |
| V     | $(\text{Al}_2\text{O}_3 + \text{K}_2\text{O})/(\text{MgO} + \text{CaO} + \text{Na}_2\text{O})$   | < 1                 | Infinite                | Positive   | No                 | Vogt (1927)<br>(see also Roaldset, 1972)             |
| CIA   | $(100)[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})]$                                   | ≤ 50                | 100                     | Positive   | No                 | Nesbitt and Young (1982)                             |
| CIW   | $(100)[\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O})]$  | ≤ 50                | 100                     | Positive   | No                 | Harnois (1988)                                       |
| PIA   | $(100)[(\text{Al}_2\text{O}_3 - \text{K}_2\text{O})/(\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} - \text{K}_2\text{O})]$            | ≤ 50                | 100                     | Positive   | No                 | Fedo et al. (1995)                                   |
| STI   | $(100)[(\text{SiO}_2/\text{TiO}_2)/((\text{SiO}_2/\text{TiO}_2) + (\text{SiO}_2/\text{Al}_2\text{O}_3) + (\text{Al}_2\text{O}_3/\text{TiO}_2))]$ | > 90                | 0                       | Negative   | No                 | de Jayawardena and Izawa (1994)                      |

For the weathering of silicate rocks, the CaO must be restricted to that derived from silicate minerals.

izing alterations associated with neotectonic delineations (e.g., Sharma and Rajamani, 2000), quantifying the engineering properties of regolith (Duzgoren-Aydin et al., 2002) and/or simply providing a better understanding of elemental mobility during weathering. In addition, weathering indices are also used to interpret the weathering history of modern and ancient sediments (e.g., Crichton and Condie, 1993; Gao and Wedepohl, 1995; Ramesh and Anglejan, 1995; Fedo et al., 1996; Colin et al., 1998; Tripathi and Rajamani, 1999; Eisenhauer et al., 1999; Gao et al., 1999; Young, 1999). Weathering indices have facilitated research on the geochemistry of the Earth's surface environment over geologic time (e.g., Nesbitt and Young, 1982; Maynard, 1992; Gall, 1992, 1994; Arndorff, 1993; Bäumler and Zech, 2000).

One way to interpret the bulk chemistry of heterogeneous weathering profiles is by using isovolumetric techniques. Millot and Bonifas (1955) (summarized in English by Millot, 1970) were the first to apply the isovolumetric method to the geochemical study of weathering profiles. This technique is based on the assumption that, during subaerial weathering, elements are removed from or added to the weathering profile without dilation or compaction. Therefore, a unit volume of weathered rock is presumed to have evolved from an equivalent volume of fresh rock (Gardner et al., 1978). Saprolite forms by isovolumetric weathering (Schoeller, 1942; Millot and Bonifas, 1955; Gardner et al., 1978; Velbel, 1990; Gardner, 1980, 1992). An empirical reaction progress diagram is created by plotting the oxide volumetric concentration (in  $\text{g cm}^{-3}$ ) against bulk density (e.g., Millot, 1970; Gardner et al., 1978, 1981; Gardner, 1980, 1992). The bulk density—*not* depth—of the sample serves as a measure of the extent of weathering (e.g., Grant, 1963, 1964). Sample depth may be inferior to bulk density as a measure of the extent of weathering, because deeper samples may be highly weathered adjacent to joints or other parent-rock discontinuities not directly related to distance from the land surface. Gardner et al. (1978, 1981) successfully applied the isovolumetric approach to understanding saprolite formation on (homogeneous) granite and diabase.

Weathering indices for weathering profile samples conventionally have been calculated using the molecular proportions of major element oxides. In

doing so, stoichiometric changes during weathering are reflected in the index value. The molecular proportion of each oxide is easily calculated from the percent of the oxide based on weight. Molecular proportions may also be used to calculate weathering indices for materials, which do not weather isovolumetrically or that have been affected by mechanical processes (e.g., bioturbation in soils). However, weathering indices calculated from molecular proportions typically are based on the assumption that aluminum is immobile (e.g., Vogt, 1927; Ruxton, 1968; Nesbitt and Young, 1982; Harnois, 1988; Fedo et al., 1995), an assumption that is not always warranted (Gardner et al., 1978; Gardner, 1980, 1992). Weathering indices calculated from volumetric concentrations and plotted against bulk density allows for the mobility of all elements. Instead, bulk density can be considered as a weathering progress variable for profiles that develop isovolumetrically. The isovolumetric technique serves as an independent standard against which each index is compared. Vertical (up-profile) weathering trends are also evaluated.

Table 1 outlines the indices evaluated in this study. Not all weathering indices found in the literature are assessed here. For example, weathering indices which include iron in their formulation are not suitable for application to weathered regoliths (Harnois, 1988), especially if the profile is developed on metamorphic rocks (Vogel, 1975). There are two limitations on the use of iron in a weathering index applied to weathered regoliths developed on metamorphic rocks. First, iron may be oxidized during metamorphism. The mobility of iron in the weathering environment depends on its oxidation state; trivalent (ferric) iron is relatively immobile, whereas divalent (ferrous) iron is highly mobile. During weathering, oxidation causes an increase in  $\text{Fe}_2\text{O}_3$  and a decrease in  $\text{FeO}$ . The weathering indices that include iron in their formulations have not provided for the differences between ferrous and ferric iron during weathering (i.e., Reiche, 1943; Eswaran et al., 1973). Because of the extra oxygen associated with ferric iron in oxide analyses, the weight percent ferric oxide is greater than the weight percent ferrous oxide, even if there is no change in the abundance of iron. This apparent increase in iron may partly offset losses of alkalis and alkaline earth, resulting in values that would skew a weathering

index to reflect a less-advanced stage of weathering. Furthermore, any increase in ferric iron is dependent on the relative concentrations of ferrous and ferric iron in the parent rock. In short, a weathering index that incorporates iron into its formulation would have to properly account for deviations from potentially complex and varied initial values of ferrous and ferric iron, and, therefore, may not yield values that are superior to indices that exclude iron.

The second concern with iron in a weathering environment is that its abundance is a reflection of redox conditions, which may not be consistent throughout a weathering profile (Harnois, 1988). For example, Gardner and Nelson (1991) described the formation of white to very slightly red-stained saprolite (“ghosts”) ovoid bodies that occur in a matrix of more intensely stained saprolite developed on granite in South Carolina. They suggested that “ghost” core stone formation occurred below the water table, as groundwater is commonly anoxic. Therefore, iron concentrations in a weathering profile may be controlled by modern or ancient groundwater levels rather than the extent of weathering. Price and Velbel (2000) described the formation of groundwater ferricretes in a weathering profile, and demonstrated that tectonic fractures in the parent rock controlled the complex redox-influenced redistribution of iron during weathering.

Chittleborough (1991) also proposed a weathering index, the Weathering Ratio, which is not considered here. This index is intended for the 20–90  $\mu\text{m}$  fraction of a soil and is based not only on the bulk chemistry of this size fraction, but also on the resistant heavy minerals present.

Recently, Duzgoren-Aydin et al. (2002) reviewed over 30 different chemical weathering indices to reassess their suitability for engineering applications. These authors applied the weathering indices to a weathering profile developed on (homogeneous) felsic pyroclastic rock weathering under subtropical conditions in Hong Kong. They concluded that, for the weathered regolith developed on pyroclastic rock, indices based on the ratio of a group of mobile oxides to one or more immobile oxides are the best candidates to characterize weathering-induced changes (Duzgoren-Aydin et al., 2002). These authors advocated avoiding weathering indices that consist of simple ratios of single oxides (e.g., the Ruxton Ratio;

Ruxton, 1968). In addition, the abundance of sesquioxides and clays in a regolith commonly results in unpredictable and poor correlations between a weathering index and the degree of weathering (Duzgoren-Aydin et al., 2002).

A useful chemical weathering index should provide values that do more than simply vary relative to one another on a given weathering profile. Ideally, a chemical weathering index should permit comparison between studies performed at different localities, on different parent materials and on weathering profiles of different ages. Based on our review of the literature, we apply the following criteria in evaluating the utility of weathering indices.

1. A chemical weathering index should be easy to use, involving chemical elements common in soil analyses (Harnois, 1988). This is desirable for wide applicability and maximum comparability with other studies.
2. A weathering index should incorporate elements with a range of mobility in the weathering environment (Harnois, 1988). Weathering indices based exclusively on the most mobile elements may not be applicable to assessing profiles or intervals representing advanced stages of weathering, because these are likely to have been depleted in highly mobile elements (Eswaran et al., 1973).
3. A useful weathering index should exhibit chemically appropriate trends with increased weathering (e.g., varying monotonically with depth) and should change greatly with increasing weathering. This is especially important in weathering profiles developed on metasedimentary parent rocks, which are commonly compositionally layered at scales much smaller than the overall dimensions of the weathering profile.
4. A useful weathering index should be applicable to a wide range of rocks and rock types, and should yield values for the unweathered parent material that are distinct from values for weathered material, regardless of rock type (Fedó et al., 1995). Metamorphosed sedimentary rocks might be expected to exhibit “weathered” chemical signatures by virtue of their pre-metamorphic history of weathering, differential erosion, and “chemical maturation” during transport in the previous pass of their protoliths through the sedimentary cycle. A useful weathering index

should allow users to distinguish between a “chemically mature” metasedimentary parent material and material post-metamorphically weathered from that parent material.

5. Ideally, a chemical weathering index should not assume that any element is immobile. This is difficult to apply in practice. Any element may be mobile in a weathering environment. At best, those elements that are least mobile should be used.

The weathering indices evaluated in this study are listed in Table 1 and discussed below.

### 2.1. Ruxton Ratio

Ruxton (1968) proposed a simple weathering index, which has been termed the Ruxton Ratio (R; Table 1) by Chittleborough (1991). Ruxton (1968) stated that his simple weathering index is best suited for weathering profiles developed on uniform acid to intermediate bedrock, with constant sesquioxide content during weathering, and which produces kaolin and/or allophane weathering products (products which have mole ratios of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  of 2:1). The Ruxton Ratio relates silica loss to total-element loss and considers alumina (and other sesquioxides) to be immobile during weathering (Ruxton, 1968). Ruxton (1968) tested R on weathering profiles developed on igneous and metamorphic rocks from humid regions around the world, and found that R correlated well with total-element loss.

### 2.2. Weathering Index (of Parker)

Parker (1970) introduced the weathering index, termed the Parker Index, or the Weathering Index of Parker (WIP; Eswaran et al., 1973; Hamdan and Burnham, 1996) for silicate rocks. Parker’s Weathering Index is based on the proportions of alkali and alkaline earth metals (sodium, potassium, magnesium and calcium) present. These elements are the most mobile of the major elements, and there is no need to assume that sesquioxide concentration remains approximately constant during weathering. The WIP also takes into account the individual mobilities of sodium, potassium, magnesium and calcium, based on their bond strengths with oxygen (Parker, 1970).

Parker (1970) applied the WIP to acid, intermediate and basic igneous rocks. However, because the WIP relies only on the mobile alkali and alkaline earth, its application to highly weathered materials (i.e., sedentary ferricretes and bauxites) is uncertain (Eswaran et al., 1973).

### 2.3. Vogt’s Residual Index

Vogt (1927) proposed a geochemical method for assessing the maturity of residual sediments; this index has been termed Vogt’s Residual Index (V; Table 1). Roaldset (1972) used this index to determine the extent to which clays have been weathered in Quaternary deposits of the Numedal Area, Norway. He used V to compare the bulk chemistry of moraine and marine clay deposits and concluded that the moraine clays were more weathered than the marine clays, suggesting that weathering ceased following deposition in a marine basin.

### 2.4. Chemical Index of Alteration

Nesbitt and Young (1982) developed the Chemical Index of Alteration (CIA; Table 1) in reconstructing paleoclimate from Early Proterozoic sediments of the Huronian Supergroup, north of Lake Huron. Nesbitt and Young (1982) used major element analyses of lutites to calculate their CIA. Their results suggested that the depositional basin of the lutites migrated through various climate zones, from approximately 32° latitude to approximately 60° latitude. These conclusions were confirmed with paleomagnetic studies. Because the CIA is interpreted as a measure of the extent of conversion of feldspars (which dominate the upper crust) to clays such as kaolinite (Nesbitt and Young, 1984, 1989; Fedo et al., 1995; Maynard et al., 1995), it has been used in numerous paleosol studies (e.g., Sutton et al., 1990; Sutton and Maynard, 1992, 1993; Gall, 1994).

### 2.5. Chemical Index of Weathering

Harnois (1988) developed the Chemical Index of Weathering (CIW; Table 1; may also be termed the ACNRATIO; Harnois and Moore, 1988). This index is identical to the CIA, except that it eliminates  $\text{K}_2\text{O}$  from the equation. The same formulation has been

employed by Maynard (1992) and subsequent workers as the  $K_2O$ -free CIA, or CIA-K. Because the CIW does not account for the aluminum associated with K-feldspar, it may yield very high values for K-feldspar-rich rocks, whether they are chemically weathered or not (Fedó et al., 1995). Like the CIA, the CIW is also essentially a measure of the extent of conversion of feldspars to clays (Nesbitt and Young, 1984, 1989; Fedó et al., 1995; Maynard et al., 1995).

### 2.6. Plagioclase Index of Alteration

Fedó et al. (1995) proposed the Plagioclase Index of Alteration (PIA; Table 1) as an alternative to the CIW. Because plagioclase is abundant in silicate rocks and dissolves relatively rapidly, the PIA may be used when plagioclase weathering needs to be monitored (Fedó et al., 1995).

### 2.7. Silica–Titania Index

The Silica–Titania Index (STI; Table 1) was developed to correlate the degree of chemical weathering of metamorphic silicate rocks in tropical regions with their engineering properties (e.g., point load strength and uniaxial compressive strength; de Jayawardena and Izawa, 1994). For fresh rock and weathering profiles developed on high grade gneisses and quartzite of Sri Lanka, de Jayawardena and Izawa (1994) found that the STI correlated well with the Ruxton Ratio (Ruxton, 1968).

### 3. Study area

The study area for the research reported here is the U.S. Forest Service Coweeta Hydrologic Laboratory

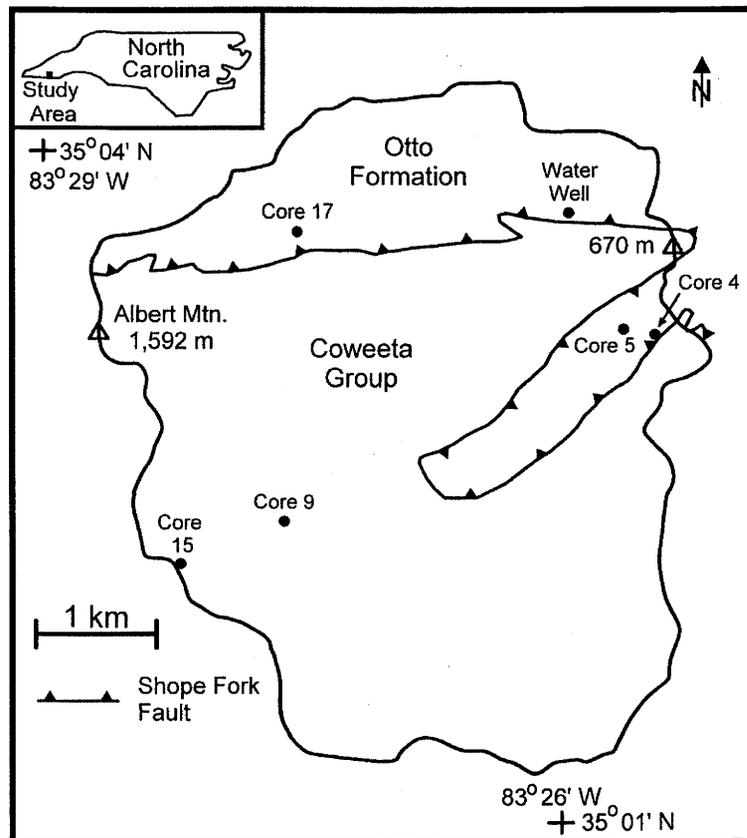


Fig. 1. Map of study area showing bedrock geology, and well and core locations.

(CHL) located in western North Carolina, within the Blue Ridge Physiographic Province (latitude 35°03' North and longitude 83°25' West; Fig. 1; Swank and Crossley, 1988). CHL is located approximately 15 km southwest of Franklin, NC and about 3 km north of the Georgia state line.

The Coweeta Basin is underlain by complexly folded, thrust faulted, amphibolite facies (staurolite–kyanite subfacies) metamorphosed sediments of the Coweeta Group (mid-Ordovician; Miller et al., 2000) and the Otto Formation (Upper Pre-Cambrian) (Hatcher, 1980, 1988, personal communication 2001). The Coweeta Group may be subdivided into three lithostratigraphic units. The basal Persimmon Creek Gneiss is dominantly a massive quartz–diorite gneiss with interlayers of metasandstone, quartz–feldspar gneiss and pelitic schist (Hatcher, 1980). The overlying Coleman River Formation is characterized by metasandstone and quartz–feldspar gneiss with lesser pelitic schist and calc-silicate quartzite. The Coleman River Formation is overlain by the Ridgepole Mountain Formation, a cleaner, coarse biotite–garnet schist, pelitic schist, metaorthoquartzite, garnetiferous metasandstone and muscovite–chlorite quartzite (Hatcher, 1980). In contrast to the compositional maturity of the Coweeta Group's sedimentary protoliths (e.g., arkoses and quartz arenites), the Otto Formation is derived from sedimentary protoliths of low compositional maturity (e.g., graywackes). The Otto Formation comprises a sequence of metasandstones, which are feldspar- and biotite-rich, and are interlayered with mafic volcanics and aluminous schists (Hatcher, 1988). The Otto Formation is predominantly biotite paragneiss and biotite schist (Hatcher, 1980). Coweeta Group and Otto Formation rocks are juxtaposed as a result of thrusting along the premetamorphic Shope Fork Fault (Hatcher, 1988; Fig. 1). The amphibolite facies regional metamorphism is associated with the Ordovician Taconic Orogeny when the Piedmont terrain was probably accreted (or reattached) to Laurentia (Hatcher, 1988; Miller et al., 2000).

The average thickness of the weathering profile (saprolite and soil) on ridges at CHL is 6.1 m (Berry, 1976, personal communication 2002). Velbel (1985) summarized evidence suggesting that the saprolite at CHL is geomorphically, geochemically and mineralogically adjusted to modern environmental conditions, and is not an ancient relict deep weathering profile.

#### 4. Methods

Typically, studies that use indices of alteration focus on the change of the index with depth in a weathering profile; in other words, they seek to use the index to quantify the changes in bulk chemistry as weathering progresses. This is equivalent to assuming that: (1) all material in the profile had the same initial composition (that of the deepest, presumably freshest sample) and (2) deeper samples are less extensively weathered than shallower samples (in other words, that extent of weathering increases with proximity to the surface and that subsurface features such as joint blocks do not influence weathering at depth).

For the purpose of evaluating weathering indices, the volumetric concentrations of the oxides (not molecular proportions) were used in the formulae for the weathering indices, and then the dimensionless indices themselves were plotted against bulk density. These diagrams will be termed herein empirical *weathering* progress diagrams (as opposed to empirical *reaction* progress diagrams used for the individual elemental oxides; Gardner et al., 1978). As such, the changes in a weathering index may be compared with bulk density, which serves as an independent measure of weathering progress. Because bulk density decreases systematically as isovolumetric weathering proceeds, chemically unreasonable trends generated from a weathering index can be identified. For example, if a weathering index increases in the direction of increased weathering (e.g., up-profile or radially outward from a corestone in the case of spheroidal weathering), it should also increase as bulk density decreases. If the index in fact decreases with decreased bulk density, it does not quantify elemental behavior in a manner consistent with the known weathering state of the sample. Any weathering index which fails to yield an appropriate (in the proper direction with increased weathering) and consistent trend is deemed inappropriate for studies of heterogeneous parent rocks. As a result of their formulation, some indices should increase in value as weathering progresses (i.e., V, CIA, CIW and PIA), while others should decrease with increased weathering (i.e., R, WIP and STI) (Table 1). Ideally, the predicted trend should be consistently observed regardless of the bedrock on which the weathering profile is developed. Indices of alteration calculated from element oxides in

Table 2

Chemical analyses of bedrock and saprolite from cores located at Coweeta Hydrologic Laboratory, North Carolina (data from Berry, 1976)

| Core sample | Bedrock <sup>a</sup> | Depth (m) | Bulk density (g cm <sup>-3</sup> ) | Weight percent oxide |                                |                                |      |      |                   |                  |                  |                               |      |       |        | Total H <sub>2</sub> O | Total |
|-------------|----------------------|-----------|------------------------------------|----------------------|--------------------------------|--------------------------------|------|------|-------------------|------------------|------------------|-------------------------------|------|-------|--------|------------------------|-------|
|             |                      |           |                                    | SiO <sub>2</sub>     | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | MnO  |       |        |                        |       |
| C15-4       | CG                   | 0.67      | 1.30                               | 41.67                | 24.97                          | 10.01                          | 4.04 | 1.13 | 1.14              | 3.11             | 2.01             | 0.09                          | 0.10 | 11.73 | 100.00 |                        |       |
| C15-7       | CG                   | 5.73      | 1.81                               | 50.37                | 21.52                          | 10.18                          | 3.17 | 0.35 | 0.40              | 5.02             | 1.43             | 0.08                          | 0.18 | 7.30  | 100.00 |                        |       |
| C15-9       | CG                   | 12.8      | 2.76                               | 64.88                | 16.10                          | 6.65                           | 1.58 | 2.00 | 2.04              | 3.59             | 1.11             | 0.13                          | 0.04 | 1.88  | 100.00 |                        |       |
| C17-2       | OF                   | 0.46      | 1.72                               | 38.77                | 27.14                          | 10.50                          | 3.08 | 2.90 | 0.15              | 1.32             | 1.00             | 0.27                          | 0.06 | 14.80 | 100.00 |                        |       |
| C17-3       | OF                   | 8.69      | 2.60                               | 71.13                | 12.66                          | 4.92                           | 1.96 | 3.17 | 2.47              | 1.43             | 0.88             | 0.17                          | 0.04 | 1.17  | 100.00 |                        |       |
| C17-4       | OF                   | 1.37      | 2.21                               | 63.44                | 15.15                          | 7.27                           | 1.90 | 0.10 | 0.12              | 1.14             | 1.88             | 0.25                          | 0.40 | 8.36  | 100.00 |                        |       |
| C4-4        | OF                   | 0.85      | 2.25                               | 51.79                | 24.21                          | 9.99                           | 1.32 | 0.03 | 0.37              | 3.17             | 1.24             | 0.25                          | 0.40 | 7.23  | 100.00 |                        |       |
| C4-6        | OF                   | 11.58     | 2.50                               | 41.88                | 24.16                          | 16.68                          | 3.14 | 0.31 | 0.54              | 3.11             | 2.42             | 0.21                          | 0.22 | 7.33  | 100.00 |                        |       |
| C5-5        | OF                   | 19.64     | 1.61                               | 66.32                | 15.76                          | 6.61                           | 1.86 | 1.40 | 1.36              | 1.61             | 1.35             | 0.06                          | 0.11 | 3.56  | 100.00 |                        |       |
| C5-6        | OF                   | 23.18     | 2.92                               | 47.62                | 25.00                          | 11.05                          | 3.64 | 2.27 | 2.54              | 3.77             | 1.82             | 0.17                          | 0.31 | 1.81  | 100.00 |                        |       |
| C9-3        | CG                   | 0.37      | 1.70                               | 48.34                | 23.05                          | 13.12                          | 2.51 | 0.02 | 0.41              | 2.69             | 1.85             | 0.11                          | 0.04 | 7.86  | 100.00 |                        |       |
| C9-4        | CG                   | 4.33      | 2.29                               | 46.96                | 24.01                          | 13.86                          | 3.17 | 0.02 | 0.47              | 3.64             | 1.84             | 0.11                          | 0.04 | 5.88  | 100.00 |                        |       |
| C9-5        | CG                   | 6.31      | 2.83                               | 73.58                | 12.27                          | 4.89                           | 1.97 | 1.11 | 0.74              | 1.61             | 1.95             | 0.24                          | 0.03 | 1.34  | 100.00 |                        |       |
| C9-7        | CG                   | 11.29     | 2.80                               | 72.04                | 12.18                          | 5.34                           | 1.73 | 2.83 | 2.19              | 1.28             | 1.22             | 0.10                          | 0.02 | 1.07  | 100.00 |                        |       |

<sup>a</sup> CG=Coweeta Group rocks, OF=Otto Formation.

volumetric concentrations yield different values from those calculated using element oxide concentrations in molecular proportions. Weathering indices calculated from elemental oxide concentrations in molecular

proportions were also used herein to evaluate the vertical changes in a weathering profile.

In order to account for wide compositional and textural variation in the study area bedrock, the data

Table 3

Chemical analyses of Otto Formation cuttings sampled from the Coweeta Hydrologic Laboratory potable water well (data from Ciamponi, 1995)

| Well sample  | Depth (m) | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | FeO  | Total Fe | Weight percent oxide |      |                   |                  |                  |                               |      |      |        |  |
|--------------|-----------|------------------|--------------------------------|--------------------------------|------|----------|----------------------|------|-------------------|------------------|------------------|-------------------------------|------|------|--------|--|
|              |           |                  |                                |                                |      |          | MgO                  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | MnO  | LOI  | Total  |  |
| COWW 0–10    | 3.05      | 60.05            | 17.67                          | 8.49                           | 0.80 | 9.38     | 1.15                 | 0.21 | 0.18              | 1.42             | 0.92             | 0.14                          | 0.18 | 8.50 | 99.80  |  |
| COWW 10–20   | 6.10      | 65.52            | 14.68                          |                                |      | 8.83     | 1.79                 | 0.87 | 0.76              | 1.18             | 1.39             | 0.18                          | 0.15 | 5.09 | 100.44 |  |
| COWW 20–30   | 9.14      | 58.09            | 19.78                          |                                |      | 7.86     | 2.39                 | 0.60 | 0.80              | 3.61             | 1.14             | 0.11                          | 0.23 | 5.08 | 99.69  |  |
| COWW 30–40   | 12.19     | 69.67            | 13.99                          |                                |      | 6.21     | 1.53                 | 0.64 | 0.74              | 1.85             | 1.24             | 0.10                          | 0.14 | 3.67 | 99.78  |  |
| COWW 40–50   | 15.24     | 63.28            | 14.90                          | 6.26                           | 2.20 | 8.70     | 3.05                 | 2.74 | 0.88              | 1.29             | 0.89             | 0.13                          | 0.19 | 3.82 | 99.87  |  |
| COWW 50–60   | 18.29     | 71.02            | 13.28                          |                                |      | 4.95     | 1.54                 | 1.86 | 1.88              | 2.09             | 1.14             | 0.12                          | 0.08 | 2.31 | 100.27 |  |
| COWW 60–70   | 21.34     | 66.47            | 15.24                          | 2.02                           | 3.80 | 6.24     | 2.00                 | 1.69 | 2.24              | 3.25             | 0.92             | 0.15                          | 0.10 | 1.44 | 99.74  |  |
| COWW 70–80   | 24.38     | 69.54            | 13.46                          |                                |      | 6.28     | 1.81                 | 1.91 | 1.95              | 2.37             | 1.27             | 0.17                          | 0.11 | 1.54 | 100.41 |  |
| COWW 80–90   | 27.43     | 64.91            | 15.97                          |                                |      | 8.39     | 2.36                 | 1.60 | 2.59              | 2.59             | 1.27             | 0.16                          | 0.16 | 1.32 | 101.32 |  |
| COWW 90–100  | 30.48     | 61.67            | 17.14                          |                                |      | 9.77     | 2.62                 | 1.54 | 2.39              | 2.92             | 1.28             | 0.18                          | 0.17 | 1.55 | 101.32 |  |
| COWW 100–110 | 33.53     | 55.24            | 19.41                          |                                |      | 13.71    | 3.51                 | 1.39 | 2.19              | 3.13             | 1.44             | 0.18                          | 0.31 | 1.52 | 102.03 |  |
| COWW 110–120 | 36.58     | 58.04            | 18.59                          |                                |      | 11.95    | 3.27                 | 1.68 | 2.65              | 2.53             | 1.75             | 0.16                          | 0.37 | 1.19 | 102.18 |  |
| COWW 120–130 | 39.62     | 65.53            | 16.23                          | 2.60                           | 3.20 | 6.15     | 2.04                 | 2.23 | 3.69              | 1.53             | 1.56             | 0.18                          | 0.12 | 1.04 | 100.30 |  |
| COWW 130–140 | 42.67     | 66.97            | 15.53                          |                                |      | 7.16     | 2.25                 | 2.21 | 3.40              | 1.37             | 1.36             | 0.18                          | 0.16 | 1.07 | 101.66 |  |
| COWW 140–150 | 45.72     | 62.17            | 16.85                          |                                |      | 10.01    | 2.57                 | 1.76 | 2.50              | 2.01             | 1.50             | 0.20                          | 0.22 | 1.28 | 101.07 |  |
| COWW 150–160 | 48.77     | 65.30            | 15.92                          |                                |      | 8.34     | 2.33                 | 2.02 | 2.98              | 1.53             | 1.88             | 0.17                          | 0.18 | 1.17 | 101.82 |  |
| COWW 160–170 | 51.82     | 64.46            | 16.05                          |                                |      | 9.07     | 2.43                 | 1.37 | 2.07              | 2.32             | 1.69             | 0.14                          | 0.17 | 1.54 | 101.31 |  |
| COWW 170–180 | 54.86     | 64.59            | 16.31                          |                                |      | 8.51     | 2.46                 | 1.85 | 2.77              | 2.00             | 1.35             | 0.16                          | 0.22 | 1.15 | 101.37 |  |
| COWW 180–190 | 57.91     | 64.35            | 15.87                          |                                |      | 8.78     | 2.56                 | 1.82 | 2.57              | 2.00             | 1.33             | 0.20                          | 0.30 | 0.92 | 100.70 |  |
| COWW 190–200 | 60.96     | 67.13            | 14.87                          | 2.93                           | 3.70 | 7.04     | 2.45                 | 2.03 | 2.47              | 2.10             | 1.45             | 0.22                          | 0.14 | 1.31 | 101.21 |  |

set was subdivided; weathering profiles developed on Otto Formation were treated separately from those developed on Coweeta Group lithostratigraphic units. The data also were subdivided on the basis of metamorphic fabric (i.e., schist or gneiss after Berry, 1976) and mineralogy (micaceous or quartzo-feldspathic). Neither of these two classification categories revealed any clustering of the data that would be considered superior to that found by grouping using the lithostratigraphic units. However, the comparison of the analyses demonstrated that pre-weathering bulk density values for the bedrock are nearly identical, regardless of the method of classification.

Bulk major element oxide analyses of rock, saprolite and soil at CHL were acquired by Berry (1976) and Ciampone (1995), and this study is based exclusively on their data (Tables 2 and 3). Only saprolite and bedrock samples collected from below the solum (i.e., from the C and R horizons; Birkeland, 1999) were used in this study. Soil-forming processes (e.g., eluviation, illuviation, bioturbation, etc.) typically disrupt isovolumetric weathering, making bulk density measurements of solum inapplicable to weathering or reaction progress diagrams. Furthermore, adsorbed ions and organic matter are ubiquitous in soil horizons, and, if not removed, may result in an overestimation of oxides, and hence skew weathering indices.

Berry (1976) provided bulk major element oxide chemical data of samples collected during a regolith coring investigation (see Fig. 1 for core locations). As Berry's (1976) study included bulk density measurements of saprolite (Table 2), his data are used to generate the weathering and reaction progress diagrams. All cores sampled complete regolith profiles (bedrock parent material and saprolite developed from that bedrock). Cores 4, 5 and 17 reached Otto Formation bedrock and penetrated saprolite developed by weathering of the Otto Formation. Core 9 sampled a regolith profile on the Coleman River Formation of the Coweeta Group; Core 15 sampled regolith developed on the Persimmon Creek Gneiss of the Coweeta Group. Berry (1976) sampled the weathering profile by driving a standard engineering split spoon into the regolith and by diamond-drilling into the unweathered rock. Major element oxide analyses (Table 2) were performed by  $\text{LiBO}_2$  atomic adsorption methods at the University of Georgia. Bulk density was measured with a Jolly Balance. Samples were weighed in air and

then weighed in water after being coated with aerosol acrylic lacquer (Berry, 1976). Furthermore, due to their lithologic similarity, Coweeta Group rocks were combined into a single data set.

Ciampone (1995) performed major element oxide analyses on saprolite and bedrock composite cuttings sampled during installation of the potable water well at CHL (Table 3). Originally, the water well was believed to have been drilled entirely into the Otto Formation to a depth of approximately 61 m (Ciampone, 1995). However, based on the proximity of the well to the Shope Fork Fault (Fig. 1) and the knowledge that the fault dips approximately  $45^\circ$  to the north (Hatcher, 1980, personal communication 2001), the water well likely encounters the fault in the subsurface. The Otto Formation, therefore, occurs in the upper portion of well, and the Coweeta Group occurs in the deeper portions of the well. The schistose Otto Formation is significantly more micaceous than the gneisses of the Coweeta Group and should, therefore, be more potassium-rich. Fig. 2 shows plots of  $\text{K}_2\text{O}$  (weight percent)

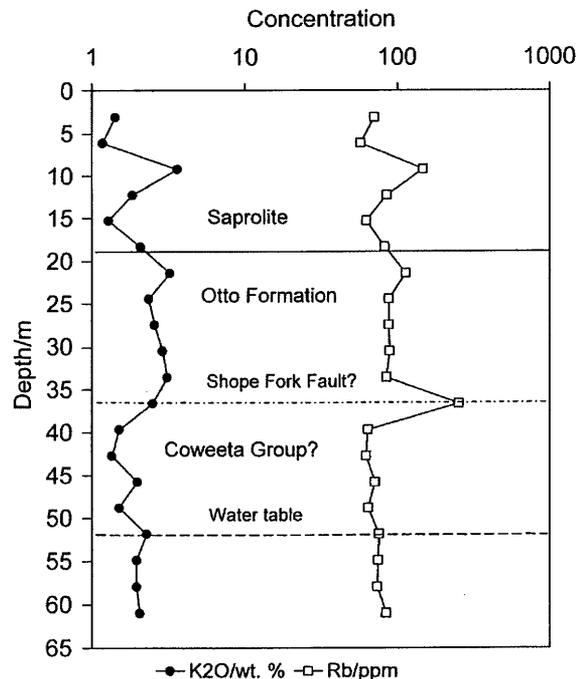


Fig. 2. Plot of  $\text{K}_2\text{O}$  and rubidium vs. depth for the water well. Note decrease in  $\text{K}_2\text{O}$  and rubidium below 37 m depth. Data from Ciampone (1995).

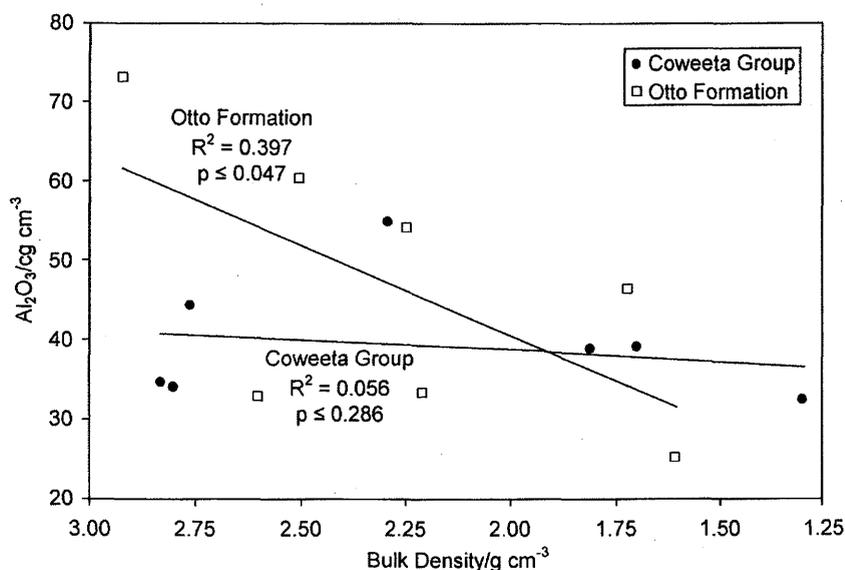


Fig. 3. Empirical reaction progress diagram showing mobilization of alumina in cores.

and rubidium (ppm) vs. depth in the water well. Potassium and rubidium concentrations are notably higher above versus below approximately 37 m depth, suggesting the transition from Otto Formation (above) to Coweeta Group rocks (below) across the subsurface expression of the Shope Fork Fault. The distinct enrichment of rubidium at approximately 37 m depth may indicate alteration along, or adjacent to, the shear zone. Regardless of the exact depth of the Shope Fork

Fault in the water well, it provides an opportunity to investigate the contribution of faulting to bedrock heterogeneity. Faulting is common in metamorphic orogenic belts, and not only do faults juxtapose bedrock of different lithologies, but they may also be a location of both high temperature (hydrothermal) alteration and/or accentuated weathering.

The composite water well samples were collected at 3-m intervals. Whole-rock geochemical analyses were

Table 4  
Weathering indices for the core samples

| Core sample | Bedrock <sup>a</sup> | Bulk density<br>(g cm <sup>-3</sup> ) | R   | WIP      | V    | CIA  | CIW  | PIA  | STI  |
|-------------|----------------------|---------------------------------------|-----|----------|------|------|------|------|------|
| C15-4       | CG                   | 1.30                                  | 1.7 | 4852.7   | 4.5  | 82.6 | 92.1 | 91.0 | 59.5 |
| C15-7       | CG                   | 1.81                                  | 2.3 | 8383.5   | 7.0  | 79.2 | 97.1 | 96.2 | 66.9 |
| C15-9       | CG                   | 2.76                                  | 4.0 | 12,349.7 | 3.6  | 68.3 | 80.6 | 76.4 | 75.9 |
| C9-3        | CG                   | 1.70                                  | 2.1 | 4530.8   | 8.8  | 88.1 | 98.3 | 98.0 | 64.2 |
| C9-4        | CG                   | 2.29                                  | 2.0 | 8090.1   | 7.6  | 85.4 | 98.1 | 97.7 | 63.0 |
| C9-5        | CG                   | 2.83                                  | 6.0 | 5782.2   | 4.0  | 79.6 | 88.9 | 87.4 | 75.5 |
| C9-7        | CG                   | 2.80                                  | 5.9 | 7988.8   | 2.0  | 66.4 | 71.4 | 69.0 | 78.8 |
| C17-2       | OF                   | 1.72                                  | 1.4 | 3179.2   | 4.9  | 87.1 | 91.0 | 90.6 | 57.6 |
| C17-3       | OF                   | 2.60                                  | 5.6 | 8313.0   | 1.9  | 64.9 | 70.0 | 67.4 | 80.2 |
| C17-4       | OF                   | 2.21                                  | 4.2 | 2625.3   | 8.1  | 92.3 | 99.2 | 99.2 | 73.4 |
| C4-4        | OF                   | 2.25                                  | 2.1 | 6511.7   | 16.2 | 87.2 | 98.5 | 98.3 | 65.8 |
| C4-6        | OF                   | 2.50                                  | 1.7 | 7875.6   | 7.3  | 86.8 | 97.7 | 97.3 | 59.6 |
| C5-5        | OF                   | 1.61                                  | 4.2 | 3961.4   | 3.8  | 78.6 | 85.5 | 84.1 | 75.6 |
| C5-6        | OF                   | 2.92                                  | 1.9 | 15,079.4 | 3.5  | 74.9 | 84.5 | 82.2 | 62.6 |

Weathering indices were calculated using oxides in volumetric concentrations (g cm<sup>-3</sup>).

<sup>a</sup> CG=Coweeta Group rocks, OF=Otto Formation.

performed by X-ray fluorescence (XRF) using a Rigaku 3070 X-ray spectrometer at the University of Cincinnati (Ciampone, 1995). Because composite cuttings from 3-m intervals were collected (rather than intact samples), bulk density could not be measured on the well samples. For this reason, Ciampone's (1995)

data were used to evaluate up-profile trends of the weathering indices (calculated using oxide concentrations in molecular proportions).

As established by the authors of the weathering indices, all calcium used in the calculations derives from silicate minerals. There are no reports of any

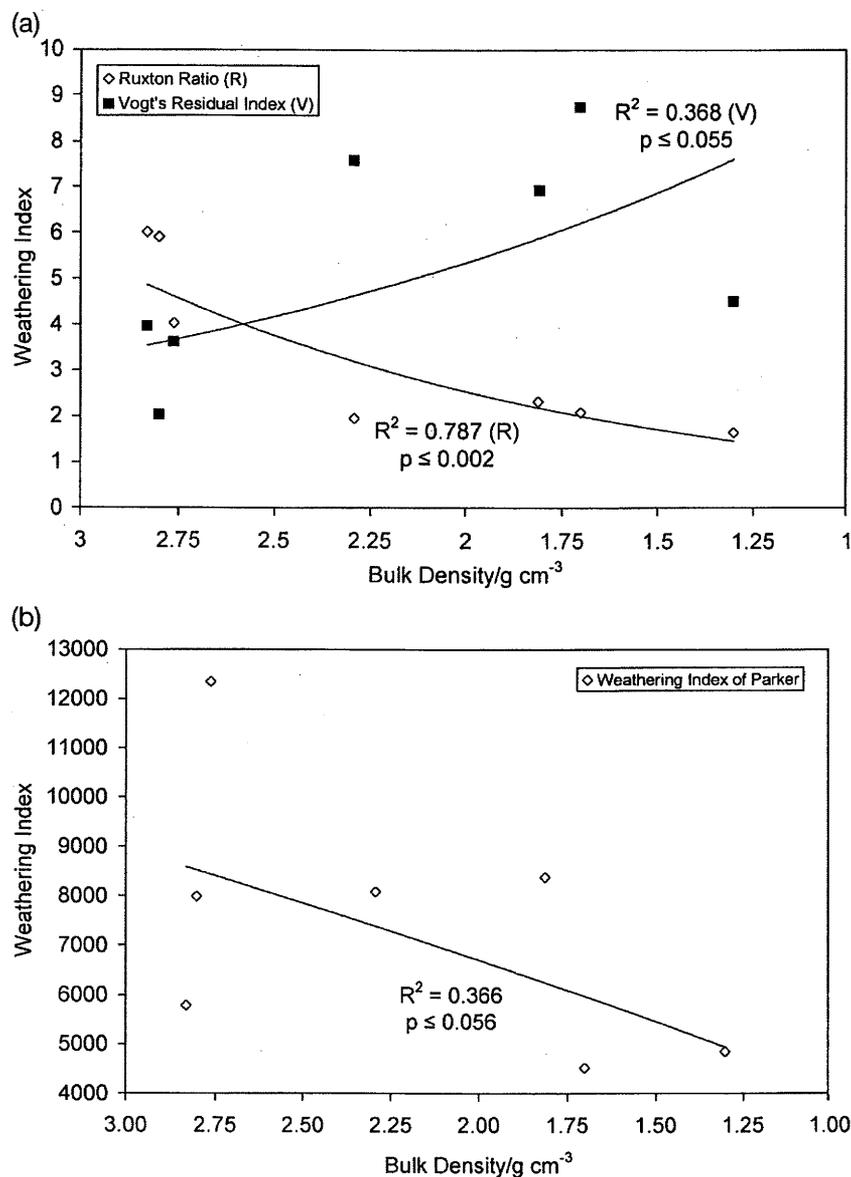


Fig. 4. Weathering progress diagrams for core samples. Weathering indices for saprolite developed on Coweeta Group rocks are: (a) Ruxton Ratio and Vogt's Residual Index; (b) Weathering Index of Parker; (c) Chemical Index of Weathering, Chemical Index of Alteration and Plagioclase Index of Alteration; (d) Silica-Titania Index; (e) Weathering Index of Parker for saprolite developed on the Otto Formation.

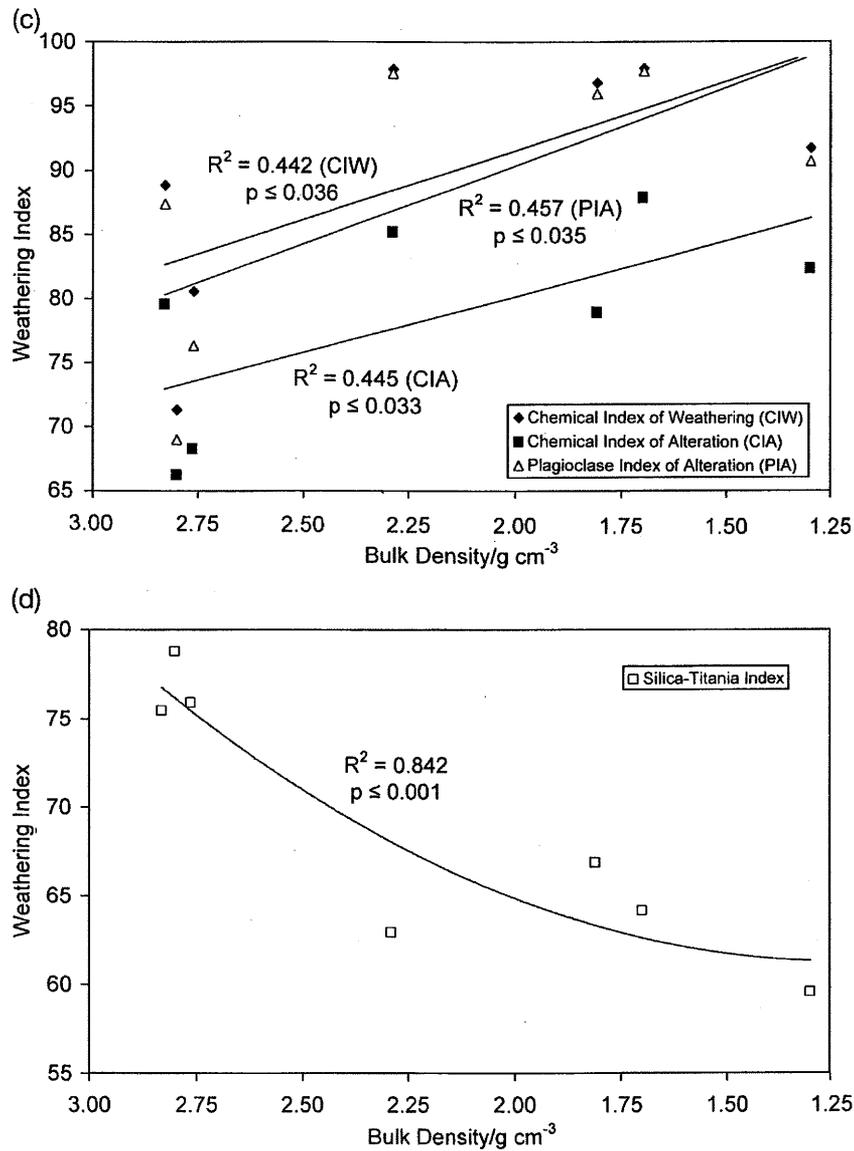


Fig. 4 (continued).

primary carbonate minerals occurring in any of the felsic bedrock lithologies at CHL (Hatcher, personal communication). Apatite, however, is present. Therefore, the CaO values have been corrected for apatite. That is,  $\text{CaO}^* = \text{mol CaO} - [(10/3) \times \text{mol P}_2\text{O}_5]$ .

Statistical interpretations of correlation coefficients for the weathering progress diagrams follow methods presented by Davis (1986).

## 5. Results

### 5.1. Aluminum mobility

Cleaves (1974), Gardner et al. (1978, 1981) and Gardner (1980) have previously demonstrated the loss of aluminum in homogeneous material using isovolumetric methods. Therefore, this study focussed

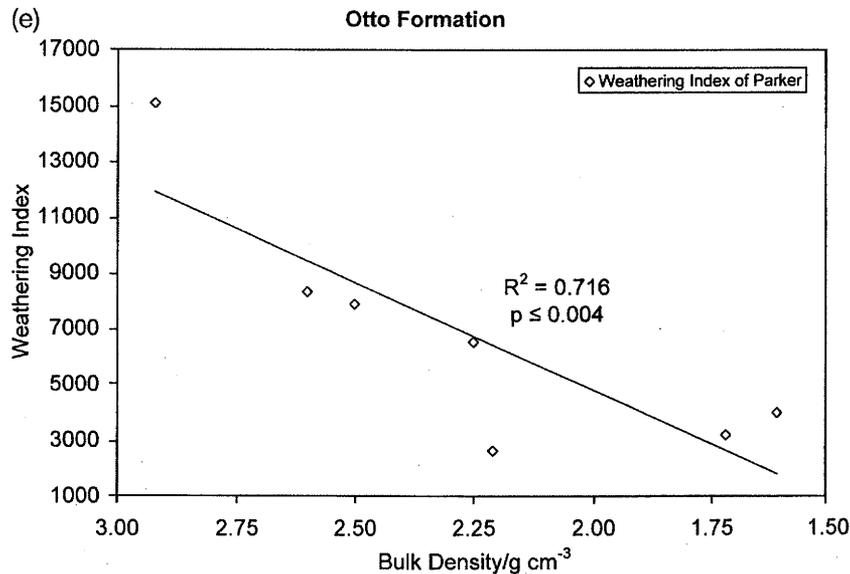


Fig. 4 (continued).

on the role of aluminum mobility in the application of weathering indices to heterogeneous fresh and weathered rock. The reaction progress diagram for aluminum (Fig. 3) reflects aluminum mobilization in saprolites developed on both Coweeta Group and the Otto Formation. Despite weak correlation coefficients (0.397 and 0.056 for saprolite developed on the Otto Formation and Coweeta Group, respectively), with relatively high corresponding  $p$ -values (0.047 for the Otto Formation correlation coefficient and 0.286 for the Coweeta Group correlation coefficient), the general trend of decreasing aluminum with decreasing bulk density is evident (Fig. 3). The poor correlation statistics of the reaction progress diagrams for alumina reflect the heterogeneity in aluminum distribution within a given lithostratigraphic unit.

### 5.2. Weathering indices

The weathering indices (calculated from volumetric concentrations) for the cores are presented in Table 4 and plotted as empirical weathering progress diagrams in Fig. 4a–e. For the Coweeta Group, all indices yield trends appropriate to the respective weathering index, with relatively good correlation

coefficients considering the pronounced heterogeneity of the materials (Fig. 4a–d). The minimum correlation coefficient for the Coweeta Group data is approximately 0.366, with a corresponding  $p$ -value of 0.056 (89% significance level; Table 5). Higher correlation coefficients and lower  $p$ -values would be desirable. However, for heterogeneous weathering mantles, we are treating  $p$ -values less than 0.06 (88% significance level) as being statistically significant.

The only weathering index that yielded a respectable correlation coefficient and appropriate trend for saprolite developed on the Otto Formation was the WIP ( $R^2=0.716$ ,  $p \leq 0.004$ ; Fig. 4e, Table 5). Although the WIP may not be applicable to highly leached sedentary ferricretes and bauxites because it includes only the mobile alkali and alkaline earth metals in its formulation, it does appear to work well with the CHL saprolite, despite the high level of parent rock heterogeneity. The R yielded an inappropriate trend with a correlation coefficient of 0.001 at a 6% significance level for Otto Formation bedrock and saprolite (Table 5). Similarly, the correlation statistics for the STI in the Otto Formation are very poor ( $R^2=0.002$  and  $p \leq 0.463$ ; Table 5). The Ruxton Ratio and Silica–Titania Index were therefore deemed unsuitable for application to heterogeneous

Table 5  
Summary of correlation statistics for weathering progress diagrams of Fig. 4

|     | Coweeta Group |                |                 |                        | Otto Formation |                |                 |                        |
|-----|---------------|----------------|-----------------|------------------------|----------------|----------------|-----------------|------------------------|
|     | $R^2$         | <i>t</i> -test | <i>p</i> -value | Significance level (%) | $R^2$          | <i>t</i> -test | <i>p</i> -value | Significance level (%) |
| R   | 0.787         | 4.714          | 0.002           | 100                    | 0.001          | 0.085          | 0.468           | 6                      |
| V   | 0.368         | 1.869          | 0.055           | 89                     | 0.028          | 0.415          | 0.346           | 31                     |
| WIP | 0.366         | 1.861          | 0.056           | 89                     | 0.716          | 3.889          | 0.004           | 99                     |
| CIW | 0.442         | 2.182          | 0.036           | 93                     | 0.059          | 0.614          | 0.281           | 44                     |
| CIA | 0.445         | 2.194          | 0.035           | 93                     | 0.160          | 1.069          | 0.163           | 67                     |
| PIA | 0.457         | 2.246          | 0.033           | 93                     | 0.071          | 0.677          | 0.262           | 48                     |
| STI | 0.842         | 5.646          | 0.001           | 100                    | 0.002          | 0.098          | 0.463           |                        |

weathering profiles and were not used in subsequent tests. A substantial decrease in correlation statistics were also noted for the V, CIW, CIA and PIA (especially for V; Table 5). Despite the poor statistical significance, these four weathering indices were retained for further analysis, but with the caveat that they only marginally represent the progress of weathering in heterogeneous saprolite. Of these four indices, the CIA yields the best correlation statistics ( $R^2=0.160$  and  $p \leq 0.163$ ; Table 5).

A second test applied to the data set was to plot each of the remaining weathering indices (WIP, V, CIW, CIA and PIA) against depth (Table 6 and Fig. 5a–c), using the bulk chemistry data from the water well (Otto Formation, Shope Fork Fault and Coweeta Group; Ciampone, 1995). For this test, the mole proportions of each oxide were used, rather than the volumetric concentration used in the weathering progress diagrams shown in Fig. 4a–e. All five of the remaining weathering indices yield appropriate up-profile trends. The WIP displays a sharp rise at approximately 10 m depth, however, the elevated value of this saprolite sample is still below the lowest value of the parent bedrock (Table 7). The elevated WIP value at approximately 10 m depth reflects a relative increase in  $K_2O$  for that sample (Fig. 2, Table 3), but without a corresponding increase in mica or feldspar abundance (Ciampone, 1995). Because the saprolite WIP values do not overlap those for the bedrock, they are best interpreted as the result of weathering. For the V, CIW, CIA and PIA, there are some saprolite samples that have index values lower than some of the values for the fresh bedrock (Fig. 5b,c), but they still display appropriate trends (that is, increasing up-profile).

Such variability is most pronounced for the CIW, CIA and PIA (Fig. 5c).

The variability in CIW, CIA and PIA values for the water well samples is noteworthy. The highest values for these indices below the base of the saprolite (which is approximately the weathering front in these heterogeneous materials) occur at approximately 34 m depth. This is near the depth at which potassium and rubidium concentrations decrease (Fig. 2). This phenomena may be attributed to the proximity of the Shope Fork Fault (which

Table 6  
Weathering indices for the water well samples (Otto Formation, Shope Fork Fault and Coweeta Group)

| Well sample  | WIP  | V   | CIW  | CIA  | PIA  |
|--------------|------|-----|------|------|------|
| COWW 0–10    | 17.0 | 5.9 | 98.1 | 90.4 | 97.9 |
| COWW 10–20   | 23.6 | 2.3 | 85.9 | 80.0 | 84.8 |
| COWW 20–30   | 45.8 | 2.9 | 90.2 | 76.6 | 88.1 |
| COWW 30–40   | 28.0 | 2.7 | 86.7 | 77.1 | 84.8 |
| COWW 40–50   | 34.0 | 1.2 | 70.9 | 66.5 | 68.8 |
| COWW 50–60   | 43.7 | 1.5 | 68.2 | 61.1 | 64.0 |
| COWW 60–70   | 57.6 | 1.6 | 70.4 | 60.6 | 64.7 |
| COWW 70–80   | 47.4 | 1.5 | 68.2 | 60.4 | 63.5 |
| COWW 80–90   | 55.9 | 1.5 | 70.2 | 62.5 | 66.0 |
| COWW 90–100  | 57.4 | 1.6 | 73.1 | 64.4 | 68.9 |
| COWW 100–110 | 59.4 | 1.6 | 77.3 | 68.1 | 73.8 |
| COWW 110–120 | 58.7 | 1.4 | 72.6 | 65.6 | 69.3 |
| COWW 120–130 | 57.7 | 1.2 | 62.6 | 58.8 | 60.1 |
| COWW 130–140 | 54.2 | 1.1 | 62.8 | 59.3 | 60.5 |
| COWW 140–150 | 51.0 | 1.4 | 71.1 | 65.2 | 68.2 |
| COWW 150–160 | 51.5 | 1.2 | 66.1 | 61.8 | 63.6 |
| COWW 160–170 | 48.5 | 1.6 | 74.3 | 66.5 | 70.9 |
| COWW 170–180 | 53.5 | 1.3 | 68.4 | 62.7 | 65.2 |
| COWW 180–190 | 51.7 | 1.3 | 69.2 | 63.2 | 66.0 |
| COWW 190–200 | 51.8 | 1.3 | 67.3 | 61.0 | 63.5 |

Weathering indices were calculated using oxides in molecular proportions.

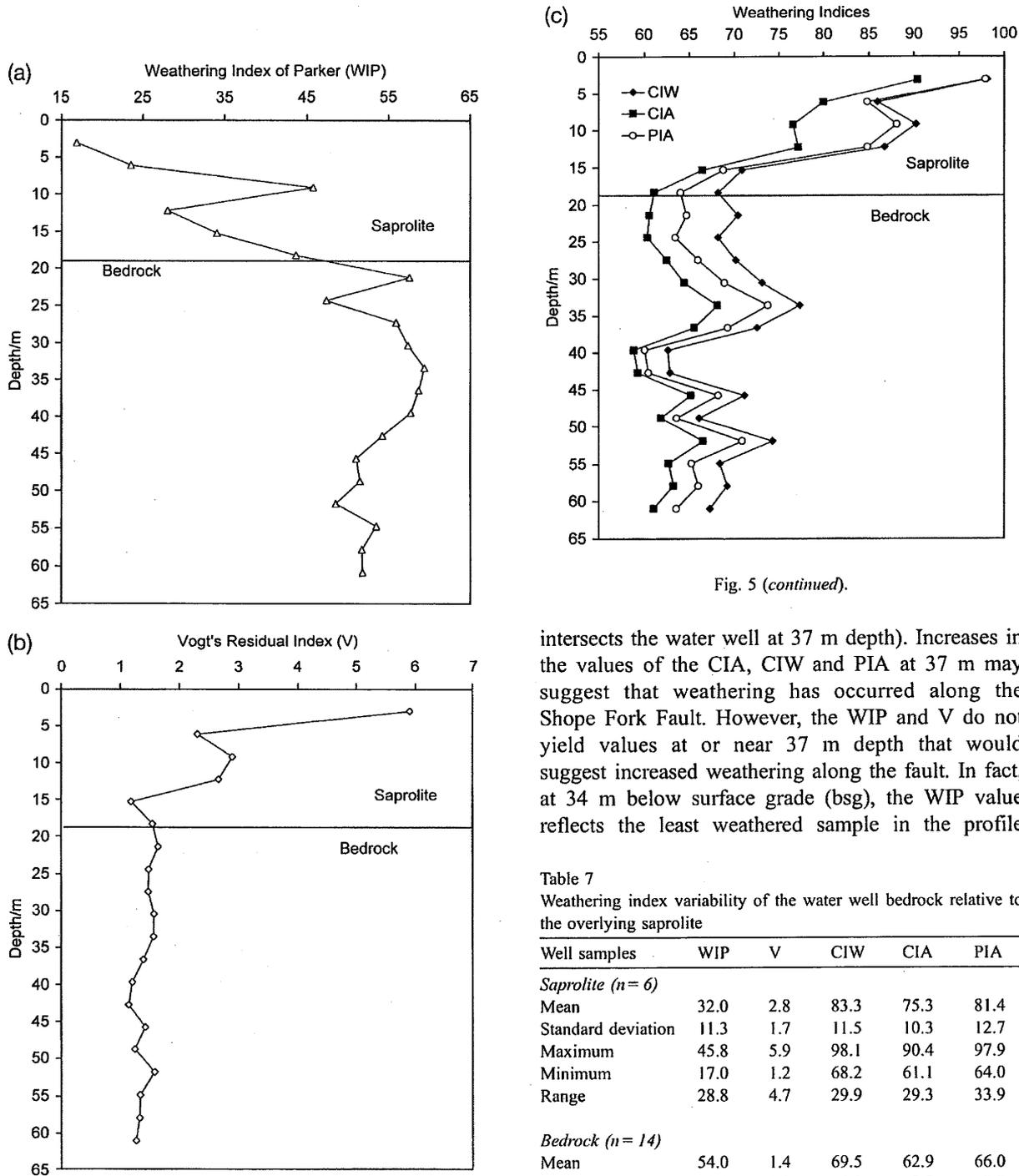


Fig. 5. Weathering indices for vertical profiles in the water well. (a) Weathering Index of Parker; (b) Vogt's Residual Index; and (c) Chemical Index of Weathering, Chemical Index of Alteration and Plagioclase Index of Alteration.

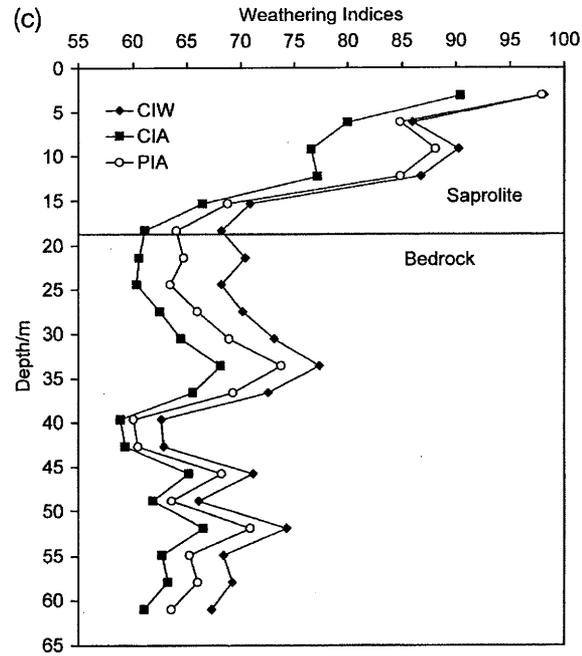


Fig. 5 (continued).

intersects the water well at 37 m depth). Increases in the values of the CIA, CIW and PIA at 37 m may suggest that weathering has occurred along the Shope Fork Fault. However, the WIP and V do not yield values at or near 37 m depth that would suggest increased weathering along the fault. In fact, at 34 m below surface grade (bsg), the WIP value reflects the least weathered sample in the profile

Table 7  
Weathering index variability of the water well bedrock relative to the overlying saprolite

| Well samples             | WIP   | V     | CIW   | CIA   | PIA   |
|--------------------------|-------|-------|-------|-------|-------|
| <i>Saprolite (n = 6)</i> |       |       |       |       |       |
| Mean                     | 32.0  | 2.8   | 83.3  | 75.3  | 81.4  |
| Standard deviation       | 11.3  | 1.7   | 11.5  | 10.3  | 12.7  |
| Maximum                  | 45.8  | 5.9   | 98.1  | 90.4  | 97.9  |
| Minimum                  | 17.0  | 1.2   | 68.2  | 61.1  | 64.0  |
| Range                    | 28.8  | 4.7   | 29.9  | 29.3  | 33.9  |
| <i>Bedrock (n = 14)</i>  |       |       |       |       |       |
| Mean                     | 54.0  | 1.4   | 69.5  | 62.9  | 66.0  |
| Standard deviation       | 3.8   | 0.2   | 4.1   | 2.8   | 3.9   |
| Maximum                  | 59.4  | 1.6   | 77.3  | 68.1  | 73.8  |
| Minimum                  | 47.4  | 1.1   | 62.6  | 58.8  | 60.1  |
| Range                    | 12.0  | 0.5   | 14.7  | 9.3   | 13.7  |
| t-test (p-values)        | 0.004 | 0.106 | 0.032 | 0.032 | 0.030 |

(Fig. 5a) and V displays negligible variation (Fig. 5b). Therefore, evidence for alteration of any kind, weathering or high temperature alteration along the Shope Fork Fault is equivocal. Thus, high values of the CIW, CIA and PIA may not always reflect weathering, and these weathering indices are sensitive to changes in bulk chemistry that may be associated with hydrothermal alteration or mylonitization during metamorphism.

Ciamponi (1995) reported that the water table in the well is located at approximately 52 m bsg. There is a noticeable change in all weathering indices at this depth (Fig. 5); the change suggests an increase in weathering. This change is much more pronounced for the CIW, CIA and PIA (Fig. 5c), demonstrating the sensitivity of these indices to factors that are not necessarily directly associated with weathering.

According to the criteria reviewed above, an index should provide appropriate trends and vary greatly with increasing weathering, despite parent rock heterogeneity. Table 7 provides a statistical comparison of the five weathering indices plotted in Fig. 5a–c. All of the weathering indices yield larger standard deviations for the saprolite relative to the bedrock (Table 7), and all of the indices provide appropriate trends (Fig. 5). In addition, the *p*-values for a *t*-test based on the saprolite and bedrock weathering indices reveals that for each weathering index, the saprolite values are statistically distinct from the bedrock (at 88% significance; Table 7).

## 6. Discussion

The objective of this study was to evaluate weathering indices with respect to their potential application to saprolite developed on heterogeneous felsic metamorphic parent materials. It is clear that no single weathering index meets all of the criteria outlined in Section 2 above, and no weathering index would give unequivocal results when applied to such weathering environments. The “best-fit” weathering index might be determined by prioritizing the criteria and evaluating each model in this light. The results of this study are summarized in Table 8.

The Ruxton Ratio failed the first test of yielding appropriate trends using isovolumetric techniques and was eliminated early on from further consideration.

Table 8  
Summary of weathering indices evaluated in this study

| Index | Easy to use (1) | Elements with a range of mobility (2) | Appropriate trends (3) | Different rock types (4) | Allows Al mobility (5) |
|-------|-----------------|---------------------------------------|------------------------|--------------------------|------------------------|
| R     | Yes             | Yes                                   | No                     | Unknown                  | No                     |
| WIP   | Yes             | No?                                   | Yes                    | Yes                      | Yes                    |
| V     | Yes             | Yes                                   | ?                      | Yes                      | No                     |
| CIA   | Yes             | Yes                                   | Yes                    | ?                        | No                     |
| CIW   | Yes             | Yes                                   | ?                      | ?                        | No                     |
| PIA   | Yes             | Yes                                   | ?                      | ?                        | No                     |
| STI   | Yes             | Yes                                   | ?                      | Unknown                  | No                     |

A “?” indicates marginal to poor performance.

The Weathering Index of Parker, however, provides both appropriate trends and statistically meaningful correlation coefficients (at an 88% significance level) for the bedrock lithologies of this study (Fig. 4b,e). In fact, the WIP satisfies all of the criteria established for a weathering index, except that it uses only highly mobile alkali and alkaline earth metals (sodium, potassium, magnesium and calcium; Table 8, column 3) in its formulation (e.g., Harnois, 1988). Alkali and alkaline earth metals may be lost during the early stages of weathering (Eswaran et al., 1973), and the WIP, therefore, may not be useful if applied to weathering profiles more strongly leached than those at Coweeta. The WIP would be zero for sedentary ferricretes and bauxites, but, as long as any of the alkali and alkaline earth metals were present in the weathering residuum, the WIP will yield a value greater than zero. Thus, despite using only alkali and alkaline earth metals, the WIP may be the weathering index most amenable to use in the study of weathered regoliths developed on heterogeneous parent rocks.

Vogt’s Residual Index yielded statistically insignificant correlation coefficients on weathering progress diagrams for saprolite developed on the Otto Formation (Table 5), but does provide a nearly ideal up-profile trend (Fig. 5b). It also relies on the assumption that aluminum is immobile during weathering, which is known to not be the case at CHL (Fig. 3). Therefore, the V should be used with caution when applied to heterogeneous weathered regoliths.

The CIW, CIA and PIA all display similar behavior for the saprolite and bedrock of this study. However, when Otto Formation data are plotted on weathering

progress diagrams, the correlation coefficients relating bulk density to extent of weathering are not statistically significant (Table 5). The same pattern among these three weathering indices was also noted for the up-profile trends of the water well (Fig. 5c). The substantial variability noted for the CIW, CIA and PIA in the bedrock appears to reflect their sensitivity to fault-related alteration that is not detected by the WIP and V. Some of the variability in CIW, CIA and PIA is also attributable to the presence of the water table at approximately 52 m bsg (Fig. 5c).

The WIP appears to be best suited for weathering profiles developed on heterogeneous parent rocks, but caution should be exercised for deeply weathered profiles, as alkali and alkaline earth metals may be readily depleted yielding a WIP of zero well before the regolith weathers to the extent of forming bauxite or sedentary ferricrete. If, for this reason, the WIP were deemed unsuitable for characterizing a weathering profile, then the V or CIA could be used, but only with extreme caution. The CIW, CIA and PIA are susceptible to subtle geochemical changes that may occur along tectonic structures (e.g., hydrothermal alteration along a fault) and at the water table, and are not necessarily directly or exclusively related to weathering. The success of the WIP may be due in part to the fact that it does not assume aluminum to be immobile (e.g., Chittleborough, 1991).

Interestingly, Duzgoren-Aydin et al. (2002) report similar results for weathering indices when compared to the weathering grade (an engineering metric determined from petrographic observations) of a regolith developed on felsic pyroclastic rocks in Hong Kong. When compared with weathering grade, the WIP and CIA correlated well, but the R and CIW correlated very poorly.

Geologically inappropriate trends and/or lack of statistical significance of correlation coefficients on weathering progress diagrams are the result of situations in which variations in the chemical content of weathering mantles due to chemical weathering do not exceed variation in the parent rock. The bedrock in the study area is metasedimentary; the sedimentary protoliths acquired a weathering signature prior to metamorphism. Therefore, a suitable weathering index must distinguish geochemical changes that occur during modern weathering, and changes of sufficient magnitude to overprint the pre-metamorphic sedimen-

tary weathering signature. For example, R is an inappropriate weathering index for saprolite developed on the Otto Formation, because the range and variability of concentrations of aluminum and silica are very similar in the bedrock and weathering residuum, and R is defined in terms of the concentrations of these elements. In this case, the changes resulting from chemical weathering do not overprint the pre-weathering chemistry of the bedrock as measured by these elements.

Weathering indices that use elements that are most mobile during weathering (i.e., alkali and alkaline earth elements) are most effective in quantifying the effects of chemical weathering relative to the unweathered bedrock and are best suited for application to heterogeneous weathering residua. The WIP is based on mobile elements and gives the "best fit" for the heterogeneous weathering mantles at Coweeta. Other indices assume some element immobility and are less useful (Table 8). This conclusion raises questions about the validity of criterion (2) above (and column 3 in Table 8), that a weathering index should incorporate elements with a range of mobility in the weathering environment (Harnois, 1988). The results from Coweeta indicate that the choice of an appropriate weathering index requires prior characterization of the bedrock and regolith.

A second factor that contributes to the success of the WIP in characterizing the weathering profiles of this study is that it allows aluminum to be mobile. The other weathering indices assume aluminum to be immobile and are not as useful in characterizing the Coweeta weathering profiles (Table 8).

As noted earlier, the WIP may not be applicable to highly leached weathering mantles, such as sedentary ferricretes or bauxites. However, ferricretes and bauxites represent very extreme cases of weathering, usually constituting only the upper-most horizons of a saprolitic weathering profile. Under such circumstances, the WIP would be suitable for the portions of the regolith that reside below the bauxite or ferricrete, with the bauxite or ferricrete yielding values of zero (still a useful value). If any alkali or alkaline earth element impurities exist within the ferricrete or bauxite (e.g., clays or micas), a bauxite or ferricrete may also yield WIP values greater than zero. In a ferricrete, none of the weathering indices evaluated would be of value, unless aluminum residua were present in the ferricrete.

## 7. Summary and conclusions

The fundamental challenge when addressing the chemical weathering of heterogeneous metamorphic rocks is to correlate a weathered sample with an unweathered bedrock precursor. Bulk density, at least in some instances, may be homogeneous among unweathered materials, regardless of bulk chemistry. However, methods that address the geochemistry of heterogeneous rock weathering are still lacking. The development of tools suitable for application to the study metamorphic silicate rock weathering is important, as heterogeneous felsic metamorphic rocks are ubiquitous in orogenic belts where chemical weathering is intense, and the consumption of atmospheric CO<sub>2</sub> high (e.g., Berner and Berner, 1997; Edmond and Huh, 1997). This study is a contribution to this effort. Our results indicate that the Weathering Index of Parker is the most appropriate index of alteration for application to felsic heterogeneous weathered regoliths. The V could also be used for a regolith leached of all alkali and alkaline earth metals, but may not yield as appropriate results as the WIP because it assumes aluminum to be immobile. Application of the CIW, CIA or PIA to heterogeneous profiles should only be done so with extreme caution, because they, too, assume aluminum immobility. The CIA may yield informative results, because it not only includes potassium in its formulation, but also combines potassium with the other alkali and alkaline earth elements. The Ruxton Ratio should not be applied to heterogeneous weathering materials. The success of the WIP may be due in part to its allowance for aluminum mobility (in contrast to other indices) (e.g., Chittleborough, 1991), and also because its formulation includes only alkali and alkaline earth metals. Due to their mobility during chemical weathering, alkali and alkaline earth elements are capable of undergoing large changes, and, hence, yielding greater compositional variations relative to the unweathered bedrock than other elements.

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