Major and trace elements distribution in a weathering profile of a granite gneiss at higher altitudes

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The major and trace element geochemistry of a weathering profile from Ranikhet granite gneiss, NW Lesser Himalaya suggests that except for K, other major elements are leached during incipient and intensive stages of weathering, while Al and Fe along with Nb and Se remained immobile even in extreme stages of weathering. Primary mineral degradation and release of ions to solutions aided by fracture pattern and gneissose structure are the main factors that governed the alteration of the weathering profile. The study reveals that mechanical weathering dominates over chemical weathering, which resulted in the formation of thin soil cover in the region.

Keywords: Granite gneiss, major and trace elements, weathering, geochemistry.

Many workers to examine various aspects have investigated the Himalayas extensively, but studies related to weathering intensity are lacking in this region. Weathering is an important natural process which modifies the earth’s surface and studies on weathering of different rock types are numerous in the literature. In this communication, geochemistry is used in an attempt to understand changes in the major and trace element compositions of the weathering profile developed on a granite gneiss in and around Ranikhet, Uttarakhand, NW Lesser Himalaya. The Pan-African age Ranikhet granite gneiss, pertains to Almora nappe, Kumaun Lesser Himalaya and intrudes into the medium-grade metasedimentary rocks that are made up of medium to coarse-grained garnetiferous-micaschists and phyllites interbedded with quartzites. Earlier investigations have revealed that two types of granites are present in the area; older (500 Ma) metamorphosed granite (augen) gneiss followed by younger (Tertiary?), weakly to non-foliated porphyritic granite. The augen gneisses form a larger part of the area and some good outcrops are available along and across the main mall road that connects Ranikhet with Chaubatia apple gardens. Petrographic studies show that the gneisses are medium to coarse-grained, in which mainly K-feldspar (some times pheithic) is phenocrystic in the groundmass of biotite, muscovite, plagioclase (mostly sodic; An$_3$–An$_9$) and quartz. The Ranikhet granite gneiss is located at an elevation of ~6000 ft (from msl) and receives low to moderate (~75 cm) annual rainfall, with temperatures ranging from 3°C to 22°C, representing subtropical humid climate.

A 4 m Ranikhet weathering profile is traversed by a network of fractures (Figure 1). The top portion is extensively weathered; however, with increasing depth, the gneiss has retained its original texture, except along fractures where it is powdered. Representative samples have been collected from the profile and were analysed for major element concentrations by XRF at the Wadia Institute of Himalayan Geology, Dehradun and trace elements by ICP-MS at the National Geophysical Research Institute, Hyderabad. The geochemical data are presented in Table 1. The analytical errors are well within the permissible limits (i.e. 5–10% for trace elements and ~5% for major oxides). Since the entire discussion is based on the nature of the samples, a detailed sample description is essential before the data are adequately interpreted. Samples are divided into three categories; I – least weathered, fresh (parent) rock (sample # C); II – incipient weathered saprolite, wherein original textures of protolith are not destroyed as a result of alteration (sample # A2); III – more altered saprock samples (sample # A1, A3, A4, A5) collected from various fracture zones. One sample each from categories I and II was collected because of their uniform textures. Among four samples of category III, a consistent prograde alteration effect was seen according to varying depths. Sample A1 which was collected near the surface below the organic-rich zone (50 cm from the top) and the sample lying at a depth of ~4 m (A5, just above the bedrock) show similar alteration effects. Whereas sample # A4, which occurs above A5 at a depth of ~3 m, is intensely altered when compared to the other three samples. This may lead to the conclusion that the water–rock interaction rate is not uniform even along the fractures and it probably depends on the fracture slopes also.

The degree of alteration of the samples can well be evaluated using chemical index of alteration (CIA), introduced by Nesbitt and Young. The CIA is calculated as:

\[
\text{CIA} = \frac{\text{Al}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{CaO}^* + \text{Na}_2\text{O} + \text{K}_2\text{O})} \times 100,
\]

where CaO* is the concentration of Ca in silicates only. Accordingly, CIA of the Ranikhet samples (Table 1) shows that the unaltered bedrock has CIA value 62 followed by saprolite with 66 and saprock samples from 72 to 75. This in turn implies that samples from saprock (fracture zones), as predicted, are intensely altered relative to saprolite and bedrock. The weathering intensity of any rock can also be depicted from A-CN-K diagram of Nesbitt and Young. The background information of this diagram is that during initial stages of weathering, Na and Ca are removed from the earlier dissolved plagioclase and those samples which have undergone weak weathering will plot close to the A-CN line. Whereas advanced weathering results in the dissolution of K-feldspar to re-
Figure 1. (Left) Geological map of the Ranikhet area (modified after Merh and Vashi\textsuperscript{15}). (Right) Photograph of weathering profile showing sample locations. The unweathered ‘C’ horizon occurs below the road.

Table 1. Major and trace element concentrations and mass-balance calculations of Ranikhet granite gneiss

<table>
<thead>
<tr>
<th></th>
<th>A-1 (Saprock)</th>
<th>A-2 (Sap)</th>
<th>A-3 (Saprock)</th>
<th>A-4 (Saprock)</th>
<th>A-5 (Saprock)</th>
<th>C (Parent rock)</th>
<th>Standard\textsuperscript{15}</th>
<th>C→A1</th>
<th>C→A2</th>
<th>C→A3</th>
<th>C→A4</th>
<th>C→A5</th>
<th>(Mass-balance calculations following Gresens\textsuperscript{15})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO\textsubscript{2}</td>
<td>61.73</td>
<td>67.04</td>
<td>61.35</td>
<td>61.73</td>
<td>60.84</td>
<td>67.97</td>
<td>72.57</td>
<td>-3.87</td>
<td>-0.63</td>
<td>-4.19</td>
<td>-4.34</td>
<td>-4.61</td>
<td>(Lost in the fluid)</td>
</tr>
<tr>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>21.64</td>
<td>18.75</td>
<td>21.60</td>
<td>22.64</td>
<td>22.14</td>
<td>18.03</td>
<td>13.65</td>
<td>4.44</td>
<td>0.80</td>
<td>4.43</td>
<td>5.31</td>
<td>5.03</td>
<td>(Always enriched)</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3}</td>
<td>3.53</td>
<td>2.91</td>
<td>3.54</td>
<td>3.20</td>
<td>3.44</td>
<td>2.57</td>
<td>2.13</td>
<td>1.10</td>
<td>0.35</td>
<td>1.11</td>
<td>0.73</td>
<td>1.01</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.96</td>
<td>0.78</td>
<td>0.94</td>
<td>0.81</td>
<td>0.99</td>
<td>0.65</td>
<td>0.75</td>
<td>0.35</td>
<td>0.13</td>
<td>0.33</td>
<td>0.18</td>
<td>0.38</td>
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<tr>
<td>CaO</td>
<td>0.41</td>
<td>0.45</td>
<td>0.44</td>
<td>0.40</td>
<td>0.31</td>
<td>0.72</td>
<td>2.11</td>
<td>-0.29</td>
<td>-0.27</td>
<td>-0.26</td>
<td>-0.31</td>
<td>-0.40</td>
<td></td>
</tr>
<tr>
<td>Na\textsubscript{2}O</td>
<td>1.00</td>
<td>1.77</td>
<td>1.06</td>
<td>0.71</td>
<td>1.00</td>
<td>2.40</td>
<td>3.36</td>
<td>-1.36</td>
<td>-0.62</td>
<td>-1.30</td>
<td>-1.67</td>
<td>-1.36</td>
<td></td>
</tr>
<tr>
<td>K\textsubscript{2}O</td>
<td>5.00</td>
<td>5.48</td>
<td>5.31</td>
<td>5.38</td>
<td>5.30</td>
<td>5.34</td>
<td>4.02</td>
<td>-0.15</td>
<td>0.16</td>
<td>0.18</td>
<td>0.21</td>
<td>0.18</td>
<td>(Nearly conserved)</td>
</tr>
<tr>
<td>TiO\textsubscript{2}</td>
<td>0.46</td>
<td>0.36</td>
<td>0.44</td>
<td>0.38</td>
<td>0.44</td>
<td>0.31</td>
<td>0.26</td>
<td>0.17</td>
<td>0.05</td>
<td>0.15</td>
<td>0.08</td>
<td>0.15</td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.03</td>
<td>0.03</td>
<td>0.04</td>
<td>0.06</td>
<td>-0.01</td>
<td>-0.01</td>
<td>0.00</td>
<td>-0.01</td>
<td>-0.01</td>
<td></td>
</tr>
<tr>
<td>P\textsubscript{2}O\textsubscript{5}</td>
<td>0.02</td>
<td>0.08</td>
<td>0.06</td>
<td>0.05</td>
<td>0.05</td>
<td>0.18</td>
<td>0.11</td>
<td>-0.16</td>
<td>-0.10</td>
<td>-0.12</td>
<td>-0.13</td>
<td>-0.13</td>
<td></td>
</tr>
<tr>
<td>LOI – H\textsubscript{2}O</td>
<td>4.89</td>
<td>3.98</td>
<td>3.52</td>
<td>4.18</td>
<td>4.32</td>
<td>1.49</td>
<td>3.59</td>
<td>2.51</td>
<td>2.17</td>
<td>2.82</td>
<td>3.01</td>
<td>(Water added in the process)</td>
<td></td>
</tr>
</tbody>
</table>

Sum | 99.67 | 101.63 | 98.30 | 99.51 | 98.86 | 99.70 | 99.02 | 1.42 | 1.23 | 0.95 | 0.67 | 1.06 | |

Trace elements (in ppm) | Se | 4 | 4 | 4 | 4 | 4 | 3 | 3 | 2 | 1.42 | 1.23 | 0.95 | 0.67 | 1.06 | |
|                | Nb | 17 | 14 | 19 | 14 | 17 | 16 | 15 | 1.47 | -1.93 | 3.02 | -2.12 | 1.15 | |
|                | Sr | 52 | 67 | 52 | 52 | 52 | 53 | 59 | -4.20 | 8.68 | -4.38 | -4.97 | -3.22 | |
|                | Cs | 20 | 19 | 24 | 20 | 20 | 25 | 8 | -3.79 | -6.03 | -0.10 | -4.06 | -3.88 | |
|                | Ba | 325 | 431 | 318 | 405 | 378 | 318 | 67 | 19.15 | 114.49 | 11.84 | 99.47 | 75.63 | |
|                | Na-K | 0.20 | 0.32 | 0.20 | 0.13 | 0.19 | 0.45 | 0.45 | |
|                | CIA | 73 | 66 | 72 | 75 | 74 | 62 | 62 | |

Density (g/cm\textsuperscript{3}) | 2.46 | 2.38 | 2.47 | 2.45 | 2.47 | 2.37 | 2.37 | |

Density calculated following the empirical method after Bottina and Well\textsuperscript{15}; Isovolumetric, i.e. Fv = 1; i.e. no volume change during transformation of fresh granite to weathered granite. Negative value = loss; Positive value = gain; * Analyzed standard values for major elements JG-1A (by Wadia Institute) and for trace elements JG-2 (by NGRI) were used.
lease K in preference to Al, so that the bulk composition trends of the residues are redirected to the $\text{Al}_2\text{O}_3$ apex. Ranikhet samples in the A–CN–K diagram (Figure 2) clearly reveal that samples from categories I and II, which are less weathered, show a trend which is sub-parallel to the A–CN join, indicating that Ca + Na are removed from the protolith relative to K during the initial stages of weathering. Whereas the trend shown by category III samples, which are sub-parallel to the A–K join, suggests the breakdown of plagioclase during the initial stages followed by the alteration of K-feldspar to release K in preference to Al, during the intense alteration stage, thus turning the trend toward the $\text{Al}_2\text{O}_3$ apex.

The geochemical data show that silica decreases with increasing intensity of alteration. $\text{Al}_2\text{O}_3$ content of the samples increases from 18% (bedrock) to 23% (most altered sample), suggesting that Al has been added (or residual enrichment). This in turn indicates that other constituents have been removed by leaching relative to Al. Similarly, slight enrichment in Fe is also noticed (from 2.57% to 3.44%) in the intensely altered samples, thus substantiﬁing the inference that Al and Fe are the more stable elements and their abundances remained largely unaffected during surface weathering processes. K is almost conserved throughout the profile. To verify this, mass-balance calculations were done and they conformed the interpretation that concentration of K is neither lost nor gained during weathering process (Table I). This may probably suggest that K-feldspar, a chief source of K, seems to have been either more resistant than the other minerals (particularly plagioclase) or, $K^+$, which might have been released during the later stages of weathering, being a larger cation might have partly fixed on clay minerals. Further, the striking decrease in Na/K ratios (0.45–0.13) of the samples during the initial weathering stages may have resulted primarily from the greater alteration rate of plagioclase compared to that of K-feldspar. This observation is in conformity with other studies which have recognized that plagioclase alters faster (~three times) than K-feldspar. Low concentration of Ca and relatively high percentage of Na support the fact that the plagioclase in Ranikhet gneisses is albite in nature and therefore, the Ca% in samples may correspond to some other accessory mineral, probably apatite. The decreasing trend exhibited by P in samples from bedrock to saprock may reflect the rapid weathering of apatite in the profile, because apatite has been considered to be unstable during weathering. Consistent increase in the concentration of Mg from bedrock to intensely weathered sample (0.65–0.99%) suggests that Mg, which might have been released from the breakdown of biotite, did not go off with solutions but adhered to secondary clay product (illite). Clay mineral studies have shown that Mg is preferentially incorporated in octahedral sites of illite. A comprehensive picture regarding the distribution of major elements in the entire profile can be seen more prominently in the fresh rock-normalized spider diagram (Figure 3). In this diagram, when compared to fresh (bed) rock, significant depletion in $\text{CaO}$, $\text{Na}_2\text{O}$ and $\text{P}_2\text{O}_5$ contents with a prominent $\text{P}_2\text{O}_5$ anomaly is evident. As discussed earlier, continuous depletion of P from incipient stages of weathering to intensive stage is noticeable and this may be attributed to the rapid alteration of apatite. The concentrations of other elements are conserved and show consistent patterns with negligible variations when compared to the parent rock.

The concentrations of trace elements corroborate the conclusions drawn from the major elements. The distribution of Rb appears to be almost constant throughout the profile, with little variation (relative depletion by ~12%) from fresh rock to most weathered residue. K-feldspar

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**Figure 2.** A–CN–K diagram for the weathering profile developed on Ranikhet granite gneiss. Two clear trends are visible in the diagram (see text for explanation). Plg, plagioclase; K-sp, K-feldspar; Ka, Kaolinite; Gi, Gibbsite; Sm, Smeectite; Mus, muscovite.

**Figure 3.** Fresh rock-normalized spider diagram of the Ranikhet weathering profile.
contains more Rb than biotite and the later mineral is readily weathered compared to K-feldspar. Alteration of biotite and subsequent exchange of Rb with clay minerals (vermiculite, alteration product of biotite) may explain the uniformity of this element in the profile. When compared to the parent rock, a considerable reduction in Cs concentration is noticed in saprolite (from 25 to 19 ppm). It shows almost matching values in the intense weathered sample (from 25 to 24 ppm). This noticeable variation suggests that the concentration of Cs has been affected chiefly by the breakdown of biotite that resulted in the reduction of values during early stages of weathering. However, the relatively higher contents of Cs in more intensely weathered saprock above indicate that the released Cs might have retained onto the clay minerals. Ba abundances increase by about 35% in the most weathered samples, which in turn suggests the retention of Ba even after the breakdown of Ba-bearing minerals such as biotite, plagioclase and K-feldspar. Sr also displays decreasing trend from fresh to intensely weathered samples and is consistent with the rapid alteration of plagioclase. Negligible variation in the concentration of Nb and Sc reveals that they are rather immobile during weathering. This observation is in accord with the predicted mobilities of these elements.

Extensive studies on continental weathering processes by many workers have shown that the process is mainly an acid-base reaction, where an acid is neutralized by a solid base to produce secondary minerals and dissolved salts, as illustrated in the following equation:

\[ 2\text{KAlSi}_3\text{O}_8 + \text{H}_2\text{CO}_3 + n\text{H}_2\text{O} \rightarrow \text{K}_2\text{CO}_3 + \text{Al}_2(\text{OH})_3\text{Si}_4\text{O}_{10} + n\text{H}_2\text{O} + 2\text{SiO}_2 \]

The detailed examination of the distribution of elements in the weathering profile of Ranikhet gneisses has led to the conclusion that the main weathering mechanism has been the alteration of primary minerals such as plagioclase, biotite and K-feldspar, etc., according to their susceptibility rates in the presence of acids (or low pH waters) to release constituent cations. The released cations are carried to fractures by migrating waters, where they interact with clay minerals causing increase in pH conditions and result in the exchange of leached cations onto the clays. This causes the removal of small cations (e.g. Na, Ca, Sr) by surface run-off, whereas the larger cations (e.g. Rb, Ba) are cycled between the soil and weathering zones. In addition, gneissosity also appears to have played a vital role in the weathering of Ranikhet gneisses. The gneisses are characterized by feldspar augens that are wrapped around by mica (mostly biotite). When the solutions (or acid waters) percolate through gneissose (weak) planes, obviously biotite will be attacked more rigorously than feldspar. This is what happened in the area, which is evident in the field also, where most of the feldspar is intact, while biotite has been intensely altered. This may be one of the explanations that validate the distribution of K, which is found almost unchanged throughout the profile.

From the above discussion, it can be inferred that apart from the parent rock mineralogy, fracture pattern and gneissose structure are the main controlling factors that influenced the weathering and alteration in the area. Another conclusion that needs attention is the despite having all favourable conditions for chemical weathering such as moderate climate which is supported by a good drainage system (or good moisture content), mechanical weathering is more dominant in the area. This is well depicted in CIA values of the profile where least weathered fresh rock and saprolite, which form a major part of the profile, show values 62 and 66 respectively, again suggesting low chemical weathering. One of the reasons that appears to be valid for the predominance of mechanical weathering over chemical weathering is a steep slope in the area, because slope influences the rate of run-off.

Natural parasitization and biological control: case of the coconut caterpillar

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Successful biological control of insect pests often depends on reliable baseline information on natural mortality imposed by natural enemies. Generating such data requires painstaking long-term studies over considerable geographical area. We attempted to produce such data on the extent of natural pupal parasitization of \textit{Opisina arenosella} (Walker) a defoliating pest of coconut palms. Pupal parasitization in 31 discrete generations across different locations in South Karnataka, India, where coconut is widely cultivated and where \textit{Opisina} frequently causes serious losses, was quantified between 1999 and 2005. Each parasitoid species makes a characteristic exit hole on the host pupa, which was used to quantify the extent of parasitization. Results show that parasitoids emerged from 44% and moths from 41% of the pupae. Consistently, \textit{Meteoridea hutsoni} (Nixon) was the dominant parasitoid of the region followed by \textit{Brachymeria} spp. Together, they contributed to 90% of the pupal parasitization. There was a negative correlation between extent of parasitization by \textit{Meteoridea} and that of \textit{Brachymeria}, and between parasitization by \textit{Meteoridea} and emergence of \textit{Opisina} moths. Extent of parasitization by \textit{Brachymeria} does not appear to have significant influence on moth emergence in the study area. Although parasitization by the two parasitoids varied with respect to seasons, the overall parasitization percentage, interestingly, remained unaffected and hovered around 50% all through the year. Finally, we comment on some of the implications of the study on the current recommendations in biological control of \textit{Opisina}, and emphasize the need for long-term data on natural parasitization before arriving at ‘recommendations’ in biological control of insect pests.

Keywords: Biological control, discrete generations, natural parasitization, \textit{Opisina arenosella}, pupal parasitoids.

Data on natural mortality in a species, generated over considerable space and time, have wide applications that include pest management. In this communication we present such data for an important pest of coconut palm, \textit{Opisina arenosella} (Walker) (Lepidoptera: Oecophoridae), and suggest its implications for biological control. \textit{Opisina}, commonly called coconut black-headed caterpillar, is the most important defoliator pest of coconut palms in India\textsuperscript{1,2} and Sri Lanka\textsuperscript{3}. Among the few species of palms that serve as its host, coconut is the only one that is cultivated. Populations breed throughout the year in five discrete generations, each generation lasting 65–75 days\textsuperscript{4}. Biological control has been the much sought-after management practice against this pest; in as much that the State Department of Horticulture, Government of Karnataka has laboratories dedicated to mass multiplication and release of larval parasitoids of \textit{Opisina} (\textit{Goniozus nepanthidis} Muesbeck (Bethylidae: Hymenoptera) and \textit{Bracon brevicornis} Wesmeal (Braconidae: Hymenoptera)) in all the taluks where the pest is known to frequent. Perhaps one of the earliest organized attempts for biological control of an insect pest in India was the campaign against \textit{Opisina}. In 1923, the erstwhile Madras Government undertook methodical mass multiplication and field releases of several parasitoids when \textit{Opisina} reached alarming proportions in the Malabar and South Canara region\textsuperscript{5}. Among the 45 species of parasitoids reported so far, four cause mortality at the egg stage (egg parasitoids), ten at the larval stage (larval parasitoids) and 31 at the pupal stage (pupal parasitoids) of the pest\textsuperscript{5,6} (we have considered the host stage that is finally killed by the parasitoid to classify it as egg, larval or pupal parasitoid). Pupal parasitoids of \textit{Opisina} have been found to be the most diverse and the most abundant\textsuperscript{7–9}. In the present study, natural parasitization of pupae of \textit{Opisina} was re-