Rare earth elements in stream waters from the Rokko granite area, Japan: Effect of weathering degree of watershed rocks

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The concentrations of major elements and rare earth elements (REE) of the stream waters from the Rokko granite area, Japan, were analyzed to examine the relationship between the degree of weathering and chemistry of the waters. The clay minerals in the related soils from the watershed areas were also examined. It was found that the relative proportion of kaolinite to total clay minerals is a good measure for the degree of weathering of the area. The Ca concentrations of the stream waters are rather high in comparison with other cations such as Na, K and Mg, and are well correlated with HCO$_3^-$ . These facts indicate that the Ca concentrations in the stream waters are largely controlled by dissolution of calcite that occurs as disseminated crystals in granites. The Ca/Na molar ratio in the waters decreases with increasing kaolinite/clay ratio in the related soils. The high Ca waters tend to occur in the fresh or weakly weathered areas, which is attributed to abundant calcite in these granites. By contrast, in the strongly weathered areas, where calcite had already been consumed via previous weathering processes, low Ca waters occur. The REE abundances, especially light REE, of the stream waters tend to be high in the strongly weathered watershed areas, and low in the fresh or weakly weathered watershed areas. This is attributed to either enhanced REE leaching from rocks in strongly weathered watershed areas due to larger solid surface areas or increased weathering of accessory minerals such as apatite. Interestingly, the magnitude of negative Ce anomalies appears to be inversely related to the degree of weathering. We suggest that the magnitude of Ce anomalies in those waters is largely controlled by mechanical filtration of CeO$_2$ during infiltration in micro-cracks or pores rather than by Eh-pH conditions.

INTRODUCTION

Chemical weathering is a fundamental geological process. Because of the predominant occurrence of granitic rocks, our knowledge of the chemistry of granite-water interaction during weathering is important not only for water quality investigations of river waters but also for worldwide environmental problems concerning acidification of soils and greenhouse effect of CO$_2$ in climate changes (e.g., White and Blum, 1995; Gaillardet et al., 1999; Dessert et al., 2001; Millot et al., 2002). It should be noted that atmospheric CO$_2$ has been affected by weathering processes through CO$_2$-bearing reactions, and the disseminated calcite in granitic rocks has recently been invoked as an important CO$_2$-bearing component (White et al., 1999). Despite such importance, studies on the relationship between water chemistry and chemical weathering of watershed rocks has not progressed significantly since the pioneering investigation of Garrels (1967). Although there are several investigations on chemical weathering (e.g., Weijden and Weijden, 1995; Nesbitt and Markovics, 1997; Braun et al., 1998; Aubert et al., 2001), precise analyses of all of the materials involved in weathering processes such as fresh basement rocks, soils and waters are required for
comprehensive understanding of the weathering processes, and thus more studies are necessary.

Many investigations show that the rare earth elements (REE) provide useful information concerning the origin and genesis of various kinds of geological materials because of their unique chemical characteristics (e.g., Henderson, 1984; Bünzli and Choppin, 1989). In fact, there are many studies dealing with REE of river waters (e.g., Goldstein and Jacobsen, 1988; Négrel et al., 1993; Dupré et al., 1996; Viers et al., 1997; Roy et al., 1999; Ingri et al., 2000; Aubert et al., 2001; Shiller et al., 2001; Biddau et al., 2002). The REE abundances in the natural waters are controlled by many factors such as leaching, precipitation, colloidal transport, complexation, ion exchange, and adsorption-desorption. Moreover, leaching processes are intimately related to chemical weathering processes. It is rather difficult to analyze all of these factors at once, and thus relatively simple geologic systems are advantageous as these systems allow unique insights into the processes of chemical weathering.

We chose to study the relationship between water chemistry and chemical weathering of the related rocks in the Rokko granite area as a relatively simple test site. The samples used in this study were collected from the small streams in the watersheds where granite or its detritus is exposed. The relatively short flow distances of those streams can almost avoid contamination of anthropogenic pollutants and effects of biological activities. The geology of the study area is well investigated, and the degree of weathering of the granites has already been studied (Kuroda et al., 1970; Miura, 1991). In this study, we report major element and REE concentrations in the stream waters as well as clay mineral compositions of the soils in order to explore REE geochemistry of river waters and chemical weathering processes.

**SAMPLES AND GEOLOGIC BACKGROUND**

Eleven water (ten stream waters and one groundwater) and related soil samples were collected from the Rokko Mountain area, which is located near Kobe, Japan (Fig. 1). The sampling
sites were chosen from the area where the rocks and sediments are composed of the Rokko granite or its detritus and where any obvious anthropogenic pollution sources are not found. The Rokko granite is a fine to coarse grained biotite granite of late Cretaceous age. Normative mineral compositions of the Rokko granites are 30–45% for quartz, 20–50% for K-feldspar, 12–28% for plagioclase, 1–8% for biotite and 0–1% for amphibole. Their silica contents are rather uniform falling within 74.5–75.5 wt.% (Ueji, 1937; Kasama, 1968; Huzita and Kasama, 1982; Terakado and Nohda, 1993).

These granites have undergone varying degrees of weathering, and the degree of weathering for the area has been examined in relation to landslide and slope failure (Fig. 2; Kuroda et al., 1970). According to Kuroda et al. (1970), the degree of weathering was divided into four grades, using the criteria listed below, on the basis of hammerblow method and naked eye observations:

1. Fresh—When a rock is struck with a hammer, it rebounds keenly, and the mineral grains are cut with a sharp crack.
2. Weakly weathered—When a rock is broken with a hammer, complex micro-fractures are observed along the crack. Secondary minerals produced by weathering are not found, but the rock is not adequate for stonework.
3. Medium strongly weathered—A hammer easily crushes a rock, making complex fragments, and weathering minerals are found.
4. Strongly weathered—Rocks and minerals can be broken by hand without hammer.

Figure 2 shows the weathering degree map after the figure appeared in Kuroda et al. (1970). Unfortunately, the weathering minerals were not specified in the above criteria, but it is likely that they correspond to clay minerals such as kaolinite (Miura, 1991).

For the purpose of later discussions, we define an index of weathering degree (WD index) for a rock on the basis of the criterion used by Kuroda et al. (1970): 1 is assigned to fresh, 2 to weakly weathered, 3 to medium strongly weathered, and 4 to strongly weathered. The intermediate values are assigned to the intermediate cases. These WD indices are basically defined for a rock, but we expand WD index to weathering degree for watershed areas. Although it is difficult to define WD index for a watershed area rigorously, because of occurrence of several different WD index rocks, introduction of the WD index is intended to treat weathering phenomena more quantitatively. When the watershed area straddles two fields (Fig. 2), then the intermediate values are adopted: For example, intermediate position between “strong” and “medium strong”, is defined as WD value = 3.5.

Miura (1991) examined the weathering minerals in the granitic rocks from 11 localities in the Rokko mountain area, and specifically focused on the weathering processes of biotite and plagioclase using X-ray diffraction and electron probe microanalysis methods. Several important aspects pointed out by Miura (1991) are: (1) The biotites in fresh rocks (locality “A” in Fig. 2) underwent considerable chloritization via possible hydrothermal alteration during late stage solidification of the magma; (2) The weathering boulders and nearby decayed rocks (“B”, Fig. 2) indicate that the chlorites are converted into mixed-layer minerals with vermiculite and partly into kaolinite, but obvious changes were not observed in biotite itself. In the strongly weathered rocks from “B” and “C”, most chlorites were converted into kaolinites, whereas the biotites remain relatively unaltered; (3) In the area around “D”, although the chloritization of biotite was not significant, the biotites underwent strong weathering and oxidation. The chlorites had changed to kaolinite through vermiculite; (4) Although the plagioclase from the area around “D” slightly changed to kaolinite in comparison with those from the other areas, the plagioclases from the Rokko Mountains are, as a whole, less weathered.

As for the history of the Rokko mountain area, prior to about 0.5 Ma, the area had temporarily been a part of a peneplain, shallow inland sea or lake. After about 0.5 Ma the area was uplifted in association with faulting (e.g., Huzita and Kasama, 1982). Miura (1991) considered that the weathering of most of the Rokko granites had taken place.
prior to the Quaternary, and the red weathering crust had already been eroded. The weathered rocks thus formed in the Rokko Mountain area extend to considerable depths, which is substantiated by many observations of the strongly weathered rocks at considerable depths in many sites of land developments, road and tunnel constructions.

**Analytical Method**

The samples were collected during late October to November in 1998. In the field, the alkalinity was measured for the non-filtered water by titration with 0.02N H$_2$SO$_4$ and final pH value of 4.8. The water samples were immediately filtered through a 0.45 µm membrane filter and stored in polyethylene bottles. For REE and major cation analyses, samples (ca. 1 kg) were acidified with HCl and stored at room temperature, while for anions and PO$_4$ and SiO$_2$ analyses, the filtered samples without acidification were stored immediately in a dry-ice box or in a freezer within about two hours.

Anions (F$^-$, Cl$^-$, NO$_3^-$, SO$_4^{2-}$) were measured by ion chromatography using Hitachi LC system. For P and silica measurements, colorimetric methods using molybdenum blue complex were applied (JSAC, 1981). Major cations (Na, K, Ca, Mg) were measured by atomic absorption method using Sr for interference suppressor on the Hitachi Z-8200. Contents of Fe and Mn were measured by standard addition technique on frame-less atomic absorption method. REE and Ba were measured by mass-spectrometric isotope dilution method using thermal ionization mass-spectrometer (JEOL 05RB). These elements were firstly separated from major elements by coprecipitation with ferric-hydroxide using about one liter sample (e.g., Masuda and Ikeuchi, 1979). Purification and further separation of light REE, heavy REE and Ba were performed by conventional cation exchange column method. In order to avoid Ba interference to La measurements, nitric acid was used for elution (Jahn et al., 1980). For some cases of the Ce data, corrections of total analytical blanks of about 3 % were made.

The clay minerals in the soil samples were identified by powder X-ray diffraction method. The fine particles in a soil sample were collected from the suspension of the water-soil budget mixed in a bucket. The X-ray diffraction patterns for oriented powder samples were taken in three ways: (1) no-treatment, (2) ethylene-glycol treatment for more than one hour at 60°C, (3) heated at 100°C for more than one hour. Although the rigorous procedure for clay mineral identification is rather complex (e.g., Shimoda, 1985), the simple procedure was adopted. For example, the 7-angstrom peak is identified as kaolinite, the 15-angstrom peak, which shifts to 17-angstrom with ethylene-glycol treatment as montmorillonite, the 14.3–14.8 peaks, as vermiculite, and the 14–14.3 peaks as chlorite (Table 3). It is true that the 7-angstrom peak of kaolinite is overlapped with the secondary peak of 14-angstrom chlorite peak, but chlorites are less abundant in the sampling region. Our mineral assignments used are not rigorous but are useful for discussions in the present study.

**Results**

The analytical results of major components and trace elements of the stream waters are presented in Tables 1 and 2, respectively.

**Major elements**

The major component data are plotted against HCO$_3^-$ contents (alkalinity) in Fig. 3. The HCO$_3^-$ concentrations for all of the samples range from 0.29 meq/l to 6.02 meq/l, but most of the values are less than ca. 3 meq/l, which is consistent with the previously reported values (Kitano et al., 1967; Kusaka and Sagawa, 1974). In the major components vs. HCO$_3^-$ plots, several features can be pointed out: (1) Positive correlations are obvious in the data of Ca, Na, Cl$^-$ and SO$_4^{2-}$, (2) Mg and K seem to be rather uniform; (3) Fe and Mn are negatively correlated with HCO$_3^-$, showing hyperbolic curves; (4) F$^-$, NO$_3^-$ and pH data may show broad positive trends; (5) In most cases, the highest HCO$_3^-$ data (No. 2) deviates largely from the trends.
The Ca depletion of this sample may be attributed to CaCO₃ saturation (Stumm and Morgan, 1996), and relative enrichments of Mg, K and F suggest relatively large contribution of biotite dissolution. Tsurumaki and Sakuramoto (1985) also examined the high F stream waters from the similar area of the Rokko Mountains, and concluded that the high F contents in those stream waters are due to high F content in biotite of the area. They also pointed out the possibility that the Ca concentrations in those high F stream waters are regulated by precipitation of CaF₂ (Ksp = 10⁻⁹.₆~10⁻¹₀.₅₆; Nordström and Jenne, 1977). Although the deviations of this sample from the general trends in Fig. 3 are not completely understood, this sample can be considered as a peculiar sample in the stream waters of the Rokko Mountains, because this sample was taken from a very small stream around which the occurrence of high F biotite is known.

### REE patterns and weathering degrees

The rare earth element abundances for the stream water samples are normalized to the chondritic values (Masuda et al., 1973) and are plotted against atomic number in Fig. 4. Most samples are characterized by light REE enrichments with large negative Ce and Eu anomalies. Moreover, the heavy REE spans are rather variable, and some samples show heavy REE enrichments as

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**Table 1. Analytical results of major elements**

<table>
<thead>
<tr>
<th>Site No.</th>
<th>pH</th>
<th>Alkalinity (neq/l)</th>
<th>Na (ppm)</th>
<th>K (ppm)</th>
<th>Ca (ppm)</th>
<th>Mg (ppm)</th>
<th>Fe (ppb)</th>
<th>Mn (ppb)</th>
<th>SiO₂ (ppm)</th>
<th>Cl (ppm)</th>
<th>F (ppm)</th>
<th>NO₂ (ppm)</th>
<th>SO₄ (ppm)</th>
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</thead>
<tbody>
<tr>
<td>Akagodani</td>
<td>1</td>
<td>7.2</td>
<td>0.472</td>
<td>6.04</td>
<td>1.3</td>
<td>11.8</td>
<td>0.74</td>
<td>29</td>
<td>5.4</td>
<td>14.5</td>
<td>5.58</td>
<td>3.0</td>
<td>7.7</td>
</tr>
<tr>
<td>Horaiiko</td>
<td>2</td>
<td>8.1</td>
<td>6.02</td>
<td>26</td>
<td>10.8</td>
<td>71.0</td>
<td>10.3</td>
<td>8.6</td>
<td>0.6</td>
<td>5.5</td>
<td>4.92</td>
<td>4.5</td>
<td>0.56</td>
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<tr>
<td>Tsurukabuto</td>
<td>3</td>
<td>8.2</td>
<td>2.77</td>
<td>16.8</td>
<td>0.93</td>
<td>54.6</td>
<td>1.37</td>
<td>5.4</td>
<td>bd</td>
<td>12.7</td>
<td>16.1</td>
<td>1.2</td>
<td>22</td>
</tr>
<tr>
<td>Uzumamori</td>
<td>4</td>
<td>7.7</td>
<td>0.797</td>
<td>8.59</td>
<td>0.63</td>
<td>16.2</td>
<td>1.17</td>
<td>25</td>
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<td>23</td>
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<td>Senjodani G.</td>
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<td>6.8</td>
<td>1.82</td>
<td>13.0</td>
<td>1.1</td>
<td>33.2</td>
<td>1.01</td>
<td>10</td>
<td>1.9</td>
<td>10.2</td>
<td>13.1</td>
<td>0.32</td>
<td>12</td>
</tr>
<tr>
<td>Senjodani R.</td>
<td>5’</td>
<td>7.2</td>
<td>0.816</td>
<td>8.67</td>
<td>0.83</td>
<td>13.8</td>
<td>0.73</td>
<td>29</td>
<td>11</td>
<td>15.8</td>
<td>7.51</td>
<td>0.50</td>
<td>8.2</td>
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<td>Ishiyagawa</td>
<td>6</td>
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<td>2.85</td>
<td>12.4</td>
<td>1.15</td>
<td>52.0</td>
<td>2.36</td>
<td>12</td>
<td>0.54</td>
<td>14.1</td>
<td>12.7</td>
<td>0.57</td>
<td>12</td>
</tr>
<tr>
<td>Sumiyama</td>
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<td>7.5</td>
<td>0.921</td>
<td>9.29</td>
<td>0.76</td>
<td>19.1</td>
<td>0.93</td>
<td>9.1</td>
<td>0.24</td>
<td>18.3</td>
<td>10.4</td>
<td>0.45</td>
<td>13</td>
</tr>
<tr>
<td>Omote-RDW</td>
<td>8</td>
<td>7.8</td>
<td>1.33</td>
<td>6.95</td>
<td>0.91</td>
<td>27.2</td>
<td>1.25</td>
<td>6.3</td>
<td>bd</td>
<td>15.7</td>
<td>12.9</td>
<td>0.10</td>
<td>7.6</td>
</tr>
<tr>
<td>DW-58</td>
<td>9</td>
<td>6.6</td>
<td>0.290</td>
<td>5.75</td>
<td>1.33</td>
<td>4.25</td>
<td>1.44</td>
<td>77</td>
<td>4.5</td>
<td>4.1</td>
<td>6.57</td>
<td>bd</td>
<td>0.65</td>
</tr>
<tr>
<td>Yamada</td>
<td>10</td>
<td>6.6</td>
<td>0.341</td>
<td>5.87</td>
<td>0.68</td>
<td>7.35</td>
<td>1.31</td>
<td>35</td>
<td>1.9</td>
<td>11.5</td>
<td>7.54</td>
<td>0.09</td>
<td>0.78</td>
</tr>
</tbody>
</table>

bd: below detection limit.

Site No.: See Fig. 1. These numbers are also used as the sample numbers.

**Table 2. REE (ppt) and Ba (ppb) concentrations for the analyzed samples**

<table>
<thead>
<tr>
<th>Site No.</th>
<th>Akago</th>
<th>Horai</th>
<th>Turuka</th>
<th>Uzug</th>
<th>Senj G</th>
<th>Senj R</th>
<th>Ishiy</th>
<th>Sumiya</th>
<th>Omote-RDW</th>
<th>DW58</th>
<th>Yamada</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>nd</td>
<td>nd</td>
<td>24</td>
<td>40.7</td>
<td>205</td>
<td>405</td>
<td>28.2</td>
<td>44.5</td>
<td>49</td>
<td>316</td>
<td>513</td>
</tr>
<tr>
<td>Ce</td>
<td>204</td>
<td>68.8</td>
<td>6.2</td>
<td>20.2</td>
<td>nd</td>
<td>22.8</td>
<td>7.91</td>
<td>12.7</td>
<td>3.88</td>
<td>951</td>
<td>171</td>
</tr>
<tr>
<td>Nd</td>
<td>392</td>
<td>177</td>
<td>37.3</td>
<td>34.6</td>
<td>189</td>
<td>32.6</td>
<td>35.1</td>
<td>34</td>
<td>32.5</td>
<td>466</td>
<td>540</td>
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<tr>
<td>Sm</td>
<td>98</td>
<td>43.7</td>
<td>10.1</td>
<td>6.38</td>
<td>36.4</td>
<td>6.35</td>
<td>7.4</td>
<td>6.98</td>
<td>5.4</td>
<td>81</td>
<td>121</td>
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<tr>
<td>Eu</td>
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<td>2.4</td>
<td>1.6</td>
<td>0.68</td>
<td>3.8</td>
<td>0.69</td>
<td>1.1</td>
<td>0.9</td>
<td>0.83</td>
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<td>Gd</td>
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<td>27.5</td>
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<td>6.52</td>
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<td>7.18</td>
<td>5.74</td>
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<td>115</td>
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<tr>
<td>Dy</td>
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<td>27.5</td>
<td>6.06</td>
<td>32.5</td>
<td>6.98</td>
<td>15.2</td>
<td>6.21</td>
<td>5.24</td>
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<td>Yb</td>
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<td>10.8</td>
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<td>nd</td>
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<td>42</td>
<td>97.5</td>
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<td>Lu</td>
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<td>12.4</td>
<td>0.51</td>
<td>1.8</td>
<td>1.9</td>
<td>8.2</td>
<td>0.66</td>
<td>0.71</td>
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<tr>
<td>Ba</td>
<td>3.69</td>
<td>42.3</td>
<td>13.2</td>
<td>17.4</td>
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<td>10.3</td>
<td>14.5</td>
<td>6.05</td>
<td>5.29</td>
<td>10.6</td>
<td>3.78</td>
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</table>

nd: not determined.
Fig. 3. Major components vs. $\text{HCO}_3^-$ plots. The concentration unit for the ordinates is mmol/l aside from $\mu$mol/l for Fe and Mn. These symbols are also used throughout the following figures.

represented by Nos. 3 and 6.

The REE abundances normalized to the local silicic rocks are illustrated in Fig. 5. The normalizing values are the average values of 12 silicic rocks in the Hyogo Prefecture that includes our study area (Terakado and Masuda, 1988). These values are similar to those of the shales such as PAAS (Nance and Taylor, 1976) or NASC (Gromet
et al., 1984) and also to those of the Rokko granites (Terakado and Fujitani, 1995). On this diagram, Ce anomalies are conspicuous, and the overall REE patterns are almost flat except for Nos. 3, 6 and 5’. As for Nos. 3 and 6, the normalized values increase almost linearly from La to Lu aside from Ce and Eu.

It was found that the REE concentrations of the waters discharged through the strongly weathered watershed areas are relatively high (open symbols in Figs. 4 and 5), while the waters from the fresh or weakly weathered areas tend to have low REE concentrations (solid symbols in Figs. 4 and 5). Because of relatively large heavy REE variations, this tendency is conspicuous, when the light REE (La-Sm) data are concerned. We chose Nd as a representative of light REE, and the Nd concentrations are plotted against the WD values in Fig. 6a. The Nd concentrations are clearly separated into high and low groups, depending on the WD values. The groundwater (No. 5) and the stream water (No. 5’) are both located on the medium-strongly weathered area in Fig. 2, but Nos. 5 and 5’ are classified into high and low REE groups, respectively. The groundwater (#5) flows through a terrace deposit aquifer composed of strongly weathered granitic soil, which is consistent with higher REE contents. It should be noted that the weakly weathered area in Fig. 2 roughly corresponds to relatively steep area as demonstrated by the thick contour intervals (Fig. 1), and such areas tend to correspond to relatively fresh areas. Therefore, relatively low REE contents for

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**Fig. 4.** Chondrite normalized REE patterns for the stream waters analyzed in this study. Normalizing values are taken from Masuda et al. (1973). The sample locality numbers are indicated. Note that open symbols are intended to show relatively weathered watershed samples, and solid symbols correspond to fresh or weakly weathered watershed areas.

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**Fig. 5.** The REE patterns of the stream waters using normalizing values of average silicic rocks (Terakado and Masuda, 1988).
No. 5′ is reasonable. The two samples, Nos. 1 and 2, are located out side the area of Fig. 2, but according to our complementary field observations for Nos. 1 and 2 areas, the weathering degrees for the areas are assigned to strong or medium-strongly weathered areas, which is consistent with their light REE enrichments. Therefore, all in all, the waters from the strongly weathered areas tend to have high REE concentrations.

**Degree of weathering and kaolinite/clay ratio**

The several clay minerals (see Table 3) were identified by X-ray diffraction (XRD) patterns. On the XRD charts, the heights of major reflection peaks of the clay minerals were measured, and are listed in Table 3. Moreover, the peak height ratios of kaolinite to the sum of all clay peaks were calculated. These apparent kaolinite/clay ratios are not the true mineral compositions but is only a measure of the relative proportion of kaolinite to other clay minerals in the soil. The kaolinite can be considered as a representative of the final weathering products, and thus, as a working hypothesis, we regard the apparent kaolinite/clay ratio as a measure of the degree of weathering. This point will be discussed later. In Fig. 6b, the apparent kaolinite/clay ratios are plotted against the WD indices which were estimated from Fig. 2 and our field observations. Although data points scatter widely, a rough relationship exists.

**DISCUSSION**

The watershed areas of the stream waters examined in the present study are restricted to the Rokko granite area. The widths of those streams are quite narrow, ranging from about several-centimeters to about one meter or so, and the lengths of these streams as far as the sampling sites are very short (usually less than a few hundred meters). Moreover, no anthropogenic pollution sources exist within these watershed areas. Furthermore, due to relatively steep mountain slope, the streams flow rapidly without stagnation, and contributions from biological activity to the water chemistry is minimal. Therefore, the chemical compositions of these waters reflects the interaction between water and granite materials.

**Significance of calcite dissolution**

The possible chemical reactions involved in the weathering of granitic rocks can be expressed by combination of several dissolution reactions of rock forming minerals as follows (e.g., Garrels, 1967, Garrels and Mackenzie, 1967):

\[
\begin{align*}
\text{Plagioclase (Ab}_{50}\text{An}_{50})
\rightarrow 4\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{2}\text{Si}_{3}\text{O}_{8} + 6\text{CO}_2 + 9\text{H}_2\text{O} \\
\rightarrow 3\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 (\text{Kaolinite}) \\
\rightarrow + 4\text{SiO}_2 + 2\text{Na}^+ + 2\text{Ca}^{2+} + 6\text{HCO}_3^- 
\end{align*}
\] (1)
REE in stream waters from the Rokko granite area, Japan

\[4\text{Na}_{0.5}\text{Ca}_{0.5}\text{Al}_{1.5}\text{Si}_{2.5}\text{O}_8 + 6.36\text{CO}_2 + 5.74\text{H}_2\text{O}\]
\[\rightarrow 2.56\text{Ca}_{0.17}\text{Al}_{2.34}\text{Si}_{3.66}\text{O}_{10} (\text{OH})_2 (\text{Montmorillonite}) + 0.308\text{SiO}_2 + 2\text{Na}^+ + 1.56\text{Ca}^{2+} + 6.36\text{HCO}_3^-\]

(2)

K-feldspar

\[2\text{KAlSi}_3\text{O}_8 + 2\text{CO}_2 + 3\text{H}_2\text{O}\]
\[\rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{SiO}_2 + 2\text{K}^+ + 2\text{HCO}_3^-\]

(3)

Biotite

\[2\text{KMg}_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2 + 14\text{CO}_2 + 7\text{H}_2\text{O}\]
\[\rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 4\text{SiO}_2 + 2\text{K}^+ + 6\text{Mg}^{2+} + 14\text{HCO}_3^-\]

(4)

Calcite

\[\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^-\]

(5)

In order to examine the observed data in the context of these reactions, the mole-base concentrations of Ca, Na, Mg and K are illustrated in Fig. 7. The linear correlation between Ca and HCO$_3^-$ is prominent, and these data points fall on the 1:2 line (Fig. 7a), which is expected from reaction (5). If Ca ions were supplied from decomposition of plagioclase as represented by reaction (1), similar concentrations of Na to Ca ions should be observed. Given that the typical plagioclase compositions of granites are about Ab$_{80}$An$_{20}$ (e.g., Tainosho, 1986), much higher Na concentrations in comparison with Ca would be expected. On the contrary, our observed Na concentrations are rather low. Moreover, Mg and K concentrations are also considerably low and seem to be independent on HCO$_3^-$ concentrations (Fig. 7c). These facts indicate that the calcite dissolution is a dominant weathering process in the Rokko mountain area.

White et al. (1999) emphasized the role of disseminated calcite in the chemical weathering of granitoid rocks from the Merced watershed in Yosemite National Park, CA, U.S.A. They found calcite occurring as fillings in microfractures, as disseminated grains within the silicate matrix, and as replacement of calcic cores in plagioclase, and analyzed the mineral chemical compositions by electron microprobe. They noticed excess Ca occurred in many surface and ground waters relative to the molar Ca/Na ratio of plagioclase stoichiometry expected from the standard plagioclase decomposition theory (Eqs. (1) and (2); Stauffer, 1990). They also conducted experiments in which the CO$_2$ saturated water was passed through columns with fresh or weathered rock grains, and analyzed the effluents. Conclusively, they showed that accessory calcite dissolution in granitoid rock contributed a significant portion of the total Ca and alkalinity in the watersheds and river basins where significant amounts of bedrock are recently exposed.

In the present study, the higher Ca concentrations of stream waters are observed for the relatively fresh granite areas rather than strongly

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Table 3. Apparent clay mineral compositions of the watershed soils. The peak heights (mm) for characteristic mineral peaks on the XRD charts are indicated.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Kaolinite</th>
<th>Montmorillonite</th>
<th>Vermiculite</th>
<th>Mica</th>
<th>Kaolinite/Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>Akagodani</td>
<td>1</td>
<td>8</td>
<td>6</td>
<td>0</td>
<td>0.57</td>
</tr>
<tr>
<td>Horaikyo</td>
<td>2</td>
<td>66</td>
<td>42</td>
<td>0</td>
<td>0.61</td>
</tr>
<tr>
<td>Tsurukabuto</td>
<td>3</td>
<td>16</td>
<td>19</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Uzugamori</td>
<td>4</td>
<td>22</td>
<td>0</td>
<td>10</td>
<td>0.69</td>
</tr>
<tr>
<td>Senjodani G.</td>
<td>5</td>
<td>103</td>
<td>0</td>
<td>22</td>
<td>0.82</td>
</tr>
<tr>
<td>Senjodani R.</td>
<td>5′</td>
<td>81</td>
<td>20</td>
<td>12</td>
<td>9</td>
</tr>
<tr>
<td>Ishiyagawa</td>
<td>6</td>
<td>7</td>
<td>6</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>Sumiyama</td>
<td>7</td>
<td>26</td>
<td>6</td>
<td>8</td>
<td>9</td>
</tr>
<tr>
<td>Omote-RDW</td>
<td>8</td>
<td>7</td>
<td>21</td>
<td>6</td>
<td>9</td>
</tr>
<tr>
<td>DW-58</td>
<td>9</td>
<td>25</td>
<td>3</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>Yamada</td>
<td>10</td>
<td>21</td>
<td>27</td>
<td>0</td>
<td>8</td>
</tr>
</tbody>
</table>

---
For example, two samples from the strongly weathered areas, Nos. 9 and 10, show the lowest Ca concentrations. This phenomenon is also demonstrated clearly from the relationship between Ca/Na ratio in water and apparent kaolinite/clay ratio of the watershed soils.

In our Ca and Na data, Ca/Na molar ratios range from 0.424 to 2.41, though seawater salt must contribute to the river water Na, because the area is very close to the Seto Inland Sea (Osaka Bay). The sea-spray effect on river waters has been discussed by many investigators (e.g., Tsurumi, 1992; Nakagawa and Iwatsubo, 2000), and thus we intriguingly correct the seawater Na contribution to our Na data. The Na concentrations are well correlated with HCO$_3^-$ values (Fig. 7b) and the intercept (0.213 mmol/l) may correspond to the average Na concentration that originated from seawater Na. However, at present, it seems to be almost impossible to find the exact value that can be applicable to all of the data measured in this study, because such sea-spray contribution to rain waters are generally variable depending on meteorological condition and distance from the sea (Tsurumi, 1992). Actually, there are two points that deviate downward from the regression line. Therefore, for the correction value of sea-spray contribution to Na, we temporarily use the value, 0.0953 mmol/l, which is the intercept for the dotted line that is parallel to the regression line and penetrates those two points (see Fig. 7b). This correction value is consistent with the Cl$^-$ data, though they are also scattered (Fig. 3). As demonstrated in Fig. 7c, Mg and K show almost constant values, indicating existence of biases probably due to the reactions other than those in Eqs. (1) to (4). If the high value, i.e., 0.213 mmol/l, is chosen, unrealistically larger corrections are made for the lower Na samples, ignoring the above-mentioned biases. Therefore, we practically chose the lower value, 0.0953 mmol/l, for the corrections.

In Fig. 8, the Ca/Na molar ratios are plotted against the apparent kaolinite/clay ratios of the soils of the sampling sites, and a rough linear correlation is seen. In the watersheds composed of fresh granites, the apparent kaolinite/clay ratios are low, and calcites in granitic materials are dissolving via ongoing weathering and supplying abundant Ca to the stream waters. By contrast, in the strongly weathered areas, the apparent kaolinite/clay ratios are high, and granites gener-
ally lack calcite, because calcite has been consumed during the past weathering processes, and thus Ca contents in the stream waters from such strongly weathered areas are relatively low.

The descriptions of calcite occurrence in the granitic rocks from Japan are sparse, but we found many calcites in thin sections of the Rokko granites. They usually occur as relatively small grains in dusty parts of feldspars, along cleavages in biotites and as fillings in microfractures. The sparse descriptions of calcite in granitic rocks are attributed to less attention of the petrologists who are interested in genetic processes of granitic magmas. Many petrologists have overlooked the calcite which is considered to be an alteration product or secondary mineral together with saussurite in granitic rocks. Although genesis of those calcites is not clear, they cannot be the result of deposition during more recent weathering processes, because calcites are found in the interior of mineral grains in relatively fresh granites. It is likely that those calcites were formed under deuteric alteration during the late Cretaceous time. In fact, it is well known that the late Cretaceous volcanic rocks (mostly ash flow or welded tuff) associated with granitic rocks in the southwestern Japan underwent varying degrees of hydrothermal alteration, but detailed descriptions of those processes are sparse (cf., Vaniman and Chipera, 1996; Terakado and Fujitani, 1998).

**The high and low REE groups in relevance to weathering**

As mentioned previously, the samples from the strongly weathered areas tend to have higher REE concentrations (Figs. 4 and 5). For example, the Nd concentrations are clearly separated into two groups depending on the WD indices (Fig. 6a). This tendency can be explained by the leaching of REE from solid materials. One possibility is that the water-rock interactions are enhanced in the larger solid surface area, since one of the major factors controlling the extent of REE leaching from solids is the surface area of the solid. The strongly weathered rocks or soils through which the stream waters flow have more micro-fractures and thus have larger surface areas than the fresh or weakly weathered rocks.

The above tendency seems to be contradictory to the Ca data. The Ca concentrations for the stream waters from the strongly weathered areas tend to be low, while the REE concentrations for them are high. Such reverse tendency can be reconciled by considering that the fresh granites contain abundant calcite, which has Ca as major element but REE as trace elements. In the strongly weathered areas, the Ca concentrations are reduced by previous consumption of calcites, while the REE concentrations are enhanced due to larger surface areas of the solids as mentioned above.

Another important factor that controls REE leaching from rocks is the effect of minor minerals having high REE concentrations (Braun et al., 1998; Aubert et al., 2001). It is known that REE are concentrated in some minor minerals such as apatite, monazite and zircon in granitic rocks (Gromet and Silver, 1983; Braun et al., 1993). The selective dissolution of these minerals can account for the observed REE variations.

Aubert et al. (2001) examined major and trace elements and Sr and Nd isotopic compositions of

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**Fig. 8. Molar Ca/Na ratio versus apparent kaolinite/clay ratio. The molar Na contents are the possible net Na values calculated by subtracting the seawater contribution as indicated in Fig. 7B from the observed Na contents.**
the granitic rocks, soils, stream waters and suspended loads in a small catchment of the Vosges mountains, France. They found that $P_2O_5$ in the soils is positively correlated with Th and negatively with La/Dy ratio, which suggests that these elements are controlled by phosphate minerals such as apatite and monazite. Moreover, Aubert et al. (2001) also measured Sr and Nd isotopic compositions for those materials, and showed that the Sr and Nd isotopic compositions of the stream and spring waters are close to the isotopic values of apatite, suggesting that the stream and spring waters would incorporate more Sr and Nd originating from apatite dissolution. Given that apatite concentrates REE especially middle ones (Gromet and Silver, 1983; Byrne et al., 1996; Hannigan and Sholkovitz, 2001), the apatite controlling model might be a possibility in the present case.

Moreover, it is known that REE tend to concentrate in the grain boundaries of rock-forming minerals (Suzuki et al., 1990). If the grain boundaries can be dissolved during weathering, those REE may contribute to higher REE in the stream waters. Furthermore, clay minerals in the weathered area rocks may more or less play a role in REE distribution between clay containing rocks and waters. Zwingmann et al. (1999) examined REE characteristics of some clay minerals from a densely faulted area in the Permian gas province of the Niedersächsische rift system, Germany. The shale-normalized REE patterns for those clays are classified into three different types: (1) a concave-type showing middle REE enrichment with positive Eu anomaly; (2) a relatively flat type; and (3) a third type is characterized by increase from LREE to HREE. They also conducted leaching experiments with dilute HCl, and the shale-normalized REE patterns for the soluble phases are similar with a concave shape with positive Eu anomaly. However, these features do not directly relate to the contention that dissolution of clay minerals supplies REE to water.

Although some REE concentrated minerals may play an important role in the overall REE concentration variations, other possibilities mentioned above must be examined further using more detailed data of related minerals and soils. The present observation, i.e., the relationship between the REE concentration and the degree of weathering, suggests usefulness of REE as a tool for examining weathering mechanisms.

Heavy REE enrichment

The enrichments of heavy REE are conspicuous in several samples especially for two samples (Nos. 3 and 6). These two samples are located on the weakly weathered and medium-strongly weathered areas (Fig. 2). As mentioned above, they are classified into the low light REE group (Fig. 6a), and correspond to weakly weathered type inferred from their WD indices, i.e., 2 and 2.5. Moreover, those samples tend to have relatively high $\text{HCO}_3^-$, $\text{SO}_4^{2-}$, and Ca, and have relatively low Fe and Mn. The higher $\text{HCO}_3^-$ and Ca indicate the larger contribution of calcite dissolution as discussed before, and such larger extent of calcite dissolution corresponds to the weakly weathered signature. It is also notable that the lower Fe and Mn suggest larger extent of Fe-Mn hydroxides precipitations.

As for the heavy REE enriched patterns, the previous investigators have suggested the significance of light REE scavenging by particulate matters in ocean and river environments (e.g., Byrne and Kim, 1990; Elderfield et al., 1990; Nozaki et al., 2000; Sholkovitz, 1992; Johannesson et al., 1999; Kuss et al., 2001). Moreover, some inorganic ligands tend to form stronger heavy REE complexes than light REE ones (Cantrell and Byrne, 1987; Wood, 1990; Lee and Byrne, 1993; Millero, 1992; Byrne and Li, 1995). Predominance of bicarbonate complexes over carbonate and other complexes was demonstrated using the methods of Millero (1992) and the computer program of PHREEQE (Parkhurst et al., 1980) for the Oasis Valley groundwater case (Johannesson et al., 1999). They also pointed out that although formation of stronger bicarbonate complexes with increasing atomic number would be a basic mechanism for greater sorption affinity for causing the lighter REE to the aquifer materials, the particle/
REE in stream waters from the Rokko granite area, Japan

Water fractionation is necessary for causing the light/heavy REE fractionation. It is interesting that the heavy REE enriched samples (Nos. 3 and 6) have the highest \( \text{HCO}_3^- \) contents excluding one extremely high sample (No. 2). This suggests that the heavy REE are dissolved in water as bicarbonate complexes. Moreover, precipitation of Fe-hydroxides and CeO\(_2\) as deduced from relatively low Fe contents and relatively larger Ce anomalies suggests scavenging of light REE in association with these precipitates as discussed below. Although more detailed investigations are necessary to obtain a more definitive conclusion, we consider that the heavy REE enrichments are enhanced by advanced water-rock interaction induced by high \( \text{HCO}_3^- \) contents, and the light REE are scavenged by sorption on the solid surfaces (cf., Otsuka and Terakado, 2002).

Ce anomaly

The magnitude of the Ce anomaly tends to be larger in the weakly weathered areas, which is shown by a plot of Ce/Ce* vs. the apparent kaolinite/clay ratio in Fig. 9. In the Ce/Ce*, Ce is the chondrite-normalized value of the measured Ce concentration, and Ce* is the interpolated chondrite-normalized value on the La-Nd linear line of the REE pattern (As for the samples, #1 and #2, the Ce* values were estimated by extrapolation of Nd-Sm lines). It is well known that Ce anomalies in water are created by precipitation of CeO\(_2\) because of its quite low solubility (e.g., Schreiber et al., 1980; Elderfield and Greaves, 1981; De Baar et al., 1988; Kagi and Takahashi, 1998; Akagi and Masuda, 1998; Takahashi et al., 2000). Thus, the correlation between Ce/Ce* and kaolinite/clay ratio can be interpreted, to a large extent, by CeO\(_2\) precipitation in the weakly weathered areas, consistent with the larger extent of Fe-Mn hydroxide precipitation as mentioned before. The filtration of these precipitates might occur more effectively during the water percolation through micro-fractures of the weakly weathered rocks rather than through relatively loosened micro-fractures in the strongly weathered rocks.

In general, the Ce anomaly is much affected by various factors such as Eh, pH and Ce concentrations. Akagi and Masuda (1998) examined thermodynamic conditions necessary for the appearance of negative Ce anomaly in water system assuming that three species, Ce\(^{3+}\), CeO\(_2\) and Ce\(_2\)(CO\(_3\))\(_3\), are dominant in the water-stable region of Eh-pH diagram. They specified the Eh-pH region in which Ce anomaly in water will appear, and proposed the calculation method for the sizes of the Ce anomaly. As demonstrated by them, although the Eh-pH condition is generally a major factor determining the size of the Ce anomaly, the Eh-pH conditions of the usual stream waters definitely fall on the large Ce anomaly region. In other words, CeO\(_2\) always forms quite easily in the stream water. In general, removal of CeO\(_2\) from the water is always necessary for creating the Ce anomaly in the water. As discussed above, the mechanism for such CeO\(_2\) removal is mechanical filtration through fracture flow.

Someone may suspect that organic materials in rocks affect REE behavior (and Ce anomaly) during water-rock interaction processes. However,
our samples were collected with special care to avoid anthropogenic pollutants and biogenic materials, which makes the contribution from organic materials minimal. Recently, Tang and Johannesson (2001) have shown that 1.4~6.2% of total dissolved REE are combined with organic materials for relatively lower level of organic material concentrations. These relatively low values are not serious for affecting REE patterns of the stream waters. Given that REE concentrations in rocks are generally much higher than those in organic materials such as plants (Akagi et al., 2002), the contribution of REE from rocks is considered to be much greater than that from organic materials.

A measure of weathering: kaolinite/clay ratio or Ca/Na ratio

The apparent kaolinite/clay ratio in the soils is related to the Ca/Na ratio and the Ce/Ce* value in the stream waters. These relationships can be interpreted by considering the degree of weathering of the watershed rocks. In Fig. 6b, however, the correlation between the apparent kaolinite/clay ratio and the degree of weathering of the watershed area is not so clear. The scatter of the points might be attributed to errors in the assessment of the WD values or a discordance between the kaolinite/clay ratio of the sediment at the sampling site and that of the overall watershed rocks and soils.

The former case seems to include the sample No. 7, which deviates somewhat from the expected correlation line (Fig. 6b). Its WD values seem to be lower than the true value. As shown in Fig. 2, it is located on the weakly weathered field, but it is also very close to the fresh and medium strong fields. Generally, there are several large faults, which border the mountain and the plain areas around No. 7, and the weathering degrees of the rocks seem to be rather advanced in some places. Thus the DW value of No. 7 would be 2.5, which is suitable for the correlation in Fig. 6b. Needless to say, such modification does not affect the good correlations seen in Figs. 6a and 8.

Moreover, the sample No. 10 also appears to deviate from the possible correlation between the apparent kaolinite/clay and WD values. It is likely that the mineral composition of the riverside sediment is more or less fractionated by water flows. In general, finer particles tend to be more transportable than coarser particles and to be less retainable in the sediments. Moreover, such fractionation might be dependent not only on the particle size but also on mineral species. Thus the mismatch between the apparent kaolinite/clay and WD value should occur. If we trust the good linear trend seen in the Ca/Na vs. kaolinite/clay diagram (Fig. 8), No. 10 sample should have higher kaolinite/clay ratio of around 0.7, and No. 5 sample of around 0.55. These values forms a good correlation line in Fig. 6b. Moreover, such change does not alter the appearance of Fig. 9.

Therefore, the Ca/Na ratio in the stream waters is more reliable measure of the degree of weathering than the apparent kaolinite/clay and WD values. It should be noticed that the coherent variations for the apparent kaolinite/clay ratio, the Ca/Na ratio in the stream waters and the Ce anomaly confirm the above conclusion.

CONCLUDING REMARKS

(1) The relatively high Ca concentrations and the Ca/HCO_3^- molar ratios of 0.5 for the stream waters indicate significant calcite dissolution during the weathering process of the Rokko granites. The fresh granites contain relatively abundant calcite crystals, whereas calcite in the weathered granite has already been consumed. Thus, fresh granite rather than weathered granite can supply much Ca to the stream water.

(2) The molar Ca/Na ratio in the waters is negatively correlated with the apparent relative proportion of kaolinite to the total clay minerals in the related soils. This relationship can be interpreted by means of the degree of weathering of the watershed rocks. In the present study, the apparent kaolinite/clay ratio is considered to reflect the weathering degree of the watershed materials.

(3) The REE abundances in the stream waters are roughly correlated with the apparent weather-
ing degree of the watershed rocks. The REE in the weathered rock tend to dissolve easily through enhanced micro-fractures or surface areas. Some REE-rich accessory minerals such as apatite may contribute to the REE in the stream water, but further studies are necessary.

(4) The Ce/Ce* ratios are positively correlated with the apparent kaolinite/clay ratios. This observation can be explained by the extent of mechanical removal of CeO₂ precipitates rather than the changes in the Eh-pH conditions. The CeO₂ precipitates are filtered through fresh or weakly weathered rocks because of their narrower microfractures or smaller porosity than the strongly weathered materials.

(5) The Ca/Na ratio in the stream waters is more reliable measure of the degree of weathering than the apparent kaolinite/clay and WD values. The coherent variations in the apparent kaolinite/clay ratio, the Ca/Na ratio in the stream waters and the Ce anomaly confirm the above conclusion.

Finally, we would like to emphasize that the apparent kaolinite/clay ratio in the soils is an important and useful parameter for better understanding the weathering processes in watershed areas, and this investigation seems to shed new light not only on the chemical weathering but also on the REE geochemistry of the natural waters.

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