Origin of Dissolved Minor Elements (Li, Rb, Sr, Ba) in Superficial Waters in a Granitic Area

CATHERINE BEAUCAIRE and GIL MICHARD
Laboratoire de Géochimie des Eaux (LA 196), Université Paris VII, France

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The behaviour of rubidium, lithium, strontium and barium in superficial waters of a granitic area are compared with the behaviour of the associated major element: potassium, magnesium, calcium and potassium. Fractionation during dissolution is important for the Rb/K couple, whereas fractionation during deposition of new-formed minerals or uptake by vegetation is important for Mg/Li and K/Ba. Auxiliary minerals seem to play an important part in the relative concentrations of strontium and calcium in the waters.

INTRODUCTION

The acquisition of solutes by superficial waters in granitic areas has been modelized in different ways by GARRELS (1967), GARRELS and MACKENZIE (1967), PEDRO (1966), TARDY (1971), SARAZIN et al. (1976), SARAZIN (1979). But no attempt has been made to discuss the behaviour of minor elements in the same way. Obviously, a first question arises: nothing is known about the behaviour of minor elements during the dissolution of a mineral; different models are possible, as summarized by PLUMMER and THORSTENSON (1977), LIPPMANN (1977) and MICHARD and Ouzounian (1978).

The study of trace alkali ions in hot spring waters issued from granites (Ouzounian et al. 1980) shows strong correlations between Li-Na and Rb-K. Ions such as Li, Rb would assume temperatures in the reservoir in depth. These relations cannot be explained with our present knowledge. Therefore, we will try to understand the behaviour of some minor elements in the waters of a well studied area: the springs of Truyère river (FOUILLAC et al., 1974; SARAZIN et al., 1976).

In this first approach we focus on rather soluble minor elements such as Li, Rb, Sr, Ba. Some attempts to study Cs behaviour have also been made, but the analytical concentrations were often below the detection limit, either in the water or in the rock for local analyse.

This first study involves:
1— A study of the location of minor elements in the different minerals of the fresh rock.
2— An experimental leaching of the rock.
3— An analytical study of minor elements in the spring waters.

PETROGRAPHIC AND ANALYTICAL STUDY OF MARGERIDE GRANITE

The granitic massif of Margeride has been divided by COUTURIE (1971) in leucogranites, dark phryroid granites, and light phryroid granites. Our study applies to the dark phryroid facies.

The granite is rich in biotites (up to 18%). The K feldspars are mainly very large macrocrystals (5–6 cm in length; about 20–25% of rock) and smaller crystals (16% of the rock). Plagioclases (33% of the rock) are Na rich ones (An_{10} to An_{30}).

The microscopic study shows several noticeable points:

Plagioclases (oligoclase, andesine) show two different stages of sericitization, and, at
Table 1. Analysis of the Margeride granite (ppm)

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>K</th>
<th>Na</th>
<th>Mg</th>
<th>Mn</th>
<th>Sr</th>
<th>Rb</th>
<th>Li</th>
<th>Cs</th>
<th>Fe</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>Whole rock</td>
<td>8,200</td>
<td>54,300</td>
<td>17,200</td>
<td>5,710</td>
<td>410</td>
<td>247</td>
<td>378</td>
<td>57</td>
<td>11.6</td>
<td>17,900</td>
<td>1,440</td>
</tr>
<tr>
<td>Plagioclase</td>
<td>11,600</td>
<td>19,900</td>
<td>20,200</td>
<td>640</td>
<td>226</td>
<td>60</td>
<td>29</td>
<td>1.3</td>
<td>1,600</td>
<td>1,020</td>
<td></td>
</tr>
<tr>
<td>K Feldspar (phenocrystals)</td>
<td>2,200</td>
<td>89,900</td>
<td>13,700</td>
<td>175</td>
<td>204</td>
<td>188</td>
<td>7</td>
<td>446</td>
<td>4,800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Feldspars</td>
<td>11,200</td>
<td>31,200</td>
<td>21,800</td>
<td>470</td>
<td>253</td>
<td>188</td>
<td>17</td>
<td>2,100</td>
<td>1,900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Biotite</td>
<td>5,200</td>
<td>73,500</td>
<td>960</td>
<td>42,300</td>
<td>3,180</td>
<td>77</td>
<td>1,200</td>
<td>486</td>
<td>60</td>
<td>17,600</td>
<td>1,500</td>
</tr>
</tbody>
</table>

Table 2. Ratio of concentration for Margeride rock forming minerals and waters.

<table>
<thead>
<tr>
<th>Ratio of elements concentration</th>
<th>medium</th>
<th>number of samples</th>
<th>mean</th>
<th>max</th>
<th>min</th>
</tr>
</thead>
<tbody>
<tr>
<td>K/Rb</td>
<td>biotite</td>
<td>13</td>
<td>120</td>
<td>140</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>feldspar</td>
<td>10</td>
<td>1040</td>
<td>1280</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>leaching</td>
<td>7</td>
<td>360</td>
<td>440</td>
<td>320</td>
</tr>
<tr>
<td></td>
<td>nat. waters (ratio) a</td>
<td>24</td>
<td>358</td>
<td>450</td>
<td>290</td>
</tr>
<tr>
<td></td>
<td>nat. waters (slope) b</td>
<td>24</td>
<td>307</td>
<td>345</td>
<td>270</td>
</tr>
<tr>
<td>K/Ba</td>
<td>feldspar</td>
<td>10</td>
<td>60</td>
<td>110</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>nat. waters</td>
<td>18</td>
<td>272</td>
<td>410</td>
<td>150</td>
</tr>
<tr>
<td>Ca/Sr</td>
<td>plagioclase</td>
<td>19</td>
<td>115</td>
<td>140</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>leaching</td>
<td>10</td>
<td>1710</td>
<td>1860</td>
<td>1550</td>
</tr>
<tr>
<td></td>
<td>nat. waters (ratio)</td>
<td>24</td>
<td>195</td>
<td>260</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>nat. waters (slope)</td>
<td>24</td>
<td>147</td>
<td>168</td>
<td>126</td>
</tr>
<tr>
<td>Mg/Li</td>
<td>biotites</td>
<td>13</td>
<td>31</td>
<td>45</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>leaching</td>
<td>12</td>
<td>24.5</td>
<td>30</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>nat. waters</td>
<td>24</td>
<td>175</td>
<td>230</td>
<td>90</td>
</tr>
<tr>
<td>Mg/K</td>
<td>biotites</td>
<td>13</td>
<td>0.92</td>
<td>1.11</td>
<td>0.70</td>
</tr>
<tr>
<td></td>
<td>leaching</td>
<td>12</td>
<td>1.18</td>
<td>1.29</td>
<td>1.04</td>
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<tr>
<td></td>
<td>nat. waters</td>
<td>60</td>
<td>2.36</td>
<td>3.65</td>
<td>1.62</td>
</tr>
<tr>
<td></td>
<td>pine needles</td>
<td>2</td>
<td>0.78</td>
<td>0.80</td>
<td>0.78</td>
</tr>
</tbody>
</table>

different places associations of sericitized plagioclases, chlorite and calcite are observed.

Biotites, sometimes chloritized, are associated with small amounts of muscovites, and apatites or zircons. These associations are related to hypogene alteration rather than to weathering.

Major minerals have been separated by classical techniques (Frantz separator, heavy liquids and analyzed by atomic absorption for major and minor elements (Table 1). This mean value has been used to calibrate data obtained on the ionic microprobe.

The location of minor elements has been studied with an ionic microprobe CAMECA. Photographic examination shows that studied elements are essentially in minerals and not at cracks or at crystal joints. The presence of very small crystals of calcite appears in some photographic plates. The quantification of minor elements has been made at several places for the different minerals.

As it is shown in Table 1, minor elements are principally related to one or two minerals:
- Lithium and cesium are in biotites, like magnesium.
- Strontium in plagioclase, like calcium.
- Rubidium both in biotite and K feldspar like potassium.
- Barium essentially in K feldspar like potassium.

Thus, rather than absolute values which are more or less difficult to assess from ionic microprobe data, we present values of typical ratios between major elements and between minor elements and associated major elements: Mg/Li, K/Rb, K/Ba, Ca/Sr. The mean value and minima and maxima values are given in Table 2.

These figures are taken as references for the concentration ratios in waters.
EXPERIMENTAL LEACHING OF ROCK

Direct comparison of chemical compositions of spring waters and rock is difficult because fractionation between minor elements and associated major elements can occur during the dissolution process and during the precipitation of new-formed minerals. For instance, Al (SARAZIN et al., 1976) and Fe (JUNDT, unpublished) data indicate deposition of disordered kaolinite and iron hydroxyde.

Thus, in order to have a first approximation of the behaviour of minor elements during dissolution, we perform an experimental leaching of the rock by artificial solutions. The composition of the solution was established to avoid Al** and Fe*** precipitation. We first use oxalic acid, which is known to be present in soil waters. Unfortunately, oxalic acid precipitates with Ca** ions and, moreover, is not stable at the contact with rock. Therefore, we use a dilute solution of ammonium salt of EDTA at pH 5.5.

The rock is divided into small cubes of about 3–5 mm. These fragments are washed three times with distilled water and stored in the EDTA solution in polyethylene flasks. Small volumes are taken from time to time and analysed by atomic absorption (flame AA for major elements and graphite furnace A-A for minor elements) or colorimetry (silica).

Results are presented on Table 3 and on Fig.1 which give the mean value of the ratios of major elements for the principal minerals of the rock.

Ca/Na  

The Ca/Na ratio is very high in leaching experiment (>20), whereas the ratio in plagioclase is about 0.33. BUSENBERG (1976–1978) has demonstrated that plagioclases are not dissolved stoichiometrically, but has not observed a too large discrepancy of the ratio between leaching and mineral. But a large discrepancy is observed for an andesine (Ab49An42Or8) containing 0.68% calcite with a Ca/Na ratio in leaching of about 10.

The high ratio observed in our experiment can be explained by the presence of secondary minerals such as apatite, calcite. The dissolution of apatite is important (\(\Sigma P_{O_4} = 2.4 \times 10^{-4} \text{M in solution}\)) but not enough to explain the high Ca** value. Then, we think that the dissolution of calcite in small amounts is rather fast.

At first, Ca** increase quickly in solution and stop. In the meantime, Na’ continue to be dissolved, and Al concentration begins to decrease: the Ca** constant top value can be related to the end of the dissolution of auxiliary minerals or to the deposition of a newly formed mineral.

K/Na  

The K/Na ratio in solution is about 1. For microcline (Ab25Or75), BUSENBERG (1976) observed dissolution rates similar to those for orthose and albite.

In our case, K feldspars are present as macrocrystals, with a slow kinetic of dissolution, so biotite must be the principal source of potassium.

Mg/K  

The ratio in solution is slightly higher than in biotites. This suggests a low contribution of K feldspar in dissolved potassium and a non-stoichiometric dissolution for

### Table 3. Experimental leaching of the Margeride granite

<table>
<thead>
<tr>
<th>Days</th>
<th>1</th>
<th>2</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>11</th>
<th>13</th>
<th>20</th>
<th>27</th>
<th>31</th>
<th>34</th>
<th>51</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>10^{-5}</td>
<td>1.60</td>
<td>1.90</td>
<td>2.30</td>
<td>2.42</td>
<td>2.50</td>
<td>2.50</td>
<td>2.50</td>
<td>3.60</td>
<td>4.00</td>
<td>3.60</td>
<td>3.96</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>10^{-4}</td>
<td>1.65</td>
<td>2.25</td>
<td>2.85</td>
<td>2.95</td>
<td>3.25</td>
<td>3.80</td>
<td>5.20</td>
<td>5.32</td>
<td>7.20</td>
<td>8.00</td>
<td>8.80</td>
<td>9.20</td>
</tr>
<tr>
<td>Ca</td>
<td>10^{-4}</td>
<td>22.40</td>
<td>33.10</td>
<td>55</td>
<td>59.50</td>
<td>57</td>
<td>86</td>
<td>86</td>
<td>87</td>
<td>87</td>
<td>89</td>
<td>87.50</td>
<td></td>
</tr>
<tr>
<td>Mg</td>
<td>10^{-4}</td>
<td>1.20</td>
<td>1.90</td>
<td>3.40</td>
<td>3.80</td>
<td>4.20</td>
<td>4.80</td>
<td>6.65</td>
<td>7.50</td>
<td>9.00</td>
<td>9.50</td>
<td>10.30</td>
<td>11.10</td>
</tr>
<tr>
<td>H2SiO4</td>
<td>10^{-8}</td>
<td>2.25</td>
<td>5.50</td>
<td>14.70</td>
<td>18.50</td>
<td>19.00</td>
<td>20.80</td>
<td>22.30</td>
<td>24.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>10^{-4}</td>
<td>1.20</td>
<td>2.36</td>
<td>4.80</td>
<td>5.36</td>
<td>5.89</td>
<td>7.05</td>
<td>8.51</td>
<td>12.10</td>
<td>(39)</td>
<td>15</td>
<td>11.20</td>
<td>11.20</td>
</tr>
<tr>
<td>Li</td>
<td>10^{-7}</td>
<td>4.00</td>
<td>7.20</td>
<td>11.70</td>
<td>13.70</td>
<td>15.00</td>
<td>20.80</td>
<td>23.00</td>
<td>33.20</td>
<td>40.80</td>
<td>42.00</td>
<td>46.80</td>
<td>48.00</td>
</tr>
<tr>
<td>Sr</td>
<td>10^{-7}</td>
<td>1.45</td>
<td>1.99</td>
<td>3.32</td>
<td>3.52</td>
<td>3.38</td>
<td>3.86</td>
<td>3.86</td>
<td>4.60</td>
<td>4.90</td>
<td>5.00</td>
<td>6.00</td>
<td>7.40</td>
</tr>
<tr>
<td>Rb</td>
<td>10^{-7}</td>
<td>0.31</td>
<td>0.51</td>
<td>0.76</td>
<td>0.88</td>
<td>0.96</td>
<td>1.18</td>
<td>1.94</td>
<td>2.50</td>
<td>3.20</td>
<td>3.40</td>
<td>4.60</td>
<td>8.60</td>
</tr>
</tbody>
</table>
Fig. 1 Correlation between elements in the experimental leaching of the Margeride granite.
range of the ratio in minerals.
biotites. (Fig. 1-b)

**Mg/Li**  The ratio in solution is consistent with the ratio in biotite. Biotite is the main source for these two elements (Table 1). There is no significant fractionation between biotite and solution. The concept of stoichiometric dissolution (PLUMMER and THORSTENSON, 1977) is applicable in this case. (Fig. 1-a)

**K/Rb**  The K/Rb ratio in solution is intermediate between observed ratios in biotite and in feldspar. If we assume stoichiometric dissolution, we can calculate the relative amounts of biotites and K feldspar dissolved; about 30% of potassium comes from biotite. This result is in contradiction with the previous result on Mg/K. Biotite dissolution is not stoichiometric at the same time for both pairs Mg-K and Rb-K. (Fig. 1-c)

**Ca/Sr**  In contrast with Ca behaviour, the dissolved amount of Sr increases continuously. Then, the Ca/Sr ratio, which is very large ($\approx 10^3$) at the beginning of the dissolution experiment, decreases abruptly when Ca increase stops. Calcite and apatite, which are the main sources of Ca in the first step, may be very poor in strontium. In the second step, only plagioclase is dissolved. This dissolution results in an undetectable increase of Ca$^{2+}$ but a significative increase of Sr$^{2+}$ in the solution. (Fig. 1-d)

**K/Ba**  Little can be deduced from these measurements owing to the lack of sensitivity of analytical methods both for atomic absorption and ionic microprobe. Nevertheless, the amount of barium in different minerals is rather high and this element does not seem to go easily to solution.

The whole results show that dissolution of minor elements is not simple. The concept of stoichiometric dissolution, which is suggested by dissolution mechanism, is not applicable, at least to some granite minerals. BUSSENBERG (1978) gave similar conclusions after dissolution experiment of plagioclases. But a careful examination of his results shows that after a first step dominated by ion exchange, the dissolution behaves roughly as stoichiometric (BEAUCAIRE, 1981). Dissolution of strontium bearing gypsum and anhydrite (DENIS, in preparation) obeys a stoichiometric law. It is obvious that precise studies on the dissolution of each granite mineral are needed.

### Table 4. Chemical composition of Margeride spring waters.

<table>
<thead>
<tr>
<th>Springs n°</th>
<th>1</th>
<th>4</th>
<th>5</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>20</th>
<th>31</th>
<th>73</th>
</tr>
</thead>
<tbody>
<tr>
<td>t (°C)</td>
<td></td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>pH</td>
<td>6.02</td>
<td>6.27</td>
<td>6.35</td>
<td>6.50</td>
<td>6.09</td>
<td>6.59</td>
<td>5.85</td>
<td>6.22</td>
<td>6.22</td>
<td></td>
</tr>
<tr>
<td>Major elements ($10^{-3}$ M)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>10.7</td>
<td>7.84</td>
<td>12.3</td>
<td>6.97</td>
<td>8.49</td>
<td>11.0</td>
<td>7.99</td>
<td>6.07</td>
<td>16.9</td>
<td>12</td>
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<td>Cl$^-$</td>
<td>2.96</td>
<td>2.94</td>
<td>2.74</td>
<td>2.96</td>
<td>2.91</td>
<td>4.01</td>
<td>2.35</td>
<td>2.96</td>
<td>2.94</td>
<td>1.0</td>
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<td>SO$_4^{2-}$</td>
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<td>4.67</td>
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<td>2.34</td>
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<td>2.81</td>
<td>1.66</td>
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<td>Σ$^-</td>
<td>26.52</td>
<td>22.92</td>
<td>23.02</td>
<td>15.81</td>
<td>18.16</td>
<td>19.91</td>
<td>16.56</td>
<td>14.35</td>
<td>25.84</td>
<td>19.52</td>
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<td>Na$^+$</td>
<td>9.19</td>
<td>8.35</td>
<td>8.59</td>
<td>8.17</td>
<td>7.57</td>
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<tr>
<td>K$^+$</td>
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<td>0.57</td>
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<td>0.81</td>
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<td>Ca$^{2+}$</td>
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<td>2.43</td>
<td>5.23</td>
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<td>Mg$^{2+}$</td>
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<td>2.39</td>
<td>2.45</td>
<td>1.30</td>
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<td>2.14</td>
<td>1.21</td>
<td>1.48</td>
<td>2.91</td>
<td>1.75</td>
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<td>Σ$^+$</td>
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<td>22.96</td>
<td>23.12</td>
<td>15.16</td>
<td>18.84</td>
<td>19.75</td>
<td>17.13</td>
<td>14.42</td>
<td>27.05</td>
<td>20.16</td>
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<tr>
<td>H$_4$SiO$_4$</td>
<td>16.8</td>
<td>14.2</td>
<td>17.2</td>
<td>15.3</td>
<td>13.7</td>
<td>15.5</td>
<td>14.6</td>
<td>11.8</td>
<td>19.5</td>
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<td>Minor elements ($10^{-7}$ M)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rb$^+$</td>
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<td>0.32</td>
<td>0.28</td>
<td>0.17</td>
<td>0.16</td>
<td>0.32</td>
<td>0.11</td>
<td>0.18</td>
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<tr>
<td>Li$^+$</td>
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<td>1.28</td>
<td>1.40</td>
<td>0.90</td>
<td>1.34</td>
<td>1.70</td>
<td>1.20</td>
<td>1.65</td>
<td>3.25</td>
<td>0.75</td>
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<tr>
<td>Sr$^{2+}$</td>
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<td>2.40</td>
<td>2.40</td>
<td>1.50</td>
<td>1.56</td>
<td>1.90</td>
<td>0.98</td>
<td>1.40</td>
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<tr>
<td>Ba$^{2+}$</td>
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<td>0.49</td>
<td>0.23</td>
<td>0.47</td>
<td>0.37</td>
<td>0.17</td>
<td>0.43</td>
<td>0.55</td>
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Fig. 2 Correlation between concentrations of dissolved species in the spring water of Margeride.
MINOR ELEMENTS IN THE WATERS OF TRUYÈRE SPRINGS

Waters of about 20 springs were sampled for ten days in October 1978, for 13 days in May 1979, and sampled again in June 1980 and October 1980.

The springs are located at an elevation of about 1,420m near the central area of Margeride massif, in a place called “Le col des trois sœurs”.

On some spring waters, temperature and pH measurements and sampling have been performed every day during the time of the study. Major element analysis has been achieved on all samples, whereas minor elements were analysed only on some samples. Anions, silica, and ammonia measurements were performed every day in auxiliary laboratory. Cations (major and minor) were measured, using acidified and then filtered (0.1 m) samples, in the laboratory in Paris.

Typical results for different springs are given in Table 4.

General correlation

For discussion, we present, first, studies of the correlation between trace element and its associated major element.

(1) Magnesium and Lithium are not correlated in the Truyère waters. The amount of Li in spring waters is quite low, in comparaison with Li content of experimental solutions. (Fig. 2-a)

(2) Magnesium and Potassium are poorly related. The ratio of magnesium to potassium is generally higher in natural waters than in experimental solutions. (Fig. 2-b)

(3) Correlation between potassium and rubidium is rather good Fig. 2-c. The trend does not vary with time. The K/Rb ratio in the natural waters is very near the ratio of experimental leaching.

(4) Ca and Sr are well correlated for the whole analysis. (Fig. 2-d)

We can see some regular trend with time: between May 1979 and June 1980, we observe a significant increase in strontium concentrations, whereas calcium concentrations stay constant. In October 1980, we have an increase in Ca concentrations and not in Sr concentrations. This evidence is true for all the spring waters. The correlation straight line does not go through origin; the slope Ca/Sr is very different from the value in the dissolution experiment and is near the Ca/Sr ratio on plagioclases.

(5) K and Ba in spring waters are slightly correlated. The waters sampled after a rainfall are significantly more enriched in barium than the others.

The lack of a good correlation reveals the complexity of the process of supply of elements to the spring waters.

Several factors are involved in this process: 1 – input of dissolved elements by rain waters; 2 – origin of elements; 3 – exchange of ions with vegetation; 4 – fixation of trace elements by newly formed minerals

1. Input of dissolved elements by rain.

The sampling and analysis of rain waters are a difficult problem. Owing to their low concentrations, sampling of rain must be very careful. Moreover, the chemical composition of rain is largely variable from one rain to another, and even during the same rain. An automatic rain sampler proved to be unsatisfactory, because it does not resist to the weathering agents. The values obtained in this study are mainly analytical results of a mixed sample of rains collected in rain-gauge stations of St Denis en Margeride and Berthaldès, 8 kmW and 5 kme, respectively, from the Truyère springs.

An interesting insight of the influence of rain can be given by the daily sampling from May 18 to 30, 1979. Waters sampled on May 20 and 24 were collected after an important rainfall. The results of this study, initiated by IUNDT (unpublished) are summarized below.

The influence of rainfalls on the chemical composition of spring waters varies drastically from one spring to another. The composition of some springs is not affected by rainfalls, some other springs record the influence of all
Fig. 3 Concentration of some elements versus time. Arrow indicates rainfall days.
the rainfalls, and, at last, a few of them record the influence of only some rainfalls.

On Fig. 3 are represented daily variations of the concentrations of major and minor elements in spring #7, which is especially sensitive in its chemical composition to the influence of rainfalls.

After a rainfall, silica and sodium concentrations decrease. On the contrary, potassium concentration increases. The influence of rainwater on the concentrations of anions, calcium and magnesium is not definite. From the data for minor elements, we can see that:

- Lithium and strontium do not seem to be affected by rain, values for May 20 or 24 are not significantly different from values for other days.
- Rubidium behaviour is completely similar to potassium behaviour. The rubidium concentration increases after rains and the enrichment factor is about the same that of potassium; this explains why the K-Rb correlation is not affected by rain.
- Barium concentration increase after rainfall is significantly higher than potassium increase. It is the same for manganese. Rainwater analysis indicates that all these elements are very abundant in rainwaters, and especially in rain under forests. The origin of this enrichment is not clear. The importance of tree leaves is certainly high and is reflected by high concentrations of both K and Rb in rain waters sampled under forests.

2. Origin of elements

The leaching experiments above give us the first steps explaining the origin of elements dissolved in water during weathering process if natural and experimental conditions are comparable. Also in nature, we must take other parameters like vegetation or rainwaters into consideration.

Elements like Li have a simple behaviour; Li is closely associated with Mg in fresh rock micas and it was shown during leaching that biotite is the main source for Li and Mg, without significant fractionation. But in natural waters, Li is easily fixed in newly formed minerals.

Other elements like Rb and Sr have also a well defined origin. Rb is principally related to K in different potassic minerals (micas and potassic feldspars). Study of leaching showed us the major contribution of biotites during dissolution process. In leaching experiments and natural spring waters, we observe a similar Rb/K ratio according to a fractionation during biotite dissolution. We must also notice the influence of rainwaters under forest, on K and Rb.

Also Sr is principally associated with Ca in plagioclases, and we can postulate that plagioclase is the major origin of Sr. But understanding of Ca behaviour is more difficult. We observe in leaching a very high Ca/Sr ratio and in this case we must take into consideration the contribution of auxiliary minerals like calcite and apatite. Moreover, the Ca/Sr ratio is rather variable in spring waters (see Fig. 2-d) and we must note that Ca/Sr ratio in leaching is higher than in spring waters. The observed correlation can be related either to the contribution of auxiliary minerals (only Ca without Sr) or to the fractionation between Ca and Sr during an uptake of dissolved elements by minerals. Though the Ca/Sr ratios in spring waters and plagioclases are comparable, we can consider in spring waters the contribution of auxiliary minerals, that is more important in leaching. The lower concentration of Ca can be explained by the dissolution of auxiliary minerals during earlier weathering of natural net-work.

In order to explain this correlation, Ca-Sr, $^{87}$Sr/$^{86}$Sr isotopic ratios are measured in minerals, leaching and natural waters. The isotopic ratio in waters are all in the range from 0.7113 to 0.7119, whereas rock leaching gives a value of 0.714 and feldspars 0.718. It appears first that this 0.711 isotopic ratio is common for granitic natural waters.

Moreover, it has been shown (Dash, 1969; Brass, 1975) that isotopic fractionation occurs during weathering process. Then it is difficult to use Sr isotopes to reveal Sr behaviour during this process. We cannot trace further the
origin of Ca in natural waters and evaluate the contribution of auxiliary minerals.

The behaviour of elements like Ba are very difficult to understand. It goes very slowly in solution and it is very easily removed from solution by weathering products. (Mac Laughlin, 1957)

3. Influence of vegetation

The uptake of soluble elements by plants is important for the chemical composition of spring water (Crozat, 1979). This influence is discussed here, because some waters spring under forests, whereas some others emerge in meadows.

The effects of forest cutting on nutrient budgets in watersheds have been studied by Likens et al. (1969). We also observe in Margeride that NO$_3^-$ is produced here by plant root bacteria and can be considered to be a “basic” ion related to an acide which attacked the parent rock, as did CO$_2$. Thus, the sum HCO$_3^-$ + NO$_3^-$ represents the amount of cations dissolved from the minerals of the rock. Therefore, we can compare compositions of spring 1 (meadow) and 31 (forest): the sums HCO$_3^-$ + NO$_3^-$ for these two springs are similar, but the concentration of NO$_3^-$ represents about half of the total for spring 1, and only 12% for spring 31. The concentrations of cations are about the same in the two springs. This shows that the nature of the vegetation has little influence on the relative concentrations of dissolved cations. It seems that it is also true for minor elements, except Li$^+$ which is definitely more abundant in the spring in the forest area.

The ratios of elements in leaves or in pine needles are representative of the ratios of uptake by the roots of the trees. Since elements with similar chemical properties, such as K and Rb, Ca and Sr, are known to be not fractionated by this uptake process (R. Heller, comm. pers.), our attention was focused on the K/Mg ratio: the ratio varies between 1.25 and 1.35 in the different samples of pine needles. This ratio is higher than the K/Mg ratio in biotites and in waters. Vegetation is a possible sink for dissolved potassium.

4. Fixation of minor elements by weathering minerals

The observation of soil profile shows the occurrence of mixed layer clay minerals: illite, chlorite, vermiculite and kaolinite (Sarazin, 1979). These minerals, except probably kaolinite, result from the degradation of biotite. A study on dissolved Al$^{3+}$ (Sarazin et al., 1976) and Fe$^{3+}$ (Jundt, unpublished) shows that spring waters are in equilibrium with low crystalline kaolinite and goethite. Dissolved ions are trapped in some of these minerals. This is particularly the case of K$^+$ (Millot, 1963; Nesbitt et al., 1980). Fixation of lithium into kaolinite has been described by Vlassov (1966) as very common. Nesbitt et al. show that rubidium is not evacuated from the weathered zones of a soil profile and, therefore, is strongly adsorbed on weathering minerals.

In the same way, Mac Laughlin (1957) studies the location of trace elements in weathering minerals and indicates that clay minerals have low Mg/Li and K/Ba ratios.

It is difficult to assess fixation of both major and minor elements on minerals from the results of water analysis. Nevertheless, it seems that this mode of removal of elements is important. The lack of correlation between Li and Mg in spring waters can be explained by a preferential trapping of Li in newly formed minerals. The large variations of potassium from one spring to another, compared with the rather small variations of sodium and silica can be explained more easily by an uptake of potassium by vegetation of weathering minerals than by a drastic change in the rate of biotite dissolution. This is also true, at a lesser extent, for calcium and magnesium. And it is well known that sodium is not easily uptaken by either vegetables or minerals.

CONCLUSION

The behaviour of trace elements during the dissolution of granitic minerals by meteoric
Origin of dissolved minor elements

water is rather complex. Fractionation between a trace element and its associated major element can be considered as the result of, at least three different processes.

1—Partition occurring during the dissolution of a mineral i.e incongruent or non stoichiometric dissolution. It can be the case for K and Rb in micas, where the dissolution is associated with an exchange of the exchangeable cations.

2—Differences in the rate of dissolution of two or more minerals containing the same major element. For instance Ca and Sr come from plagioclase (with low Ca/Sr ratio) and from important accessory minerals with high Ca/Sr ratio) and from important accessory minerals with high Ca/Sr ratio (apatite, calcite). The Ca/Sr ratio in water reflects the relative amounts of minerals dissolved by this water.

3—Deposition or trapping of the trace element in newly formed minerals: this is experimental dissolutions give a Mg/Li ratio similar to the ratio in biotite; but Mg/Li is far greater in natural waters.

Moreover inputs of trace or major elements by rainwater and vegetation are important (especially for K and Rb), as well as outputs in vegetation.

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