Contrasting alteration processes in hydrothermally altered dolerites from the Betic Cordillera, Spain

J. JIMÉNEZ-MILLÁN1,*, I. ABAD1 AND F. NIETO2

1 Departamento de Geología, Universidad de Jaén, 23071 Jaén, Spain, and 2 Departamento de Mineralogía y Petrología and IACT, Universidad de Granada-CSIC, 18002 Granada, Spain

(Received 26 September 2007; revised 21 January 2008)

ABSTRACT: Dolerites from the Sierra de San Pedro (Betic Cordillera, south Spain) develop three main types of microsystems during hydrothermal alteration: (1) centimetre-sized veins cross-cutting the dolerites; (2) microfractures in feldspar and diopside grains; and (3) alterations involving primary-igneous mafic phyllosilicate grains. The vein and microfracture sites developed alteration assemblages of randomly oriented smectites (saponite and beidellite) and halloysite. At these sites, the alteration mechanism was governed by complete dissolution of the parent material with subsequent crystallization of the products, with no parent-mineral crystallographic control. Pseudomorphed mafic phyllosilicate sites are characterized by oriented complex mineral assemblages made of chlorite, chlorite/smectite mixed layers, corrensite, saponite and relics of biotite. These assemblages formed during the initial high-temperature stage of the hydrothermal process. In these microsites, the alteration sequence was controlled by the parent-mineral structure and chemistry with products determined by structural relations with the parent phyllosilicate. Alteration of one phyllosilicate to the next most-stable proceeds via interstratification of the parent and product phyllosilicates.

KEYWORDS: pseudomorphed biotite, interstratification, microfractures, fluid circulation, dissolution.

Cracks in rocks are a common cause of hydrothermal alteration in a variety of rock types and these conduits are likely to affect alteration rates and products. Fluid access to minerals determines the extent to which distinct mineral-chemical microsystems can operate during alteration. As a result, the mineralogy and chemistry of the products from open-conduit systems can be completely different from the products of internal mineral alterations, which are generally characterized by secondary pseudomorphs after the primary minerals.

It is primarily the structure and composition of the parent material and the fluid characteristics in hydrothermal systems that control the various alteration mechanisms and alteration products. Low-temperature alteration of phyllosilicates commonly develops along layer replacements where the structure and orientation of the products can be inherited from the parent phyllosilicate (Ahn & Peacor, 1987; Banfield & Eggleton, 1988; Dong et al., 1998; Jiang & Peacor, 1991; Banfield & Murakami, 1998), although dissolution-neocrystallization has also been proposed for the formation of the alteration products (see Banfield & Murakami, 1998 for example). In the alteration of other silicates, regardless of the parent mineral and alteration product, the predominant mechanism described is dissolution/precipitation, where the

* E-mail: jmillan@ujaen.es
DOI: 10.1180/claymin.2008.043.2.09

© 2008 The Mineralogical Society
precipitated clay mineral or hydroxide bears no crystallographic relation to the reactant (Eggleton, 1986). The defect state of the parent material affects alteration in providing pathways for fluids (Sheets & Tettenhorst, 1997).

The intrusion of subvolcanic bodies in the Subbetic Zone of the Betic Cordillera during the Jurassic generated hydrothermal systems that produced intense alteration of the igneous and sedimentary host materials. The development of a fabric with macro- and micro-veins as well as the diversity of the mineralogical composition of the parent rocks has provided a unique environment to carry out a study on the alteration mechanisms of a variety of minerals during the evolution of a hydrothermal system. X-ray diffraction (XRD), optical microscopy and scanning and transmission electron microscopy (SEM and TEM) have been used to characterize reactant and product phases, and to compare the processes of hydrothermal alteration in minerals of diverse structure and composition.

GEOLOGICAL SETTING

The Betic Cordillera (southern Spain) is the westernmost European Alpine chain (Fig. 1a). The External Zones (Prebetic and Subbetic) of this cordillera are mainly composed of sedimentary rocks deposited from the Triassic to the early Miocene on the south Iberian continental margin (Vera et al., 1997). The Subbetic Zone corresponds to a part of the margin in which early Jurassic pelagic facies dominated. Four palaeogeographic domains can be observed in this zone in the middle and late Jurassic, although Jurassic igneous activity appears only in the Median Subbetic (Portugal et al., 1995; Vera et al., 1997; Molina & Vera, 1999). The composition of the igneous rocks is mafic, with a transitional-alkaline affinity (Portugal et al., 1995). Radiometric dating shows maximum igneous activity from 170 to 155 Ma (Portugal et al., 1995; Vera et al., 1997), coinciding with the main phase of intracontinental rifting of the South Iberian continental margin. Although basalts with pillow-lava flows dominate, some subvolcanic intrusive dykes, sills and laccoliths are also found. The host rock generally corresponds to the Zegri Formation, which consists of Domerian to Bathonian limestone and marl rhythmites (Molina & Vera, 1999). The volcanic edifices are overlain by oolitic limestones deposited on isolated shallow-marine carbonate platforms interpreted as guyots (Vera et al., 1997; Molina & Vera, 1999). The Zegri Formation also contains local intrusive bodies of stratiform dolerites 60–100 m thick which originated during the most active phases of Subbetic volcanism (Aalenian–Bajocian). These bodies crop out in small areas (a few square kilometres) and produced contact metamorphism in the host rocks. One of the best examples lies in the Sierra de Priego de Córdoba (Abad et al., 2003). This work focuses on a contemporaneous intrusive body in the surroundings of the Sierra de San Pedro (Molina & Vera, 2000), located in the province of Jaén (south Spain) (Fig. 1b), where the intrusion covers an area of 5 km² with a maximum thickness of 100 m. The stratiform dolerites intrude between Aalenian and Bajocian rocks of the Zegri Formation. The samples were collected from a
laccolith profile of dolerite facies from the Sierra de San Pedro containing plagioclase, diopside, olivine and biotite as components of the original, unaltered dolerite assemblage. Here, the intrusion is strongly brecciated and crosscut by a network of fractures filled by greenish phyllosilicates. Samples were taken from fissures in the dolerite filled with phyllosilicates and also from the altered dolerite in contact with the fractures (Fig. 2a). As shown in Figs 2a and 2b, the cracks are filled with a pale-green material which is soft and smooth to the touch, as well as a white calcareous material.

**ANALYTICAL METHODS**

Samples were studied by optical microscopy, XRD, SEM (with an energy dispersive X-ray (EDX) microanalyser), electron microprobe (EMP), and high-resolution and analytical electron microscopy (HRTEM/AEM).

The XRD data were obtained from powders and oriented aggregates (whole-rock samples and <2 μm fraction) with two different diffractometers: (1) a Philips 1710 powder diffractometer with Cu-Kα radiation, a graphite monochromator and automatic divergence slit (Universidad de Granada); and (2) a Siemens D-5000 diffractometer using Cu-Kα radiation (Universidad de Jaén). Dry samples were scanned from 3º to 62°2θ and glycolated samples were scanned from 2º to 30°2θ to corroborate the identification of expandable clays.

The SEM study was performed on polished samples with a JEOL 5800 SEM equipped with a Link Isis microanalyser at 20 kV (Universidad de Jaén). Observations were made using backscattered-electron images (BSE) in the atomic-number contrast mode.

Mineral compositions were determined using a JEOL 8600 Superprobe automated EMP with four wavelength-dispersive spectrometers (WDS) and one energy-dispersive spectrometer (EDS) from Tracor Northern (Noran) TN 5500 (Johns Hopkins University). The EMP was operated under the following conditions: accelerating voltage 15 kV, probe current 20 nA and electron beam diameter <5 μm. The following compounds were used as calibration standards: albite, orthoclase, anorthite, enstatite, rhodonite, anatase and fayalite. Data correction was performed with the CITZAF programme (Armstrong, 1989).

The HRTEM studies were carried out with a Philips CM20 (STEM) operating at 200 kV (Centro de Instrumentación Científica, C.I.C., Universidad de Granada). The point-to-point resolution was 2.7 Å in the TEM mode and 50 Å in the STEM mode. Copper rings were attached to representative areas of the thin sections. These areas were detached through gentle heating and further thinned with a Gatan dual ion mill. Chemical analyses of particles were obtained from thin edges in the STEM mode with an EDAX microanalysis system. A (200 × 1000 Å) scanning area with the long axis oriented parallel to the phyllosilicate packets was used for each analysis with a 50 Å beam diameter. Counting times of 200 s were used except for Na and K, which were analysed using 30 s counting times. Albite, olivine, biotite, spessartine, muscovite, chlorite and titanite were used to obtain K-factors for transformation of intensity ratios to concentration ratios according to the Cliff & Lorimer (1975) approximation.

**Fig. 2.** (a) Altered dolerite with fractures filled by pale-green phyllosilicates. A lithic fragment is indicated the arrow. (b) Detail of a fracture filled by calcite (white) and phyllosilicates (green).
MINERALOGY AND PETROGRAPHY

We studied samples from: (1) the fracture network which crosscuts the doleritic outcrop and is filled with greenish phyllosilicates; and (2) the altered dolerite in contact with these fissures.

XRD data

Material filling the dolerite fractures. Although feldspars (plagioclase and K-feldspar) and calcite can be found, the main phases are phyllosilicates. Pale-green material filling the fractures have XRD patterns of oriented aggregates showing mainly expandable phases, with a basal spacing of $\sim$15.56 Å which expands to 16.74 Å after ethylene glycol treatment (Fig. 3a). This is characteristic behaviour of smectite, caused by non-uniform basal distances, presumably related to the presence of variable amounts of interlayer water molecules. The XRD patterns of the random powder samples show that the smectite is dominantly trioctahedral in nature with a reflection located at 1.53 Å.

Altered dolerite. In the samples of altered dolerite in contact with the green phyllosilicate-filled fractures, the XRD patterns of oriented aggregates (Fig. 3b) reveal the presence of corrensite, smectite, plagioclase, K-feldspar and diopside. The corrensite is characterized by a basal spacing of 30.46 Å and the different orders of the diffraction (00l) define spacings that can be considered as coherent, with the smectite and chlorite layers forming an ordered interstratification of corrensite. Smectite has a basal spacing of 14.88 Å that expands to 16.37 Å after ethylene-glycol treatment. Furthermore, the presence of a wide peak at 1.53 Å and a weak diffuse peak at 1.49 Å in the XRD patterns of the random powder samples reveals that, although trioctahedral smectites dominate, dioctahedral smectites are also present.

Optical microscopy, SEM and TEM characterization

Material filling the dolerite fractures. Fractures are filled by randomly oriented smectite of saponitic composition (Table 1) with a Mg content (up to 1.84 a.p.f.u.) always greater than the Fe content (up to 1.11 a.p.f.u.). Relics of lithic fragments (up to 40 cm) of altered dolerite can be identified inside the fissures (Fig. 2b).

Altered dolerite. The BSE images show that grains of labradorite, K-feldspar, albite, diopside, mafic phyllosilicates, Fe and Ti oxides, and apatite seem to develop a fine-grained hypidiomorphic

![Fig. 3. XRD patterns of air-dried (AD) and ethylene glycol (EG) solvated materials: (a) sample of material filling the dolerite fractures; (b) sample from the altered dolerite.](image-url)
equigranular texture, which suggests they are associated with the dolerite igneous assemblages (Figs 4a and 4b). However, the original igneous texture of dolerite is difficult to observe because it is highly-altered and grains are intensely cracked and crosscut by a network of greenish-brown phyllosilicate veins. Alteration products are found in a variety of textural microsites including veins (Figs 4b and 4c) and altered grains of diopside (Fig. 4d), feldspars (Fig. 4e) and pseudomorphed mafic phyllosilicates (Figs 4e and 4f).

Different observations have been made of these microsites:

(1) Vein materials. Optical microscopy and BSE images show that, in general, microveins are present throughout the samples, giving the texture a certain chaotic appearance. This network of veins crosscutting the igneous matrix is filled with phyllosilicates. Smectite aggregates dominate, consisting of up to 1 mm randomly-oriented flakes (Fig. 4c). Some unreacted fragments of diopside and feldspars can be observed within the smectite aggregates (Figs 4b and 4c). The low-magnification TEM images of the altered doleritic material also show the typical texture of the smectitic phases at the nanometre scale, forming aggregates of bent and unoriented packets that coalesce or open (Fig. 5). However, trioctahedral and dioctahedral smectite species are texturally indistinguishable in the TEM images. Compositionally, EMP and AEM analyses reveal that saponite is the dominant phyllosilicate in the veins. Saponite composition is characterized by an interlayer charge of up to 0.3 a.p.f.u. and the predominance of Ca. However, smectite analyses with intermediate compositions between the theoretical values of saponite and beidellite were also obtained (Table 2, analyses 4 and 5). Beidellitic

Table 1. Representative analyses of smectites normalized to O$_{10}$(OH)$_2$ in the centimetric fractures crosscutting the dolerite.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>$^{IV}$Al</th>
<th>$^{V}$Al</th>
<th>Mg</th>
<th>Fe</th>
<th>$^{VI}$Σ</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Σinter.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>3.44</td>
<td>0.56</td>
<td>0.31</td>
<td>1.41</td>
<td>1.11</td>
<td>0.00</td>
<td>2.84</td>
<td>0.00</td>
<td>0.01</td>
<td>0.28</td>
</tr>
<tr>
<td>2*</td>
<td>3.32</td>
<td>0.68</td>
<td>0.43</td>
<td>1.50</td>
<td>0.97</td>
<td>0.00</td>
<td>2.90</td>
<td>0.01</td>
<td>0.01</td>
<td>0.20</td>
</tr>
<tr>
<td>3**</td>
<td>3.34</td>
<td>0.66</td>
<td>0.42</td>
<td>1.52</td>
<td>0.99</td>
<td>0.01</td>
<td>2.94</td>
<td>0.03</td>
<td>0.08</td>
<td>0.09</td>
</tr>
<tr>
<td>4**</td>
<td>3.39</td>
<td>0.61</td>
<td>0.41</td>
<td>1.50</td>
<td>0.97</td>
<td>0.01</td>
<td>2.89</td>
<td>0.03</td>
<td>0.01</td>
<td>0.18</td>
</tr>
<tr>
<td>5**</td>
<td>3.43</td>
<td>0.47</td>
<td>0.46</td>
<td>1.84</td>
<td>0.69</td>
<td>0.01</td>
<td>3.00</td>
<td>0.03</td>
<td>0.01</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Total Fe considered as Fe$^{2+}$.
* EMPA analyses
** AEM analyses

Table 2. Representative analyses of smectites normalized to O$_{10}$(OH)$_2$ in the microveins of the altered dolerite.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>$^{IV}$Al</th>
<th>$^{V}$Al</th>
<th>Mg</th>
<th>Fe</th>
<th>$^{VI}$Σ</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Σinter.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>3.19</td>
<td>0.81</td>
<td>0.55</td>
<td>1.85</td>
<td>0.58</td>
<td>2.98</td>
<td>0.00</td>
<td>0.00</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>2*</td>
<td>3.35</td>
<td>0.65</td>
<td>0.56</td>
<td>1.59</td>
<td>0.63</td>
<td>2.79</td>
<td>0.01</td>
<td>0.00</td>
<td>0.24</td>
<td>0.25</td>
</tr>
<tr>
<td>3*</td>
<td>3.33</td>
<td>0.67</td>
<td>0.64</td>
<td>1.55</td>
<td>0.59</td>
<td>2.78</td>
<td>0.01</td>
<td>0.00</td>
<td>0.22</td>
<td>0.24</td>
</tr>
<tr>
<td>4**</td>
<td>3.85</td>
<td>0.15</td>
<td>0.68</td>
<td>1.47</td>
<td>0.50</td>
<td>2.65</td>
<td>0.00</td>
<td>0.00</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>5**</td>
<td>3.58</td>
<td>0.42</td>
<td>0.82</td>
<td>1.44</td>
<td>0.44</td>
<td>2.71</td>
<td>0.00</td>
<td>0.00</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>6**</td>
<td>3.77</td>
<td>0.23</td>
<td>1.97</td>
<td>0.05</td>
<td>0.02</td>
<td>2.04</td>
<td>0.00</td>
<td>0.06</td>
<td>0.05</td>
<td>0.11</td>
</tr>
<tr>
<td>7**</td>
<td>3.90</td>
<td>0.10</td>
<td>1.85</td>
<td>0.12</td>
<td>0.05</td>
<td>2.03</td>
<td>0.00</td>
<td>0.07</td>
<td>0.03</td>
<td>0.10</td>
</tr>
<tr>
<td>8**</td>
<td>3.49</td>
<td>0.51</td>
<td>1.94</td>
<td>0.14</td>
<td>0.09</td>
<td>2.17</td>
<td>0.00</td>
<td>0.05</td>
<td>0.05</td>
<td>0.10</td>
</tr>
<tr>
<td>9**</td>
<td>3.91</td>
<td>0.09</td>
<td>1.73</td>
<td>0.21</td>
<td>0.09</td>
<td>2.02</td>
<td>0.00</td>
<td>0.15</td>
<td>0.03</td>
<td>0.18</td>
</tr>
<tr>
<td>10**</td>
<td>3.68</td>
<td>0.32</td>
<td>1.90</td>
<td>0.10</td>
<td>0.09</td>
<td>2.09</td>
<td>0.00</td>
<td>0.08</td>
<td>0.03</td>
<td>0.11</td>
</tr>
</tbody>
</table>

1 to 5: saponite analyses; 6 to 10: beidellite analyses.
* EMPA analyses
** AEM analyses
Fig. 4. BSE images showing the different textural microsites occupied by alteration products: (a) and (b) textural appearance of the altered dolerite; (c) segment of a vein (see arrows) filled with aggregates of smectite around fragments of diopside; (d) altered and very fractured grains of diopside; (e) and (f) examples of pseudomorphed mafic phyllosilicates (PMP) in the altered dolerite. Mineral abbreviations according to Kretz (1983). Sm: smectite.
Smectites were analysed by AEM and have interlayer contents <0.2 a.p.f.u. with K slightly greater than Ca.

(2) Diopside. BSE images show diopside crystals (Si$_{1.92}$O$_6$Al$_{0.20}$Fe$_{0.22}$Mg$_{0.75}$Ti$_{0.03}$Mn$_{0.01}$Ca$_{0.8}$Na$_{0.02}$) with cracks along the cleavages planes (Fig. 4c). Consequently, initial alteration is apparently cleavage-controlled. However, diopside is also replaced by fine-grained saponite (Table 3) along irregular veinlets (Fig. 4d).

(3) Feldspars. At the SEM scale, prismatic grains of labradorite with an internally fractured network are commonly observed. Smaller albite crystals are included in labradorite, whereas K-feldspars in general are unaltered (Figs 4a and 4b).

The TEM images of smectite in direct contact with feldspar grains can be observed. Figure 6 shows that smectite packets from a randomly orientated aggregate are partly bent, wrapping around K-feldspar crystal surfaces. At high resolution, these smectites develop packets of 10 Å layers with some fissures probably promoted by the high-vacuum conditions (Fig. 7). Some high-resolution images, taken close to plagioclase crystals, show slightly bent 10 Å-spaced lattice fringes sometimes intergrown with 20 Å-spaced layers (probably

Table 3. Representative analyses of smectites normalized to O$_{10}$(OH)$_2$ and halloysites normalized to O$_{10}$(OH)$_8$ in microfractures of diopside and feldspar.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>$^{IV}$Al</th>
<th>$^{VI}$Al</th>
<th>Mg</th>
<th>Fe</th>
<th>$^{VI}$Σ</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Σinter.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>3.13</td>
<td>0.87</td>
<td>0.31</td>
<td>1.41</td>
<td>1.23</td>
<td>2.96</td>
<td>0.02</td>
<td>0.01</td>
<td>0.31</td>
<td>0.33</td>
</tr>
<tr>
<td>2**</td>
<td>3.67</td>
<td>0.33</td>
<td>0.60</td>
<td>1.63</td>
<td>0.55</td>
<td>2.78</td>
<td>0.00</td>
<td>0.00</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>3**</td>
<td>3.83</td>
<td>0.17</td>
<td>0.70</td>
<td>1.47</td>
<td>0.49</td>
<td>2.66</td>
<td>0.00</td>
<td>0.00</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>4**</td>
<td>3.73</td>
<td>0.27</td>
<td>0.79</td>
<td>1.55</td>
<td>0.41</td>
<td>2.75</td>
<td>0.01</td>
<td>0.00</td>
<td>0.10</td>
<td>0.11</td>
</tr>
<tr>
<td>5**</td>
<td>3.84</td>
<td>0.16</td>
<td>1.87</td>
<td>0.05</td>
<td>0.05</td>
<td>1.97</td>
<td>0.10</td>
<td>0.09</td>
<td>0.05</td>
<td>0.24</td>
</tr>
<tr>
<td>6**</td>
<td>3.85</td>
<td>0.15</td>
<td>1.87</td>
<td>0.05</td>
<td>0.03</td>
<td>1.96</td>
<td>0.19</td>
<td>0.07</td>
<td>0.03</td>
<td>0.29</td>
</tr>
<tr>
<td>7**</td>
<td>4.03</td>
<td>0.00</td>
<td>3.79</td>
<td>0.09</td>
<td>0.11</td>
<td>3.99</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8**</td>
<td>3.88</td>
<td>0.12</td>
<td>3.76</td>
<td>0.09</td>
<td>0.23</td>
<td>4.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9**</td>
<td>3.95</td>
<td>0.05</td>
<td>3.79</td>
<td>0.14</td>
<td>0.14</td>
<td>4.06</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10**</td>
<td>4.03</td>
<td>0.00</td>
<td>3.68</td>
<td>0.18</td>
<td>0.18</td>
<td>4.03</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1 and 2: saponite analyses in diopside microfractures; 3 and 4: saponite in feldspar microfractures; 5 and 6: beidellite in feldspar microfractures; 7 to 10: halloysite in feldspar microfractures.

* EMP analyses
** AEM analyses
illite, since this type of polytype has not been described for smectite) (Fig. 8). The SAED pattern (Fig. 8, inset) corroborates the variable orientation of these packets. AEM analyses of smectite filling feldspar fissures reveal the presence of Mg-rich smectites with Ca in the interlayer and Al-rich smectites with a Na interlayer content between 0.1 and 0.2 a.p.f.u. and K and Ca in lesser amounts (Table 3), as well as smectite analyses with intermediate composition between saponite and beidellite.

Spheres with diameters from 500 Å to ~1000 Å (Fig. 9) that experienced rapid damage under the electron beam occur in altered plagioclase. The SAED patterns from these layers reveal 7.4 Å periodicity and kaolinite-like chemical analyses slightly Fe-enriched (Table 3). The spherical material is very similar to spherical halloysite reported by Dixon & McKee (1974), Robertson & Eggleton (1991), Singh & Gilkes (1992), and Huertas et al. (2004). Hence, on the basis of the material morphology, chemical composition and SAED pattern, it is interpreted as spherical halloysite.

**Pseudomorphs of mafic phyllosilicates.** At the optical microscope scale, brown, weakly pleochroic, hypidiomorphic phyllosilicate crystals up to 1 mm in size are observed. Most of the grains develop wide spaces between cleavage planes and may be internally folded or broken. These grains contain alternating domains with different birefringence. Such features suggest they were original igneous grains of biotite now affected by alteration. Small elongated grains of rutile and Fe-oxides were found within and surrounding partially-altered igneous biotite grains.

In the BSE images, different grey bands can commonly be distinguished inside the altered biotite (Figs 4e and 4f), producing a broad compositional variation in the EMP results. Microanalyses are always Fe- and Mg-enriched and there are significant differences in the K, Ti and Si contents. The K- and Ti-rich compositions from brighter bands can be normalized to $\text{O}_{10}(\text{OH})_2$, producing structural formulae with octahedral cations close to 3 and interlayer contents up to 0.7 a.p.f.u., close to
the composition of a trioctahedral mica such as biotite (Table 4, analyses 1 and 2). Some bright zones produce Fe-rich analyses whose normalization to O10(OH)8 results in structural formulae in the range of those commonly observed for chlorite, with a sum of octahedral cations near 6 and small interlayer cation contents (Table 4, analyses 3 and 4). Darker areas provide two types of Mg-rich analyses. Some of these analyses can be correctly normalized to O10(OH)2, producing structural formulae similar to those of the saponite-filling veins. However, the best normalization for some of these analyses is obtained considering 50 charges (the sum of smectite and chlorite), which produces a sum of octahedral cations near 9, which is close to the ideal composition of an interstratified trioctahedral chlorite/smectite (Table 4, analyses 5 to 11). The sum of the structural formulae of the average saponite with the average chlorite from these grains produces structural formulae in the range of the interstratified mineral phases obtained in this study. A great number of the EMP analyses obtained can be interpreted as mixtures of the phyllosilicates that form these grains.

The TEM lattice-fringe images corroborated the existence of complex intergrowths of phyllosilicates in partially- and largely-altered mafic pseudomorphs. Figure 10 shows some areas with a predominance of 10 Å periodicity produced by the presence of collapsed smectite and layers of relict biotite relicts normalized to O10(OH)2; 3 and 4: chlorites normalized to O10(OH)6; 5 to 11: chlorite/smectite mixed layers normalized to O20(OH)10; 12 to 15: saponites normalized to O10(OH)2.

** EMP analyses

** AEM analyses

Table 4. Representative analyses of clay minerals in pseudomorphed mafic phyllosilicate grains.

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>IV Al</th>
<th>VAl</th>
<th>Mg</th>
<th>Fe</th>
<th>Ti</th>
<th>V1Σ</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Σinter.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1*</td>
<td>2.82</td>
<td>1.18</td>
<td>0.00</td>
<td>1.12</td>
<td>1.63</td>
<td>0.27</td>
<td>3.02</td>
<td>0.02</td>
<td>0.56</td>
<td>0.03</td>
<td>0.61</td>
</tr>
<tr>
<td>2*</td>
<td>2.90</td>
<td>1.09</td>
<td>0.00</td>
<td>1.59</td>
<td>1.01</td>
<td>0.32</td>
<td>2.91</td>
<td>0.07</td>
<td>0.47</td>
<td>0.07</td>
<td>0.61</td>
</tr>
<tr>
<td>3*</td>
<td>3.26</td>
<td>0.74</td>
<td>0.58</td>
<td>2.29</td>
<td>3.05</td>
<td>0.05</td>
<td>5.97</td>
<td>0.01</td>
<td>0.01</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>4*</td>
<td>3.38</td>
<td>0.62</td>
<td>0.85</td>
<td>1.70</td>
<td>3.20</td>
<td>0.01</td>
<td>5.75</td>
<td>0.01</td>
<td>0.14</td>
<td>0.04</td>
<td>0.19</td>
</tr>
<tr>
<td>5*</td>
<td>6.43</td>
<td>1.57</td>
<td>0.94</td>
<td>4.64</td>
<td>3.57</td>
<td>0.01</td>
<td>9.17</td>
<td>0.01</td>
<td>0.07</td>
<td>0.09</td>
<td>0.17</td>
</tr>
<tr>
<td>6*</td>
<td>6.57</td>
<td>1.43</td>
<td>1.36</td>
<td>3.85</td>
<td>3.64</td>
<td>0.00</td>
<td>8.85</td>
<td>0.04</td>
<td>0.04</td>
<td>0.14</td>
<td>0.22</td>
</tr>
<tr>
<td>7*</td>
<td>6.56</td>
<td>1.44</td>
<td>1.26</td>
<td>4.52</td>
<td>2.85</td>
<td>0.03</td>
<td>8.67</td>
<td>0.02</td>
<td>0.03</td>
<td>0.36</td>
<td>0.41</td>
</tr>
<tr>
<td>8**</td>
<td>6.19</td>
<td>1.81</td>
<td>1.99</td>
<td>1.71</td>
<td>5.21</td>
<td>0.00</td>
<td>8.91</td>
<td>0.01</td>
<td>0.01</td>
<td>0.03</td>
<td>0.05</td>
</tr>
<tr>
<td>9**</td>
<td>5.88</td>
<td>2.12</td>
<td>2.05</td>
<td>2.17</td>
<td>4.81</td>
<td>0.00</td>
<td>9.04</td>
<td>0.03</td>
<td>0.01</td>
<td>0.06</td>
<td>0.10</td>
</tr>
<tr>
<td>10**</td>
<td>6.31</td>
<td>1.69</td>
<td>1.04</td>
<td>5.16</td>
<td>2.26</td>
<td>0.43</td>
<td>8.45</td>
<td>0.01</td>
<td>0.02</td>
<td>0.04</td>
<td>0.07</td>
</tr>
<tr>
<td>11**</td>
<td>6.16</td>
<td>1.84</td>
<td>1.44</td>
<td>3.23</td>
<td>4.53</td>
<td>0.00</td>
<td>9.20</td>
<td>0.02</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
</tr>
<tr>
<td>12**</td>
<td>3.25</td>
<td>0.75</td>
<td>0.38</td>
<td>1.33</td>
<td>0.81</td>
<td>0.30</td>
<td>2.81</td>
<td>0.00</td>
<td>0.07</td>
<td>0.04</td>
<td>0.11</td>
</tr>
<tr>
<td>13**</td>
<td>3.14</td>
<td>0.86</td>
<td>0.36</td>
<td>1.38</td>
<td>0.84</td>
<td>0.30</td>
<td>2.88</td>
<td>0.00</td>
<td>0.06</td>
<td>0.04</td>
<td>0.10</td>
</tr>
<tr>
<td>14**</td>
<td>3.65</td>
<td>0.35</td>
<td>0.62</td>
<td>1.02</td>
<td>0.69</td>
<td>0.25</td>
<td>2.58</td>
<td>0.00</td>
<td>0.04</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>15**</td>
<td>3.39</td>
<td>0.61</td>
<td>0.48</td>
<td>1.21</td>
<td>0.76</td>
<td>0.30</td>
<td>2.75</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Total Fe considered as Fe2+

Fig. 10. Lattice-fringe image of an altered mafic pseudomorph. Some areas show predominance of 10 Å periodicity (collapsed smectite and layers of relict biotite in coherence with AEM data, Table 4: analyses 12–15). Contrast differences, several dark fringes and one light fringe, produce stacking sequences (see arrow) of 40 Å or more. The SAED pattern shows streaking along c* in addition to the 10 Å periodicity.
biotite. In detail, there are contrast differences (see arrow): several dark fringes and one light fringe, which initiate stacking sequences due to super-periodicities of 40 Å or more. The AEM analyses from these areas with 10 Å periodicity indicate the presence of Mg-rich smectites with Ti contents of ~0.2–0.3 a.p.f.u. (Table 4, analyses 12 to 15).

In some areas, thin and discontinuous packets showing 10 Å or 14 Å periodicities may be recognized. They do not present clear boundaries and are surrounded by poorly crystalline material (Fig. 11). The AEM data from these packets show deviations from pure chlorite with small contents of octahedral elements and compositions corresponding to different degrees of smectite contamination. The structural formulae from these analyses adjusted to 50 charges are close to a mixture of both phases (Table 4, analyses 8 to 11).

In some lattice-fringe images, a random sequence of chlorite and smectite layers is observed. Figure 12 shows that 14 Å and 10 Å layers form some packets of an ordered interstratified phase of 24 Å layers identified as corrensite. In general, the proportion of 14 Å layers is slightly greater than the proportion of 10 Å layers. The AEM data from these areas correspond to chlorite/smectite interstratifications normalized to O$_{20}$(OH)$_{10}$. As saponitic smectite has been recognized in this zone, we can conclude that disordered interstratification between chlorite and trioctahedral smectite occurs with rare packets of several 24 Å layers (collapsed smectite + chlorite).

DISCUSSION

Alteration sites and mechanisms

Alteration reactions are controlled by the nature of the parent minerals, chemical composition of solutions, and fluid-flow dynamics of the reaction site, which also control the reaction chemistry of the sites (Nahon, 1991). In partly-altered rock, where fracture networks account for flow paths, the hydrothermal solution can affect the rate and products of alteration. Minerals altering at a distance from the fissures that traverse the altered rock show different secondary-product assemblages and chemistry compared to minerals adjoining the fractures (e.g. see Alt & Teagle, 2003).

In these rocks, the nature and texture of the alteration products indicate that three different types
of microsystems are active during the process of hydrothermal alteration: (1) the entire crystals of the primary igneous mafic phyllosilicates; (2) centimetre-sized veins cross-cutting the dolerites; and (3) microfractures in feldspars and diopside grains. Pseudomorphed mafic phyllosilicate sites typically have oriented complex-mineral assemblages (chlorite, chlorite/smectite mixed layers, corrensite, saponite and relics of biotite) that contain evidence of the initial high-temperature stage of the hydrothermal process. Chlorite, chlorite-smectite mixed layers and corrensite do not appear outside the pseudomorphosed biotite crystals. Veins developed almost monomineralic alteration assemblages of randomly oriented smectites (saponite and beidellite). In the mineral microfracture sites, saponite is the main alteration product in relation to diopside, whereas saponite, beidellite and halloysite appear in feldspar microfractures.

The differences in products, alteration mechanisms and possibly rates of alteration, are probably related to the solution properties in the micro- and nano-sites (Hochella & Banfield, 1995). Solution properties and contact time with reacting minerals are known to affect the presence or absence of secondary minerals (Mazer et al., 1992), the nature of the secondary minerals (Anand et al., 1985) and the orientation of secondary minerals in relation to the parent minerals (Eggleton & Boland, 1982; Le Gleuher et al., 1990; Banfield & Barker, 1994).

In fracture sites, the parent minerals have a large surface area in contact with the solution and, therefore, ionic diffusion to and from the reacting surface is rapid. The chemical composition of the solution also affects the final composition and product-type, as seen by the general homogeneity in the Mg-Fe-rich products in the fissures, where Mg and Fe would be sourced from the connected microfractures. In contrast, solution movement along pseudomorphed igneous phyllosilicate, probably unaffected by the fracture network, is more likely to produce very small and confined ionic transport (Hochella & Banfield, 1995). The narrow passages and lack of space in the ‘internal’ alteration sites would be an important factor favouring inheritance of structural and chemical modules by the products from the parent mineral by way of minimizing surface energy (Eggleton & Boland, 1982; Veblen, 1991; Banfield & Barker, 1994; Hochella & Banfield, 1995; Banfield & Murakami, 1998).

In the vein areas, SEM and low-magnification TEM images of feldspars suggest that the alteration fronts extend into parent minerals from surface imperfections probably related to mineral cleavage. Nonetheless, the orientation, chemistry and morphology of products point to a dissolution-precipitation mechanism for their origin from the surrounding mineral assemblage. None of the products show any crystallographic relations with the surrounding minerals and are randomly oriented, pointing to a lack of crystallographic control on the formation of secondary products. The alterations of diopside to saponite and feldspars to smectites and halloysite would involve the complete dissolution of the parent minerals. Even in the case of formation of the 1:1 phyllosilicate halloysite from a layer silicate, replacement of tetrahedral Al by Si is required, which points to dissolution of the parent-layer silicates. A considerable influx of Al into the areas occupied by halloysite and Al-smectite would be required. This extra Al must have been acquired from nearby sites, which were the locus of the feldspar dissolution reaction. Aluminium released from the feldspar dissolution reaction could migrate short distances to junctions of layer silicate grains where water is considered to be present as a pervasive fluid. The Mg and Fe influx required for saponite formation are most probably related to the massive alteration of mafic minerals along fissures.

Igneous minerals from fracture areas appear to have been transformed into smectite through a dissolution and precipitation process without the formation of a metastable intermediate phase. The major chemical constituents were mobilized, at least locally, during the dissolution of these minerals to form smectite. The resultant textures are similar to those described by Banfield et al. (1991). Randomly oriented smectitic flakes fill fractures and pores formed during the dissolution of the igneous minerals, particularly feldspars and diopside. The observed variations in the chemical composition of smectites suggest that smectite precipitation is controlled by the nature of the parent material and the fluid that produces the hydrothermal alteration. Veins and fractures in feldspars were found to contain dioctahedral smectite and Mg-rich trioctahedral smectite with compositions close to saponite. Saponite represents the most common secondary mineral formed during low-temperature alteration of oceanic
basalts (Alt, 1999), where substantial amounts of Fe and Mg are liberated during the breakdown of primary phases such as olivine and pyroxene. Observations at the nanometre scale show that the trioctahedral smectite textures are similar to those observed for the dioctahedral species. Consequently, both smectites are interpreted to have formed by a similar process of dissolution and crystallization from the igneous minerals, involving an aqueous fluid as the transport medium and source of Mg, although direct precipitation from the fluids as suggested by Fiore et al. (2001) cannot be conclusively ruled out. Hydrothermal alteration of mafic rocks commonly produces mixtures of saponitic and beidellitic smectites (Pichler et al., 1999; Clayton & Pearce, 2000). A miscibility gap between these two smectites below 400°C was suggested by the synthesis experiments of Decarreau et al. (1992) and Yamada et al. (1999). Although Grauby et al. (1993) synthesized mixtures of Al-dioctahedral and Mg-trioctahedral smectites, their XRD and IR data have shown that the clay particles were made up of clusters of two different lattices, and solid-solution presents a wide miscibility gap. Given that clay particle microanalyses from dolerite veins and feldspar fractures show continuity between dioctahedral aluminous and trioctahedral magnesian smectites, the compositionally-intermediate smectites seem to correspond to weighted compositions of di- and tri-octahedral phases stacked together in the same particle.

The preceding dissolution-precipitation mechanisms, which show no direct crystallographic control of the parent on the products, are in contrast to the reaction mechanisms occurring in the biotite pseudomorphs in the same rocks where crystallographic and chemical control on alteration products is maintained. The SEM and TEM observations indicate that pseudomorphed phyllosilicate grains with igneous characteristics are alteration products of igneous biotite. Chlorite, corrensite and complex mixed-layered phases have previously been described during diagenetic and low-grade replacement of biotite (Jiang & Peacor, 1994; Li et al., 1998; Barrenechea et al., 2000). Hence, biotite appears to be replaced during an early hydrothermal process, first by chlorite and then by complex assemblages of corrensite-chlorite-berthierine-saponite layers. Rutile developed along cleavage planes, with the Ti needed for rutile formation sourced from biotite alteration. The altered biotite has zones parallel to (001) containing chlorite, berthierine, corrensite and saponite. The parallelism of c* of biotite, chlorite and corrensite suggest the replacement of biotite could be topotactic (Fig. 12). Consequently, chlorite, berthierine and corrensite have a common origin, probably related to the evolution of the hydrothermal process inside the primary biotite grains.

**CONCLUSIONS**

Our observations of different alteration reactions and products suggest that reaction mechanisms, and possibly the rate of alteration, differ among different microsites. Dissolution of the parent material and subsequent crystallization of products was the dominant low-temperature alteration mechanism where there was little or no parent-mineral crystallographic control on the products, such as smectites and halloysite in veins and microfracture sites.

The formation of halloysite and Al-smectite required a considerable influx of Al to the hydrothermal fluids, which was provided by feldspar dissolution from nearby sites. The addition of Mg and Fe to the hydrothermal fluids at these microsites via alteration of mafic minerals resulted in the formation of saponite. In contrast, the direct replacement of biotite layers was the dominant mechanism in the pseudomorphed mafic phyllosilicate sites, where parent minerals and products have structural and chemical relations.

Biotite contains substantial Ti that is inferred to have been the source of Ti for the authigenic oxides. The occurrence of pseudomorphed biotite in microsites emphasizes the strong influence of parent-mineral structure and composition on the secondary products. Our findings indicate that in microenvironments lacking free solutions and pore-space, the alteration of one phyllosilicate to the next most stable one proceeds via interstratification of the parent and product phyllosilicates, a mineral-alteration sequence facilitated by structural similarities of the parent and product minerals. Nevertheless, the absence of interstratifications during alteration in fracture sites may indicate that the localized reaction rate was rapid and favoured the formation of the discrete phyllosilicate product, rather than an intermediate interstratified mineral.
ACKNOWLEDGMENTS

We thank J.M. Molina (University of Jaén) and J.A. Vera (University of Granada) for their help with the field work, K. Livi (Johns Hopkins University) for his advice on the EMP, and M.M. Abad (C.I.C., University of Granada) for her help with HRTEM work. C. Laurin is acknowledged for revising the English. We are grateful to G. Giorgetti and an anonymous reviewer for their helpful comments and suggestions. Financial support was supplied by the Research Project BTE2003-07867 (Spanish Ministry of Science and Technology) and Research Groups RNM-179 and RNM-325 of the Junta de Andalucía.

REFERENCES


