MOBILE TRACE ELEMENTS AND FLUID-DOMINATED PROCESSES IN THE RONDA PERIDOTITE, SOUTHERN SPAIN

MÁRIA DOLORES PEREIRA
Departamento de Geología, Universidad de Salamanca, E–37001 Salamanca, Spain

DENIS M. SHAW
School of Geography and Geology, McMaster University, Hamilton, Ontario L8S 4M1, Canada

ANTONIO ACOSTA
School of Geology and Geophysics, University of Oklahoma, 100 East Boyd Street, Norman Oklahoma 73019–0628, U.S.A.

ABSTRACT

Intrusion of the Serranía de Ronda peridotite massif, in southern Spain, during the Alpine orogeny caused partial melting of the Hercynian migmatites lying below and generation of leucogranitic magma that intruded the peridotite as subvertical dikes. Incorporation of B, Cl and Br from marble and evaporite country-rocks account for a high content of volatiles in the melt, facilitating its intrusion and provoking hydrothermal alteration of adjacent, slightly altered peridotite to serpentinite. In comparison with the mantle composition favored by McDonough & Sun (1995), our peridotite compositions are notably enriched in the elements Br, Cl, As, and B, but impoverished in the incompatible elements P, Al, Ti and Na; compatible major and trace elements have similar abundances in both. The peridotites and serpentinites have similar concentrations of many major and trace elements, but some incompatible elements, including B, Li, Th and the LREE, are more abundant in serpentinites, approaching the content in granites. In a profile of serpentinization adjacent to a granite dike, B concentrations decrease away from the granite, and Br, Cl increase slightly. High oxygen isotope ratios in serpentinite and peridotite, compared to similar rocks elsewhere, indicate an interaction with fluids of igneous derivation. Granites have high values of δ18O, which conform to their origin from melting of metamorphic rocks.

Keywords: Ronda massif, peridotite, serpentinization, boron, chlorine, bromine, Spain.

SOMMAIRE

La mise en place du massif péridotitique de Serranía de Ronda, dans le sud de l’Espagne, lors de l’orogénèse Alpine, a provoqué une fusion partielle de la croûte hercynienne migmatitique sous-jacente et la génération d’un magma leucogranitique qui a recouvert la péridotite sous forme de filons sub-verticaux. L’inclusion de B, Cl et Br provenant du marbre et des évaporites du socle explique la teneur élevée en composants volatils du magma, ce qui en a facilité la mise en place et a causé l’altération hydrothermale en serpentinites des roches péridotitiques encaissantes légèrement altérées. En comparaison avec la composition du manteau favorisée par McDonough et Sun (1995), nos compositions de péridotite sont enrichies en Br, Cl, As, et B de façon importante, mais appauvries en éléments incompatibles P, Al, Ti et Na; par contre, les éléments compatibles majeurs et en traces ont des teneurs semblables. Les péridotites et les serpentinites possèdent des concentrations semblables de plusieurs éléments majeurs et en traces, mais certains éléments incompatibles, y inclus B, Li, Th et les terres rares légères, sont enrichis dans les serpentinites, s’approchant des teneurs dans les granites. Dans un profil de serpentinisation près d’un filon de granite, les concentrations en bore diminuent en se rapprochant du granite, et Br et Cl augmentent légèrement. Les valeurs élevées du rapport δ18O dans la serpentinite et la péridotite, par rapport aux valeurs typiques, indiquent une interaction avec une phase fluide dérivée d’une source ignée. Les granites ont une valeur de δ18O élevée, ce qui concorde avec leur origine par fusion du socle métamorphique.

(Mots-clés: massif de Ronda, péridotite, serpentinisation, bore, chlor, brome, Espagne.)

(abridged by the editor)

© E-mail addresses: mdp@usal.es, shawden@mcmaster.ca, aacosta@hoth.gcn.ou.edu
INTRODUCTION

The ultramafic massif of the Serranía de Ronda, southwestern Spain, is an E–W elongate tectonic slab that crops out over 350 km², the largest body of such mantle-derived material on Earth (Obata 1980, Tubía 1988, 1994). It was emplaced during the Alpine orogeny, during the geodynamic evolution of the central and western Mediterranean region, when the opening of the Alboran Sea took place. The Ronda peridotite is associated with high-grade metamorphic crustal rocks and shows a sheet-like geometry, with a maximum thickness of about 4.5 km (Acosta 1997, and references therein). The sheet is located above a tectonically inverted metamorphic sequence, dipping 30–40°. At the contact, the metasediments are low-pressure peraluminous migmatites and Permo-Triassic marbles and meta-evaporites (Torres-Roldan 1983). The massif is cut by many subvertical dikes of granitic composition, with variable widths, from a few centimeters up to 10 meters (Figs. 2a, b); the adjacent peridotite is altered to dense serpentinite. There is widespread partial serpentinization throughout the Ronda massif (Lorand 1985, Sánchez-Rodríguez & Gebauer 2000), from interaction of the massif with fluids (Thompson & Melson 1970) during or after its ascent. In this work, we consider the effects of the granitic dikes on the genesis of the dense serpentinites, particularly with respect to the extent of transfer of trace and volatile elements, under the influence of melt-generated fluids.

ROCK TYPES

Ultramafic rocks

The Ronda massif consists mainly of partially serpentinized peridotite, consisting of layers of various mafic and ultramafic rocks (Westerhof 1977, Doblas & Oyarzun 1989, Gervilla & Remaidi 1993). The mineralogy of the peridotites has been studied in detail by many authors (e.g., Obata 1980, Tubía 1988, Gervilla 1990), who have described various facies containing olivine + orthopyroxene + clinopyroxene ± garnet ± chromite and other opaque phases. Many have identified a large-scale zonation from plagioclase peridotite below, spinel peridotite at intermediate levels, to garnet peridotite in the uppermost part of the ultramafic slabs (Obata 1980, Tubía 1994). The samples we have studied do not contain garnet, and invariably contain volumetrically significant hydrated minerals; they represent the spinel peridotite from the intermediate level.

For the purposes of this paper, we use the name peridotite as a field term for rocks that are coarse grained and massive; those we call serpentinite are finer grained, sheared and fractured, with little textural resemblance to the major rocks of the massif.

Granite dikes

Agmatitic dike breccias occur in the lower zone of the Ronda sheet, containing metapelitic enclaves 2–3 cm across in a leucogranitic groundmass. The leucogranite consists of quartz, microcline and sodic plagioclase as essential minerals, and is characterized by the presence of tourmaline and, in some cases, cordierite. The abundance of enclaves decreases toward the central part of each dike, which changes from agmatite to leucogranite; in the uppermost zone of the peridotite, the enclaves are absent. Near the top of the sheet, a conspicuous differentiation has led to complex geometrical relations among granite, aplite, and pegmatite, with abundant mafic intrusions and occasional luxullianitic texture, where large crystals of tourmaline contrast with a groundmass of quartz and feldspar (Acosta & Menéndez 1995, Acosta 1997). The tourmaline- and cordierite-bearing leucogranites are rich in boron (500–1250 ppm B) (Acosta et al. 2001).

The Ronda leucogranites were generated by partial melting of underlying migmatites during the emplacement of the ultramafic massif in the crust (Tubía 1988, Acosta & Menéndez 1995, Acosta 1997, Acosta et al. 2000). Heat for melting was provided by the massif (at a temperature of 900–1000°C; Tubía & Cuevas 1986) and perhaps by frictional heating along the thrust plane (Acosta et al. 2000). This plane may have also acted as a channel for a volatile-rich phase released from the Permo-Triassic country rocks, which helped promote the partial melting and lowered the viscosity. Pods of the partially molten material were emplaced as agmatitic dikes along fractures in the peridotite body. The dike material ascended quickly enough (Petford et al. 1994, Acosta et al. 2000) to avoid extensive chemical interaction with the peridotite, other than the local alteration discussed below.

Migmatites

The migmatites can be described as diatexites, and have been grouped in pelitic and quartzofeldspathic units (Acosta 1998, Acosta et al. 2001). They underlie the peridotites and constitute the upper part of an inverted metamorphic sequence (Tubía et al. 1997). Migmatites have a low boron content (~10 ppm) similar to that in other Hercynian migmatites (e.g., the Peña Negra massif in central Spain, with 20 ppm; Pereira & Shaw 1997).

SAMPLES AND ANALYSIS

Sets of samples were collected from outcrops where peridotite, serpentinite and intrusive veins of granite occur adjacent to each other (Fig. 2b). Their compositions are in Table 1. In one locality, known as Peñas Blancas, within the Sierra Bermeja complex, we were able to
Fig. 1. Location of the Ronda ultramafic massif within the Betic Cordillera. Section c – c’ is shown in Figure 2a. Modified from Tubía (1988) and Balanyá & García-Dueñas (1991).
collect samples of serpentine along a profile from an intruded leucogranite dike for a distance of over 75 m in the peridotite, permitting a comparison (see below) of alteration with distance (Tables 2a, b).

Samples were analyzed for major elements by X-ray fluorescence at the University of Granada and for boron, halogens and some other trace elements at the Nuclear Reactor of McMaster University, using neutron activation analysis (Pereira & Shaw 1997); oxygen isotope analyses of the whole rocks were carried out at Queen’s University, Kingston, Ontario.

**Chemical Features of the Rocks**

*Relationships among rock types*

Average compositions for peridotite, serpentine and granite were calculated from the data in Tables 1, 2a, 2b, and are set out in Table 3.
The average Ronda peridotite has a composition similar to the mantle, as defined by McDonough & Sun (1995). The abundances of Mg, Fe, and Mn are similar, as is the case for the compatible trace elements Cr, V, Sc, Co and perhaps Zn (Figs. 3a, 3b); this, however, is not the case for P, Ti, Al, Ca and Na and many incompatible trace elements, including the light rare-earth elements (LREE), which all are depleted, with many abundances being below the detection limit (e.g., K, Na, Ti, Al, Ca, Mg).
Ba, Cs). Such behavior is shown by other continental ultramafic massifs and xenoliths, as reviewed by McDonough & Sun (1995) and displayed in their Figure 2 (similar to Figs. 3a and 3b).

By contrast, the Ronda peridotite is notably enriched in the elements B, Cl, As, and Br relative to the composition of the mantle (Table 3). These are volatile-soluble elements and will be discussed further below; unfortunately, these elements are not included among the rock series shown in Figure 2 of McDonough & Sun (1995).

Next, comparing the peridotite and serpentinite compositions in Table 3, it is clear that the major elements do not differ much, except for Ca. The similar LOI values (Fig. 3a) show that all are in fact hydrated, but one composition (B–116–S) is anomalous, with a LOI much lower than the ideal formula value of 13% for a serpentinite-dominant rock (Kyser et al. 1999); this rock must have been misclassified. The trace elements Br, Co, Zn, Sc are also at similar levels (Fig. 3a) in peridotites and serpentinites. Values of Br/Cl show little variation, except for one higher value in the serpentinite B–116–S, which corresponds to the low Cl concentration. By contrast, other incompatible elements, including B, Li, Sb, the LREE, Ba and Th are at higher concentrations in serpentinites, intermediate between peridotites and granites (Fig. 3b).

The granites are predominantly peraluminous, with the aluminum saturation index \[ASI = \text{mole fraction } Al_2O_3 / (CaO + Na_2O + K_2O)\] ranging from 1.40 to 0.92, with an average of 1.06; ASI values decrease with SiO\(_2\), TiO\(_2\), and FeO\(_{total}\), the most silicic dikes being metaluminous (Acosta 1997). Major-element concentrations in the granites reflect the abundance of quartz and feldspars; the incompatible lithophile elements, including B, Li, Hf, the LREE, Th, Ba, Cs are abundant (Fig. 3b), as also are the chalcophile elements As and Sb. Alpha-track analysis on thin sections of the high-B granites mentioned earlier shows that the boron in these rocks (Tables 1, 2b) is concentrated in tourmaline, and no other phase (Perere & Shaw 1996). So, a boron-rich source is necessary, which is provided in the underlying Permo-Triassic marbles and meta-evaporites already mentioned (Acosta et al. 2001), although the migmatites constitute the silicate source of these leucogranites.

Oxygen isotope (\(^{18}O\)) values for the serpentinites (Table 1) are high (5.7–10‰) compared to the bibliographic values given for such rocks (5.5–7.4‰: e.g., Kyser et al. 1999); they are values more appropriate for granitic rocks. In fact, the \(^{18}O\) values for the granites are high (12.2–13.6‰) and in the range found by Li et al. (1991) for gneisses and metasedimentary rocks, in accord with their formation by anatexis of migmatites. These felsic dikes are related therefore to the local serpentinitization.

**Alteration profile**

In the profile developed in altered peridotite, the granitic dikes appear to have been volatile-rich, producing a local intense serpentinization in narrow zones (20–50 cm) at contacts with peridotite. Regarding the mineralogy, both peridotite (#–P) and serpentinite (#–S) are made up mainly of pyroxene, altered to Fe-oxides, some olivine and various amounts of serpentine-group minerals. “Peridotite” preserves granoblastic textures, whereas “serpentinite” invariably shows a mesh texture made up of serpentine-group minerals. Pyroxenes present evidence of deformation twins very commonly, but these can be observed better in peridotite samples; in serpentinites, the pyroxene has been converted to serpentine mesh. In serpentinite samples, olivine is present as skeletal remains, in some cases included in chromian spinel. This accessory mineral is much more abundant in fresh samples than in serpentinite, where in some cases it is totally absent.

The behavior of the elements in relation to distance from a granitic dike is documented in Tables 2a, 2b and in Figures 4a, b, c. Samples LOR–4 and LOR–5 were both very close to the granite, with the latter being closer; they have therefore been arbitrarily assigned

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**TABLE 3. MEAN CONCENTRATION OF MAJOR AND TRACE ELEMENTS IN PERIDOTITE, SERPENTINITE AND GRANITE FROM THE RONDA MASSIF, COMPARED WITH AVERAGE MANTLE**

<table>
<thead>
<tr>
<th>Element</th>
<th>Peridotite (P)</th>
<th>Mantle (M)</th>
<th>P/M</th>
<th>Serpentinite (S)</th>
<th>Granite (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si (wt%)</td>
<td>18.82</td>
<td>21.40</td>
<td>0.90</td>
<td>21.86</td>
<td>35.88</td>
</tr>
<tr>
<td>Ti</td>
<td>0.05</td>
<td>0.12</td>
<td>0.41</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>Al</td>
<td>0.92</td>
<td>2.35</td>
<td>0.39</td>
<td>1.22</td>
<td>6.85</td>
</tr>
<tr>
<td>Fe</td>
<td>6.05</td>
<td>6.26</td>
<td>0.97</td>
<td>5.12</td>
<td>3.4</td>
</tr>
<tr>
<td>Mg</td>
<td>23.41</td>
<td>22.80</td>
<td>1.02</td>
<td>19.92</td>
<td>1.1</td>
</tr>
<tr>
<td>Mn</td>
<td>0.10</td>
<td>0.19</td>
<td>0.92</td>
<td>0.08</td>
<td>0.01</td>
</tr>
<tr>
<td>Ca</td>
<td>0.96</td>
<td>3.53</td>
<td>0.32</td>
<td>0.91</td>
<td>4.06</td>
</tr>
<tr>
<td>Na</td>
<td>0.01</td>
<td>0.27</td>
<td>0.11</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>K</td>
<td>0.02</td>
<td>0.01</td>
<td>0.00</td>
<td>0.04</td>
<td>0.00</td>
</tr>
<tr>
<td>P</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>LOI</td>
<td>10.32</td>
<td>14.59</td>
<td>0.72</td>
<td>13.1</td>
<td>3.3</td>
</tr>
</tbody>
</table>

P: means of peridotite compositions in Tables 1, 2a, and 2b. M: mantle composition from McDonough & Sun (1995, Table 5, Col. 2). G: means of serpentinite compositions in Table 1 only. b.d.:
stances of 0.2 and 0.1 meters, respectively. Most elements show relatively constant profiles of concentration in the ultramafic rocks, with an abrupt change at the transition to granite. An exception, however, is in the behavior of B, Cl and Br. The highest concentrations of B are in the leucogranite, and the content decreases with distance away from the dike (Fig. 4c). For halogens, there is a slight increase in concentration away from the granite dike.

Concentration anomalies appear in samples LOR–10 and LOR–5, respectively at distances of 15 and 0.2 m from the granite. LOR–10 has lower abundances than its neighbors of Al, Fe, Mn, Ca, Cr, V, Sc, La, Sm, and slight increases in B, Br. LOR–5 has similar low values for Al, Ca and V, and a slight increase in Mg. The behavior of As and Sb seems anomalous also, with slight increases at those distances. These anomalies suggest that both rocks have lost clinopyroxene and consist entirely of serpentine-group minerals, as a result of leaching provoked by volatile introduction through cross-cutting shears, which are abundant in the section. This same effect has been observed by Esteban et al. (2003) in the mafic complex of Carratraca, northeast of our working area, as well as within the Bermeja massif. Our data show that the local serpentinization occurred at the time of intrusion of the dikes, at 22.2 Ma (Priem et al. 1979, Acosta et al. 2000). Local rodingitization of these dikes took place probably during this serpentinization, as the general serpentinization affecting Ronda massif had taken place earlier, largely induced by surface water, percolating down shear zones, as the δ18O values are lower than for serpentinites related to granitic dikes; they are more in accord with values recorded for such rocks from other regions (e.g., Li et al. 1991, Kyser et al. 1999).

Evidence presented in the previous section shows B, Cl, Br, and As to be concentrated in the Ronda ultramafic rocks relative to the mantle. The gradational changes in their concentrations (except for As) with distance from the granite dike appears to be a feature of the alteration, and may be attributed to volatile components emanating from the granite.

**Summary**

Intrusion of the Ronda peridotite slab during the Alpine orogeny caused partial melting of the Hercynian migmatites lying below. The leucogranitic melt formed dikes that intruded the massif and provoked locally intense serpentinization of an already slightly altered peridotite, by release of fluids. Calcium metasomatism affected some of the granitic dikes during the serpentinization, leading to a rodingitization process, which has been described recently by Esteban et al. (2003).

In comparison with the mantle composition favored by McDonough & Sun (1995), the Ronda ultramafic rocks show similar abundances of compatible major and trace elements; this, however, is not the case for P, Ti, Al, Ca and other incompatible major and trace elements, including the LREE, which all are depleted. By contrast, the elements Br, Cl, As, and B are notably more abundant in the Ronda peridotite relative to the mantle, as a result of transport in the fluids emitted from the granite. These same elements (except As) show gradational changes in concentration in a profile of serpentinization adjacent to a granite dike, again caused by the volatile phase.

Many major and trace elements have similar concentrations in the peridotites and serpentinites, but some incompatible elements, such as B, Li, Th and the REE,
are more abundant in serpentinites, at levels intermediate between peridotites and granites (Fig. 3b).

Oxygen isotope analysis shows that $\delta^{18}O$ values in serpentinite and peridotite are higher than those encountered for similar rocks elsewhere, and the granites have high values, which conform to their origin from melting of metamorphic rocks.

Chemical anomalies have been observed where the serpentinites are affected by shears connected to the regional extension processes that affected the Ronda massif (Tubía 1994, Tubía et al. 1997), permitting fluids to permeate and react with peridotite–serpentinite mineral phases.

In conclusion, the behavior of boron and halogens involved in the alteration process of Ronda peridotite was caused by fluids derived during intrusion of the abundant cross-cutting leucogranite dikes, affecting an already slightly altered peridotite.

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