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D, O and C isotopes in podiform chromitites as fluid tracers for hydrothermal alteration processes of the Mayari–Baracoa Ophiolitic Belt, eastern Cuba

J.A. Proenza a,*, P. Alfonso a, J.C. Melgarejo a, F. Gervilla b, J. Tritlla c, A.E. Fallick d

aDepartament de Cristallografia, Mineralogia i Dipòsits Minerals (CMDM), Universitat de Barcelona, C/Marti i Franqués s/n, 08028 Barcelona, Spain
bInstituto Andaluz de Ciencias de la Tierra, Facultad de Ciencias, Avenida Fuentenueva s/n, 18002 Granada, Spain
cCentro de Geociencias, Campus Juriquilla, U.N.A.M. Carretera Queré-LP, km 15.5, 76230 Querétaro, Mexico
dIsotope Geosciences Unit, SUERC, East Kilbride, Glasgow, UK

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The Mayari–Baracoa Ophiolitic Belt (MBOB, eastern Cuba) is composed of two large, chromite-rich massifs: Mayari-Cristal and Moa-Baracoa. The chromitites and hosting dunites were firstly affected by a regional serpentinization event, a subsequent episode of hydrothermal alteration (chloritization mainly) and, finally, these already altered bodies were crosscut by thin calcite-dominated veins. Analysed serpentines from serpentinized chromitites and dunites present very similar isotopic compositions (δ18O = +4.7‰ to +6.3‰ and δD = −67‰ to −60‰), suggesting that the serpentinization process took place at moderate temperatures, in an oceanic environment. Serpentinite formation by interaction with ocean water is also supported by the isotopic composition of chlorite and calcite. These results suggest that the serpentinization, chloritization and fracture filling processes of the Mayari–Baracoa Ophiolite Belt took place in a subocean floor scenario and, thus, that the Mayari–Baracoa serpentines represent a good example of serpentine formed during interaction with seawater. The oceanic origin of the serpentines from serpentinized chromitites and dunites from the MBOB indicate that the serpentinization of the mantle sequence occurred pre-thrusting (pre-emplacement in age).

Keywords: Fluids; Serpentinization; Stable isotopes; Ophiolites; Cuba

1. Introduction

Hydrogen and oxygen isotopic studies on serpentine provide valuable information about the fluids involved in the serpentinization process (Wenner and Taylor, 1973; Sakai et al., 1990; O'Hanley, 1996). However, most of the δD and δ18O data from ophiolitic serpentines have been gathered from serpentinized peridotites, but few data exist in the literature on the serpentine forming the matrix of the chromitites. In this paper, we provide a new data set of hydrogen and oxygen isotopic compositions of serpentines and chlorites both from the silicate matrix of chromitite bodies and from the dunites enveloping chromitites in the Mayari–Baracoa Ophiolite Belt (MBOB), and C and O isotopic
composition from the calcite veins that crosscut the ores, in order to give a new insight into the source and behavior of the fluids involved in the hydrothermal alteration processes of ophiolitic mantle sequences.

2. Geological setting

The MBOB (Upper Jurassic–Lower Cretaceous age) is located in the easternmost part of the E–W trending Cuban Ophiolite Belt (Fig. 1). It is composed

![Diagram](image-url)
of two large chromite-rich massifs: the Mayari-Cristal (MC) and Moa-Baracoa (MB) (Proenza et al., 1999a).

The western part of MC massif (Mayari district) contains abundant chromitite pods, made up of Cr-rich chromite that are included within dunites in the interlayered harzburgite-dunite unit. However, in the easternmost part of the MC massif (Sagua de Tánamo district), the chromitite pods contain both Cr-rich and Al-rich chromite ores, in an area characterized by the imbrication of different tectonic sheets of ophiolite-related ultramafic rocks (Fig. 1).

The whole MB massif can be considered as a single mining district (Moa-Baracoa district) containing more than 100 chromite occurrences. The chromitite pods in MB massif occur in the mantle–crust transition zone, characterized by the interbedding of ultramafic and gabbroic rocks (Fig. 1). These chromitite pods are made up by Al-rich chromite ores (Proenza et al., 1999a).

3. Petrography and mineral chemistry

Primary mineralization is formed mainly by chromite and olivine with local minor amounts of clinopyroxene, orthopyroxene, amphibole and plagioclase (Proenza et al., 1999a). Three main hydrothermal alteration stages can be distinguished: olivine serpentinization, serpentine chloritization and hydrothermal vein filling.

Serpentinization in MBOB was a regional process that affected both the chromitite bodies and the host rocks (dunite and harzburgite), replacing the olivine grains by an assemblage of serpentine plus magnetite. Typically, the serpentine phase altering the Mayari–Baracoa chromitites and dunites displays a pseudomorphic mesh texture after olivine. This texture indicates that the serpentine phase present is lizardite (O’Hanley, 1996). However, chrysotile and antigorite were also recognized in some of the samples. Lizardite is Al-enriched with respect to the coexisting antigorite, with aluminum substituting both tetrahedral silicon and octahedral magnesium. Antigorite is slightly richer in SiO₂.

The chloritization took place largely in the chromitite bodies and their vicinity, and consists in the replacement of serpentine by chlorite. Chlorite compositions cover a wide range of silica contents (Si = 4.9–6.6 atoms p.f.u.). It has a very low Fe content (<0.8 wt.% FeO) and a Fe/(Fe + Mg) ratio of approximately 0.01, and this chlorite can be classified as clinochlore (Proenza et al., 1999b).

Finally, the chromitite bodies of the MBOB were crosscut by a swarm of small, millimeter-thick fractures containing Cr-rich clinochlore, uvarovite, rutile and titanite, with the remaining open space being filled up by a late blocky calcite. All this assemblage display an open space filling texture.

4. Samples and analytical procedures

Serpentinized chromitite and dunite samples were collected from the three mining districts of the MBOB (Fig. 1). The mineralogy and purity of the separated samples (serpentine and chlorite) were checked using an optical microscope and X-ray diffractometry. The purity of the final separates was better than 95%.

Oxygen and hydrogen isotope analyses were carried out at the Scottish Universities Environmental Research Centre (SUERC). Laser fluorinations were performed with a CO₂ laser system; the fluorination agent was CIF₃. The δ¹⁸O values were measured on a VG-SIRA 10 mass spectrometer. Hydrogen isotopic analyses were performed with 10–20 mg of sample using conventional methods. The δD was measured on a VG602 mass spectrometer. Oxygen and carbon isotope analyses of calcite from carbonate-filled fractures crosscutting the chromitite pods were carried out at the Servicio General de Análisis de Isótopos Estables of the Salamanca University (Spain).

The chemical composition of serpentine and chlorite was analysed using a CAMECA SX50 electron microprobe at the University of Barcelona.

5. Isotopic results

Serpentine from all serpentinized chromitites of three mining districts exhibits a narrow range in δ¹⁸O (+4.7‰ to +6‰) and δD values (−66‰ to −60‰) (Fig. 2a).

Serpentines from the serpentinized dunite enveloping the chromitite pods were also analysed. The isotopic composition of two samples from the Moa-Baracoa district are δ¹⁸O=+6.2‰ and +6.3‰ and...
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Fig. 2. (a) A δD versus δ18O plot of the serpentine from MBOB. The isotopic ranges are from: “oceanic serpentines” (Wenner and Taylor, 1973), “continental serpentines” (Wenner and Taylor, 1974), “ophiolitic serpentines” (Wenner and Taylor, 1973), and Izu-Ogasawara-Mariana forearc serpentines (Sakai et al., 1990). (b) δ13C vs. δ18O of calcite vein cross-cut chromitite of the MBOB compared to other carbonates in ophiolite: (1) carbonate in serpentinite, Arosa-Platta nappe (Switzerland, Burkhard and O’Neil, 1988); (2) carbonate in serpentinite, Valmalenco (Italy, Burkhard and O’Neil, 1988); (3) composition of Deep Sea Drilling Project basalt calcite (Cocker et al., 1982). The temperature scale is based on calcite-water fractionation (O’Neil et al., 1969), and the assumption that calcite was deposited in equilibrium with seawater (δ18O = 0‰).
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\[ \delta D = -67\%o \text{ and } -65\%o, \text{ respectively. These compositions are very close to the serpentine sampled in the chromitite pods. In contrast, two serpentine veins (chrysotile) in serpentinized dunites from the Mayari district (samples CL-1 and CL-4B) show } \delta D \text{ values (} -68\%o \text{ and } -63\%o \text{) similar to those from the Moa-Baracoa dunite, but exhibit a higher } \delta ^{18}O \text{ composition (+10.3\%o and +11.3\%o) (Fig. 2a).} \]

The isotopic composition of chlorite forming the matrix of chromitites shows considerable variations in \( \delta ^{18}O \) values (+4.7\%o < \( \delta ^{18}O \) < +7.5\%o), as well as variable and relatively high \( \delta D \) values (−52\%o < \( \delta D \) < −10\%o) (Fig. 2a).

Calcare veins, crosscutting chromitites and the enveloping dunites, have a range of \( \delta ^{13}C \) values near zero (−0.6\%o < \( \delta ^{13}C \) < +2.6\%o PDB) and \( \delta ^{18}O \) values from +12.2\%o to +14.9\%o (Fig. 2b).

6. Discussion

The oxygen and hydrogen isotopic compositions of the serpentine after chromitites and dunites fall within the range of "oceanic serpentine" \( (\delta ^{18}O = +0.8\%o \text{ to } +6.7\%o, \delta D = -68\%o \text{ to } -35\%o) \) defined by Wenner and Taylor (1973) (Fig. 2a), and confirmed more recently by Agrinier et al. (1995). These serpentines have been interpreted as formed by seawater-derived fluids at temperatures between 200 and 350 °C.

Calcare veins, crosscutting chromitites and the enveloping dunites, have a range of \( \delta ^{13}C \) values near zero (−0.6\%o ≤ \( \delta ^{13}C \) ≤ +2.6\%o PDB) and \( \delta ^{18}O \) values from +12.2\%o to +14.9\%o (Fig. 2b).

7. Conclusions

Our data suggests that in the MBOB the serpentinization, chloritization and fracture filling processes probably occurred during a subocean-floor alteration stage. Thus, the Mayari–Baracoa serpentines represent a good example of serpentine formed in an oceanic environment. Moreover, we conclude, in agreement with O’Hanley (1996), that the ophiolite
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Serpentine field defined by Wenner and Taylor (1973) must be considered purely descriptive.

Finally, the origin of the Mayari-Baracoa serpentine is clearly linked to ocean water circulation through the whole ophiolite sequence, suggesting that the serpentinization of the mantle sequence occurred pre-thrusting (pre-obduction), and probably took place in a suprasubduction setting (fore arc environment or spreading axis of a back arc basin). The evolution of this scenario caused the retreat of the isotherms as the obducted slab was elevated, giving rise to a retrograde cooling path changing the alteration mineralogy as the obduction proceeded.

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