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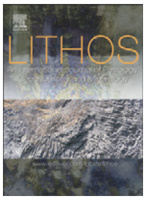

Oriented quartz + calcic amphibole inclusions in omphacite from the Saualpe and Pohorje Mountain eclogites, Eastern Alps—An assessment of possible formation mechanisms based on IR- and mineral chemical data and water storage in Eastern Alpine eclogites

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ABSTRACT

The composition of mineral phases and their modal proportions have been determined for three representative Eoalpine eclogites from the Saualpe type locality/Eastern Austria (sample SKP31) and the Pohorje Massif/Slovenia (CM31/03 and CM15/01) using electron microprobe, laser ICP-MS, IR spectroscopy and modal analysis to evaluate possible mechanisms for the formation of composite oriented calcic amphibole + quartz inclusions (COIs) in omphacite and to assess the relative importance of hydrous and nominally anhydrous phases as H_2O carriers in these eclogites.

For omphacites in CM31/03 with a zonal distribution of COIs, a comparison of water and trace element concentrations of areas containing COIs and those free of COIs and a comparison with the trace element concentration of calcic amphibole indicate that COIs have formed through an open-system alteration of clinopyroxene and not through a closed system exsolution process. In sample SKP31, both textural and mineral chemical evidence suggests that COIs did not form by exsolution involving a Ca-Eskola component in clinopyroxene but formed by progressive growth under eclogite-facies P-T conditions and prior to the onset of retrogressive symplectite formation analogous to the formation of poikiloblastic quartz–calcic amphibole grains in the matrix.

Bulk H_2O contents of the eclogites are between ca. 750 and 2150 ppm with 6–25% of the total water contributed by nominally anhydrous minerals (NAMs). Because of high modal amounts of 37–65%, omphacite is the major nominally anhydrous water carrier, containing 145–580 ppm H_2O with significant concentration variations on a thin section scale. Due to their very low H_2O concentrations of <5–10 ppm (garnet, kyanite) or insignificant modal amounts ≤3% (rutile) the remaining NAMs contribute less than 1.5% to the bulk eclogite H_2O content. Calcic amphibole forming part of COIs may be a major carrier of H_2O as evidenced by CM31/03 containing both COIs and texturally primary calcic amphibole. In this sample calcic amphibole of the COIs contributes 63% whereas primary calcic amphibole only accounts for 13% of the bulk water. The relative order of H_2O concentrations in NAMs is $H_2O_{\mathrm{rutile}} > H_2O_{\mathrm{omphacite}} \gg H_2O_{\mathrm{garnet}}$ for CM31/03 and CM15/01 and $H_2O_{\mathrm{rutile}} \approx H_2O_{\mathrm{omphacite}} \gg H_2O_{\mathrm{garnet}}$ in SKP31.

1. Introduction

Omphacitic clinopyroxenes containing oriented rods/needles of quartz and more rarely coesite are frequently found in mafic eclogites (Page et al., 2005, and references therein). These oriented inclusions are commonly interpreted as an exsolution texture formed by the retrogressive breakdown of a non-stoichiometric Ca-Eskola component ($Ca_{0.5}\square_{0.5}AlSi_2O_6$) in clinopyroxene during exhumation according to a reaction 2 $Ca_{0.5}\square_{0.5}AlSi_2O_6 = CaAl_2SiO_6 + 3\ SiO_2$, thereby producing a Ca–Tschermak enriched pyroxene while releasing SiO_2. Because some of these localities record ultrahigh-pressure (UHP) metamorphic conditions as evidenced by coesite- and/or diamond-bearing assemblages (Smith, 1984; Shatsky et al., 1985; Katayama et al., 2000; Song et al., 2003; Zhang et al., 2005) the presence of oriented quartz inclusions in clinopyroxene in combination with thermobarometric calculations have often been used to claim UHP conditions even if only indirect evidence for the former presence of UHP phases could be presented (e.g. Schmädicke and Müller, 2000; Tsai and Liou, 2000; Zhang et al., 2002; Liati et al., 2002; Dobrzhinetskaya et al., 2002; Janák et al., 2004). Using phase analysis

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in a simplified CaO–MgO–Al_2O_3–SiO_2–TiO_2 model eclogite, Day and Mulcahy (2007) showed that formation of SiO_2-lamellae need not be related to a CaEs component in omphacite but may result from reactions of minor/accessory phases such as rutile or kyanite with stoichiometric pyroxene phase components. Likewise, these authors showed that vacancies in omphacite may be consumed by SiO_2-conserving reactions so that a high vacancy content of a pyroxene does not imply a high potential to produce free silica.

In some cases, calcic amphibole was identified intergrown with the oriented quartz inclusions, thus forming composite oriented calcic amphibole-quartz inclusions (COIs) (Terry and Robinson, 2001; Liati et al., 2002; Page et al., 2005; Miller and Konzett, 2005). The presence of amphibole requiring a hydrous fluid for its formation shows that mechanisms more complex than the simple CaEs breakdown reaction as defined above must have been responsible for the formation of COIs. Page et al. (2005) pointed out that composite inclusions need not be at all related to a former CaEs component in clinopyroxene but may form instead by secondary breakdown reactions involving a hydrous fluid. Page et al. (2005) also challenged the significance of oriented quartz + calcic amphibole as UHP indicators and reported their extensive growth in clinopyroxene from an eclogite equilibrated at 600–700 °C and approximately 1.5 GPa. Additional evidence for a HP origin of oriented quartz inclusions had already been presented by Gayk et al. (1995) describing an occurrence of oriented quartz needles in clinopyroxene from a felsic high-pressure granulite equilibrated around 1.8 GPa and 1100 °C. This is in agreement with experimental results by Konzett et al. (2008) who stabilized clinopyroxene with a significant CaEs component at 2.5 GPa and 850 °C in a basaltic bulk composition. These authors showed that $CaEs_{ss}$ in clinopyroxene is strongly dependent upon bulk composition and temperature but shows very little pressure dependence.

In order to assess possible formation mechanisms of COIs in eclogitic clinopyroxene with special emphasis on potential sources of hydrous fluid and to evaluate the water storage capacity of typical Eastern Alpine eclogites we present the results of an IR and mineral chemical investigation of eclogites containing COIs in omphacites from the Koralpe/Austria representing the eclogite type locality and from the Pohorje Mountains/Slovenia, together forming the southernmost portion of the Eoalpine eclogite zone of the Eastern Alps.

2. Geological setting

The Saualpe–Koralpe–Pohorje (SKP) complex is part of the southernmost Austroalpine nappe system and represents portions of the former southern margin of the Alpine Thethys immediately north of the Periadriatic lineament (e.g. Stampfli and Mosar, 1997) (Fig. 1). This Austroalpine domain was dissected and accreted to the European continental margin during closure of the Meliata and Vardar oceans, and collision of the Apulian microplate with Europe. The lithology of the SKP complex is dominated by ortho- and paragneisses with intercalations of eclogite bodies ranging in size from a few to several hundred meters. A more detailed description of the tectonic and geological situation is given by Miller et al. (2005) (with references therein) and need not be repeated here. Peak-metamorphic conditions for the SKP complex are controversial: a number of studies (Miller, 1990; Miller and Thöni, 1997; Sassi et al., 2004; Miller et al., 2005; Miller and Konzett, 2005; Miller et al., 2007) derived HP-conditions of 2.2–2.8 GPa at 670–760 °C that were reached around 90 Ma. Janák et al. (2004, 2006) on the other hand, postulated UHP conditions for the Pohorje Massif based on calculated phase equilibria and textural observations involving oriented quartz inclusions in clinoproxene and radial cracks around quartz inclusions in garnet.

3. Sample preparation and analytical techniques

The major element composition of minerals was analyzed using a JEOL XJS 8100 electron microprobe with 15 kV acceleration voltage and a 20 nA beam current and acquisition times of 20 s and 10 s on peaks and backgrounds of the X-ray lines. The following standards were used: Si, Al, Ti: synthetic SiO_2, Al_2O_3 and TiO_2; Fe, Mn, Mg, Ca, Na, K: natural almandine, tephroite, diopside, bytownite, jadeite and orthoclase. In addition, a diopside standard (USNM-standard 117733; Jarosevich et al., 1980) was analyzed before and after each analytical session in order to increase the reliability of clinopyroxene analysis especially with respect to total cation sums. Raw counts were corrected using the PRZ correction procedure.

In-situ trace element analyses of individual mineral phases were carried out using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the CNR-IGG, Unit of Pavia, Italy. The laser probe consists of a Q-switched Nd:YAG laser, model Quantel (Brilliant), whose fundamental emission in the near-IR region (1064 nm) is converted to 266 or 213 nm by harmonic generators. The laser was focused to a spot diameter of 40–60 μm and the ablated material was analyzed by using, alternatively: (i) a double focusing sector–field analyzer Element I (ThermoFinnigan MAT), in which the standard field regulator power stage of the magnet and the ICP torch were upgraded to those of the Element II model; (ii) an Elan DRC-e mass spectrometer. Helium was used as carrier gas with Ar admixed downstream of the ablation cell. NIST SRM 610 was used as external standard and Ca or Si as internal standard. Precision and accuracy of individual analyses were assessed from repeated analyses of the BCR-2 or NIST SRM 612 standards and yielded results usually better than 7% (1σ) and 10% (at ppm level), respectively. Detection limits were typically in the range of 100–500 ppb for Sc, 10–100 ppb for Sr, Zr, Ba, Gd and Pb, 1–10 ppb for Y, Nb, La, Ce, Nd, Sm, Eu, Dy, Er, Yb. Hf and Ta, and usually <1 ppb for Pr, Th and U. A detailed description of instrumental parameters and quantification procedure is given in Tiepolo et al. (2003).

X-ray single crystal diffraction data were collected at room temperature using an Oxford Diffraction Gemini R Ultra four-circle diffractometer equipped with graphite monochromated MoKα radiation at 50 kV and 40 mA and a 135 mm diameter Ruby CCD detector. Reflections with intensities smaller than 0.2% of the type $h0l$: $h+l=2n+1$ violating $P2/n$ symmetry were proven to originate from $\lambda/2$ effect and thereafter ignored in the structure refinement. Lattice parameters were found to be very similar to omphacites of comparable chemical composition (cf. McCormick, 1986; Boffa-Ballaran et al., 1998). Structure refinements based on F_o^2 were performed using the program SHELXL-97 (Sheldrick, 2008) starting from positional and displacement parameters as in the above mentioned samples. Likewise the site-occupation of the M positions was taken from these samples as staring values for the structure refinement, which eventually converged to an $R1$-value smaller 0.004 for all studied samples.

The density of oriented inclusions in omphacites was determined based on high-quality BSE images (0.25 pixels/μm) using the NIH image software. Only those sections were selected where the long axes of the quartz–calcic amphibole needles are ± parallel to the sample surface.

IR absorption measurements of omphacite, garnet and kyanite were performed on a PerkinElmer 1760X FTIR spectrometer connected to a PerkinElmer IR microscope using doubly-polished self-supporting sections with a thickness of 0.145–0.195 mm. In addition selected individual garnet and rutile grains were handpicked from a mineral concentrate (cf. Miller et al., 2005) and embedded in epoxy resin for IR-analysis. Due to their small crystal size, garnet grains were polished to a thickness of 0.125 mm and rutiles to 0.085 mm.

A ceramic light source, a KBr beam splitter and a MCT detector were used to collect spectra in the wavenumber range from 600 to 4000 cm^{-1}. The IR microscope was equipped with three 6×/0.6 N.A. mirror (Cassegrain) lenses in condenser, objective and detector position. A dual aperture system was set up to constrain the measured sample areas and to avoid any stray light. Therefore, selected regions of the polished sample slabs were adjusted on the centre of a flat metal aperture with 100 μm diameter and, in addition, a second