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RODINGITISATION OF A BASALTIC DYKE INDUCED BY H_2O-$CaCl_2$-NaCl-H_2-CH_4 REDUCED FLUIDS IN THE BELLECOMBE SERPENTINITE, PIEMONTE ZONE, AOSTA VALLEY, ITALIAN WESTERN ALPS.

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We report fluid inclusion data in gem quality vesuvianite from coarse-grained veins within a fine-grained rodingite of the Piemonte Zone exposed in the Bellecombe serpentinite, Aosta Valley, Italian Western Alps. The fine-grained rodingite, derived from basaltic dykes, is hosted in a lherzolite-derived antigorite serpentinite. The rodingitic mineral assemblage (garnet + diopside + vesuvianite + titanite + chlorite + opaques ores) is considered to be coeval with the serpentinisation of the host lherzolite, which occurred during the late-Alpine greenschist-facies metamorphic event. This event is poorly constrained in the range T = 400-500°C and P = 0.2-0.5 GPa (Borghi et al., 1996). A network of at least five generations of polyphase mono- and/or poly-mineralic coarse-grained veins cross-cuts the fine-grained rodingite: chlorite + diopside veins (Type I), grossular-rich garnet veins (Type II), andradite-rich garnet + chlorite ± diopside ± apatite ± titanite ± opaque ores veins (Type III), vesuvianite veins (Type IV), chlorite veins (Type V). The studied vesuvianite occurs as clear gem-quality crystals in Type IV veins, which developed towards the latest phases of the rodingitisation process.

Primary (in the sense of Roedder, 1984) two phase (L+V=L) liquid dominated [df = 0.8; df = L/(L+V)] aqueous inclusions (size =10 - 50 μm) have been recognised in vesuvianite. The microthermometric measurements show temperatures of freezing for the aqueous fluid (T_f) below -60°C. Eutectic temperatures (T_e) are not visible but melting in the inclusions is always observed at -42°C. Hydrohalite melts (T_{mhy}) between -34 and -19.8°C, and ice (T_{mice}) between -19.6 and -5.9°C, with most measurements at -7.7°C. Homogenisation temperatures to the liquid phase (Th_L) are between 240 and 381 °C, with most data at 285°C. Such a microthermometric record corresponds to a H_2O-NaCl-$CaCl_2$ system, with a mean salinity of 6 wt% NaCl + 6 wt% $CaCl_2$, and density of 1.09 g/cm^3 (Bakker, 1999).

Raman analyses in the gas bubble always show the presence of well defined peaks for molecular H_2 at 4156 cm^{-1} (Fig. 1). An additional peak at 2918 cm^{-1} indicates that CH_4 is also present.

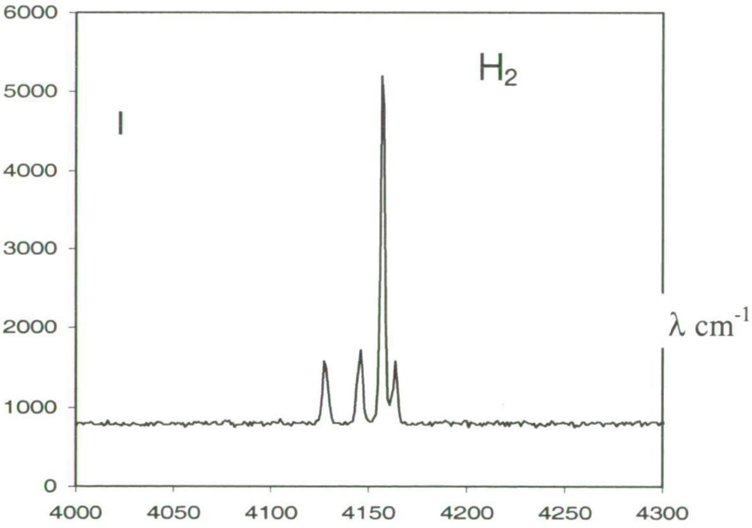

Fig. 1 - Raman spectrum of H_2 in fluid inclusions in the 4000 cm^{-1} region.

Quantitative analyses (n. 13) indicate 78–90 mole % H_2 and 22–10 mole % CH_4. The high-quality of the hydrogen Raman signal (Fig. 1) suggests that the molar volume of the gaseous part of the fluid should not be extremely high, and probably in the range 500 – 1000 mole cm^{-3} (i.e. 0.008 – 0.004 g/cm^3). Based on the relative size of the bubble, the H_2+CH_4 content in the fluid can be tentatively estimated between 1 and 0.4 mole %.

Microthermometry and Raman analyses indicate that the fluid in the inclusions is a complex mixture dominated by saline (6 wt % $CaCl_2$ + 6 wt % NaCl) aqueous fluids with minor H_2 (probably ≤ 1 mole %) and traces of CH_4. Since the precise molar volume of the H_2-CH_4 gas mixture is unknown, isochores based on the H_2O-NaCl-CaCl have been calculated (Bakker, 1999). These correspond to P ≅ 0.12 GPa at temperatures of 400 °C: they are not in agreement with the greenschist-facies conditions of T = 400-500°C and P = 0.2-0.5 GPa estimated for the second Alpine tectono-metamorphic event (Borghi et al., 1996). The effect of H_2 on the isochores is significant and can be calculated from Henry's law equation: 1 mole % H_2 in a fluid with calculated salinity would shift isochores towards higher pressures by 0.1 GPa (Bakker, 1999). This implies that the presence of 1 mole % of H_2 or less in studied fluid inclusions (amount estimated from Raman study) would give fluid isochores in equilibrium with the rodingitisation event.

Present data allow us to propose that the rodingitisation process is associated to a complex H_2O-H_2-CH_4-$CaCl_2$-NaCl fluid mixture. In the C-O-H system at the inferred P (0.2 GPa) and T (400°C), such a fluid composition ($X_{H2O}=0.988$, $X_{H2}=0.010$ $X_{CH4}=0.002$; $H_2/(H_2+CH_4)=0.86$) is indicative of f_{O2} conditions at QFM-2 (log $f_{O2}=-30.59$) and carbon activities (a_C) < 0.001.

Only in exceptional cases fluid inclusion studies have reported the presence of detectable H_2 from metamorphic environments (e.g.: Peretti et al., 1992). In fact, to be stable in fluids in considerable amounts, H_2 requires not only low oxygen fugacity conditions but also very low C activity, otherwise CH_4 would be the stable fluid phase. Similar conditions can be achieved during serpentinisation processes. H_2 can be produced through reactions between serpentinising aqueous fluids and mafic rocks such as: FeO (silicate) + $0.5H_2O$ = $FeO_{1.5}$ (silicate/oxide) + $0.5H_2$. Serpentinisation reactions can also account for an enrichment of Ca^{2+} in the aqueous fluid through breakdown of clinopyroxene and Ca-bearing orthopyroxene.

From the results of the present study, it may be concluded that the rodingitisation of the Bellecombe basaltic dyke was coeval with the serpentinisation of the hosting ultramafic rocks and was favoured by the infiltration of Ca-rich H_2–bearing reducing aqueous solutions derived from the serpentinising metamorphic aqueous fluids.

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