

## Geochemistry of devolatilization (and exhumation) in W. Alps HP and UHP metasedimentary suites

G. BEBOUT<sup>1,2</sup>, P. AGARD<sup>3</sup>, R. KING<sup>1,2</sup> AND E. NAKAMURA<sup>2</sup>

<sup>1</sup>Earth & Environmental Sciences, Lehigh University, Bethlehem, PA 18015, USA. (geb0@lehigh.edu)

<sup>2</sup>The Pheasant Memorial Laboratory, Institute for Study of the Earth's Interior, Okayama University at Misasa, Tottoriken, 682-0193, JAPAN.

<sup>3</sup>Laboratoire de Tectonique, Universite PM Curie, Paris Cedex 5, FRANCE

### Abstract

Subduction-zone metamorphic rocks are notorious for their superposition of prograde mineral assemblages and exhumation-related assemblages. We have undertaken a whole-rock-EPMA-SIMS analysis of records of prograde devolatilization and exhumation in metasedimentary suites in the W. Alps, Italy (Schistes Lustrés, Cottian Alps, SL; coesite-bearing Lago di Cignana, LDC). Together, the suites represent peak conditions of 1.5 to 2.9 GPa, 300-625°C; however, prograde histories in the higher-grade SL and at LDC are highly obscured by overprinting during underplating and exhumation (Reinecke, 1998; Agard et al., 2002). In the lower-grade SL, heterogeneity in mica trace element content (B, Li, Be, Cs, Ba, Sr; by SIMS) exists at sub-mm scales, not obviously related to mica texture or grain size. In the high-grade SL and at LDC, multiple coarse-grained mica generations (at LDC, some paragonitic) have different trace element contents and, in one LDC sample, white-mica inclusions in garnet contrast in trace/major element chemistry with matrix micas. Other than in B contents, white-mica does not *obviously* vary systematically in trace element contents across grade, with any prograde variation variably obscured by exhumation. Low-grade SL contains very minor fine-grained tourmaline with  $\delta^{11}\text{B}_{\text{SRM951}}$  ranging widely from -10 to +15‰; some higher-grade SL contains abundant, coarse-grained tourmaline with  $\delta^{11}\text{B}$  of -12 to -1‰ consistent with B derivation from devolatilizing lower- $\delta^{11}\text{B}$  micas, perhaps during initial underplating and exhumation. Tourmaline in siliceous LDC rocks preserves distinct generations of low- $\delta^{11}\text{B}$ , high-Mg tourmaline attributable to UHP metamorphism and high- $\delta^{11}\text{B}$ , lower-Mg tourmaline attributed to exhumation (Bebout and Nakamura, 2003). Highly overprinted more pelitic LDC rocks contain texturally late-stage, zoned tourmaline with  $\delta^{11}\text{B}$  of -7 to +1‰ similar to that in high-grade SL, compatible with a late-stage origin of B from devolatilizing white-micas.

### References

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## Solubility of CO<sub>2</sub> in hydrous rhyolitic to basaltic melts

H. BEHRENS, F. HOLTZ, S. OHLHORST, N. TAMIC, M. FREISE, AND R. BOTCHARNIKOV

Institute of Mineralogy, Uni Hannover, Germany  
 (h.behrens@mineralogie.uni-hannover.de)

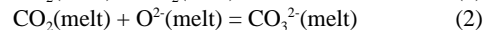
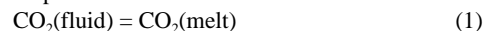
Although the concentration of CO<sub>2</sub> in magmas is usually low compared to H<sub>2</sub>O, it is often the first component to reach saturation during pressure release due to its low solubility in the melt. Hence, to understand the kinetics of magma degassing, the solubility of CO<sub>2</sub> in the melt must be known as a function of T, P and fluid composition.

In the present work, the solubility of CO<sub>2</sub> in rhyolitic, dacitic and basaltic melts equilibrated with H<sub>2</sub>O-CO<sub>2</sub> fluids was experimentally investigated at temperatures above the liquidus and pressures ranging from 100 to 500 MPa. In the experiments a single glass piece, liquid water and a CO<sub>2</sub> source (mostly Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) were loaded into noble metal capsules and processed for 10 – 200 h in internally heated gas pressure vessels. Rapid quench was required for dacitic and basaltic compositions to get bubble-free and crystal free glasses (quenched melts). Fluid composition after the run was measured gravimetrically or was deduced by mass balance. Volatile concentrations in the glasses were analyzed by IR and SIMS.

IR spectra confirm that carbon dioxide is dissolved in rhyolitic glasses only as molecular CO<sub>2</sub> and in basaltic glasses only as carbonate. In dacitic glasses both carbon species are present with the relative abundance of molecular CO<sub>2</sub> decreasing with increasing H<sub>2</sub>O content of the glass. At constant T and P the solubility of CO<sub>2</sub> varies non-linearly with mol fraction of CO<sub>2</sub> in the fluid ( $X_{\text{CO}_2,\text{n}}$ ) for all melts. The total CO<sub>2</sub> concentration is approximately constant in rhyolitic and dacitic melts at 200 and 500 MPa in the  $X_{\text{CO}_2,\text{n}}$ -range 0.8 -1.0. Basaltic melts show a maximum in CO<sub>2</sub> solubility for water-rich fluid compositions.

The maximum CO<sub>2</sub> content which can be dissolved in the melt at 500 MPa increases from rhyolite to basalt (2500 ppm CO<sub>2</sub> in rhyolite at 1100°C (Tamic et al. 2001), 2900 ppm in dacite at 1250°C, 4300 ppm in basalt at 1120°C). The small difference in the experimental temperatures is expected to be of minor importance.

The dissolution of CO<sub>2</sub> in the melt can be considered as a two step reaction:



The non-linear variation of total CO<sub>2</sub> solubility with  $X_{\text{CO}_2,\text{n}}$  indicates that the equilibrium constant for both reactions ( $K_1$  and  $K_2$ , respectively) increase strongly with dissolved water. A new thermodynamic model is proposed to describe the CO<sub>2</sub> solubility in hydrous melts assuming a simple log linear dependence of  $K_1$  and  $K_2$  on dissolved H<sub>2</sub>O.

### References

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