

## Influence of mantle-wedge flow on the composition of fluids released by subducting slabs

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Models of subduction zones that include shear heating and non-Newtonian mantle wedge rheology show that, upon reaching the wedge tip, slab-surface temperature increases dramatically over a narrow depth range [e.g. 1]. This leads to pronounced, nearly isobaric changes in metamorphic facies and significant devolatilization in the uppermost slab at the wedge tip. For subducting systems in which the slab fluid is dominated by H<sub>2</sub>O, this region will also mark a profound transition in the nature and composition of the fluid exiting the slab. Using the Central American subduction system as a model [2], the pressure (*P*) at which the slab top comes into contact with flowing mantle is ~1.7 GPa. At shallower depths, temperatures (*T*) in the subducting crust are low (less than ~400°C), and *T* gradients along vertical flow paths are minimal. At these levels, the composition of slab-top fluids can be modeled using extrapolated thermodynamic properties of aqueous solutes [3, 4]. MORB-equilibrated fluid is calculated to be dilute (up to ~1 wt% total dissolved solids), with simple ions, ion pairs and monomeric species the predominant solutes. However, at the wedge tip, the large nearly isobaric rise in *T* leads to dramatically different aqueous solutions. Experimental studies of model feldspar-quartz systems reveal total dissolved solids of >20 wt% oxides. The solutes are >90% polymerized aluminosilicate species [e.g. 5], which strongly enhance the capability for mass transfer [4]. Values of *dT/dP* along flow paths of fluids rising from the slab interior also increase significantly at the wedge tip. At this depth and below, the large *dT/dP* of fluid rising through the slab will lead to increasing element stripping from slab lithologies. The thermal structure imposed by non-Newtonian wedge rheology and plausible magnitudes of shear heating thus leads to a major transition in metasomatic mass transfer from the slab at the wedge tip.

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## PVTx properties of sulfate-bearing aqueous fluids

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Sulfates (SO<sub>4</sub><sup>2-</sup>) are among the most relevant chemical species present in deep geological fluids. They play an important role on the complexation and transport of metals (namely gold) and the formation of ore deposits in volcanic settings. The precipitation of sulfate minerals (*e.g.* anhydrite) is often related to hydrothermal activity on the seafloor, but may also occur during ore deposit formation and sulfur-rich magmatism [1, 2]. Sulfates are also common daughter minerals in saline fluid inclusions, recording the presence of sulfate-bearing fluid in deep-seated environments. The fluid-rock interactions in this environments involve *T* as high as 500°C and may control the composition and evolution of fluids at depth. There is however a dearth of thermodynamic data for sulfate-bearing aqueous fluids at elevated *P* and *T*. The lack of these data limit the quantitative modeling of fluid-rock interactions involving sulfate-rich fluids, as well as the accurate interpretation of sulfate-bearing fluid inclusion data.

The goal of this study was to determine the PVTx properties of sulfate-rich aqueous fluids (H<sub>2</sub>O-Na<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O-MgSO<sub>4</sub> mixtures) with variable salinities (0.5 - 1m) from acoustic velocity (*V<sub>p</sub>*) measurements using Brillouin scattering spectroscopy. Experiments were conducted along isothermal path up to 400 °C and 5 GPa using externally heated diamond anvil cells (DAC). The *V<sub>p</sub>* at room conditions are in good agreement with the results obtained by Millero *et al.* [3]. Anomalous changes in the *V<sub>p</sub>*-pressure relations are observed between 0.2-0.4 GPa and may be ascribed to the liquid-liquid transition in the solvent [4, 5]. The acoustic velocity *V<sub>p</sub>* data as a function of *P*-*T* are used to determine the density of these solutions up to 400°C and 5 GPa. The PVT relations were further fit using modified Redlich-Kwong (MRK) equations of state (EoS) to develop a predictive model for the properties of sulfate-bearing solutions in high pressures environments.

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