

Thermodynamics of carbon-bearing fluids and oxidized carbon speciation equilibria in subduction zone fluids

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Subduction zones play an important role in the deep carbon cycle as allow the reintroduction of C into the mantle and the recycling through arc magmatism. The occurrence of diamond-bearing fluid inclusions in HP rocks of oceanic origin suggests that C can be efficiently transferred from the slab to the mantle wedge through dissolution reactions driven by slab-derived aqueous fluids (Frezzotti *et al.*, 2011). A better understanding of the role of aqueous fluids on C recycling thus relies on the development of robust thermodynamic models of the properties of C-bearing aqueous species at relevant conditions.

In this contribution, we present first experimental data on the thermodynamic properties of oxidized carbon species at high P-T that have been used to constrain a model of the speciation of oxidized carbon in aqueous fluids at subduction zone conditions. The thermodynamic properties of oxidized C-bearing aqueous fluids were determined up to 650 °C and 4 GPa from acoustic velocity measurements performed on Na₂CO₃ and NaHCO₃ aqueous solutions with various concentrations (0.1 to 1 m). Experiments were conducted on externally heated diamond anvil cells by Brillouin scattering spectroscopy. Densities of the fluids directly obtained from the measured acoustic velocities were used to calibrate an equation of state (EoS) able to predict the thermodynamic properties of carbonated fluids at high P-T conditions. Further, the derived partial molar volume and compressibility of aqueous CO₃²⁻ and HCO₃⁻ ions were used to constrain the effect of P on the equilibrium constant controlling the speciation of oxidized carbon in high temperature fluids: $\text{HCO}_3^- = \text{H}^+ + \text{CO}_3^{2-}$ (Eq.1). The calculated volume of reaction $\Delta\bar{V}_r$ for Eq.1 is negative at the investigated P conditions, indicating that aqueous carbonate ions CO₃²⁻ are the dominant C-species in high P oxidized fluid. This observation is consistent with direct investigations of the speciation of fluids in equilibrium with carbonate minerals by Raman spectroscopy. The predicted stability of aqueous CO₃²⁻ in high P fluids and the enhanced solubility of carbonate minerals under P, indicate that CO₃²⁻ ions may be major components in slab-derived fluids and may thus control the mobility of other rock-forming elements in subduction zones.

Branched tetraethers derived temperature reconstruction from northwestern Black Sea: Proposition of correction and associated sensitivity test

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Proxies based on branched GDGT (glycerol dialkyl glycerol tetraether) core lipids are promising tools to reconstruct past continental temperatures. However their use is not always straightforward, notably because of the uncertainties on the source of these biomarkers.

Here we study the relative distribution of branched GDGTs (brGDGTs) in lacustrine sediments from a core retrieved in the northwestern Black Sea (from 40 to 9 cal ka BP). We first discuss the origins of the branched GDGTs. Comparisons to geochemical proxies from the same core support a dominant terrestrial origin of the brGDGTs during the last glacial, and a strong decrease of the soil derived brGDGTs relative proportion toward the Holocene. As this lowering of the soil vs. lacustrine derived brGDGTs is prone to bias the temperature signal reconstructed with a soil calibration, we propose a correction of this signal with a binary mixing model. We further test the sensitivity of this model with a Monte Carlo method. The resulting signals are consistent with (discrete) independent temperature reconstructions from the study area. Moreover the temperature relative evolution provides insights into the millennial scale climate variability in central and eastern Europe. Notably, the imprints of Heinrich event cold spells and late glacial climatic oscillations are in line with other regional paleorecords from the northern hemisphere.