

FLUIDS IN THE CRUST

**Redox effects on calcite-portlandite-fluid equilibria at forearc conditions: Carbon mobility, methanogenesis, and reduction melting of calcite†**

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**ABSTRACT**

Oxygen fugacity ( $f_{\text{O}_2}$ ) is a fundamental parameter that controls carbon mobility in aqueous fluids in geological environments such as subduction zones, where reduced serpentinite fluids have the potential to infiltrate oxidized carbonate-bearing lithologies. Using experiments and calculations, we describe how mineral-fluid equilibria evolve as  $f_{\text{O}_2}$  decreases in the model Ca-C-O-H system at forearc conditions (300–700 °C and 2–10 kbar). Experimental calcite solubility was constant at  $f_{\text{O}_2}$  values from quartz-fayalite-magnetite (QFM) to hematite-magnetite (HM). At lower  $f_{\text{O}_2}$  values of iron-magnetite (IM) or wüstite-magnetite (WM), calcite reacted with  $\text{H}_2$  to form methane plus portlandite or melt. These results were consistent with thermodynamic calculations and indicate that carbon mobility, as parameterized by total aqueous carbon ( $[\text{C}_{\text{TOT}}]$ ), is strongly dependent on  $f_{\text{O}_2}$ . At constant pressure and temperature, carbon mobility is minimized at oxidizing conditions, where  $[\text{C}_{\text{TOT}}]$  is controlled by calcite solubility. Carbon mobility is maximized at the most reducing conditions because all the carbon in the system is present as  $\text{CH}_4$ . An intermediate region of carbon mobility exists in which calcite is stable with a  $\text{CH}_4$ -bearing fluid. As pressure increases from 2 to 10 kbar, the  $f_{\text{O}_2}$  range over which calcite is stable with a methane-rich fluid shifts to more reducing conditions. The variety of geological conditions with the potential for redox enhancement of carbon mobility becomes more restricted with depth. Reduction melting was observed at 700 °C and 6 kbar, and at 650 °C and 10 kbar, due to the partial reaction of calcite to portlandite at conditions above the hydrous melting curve of calcite+portlandite. Although likely metastable in the present experiments, reduction melting may occur in nature whenever  $\text{H}_2$  partially reduces carbonate minerals at pressures and temperatures above the hydrous melting curve of calcite+portlandite. Whether it causes melting or not, calcite reduction is likely an important mechanism for abiogenic methanogenesis in natural systems such as subduction zone forearcs or similar environments with the potential for interaction of reduced fluids with carbonate minerals. Because calcite solubility at oxidized conditions is already known to increase substantially with pressure, the additional increase in carbon mobility provided by calcite reduction implies that subduction zones may host some of the most carbon-rich aqueous fluids on Earth.

**Keywords:** Carbon cycle, subduction zones, fluid-rock interaction, serpentinization, forearc mantle, methanogenesis