

## Mantle melting and volatiles: Redox-controlled solution mechanisms and C-isotope fractionation in coexisting silicate melt and COH fluid

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Carbon solubility mechanisms in melts and fluid and C isotope partitioning within and between melts and fluids in alkali aluminosilicate – C-O-H systems under oxidizing and reducing conditions have been determined experimentally to aid our understanding materials transport processes in the Earth. The experimental data were recorded while the fluids and melts were at equilibrium in a hydrothermal diamond anvil cell at temperatures and pressures to 850°C and >1300 MPa and controlled redox conditions. Vibrational spectroscopy was used for structural determination and to determine carbon isotope fractionation within and between coexisting melt and fluid.

The solution equilibria were (1)  $2\text{CH}_4 + \text{Q}^n = 2\text{CH}_3^- + \text{H}_2\text{O} + \text{Q}^{n+1}$  and (2)  $2\text{CO}_3^{2-} + \text{H}_2\text{O} + 2\text{Q}^{n+1} = \text{HCO}_3^- + 2\text{Q}^n$ , under reducing and oxidizing conditions, respectively, and where the superscript, n, in the  $\text{Q}^n$ -species denotes number of bridging oxygen in the silicate species (Q-species). The abundance ratios,  $\text{CH}_3/\text{CH}_4$  and  $\text{HCO}_3^-/\text{CO}_3^{2-}$ , increase with temperature. The enthalpy change associated with the species transformation differs for fluids and melts and also for oxidized and reduced carbon (Reducing:  $\Delta H_{(1)}^{\text{fluid}} = 16 \pm 5$  kJ/mol,  $\Delta H_{(1)}^{\text{melt}} = 50 \pm 5$  kJ/mol; oxidizing  $\Delta H_{(2)}^{\text{fluid}} = 81 \pm 14$  kJ/mol). For the exchange equilibrium of  $\text{CH}_4$  and  $\text{CH}_3$  species between fluid and melt, the temperature-dependent equilibrium constant,  $(X_{\text{CH}_4}/X_{\text{CH}_3})^{\text{fluid}}/(X_{\text{CH}_4}/X_{\text{CH}_3})^{\text{melt}}$ , yields  $\Delta H = 34 \pm 3$  kJ/mol [1]. The carbon isotope fractionation factors,  $\alpha$ , between melt and fluid differ from 1 even at magmatic temperatures and are governed by these equilibria and can be fitted to functions of the form  $\ln \alpha = a + b/T$ . For example, the  $\Delta H$  derived from such fits equals  $3.2 \pm 0.7$  kJ/mol and  $9.5 \pm 0.8$  kJ/mol for the  $^{13}\text{C}/^{12}\text{C}$  fractionation under oxidizing and reducing conditions, respectively. From such experimental data, it is suggested that  $\delta^{13}\text{C}$ -differences between coexisting ( $\text{CO}_2 + \text{H}_2\text{O}$ ) fluid and silicate melts in the upper mantle increases from about 40 to > 100 ‰ and with reduced  $\text{CH}_4 + \text{H}_2\text{O} + \text{H}_2$  by > 100% in magmatic temperature ranges. Temperature, therefore, during melting and crystallization is an alternative with which to explain C isotope variations in mantle- derived magma.

[1] Mysen, (2015) *Amer. Mineral* **100**, 872-882.