

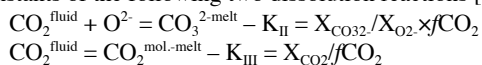
Solubility of CO₂ in rhyolitic melts as a function of depth, temperature, and oxygen fugacity – implications for carbon flux in subduction zones

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Partial melt of subducting sediments is thought to be a critical agent in transport of trace elements and water to arc basalt source regions. Sediment melts may also carry CO₂ to arc basalt source regions, however, the carrying capacity of CO₂ in rhyolitic melts of appropriate composition and at conditions relevant for subducting slab is unknown. In particular, the solubility of CO₂ in rhyolitic sediment melt may vary significantly as a function of fO_2 , i.e. from graphite-saturated or organic carbon-bearing domains to carbonate/CO₂-saturated conditions. Yet no studies have constrained the sediment partial melt CO₂ carrying capacity under graphite saturated conditions.

We conducted experiments over 1.5 to 3.0 GPa and 1300°C on a model, natural rhyolitic melt under nominally anhydrous to hydrous conditions. CO₂ content of experimental glasses in equilibrium with CO₂-rich vapor phase was determined using FTIR spectroscopy. CO₂ was found to be dissolved both as molecular CO₂ (CO₂^{mol.-melt}) and as carbonates (CO₃^{2.-melt}). Speciation-specific CO₂ solubility data were used to constrain the pressure-dependence of equilibrium constants of the following two dissolution reactions [1] –



Further, using the thermodynamic framework given by [2], here we calculated the CO₂ content of silicate melt as a function of P, T, and fO_2 for graphite-saturated conditions, by combining the P-dependence of K_{II} and K_{III} constrained in [1] and P-T- fO_2 dependence of K_{I} of the reaction: C + O₂ = CO₂^{fluid} given by [2]. Experiments at lower temperatures are underway to constrain the T-dependence of K_{II} and K_{III} .

Using the model above, we have calculated the total CO₂ content (CO₂^{mol.-melt} + CO₃^{2.-melt}) of a sediment partial melt for a variety of subduction P-T paths [3] at fO_2 values at or below the graphite-CO₂ equilibrium. Our study suggests that ≥1 wt.% CO₂ may be dissolved in sediment partial melt at graphite saturation even at fO_2 ~FMQ-3.

[1] Duncan and Dasgupta. (in review) *GCA*; [2] Holloway *et al.*, (1992) *EJM*, 4, 105-114; [3] Syracuse *et al.*, (2010) *PEPI*, 183, 73-90.

The Caribbean plateau and OAE2: resolution of timing and trace metal release

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Initial volcanism that formed a large part of the Caribbean ocean plateau coincided with ocean anoxic event 2 (OAE2), which occurred close to the Cenomanian/Turonian (C/T) boundary (~94 Ma). Increased trace metal delivery to the surface ocean during volcanic activity associated with this ocean plateau has been suggested as the cause for the depletion of seawater oxygen concentration and deposition of organic rich sediments [1]. This link is supported by isotopic excursions (Sr, Nd, Pb, Os) across the OAE2 that indicate a volcanic source. An interval of trace metal anomalies occurs in pelagic carbonate and black shale sequences of the Rock Creek Canyon section, Pueblo, Colorado at the onset of the δ¹³C global positive event [2]. The presence of these metal anomalies and isotopic profiles indicates a relationship between ocean plateau formation and ocean anoxia.

To further explore a direct connection between this ocean plateau and OAE2, we determined the distribution of major, minor and trace element abundances in marine sediments from an additional 7 globally distributed sites (Bass River, New Jersey; central Kerguelen Plateau; Baranca el Cañon, Mexico; Totumo, Venezuela; and Bottaccione, Calabianca and Novara di Sicilia, Sicily). After normalizing element concentrations to Zr, an interval of metal anomalies is present in all 8 sites. The changes in the trace metal patterns and concentrations among these sites is consistent with modeled late-Cretaceous surface circulation and a source of metals being the Caribbean plateau.

[1] Sinton&Duncan (1997) *Econ. Geol.*, **92**, 836-842. [2] Snow *et al.*, (2005) *Paleoceanog.*, **20**, PA3005.