

## Melting and Redox Control of the Deep Carbon Cycle

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The deep carbon cycle is governed by a combination of melting and redox reactions. While in the uppermost mantle, slab-derived CO<sub>2</sub> may remain in its oxidized state, reduction and immobilization is inevitable in the deeper mantle.

Melting of subducted carbonated sediments produces carbonate-saturated phonolitic silicate melts to ~5 GPa but requires temperatures in excess of what is normally reached at subarc depth. The Italian ultrapotassic CO<sub>2</sub>-rich kamafugites are mostly interpreted through assimilation of carbonate in the Apennine crust but experiments demonstrate that they derive from subducted sediments and their phonolite melts. Melting occurs at the trailing slab edge and the migration of the already ultrapotassic CO<sub>2</sub>-rich phonolites leads to hybridization in the mantle, where heavily undersaturated kamafugites (~43 wt% SiO<sub>2</sub>) form through reaction with olivine and cpx under CO<sub>2</sub>-rich conditions. Upon rise, these kamafugites exsolve carbonatites and the observed trace concentrations of the Apennine carbonatites and kamafugites match our experimental element partition coefficients.

Above 5 GPa, melts of subducted carbonated crust are alkali-rich carbonatites. Upon migration into metal-saturated mantle at >8 GPa, these carbonatites are reduced to diamond and immobilized leading to mantle domains with abundant Fe<sup>3+</sup> in garnet (and perovskite in the lower mantle) with most Fe<sup>0</sup> oxidized and the carbon reduced to its elemental state. Interestingly, the eutectic between Fe<sup>0</sup> and C lies >200 °C below the adiabat leading to mantle domains with a small Fe-C-metal melt fraction that is probably inconspicuous as this melt will remain isolated at grain boundaries.

While redox freezing leads to carbon enriched domains in the mantle, the inverse process occurs upon decompression when the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio in garnet approaches again zero. As a consequence of the reduction of Fe<sup>3+</sup> any coexisting carbon is reoxidized and a first carbonatitic melt fraction forms from carbon bearing mantle. This process may occur under mid-ocean ridges as well as in hotspots and may ultimately be responsible for the first melts to occur in mantle upwellings.

Further progress in our ability to predict the deep carbon cycle critically depends on thermodynamic modelling: After determining the high-pressure melting of siderite, of the highly non-ideal magnesite-siderite binary and of the liquidus surface of the Ca-Fe-Mg-carbonate ternary (at 3.5 GPa), we are presently developing a carbonate melt model.