

## Chloride degassing and its effects on the evolution of magmatic redox state

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Magmatic  $fO_2$  is a parameter that plays an important role in ferromagnesian and sulfide phase equilibria, the speciation of redox sensitive volatiles, and the physical properties of silicate liquids. We have performed redox controlled experiments to investigate iron partitioning behavior between a coexisting chloride rich volatile phase and silicate liquid. The results of these experiments suggest that volatiles with relatively modest chloride contents may contain several wt % Fe as a chloride species. These experimentally generated data suggest that the degassing of chloride rich volatiles may reduce the concentration of the FeO component of the melt. Notably, the preferential scavenging of ferrous iron from the melt must increase the  $Fe^{3+}/\Sigma Fe$ , consequently causing the  $fO_2$  residual degassed melt to also increase.

These data support a model wherein the degassing of a chloride-rich volatile phase may significantly increase the oxidation state of the residual melt. Model calculations indicate that the magnitude of the induced oxidation ranges from 0.5 to 1.0 log unit; where this value depends on the partition coefficient value and the volatile phase-melt ratio used in the calculation. The oxidation of magmas during degassing and ascent may have marked effects on the identity and composition of the hypersolidus phase assemblage. Most saliently, this oxidizing effect may be manifested in sulfide saturated arc magmas as the destabilization of coexisting immiscible sulfide liquids or crystalline magmatic sulfides. Such an iron scavenging based oxidation process has important implications for the remobilization of sulfide bound chalcophile metals as well as the petrologic interpretation of compositional zoning patterns in crystallizing ferromagnesian phases.

## Carbonatites and Pb isotopes – Insights into terrestrial evolution

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Information concerning the depleted mantle has come from studies of oceanic basalts but these cover only a small amount of geological time, at best back to a few hundred million years. Carbonatites, however, ranging in age from 3.0 Ga through to the present, provide a means of monitoring the secular evolution of the sub-continental mantle. Initial Pb isotopic ratios in carbonatites and alkaline complex rocks from the Canadian and Fennoscandian Shields appear to trace the evolution of “depleted” subcontinental mantle over the past 2.7 Ga.  $^{87}Sr/^{86}Sr$  and  $^{206}Pb/^{204}Pb$  ratios from Archean carbonatites from Canada tend to cluster closely around model “bulk silicate Earth” values in isotope correlation diagrams suggesting a mantle not yet depleted. A marked depletion event >3.0 Ga indicated by the Sm-Nd and Lu-Hf systems indicates sampling of considerably older, depleted mantle sources. Mantle differentiation processes appear to have changed in some fundamental way around 3 Ga with extraction of sialic crust. The similarity in isotopic compositions of young carbonatites (<100 Ma) to some OIB components (FOZO, HIMU, EM1) with little or no involvement with DMM suggests similar sources, and sub-lithospheric, deep-seated magmatism. Analogues to present day mantle components are not recognized in Archean carbonatites. Binary mixing of mantle sources (e.g. HIMU and EM1 for many young carbonatites) can be traced back to at least 1900 Ma.