

Geothermobarometric and fluid inclusion data of historic lavas of Fogo Volcano, Cape Verde islands

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Fogo is one of the most active oceanic volcanoes and the only island of the Cape Verde archipelago with historic volcanic activity. The 1995 eruption has been preceded and accompanied by seismic activity beneath the submarine Fogo-Brava-platform and also on the adjacent island of Brava. We have carried out a geobarometric study of basaltic to tephriphonolitic volcanic rocks from several historic eruptions of Fogo in order to reconstruct the depths of magma reservoirs and magma pathways prior to eruption. Our investigations focused on the most recent eruptions of 1995 and 1951. The eruption of 1995 was mineralogically and chemically zoned; the early ejecta were phonotephritic, the later main volume was tephritic in composition. Clinopyroxene-melt thermobarometry of 75 clinopyroxene phenocrysts in nine samples of 1995 yields a dominant pressure range of 400-690 MPa (average 510 MPa). There is no systematic pressure difference between the tephrites and the phonotephrites. For the 1951 eruption 87 clinopyroxene phenocrysts in eight samples yield a range of 380-710 MPa (average 500 MPa). Six clinopyroxene phenocrysts of a lava flow from 1694 yield a pressure range of 450-500 MPa. These pressures are interpreted to reflect different fractionation levels at ca. 15-24 km depth, within the uppermost mantle, where melt and phenocrysts last equilibrated.

Microthermometry of CO₂-rich fluid inclusions in clinopyroxene and olivine phenocrysts of the 1995 eruption yields a slightly different pressure range. Inferred pressures range from 260-580 MPa with a maximum between 360 and 420 MPa. There is thus considerable overlap with the cpx-melt data and a spread to lower pressures, which indicates limited reequilibration of fluid inclusions during magma transit to the surface. Our data suggest that the 1995 magmas ascended from mantle depth to the surface with only short residence times at crustal levels, probably on the order of one day. This conclusion is in accordance with the absence of plagioclase phenocrysts and microphenocrysts in the vast majority of Recent Fogo lavas.

Ab initio studies of Fe isotope fractionation in Fe sulfides

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Iron sulfide compounds form in many natural and microbial processes involving the reduction of iron and/or sulfur. ⁵⁶Fe/⁵⁴Fe ratios in sedimentary pyrites deposited before the rise of atmospheric oxygen were much lighter than those of today [1]. The Fe isotope signatures of such minerals as pyrite depend on the fractionation between their dissolved precursors and upon the reservoirs from which the iron is taken. Understanding of redox and non-redox effects on equilibrium iron isotope fractionation in Fe sulfides will help us decipher modern and ancient Fe-isotopic signatures.

Here we predict ⁵⁶Fe/⁵⁴Fe fractionations in Fe-S and Fe^{II}-Cl complexes with 3 sets of ab initio models, extending our previous studies of aqueous ferric chloride complexes [2]. In B3LYP/6-31G(d) models, 1000 ln β₅₆₋₅₄ (reduced partition function ratios) of Fe^{III}(H₂O)₆, Fe^{III}Cl²⁺(H₂O)₅, Fe^{III}Cl₂⁺(H₂O)₄, Fe^{III}Cl₃(H₂O)₃, Fe^{III}Cl₄⁻, Fe^{III}Cl₅²⁻(H₂O)₂, Fe^{III}Cl₆³⁻ show roughly linear decreases of ~0.9‰/Cl. The Fe^{II}-S series and the Fe^{II}-Cl series show slightly smaller decreases of ~0.6‰/S and ~0.6‰/Cl respectively. 1000 ln β for the tetrahedral complex Fe^{III}Cl₄⁻ is slightly larger than Fe^{III}Cl₃(H₂O)₃, most likely due to the smaller coordination number. Surprisingly, tetrahedral ferrous species such as Fe^{II}Cl₄²⁻ will not have the abnormally high ⁵⁶Fe/⁵⁴Fe, demonstrating that in this case, the change of bond partners is more significant than the change in coordination number.

Redox fractionations between equivalent species (e.g., Fe^{III}Cl₂⁺(H₂O)₄ vs. Fe^{II}Cl⁺(H₂O)₅) range from 2.7 to 3.9‰, the oxidized member being heavier. Fractionation between ferric and ferrous Fe modeled with an inner hydration sphere of 6 waters, is 3.2‰ when calculated with the same basis set and method. A model of the tetrahedral iron sulfide site in the iron protein rubredoxin (Fe-(SH-R)₄) shows a 2.6‰ difference between the ferric and ferrous versions.

We also compare the effects of coordination number and bond length in sulfide species. Fe^{II}(SH)₄ is predicted to have higher ⁵⁶Fe/⁵⁴Fe than Fe^{II}(SH)₆ suggesting that the mineral mackinawite (tetrahedral coordination of Fe) will have higher ⁵⁶Fe/⁵⁴Fe than triolite or pyrrhotite (octahedral coordination of Fe). Trends in equilibrium iron isotope fractionation among the ferric chloride complexes appear as reasonable predictors of trends in other sequences of Fe-ligand complexes.

[1] Rouxel, Bekker, Edwards, (2005) *Science* **307** 1088-1091

[2] Hill & Schauble (2008) *Geochim. Cosmochim. Acta* **72** 1939-1958.