Hf and Nd Isotope Decoupling in the Lesser Antilles Island Arc

DAWN MUNDAY¹, MATTHEW THIRLWALL¹, TERRY SMITH², JON DAVIDSON³

¹Royal Holloway Univ. London, Surrey TW20 0EX, UK d.munday@gl.rhul.ac.uk m.thirlwall@gl.rhul.ac.uk

New Hf isotopic analyses have been carried out on several islands in the Lesser Antilles island arc. ¹⁷⁶Hf/¹⁷⁷Hf ranges from 0.28309-0.28311 on Dominica, 0.28273-0.28313 on Bequia and 0.28306-0.28317 on Grenada, with external precision <0.000010 2sd. When these analyses are plotted relative to ¹⁴³Nd/¹⁴⁴Nd decoupling between Hf and Nd is visible, both at the lower and upper ends of the Nd-Hf isotopic range. Hf-Nd isotopic data for the southern part of the arc (Grenada and Bequia) form a tight linear array extending to _Hf-Nd data arrays and parallel to the array published for Martinique (Woodhead et al., 2001), but offset to lower _Hf by ca. 2.5 units. Data from Dominica lie at the depleted end of the Martinique data array and form a very tight field offset ~3 _Hf units above the Grenada-Bequia array.

Correlations with _18O indicate that both the Bequia and Martinique arrays result from high level assimilation of sediment in the arc crust, while the higher _Hf for a given _Nd in the north may relate to a greater pelagic component to the sediment in the north. At the depleted end, the Grenada-Bequia field extrapolates to the average composition of Pacific MORB and of Atlantic MORB away from hotspot influences, but the Martinique-Dominica data field extrapolates to a possible mantle wedge composition more closely resembling Indian MORB compositions. Given that Indian MORB mantle is an unlikely component in the Antilles lithosphere, alternative scenarios must be considered that could yield the higher _H in parental lavas for Dominica and in Martinique prior to high-level assimilation. Although the Caribbean plate may have formed above the Galapagos hotspot, published Galapagos data provide no evidence of a high _H component (Blichert-Toft & White 2001).

In the subduction zone, generation of the Hf-Nd isotope compositions of Dominican lavas from the same wedge source as observed in Grenada would require either preferential transport of sediment Nd from the subduction zone relative to Hf, or would require that the subducted sediment had much higher _Hf or Nd/Hf ratios than that assimilated in the arc crust. Both hypotheses are difficult to reconcile with the detailed relationships shown within Dominica.

References

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Oxidation of the mantle wedge

JAMES E MUNGALL

Dept of Geology, University of Toronto, 22 Russell St, Toronto, ON, M5S 3B1, mungall@geology.utoronto.ca

The flux of chalcophile elements Cu, Au and the platinum group elements from the mantle to the crust is the first-order control on their crustal abundances and also their availability to form exploitable ore deposits. The removal of significant amounts of chalcophile elements from the mantle wedge into arc magmas can only occur if sulfide is absent from the source, requiring either extreme mantle depletion to form boninitic magmas, or oxidation of the mantle wedge to values of $\log fO_2 > FMQ+2$ resulting in the complete oxidation of sulfide to sulfate. The only agent capable of oxidizing the mantle wedge sufficiently to destroy sulfide is ferric iron. I have applied empirically calibrated HKF parameters (E. Shock pers comm, 2000; Johnson et al., 1992) and the NIST model for the dielectric constant of water (Fernandez et al., 1997) to estimate partial molar thermodynamic properties of aqueous solutes at 600 $^{\circ}\text{C}$ to pressures as high as 30 kbar. The modelled total concentration of species containing Fe⁺³ remains below 10 ppm at pressures less than 25 kbar, but rises rapidly as the critical end point in the system silicate melt water is approached near 30 kbar. Comparison of these model results with estimates of the redox state of iron in slab melts (MELTS software; Ghiorso and Sack, 1995) shows that in terms of the total flux of Fe₂O₃ out of the slab per unit mass of water brought into the system by the slab, slab melts will carry as much as 10,000 times more Fe₂O₃ than can dehydration fluids. The exception to this would be the generation of a slab fluid at pressures above the silicate-water critical end point, where ferric iron concentration approaches that seen in silicate melts. Large-scale fluxes of chalcophile elements from the mantle wedge into the upper arc crust due to oxidation of mantle sulfide can therefore result only from either melting of the subducting slab, or from the release of a supercritical iron-rich fluid at pressures > 30 kbar.

References

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² SmtTESMITH@aol.com

³ J.P.Davidson@durham.ac.uk