

Stability of Reduced Carbon in the Mantle

PATRICK T. HASTINGS JR.^{1*}, ANTHONY C. WITHERS¹ AND
MARC M. HIRSCHMANN¹

¹University of Minnesota, Minneapolis, United States,
phasting@umn.edu (* presenting author)

Reduced carbon in the mantle is commonly thought to be chiefly in diamond, but experiments suggest that at >250 km the mantle contains small amounts (0.1-1 %) of FeNi alloy. [1, 2, 3]. Thus, alloy may be a significant host of reduced C [4], but little is known about C solubility of FeNi alloy under mantle conditions.

To determine the carbon solubility in FeNi alloy and melt, we conducted experiments in the system Fe-Ni-C with bulk compositions having 5 wt. % C and variable Fe/(Fe+Ni) at 3 to 7 GPa and 1000 – 1400°C. Experiments at 3 GPa and 1000-1250 °C were performed in an end loaded piston cylinder apparatus; those at 5 and 7 GPa and 1200-1400°C were performed in a 1000 ton Walker-style octahedral multianvil.

At 3 GPa, Fe-rich melts contain up to 4.5 wt. % C, but Ni-rich (>25 mole% Ni) compositions remain subsolidus at 1250°C. The solubility of carbon in pure Fe and Ni metal are 2 wt. % and 1 wt. % respectively, but in the alloy passes through a minimum of 0.4 wt. % for Fe_{0.2}Ni_{0.8}. Assuming that these concentrations apply at higher temperatures and pressures (as will be tested by future experiments) allows a first estimate of the potential storage of C in FeNi alloy in the mantle. If the mantle at 250 km contains 0.1-0.2 wt.% Ni-rich (Fe_{0.4}Ni_{0.6}) alloy, increasing with depth to 1 wt.% Fe-rich (Fe_{0.88}Ni_{0.12}) alloy at 700 km [1,2], then maximum storage of C in alloy rises from 5 ppm in the deep upper mantle to 180 ppm in the shallow lower mantle. For mantle similar to the MORB source, with ~10-30 ppm C [5], alloy cannot store all C in the deep upper mantle but can in the lower mantle. For OIB sources with 33-500 ppm C [5], complete storage in alloy is less likely. Additional phases will be diamond in the upper mantle, as our experiments and previous work [6] indicate that carbide is not stable in equilibrium with Ni-rich alloy, and carbide melt in the lower mantle.

[1] Frost et al (2004) *Nature* **428** 409-412 [2] Frost and McCammon (2008) *EPSL* **36** 389-420 [3] Rohrbach et al. (2011) *J.Petrol* **52** #717-731 [4] Dasgupta et al. (2009) *GCA* **73** 6678–6691 [5] Dasgupta and Hirschmann (2010) *EPSL* **298** 1-13 [6] Romig and Goldstein (1978) *Metal Trans. Met. AIME* **9a** 1599-1609

Rare earth elements in Andaman Island surface seawater: Geochemical tracers for the monsoon

ED HATHORNE^{1*}, MARTIN FRANK¹, P.M. MOHAN²

¹GEOMAR | Helmholtz Centre for Ocean Research Kiel, Wischhofstr. 1-3, Kiel, Germany, ehathorne@geomar.de (* presenting author)

²Department of Ocean Studies and Marine Biology, Pondicherry University, Port Blair 744 103, Andaman & Nicobar Islands, India

The Asian summer monsoon affects the lives of billions of people. With the aim of identifying geochemical tracers for the monsoon related freshwater input from the major rivers draining into the Bay of Bengal and Andaman Sea we have taken surface seawater samples from various locations up and down the Andaman Islands during 2011. Importantly, in some locations samples have been taken in March, July and November, covering most of a seasonal cycle and different monsoon phases. Samples were collected from the side of small wooden boats or while swimming and were filtered within a few hours at 0.45 or 0.22 microns using the vacuum produced by a water jet or a hand operated peristaltic pump. Filtered and unfiltered samples were acidified to < pH 2 and analysed for Y and the REEs with an automated online preconcentration ICP-MS technique [1].

The local input of REEs from streams and sediment rich areas such as mangrove environments is clearly identified by middle REE enrichments in the shale normalised patterns of some samples. These middle REE bulges accompany large increases in dissolved REE concentrations at some locations, especially for the July samples obtained during the peak monsoon season with frequent storms. Y/Ho fractionation also occurs during the local input of dissolved REEs with affected samples having lower Y/Ho ratios. Conversely, some samples, in particular those taken after heavy rainfall in March, show strong REE scavenging accompanied by the preferential removal of dissolved light REEs and higher Y/Ho ratios.

The time series at a location away from local input sources shows remarkably similar REE patterns and concentrations in March and July. Then in October-November, following the peak in monsoon river discharge, the dissolved REE concentration increases by almost a factor of 2. The notable exception to this seasonal pattern is the Ce anomaly which is around 0.3 in March and November but 0.6 in July, implying less oxidative removal of Ce(IV) during the peak summer monsoon rains. With the exception of elevated dissolved Ce concentrations, the North Pacific Deep Water normalised REE patterns are similar to those reported for offshore samples from the Bay of Bengal and Andaman Sea [2]. These seawater normalised patterns are distinctive having a middle REE enriched arc with similar light and heavy REE values suggesting the input from large rivers in the region is traceable using seawater REE chemistry.

[1] Hathorne et al. (2012), Online preconcentration ICP-MS analysis of rare earth elements in seawater, *Geochem. Geophys. Geosyst.*, **13**, Q01020, doi:10.1029/2011GC003907.

[2] Amakawa et al. (2000), *Geochim. Cosmochim. Acta* **64**, 1715-1727.