Temporal change from young HIMU to EM1 source along the Pitcairn-Gambier chain

H. DELAVAULT[1], C. CHAUVEL[2]

[1] (helene.delavault@ujf-grenoble.fr)
[2] (catherine.chauvel@ujf-grenoble.fr)

Plume volcanism is one of the most puzzling features of present-day activities of the earth. The origin of this type of volcanism is matter of debate but it is generally agreed that its source is hot material containing some potentially recycled material. Most studies concentrate on strong plumes (Hawaii, Réunion) but weaker plumes such as Polynesia or St Helena can provided complementary information.

Here we present geochemical data on samples coming from the Pitcairn-Gambier alignment in Polynesia. This chain consists of Mururoa (11.9-10.7 Ma), Fangataufa (11.5-9.6 Ma), Gambier (7.1-5.3 Ma) and Pitcairn Islands (0.95 Ma) as well as the Pitcairn seamounts (0.45 Ma). We report trace elements and Pb isotopic data on basaltic samples with MgO>7% and we use these data to constrain the source of magmas and its evolution through time.

The most striking feature is the presence of Nb (and Ta) positive anomalies (defined as Nb/Nb* with Nb*=(Th+La)/2) in most lavas. In addition, the size of this Nb anomaly decreases with time: it equals 1.6-1.7 in Mururoa, Fangataufa and Gambier lavas; the value decreases to 1.2 in the younger Pitcairn Island and it is absent in the most recent lavas of Pitcairn seamounts. Because the size of the Nb anomaly is not correlated to MgO, its presence cannot be associated with fractionation of a mineral phase. We believe that it is a source feature because it correlates with Pb isotopic compositions that also decrease with time: $^{206}Pb/^{204}Pb$ is about 19.57 in Mururoa, 19.04 in Gambier, 18.31 in Pitcairn Island and finally only 17.71 in the Pitcairn seamounts.

To our knowledge, the only islands where positive Nb anomalies were observed are Tubuai and Mangaia, two HIMU Islands with $^{206}Pb/^{204}Pb>21$ but in both islands, the size of the Nb anomaly never exceeds 1.5. The similarities between the trace element and isotopic characteristics of typical HIMU islands and the old islands in the Pitcairn chain suggest that they share a common origin but the lower Pb isotopic ratios observed in Mururoa, Fangataufa & Gambier suggest a more recent enrichment of U and Th relative to Pb. Finally, both trace element and isotopic changes through time along the Pitcairn-Gambier chain suggest that the source that melted to produce the lavas, started with "young HIMU" characteristics and evolved with time to a clear EM1 type in the most recent volcanic products.

DFT studies of the interaction of water with (Fe,Ni)-sulfide surfaces and clusters

NORA H. DE LEEUW,* ALBERTO ROLDAN, SAIMA HAIDER, DAVID SANTOS CARBALLAL AND UMBERTO TERRANOVA

Department of Chemistry, University College London, London WC1H 0AJ, UK. (n.h.deleeuw@ucl.ac.uk)

Reactive iron sulfide compounds that are formed at hydrothermal vents are implicated as catalysts in Origin of Life theories, which suggestion is lent credence by their widespread presence as redox centres in contemporary enzymes – thereby also suggesting their potential as benign modern-day catalysts for CO_2 conversion. These applications highlight the need for a thorough understanding of the properties of these minerals and especially their surface reactivity as well as nucleation and growth from solution.

We have used Density Functional Theory calculations (GGA+U [1]) to investigate the interaction of water with the spinel-structured greigite Fe_3S_4 and violarite $FeNi_2S_4$ minerals, and compared them with the oxide analogue magnetite Fe_3O_4. We have studied water adsorption at the (001) and (111) surfaces, where the metal ions are in different oxidation states. Using the Nudged-Elastic-Band and Dimer methods we have calculated the energy barriers to the dissociation of water at the surfaces, and the role of co-adsorbed water, through a number of pathways, where the presence of nickel in the surfaces notably affects the surface reactivity towards water, which also influences the co-adsorption and activation of CO_2 at the surfaces.

We also present preliminary findings on *ab initio* molecular dynamics simulations of the nucleation of $(FeS)_n$ clusters from aqueous solution. Iron sulfides are widespread in the environment, but although the formation of the principal geologically stable iron sulfide, pyrite (FeS_2), via meta-stable Fe-S precursors, is reasonably well understood, still little is known about the reactions that control the nucleation and growth of the precursor Fe-S compounds that are crucial in the pyrite pathway, e.g. mackinawite and greigite. Field and laboratory data have shown the existence of small aqueous species (FeS_{aq}), whose role in the formation mechanism of the first condensed FeS mackinawite phase is crucial [2]. However, despite these studies, the stoichiometry and size of FeS_{aq} are still unknown. Our simulations predict hydration shells and stability constants and compare with experiment, where available.

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DOI: 10.1180/minmag.2013.077.5.4