Letters of Intent: EPR
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Oxygen isotope ratios of PO4 (d18Op) as an enzymatic activity indicator and environmental/biomass temperature recorder in deep-sea hydrothermal systems: Ground-truthing studies at 8-11°N EPR

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The primary goal of the proposed research is to investigate the application of oxygen isotope ratios of phosphates (d18Op) as a geochemical signature of modern and past microbial/enzymatic activity as well as a vent biomass and environmental temperature recorder in MOR hydrothermal systems and oceanic crust. The approach to proposed research will include controlled laboratory calibration studies and analysis of natural samples formed under known or measured temperature conditions in order to groundtruth d18Op temperature and biological signatures. Targeted samples will be obtained during a series of add-on dives (proposed here) during 3 cruises proposed by K. Von Damm to the 8-11°N EPR Integrated Study Site and recently funded through R2K. Additional samples of pristine and altered oceanic crust obtained during ODP Leg 206, and samples acquired during the R/V Atlantis Voyage 7 Leg 6 "AdVenture 9" cruise to 9oN and 21oN EPR (Jan-Feb. 2002, K.von Damm, chief scientist) will also be targeted.

Recent laboratory experiments and field studies indicate that the d18Op of dissolved inorganic phosphate (DIP) in microbial culture media and in all natural aquatic systems studied thus far (marine water column, rivers, groundwater), records microbial and enzymatic activity as well as ambient water d18O and environmental temperature (Blake et al., 1997, 1998a,b, 2001, Colman et al., 2002; Colman 2002). Thus, it is hypothesized that phosphate in a variety of related forms (e.g., adsorbed PO4, authigenic minerals, biomass), should also record temperature and evidence of microbial/enzymatic activity in d18Op values. Several aspects of the O isotope systematics of microbial metabolism of phosphate have already been characterized as part of previous and ongoing studies by the P.I. Importantly, these studies provide a context for interpretation of d18Op values of natural samples and new hypotheses that will be tested in deep-sea/sub-seafloor systems and laboratory studies proposed.

Phosphate is potentially present in considerable abundance in MOR hydrothermal systems in association with iron-oxide and oxyhydroxide deposits (Fe-PO4), and seafloor weathering of iron-sulfides (Mills and Elderfield, 1995; Feely et al., 1996). Magnesium hydroxide chimney deposits, recently discovered for the first time at the 'Lost City' hydrothermal field (Kelly et al., 2001), are also potential sinks for PO4 (Karl and Tien, 1992). As an essential nutrient and key component of critical biomolecules such as DNA, membrane lipids, and ATP, PO4 concentrated within tissues and cells of the abundant micro- and macro-organisms that live in and around hydrothermal vents and in microbes inhabiting the sub-sea floor and oceanic crust, is another important reservoir of PO4 in MOR systems (Parkes et al., 1994; Delaney et. al., 1998, Holden et. al., 1998; Fisk et. al., 1998: Furnes and Staudigel, 1999).

Current explanations for the occurrence of hydrothermal Fe-PO4 deposits are that reduced iron , Fe2+, in venting fluids becomes oxidized either by oxygenated seawater (e.g. Feely et al., 1994a, b; 1996) or by Fe-oxidizing bacteria (Emerson and Moyer, 2002), followed by scavenging of DIP from ambient seawater via adsorption or co-precipitation (Berner, 1973; Feely et. al., 1994a,b,) The d18Op of Fe-PO4 should then reflect the d18Op of DIP in ambient seawater. Studies of numerous hydrothermal vent sites identified over the past two decades have concluded that most of the heat flux from MOR hydrothermal systems is not associated with the highly prominent black smokers with vent fluid temperatures of 300-400°C, but rather, with the relatively low- temperature (<50°C) diffuse-flow systems, off of the main axis of rifting (Mills et al., 1996 and references therein). At the low temperatures of diffuse-flow hydrothermal systems and over the relatively short lifespans of many actively venting sites (e.g., Shanks et al., 1998), PO4 would not undergo significant abiotic O isotope exchange with water (Longinelli et al., 1976 Blake et al., 1997; Lecuyer et al., 1999; O.Neil et al., 2003). At low temperatures, PO4-water O isotope exchange and alteration of PO4 isotopic signatures requires catalysis by enzymes (Tudge, 1960; Kok and Varner, 1967;

Blake et al. 1997, 2001, Lecuyer, 1999). As described below, enzyme/microbially-mediated PO4-water O isotope exchange also records the ambient temperature at which exchange occurs. Thus, recording of ambient temperature in d18Op values at low temperature, implies the presence of enzymatic/biological activity.

Relevance to R2K and ISS objectives:

Proposed research will address fundamental questioned raised in the RIDGE 2000 Science Plan and 8-11°N EPR Integrated Studies Site (ISS) Implementation Plan, including noted "community data needs" for vent chemistry and temperature data. Question 3.4 of the ISS goals "what are the interactions between biological activity, vent chemistry, physical processes and hydrothermal features" and the question of "effects of organisms on hydrothermal system chemistry", specifically PO4 chemistry and d18Op values of hydrothermal Fe-oxide deposits and oceanic crust, will be addressed.

The P.I. is actively seeking additional collaborators and sample collection opportunities as part of previously funded and proposed future studies.