Drilling in Serpentine Sea

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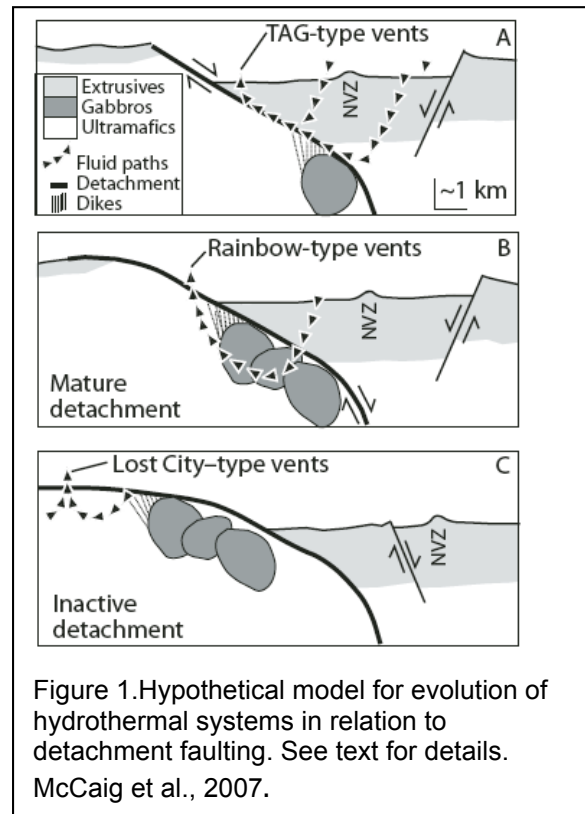Andrew McCaig, University of Leeds, UK

I. ABSTRACT

In recent years there has been a profound rise in appreciation of the importance that exposure of mantle material, and resultant reactions with seawater to produce serpentinite play as fundamental, and central Earth processes. Serpentinization profoundly affects the rheology, gravity, and seismic structure of ocean crust formed by slow-spreading. Because magnetite is a product of serpentinization, hydration of olivine-rich rocks has a major effect on the magnetic signature of the ocean floor. The geochemical consequences of serpentinization are also important to sea floor studies. Serpentinite-hosted hydrothermal vents are common along slow and ultraslow spreading ridges. These vents host unique microbiological ecosystems supported by hydrogen and methane released during peridotite-seawater interactions. Serpentinization is also common away from mid-ocean ridges, in fore-arc regions and at rifted continental margins. Serpentine formation and dehydration plays a dominant role in subduction zone processes (element cycling, seismogenesis, mantle wedge dynamics), and the planetary water cycle.

II. INTRODUCTION

Exposure of mantle material and serpentinization of peridotite are integral parts of the architecture of slow- and ultra-slow spreading ridges. Seawater reacts with peridotite as detachment faults unroof mantle material, and peridotite hosts black smoker type and cooler off-axis hydrothermal systems. Thus, understanding serpentinization processes is a fundamental part of understanding the exposure of mantle material and the evolution of oceanic lithosphere formed at slow spreading ridges.

Serpentinization is a process that turns dry, dense, mechanical strong and weakly magnetic peridotite into a low-density, weak, highly magnetic rock with >10 wt.% H_2O. The chemical and physical changes of this transformation are so radical that the implications of serpentinization in all geotectonic settings where it occurs are extreme. A number of recent microscopic (Dodony and Buseck, 2004), experimental (Normand et al., 2002; Allen and Seyfried, 2003), and theoretical (Wetzel and Shock, 2000; Sleep et al., 2004; Alt and Shanks, 2003) studies have addressed the geochemical and mineralogical transformations associated with serpentinization of abyssal peridotite (also see Evans, 2004; Früh-Green et al., 2004; Mével, 2003; Schroeder et al., 2002; Fryer, 2002; Andréani et al., 2007). Despite the current interest in serpentinization, the underlying peridotite-water reactions remain poorly constrained. Study of, and our resultant understanding of serpentinization has been fragmented and haphazard. Here we emphasize the need for an integrated understanding of serpentinization processes in different tectonic/magmatic/hydrothermal settings in oceanic lithosphere.

McCaig et al. (2007) present a hypothetical model (Figure 1) whereby hydrothermal activity could evolve as detachment faulting proceeds and foot- and hanging-walls age, from TAG-like venting in the young mafic hanging wall, to Rainbow-like high-T ultramafic hosted systems in the exposed footwall, to lower-T off-axis Lost City type activity. This model is hypothetical and untested, but it illustrates some of the integral linkages between serpentinization and processes of crustal formation and evolution. Such a model provides a kind of "straw man" that could provide a basis for developing integrated models of serpentinization in relation to formation of ocean crust at slow and ultraslow spreading ridges. Drill cores from serpentinized massifs in the oceans will allow us to approach the problem of serpentinization and its relationship to crustal formation and evolution in new ways, by selecting appropriate tectonic/magmatic/ hydrothermal settings. Drill cores are critical, as the phase relations are minimally disturbed by later-stage reactions related to orogenesis or weathering that affect serpentinites exposed in mountain belts or at the seafloor.

Figure 1.Hypothetical model for evolution of hydrothermal systems in relation to detachment faulting. See text for details. McCaig et al., 2007.

Ocean drilling provides an unparalleled opportunity to understand peridotite-water interaction and the highly unusual compositions of interacting fluids that have puzzled petrologists and geochemists for decades. The fluids, rich in hydrogen and abiotic hydrocarbons (Proskurowski et al., 2008), support unique ecosystems and are believed to be excellent analogues of hydrothermal sites where life may have originated (Martin et al., 2008). Serpentinization provides a direct tie between mantle and microbes, as well as linking these with magmatism and tectonics, and is an ideal topic for transdisciplinary science in a new drilling program.

This white paper addresses the need for systematic and comprehensive petrological, chemical, structural, and microbiological studies of drill core samples from deep sections of ultramafic basement from different (mid-ocean ridge, rifted continental margin, fore-arc) settings. These studies should be supplemented by drill hole observatory science and experimentation to determine rates of crucial reactions and examine the consequences of serpentinization for the deep biosphere.

III. RELEVANCE

1) *Serpentinization Is An Integral Part Of Seafloor Spreading* - Lithospheric heterogeneity is a basic consequence of the varying influences of magmatism and tectonics at slow and ultraslow spreading ridges. This heterogeneity includes variable amounts of peridotite and olivine-rich gabbroic rocks, and variable influences on this peridotite from tectonics, magmatic intrusions, and fluids. The type and sequence of serpentinization reactions depend on the conditions of water-rock reactions, chiefly the protolith composition, temperature, and fluid flux. ODP drill cores have shown that peridotite-seawater interactions take place under a wide range of temperature and redox conditions and involve

fluids with highly variable pH and silica activities (e.g., Bach et al., 2004). It has recently become apparent that the protolith composition, the presence or absence of magmatic intrusions, and structural features (e.g., detachment faults, fault gouges, trapped melt) contribute to the large diversity in serpentinization and related processes (rodingitization, steatitization) (Boschi et al., 2006; Frost et al., 2008; Bach and Klein 2009). Serpentinization leads to dramatic changes in the rheology and magnetic properties of lithosphere (Dyment et al., 1997; Escartin et al., 1997; Schroeder et al., 2002). Thus, serpentinization is an integral part of formation of heterogeneous ocean crust and reflects the variable interplay of magmatism, tectonics, and fluid flow. Drilling of serpentinite is needed to further understand serpentinization processes resulting from these variable influences, as outlined below, but the understanding gained by study of serpentinization will in turn enable further insights into interactions among magmatic, tectonic, and hydrothermal processes during formation of heterogeneous oceanic crust.

2) *Seawater-Ocean Lithosphere Chemical Exchange* - Serpentinization of peridotite results in significant uptake of H_2O, C, S, B, Cl, and LREE, and generation of hydrogen and methane. However, reaction pathways and rates of serpentinization are incompletely understood and do not allow us to predict hydrogen generation or CO_2 uptake related to serpentinization at the scale of ridge segments let alone at a global scale. The consequences of serpentinization of roughly 25% of seafloor formed at slow spreading ridges (Cannat et al., 2005) for global exchange budgets are also poorly known, although serpentinization is likely to change estimations of fluxes significantly for some elements (B, Sr, Li, Os, etc.), and may be equivalent to seawater exchange with mafic crust for other elements (e.g., S, C). Additionally, new insights are critically needed to assess the potential of serpentinization systems for carbon capture and storage, which may be considerable (Kelemen and Matter, 2008).

3) *Deformation and Magmatic-Tectonic-Hydrothermal Linkages* – Magmatism and melt impregnation exert important effects on deformation, fluid flow and water-rock interactions, with important feedbacks among these processes. Structural models of detachment faulting (Tucholke et al., 1998; Escartin et al., 2003; Ildefonse et al, 2007) highlight the crucial role of weakening the shear strength in the lithosphere by the formation of serpentine and talc. Interesting feedback mechanisms between hydration-promoted melting, hydration, detachment faulting, and mass transfers were recently proposed by Jöns et al. (2009). They showed that melt impregnations play a crucial role in the development of detachment faults. Magmatic components in mantle sections change the phase relations such that hydration can take place at temperatures >200°C higher than where unimpregnated mantle rocks would hydrate. The hydrated talc-chlorite-tremolite bearing rocks are mechanically much weaker (e.g., Escartin et al., 1997; 2008) than the surrounding mantle rock, and accommodate all the strain at temperatures higher that where strain localization usually takes place (greenschist facies conditions). Deformation leads to further hydration, promoting further weakening the rock. These feedbacks help explain many geochemical, mineralogical, and structural features of detachment fault rocks. Fluid flow is channelized in these faults and high fluid fluxes can lead to metasomatic mass transfers and hydrothermal deposit formation (McCaig et al., 2007). This mechanism can explain why seafloor hydrothermal systems commonly sit near the termination of detachment faults (Escartin et al., 2008). Other evidence from fault rocks, however, suggests low water/rock ratios (Boschi et al., 2006, 2008), pointing out the need for further work to understand the role of detachment faulting in fluid flow, and the relation of faults to serpentinization of host rocks.

4) *Ultramafic-Hosted Black Smoker Type Hydrothermal Systems* – Submarine hydrothermal systems hosted in mafic crust have been studied for nearly 40 years and are reasonably well-known. In contrast, ultramafic-hosted high temperature hydrothermal systems, where black smoker hydrothermal vents and/or sulfide mineralization co-occur with mantle peridotites that are exposed by detachment faulting are poorly understood. In the Atlantic,

~350-365°C black smoker vents and sulfide deposits occur at Rainbow (36°14'N), Logatchev (14°45'N), and Nibelungen (18°S); and sulfide mineralization has been observed in serpentinite talus at Saldanha and Ashadze (36°34'N and 13°N) (Douville et al., 2002; Dias and Barriga, 2006; Schmidt et al., 2007; Melchert et al., 2008; Mozgova et al., 2008; Petersen et al., 2009). Sulfide deposits and hydrothermal plumes indicate that such activity is common on the SW Indian and Gakkel Ridges (Baker et al., 2004; Edmonds et al., 2003). Although hosted in peridotite, the high temperatures and flow rates of these systems require a magmatic heat source, and fluid compositions indicate influences from mafic as well as ultramafic rocks (Douville et al., 2002; German and Lin, 2004; Seyfried et al., 2004, 2009; Schmidt et al., 2007). Reactions in the subsurface have thus far been inferred from measured vent fluid chemistry, experiments and modeling, the true nature of subsurface mineralogy, chemical reactions, and flow pathways that support these hydrothermal systems is unknown. In particular, the relationship of mafic intrusions to peridotite and serpentinization reactions in the "root zone" or deep "reaction zone" that support the observed surface expressions has never been observed. Drilling is key to understanding reactions at depth, the heat source, and for establishing linkages between serpentinization, hydrothermal activity, magmatism and tectonics at the slow-spreading end-member.

5) *Hydrogen Generation* – A trademark of peridotite-seawater interactions is the production of large amounts of hydrogen and methane. Understanding the phase relations and their dependence on rock composition, water-to-rock ratios, and temperature is of paramount importance in unraveling the enigma of strongly reduced conditions in serpentinization. This process is commonly often considered a single-step reaction of olivine to serpentine, brucite, and magnetite:

$$10\ Mg_{1.8}Fe_{0.2}SiO_4 + 13\ H_2O \rightarrow 5Mg_3Si_2O_5(OH)_4 + 3\ Mg(OH)_2 + 2/3\ Fe_3O_4 + 2/3\ H_2$$
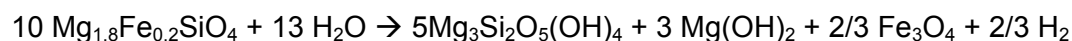
This reaction is not useful in describing hydrogen production, because Fe is not allowed to partition into any secondary phase but magnetite. More recently, the role of silica activities and Fe-Mg exchange equilibria in controlling hydrogen production during serpentinization has been highlighted (Allen and Seyfried, 2003; Bach et al., 2006; Evans, 2008; Frost and Beard, 2007; McCollom and Bach, 2009; Sleep et al., 2004; Klein et al., in press). It was shown that olivine is stable at T>350°C in the presence of an aqueous fluid. Cooling the system the system to lower T, leads to a cascade of chemical events associated with serpentinization, including an increase in the Mg# of the serpentine minerals, the destabilization of most ferrous iron silicates, the formation of unusual minerals in the serpentinite proper (e.g., metallic Ni-Fe alloys), and metasomatic alteration of adjacent rocks (rodingitization). Hydrogen fugacities during this stage are so high that CO_2 in the fluid is partly reduced to methane and other hydrocarbons. Serpentinization causes hydrogen and methane fluxes into the oceans that are an order of magnitude greater than the fluxes associated with magmatic accretion of the oceanic crust (Cannat et al., in press).

6) *Hydrogen Ecology* - Serpentinite-hosted vent fields are common along slow and ultraslow spreading ridges (Charlou and Donval, 1993; Bach et al., 2002; Baker et al., 2004; Edmonds et al., 2003). Hydrogen and methane released during peridotite-seawater interactions (Kelley et al., 2001; 2005; Charlou et al., 2002) support microbial communities that form the base of the food web in unique ecosystems associated with serpentinite-hosted hydrothermal systems and allowing microbial activity in hydrothermal plumes to thrive (Schrenk et al., 2004; O'Brien et al., 1998; Mottl et al., 2003; Kelley et al., 2005). Because hydrogen drives methanogenesis, organosynthesis, and microbial metabolism in serpentinite-hosted hydrothermal systems (Kelley et al., 2005; Proskurowski et al., 2008; Schrenk et al., 2004) and in ultramafic basement rocks (Alt and Shanks, 1998; Alt and Shanks, 2003; Alt et al., 2007; Delacour et al., 2008a; Delacour et al., 2008b), a detailed understanding of its production is essential.

7) *Continental Rifted Margins*: At volcanic rifted margins (e.g. Iberia) rifting can expose tens of thousands of square kilometers of peridotite at the surface (Whitmarsh et al., 1997). Long-lived serpentinite-hosted hydrothermal systems have been identified within the exposed peridotites (Beard and Hopkinson, 2000). Serpentinization of such large volumes of mantle rocks should produce discernable excursions in ocean geochemistry. Additionally, it has been proposed that serpentinization of the exposed mantle can promote expansion of the ocean basin in a manner analogous to MOR magmatism and even yield a magnetic signature that can be interpreted as a record of the expansion. One issue that arose with Iberian margin serpentinites in particular concerns the carrier of the magnetic signal. It turns out that minerals other than magnetite, including iron-nickel sulfides and metal phases such as awaruite, may make a large contribution to the magnetic signature (Zhao et al., 2001). Thus the nature and products of serpentinization reactions are important in interpreting the magnetic record and, particularly, the timing of ocean expansion.

8) *Subduction Zones:* Serpentinization of the mantle wedge is an integral part of cycling of elements, particularly volatiles, in subduction zones. The mantle wedge is serpentinized and metasomatized by fluids derived from dewatering of subducting sediments and dehydration of sediment and basement (Fryer and Salisbury, 2002; Mottl et al 2003; Alt and Shanks, 2006; Savov et al.,2005). These fluids can vent at the seafloor along with serpentinite protusions, as in the Marianas, where they support communities of bacteria and archaea (Mottl et al., 2003; Takai et al., 2004). At greater depths, metasomatized serpentinite in the mantle wedge can be dragged downward to dehydrate and metasomatize the deeper mantle wedge and affect arc volcanism. Because of the high P-T stability of serpentine, subducted serpentinite can carry volatiles to great depths beneath arcs, and even return volatiles to the mantle (Ulmer and Trommsdorff, 1995; Kerrick, 2002; Rüpke et al., 2004). Geophysical data indicate that suboceanic mantle is serpentinized as the lithosphere flexes outboard of subduction zones, suggesting recycling of additional H_2O and other elements added to the lithosphere far from mid-oceanic ridges (Ranero and Salleres, 2004).

9) *Planetary Serpentinization*: Much debated in astrobiology and space science is the significance of serpentinization processes on extraterrestrial bodies for their atmosphere and putative biosphere (e.g., Schulte and Shock, 2004; Schulte et al., 2006; Sleep et al., 2006; Atreya et al. 2007). Infrared absorption spectra of Ceres, a dwarf-planet in the asteroid belt, are indicative of brucite, serpentine and Mg-carbonates (Miliken & Rivkin, 2009), a mineralogy consistent with terrestrial serpentinites. Methane formed via Sabatier reactions during serpentinization could have and/or may currently contribute to the atmospheric methane observed on Mars and Europa (e.g., Atreya et al. 2007). These results indicate that hydration of ultramafic rocks may profoundly impact surface environments on other planets in our solar system and beyond. Drilling active serpentinization systems on slow-spread ridges, continental margins and fore-arc settings will lead increase our understanding of serpentinization processes and facilitate an evaluation of analogue processes on Mars, Europa, Ceres and elsewhere.

IV. NEED FOR FUTURE DRILLING

The prominent rheological, geochemical, and microbiological role in different geotectonic settings make serpentinization a key process in the System Earth. The following selected (unprioritized) examples address how future ocean drilling could crucially facilitate further understanding of serpentinization and its role in Earth processes.

* Examining the role of serpentinization in the formation and evolution of mid-ocean ridge detachment faults and non-volcanic rifted margins is of key importance in understanding slow-spreading divergent plate boundaries. Drilling is necessary to sample faults and associated host rocks, to understand the development of detachment faults and exposure of

core complexes, and in particular how hydrothermal systems and seawater influence and their relative roles evolve in relation to tectonics and magmatism. Comprehensive drilling, using conventional and seabed drill rig techniques, are required to achieve this goal.

* Drilling deeply into systems influenced by active serpentinization (e.g., Lost City, Rainbow or Logatchev?) from serpentinite into unaltered or slightly altered peridotite will allow examination of the serpentinization reaction front. Drilling is essential in unraveling the reaction pathways leading to the high hydrogen and hydrocarbon fluxes at the seafloor. Only fresh drill cores carry the required information, since dredged materials suffer from severe and irreversible seafloor weathering overprints.

* Ultramafic–hosted hydrothermal systems are unique seafloor habitats fueled by abiotic hydrogen and hydrocarbons produced in water-rock reactions. Drilling is needed to understand the subsurface structure of these systems and test models for subsurface reactions based on vent fluids and geochemical modeling. Drill cores will enable examination of questions concerning flow pathways, shallow stockwork zones, deep reaction zones, gabbro-peridotite relationships and the relative roles of gabbro vs peridotite in setting vent fluid chemistry.

* Serpentinite in subduction zone controls tectonics and geochemical cycling in one of the most prominent process zones on Earth. Samples of serpentinized mantle wedge are critical in assessing reaction pathways and fluid evolution during interactions of fluids expelled from the subducting slab and the overlying mantle. The "Mantle Wedge" may be too deep everywhere to reach by drilling, so sampling of this material as deposited at serpentinite seamounts, such as in the Marianas, may be the best approach. In addition, there are other, tectonically uplifted areas where oceanic mantle wedge material is accessible by drilling (e.g., Mariana and Tonga fore arc).

* The production of bore holes by ocean drilling, in particular in areas of active serpentinization, present opportunities for long-term active study and experimentation in the ocean crust. Geochemists, hydrogeologists, and microbiologists have been developing the means with which to use subseafloor borehole observatories (CORKs) for a variety of purposes – for example, to retrieve representative samples of crustal fluids, for conducting in-situ experiments under native crustal conditions, or for conducting active perturbation/ tracer experiments in order to learn about how fluid flows in the crust. CORKed observatories have not yet been used for study of serpentinization, but could provide exciting opportunities to directly test hypotheses, for example about reaction pathways and resultant fluid chemistries and microbial communities. CORK observatories enable repeated sampling, experiments and analysis post-drilling, after the perturbation due to emplacement has dissipated. Rock core that can be recovered via drilling is always an incomplete record of the target crustal section; CORKed observatories enable extension of the necessarily limited recovered section to the broader crustal context. The state-of-the-art in use of CORKed observatories, and in particular recent developments as applied to coupled geochemical/biological experiments is discussed in a recent paper (Orcutt et al., 2009b) another white paper (Orcutt et al., 2009a). These recent developments make this an ideal time to develop plans for drill core recovery in actively serpentinizing systems coupled with CORKed observatories for long-term study of these exciting systems.

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