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#### Scientific Objectives: (250 words or less)

Requested ICDP funds: (in US\$)		Estimated Total Project Budget (ICDP funds plus other sources):	
Planned Start:		Estimated Duration in Month (On-site operations only):	
Requested Operational Support:	Drill Engineering (Please contact ICDPs Operational Support Group if required)		
	Downhole Logging (Please contact ICDPs OSG if required)		
	Field Lab Equipment (Please contact ICDPs OSG if required)		
	Training Course (Please contact ICDPs OSG if required)		

#### Summary of Support Requested from ICDP

Details such as a Budget Plan, Management Plan, and Drilling Plan to be provided as attachment to the Proposal. OSG contact: U. Harms (<u>ulrich@gfz-potsdam.de</u>), Phone: +49 331 288 1085

COLUMBIA UNIVERSITY IN THE CITY OF NEW YORK DEPARTMENT OF EARTH & ENVIRONMENTAL SCIENCES LAMONT DOHERTY EARTH OBSERVATORY

January 9, 2014

Prof. Brian Horsfield Dr. Uli Harms International Continental Drilling Program GFZ Potsdam

Dear Brian and Uli,

With this letter, please find our revised proposal for the Oman Drilling Project.

In this cover letter, as you suggested at our meeting in Potsdam in October, we offer a brief summary of the revisions we made, in the context of the reviews of our 2013 proposal.

Our primary focus in revising the proposal was to cut the overall cost of the Project by prioritizing our planned holes, and then eliminating all but the most essential targets. In doing this, we wished to respect the input of the participants in the 2012 Oman Drilling Workshop, and follow the advice of reviewers who generally praised the broad, multi-disciplinary nature of the proposal and the proponent group. Thus, we retained *all* of the scientific goals identified at the workshop and in the 2013 proposal, and simply reduced the number of holes, and target depths, that were designed to address a specific subset of goals. With some trepidation, we also reduced the funds allocated for project management, and for project coordination meetings. We dropped our plan to purchase a (much-needed) XRF core scanner for the core description lab onboard the Joides Resolution (JR). We now plan to seek funds for the core scanner via the Qatar Foundation, with the idea of installing it at Sultan Qaboos University in Oman rather than on the JR. In any case, this equipment purchase is no longer a part of the ICDP proposal budget.

As a result, this revised proposal reflects the outcome of a substantial prioritization process, as requested by reviewers. We now plan a total of 3050 meters of diamond drilling and 2000 meters of rotary drilling, compared to last year's proposed 5450 and 3450 meters, respectively. This and other priority decisions reduced the overall cost to \$3,896,665 from \$6,775,596, and our request to ICDP from \$3M to \$1,948,332.

We added an important, though short, section addressing the nature of existing seismic data, which demonstrate that internal structure within the Samail ophiolite cannot be imaged by seismic reflection or refraction. Additional seismic experiments aimed at site characterization for this project would be a waste of time and money.

We added a brief clarification of how understanding of natural mineral carbonation is relevant to proposed design of engineered systems for  $CO_2$  capture and storage (CCS). A reviewer wondered how useful natural data could be, given the goal – in some proposed, engineered systems – to dramatically enhance reaction rates using  $CO_2$ -rich fluids and/or catalysts. Keeping in mind that our ICDP proposal is not aimed at designing CCS systems, we did not want to overemphasize this topic by adding a long discussion. Instead, we simply noted that one proposed method,  $CO_2$  capture from hydrothermally circulating seawater, simply involves stimulation of convection via drilling and hydraulic fracture, and then will proceed by the same rate and reaction mechanisms as natural systems.

If we had the space and the inclination to add additional information on CCS, we would have described our hypothesis that the Cretaceous, higher temperature mineral carbonation system, near the basal thrust of the ophiolite during its emplacement, involved rapid reaction with CO2-rich fluids at ~ 100°C, and so is actually a close analogue to the rate and fluid composition for other, proposed CCS systems. The natural, carbonated peridotites in this setting probably formed very rapidly indeed.

In Appendix 5, in addition to modifying our plans for each site based on the prioritization process described above, we added (1) substantially more site survey data, (2) a short section on our observations of the depth to the water table in water monitoring wells near the proposed drill sites in Appendix 5, (3) a short section on accessibility of drill sites via existing gravel roads and tracks, and (4) a short section on contingencies that could affect core recovery and hole completion.

Lamont Doherty Earth Observatory 211 Comer Laboratory P.O. Box 1000 61 Route 9W Palisades, NY 10964-8000 USA Columbia University 557 Schermerhorn Extension Mail Code 5505 New York, NY 10027 USA http://eesc.columbia.edu/

In addition, we added a short section in Appendix 5 making clear that there are no "previously drilled cores ... present at Lamont", as one reviewer suggested, and no cores from our target lithologies in the Samail ophiolite that are available anywhere else for that matter.

We were unclear on how to respond to a reviewer request for us to "develop a phased program". The timing of each part of the proposed project was and is given in the table in Section 10, on page 28. Once this project is complete, proponents may decide to submit a follow-up proposal for more extensive drilling, including objectives at some of the sites that were dropped during this revision process. However, we have not designed a formal plan for such a second phase.

Similarly, we were uncertain how to respond to reviewer advice that we "consider image logging" in boreholes. Use of an optical televiewer tool was and is included in Table 2 in Section 5.1, which describes our plans for geophysical wireline logging.

We were encouraged by the generally positive reviews of our previous proposal, and by your positive input at our meeting in October. As a result, we are optimistic that this revised proposal with meet with ICDP approval, so that we can move forward on the permitting and contracting process with our Omani partners in 2014. Another yearlong delay would likely damage our credibility with these partners. Thus, we hope that issues identified during the upcoming review process could be addressed via conditional approval of the proposal, followed by required modification to address any continuing problems.

In this context, an important development is that the Sloan Foundation solicited a proposal from me, for support of field projects related to their Deep Carbon Observatory. They suggested that the proposal include \$350,000 in matching funds, to facilitate startup of the Oman Drilling Project. (See supporting letter from Craig Schiffries and Robert Hazen of the Deep Carbon Observatory, in Appendix 17). In this proposal, we decided to budget funds to drill one hole at the active alteration site, Site BA1, including equipment for geophysical logging and water sampling. Of course, the Sloan funds will be considered as part of the overall matching funds if and when the overall ICDP project is approved. Meanwhile, the Sloan proposal was submitted today, and we are optimistic that it will be approved by the end of February. We hope that this confirmed funding will provide a concrete starting point and catalyst to begin specific steps in the permitting process in Oman.

On behalf of Jürg Matter, Damon Teagle and myself, thank you in advance for your continuing advice and assistance with the Oman Drilling Project.

Sincerely,

Peter B. Kelemen Arthur D. Storke Professor & Vice Chair Dept. of Earth & Environmental Sciences

peterk@LDEO.columbia.edu http://www.ldeo.columbia.edu/user/peterk

# 1. Introduction

The Samail ophiolite, along the northern coast of the Sultanate of Oman and the easternmost United Arab Emirates, is the largest and best sub-aerial exposure of oceanic crust and upper mantle in the world. The term "ophiolite" is used to identify blocks of oceanic crust and upper mantle, formed at spreading ridges, and later exposed on land. Key features of ophiolites are seafloor lava flows ("pillow basalts"), a continuous layer of dikes intruding dikes ("sheeted dikes") attesting to genesis of the crust at a spreading center, a layer of plutonic igneous rocks ("cumulate gabbros") rich in Mg and Ca, formed by partial crystallization of the magmas subsequently erupted as lavas and dikes, and underlying mantle peridotites that underwent partial melting to form the magmas that, in turn, comprise igneous oceanic crust (Figure 1).

Scientific drilling in the Samail ophiolite will improve understanding of the spectrum of processes that create and modify the oceanic crust and shallow mantle from its primary setting on the ocean floor to its modern setting in the mountains of Oman. These processes involve mass and energy transfers between the mantle, crust, hydrosphere, atmosphere and biosphere over a range of temperatures from ~1350 to 20°C, depths from 20 km below the paleo-seafloor to the surface, and tectonic settings from spreading ridges and subduction zones to the modern subaerial hydrology and surficial weathering.

Decompression melting of upper mantle peridotite, rising to fill the gap created by rifting of the plates at mid-ocean spreading ridges, and the consequent eruption and intrusion magma to form new ocean crust, are the primary steps in the plate tectonic cycle. These processes have repaved more than 60% of Earth's surface in the last 200 million years and are the principal mechanism of mass and heat transport from the interior of Earth to the surface. Hydrothermal circulation of seawater-derived fluids, at the spreading ridges and on the vast, submarine ridge flanks, forms base metal deposits and buffers the chemical and isotopic composition of the oceans. Alteration by seawater-rock exchange adds volatiles and other chemical tracers to the oceanic crust. The extreme thermal and chemical gradients within oceanic plates provide fertile ecological niches for novel microbial communities. Following subduction of oceanic crust, volatiles and tracers are returned to the crust by fluid transport and arc volcanism, or recycled into the deep mantle.

Over the past decade there has been growing recognition of the importance of serpentinization (hydration) of upper mantle peridotite in global chemical and tectonic cycles. Reactions between seawater and the minerals comprising peridotite, olivine and pyroxene, transform dense, strong, anhydrous materials into weak, hydrated, low-density serpentinites. These reactions alter tectonics along oceanic spreading ridges and in subduction zones. The juxtaposition of mantle rocks with oxidized surface waters (seawater, ground water) provides a chemical environment of extreme contrasts resulting in strongly exothermic reactions that form high pH fluids, hydrogen, and abiotic hydrocarbons, potentially key ingredients for the origin of life on Earth, creating fertile environments for the development of unique microbial communities at present.

The discovery on the Mid-Atlantic Ridge of Lost City, a large hydrothermal carbonate mound hosted by serpentinized peridotes [*Kelley et al.*, 2001], combined with observations of fully carbonated peridotite in numerous ophiolites (e.g., "listvenites", well exposed in Oman), has highlighted the potential for engineered capture and storage of anthropogenic carbon dioxide by mineral carbonation in peridotite. The presence of listvenites in mantle peridotites thrust over sediments in Oman suggests the presence of hitherto unrecognized, globally significant reservoirs for carbon in the "leading edge of the mantle wedge" above subduction zones. Active

hyperalkaline springs depositing travertine terraces in Oman attest to on-going serpentinization and "Lost City"-type reactions occurring in the Samail ophiolite today, providing opportunities to understand both ancient and modern mineral carbonation processes through drilling and subsurface experimentation.

The Oman Drilling Project, proposed here, will harness information from drill core, geophysical logs, fluid and gas samples, hydrological tests, in situ experiments, and continued detailed field mapping to address the spectrum of multi-disciplinary and inter-related science questions that connect the deep mantle and the ancient ocean floor with modern hydrology and ongoing biogeochemical reactions in the mountains and wadis of the Samail ophiolite.

# 1.1 Development of the Oman Drilling Project

Scientific drilling focused on the formation and evolution of the Samail ophiolite at an oceanic spreading ridge was first proposed to the International Continental Drilling Program (ICDP) in 1998. Although ICDP offered \$40,000 in workshop support, international events during and after 2001 suggested that the project should be postponed. However, our original goals remain compelling. They represent essential steps toward the Mantle to Moho (M2M) Project, proposed to the Integrated Oceanic Drilling Program (IODP), to drill a complete, intact section of oceanic crust and upper mantle in the Pacific (see Appendix 1). In addition, scientific developments over the past decade augmented our original plan, reflecting increasing interest in low temperature alteration and weathering, and the associated sub-surface biosphere supported by the chemical potential energy inherent in exposure of mantle peridotite at the Earth's surface. This interest is motivated, in part, by the possibility of geological carbon capture and storage via engineered, accelerated mineral carbonation in Oman.

A workshop proposal to the ICDP in January 2011 led to the Workshop on Scientific Drilling in the Samail Ophiolite, held in Palisades, New York (September 2010), supported by ICDP (\$50k), the Sloan Foundation's Deep Carbon Observatory (DCO, \$30k) and the US National Science Foundation (NSF, \$10k). There were 77 attendees from 11 countries, including 20 early career scientists. This proposal presents the science goals and drilling plans refined by the participants in working group and plenary sessions. Appendix 2 provides more information. We submitted a full proposal to ICDP in January, 2013, which was declined with encouragement for us to revise and resubmit. Reviews focused on a need for prioritization of drilling objectives. This revised proposal, submitted in January 2014, reflects the requested prioritization, with a total of 3050 meters of diamond drilling and 2000 meters of rotary drilling, compared to last year's proposed 5450 and 3450 meters, respectively. This and other priority decisions reduce the overall cost to \$3,896,665 from \$6,775,596, and our request to ICDP from \$3M to \$1,948,332.

# **1.2 Advancement of the ICDP Science Themes**

The Oman Drilling Project will make fundamental progress toward the central ICDP objective of "understanding the composition, structure and evolution of the Earth's crust and the processes that continue to modify it." The formation and evolution of oceanic plates (crust and shallow, residual mantle) is the major mechanism of thermal and chemical exchange between the Earth's interior and the crust, oceans, atmosphere, and biosphere. We will substantially improve understanding of mid-ocean ridge mantle and crustal processes, and estimates of the chemical fluxes exchanged between the ocean plates and the oceans by high temperature hydrothermal alteration near spreading ridges, and later during low temperature weathering.

We will also address other, key ICDP priorities including the wise use of Earth's energy, mineral, and water resources and the critical interactions between the biosphere and the Earth's crust. Ocean floor hydrothermal systems, powered by the cooling and crystallization of the lower oceanic crust, have produced mineral deposits that have been sources of base metals since the birth of civilization, yet the deep source of these metals remains poorly known. In parallel, understanding natural mineral carbonation reactions during the obduction of the Samail ophiolite and on-going carbonation processes during weathering will yield essential information on the Earth's carbon cycle, and insight into design of engineered systems for permanent capture and storage of anthropogenic carbon dioxide. Hydrogen and abiotic hydrocarbons produced by exothermic serpentinization reactions provide vital energy and ingredients that should support an extensive subsurface biosphere, which so far is largely undiscovered. Although there are abundant geochemical indicators of microbial activity in ancient rocks, evidence of present-day, sub-surface biological activity in these environments remains elusive.

### 1.3 The Samail ophiolite and oceanic crust

In the early 1970's, it was recognized that the thickness and seismic properties of the igneous oceanic crust in the Samail ophiolite were similar to those of Pacific crust formed at intermediate- to fast-spreading ridges [*Christensen and Smewing*, 1981; *Glennie et al.*, 1973]. Since that time, the ophiolite has been recognized as the best place on Earth for sub-aerial, three dimensional study of oceanic crust. Indeed, the widely accepted paradigm for the structure of Pacific crust is based largely on observations in the ophiolite. This led to accelerating interest in studies in Oman and the UAE that can be applied to understanding ridge processes worldwide.

In more detail, the tectonic provenance of the ophiolite – and the extent to which specific features are representative of processes at "normal" mid-ocean ridges – are subjects of continuing debate. Because of this uncertainty, ophiolite studies must always be viewed as part of a dialectical conversation, inspired, supplemented and corrected based on direct observations of active spreading centers in a variety of tectonic environments. Four decades of research and discussion have affirmed the great value of combining data and inferences based on observations from Oman with geophysical surveys, dredging and drilling along active submarine spreading ridges. In the past, this dialectic mainly focused on igneous and metamorphic processes near the ridge axis. Recently, the discussion has broadened to include off axis alteration and weathering. Our proposed project follows in this fruitful tradition.

In this project, we will focus on study of processes common to all submarine spreading centers, and the subsequent evolution of oceanic crust and upper mantle rocks at and near the Earth's surface. Of course, every place is unique, and processes vary depending on local history and boundary conditions. This understanding will always be part of the data gathering and interpretation we propose. However, we seek understanding of the factors that shape the two thirds of the solid Earth surface composed of oceanic crust and upper mantle. Doing this requires a clear understanding of the local context, but we will not emphasize lines of inquiry that are primarily relevant to regional geology. There are many fascinating aspects of the geological history of the Samail ophiolite that will not be a primary focus of the proposed study.

### 1.4 Regional setting and geologic history of the Samail ophiolite

The Samail ophiolite is the largest, best-preserved, best-exposed, and most intensively studied block of oceanic crust and shallow mantle in the world. The ophiolite was gradually thrust onto the Arabian continental margin from about 95 to 80 million years ago. The desert climate of Oman limits surficial weathering and supports only sparse vegetation (unlike the ophiolites of Papua New Guinea and New Caledonia). Further, large regions of the Samail ophiolite preserve an intact stratigraphy, from pelagic and metalliferous sediments to pillow basalts, sheeted dikes, gabbroic plutonic rocks, and residual upper mantle peridotites that underwent partial melting to form the magmas that comprise the overlying igneous oceanic crust. During emplacement onto the Arabian continental margin, this stratigraphy was tilted and eroded, exposing sections extending from the paleo-seafloor to 10 or 20 km depth below the crust-mantle transition zone, in residual mantle peridotites. These cross-sectional exposures represent an exceptional, unique natural laboratory for studying crustal formation and evolution at submarine spreading centers, and low temperature alteration of mantle rocks exposed at the Earth's surface.

Ore deposits formed at the Samail spreading ridge have been mined in Oman for more than 5000 years, providing one of the key sources of copper for early civilization in the Middle East. The presence of chemically unusual rocks – now recognized as outcrops of the Earth's upper mantle – has been known in Oman since at least 1850.

Geological mapping is comprehensive at 1:100,000, with some areas mapped at 1:25,000, and more than 1000 papers have been published on the Samail ophiolite and the regional geology of



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the Oman mountains. Mapping and interpretation [*Lippard et al.*, 1986; *Nicolas et al.*, 2000] has subdivided the Samail ophiolite into approximately 15 "massifs"; spatially separated fragments of an initially elongate, continuous sheet of oceanic crust and upper mantle in extending for more than 350 km along strike in a SE-NW direction, roughly parallel to the strike of the sheeted dikes and thus to the spreading center at which the oceanic crust formed (Figure 1).

Geochemical investigations [e.g., *Koepke et al.*, 2009; *Pearce et al.*, 1981] indicate a polygenetic origin for the Samail ophiolite, with a first phase producing lavas and gabbros similar to typical "mid-ocean ridge basalts" (MORB) and related plutonic rocks. Later magmatic phases produced lavas that are highly depleted in incompatible trace elements, with affinities to lavas erupted in the early phases of western Pacific, subduction-related arc volcanism. These later lavas are related to distinctive, orthopyroxene-bearing pyroxenites and gabbronorites indicative of high SiO<sub>2</sub> contents in primitive magmas. Although debate continues, most workers agree that all of the Samail ophiolite lavas have geochemical affinities with lavas in subduction-related volcanic arcs, and that the spreading ridge that formed the crust was in the hanging wall of a subduction zone. However, the later stages of arc-related magmatism, intruding and disrupting the more MORB-like crust formed at the Samail spreading ridge, are more strongly developed in the northern ophiolite massifs [e.g., *MacLeod et al.*, 2013]. As a result, our proposed drilling will focus on the simpler, southernmost parts of the ophiolite, the Samail and Wadi Tayin massifs (Figure 1). Among all ophiolites worldwide, these massifs are the closest analogs to the Pacific crust and upper mantle that comprise a substantial fraction of the Earth's tectonic plates.

Recent, precise U/Pb zircon ages have refined older radiometric dates. Spreading ridge magmatism extended from 96.25 to 95.50 Ma [*Rioux et al.*, 2012b; *Rioux et al.*, 2013; *Warren et al.*, 2005]. The zircon data combined with older  $^{40}$ Ar/ $^{39}$ Ar ages on hornblende and micas indicate that metamorphism (and minor partial melting) along the basal thrust of the ophiolite had initiated by 94.9 Ma, giving a minimum age for the initiation of thrusting [*Rioux et al.*, 2013]. The striking overlap of igneous and metamorphic ages indicates that thrusting began near an active spreading center. Probably, the ophiolite was "obducted" – eventually onto the continental margin – because it was young and hot, with a density too low to be subducted.

Thrusting of the ophiolite, together with an underlying blanket of allocthonous, pelagic sediments (the Hawasina Group) continued until about 80 Ma. The ophiolite was subaerially exposed and eroded, and then unconformably covered by shallow marine sediments during a Late Cretaceous to Early Miocene transgression. Late Miocene – Early Pliocene tectonism formed spectacular anticlinoria cored by autochthonous Proterozoic to Mesozoic sediments of the Arabian continental margin that now separate the different ophiolite massifs. Cooling ages interpreted in terms of uplift and erosion yield Pliocene-Quaternary uplift rates averaging ~ 0.3 mm/yr. Although the ophiolite preserves many high temperature contacts, metamorphic parageneses and structural relationships formed at the submarine spreading center, some faulting and deformation in the massifs must have accompanied Miocene-Pliocene folding and uplift. Metamorphic temperatures remained below 100°C during this episode [*Poupeau et al.*, 1998]. Hence, the only higher temperature metamorphism affecting the ophiolite occurred at and near the spreading center and the nearby, newly initiated subduction zone.

Ophiolite massifs seaward of the Miocene-Pliocene anticlinoria dip offshore beneath a broad apron of fluvial conglomerates. Ophiolite massifs inboard of the watershed in the Oman mountains, including the Samail and Wadi Tayin massifs, are isolated klippe, overlying a variable thickness blanket of allocthonous Hawasina sediments, which in turn overlies the authochthonous Arabian margin sediments. Topographically corrected, Bouger gravity anomalies [*Ravaut et al.*, 1997] indicate that, at their approximate centers, the Samail and Wadi Tayin massifs are composed mainly of partially hydrated (serpentinized) residual mantle peridotite extending to depths greater than 5 km below the present-day erosional surface. These interpretations are consistent with large scale seismic reflection and refraction lines crossing the coast and the Oman mountains just NW of the Samail and Wadi Tayin massifs [*Al Lazki et al.*, 2002] and in the United Arab Emirates [*Callot et al.*, 2010; *Naville et al.*, 2010].

At this juncture, it is crucial to note that seismic surveys cannot detect structure within the ophiolite despite the obvious lithological boundaries within it. Seismic P-wave velocities (Vp) in the crust and mantle are variable and reach a maximum of ~ 5 km/s, due to extensive, multi-scale fracture networks, together with extensive alteration (serpentinization) of mantle peridotite. Even crucial lithological boundaries within the ophiolite, such as the crust-mantle transition, are not imaged. Indeed, sophisticated seismic techniques are needed simply to map the base of the ophiolite, where peridotite overlies limestone with Vp ~ 6 km/s [*Jardin et al.*, 2013; *Naville et al.*, 2010]. Smaller scale seismic surveys (100 m to 7 km) did not detect reflection or refraction boundaries, although site-specific, fracture-related anisotropy was different in peridotite and gabbro, allowing limited, local detection of the crust-mantle boundary [*Ildefonse et al.*, 2000]. Additional seismic surveys for the purpose of characterizing the lithologies in our proposed 250 to 600 m boreholes would be a waste of time and money.

The present day hydrology of the ophiolite was studied by Dewandel et al. [2005], with a focus on the mantle exposures and the crust (gabbro) – mantle transition zone. They estimated a permeability of  $10^{-14}$  m<sup>2</sup> for the fractured mantle peridotite within a few hundred meters of the surface. In catchments underlain by peridotite, water in seasonal and perennial streams within "wadis" (canyons), and most ground water sampled in wells, originated as rainwater and was modified by surficial weathering of the peridotite to produce Mg-HCO<sub>3</sub> rich waters. Neal and Stanger [1985] documented the presence of alkaline springs (pH up to 12) in peridotite catchments, similar to previously studied alkaline springs in peridotite from the California Coast Ranges and other localities. These record ongoing serpentinization and mineral carbonation in subsurface, peridotite-hosted aquifers [*Kelemen and Matter*, 2008; *VanTongeren et al.*, 2008]. The fracture density, permeability, fluid fluxes, microbial communities and reaction rates in these subsurface environments remain almost entirely unknown.

# 2. Motivation and Goals of the Oman Drilling Project

The overarching goal of scientific drilling in the Samail ophiolite is to understand the full spectrum of processes that create and modify oceanic crust and shallow mantle, involving mass and energy transfer between the mantle, the crust, the hydrosphere, the atmosphere and the biosphere over a range of temperatures from ~ 1350 to 20°C, depths from the surface to 10 or 20 km below the paleo-seafloor, and tectonic settings from spreading ridges to the deep ocean to surficial weathering to subduction zones. Less comprehensive proposals would likely address a few of these processes. Indeed, some proposed drill sites are ideally suited to addressing specific issues. However, all sites will provide crucial data on multiple processes.

In this section, we provide overviews of our broad scientific objectives. In Section 2.5, we will illustrate how each drill site will address these objectives.

### 2.1 Igneous and metamorphic processes at oceanic spreading centers

The remarkable exposures of the Oman mountains, with close affinities to ocean lithosphere formed at intermediate to fast spreading rates, means that the Samail ophiolite has long been an inspiration and testing ground for hypotheses about processes at spreading centers. Many of these ideas remain at the forefront of ocean lithosphere investigations and include:

- ductile flow in the upper mantle (focused vs plate driven upwelling; Figure 2) [e.g., *Ceuleneer et al.*, 1996; *Nicolas and Violette*, 1982]
- melt extraction and transport in the mantle (cracks vs porous conduits) [e.g., *M. G. Braun and Kelemen*, 2002a; *Kelemen et al.*, 1995; *Nicolas*, 1986]
- accumulation of melt in the crust-mantle transition zone
- [e.g., Boudier and Nicolas, 1995; Korenaga and Kelemen, 1997]
- deformation of the lower crust (gabbro glacier vs sheeted sills; Figure 3) [e.g., *Kelemen et al.*, 1997; *Nicolas et al.*, 1988]
- near-ridge hydrothermal circulation and alteration (shallow vs deep; Figure 3)
- [e.g., Bosch et al., 2004; L Coogan et al., 2002; Manning et al., 2000; VanTongeren et al., 2008]
- melt transport, porosity and crystallization in lower crustal cumulates [e.g., *Korenaga and Kelemen*, 1998; *Nicolas and Ildefonse*, 1996]
- freezing, intrusion, stoping and metamorphism at the dike-gabbro transition (Figure 4) [e.g., *Boudier and Nicolas*, 2011; *France et al.*, 2009; *MacLeod and Rothery*, 1992; *MacLeod and Yaouancq*, 2000]

These topics have been addressed via seagoing research when possible, and in turn observations from the oceans have lead to refinement or modification of ideas about the ophiolite. However, ocean drilling is expensive and drilling intact ocean crust has proved slow and challenging. ODP Hole 1256D, the deepest hole into fast spreading Pacific crust [*Teagle et al.*, 2006; *Teagle et al.*, 2012; *Wilson et al.*, 2006], has taken four ocean drilling expeditions to penetrate only as far the dike-gabbro transition zone. Rotary coring and the difficulties of cleaning deep, uncased holes result in biased, low rates of core recovery, compromising attempts to quantitatively describe the oceanic basement [e.g., *Tominaga et al.*, 2009]. High rates of core recovery (approaching 100%) are routine for diamond-coring on-land. Core from the Samail ophiolite will provide an invaluable archive to test well-formed hypotheses in sections of the oceanic crust that remain inaccessible in the modern oceans.

Proposed investigations in drill core samples of the Oman mantle section include studies combining geochemistry to characterize mantle heterogeneity and crystallographic preferred orientations indicative of solid state mantle flow trajectories, and studies of the relative age and spatial relationships of melt transport features relevant to evaluating the nature and importance of "mantle diapirs" in Oman (Figure 2), and to understanding the mysterious processes by which partial melt from a region hundreds of kilometers wide in the mantle is focused into a two to four kilometer wide zone of crustal accretion along oceanic spreading ridges.

We will concentrate our investigations of the formation of the oceanic crust on the accretion of the lower oceanic crust, from the sheeted dike-gabbro to the crust-mantle transitions, as this is where the greatest knowledge gaps exist and ocean floor sampling has been least successful.



**Figure 2:** The magmas from which oceanic crust crystallizes form via partial melting of the mantle as it rises and decompresses beneath spreading centers, driven by the divergence of the tectonic plates. The mechanism that drives focusing of the partial melts, to form igneous oceanic crust over a narrow region, just a few kilometers wide at the spreading center, is not well understood. Is this due to coalescing melt transport within a wide region of solid mantle upwelling, or to highly focused solid upwelling? Study of melt transport veins and solid deformation structures in the Samail ophiolite mantle will resolve this.

Analyses of drill core from the Oman lower crust will be used to address well-posed, longstanding, unresolved questions. These include the extent of porous flow versus magmatic injection in dikes and sills, the extent of solid-state versus crystal mush deformation of the lower crust and its variation with depth, the modification of lower crust composition via hydrothermal alteration, the transition from relatively coarse gabbros to fine-grained sheeted dikes, and the role of fluids in controlling the nature and rate of cooling of the lower crust. These processes are the primary controls on heat and mass input from the mantle to the oceans, but their extent and interplay remain controversial after decades of discussion. Study of chemical variation with depth, the extent of crystallographic preferred orientation, and zoning within minerals indicative of cooling rates over a variety of different temperature intervals, should provide clear resolution of these questions, or at least comprehensive constraints on remaining hypotheses.



**Figure 3:** Lower oceanic crust crystallizes from subsurface magma beneath spreading centers, forming gabbros. The site of crystallization is poorly known. Does it occur in a "shallow melt lens", after which gabbros undergo ductile flow downward and outward (left), or do gabbros crystallize from stacked melt lenses throughout the crust (right)? Study of chemical variation and crystal orientation in the lower crust

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of the Samail ophiolite will resolve this question. Crystallization of gabbro in a shallow melt lens requires rapid removal of heat by hydrothermal convection in the upper crust. Crystallization of gabbro at a range of depths requires hydrothermal circulation down to the base of the crust. Measurement of mineral zoning in Oman gabbros, interpreted in terms of cooling rates, will resolve which process was predominant. Figure modified from Kelemen et al. [1997].



**Figure 4:** Gabbros intruding blocks of hydrothermally altered sheeted dikes in the Wadi Gideah section of the Wadi Tayin massif. Study dike-gabbro transitions will provide essential information heat and mass transfer between oceanic lower crust, upper crust, and the oceans. From France et al. [2009].

### 2.2 Mass transfer into the shallow mantle above subduction zones

A close correspondence between 96 to 95 Ma igneous ages in the crust, and the oldest ages of metamorphic rocks along the basal thrust (ca. 95-94 Ma), indicates that thrusting of the ophiolite over adjacent oceanic crust and nearby sedimentary rocks began during or immediately after initial formation of igneous crust [*Rioux et al.*, 2012a; *Rioux et al.*, 2013]. Metamorphic rocks emplaced along the basal thrust, between overlying peridotite and underlying metasediments, record hot subduction zone conditions up to 800-900°C, 650-900 MPa [*Ghent and Stout*, 1981; *Hacker and Gnos*, 1997]. In some localities, at much shallower depths and lower temperatures, hanging wall peridotites underwent 100% carbonation at ~100°C, to form "listvenites", rocks composed entirely of magnesite + quartz + chromite [*Falk*, 2013; *Falk and Kelemen*, 2013; *Kelemen et al.*, 2011; *Streit et al.*, 2012] (Figure 5). Sr isotope ratios in listvenites are elevated relative to seawater, like those in metasediments below the basal thrust. Based on a Rb/Sr mineral isochron from a fuchsite-bearing sample yields 97 ± 17 Ma (2  $\sigma$ ), the listvenites formed by metasomatic introduction of CO<sub>2</sub>-bearing fluids from underlying metasediments during emplacement of the ophiolite. Thus, the "leading edge of the mantle wedge" may be a globally important, hitherto unappreciated reservoir for carbon [*Kelemen et al.*, 2013a; b].

Drilling and outcrop studies of the thrust contact between metasediments and overlying mantle peridotites (Figure 6), will allow direct study of chemical and physical processes of mass transfer in a subduction zone. Ideas and observations can be quantified via detailed 1D geochemical and structural transects in drill core(s), combined with mapping of the surrounding 3D geology.

Of particular interest will be identifying the footwall source(s) of carbon-rich fluids, the mechanical processes of fluid migration, the diffuse or localized nature of hanging wall alteration, the overall balance of low temperature mass transfer, the pressure and temperature range over which mass transfer was active, and the extent to which Oman observations can be extrapolated to subduction zones worldwide. Observations there will be interpreted in the context provided by investigations of other settings, especially along active subduction zones in different stages of evolution.



**Figure 5:** Fully carbonated lenses (magnesite + quartz + chromian spinel) within partially serpentinized mantle peridotite, near the base of the mantle section of the Samail ophiolite, where peridotites were thrust over metasediments. The lenses are parallel to the basal thrust. The thinner lower lens is about 10 meters thick, the thicker upper lens is about 200 meters thick. Together, they contain about 1 billion tons of  $CO_2$  in solid carbonate minerals. P. Kelemen photo.



**Figure 6:** Modified from Oakley et al. [2007]. Red area indicates approximate position of the Samail mantle section during thrusting over the metamorphic sole and metasediments of the Hawasina Group. Study of alteration of hanging wall peridotites and footwall metasediments will provide an essential complement to studies of mass transfer in subduction zones worldwide.

# **2.3** Modern mineral carbonation, serpentinization, hydrology and subsurface biosphere in mantle peridotite

There is increasing recognition that investigating ongoing alteration of peridotite, and the related, subsurface microbial ecosystem in the Samail ophiolite, holds as much promise – for contributing to fundamental understanding of global processes – as studying the Cretaceous formation and evolution of oceanic plates in Oman. Alteration of mantle peridotite – via serpentinization (hydration), carbonation and oxidation – is an essential process in Earth dynamics. Almost everyone has seen altered peridotites – whether they know it or not – as a popular ornamental stone used for building facades and kitchen counters, soapstone amulets and

monumental statues. Mineral parageneses in altered peridotite comprise part of the canon of metamorphic petrology. Unlike most iconic metamorphic processes, occuring in obscurity, deep in the Earth, peridotite alteration is ongoing and accessible, occurring at appreciable rates near the surface. For example, in their classic paper Barnes & O'Neil [1969] estimated that dissolved Ca in one alkaline spring was extracted from  $10^3$  to  $10^4$  tons/yr of peridotite.

And no wonder. At low pressures, say at 2 kb, mantle peridotite is unstable in the presence of water below ~ 700°C, unstable in the presence of CO<sub>2</sub>-rich fluids below ~ 500°C, and unstable at any temperature in the high oxygen fugacity that prevails near the Earth's surface. Below 200°C, the energy density (free energy per unit mass) for peridotite hydration and carbonation is ~ 500 kJ/kg, about 1% of the energy density in liquid hydrocarbon fuels [*Kelemen and Hirth*, 2012]. Where plate tectonics, coupled with erosion, exposes fresh peridotite on the surface, as in the Samail ophiolite, this creates a chemical potential gradient that is unparalleled on Earth in magnitude and extent, like a giant battery, which then proceeds to burn itself out.

The energy from this chemical dynamo drives many of the fundamental processes that shape the Earth. Hydration followed by subduction, supplies huge volumes of water to drive arc volcanism, and maintains or even increases the hydrogen content of the Earth's mantle over time. Peridotite alteration controls the rheology of oceanic plates and subduction zones, causes forearc uplift, and lubricates the mantle. It is essential in the global water and carbon cycles. It produces some of the most reduced fluids on the surface of the Earth, and generates steep compositional gradients that are exploited by chemosynthetic organisms. It has been invoked as an essential ingredient in the origin of life, because it creates ideal conditions (low Eh, FeNi metal catalysts) for abiotic synthesis of organic compounds. Enhanced peridotite carbonation could play a significant role in  $CO_2$  storage, or even a practical and inexpensive route to geological  $CO_2$  capture.

Tectonic uplift and erosion of the Samail ophiolite has brought a vast mass of mantle rocks into the modern weathering domain, providing a unique opportunity to investigate the active serpentinization of mantle peridotite [e.g., Clark and Fontes, 1990; Kelemen and Matter, 2008; Kelemen et al., 2011; Paukert et al., 2012; Streit et al., 2012]. The reaction of groundwaters with peridotite at low temperatures forms pH~8, Mg-HCO<sub>3</sub>-rich, oxidized fluids in the near surface (Type I fluids in Figure 7; following Barnes and O'Neil [1969], Neal and Stanger, [1985], Bruni et al. [2002], and Dewandel et al., [Dewandel et al., 2005]. When isolated from the atmosphere at depth (>50 m?), Type I fluids continue to react with peridotite to produce pH 12, Ca-OH-rich, highly reduced fluids with no dissolved C or Mg (Type II fluids). This reaction produces very large volumes of serpentine and Mg-carbonate minerals in the subsurface but these deposits have never been sampled in situ. Calcite travertine deposits are precipitated when Type II fluids emerge in springs and react with the atmosphere. Reduced fluids at depths become saturated with the FeNi alloy awaruite. The modern peridotite alteration system in Oman produces oxygen fugacity gradients ranging from bars to nanobars, and pH gradients from 6 to 12. However, the location of the reactions and sub-surface mineral precipitation zones, the fluid residence times, the length scales of fluid flow and chemical gradients, and the sources of essential chemical components (e.g., Ca) remain poorly established.



Figure 7: Schematic diagram showing the chemical evolution of groundwaters fluids during reaction with mantle peridotites, [adapted from Dewandel et al., 2005]..

Pioneering studies of peridotite-hosted alkaline springs [*Neal and Stanger*, 1985] and bedrock hydrology [*Dewandel et al.*, 2005] in the ophiolite are now commonly-cited foundations for research on weathering of Oman peridotites, focused primarily on mineral hydration (serpentinization), mineral carbonation, and generation of H<sub>2</sub> and CH<sub>4</sub> [e.g., *Boudier et al.*, 2010; *Kelemen et al.*, 2011; *Oeser et al.*, 2012]. Closed-system interpretation of <sup>14</sup>C data yields ages of 0 to > 50 kyr for carbonate veins in serpentinized peridotites with an average of about 26 yr, and a similar range in ages of travertine terraces at alkaline springs [*Clark and Fontes*, 1990; *Kelemen and Matter*, 2008; *Kelemen et al.*, 2011; *Mervine et al.*, 2013] consistent with mineral thermometry indicating near-surface crystallization at 20 to 60°C [*Streit et al.*, 2012], and with observations of alkaline spring water [*Paukert et al.*, 2012], demonstrating that subsurface serpentinization and mineral carbonation are active, ongoing processes in Oman. Perhaps this is not surprising, given the huge reservoir of chemical potential energy represented by outcrops of peridotite far from equilibrium with the high fO<sub>2</sub>, fH<sub>2</sub>O and fCO<sub>2</sub> in the atmosphere and surface waters.

On the other hand, active alteration in Oman, continuing over 10's of thousands of years in specific sites, poses something of a puzzle. In igneous and metamorphic rocks, fluid porosity and permeability may be negligibly small, so retrograde processes are supply limited. Furthermore, fluids enhance diffusion and so act as catalysts for recystallization. Prograde reactions produce fluids, in a positive feedback, while retrograde reactions may consume all available fluid long before recrystallization is complete. Finally, in an initially open system, retrograde reactions may increase the solid volume. This may fill porosity, destroy permeable flow networks, and armor reactive surfaces, limiting fluid supply and slowing reaction rates. Thus, rocks overcome by these limitations often contain a hodge-podge of disequilibrium mineral assemblages formed by incipient, but arrested, retrograde metamorphism. Commonly peridotites in outcrop are 10 to 60% hydrated, with abundant relicts of the original, mantle minerals.

However, 100% hydrated peridotites, known as serpentinites, are common. Less familiar, but of increasing scientific interest, are "listvenites", 100% carbonated peridotites composed of, magnesite + quartz. How do these form, when retrogression is self-limiting? Two end-member explanations have been offered. Many metamorphic petrologists consider that such reactions occur at constant volume, in which expansion due to decreasing solid density is balanced by dissolution and export of chemical components in a fluid. However, with notable exceptions, most studies of serpentinites, and our work on listvenites in Oman, suggest that alteration was nearly isochemical except for addition of  $H_2O$  and/or  $CO_2$ .

Alternatively, increasing stress due to volume expansion in an elastically confined volume may cause fractures, which in turn increase or at least maintain permeability and reactive surface area, in a positive feedback mechanism that allows retrograde reactions to proceed to completion [*Iyer et al.*, 2008; *Jamtveit et al.*, 2009; *Kelemen and Hirth*, 2012; *MacDonald and Fyfe*, 1985]. This, and other similar processes involving regulation of permeability via (bio) chemical feedbacks, forms a central hypothesis motivating our proposed drilling of actively altering peridotite.

In some subsurface locations, extreme chemical gradients in altering peridotite are present on a centimeter to millimeter scale, for example in the wall rock surrounding a crack with percolating groundwater. The presence of these gradients has important consequences for the subsurface biosphere and possibly the origin of life. Chemosynthetic organisms thrive in geochemical gradients, where they can catalyze spontaneous reactions resulting from disequilibrium, and make a metabolic "profit". The peridotite alteration environment could be one of the best habitats on Earth for chemosynthetic organisms. Microbial communities in these settings may provide analogs for subsurface life on the early Earth and/or on other less differentiated planets, where surface rocks retain a near chondritic composition. The combination of low fO2, reduced carbon species, and the presence of FeNi metal alloys in serpentinizing peridotite, promotes abiotic synthesis of complex hydrocarbon species [e.g., *McCollom et al.*, 2010].

Deep biosphere habitats are generated during serpentinization because reduced conditions are reached that can lead to the production of  $H_2$  via reduction of  $H_2O$ , ideal for sulfate reduction, methane generation, and abiotic or biotic organic synthesis [*Shock and Canovas*, 2010]. Sulfate reduction to form sulfide minerals, and autotrophic methanogenesis, in which microbes gain energy from the reduction of dissolved inorganic carbon, are enabled by serpentinization.

Sulfur and carbon additions and isotopic shifts in ocean floor and ophiolitic peridotites provide abundant evidence for microbial activity during serpentinization [e.g., *Alt et al.*, 2013; *Alt and Shanks*, 1998; 2011; *Alt et al.*, 2007; *Delacour et al.*, 2008; *Schwartzenbach et al.*, 2012]. Also, organic matter derived from biomolecules associated with hydrogarnets in serpentinized peridotites from the Mid-Atlantic Ridge [*Ménéz et al.*, 2012] supports the argument that altered ultramafic rocks host microbial communities that are intimately involved in geochemical exchanges between the mantle and seawater. However, so far studies of active, subsurface peridotite alteration environments have found very little life (D. Cardace, M. Schrenk, A. Templeton, I. Tiago, pers. comm. 2012). Are there nutrient limitations, or toxic constituents? Perhaps investigators have been looking in the wrong places, where alkaline Type II waters have already equilibrated with peridotite, rather than in the reaction zone where Type I waters are converted to Type II. Alternatively, perhaps this energetic but geochemically extreme environment is inaccessible along almost all available evolutionary pathways?

Low temperature alteration and weathering of the Samail ophiolite today is very similar to processes on the seafloor, and in other ophiolites. Thus, high pH alkaline spring waters in peridotite catchments in Oman are very similar in composition to those from the peridotite-hosted Lost City hydrothermal vents on the Atlantic seafloor. There are important differences, which should be emphasized and quantified in all work on this topic, but the general processes of far-from-equilibrium interaction between exposed mantle rocks, the hydrosphere, the atmosphere, and the biosphere, are very similar. Alkaline springs in Samail are also similar to those in other ophiolites, with the best known examples in the California Coast Ranges, the Ligurian ophiolites, and New Caledonia [e.g., *Barnes et al.*, 1978]. However, the arid climate of Oman has enabled the preservation of dozens of extensive travertine terraces formed by these springs, and of carbonate veins – formed in the subsurface and later exposed by erosion – that have been largely dissolved away from surface outcrops in colder areas with more precipitation.



Figure 8: A. Travertine at an alkaline spring in a peridotite catchment, near the village of Falaij, Oman. B. Carbonate veins in serpentinized peridotite, near the town of Birkat al Mawz, Oman. P. Kelemen photos.

Drilling in Oman will provide opportunities to test the past habitability of peridotites and gabbros when they were altered, and to examine where and how active serpentinization supports living subsurface microbial

communities. Onland studies will complement observations from similar, submarine systems. Thus, proposed, highly-ranked IODP drilling in the vicinity of the Lost City hydrothermal system (IODP Proposal 758), a site of ongoing peridotite alteration near the Mid-Atlantic Ridge, will form a fertile partnership with studies of similar systems in Oman.

### 2.4 Carbonation of peridotite for geological carbon capture and storage

Previous sections of this proposal describe natural systems in Oman, in which alteration has converted silicates in peridotite into Mg-Ca carbonate minerals, both in a  $\sim 100^{\circ}$ C subduction zone setting and in the present day weathering environment. Understanding natural mineral carbonation systems in Oman, which in some cases have formed carbonate minerals from all of the Mg and Ca present in peridotite protoliths, can provide insight into design of potential, engineered systems for geological capture and storage of carbon springs [*Kelemen and Matter*, 2008; *Kelemen et al.*, 2011], addressing a major societal challenge. These processes may have the potential to make a large contribution, storing gigatons of CO<sub>2</sub> per year in inert, stable, non-toxic carbonate minerals and were the subject of a sister workshop on "Geological Carbon Capture and Storage in Mafic and Ultramafic Rocks", held in Oman in January 2011 (Appendix 3). As noted above, it is somewhat surprising that peridotites can undergo 100% carbonation, but they do in some circumstances. It is important to learn the spontaneous natural mechanisms for

efficient mineral carbonation. These can then be emulated and enhanced in order to achieve rapid reaction with minimal additional energy input.

### 2.5 Specific science objectives of the Oman drilling project

Arranged from deep to shallow, high temperature to low, and ancient to modern, the headline objectives of the Oman Drilling Project are:

*Mantle melting, upwelling, and melt transport processes at fast spreading mid-ocean ridges* **Objective OB-1:** What are the solid-state mantle and lower crust flow trajectories? How do "mantle diapirs", with steep flow trajectories, relate to surrounding mantle with horizontal trajectories due to corner flow beneath the ridge? Is there a shear-sense inversion due to rapid mantle upwelling beneath slowly spreading crust? **Measurement**: Trajectories will be measured via crystal shape and lattice preferred orientation (LPO). Gradual transition from steep to inward dipping to outward dipping indicates rapid upwelling in the diapir "fed" the surrounding mantle and crust. A sharp change indicates that the diapir is a late intrusion into an older oceanic plate. A shear sense inversion indicates that mantle upwelling was more rapid than crustal spreading. **OB-2:** What is the spatial relationship between mantle melt transport features and "mantle diapirs", and how is melt focused from a partial melting region ~100 km wide into a zone of crustal accretion at a mid-ocean ridge a few km across, and the crust? Were transport features deformed in the diapir and surrounding mantle**? Measurement**: The attitude of planar features, crystal shape and LPO in melt transport features.

#### Accretion of the lower oceanic crust at fast spreading mid-ocean ridges

**OB-4**: Do new melts enter the lower oceanic crust by porous flow or by magmatic injection in sills or dikes? **Measurement**: Chemical variation in layered gabbros constrains the amount of porous flow of melt that can have passed through the rocks [*Korenaga and Kelemen*, 1998]. **OB-5**: What is the extent of solid state versus crystal mush deformation and how does this vary with depth in the lower oceanic crust? **Measurement**: Shape and LPO of plagioclase and olivine will constrain the amount of deformation. Work on drill core will define the presence or lack of high strain "shear zones" as well as the overall vertical trend.

**OB-6:** What is the vertical distribution of cooling via hydrothermal convection versus thermal diffusion? **Measurement**: Geothermometry, cooling rate estimates (zoning profiles in minerals), isotope data yielding water/rock ratios, and volumetric proportion of hydrothermal alteration. **OB-7:** How is the lower oceanic crust modified by hydrothermal alteration? **Measurement**: Comparison of the composition of altered and unaltered rocks along strike in layered gabbros. **OB-8:** What is the role of discrete crustal scale faults in channeling deep hydrothermal circulation and the extraction of heat from the lower crust. **Measurement**: Spatial distribution and width of hydrothermally altered zones.

#### Hydrothermal mass transfer from sediments to peridotite across the basal thrust

**OB-9:** What is/are the source(s) of carbon-rich fluids responsible for the complete carbonation of specific horizons of shallow Samail mantle? **Measurement**: Isotope studies of metasediments, carbonates, surrounding peridotite,

**OB-10:** What were the mechanical processes of fluid migration and alteration? **Measurement**: Crack and vein composition, spacing and width, SEM and TEM studies of crystal plastic deformation at crack tips, anisotropy of magnetic susceptibility.

**OB-11:** What were the pressure-temperature-fluid conditions of mineral carbonation and the mass transfer fluxes? **Measurement**: Geothermometry, fluid inclusion studies, metamorphic petrology of observed mineral assemblages.

#### The hydrology, geochemistry and microbiology of a modern peridotite catchment

**OB-12:** What is the extent of sub-surface hydration in the Semail ophiolite peridotites and are there vertical and lateral gradients in serpentinization? **Measurement**: Sampling fluids and core in spatially related boreholes at a variety of depths.

**OB-13:** What is the vertical extent and distribution of hydrothermal veins and diffuse alteration, fracture densities and permeabilities, and potential pore-scale habitats for microbes?

**Measurement**: Crack and vein mineralogy, spacing, <sup>14</sup>C, isotope ratios, as well as fluid contents. **OB-14**: What are the present day rate and spatial distribution fluid flow? **Measurement**: multi-scale permeability, conductivity, dispersivity, flow rate in boreholes and core.

**OB-15:** What are the variations of physical conditions and properties, fluid compositions, biogeochemical reactions, and microbial density and diversity with depth and flow path from meteoric recharge to alkaline spring discharge? Is there a vigorous sub-surface biosphere in the peridotite alteration environment or – despite the availability of chemical energy, are there nutrient limitations or toxins that limit microbial abundance? **Measurement**: As above, plus microbial density, DNA and protein sequence, incubation studies, comparison of different sites..

Carbonation of Peridotite for Geological Capture and Storage

**OB-16:** How do natural systems overcome the negative feedbacks of volume expansion during fluid-rock reactions to produce 100% carbonated rocks? **Measurement**: Crack and vein density and geometry, texture, nature and timing of vein mineral crystallization.

**OB-17:** What are the sources of carbon and essential cations (Mg, Ca) tracers that precipitate sub-surface carbonates and surficial travertines? **Measurement**: isotope and other tracer studies. **OB-18:** What are the water and carbon budgets for mineral carbonation and what by-products (economic, toxic or otherwise) are produced? **Measurement**: Fluid and mineral compositions.

# 3. Why drill the Samail ophiolite?

The Samail Ophiolite offers the best opportunity for the subaerial study of the mantle, igneous and hydrothermal processes that form new oceanic lithosphere at fast spreading rates. The ophiolite is very well exposed, with ~30-50% bedrock outcrops in the lower crust and upper mantle sections, and respectable exposure of the upper gabbros, sheeted dikes and the lavas in the southern massifs. Given the huge existing literature on Oman and the excellent exposure of the ophiolite, why is drilling necessary? The answer is two fold: (1) many of the pressing science questions require the objective quantification of geological features, and (2) we wish to undertake sampling and experimentation of active hydrological, geochemical and microbial processes associated with ongoing serpentinization of peridotite.

### 3.1 Objective quantification of geological features

Although there are extensive outcrops in the lower crust and upper mantle of the Samail ophiolite, these are biased to lithologies that are resistant to weathering and erosion – mainly unaltered, crystalline igneous rocks. Fault zones and lithologic boundaries are commonly weathered, yet these may be the most important conduits of fluid flow and hydrothermal chemical exchange. The mountains in Oman are steep, blocky and often covered with scree so that surface sampling and detailed logging generally takes place only along restricted, water worn outcrops along wadis (canyons).

Most outcrops tend to be strongly jointed, with fractures tending to open along pre-existing veins. Sampling with a hammer typically exploits existing joins and fractures, biasing sampling toward more altered edges (vein halos). Many of the observations critical to testing the

hypotheses posed above require unbiased quantitative spatial data that are almost impossible to objectively acquire from surface outcrops. These include fracture densities, mineral fabrics, intrusive features, the scale of compositional heterogeneities, fault zones, cross cutting relationships, lithologic boundaries, and the spacing and extent of hydrothermal veins and their alteration zones. Drill core imposes a 1-dimensional discipline that is challenging to emulate in even the freshest outcrops. The quantification of deep crustal hydrothermal fluid fluxes, chemical exchange budgets, and subtle changes in mantle mineral fabrics are imperative to improve our knowledge of ocean ridge mantle and magmatic processes.

Diamond drill core will allow us to take strip samples and make quantitative composite samples to geochemically quantify the bulk composition of the crust, hydrothermal exchange and the abundance of veins and micro-intrusions in gabbros and the mantle. Continuous sensor-track measurements of physical properties (e.g., density, natural gamma, magnetic susceptibility), and whole round and split surface high resolution images will provide non-destructive archives of the core and enable core log integration, core re-orientation into the geographic framework, and geological calibration when combined with the wireline geophysical logs.

The near 100% recovery we can anticipate from on-land diamond coring, coupled with the level of intensity of visual core description and instrumental scanning typical of ODP and IODP cruises, will be powerfully complemented by geophysical logs, regional and local detailed mapping, extensive two- and three-dimensional outcrop surfaces that provide context, and by the opportunity to collect arbitrarily large, equant outcrop samples when needed. Our project will allow direct comparison of drill core and downhole observations with outcrops. These can then be used to evaluate drill core observations obtained over decades by scientific ocean drilling. Such a process will provide a clearer view of the extent to which different aspects of ocean drilling results are representative of the invisible, three dimensional world beneath the seafloor.

### 3.2 Sampling active systems

Active, subsurface processes in the ophiolite today, mainly fluid flow, chemical weathering, fracturing induced by weathering, and microbial activity, cannot be observed without drilling. Despite more than 40 years of ocean drilling there are very few data on the depth extent, age and rate of low temperature alteration and weathering processes in oceanic crust and upper mantle. One of the most interesting parts of the ongoing weathering process in the Samail peridotites is the relatively rapid uptake of  $CO_2$  – via reaction of rocks with groundwater and then via uptake of atmospheric  $CO_2$  by alkaline fluids on the surface – to form solid carbonate minerals. The subsurface processes –forming ~ 10 times more carbonate than is deposited at the surface and producing alkaline vent fluids– have never been observed (Figures 7 and 8).

These subsurface reaction zones are accessible via drilling in Oman. Assuming that alkaline fluids do not cool significantly during ascent, spring temperatures of 40°C or less (average 27°C, close to the mean annual temperature in Oman) together with the observed geotherm (40°C at 300 m depth in boreholes) suggest that all of the springs have source depths  $\leq$  300 meters (Neal & Stanger, 1985; Matter, Kelemen and co-workers unpublished data). Alkaline waters with pH 11 to 12 were present throughout the lower three quarters of a 400 meter well sampled in January 2012, so we infer that the reaction zone – forming these waters from pH 8, Mg-HCO<sub>3</sub> waters – is probably within 400 meters of the surface, and "upstream" from this well. Tellingly, dissolved H<sub>2</sub> contents in the well water were 10 to 100 times higher than in alkaline springs sampled on the surface, attesting to degassing during ascent and/or mixing of end-member fluids with shallow

ground water to produce surface spring compositions (Matter, Shock, Kelemen and co-workers). Via drilling, we will sample end-member fluid reactants and the subsurface reaction zone where there is ongoing mineral carbonation and hydration. We will determine flow rates and hydrological properties. The results will be highly significant for understanding weathering, the natural carbon cycle, and potential engineering mechanisms to increase subsurface mineral carbonation rates for geological  $CO_2$  capture and storage.

Drilling will also allow sampling and radiometric dating (<sup>14</sup>C, Uranium decay series) of recent carbonate veins at depth that record previous episodes of reaction and mineral precipitation. Previous work has shown that carbonate veins that formed in the subsurface, subsequently exposed by erosion, commonly contain measurable <sup>14</sup>C, yielding <sup>14</sup>C "ages" of < 50,000 years. Clearly, the next step in understanding ongoing CO<sub>2</sub> uptake by subsurface mineral carbonation is to drill, sample, and date carbonate veins at depth, including those forming at the present time.

There are no data worldwide on the nature and extent of the subsurface biosphere in weathering mantle peridotite, more than 50 m below the surface. The chemical potential energy, inherent in tectonic emplacement of mantle peridotite near the Earth's surface, should sustain rich and varied subsurface communities of chemosynthetic micro-organisms. However, in contrast to predictions of biogeological studies of alkaline springs, and short boreholes in peridotite in California, have yielded very low cell counts and diversity. Potential explanations for this are that (a) highly alkaline waters have already reacted with and equilibrated with peridotite upstream, so there is little remaining potential energy in the systems where they are sampled, (b) the subsurface reactions that transform Mg-HCO<sub>3</sub> waters to Ca-OH alkaline fluids by precipitating Mg-carbonate minerals, consume almost all the carbon, leaving little available for microbes, or (c) most microbial electron transfer mechanisms are adapted for low to moderate pH environments, not the high pH environment represented by alkaline fluids. For all of these reasons, we believe that prior sampling may have been in the "wrong place"; we should seek the reaction zone where pH 8 groundwater is transformed into pH 12 alkaline water, where dissolved oxygen and carbonate from the surface are abundant but first encounter meet the highly reducing environment imposed by peridotite alteration reactions. This will require several holes in a region of active peridotite alteration, to locate and sample geochemical transition zones.

Presently there are no measurements on the apertures and spacing of fractures in subsurface lithologies in the Samail ophiolite, and the subsurface permeability of the ophiolite lithologies remains largely unknown except for the pioneering work of Dewandel et al. [2005]. Investigations of ongoing alteration and the associated subsurface biosphere are ideally suited to studies of cores and in boreholes. Core will be used to observe the vertical extent and distribution of vein lithologies and diffuse alteration, variation of fracture density and permeability, and the pore-scale habitat of microbial communities. Downhole measurements and fluid sampling will determine the multi-scale variation of fluid composition and flow, crack aperture, porosity, permeability, temperature, stress, microbial density and species diversity. In-hole experiments will determine geochemical transport properties and allow microbial culture and incubation experiments. Hole-to-hole measurements will characterize the nature and frequency of natural fracture events, due to volume changes during ongoing alteration, changing temperature, and precipitation events, monitor microseismicity induced by fluid injection for permeability and geomechanical measurements, and monitor the results of reactive tracer experiments.



# 4. Drill Site Selection and Proposed Work

The proposed drilling program is a direct outcome of working group discussions at the ICDP Oman Workshop (see Appendix 2), and will achieve the science goals of this proposal. In compiling these plans, we used cost information provided by Mawarid Mining LLC and Lalbuksh Irrigation and Drilling Company LLC, both Oman based companies actively exploring for and mining copper and chromite deposits in the ophiolite. These companies have offered to provide their equipment and personnel on contract for this project. A

summary of this cost information is provided in Appendix 4. Because drilling costs per meter increase with depth, but startup costs are a larger proportion of the total for short holes, the data yield an approximately constant value of \$250 per meter for wireline diamond drilling and coring (Figure A4-1). Because of the robust properties of the target lithologies, drillholes will not be cased, other than near surface collars to protect the hole. Water for lubrication will be supplied from drinking water trucks that routinely supply villages, at a surprisingly low cost.

For water sampling and some geophysical logging, it will be necessary to drill additional holes using rotary drill bits. Less detailed information from Lalbuksh yields an approximate cost of \$140 per meter for rotary drilling of 6-inch boreholes without coring. At Site BA1, where microbiological sampling is a top priority, we will attempt to minimize the use of lubricants and drilling mud, subject to on-site cost/benefit analysis.

Comparing wireline logs to observations on drill core is far more effective when the core can be oriented using criteria independent of geophysical logging data. In order to accomplish this routinely, we will orient inclined drill holes so that the core intersects known, planar horizons (layering in gabbros, intrusive contacts, etc) at an appreciable angle.

By merging the recommendations of the three final working groups at the Oman Drilling Workshop, and then eliminating all but the highest priority sites, we have compiled the plan proposed here. The different drill sites described in Appendix 5, with regional locations as shown in Figure 9, are keyed to the overarching science themes outlined in Section 2, based on the theme for which each hole is ideally suited. Other science goals can also be achieved at each site. Table 1 provides information on specific objectives that will be addressed at each hole.

 Table 1: proposed drill sites (OB columns refer to objectives in Section 2.5)

0		1 1			1	•		,			
site	lat	description	1*	2 <sup>nd</sup>	layer	hole	az	incl	mode	depth	cost
	lon		OB	OB	dip (°)		(°)	(°)		(m)	US\$
MD1	23.109N	Maqsad diapir,	1,2	4-6,	00	А	360	90	core	400	\$100,000
	57.957E	crust-mantle		9-18							
GT1	22.890N	W. Gideah	4-8	12	25 SSW	А	360	90	core	400	\$100,000
	58.520E	lower crust			25 SSW	В	360	90	rotary	400	\$56,000
GT2	22.852N	W. Gideah	4-8	12	20 SSW	А	360	90	core	400	\$100,000
	58.520E	mid-crust									
GT3	22.796N	W. Gideah dike-	4-8		10 SSW	А	360	70	core	400	\$100,000
	58.533E	gabbro trans									

#### igneous and metamorphic processes at oceanic spreading ridges

#### mass transfer into the shallow mantle at subduction zones

site	lat	description	1*	2 <sup>nd</sup>	layer	hole	az	incl	mode	depth	cost
	lon		OB	OB	dip (°)		(°)	(°)		(m)	US\$
BT1	23.366N	MOD Mtn	9-11	1,	40 S	А	360	70	core	250	\$67,000
	58.184E	basal thrust	16-18	12-15							

#### low temperature alteration hydrology, and microbial communities in peridotite

site	lat	description	1*	2 <sup>nd</sup>	layer	hole	az	incl	mode	depth	cost
	lon		OB	OB	dip (°)		(°)	(°)		(m)	US\$
BA1	22.866N	Batin	12-18	1	NA	А	360	90	rotary	400	\$56,000
	58.710E	active			NA	В	360	90	rotary	400	\$56,000
		alteration			NA	С	360	90	rotary	400	\$56,000
					NA	D	360	90	rotary	400	\$56,000
					NA	Е	360	90	core	600	\$153,500
					NA	F	360	90	core	600	\$153,500

totals

	days	depth	cost
		(m)	US\$
total meters & cost, diamond drilling and coring		5450	\$774,000
total meters & cost, rotary drilling		3450	\$280,000
total meters & cost		8900	\$1,054,000
total days startup	48		
total days drilling	101		
total days	149		

# 5. Geophysical logging, hydrology, fluid & microbial sampling

# 5.1 Geophysical wireline logging

Down-hole geophysical wireline logging is an essential part of the project. Wireline logs will be recorded at each drilling site to obtain continuous records of in situ physical and chemical properties of the lithology and formation fluids (Table 2). Wireline logs are needed to complement incomplete core recovery, to pin individual core sections to specific borehole geophysical measurements, and to geographically orient the recovered core sections. The integration of core and wireline data will determine relationships between physical properties, fluid flow, deformation, and the extent of alteration. Focus will be given to the determination of vertical variation of fracture and crack density and width, porosity, permeability, differential stress, fluid composition, and temperature. Comparing wireline logs to observations on drill core is more effective when the core can be oriented using criteria independent of geophysical logging data. To accomplish this routinely, we will orient drill holes so that the core intersects known, planar horizons (layering in gabbros, intrusive contacts, etc) at an appreciable angle.

	1 9	88 8
Properties	Tools / methods	Note
Magnetic	Magnetic susceptibility	Lithology ID, core to wireline correlation
Porosity	Electrical resistivity, sonic, acoustic, dual induction, single induction, dual laterolog	Lithology ID, rock strength & elasticity, seismic velocity, fracture and permeability indication
Permeability, borehole flow	Heat-pulse flowmeter, impeller flowmeter, magnetic susceptibility	Multi-scale permeability and porosity distribution
Formation lithology	Spectral gamma (total gamma plus U, Th, K counts), magnetic susceptibility, optical televiewer, sonic	Extent and orientation of alteration, cracking, veins
Borehole geometry	4-arm caliper	Fracture, fault & borehole breakouts (stress) ID, well- to-well correlation
Borehole fluid	pH, Eh, p, T, C <sub>w</sub>	Vertical variation of fluid composition
Borehole images	Acoustic & optical televiewer	Lithology, fracture/crack spacing, orientation and width, local stress, core orientation

The wireline logging will be conducted with slimhole equipment from the Borehole Geophysics Group at the University of Montpellier, France (Dr. Philippe Pezard). All the proposed probes can be operated in small diameter (3"), open boreholes. Two logging engineers from Univ. Montpellier will conduct the logging. The geophysical wireline logging requires funding of US\$285,870 (Appendix 6).

# 5.2. Fluid sampling and borehole tests

Fluid sampling for chemical, isotopic and microbial analysis as well as hydrological borehole tests will be critical for the study of physical, chemical and geomicrobial processes. Fluid sampling will be conducted in selected holes in the crustal and mantle section. There are distinct differences in the hydrologic environment between the crustal (gabbro; Na-Ca fluids) and the mantle sections (peridotite; Mg-HCO<sub>3</sub> and Ca-OH fluids; Figure 7), which result in different chemical composition of the groundwater.

Relatively inexpensive boreholes will be drilled with a rotary bit, without coring, for water sampling. The target diameter for these holes is 6", which will allow us to conduct pumping and tracer tests using packers to study the subsurface permeability and solute transport in fractured peridotite. The following tests will be conducted at water sampling sites:

**Pumping tests:** Pumping tests will be conducted using a straddle-packer system to evaluate the transmissivity and storativity of specific intervals. Water levels will be measured continuously before, during and after pumping using pressure transducers. Borehole televiewer and vertical flow meter logs (Table 2) will be examined prior to the tests to locate likely permeable zones.

**Injection tests:** In case of very low permeability, we will perform injection tests in isolated zones using straddle-packers. As for pumping tests, injection tests measure permeability and storativity but they can be employed over a wider range of permeabilities. We will use groundwater that was pumped prior to the injection test and stored in a tank as an injection fluid.

**Push-pull tracer injection tests**: Single-well push pull tracer tests will be conducted in isolated zones with straddle-packers to quantify solute transport, mass transfer, and effective porosity. In addition, these tests can be used to determine in situ microbial activities [e.g., *Istok et al.*, 1997]. The tests consist of a pulse-type injection of tracer solution including biologically reactive components followed by an extraction phase during which the tracer solution is pumped back. Changes in the solute concentration will be measured to obtain breakthrough curves. The quantities of reactant consumed and products formed will be computed.

**Fluid samples** will be collected, again using straddle packers to ensure that fluids are derived from a specific depth interval, with gas-tight sample chambers to avoid degassing during transport to the surface. A more extensive sampling campaign with repeated collection of fluid and dissolved gas (mainly H<sub>2</sub>, CH<sub>4</sub>) samples will be conducted at the proposed multi-borehole BA1 Site where peridotite is undergoing alteration. Alkalinity, electrical conductivity, pH, temperature, redox potential as well as spectro analysis for dissolved oxygen, ammonia, nitrate, sulfide, silica and phosphate will be analyzed on site in the field. Fluid and gas samples will be shipped to off-site labs for further chemical and isotopic analysis.

Borehole testing and fluid sampling will be conducted by the project teams and their research groups. Two research associates will conduct the packer tests while the PIs and project manager will oversee the tests at the multi-well test site, and are responsible with their team members for the fluid and dissolved gas sampling. The total cost of the borehole packer and fluid sampling experiments is estimated at US\$447,721 (Appendix 7).

### 5.3 Microbiological Sampling

Petrological and geophysical questions drive selection of several of the proposed drill sites, but much the core from these sites will be valuable for geobiological studies. Evidence of microbial activity may be preserved in core, especially where they intersect zones of serpentinization and other types of alteration. Many forms of fossil evidence of microbiological activity can be sought in cores, and preserving some types of evidence poses minimal constraints on sample handling. Sampling for living microbes requires more stringent methods. These will be applied chiefly during drilling into the active serpentinization system at Site BA1.

#### 5.3.1 Sulfur Isotope Records

Freezing of core samples for sulfide analysis, or packaging in an inert atmosphere, will inhibit sulfide mineral oxidation. This generally has not been done with the samples from IODP holes used for sulfur isotopic investigations of microbial activity [e.g., *Alt and Shanks*, 2011; *Schwartzenbach et al.*, 2012]. We anticipate that samples from all cores taken for petrologic and geophysical studies will be amenable for sulfur isotopic investigations of past microbial activity.

#### 5.3.2 Microbiological and organic geochemistry sampling of core

There are well established techniques for sampling drill cores to minimize microbial contamination following more than a decade's research on the sub-surface biosphere [e.g., *Ménez et al.*, 2012]. Core samples for microbial sampling will be identified at the rig-site on recovery, quickly sub-sampled using organic-free tools wrapped in muffled aluminium, flash frozen in liquid nitrogen, and shipped to Sultan Qaboos University, where an anaerobic chamber in the lab of Prof. Raeid Abed will be used to further prepare selected samples by removing the periphery of the core and preserving cm-sized sub-samples of the center. These sampling efforts will be carefully coordinated with core logging to maintain a balance of efficiency and comprehensive descriptions during the coring process.

In the laboratory at SQU, flash-frozen core centers will be logged and transferred to -80°C freezers for long term preservation (and use for DNA, RNA, and lipid analyses). Samples for cultivation and activity experiments will be processed under anoxic conditions in an anaerobic chamber to evaluate the abundance and characteristics of viable microorganisms and their metabolic activities. This will be primarily accomplished using standard microbiological approaches such as microscopic cell counts and spectrophotometry, as well as more sensitive approaches such as stable isotope tracing of microbial metabolism. Several incubator ovens will be necessary to cover different chemical/thermal conditions.

#### 5.3.3 Minimizing Contamination during Drilling

Drilling into zones of active serpentinization (BA1 and SA1), where a primary goal is to obtain geochemical and microbial samples, will use procedures to minimize contamination. The strategy developed over the years in IODP and other projects is to use anthropogenic organic tracers, such as perfluorocarbons, and microscopic latex beads on the scale of microbial cells to document the extent of contamination of the core during drilling [*Santelli et al.*, 2010]. Where possible at Site BA1, we will store groundwater pumped from rotary drill holes, and/or the existing water monitoring well there, as a drilling fluid. It may also be possible to obtain desalinated, relatively pure water for drilling at this site, from one of the many desalination plants recently completed in Oman.

The total cost of the microbiological sampling is estimated at US\$345,572 (Appendix 8).

# 6. Core description & scanning, publication, sampling & curation

### 6.1 Core description & scanning

Cores recovered by the Oman Crustal Drilling Campaign will be visually and instrumentally described at modern Integrated Ocean Drilling Program (IODP) standards. There is a wealth of experience to train new scientists in the systematic IODP core logging approaches because many of the proponents of the Oman Drilling Project have served as shipboard scientists, Chief Scientists, and proponents on multiple IODP cruises.

Following drill site labeling, basic curation (depth, interval, way-up), general description of rock types in each section, microbiological (and other ephemeral property) sampling, drill cores will be sealed for transport and stored in Muscat, Oman by the Geological Survey of Oman at no cost to this project. Detailed core description, instrumental scanning, and sampling will be undertaken at a later date by members of the extended science party (proponents + post-docs and graduate students) working in a shipboard expedition mode.

The IODP riserless drill ship, RV JOIDES Resolution (JR), has a recently upgraded, state of the art laboratory for formal curation, and the visual and instrumental description of drill core, including advanced digital database and archiving capabilities. Due to budgetary constraints the JR will not be in continuous, year-round operation at sea for the next five years or more. As a result, it is available for use for at least two months per year in 2015-2017 (see supporting letters from the US National Science Foundation and IODP TAMU, Appendix 17).

Diamond drill cores will be secured for transport, containerized in Oman, and shipped to the JR in port. Scientists will travel to the JR, live and eat onboard, and engage in 24 hour core description operations as if they were at sea on an IODP drilling cruise. Logging of the core will take place for two months per year over three years. The core will be logged in topical groups, so that science teams to log the core can be selected based on research expertise.

We have investigated alternatives including logging core at the IODP Repository in Bremen, the Geological Survey in Berlin, and the IODP Gulf Coast Repository at Texas A&M University, but the JR has the best combination of facilities and is the most cost- and time-effective solution.

The cost to describe ~3000 m of drill core to IODP standards will be US\$706,000 (Appendix 9).

# 6.2 Publication of Oman drilling project reports

We will ensure the systematic and complete publication of basic observations from geophysical logging, water sampling, and core description will be undertaken in a standardized and accessible manner, analogous to the electronic, open-access Initial Reports volumes of the IODP. This is in addition to numerous, anticipated research papers that will report on more specific results of this project in peer-reviewed, international journals. IODP Publications Services at Texas A&M University has offered to help us assemble and publish an Initial Report volume on Phase I of the Oman Crustal Drilling Campaign, with a total cost of US\$150,000 (Appendix 10).

# 6.3 Permanent archiving and storage of drill core

The American Museum of Natural History has offered to permanently curate and store core, and to process sampling requests from research scientists that are submitted more than two years after the core is logged. Other options were considered – including storage in Oman or at the Geological Survey in Berlin. We have selected the AMNH because of their past role in curating and storing the core from the first and largest ICDP undertaking, the Hawaiian Drilling Project. Costs for sorting and storage are estimated at US\$17,900 (Appendix 11) as outlined in a letter of support from Dr Edmond Mathez of the AMNH (Appendix 17). We note that if, at some time before completion of this project, the Omani government or Sultan Qaboos University were to offer permanent storage facilities at a similar cost, this might be preferable.

### 6.4 Off-site analyses of samples and data

A systematic and comprehensive suite of off-site analyses of core, water and biological samples will be undertaken on the samples from this drilling project. Funding for sample analysis will be

entirely supported by research grants to the proposal PI's and to other scientists from international and national funding agencies and private foundations. (Appendix 15).

Analyses of core samples will include electron microprobe, laser ICP-MS and ion probe analyses of minerals in thin section, whole rock trace element analyses via XRF, ICP-MS, and volatile element analyzers (e.g., S, C, H<sub>2</sub>O); carbon isotope measurements for <sup>14</sup>C geochronology, light stable isotope measurements on whole rocks and powders, including clumped C-O isotope measurements for carbonate mineral thermometry, heavy radiogenic isotope measurements and zircon geochronology via multi-collector ICP-MS and/or TIMS, and high precision zircon geochronology via TIMS. We will adopt a "Pool" sampling approach where possible, in which collaborative teams of investigators will share samples (thin sections and powders) to ensure that a representative sample suite is comprehensively analyzed for a standard suite of geochemical parameters (e.g., for whole rock samples: major, trace, and volatile elements; Fe<sup>3+</sup>/Fe<sup>tot</sup>;  $\delta D$ ,  $\delta^{18}O$ ,  $\delta^{34}S$ , <sup>87</sup>Sr/<sup>86</sup>Sr) to provide a reference dataset for more time consuming and specialist analyses (e.g., U-Pb,  $\delta^{11}B$ ,  $\delta^{7}Li$ ).

Core samples will also be subjected to magnetic and physical properties (e.g.,  $\rho$ , vp, vs, porosity, etc) testing to determine essential properties for correlation with wireline measurements and regional geophysical measurements. Rock and mineral fabrics will be determined by electron back scatter distribution (EBSD), mineral shape analysis, and X-ray goniometry.

Analyses of water samples will include <sup>3</sup>H-<sup>3</sup>He and radiocarbon and noble gas analysis for geochronology.,Samples will be analyzed for dissolved organic and inorganic carbon by carbon analyzer, major and trace elements by ion chromatography, ICP-AES, and ICP-MS using the NIST standards. Dissolved gas concentrations (H<sub>2</sub>, N<sub>2</sub>, Ar, CH<sub>4</sub>, hydrocarbons) will be analyzed by gas chromatograph, as well as stable isotopes ( $\delta^{18}O$ ,  $\delta^{2}H$ ,  $\delta^{13}C_{DIC}$ ,  $\delta^{13}C_{DOC}$ ) by gas source IRMS or by laser spectroscopy. As for the core sample analysis, we will use a "pool" sampling approach, in which the different investigators share samples and the same samples get analyzed for the same parameters in different laboratories for the purpose of quality control and to ensure the comprehensive analysis of the sample set.

Microbial cultures and incubation experiments initiated at the time of sampling will determine the identity and biotechnological potential of the organisms isolated as well as their metabolic capabilities. Frozen samples will be used for extraction and characterization of biomolecules. DNA can be extracted for characterization of the microbial community diversity in subsurface core samples [Flores et al., 2011; Lin et al., 2006; Sahl et al., 2008; Santelli et al., 2008], as well as their metabolic and physiological characteristics using techniques known as quantitative PCR. metagenomics and metatranscriptomics [Brazelton et al., 2011; Canfield et al., 2010; Flores et al., 2011; Inskeep et al., 2010]. If treated appropriately, RNA can be extracted from the core section, to evaluate the active (transcribing) portion of the microbial population and their activities [Jones and Lennon, 2010]. Coupled to these data, lipids can be retrieved from the frozen core samples and serve as a bridge between microbiological analyses and organic geochemical analyses. Finally, the abundance of microbial populations and their relationships to mineral phases can be evaluated using scanning and transmission electron microscopy, fluorescence in-situ hybridization and other advanced imaging techniques. Examples of new approaches well-suited to analysis of microbial communities associated with serpentinized rocks include micro-FTIR [Igisu et al., 2012], micro-Raman [Ménez et al., 2012] and cathodoluminescence spectroscopy [Rommevaux-Jestin and Menez, 2010], as well as synchrotron-based x-ray microscopy [Menez et al., 2007] and x-ray fluorescence

microspectroscopy [*Mayhew et al.*, 2011; *Templeton et al.*, 2009]. Bulk and spatially-resolved C, S and Fe isotopic analyses can also be conducted on the same suite of samples [*Alt and Shanks*, 2011; *Rouxel et al.*, 2008]. All of these techniques can be applied to samples frozen, fixed or preserved in ethanol or RNA later upon sampling and serve to relate bulk analyses to local environments of the microbial populations.

# 7. Expected benefits of the proposed work

The Oman drilling project will address an array of fundamental science topics on which scientific consensus has not yet been achieved or in emerging fields requiring initial exploration. Data from core, geophysical logs and water samples will resolve long-standing uncertainties, provide strong constraints on developing hypotheses, and provide initial data in emerging fields.

A web site reporting on the progress and results of this project will be coordinated by a project manager and administrative assistant, using the web site facilities of ICDP. This site will provide open access to the Oman Drilling Project Initial Reports when published, as well as a comprehensive list of proponents and a bibliography of abstracts and published articles. All data resulting from the project will be available on the site, following the IODP database format.

Societal benefits from this project will include the incalculable benefit of the basic research described above. More tangible benefits will include increased understanding of natural mineral carbonation processes, at high temperature near magmatic ocean ridges, at moderate temperature above subduction zones, and at low temperature in the present day alteration environment. Understanding of these processes can be used to design engineered methods for geological  $CO_2$  capture and storage.  $CO_2$  capture from shallow seawater, mineral carbonation at depth, return of carbon-depleted water to the sea surface, and uptake of  $CO_2$  from the atmosphere, may constitute a relatively cost-effective method for distributed air capture of  $CO_2$  coupled with geological storage. Unfortunately, distributed air capture of  $CO_2$  may become necessary in the second half of this century, if unchecked greenhouse gas emissions lead to an unsustainable global climate. *This method of in situ mineral carbonation involves direct emulation of natural mineral carbonation to induce hydrothermal circulation of seawater through sub-seafloor peridotite.* 

Understanding the process of "reaction-driven cracking" is likely to have major societal benefits. In this process, solid uptake of  $H_2O$ ,  $CO_2$ ,  $O_2$ , and other components from fluids, increases the solid volume, causing high stress and fracture. Fractures, in turn, enhance fluid flow and expose reactive mineral surfaces in a positive feedback mechanism. Although this is observed in hydration and carbonation of tectonically exposed mantle peridotite, the conditions favorable for this mechanism – as opposed to constant volume replacement, and to self-limiting filling of pore space and armoring of reactive surfaces – are poorly understood. Improved understanding could permit engineered applications that create a dense fracture network for fluid transport at the grain scale, not only for  $CO_2$  capture and storage, but also for generation of geothermal power, in situ mining and extraction of hydrocarbon resources from "tight" reservoirs.

The most substantial educational benefit from the proposed Oman drilling project will be involvement of Omani undergraduate and graduate students from Sultan Qaboos University (and perhaps other Omani Universities) in all aspects of the project. Omani students will participate in water sampling (Section 5.2), and travel to the JOIDES Resolution for extensive experience with core observations (Section 6.1) in the world's best laboratory for this purpose, working shoulder-

to-shoulder with high experienced international scientists. Numerous international graduate students and early career researchers will also take part in this project.

The proponents of the Oman drilling project have a strong record of public and media engagement [e.g., huge media impact of *Teagle and Ildefonse*, 2011]. We anticipate that this will continue anticipate major interest from an international audience. In addition we would like to generate enthusiasm and interest in the local Omani and regional population beyond geologist at Sultan Qaboos University. We will do this through public lectures to schools, learned societies, and displays in local libraries and museum. We plan to publish a richly illustrated children's book describing the Samail ophiolite and the unique geology of Oman that will be available in Arabic as well as other international languages [e.g., *Laverne*, 2008] <u>http://www.christine-laverne.com/en/livres-de-geologie/</u>.

# 8. Project Management

A Project Steering Committee (PSC) will oversee all aspects of this project through completion of the Initial Reports volume and archiving of the core at the American Museum of Natural History. The PSC will meet at least twice a year, once in Oman and once elsewhere. The Chair of the PSC will be Prof. Peter Kelemen. Other members of the PSC will have responsibilities to oversee specific aspects of the project (Appendix 13).

The PSC or their designated representatives will coordinate off-site analyses of rock, water and biological samples. Access to Oman Drilling Project samples and data will be overseen by the Sample Oversight and Allocation Committee, a sub-group of the PSC (Teagle, Kelemen, Goddard, Shock, Schrenk) following the sample allocation procedure in Appendix 14).

The PSC will coordinate proposals for additional funding from international and national funding agencies and private foundations (see Appendix 15), and discuss and approve any necessary changes to the drilling plan and the budget. They will act as, or will appoint, two Chief Scientists to oversee each drilling season, and two Chief Scientists for the two, two month core logging efforts onboard the R/V JOIDES Resolution. They will be the editors of the Initial Reports volume and oversee publication requirements.

The 38 Principal Investigators on this proposal will participate in many aspects of detailed site selection, drilling, geophysical logging, water sampling, core logging, and biogeological sampling, and will ensure that there are sufficient, highly qualified volunteers for the basic characterization of core and boreholes outlined in this proposal.

A Project Manager, on contract to ICDP and reporting to the PSC, and will have operational responsibility for day-to-day coordination of proposed travel, drilling and sample shipment. A co-located Administrative Assistant will assist the Project Manager. The Project Manager will be employed for 75 days in the field in years 1 and 2, and in addition for 5-day weeks in in the office the remainder of year 1, three months in year 2, and month in year 3. The Administrative Assistant will be employed 6 months in years 1 and 2, and 3 months in year 3. The estimated costs for the management and administrative positions totals US\$429,602 (Appendix 12A).

The PSC will meet annually in years 1-4 at a cost of \$40,000 per year. Sixty members of the Science Party (all scientists involved in the drilling and logging process), will meet in Oman in years 2 and 4 at a cost of \$190,000 per year. Thus, the total cost of project coordination meetings will be \$460,000 (Appendix 12B).

Activity	Cost USD\$
Diamond coring and rotary drilling costs (Table 1)	\$1,054,000
Geophysical wireline operations (Appendix 6)	\$285,870
Borehole tests and fluid sampling (Appendix 7)	\$447,721
Microbial sampling and geobiological experiments (Appendix 8)	\$345,572
Description of drill core (Appendix 9)	\$706,000
Initial Reports Volume (Appendix 10)	\$150,000
Permanent archiving and storage of the OCDC Drill Core at the AMNH (Appendix 11)	\$17,900
Project management (Appendix 12)	\$429,602
Project coordination meetings (Appendix 12)	\$460,000
Permitting Fees for Drilling (Appendix 16)	\$10,000
Total Costs	\$3,896,665
Request from ICDP	\$1,948,332

# 9. Budget summary

# 10. Time Table

1
obtain matching funds, especially for drilling costs, geophysical logging, water sampling and hydrology, microbiological sampling; obtain permits for drilling in Oman, refine site selection
rotary drilling of two 400-m holes at Site BA1 and one 200-m hole at Site GT1 (1000 m total)
wireline diamond drilling and coring at Sites MD1, GT1, BT1 (1650 m total)
water sampling at Sites BA1, GT1
geophysical logging at all drilled sites in year 1
core sample shipment to Joides Resolution
rotary drilling: two 400-m holes at Site BA1 plus deepening to 400-m at Site GT1 (1000 m total)
wireline diamond drilling at Sites GT2, GT3 and BA1 (1400 m total)
core description Sites MD1, GT1, BT1 (1650 m total)
water sampling at Sites GT1, BA1
geophysical logging at all drilled sites in year 2
core sample shipment to Joides Resolution logging lab
core description Sites GT2, GT3 and BA1 (1400 m total)
core sample shipment from Joides Resolution to American Museum of Natural History
begin preparation initial reports volume
curation and permanent storage of core
completion of initial reports volume

Drilling will take place during November though March, avoiding the hottest months of the year. Geophysical logging will be undertaken as soon as possible after drilling to minimize hole

stability problems. It will also be desirable to sample water in holes several times in order to assess and minimize the effects of contamination during drilling. Rotary drilling and sampling at Site BA-1 in year 1 will enable us to determine the site of the active reaction zone, in preparation for choosing the locations of the two cored, diamond drill holes to be drilled at this Site.

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