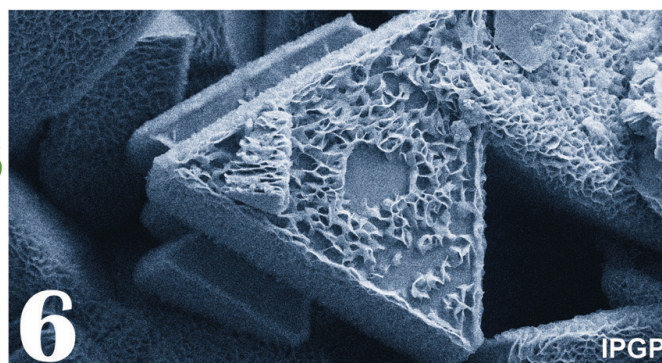


# 4th Serpentine days 2016



**25-29 September - Sète, France**

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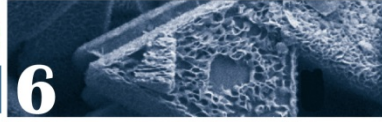
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**4th** **Serpentine** **days**  
25-29 September  
Sète, France

**2016**



## THE LOST CITY HYDROTHERMAL FIELD AS A SPECTROSCOPIC AND ASTROBIOLOGICAL ANALOG FOR NILI FOSSAE, MARS

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### Serpentinization, Mars, Habitability

The Lost City Hydrothermal Field (LC) is a submarine site of serpentinization, west of the mid-Atlantic ridge near 30°N (Kelley, 2001). The site presents a unique environment where the alteration of source rocks provides biologically viable energy. The LC serpentinites and associated alteration products are produced by the fluid interaction and hydration of ultramafic rocks. Fluid/rock interactions at temperatures <150°C produce alkaline vent fluids enriched in CH<sub>4</sub> and H<sub>2</sub>, sustaining microbes through an abiotic process (e.g., Brazelton, 2006). We have acquired a suite of variably altered serpentinites, meta-gabbros, talc-rich and amphibole-rich fault rocks, and carbonates from the LC to assess their spectral signatures in the near- and thermal-infrared wavelength regions (NIR and TIR). This has provided 1) a confirmation of the mineralogy of these rocks using a non-destructive method, 2) a detailed understanding of the spectral and mineralogical variability within a given rock type from a low-T serpentinizing setting, and 3) a spectral library with measurements similar to those acquired of the martian surface.

Bulk-rock compositions were determined for the LC samples, the non-carbonate rocks were dominated by serpentine (mostly lizardite and chrysotile), amphibole (mostly tremolite), and talc. NIR reflectance measurements uniquely identified the serpentinites and carbonates. Reflectance measurements for the talc-rich fault rock, the amphibole-rich fault rock, and the meta-gabbro were nearly indistinguishable, though their rock types can be confirmed from the TIR measurements, illuminating the sensitivities of the two wavelength regions. Our NIR measurements were then directly compared to similar measurements made of the martian surface using CRISM NIR instrument.

We have aggregated CRISM observations of phases associated with low-T serpentinization in the Nili Fossae region of Mars. Previous studies have shown the presence of olivine (Hamilton, 2005), carbonate (Ehlmann, 2008), serpentine and talc/saponite/amphibole (Ehlmann, 2009; Brown, 2010; Viviano, 2013). We have also added new observations of serpentine, talc/saponite, and Mg-carbonate from more recent CRISM data. Interestingly, we observe the same NIR spectral signatures in both the LC and Nili Fossae, with the exception of the major metal cation type of the carbonates. On Mars, the observed suite of minerals (olivine+serpentine+carbonate+talc/saponite/amphibole) are all within close regional proximity, sometimes within the same image. Additionally, this suite of minerals implies that H<sub>2</sub> was produced during the time of alteration, providing an energy source and a habitable environment for putative life in Nili Fossae's past. Though the geologic setting present in Nili Fossae was most certainly uniquely Martian and may have looked quite different from the LC, the geochemical environment implied by the observed spectral signatures is one that is known to support microbial life on Earth.

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**MAGMATIC INTRUSIONS IN EXHUMED MANTLE OF MAGMA-POOR RIFTED MARGINS: EVIDENCES FOR THE CLOSE ASSOCIATION BETWEEN DESERPENTINIZATION, CHLORITIZATION AND RODINGITIZATION PROCESSES.**

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**Deserpentinization, Ocean-Continent Transition (OCT), chloritization, Sr-Nd-B isotopes.**

Recent studies have demonstrated that tectonic, magmatism and hydration are key features that control the oceanization process from the rifting to the establishment of the first oceanic crust. In this frame, studying Ocean-Continent Transitions (OCTs) offers a unique opportunity to investigate the interactions between magma, mantle and fluids and assess their feedback mechanism and enhancers. The Upper Penninic Platta nappe (Southeastern Swiss Alps) is probably the best example of fossil OCT documented so far: This unit corresponds to the exhumed mantle section of the Liguro-Piemont magma-poor-rifted margin that has been well-preserved and only weakly affected by alpine metamorphism (prehnite-pumpellyite facies). This section is characterized by numerous rodingitized gabbroic dikes and bodies intruding the present-day strongly serpentinized peridotites. The aim of this study is to estimate whether the magmatic intrusions occurred before, during and/or after the mantle serpentinization on the basis of petrological and geochemical approaches.

Mineralogical observations and Raman spectroscopy show that rodingites consist of an assemblage of chlorite and multiple generations of clinopyroxene, while the mantle section away from the contact is mainly composed of serpentines (lizardite ± chrysotile) and relics of primary minerals (olivine + pyroxenes). At the contact with dikes, the mantle is turned into a chlorite reaction zone where clinocllore has almost completely replaced the serpentine, suggesting a process of deserpentinization and subsequent chloritization of the mantle rocks.

Radiogenic (Sr, Nd) and stable (B) isotopic data show that magmatic intrusions and their contacts have very similar compositions. This demonstrates that rodingitization and chloritization processes occurred after the circulation of fluids of a single origin. We argue that fluids released during the mantle deserpentinization in response to the magmatic intrusions are responsible for both rodingitization and chloritization processes.

## CONTROLS ON SERPENTINITE DISTRIBUTION IN THE GREAT SERPENTINE BELT OF AUSTRALIA

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The Great Serpentine Belt (GSB), a dismembered sequence of variably serpentinized peridotite bodies along the Peel Fault System (PFS) in New South Wales, Australia, provided some of the initial insights for the kernel pattern model for serpentinization (O'Hanley, 1992). However, our recent work on the GSB suggests that kernel pattern serpentinization is not pervasive on a regional scale and other factors need to be considered.

Kernel pattern serpentinization describes the reaction-driven generation of orthogonal fracture sets by volume expansion as harzburgite is converted to serpentine. A study of 2-dimensional fracture patterns with an orthopyroxenite dyke suggests the fracture networks result from hierarchical fracturing (Iyer et al., 2008), reflecting a fractal distribution. In this model, an initial fracture set defines polygonal domains with subsequent fractures within the domains emanating as a set of smaller arrays aligned perpendicular to the polygonal boundaries. The two concepts can be integrated, with kernel pattern serpentinization resulting by fluid ingress and reaction-front development along the evolving hierarchical fracture sets. The larger the fracture set, the greater the fluid ingress, the greater the degree of kernel pattern serpentinization. However, the fractal distribution is not well preserved at regional scale due to late strike-slip shearing.

A regional fracture study of the GSB has found kernel pattern serpentinization is preferentially preserved within regions of low shear strain commonly at the junction between major PFS parallel shear zones and subordinate oblique splays. The main shear zones are aligned NNW and splays are aligned NE. Serpentinization in the major (km-thick) shear zones is generally complete, and kernel pattern development has been destroyed by ongoing dynamic recrystallization along the PFS. Only relict cm-scale, lensoid phacoids remain in a matrix of sheared serpentine, but the initial fracture sets are still preserved as rare picrolite veins aligned perpendicular to phacoid boundaries. Superimposition of late strike-slip shearing along the PFS shows that serpentinization was also controlled by large-scale tectonic processes.

Iyer, K, B Jamtveit, J Mathiesen, A Malthe-Sørensen, and J Feder. 2008. Reaction-assisted hierarchical fracturing during serpentinization. *Earth and Planetary Science Letters* 267 (3):503-516.

O'Hanley, D.S. 1992. Solution to the volume problem in serpentinization. *Geology* 20 (8):705-708.

**DECIPHERING THE PARAMETERS AFFECTING SERPENTINIZATION REACTIONS:  
FIELD AND EXPERIMENTAL APPROACHES**

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**Tectonics, kinetics, thermochemical conditions**

The hydrothermal alteration of ultramafic rocks is a widespread process described in many geological settings, wherever warm aqueous fluids react with mantle-forming minerals (olivine, pyroxenes) to precipitate Mg-phylosilicates (serpentine, brucite, talc). It presents several fundamental and societal implications: it alters the physical, mechanical and chemical properties of ultramafic rocks, and it is accompanied by a redox reaction producing hydrogen that, in the presence of CO<sub>2</sub>, controls the balance between CO<sub>2</sub>-mineralisation and abiotic CO<sub>2</sub>-reduction. The P-T range under which this serpentinization reaction can occur on Earth varies from deep subduction zones to shallow lithospheric environments as in present-day hydrothermal systems on land and at mid-ocean ridges. To better evaluate the impact of serpentinization under those highly variable contexts it is determinant to identify which parameter(s) can affect the serpentinization reaction, in particular its kinetics, and the nature of the products, including its capacity to generate hydrogen – a mandatory for associated redox reaction possibly involved in life appearance and development. Experimental data provide some clues on the effect of pressure and temperature, even if they are sometimes controversial and do not cover yet the required P-T field. But natural observations of slow-spreading ridge systems underlines the strong heterogeneity of chemical reactions even at the  $\mu\text{m}$ -scale, suggesting that in addition to the effect of the wide P-T range, several other parameters such as water and element transport, and composition of the serpentinizing fluid, can considerably affect serpentinization and associated reactions. They can vary with the local tectonics and thermal regime of the lithosphere. The effect of these parameters and their possible implications in natural systems will be discussed in light of available literature and recent experimental studies that tested the effect of fluid composition on serpentinization kinetics.



## MECHANOCHEMICAL FEEDBACKS DURING HYDRATION OF ULTRAMAFIC ROCKS

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### Serpentinisation, tectonics, fluids

Controlled by fluid-induced reactions, retrograde metamorphism processes are dependent on the fluid supply to the rock. Ultramafic rocks have very low permeability and will stay under a metastable state under pressure and temperature changes in the field of retrograde metamorphism, unless a reactive fluid get into the rock (Jamtveit et al., 2016). Fluids can penetrate through fractures which opened because of tectonics or volume changes induced by metamorphic reactions (Iyer et al., 2008; O'Hanley, 1992). Fracturation process is a way of initiating and maintaining the metamorphism process (Plumper et al., 2012) as fluid penetration enables reactions, creates more fractures and a deeper fluids penetration.

The serpentinisation is the process of peridotite hydration. It is mainly affecting the oceanic lithosphere as it combines presence of water and a thin crust (meaning that peridotite is closer from the surface). Ridge axis is a privilege area for serpentinisation (Iyer et al., 2010) as subject to intense fracturation due to tectonics (Kong et al., 1992; Rouméjon and Cannat, 2014), creating pathway for sea water through the crust, and even inducing mantle exhumation at slow ridges (Karson et al., 1987; Tucholke, 1998). Water circulation is often accompanied by hydrothermalism as convection cells are formed, this process is also creating fracturation and potentially seismicity due to serpentinisation, heat transport and water progression (Cannat et al., 2010; Guillot et al., 2015). Serpentinisation is also taking place in subduction zone were the crust is again fractured by bending of the plunging plaque (Iyer et al., 2012; Ranero et al., 2003).

The amount of water in the mantle is crucial because serpentinisation is inducing strong changes in the mantle rheology like weakening it and decreasing its density. These changes have big consequences on the processes occurring at plaques boundaries and more generally on the mantle behavior, but also on volatiles global cycles.

The goal of this project is to understand how tectonic stress affects the rate and progress of serpentinisation. It is aiming at combining seismic studies with petrological and chemical approach. Samples from Feragen ophiolite in Norway, which is a "fossilized" serpentinized system, and from the ICDP Oman Drilling Project (<http://www.omandrilling.ac.uk/>) will be studied. Samples from Oman will provide insight in a system under on-going serpentinisation and carbonation. It will also be possible to measure in-situ different parameters which are not accessible on a "fossilized" system like stresses, fluid pressure and composition, temperature, etc. The collaboration with seismologists will also give the possibility to distinguish tectonics and reaction driven events.

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## PHYSICAL PROPERTIES OF OCEANIC LOWER CRUSTAL AND UPPERMOST MANTLE ROCKS FROM ATLANTIS MASSIF, MID-ATLANTIC RIDGE

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### Serpentinite, gabbro, physical properties

The degree of serpentinization depends on the access of water to fresh peridotite and the time for the reaction to develop. In a wide range of geological settings beneath the oceans, serpentinite co-exists with gabbro. When the serpentinization is incomplete the physical properties of both types of rock, for example density and seismic velocity (compressional,  $V_p$ , or shear,  $V_s$ ) are very similar. Hence, distinguishing them by remote geophysical methods such as gravity or seismic surveys is challenging and commonly requires in situ observations from direct sampling.

We have measured and analyzed the physical properties of four new serpentinite samples from the southern wall of the Atlantis Massif, acquired during IODP Expedition 357, and compared them with the properties of gabbro samples acquired previously at the Central Dome of the Atlantis Massif (IODP expedition 304-305). The physical property measurements include ultrasonic P- and S-wave velocities and their attenuation, electrical resistivity and the permeability over a wide range of effective pressures. From these measurements, we calculate the elastic constants of the rocks (i.e.,  $V_p/V_s$ , Poisson's ratio, Young's modulus, bulk modulus, and shear modulus). Furthermore, we calculate the full 9-component electric resistivity anisotropy tensor from the measurements, and we compare the anisotropy of serpentinite and gabbro samples. Because the electrical resistivity has one of the widest ranges of values of any common physical property of solids, its anisotropic variation is more easily detectable than that of seismic velocities. Any significant difference of electrical resistivity or its anisotropy between partially serpentinized peridotite and gabbro might enable us in future to distinguish remotely between these rock types by electromagnetic techniques. We also compare the measurements of permeability with the electric resistivity anisotropy and thereby explore the possibility to use electrical resistivity anisotropy as a proxy for permeability anisotropy. The estimation of permeability using electric resistivity may thus provide a tool that contributes towards the estimation of the hydrocarbon flow rates.



## MG ISOTOPES AS TRACERS OF REACTION PATHWAYS DURING SERPENTINIZATION: AN EXPERIMENTAL APPROACH

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### Mg isotopes, Serpentinization, Reactive percolation experiments.

Magnesium is a major element in the oceans, and one of Earth's most abundant rock-forming elements, particularly in mantle rocks which contain >99% of the Mg inventory of our planet. Magnesium is fluid mobile and has three naturally occurring stable isotopes, <sup>24</sup>Mg, <sup>25</sup>Mg and <sup>26</sup>Mg, with relative abundances of 78.99, 10.00 and 11.01% respectively. The relative mass difference between <sup>26</sup>Mg and <sup>24</sup>Mg is > 8%, among the largest of the non-traditional stable isotope systems and low temperature geological processes can produce large mass dependent isotopic fractionations.  $\delta^{26}\text{Mg}$  values show a variation of > 7‰ at Earth surface conditions, from carbonates with  $\delta^{26}\text{Mg} \approx -5\text{‰}$  to secondary silicate minerals with  $\delta^{26}\text{Mg} \approx +2\text{‰}$ . Consequently, Mg isotopes have the potential to be excellent tracers of geological processes that occur at the Earth's surface.

Serpentinization is one of the major processes affecting the ultramafic lithosphere exposed to reaction with seawater at slow spreading mid-ocean ridges. These hydration reactions play major roles in modifying the rheological, physical and geochemical properties of the oceanic lithosphere before its recycling at subduction zones. Hydration of mantle peridotites is a major mechanism of mass exchange between the mantle and the Earth's surface, with important consequences for mantle dynamics and global geochemical cycling. Serpentinization involves a number of interdependent dissolution-precipitation and reduction-oxidation reactions. However, we presently have only limited knowledge on reaction pathways and the kinetics of serpentinization reactions. Because Mg-rich secondary minerals (e.g. serpentine, brucite) precipitate during serpentinization, Mg isotopes could be a useful tool to decipher these fluid-rock interactions.

We are conducting a suite of reactive percolation experiments using artificial seawater labeled with Mg isotopes injected into mantle rock analogs at temperatures (190°C) and pressures (25 MPa) appropriate for mid-ocean ridges. These experiments are being run on the ICARE3 flow through reactor by injecting the fluid at a controlled flow rate into pressed olivine (Fo<sub>91</sub>) powders with an initial grain size ranging from 100 to 150 μm. Changes in fluid chemistry and isotopic signature are being monitored by collecting reacted water samples at regular intervals. The primary and secondary mineral composition of the reacted powder will be investigated at the end of each experiment through isotopic analysis, X-ray diffraction, thermogravimetry and electron microscope inspection.

This new study will allow us to utilize Mg isotope tracers to better understand the dissolution-precipitation reaction paths of the serpentinization process. This new information will be used to develop improved reactive tracer transport models for hydrothermal cooling of the lower oceanic crust and reactions in the upper mantle.

## THE DNA DOUBLE HELIX X-RAY IMAGING, A TRIBUTE TO ROSALIND FRANKLIN

Boudier, F.<sup>1</sup>

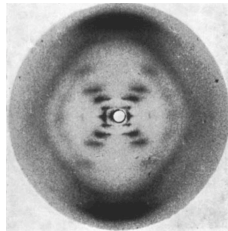
Géosciences Montpellier, CNRS & Univ. Montpellier, 34095 Montpellier, France

In 1962, Watson, Crick and Wilkins received the Nobel price for the discovery of the structure of DNA. Notably absent was Rosalind Franklin whose X-ray photographs of DNA contributed directly to the discovery of the double helix.

Rosalind Franklin born 1920 in a British Jewish family in London, graduated in Physics-Chemistry at Cambridge. After her PhD obtained at Cambridge University in 1947, she joins CNRS in Paris where she is instructed in X-ray diffraction in the lab of Jacques Méring during three years. Back in UK, in 1950, Rosalind joined the King's College in London, and was invited to work on application of X-ray technics to structure of DNA. At the end of these three years of intense involvement, she will get the famous photographs of helical double fiber structure B form of DNA. These results were published in Nature, april 1953, in a series of five articles including the celebrated double helix DNA model of Watson and Crick, inspired from diffraction images of Franklin and Gosling. James Watson and Francis Crick, biochemists at Cavendish Laboratory had knowledge of the X-ray images through Maurice Wilkins, Franklin's collaborator at King's College. Conversely, Rosalind Franklin's article contains an analytical review of Watson and Crick's model.

In march 1953, Franklin relocated to Birkbeck College where she studied the structure of tobacco mosaic and the structure of RNA.

In 1962, Watson, Crick and Wilkins received the Nobel Price in Medical Science. By then Franklin died in 1958, at the age of 37, from cancer probably related to unprotected exposition to X-ray. The fact that her name was not associated at Nobel Honour is still questioned.



Franklin, R. E. & Gosling, R. G. (1953). Molecular Configuration in Sodium Thymonucleate. *Nature* 171, 740-741.

Watson, J. D. & Crick, F. H. C. (1953). Molecular structure of Nucleic Acids : A Structure for Deoxyribose Nucleic Acid. *Nature* 171, 737-738.

## CAN SERPENTINIZATION ANSWER THE QUESTION “IS THERE LIFE ON MARS?” ?

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<sup>2</sup> Laboratoire de Géologie de Lyon – Terre, Planètes, Environnements, ENS Lyon & Université de Lyon, Lyon, France

### Mars, Remote Sensing, Geochemical Modelling

Mars today is cold and dry but morphological and mineralogical evidences show that it could have been wetter and warmer in the past (i.e. Carr and Head, 2010; Carter et al, 2015).

It has long been admitted that atmospheric escape processes would be responsible for the diminution of global liquid water budget of the planet (Lammer et al, 2013 and references therein). However it fails to completely explain the massive loss of volatile elements (Lammer et al, 2013), the storage of those elements in the crust is so a reasonable possibility.

Serpentinization has already been suggested but quantification was missing (Quesnel et al, 2009) and serpentine detections have been reported on Mars (i.e. Ehlmann et al, 2008 and Bultel et al, 2015).

Here we present a combination of remote sensing study with CRISM data and geochemical modelling with EQ3/6 to better evaluate the contribution of serpentinization to the storage process of water in the Martian crust.

We conduct a systematic analysis of Noachian crustal outcrops imaged by CRISM. We report around thirty different detection of serpentine or possible serpentine in Noachian terrains. The serpentine is never the main hydrated mineral present in the outcrops. It is often associated with talc, Fe/Mg-smectites, chlorites and carbonates. Our detections are geographically linked to high faulted region of impact craters which could imply subsurface processes to form the serpentine.

We conducted geochemical models with EQ3/6 to reproduce the mineralogical assemblages. Our conclusion is that the serpentinization should have occurs at low temperatures (<200°C) in a fluid dominated system with a basaltic rock with a high amount of olivine (30%).

We predict that a relatively small amount of dihydrogen (around  $10^{-8}$  mmol) would be formed during the serpentinization of the Martian crust and that the environments favor the formation of methane in also a relatively small amount (around  $10^{-3}$  mmol). It is unlikely that those amounts will play a role in the evolution of the composition of the atmosphere as suggested in Sanders et al., (2016). We suggest being more than careful concerning the astrobiological potential of the serpentinization of the Martian crust because of the low efficiency of the iron oxidation at low temperature.

Since the geochemical modelling does not take into account some mineralogical phase ( $\text{Fe}^{3+}$ -phyllosilicates) or kinetic parameters, we suggest an experimental work on low temperature serpentinization of olivine alone, pyroxene alone and olivine-rich basaltic rock. A first attempt of this work is currently in progress with olivine reacting in a close system at 120°C in a fluid dominated system. The result of this experiment should lead to a better understanding of the significance of serpentinization for life emergence.

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## LINKING BETWEEN TEXTURAL AND GEOCHEMICAL SIGNATURES OF OPHICARBONATES FROM OCEAN TO DEEP SUBDUCTION

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### Ophicarbonates, C isotopes, C cycle

Understanding how oceanic lithosphere is affected by chemical and physical processes in the subduction environment is key to elucidating the cycling of elements on Earth. In particular, the deep carbon (C) cycle and C mobility in the subduction environment are topics of recent debate in the scientific community.

Here, we present textural and geochemical data for ophicarbonate rocks (i.e., carbonate-bearing serpentinites) re-equilibrated at differing P-T conditions as representing a prograde subduction history. In order of increasing peak P-T conditions, we focus on the N. Apennines (Italy) ophicarbonates (not subducted), sub-blueschist and blueschist-facies ophicarbonates from the Voltri Massif (bVM) and the Queyras (Q), respectively (W. Alps), and eclogite-facies ophicarbonates from the Voltri Massif (eVM).

The oceanic ophicarbonates display breccia-like textures linked to hydrothermal and sedimentary origin. Their carbonate geochemical signatures for  $\delta^{18}\text{O}$  and  $\delta^{13}\text{C}$  are +15.6 to +18.2‰ and +1.1 to +2.5‰, respectively, and their  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7058 to 0.7068) appears to reflect equilibration with seawater during Jurassic time. Intense shear deformation characterizes the ophicarbonate rocks from bVM and Q, where strong calcite recrystallization occurred, potentially by dissolution and reprecipitation. The isotopic compositions of the bVM overlap those of the oceanic ophicarbonates, whereas the most deformed samples from the Q show enrichment in radiogenic Sr (0.7075), depletion in  $\delta^{13}\text{C}$  (to as low as -2.0‰), with  $\delta^{18}\text{O}$  approaching +20‰ (Collins et al., 2015). These textural and geochemical features suggest that the bVM and deformed Q rocks experienced interaction with fluids in closed and open system, respectively. High-pressure-metamorphosed eVM ophicarbonates show strong shear textures, with coexisting antigorite and dolomite and, in some cases, relict nodules of magnesite enclosed in the foliation are still recognizable. Dolomite-bearing rocks have  $\delta^{13}\text{C}$  of +0.4 to 1.0‰ and  $\delta^{18}\text{O}$  of +11.6 to +12.1‰ and the magnesite-bearing samples have comparable isotopic signatures. The Sr isotopic ratios for these rocks are 0.7080 and 0.7097, respectively. These data seemingly reflect interaction with externally-derived, hot metamorphic fluids with radiogenic Sr component and high O:C ratios.

We suggest that the infiltration of fluids during early stages of subduction can trigger the dissolution of the carbonate minerals, thus allowing mobilization of C. The ability of these new carbonates to record the composition of the fluids, allow us to determinate their origin (i.e., closed vs. open system). The dissolution/precipitation process can be monitored and tracked by C-O and radiogenic Sr isotopes and may have important implications in our understanding of the subduction factory processes and to better evaluate the global and deep C cycle.

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**AQUEOUS GEOCHEMICAL DYNAMICS AT THE COAST RANGE OPHIOLITE MICROBIAL OBSERVATORY (CROMO)**

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**Keywords: Serpentinization, water-rock reactions, Coast Range Ophiolite Microbial Observatory (CROMO)**

Serpentinization is a water-rock reaction that drives the evolution of micro- to mega-scale habitability in ultramafic rocks, through the aqueous alteration of primary minerals in parent rocks, and concurrent production of H<sub>2</sub>, CH<sub>4</sub>, and (possibly) biologically useful organic compounds. This process pervades extensive areas of silicate planetary bodies, in geologic settings as diverse as cratered fracture zones and fault systems in ultramafic rocks, hydrothermal flow systems operating near crust/mantle interfaces, and deep subsurface groundwater flow systems. Serpentinization causes transformations in mineralogy, rock geochemistry, and co-occurring associated water chemistry, including redox-sensitive dissolved species, which together control the feasibilities of prominent microbial metabolisms. At CROMO, a NASA Astrobiology Institute-funded initiative, the existing groundwater well array allows monitoring of shallow, open-system groundwaters and deeply sourced, closed-system groundwaters in one geographic locale. In this report on the increasingly resolved geochemical patterns at CROMO, documented shifts in pH, conductivity, oxidation-reduction potential (ORP), dissolved oxygen (DO), and major ion geochemistry are discussed and contrasted with other terrestrial sites of serpentinization (marine and continent-hosted). The particular utility of CROMO wells as means of responding to pertinent hypotheses in geomicrobiology (e.g., how serpentinization-linked geochemical parameters influence habitability, how surface and subsurface mineral assemblages relate) in terrestrial and extraterrestrial settings is also considered.



**EARLY MARS SERPENTINIZATION-DERIVED CH<sub>4</sub> RESERVOIRS, H<sub>2</sub> INDUCED WARMING  
AND PALEOPRESSURE EVOLUTION**

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**Martian atmosphere, Martian crust, Martian dynamo, Martian water**

CH<sub>4</sub> has been observed on Mars both by remote sensing and in situ during the past 15 years. It could have been produced by early Mars serpentinization processes that could also explain the observed Martian remanent magnetic field. Assuming a cold early Mars, a cryosphere could trap such CH<sub>4</sub> as clathrates in stable form at depth. The maximum storage capacity of such a clathrate cryosphere has been recently estimated to be  $2 \cdot 10^{19}$  to  $2 \cdot 10^{20}$  moles of methane. We suggest that large amounts of serpentinization-derived CH<sub>4</sub> stored in the cryosphere have been released to the atmosphere at the end of the Noachian and the beginning of the Hesperian. Due to rapid clathrate dissociation and photochemical conversion of CH<sub>4</sub> to H<sub>2</sub>, these episodes of massive CH<sub>4</sub> release may have resulted in transient H<sub>2</sub>-rich atmospheres, at typical levels of 10-20% in a background 1-2 bar CO<sub>2</sub> atmosphere. The collision-induced heating effect of H<sub>2</sub> present in such an atmosphere has been shown to raise the surface temperature above the water freezing point (Ramirez et al., 2014, *Nature Geosciences* 7, 59-63). We propose that the early Mars cryosphere had a sufficient CH<sub>4</sub> storage capacity to have maintained H<sub>2</sub>-rich transient atmospheres during a total time period up to several Myr or tens Myr, having potentially contributed to the formation of valley networks during the late Noachian and early Hesperian.



## SQUEEZING THE SPONGE: THE BEHAVIOUR OF FLUID MOBILE ELEMENTS AND BORON ISOTOPES DURING SERPENTINITE DEHYDRATION

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### Key words: Boron, Subduction, Dehydration

Subduction zones are the main drivers of global volatile recycling through the supply of water to the mantle wedge which triggers arc volcanism. Serpentinites may contribute greatly to this process due to their high water content and widespread presence in oceanic lithosphere (Ulmer and Trommsdorff, 1999). Serpentinites also hold large amounts of fluid mobile elements (including B and Li) which are expelled during subduction dehydration and thus can be used to trace the presence of serpentinite-derived fluids in arc magma sources (Scambelluri and Tonarini, 2012). Boron isotopes, in particular, are a powerful tracer of serpentinites due to their distinct signature ( $\delta^{11}\text{B} = +5$  to  $+40\%$ ) (Vils et al, 2009) and the signature of their expelled fluids ( $\delta^{11}\text{B}$  up to  $+15\%$ ) (Benton et al, 2001), whereas the mantle has a low  $\delta^{11}\text{B}$  ( $\sim -10\%$ ) (Chaussidon and Marty, 1995). However despite its fluid mobile nature, B-rich metamorphic olivine has been found in dehydrated serpentinites in the field (De Hoog et al, 2014; Scambelluri et al, 2004) as well as in experiments (Tenthorey and Hermann, 2004). This retention of B in olivine potentially fractionates B isotopes during serpentinite dehydration, but details of this process remain largely unconstrained. The aim of this study is to analyse the B and  $\delta^{11}\text{B}$  distribution between phases (olivine, serpentine, chlorite) in dehydrated serpentinites from different metamorphic grades which will allow the tracking of B behaviour throughout the subduction cycle. Current samples are sourced from Alpine ophiolites, the Cerro del Almirez ultramafic massif and the Mid-Atlantic ridge.

Preliminary results show that B distribution is highly variable between both different phases and different localities. Boron-rich olivine (7.1-37.1 ppm) is reported in samples from Monviso, Almirez, Voltri and Zermatt.  $\delta^{11}\text{B}$  values of olivine and serpentine in these samples are variable; serpentine > olivine in Monviso ( $\sim +21.0\%$  vs  $+11.0\%$ ) and Almirez, serpentine < olivine in Zermatt ( $\sim +12.0\%$  vs  $+18.0\%$ ) and similar  $\delta^{11}\text{B}$  values of both phases in Voltri ( $\sim +20\%$ ). Furthermore, B and  $\delta^{11}\text{B}$  values differ between mesh textured serpentine and bastite; samples from Chenaillet show similar B concentrations with bastites preserving lower  $\delta^{11}\text{B}$  values, whereas Monte Maggoire serpentine show similar  $\delta^{11}\text{B}$  values with bastites preserving higher B concentrations. Understanding the variations between bastite and mesh textured serpentine may be key to understanding the variable relationship between  $\delta^{11}\text{B}$  in B-rich olivine and serpentine. Therefore, this study demonstrates the importance of combining microtextural information with geochemical data in understanding boron behavior in serpentinites, potentially allowing attribution to different fluid processes or conditions during subduction or provide other reasons for B variability.

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## LOCAL STRESS FIELD DURING SERPENTINE DEHYDRATION INFERRED FROM ORTHOPYROXENE INVERSION TO CLINOENSTATITE

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**Keywords:** clinoenstatite, dehydration reactions, local stress

The release of fluid during dehydration reactions has important consequences for the subduction dynamics, since fluids might affect the rheology of the mantle wedge and the subduction interface. Additionally fluids control large scale chemical recycling through arc magmatism. How dehydration reactions and fluid transport proceed at the microscopic scale is however poorly constrained. Under poorly drained conditions, fluid pressure gradients are produced during dehydration creating small-scale variations in the stress magnitude and orientation. These local stress variations might be recorded in minerals such as orthopyroxene where shear stresses on (100) planes parallel to the [100] direction result in the inversion to low clinoenstatite (*i.e.* martensitic transformation). Experiments show that maximum critical resolved shear stress is reached by applying axial compression at 45° to the a- and c- axes (Coe & Kirby, 1975). Occurrence of clinoenstatite has been reported in natural peridotites (Frost, 1978; Padrón-Navarta et al., 2015) and Padrón-Navarta et al. (2015) showed that clinoenstatite might be produced by flexural deformation of elongated enstatite crystals.

We have studied calcium-free low temperature clinoenstatite (LCen,  $P2_1/c$ ) lamellae in orthoenstatite (Oen, Pbcn) in peridotites produced by dehydration of serpentinites from Cerro del Almirez (Spain) (Padrón-Navarta et al, 2015) to determine stress orientations. Optical microscopy and EBSD analyses were used to determine the orientations of both the host orthoenstatite and the clinoenstatite lamellae. LCen lamellae are observed in almost all OEn crystals oriented with the  $\langle b \rangle$  axis roughly normal to the thin section. For each Oen-LCen pair, we infer the orientation of the main principal compressional stress with Mtex code. We have also calculated orientations from OEN grains with LCen lamellae that were not detected by EBSD. The orientation of the compressional stress at the sample scale is highly variable and consistent between measured and calculated data. Based on these observations we conclude that dehydration reactions and the associated compaction generate local stresses with variable orientation and magnitudes sufficient to produce the inversion of orthoenstatite to clinoenstatite by a martensitic transformation.

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**UNRAVELING ALTERATION HISTORIES IN SERPENTINITES AND ASSOCIATED ULTRAMAFIC ROCKS FROM SYROS, GREECE WITH MAGNETITE (U-TH)/HE GEOCHRONOLOGY**

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**geochronology, magnetite, trace elements**

Serpentinization is a widespread process that impacts large-scale geodynamic processes along plate boundaries including continental breakup, seafloor spreading and subduction. The timing of serpentinization is critical for our understanding of these processes, but direct dating of serpentinites has been challenging or impossible due to the lack of minerals with well-established dating techniques. This study presents a novel (U-Th)/He methodology using magnetite to constrain the timing of both the cooling of exhumed ultramafic rocks and the low-temperature fluid alteration of serpentinites. In order to prove the viability of magnetite He dating in these settings, magnetite ages were obtained from two ultramafic lithologies of the Kamos mélange belt, a high-pressure low-temperature (HPLT) subduction complex on the island of Syros, Greece. Magnetite (U-Th)/He measurements of internal fragments from large grains within a chlorite schist and a serpentinite record Mid-Miocene exhumation-related cooling ages, whereas smaller grains from the serpentinite record mineral formation associated with Pliocene normal faulting. These age data, combined with magnetite trace elements, reveal evidence for multiple episodes of fluid-rock alteration, which has implications for the cooling history and local geochemical exchanges of this HPLT terrane. This method provides a new tool that may be expanded to investigate the processes and timescales of serpentinization from a variety of tectonic settings.

## H<sub>2</sub> PRODUCTION FROM INDUSTRIAL FERROUS WASTES BASED ON A GEO-INSPIRED PROCESS

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### Hydrothermal, dihydrogen, steel slags

Native H<sub>2</sub> produced at slow-spreading centers could be seen as a natural energy resource. In addition to the fact that oceanic H<sub>2</sub> reserves are difficult to estimate, today, the relative low price of H<sub>2</sub> produced at the industrial scale from fossil fuels limits the economic interest for this resource. With potentially lower exploitation costs, H<sub>2</sub> exhalations on-shore appear as more attractive although research is still needed to evaluate the corresponding H<sub>2</sub> reserves and formation processes. The way to consider the energetic relevance of native H<sub>2</sub> might not be to focus on the resource itself but rather on the way the resource is produced geologically. In particular, RedOx reactions involving magnetite (Fe<sub>3</sub>O<sub>4</sub>) crystallization along with H<sub>2</sub> production by water splitting under the hydrothermal conditions prevailing in oceanic environments, can be simulated in the laboratory (e.g., Marcaillou *et al.*, 2011). Can this geo-inspired process be successfully applied to ferrous-rich matter available at the industrial scale? Steel slags which contain around 10-20 wt.% FeO, is a good candidate with a yearly production of 140 to 220 Mt worldwide. Despite the production of secondary aggregates for civil engineering applications, a significant part of steel slags are currently not enhanced and simply stored on site. By using experimental and characterization methods developed to investigate oceanic serpentinization reactions in the laboratory (Malvoisin *et al.*, 2012), we were able to demonstrate the potential of BOF slags to produce above 5 NL H<sub>2</sub> per kg of slag at 523 K in 3 days (Malvoisin *et al.*, 2013). The next step is now to optimize the H<sub>2</sub> production process in terms of kinetics and yield. Ferrous iron being mostly hosted by wüstite (Fe,Mg)O in steel slags, we investigated by *in situ* solution and gas sampling, the hydrothermal oxidation of reagent grade FeO used as model compound for wüstite in steel slags. The initial aqueous medium was either composed of pure water or a mild acidic solution. Whereas, after 65 h, H<sub>2</sub> yield is negligible in pure water at 423 K, the reaction,  $3 \text{FeO}_{(s)} + \text{H}_2\text{O}_{(g)} \rightleftharpoons \text{Fe}_3\text{O}_{4(s)} + \text{H}_{2(aq)}$ , reached near completion at the same temperature within 10 h in a solution containing 0.05 mol/l acetic acid. Increasing acetic acid concentration by one order of magnitude did not yield significantly more H<sub>2</sub>. Acidic conditions increased FeO dissolution kinetics and, consequently, improved H<sub>2</sub> yield. The specific efficiency of acetic acid resides in its thermal stability as well as in its potential of ligand-promoted Fe(II) dissolution. We show that the presence of large amounts of CaO in steel slags will counteract the positive kinetics effect of mild acetic acid solutions by shifting the pH towards basic values. Two options are under study to overcome this pH issue, (1) the prior de-calcification of the slag (Eloneva *et al.*, 2008) and (2) the incorporation of carbonic acid through CO<sub>2</sub> injection in the hydrothermal reactor to both lower the pH and sequester CO<sub>2</sub>.

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## ADSORPTION OF NUCLEOTIDES ONTO SERPENTINE AND PHYLLOSILICATES: SIGNIFICANCE FOR THE ORIGIN OF LIFE

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### adsorption, nucleotides, origin of Life

The concentration of prebiotic organic building blocks may have promoted the formation of biopolymers in the environment of the early Earth. We therefore studied the adsorption of RNA and DNA monomers on minerals that were abundant in the early Earth environment as the result of aqueous or hydrothermal alteration of the primitive seafloor.

We focused our study on iron- and magnesium-rich swelling clays (nontronite, montmorillonite) and non-swelling phyllosilicates (chlorite, lizardite, chrysotile); pyrophyllite served as a Mg-Fe free reference mineral. Adsorption experiments were carried out under standard conditions of pressure and temperature and controlled pH. Under such conditions, this work is also relevant to the preservation of nucleic acids in Fe-Mg-rich terrestrial and Martian soils. We compared the adsorption of the different monomers on individual minerals, as well as the adsorption of single monomers on the whole suite of minerals. We found that DNA monomers adsorb much more strongly than RNA monomers, and that any monomer containing the G nucleobase adsorbed more strongly than one containing the C nucleobase. At high surface loadings (greater than about 1 mM monomer in aqueous solution) we also found a dramatic increase in the slope of adsorption isotherm on the swelling clays, leading to large increases in the amounts adsorbed. Data were processed in order to understand the adsorption mechanism of nucleotides onto mineral surfaces.

We infer that all nucleotides behave as homologous molecules in regard to their adsorption onto the studied mineral surfaces. At low to moderate surface loadings, their adsorption is best explained by a single mechanism common to the suite of minerals of the present study. At pH 7, adsorption certainly proceeds by ligand exchange between the phosphate group and the hydroxyls of the broken edges of phyllosilicates leading to the saturation of lateral surfaces. Below pH 4, swelling clays also adsorb nucleotides through cation exchange on basal surfaces, whereas non-swelling phyllosilicates do not. However, at high surface loadings an additional mechanism stabilizing adsorption occurs.

Given the proposed adsorption mechanisms, the possibility of a favorable polymerization at the mineral-water interface is discussed. We propose that Fe-Mg rich phyllosilicates tightly bind nucleotides, under ambient conditions, and concentrate them up to 1000 times the solution concentration upon saturation. The concentration effect may be enhanced by hydrothermal conditions over a range of (P,T) conditions that are currently under refinement.

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**SHARP OXIDATION GRADIENTS AND ALTERATION OF MANTLE PERIDOTITE:  
 INSIGHTS FROM WADI FINS, OMAN**

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**Oxygen fugacity, Sulfides, Geochemical modeling**

Sulfide and oxide mineralogy of altered mantle peridotite in Wadi Fins in eastern Oman record sharp oxygen fugacities ( $fO_2$ ) changes in scales of 10–15 cm. Hand samples show four evident compositional changes in the rocks and were classified based in their color: black cores, green alteration zone, red alteration zone and white carbonate. The black cores (5 cm in diameter) are characterized by primary mantle minerals (olivine, orthopyroxene and spinel) and exhibit low degrees of serpentinization (20–30%). Bulk rock major element composition of the cores is similar to Oman harzburgite from Wadi Tayin (Hanghøj et al. 2010). Secondary sulfide assemblages (pentlandite-heazlewoodite and chalcocite-bornite) characteristic of early stages of serpentinization at low  $fO_2$  and  $fS_2$  occur along serpentine/brucite veins in the cores of this rocks. Green and red alteration zones show signs of pervasive alteration of the original rock. The mineralogy of this alteration zones is dominated by poorly crystalline serpentine and talc/saponite-like hydrated minerals with composition similar to a “deweylite” assemblage (Beinlich et al. 2010; Bish & Brindley, 1978). Both alteration zones exhibit 20–30% MgO depletion compared to the black cores. The green zones show also a similar ~25% FeO depletion. This FeO depletion in the green zones is complemented with ~50% enrichment in the red zones. We interpret this depletion and enrichments as mobilization of ferrous iron short distances from inner green zones into oxidized outer red zones where iron is reprecipitated as goethite along grain boundaries with increased  $fO_2$  with MgO removal from the rocks. The green and red alteration zones sulfide and oxide mineralogy shows this progressively higher  $fO_2$  away from the cores with Ni-rich sulfides (green zone) and iron hydroxides (red zone) (Frost, 1985; Klein & Bach, 2009; Schwarzenbach et al., 2012). The white carbonate is mainly calcite likely derived from the limestones overlaying the peridotites. Clumped isotope thermometry of carbonate veins in the area record alteration temperatures between 30–60°C. We used EQ3/6 (Wolery & Jarek, 2003) for reaction path modeling of a rock with composition of average Oman harzburgite with seawater at 60°C. Model results show changes in mineralogy and fluid composition with increasing water/rock (w/r). Low w/r are characterized by serpentine, brucite and magnetite as secondary minerals with Mg, Fe and Si in the fluid remaining constant. Increasing w/r results in increasing  $fO_2$ , a shift of the main iron mineral from magnetite to goethite and a decrease of iron concentration in the fluid. Mg concentration in the fluid increases with w/r this increase is complemented with a secondary mineralogy richer in SiO<sub>2</sub> (talc and chlorite). All this is consistent with magnesium and iron mobility inferred from rock composition and supports the idea of FeO mobility over a short distance and MgO removal from the rocks.

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## ASSESSING SULFUR REDOX STATE AND DISTRIBUTION IN ABYSSAL SERPENTINITES USING X-RAY ABSORPTION SPECTROSCOPY

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### Sulfur Redox State, Abyssal serpentinite, X-ray absorption spectroscopy

At mid-oceanic ridges, the serpentinisation is recognized as a sink of sulfur under various oxidation states ( $S^{2-}$ ,  $S^-$ ,  $S^0$  and  $S^{6+}$ ). This element sequestration is usually attributed to secondary minerals crystallization, such as sulfides (e.g. pyrite, pyrrhotite) or sulfates (e.g. anhydrite); however, little is known about sulfur distribution in abyssal serpentinites especially about the role of serpentine minerals as a potential carrier of sulfur. We investigate for the first time the distribution and redox state of sulfur at micro-scale combining in situ geochemical (SIMS) and spectroscopic (X-ray absorption near edge structure: XANES) measurements. We present data acquired in natural samples from three different locations: the SWIR (South West Indian Ridge), the Rainbow and the MARK (Mid-Atlantic Ridge, Kane Fracture Zone) areas. Serpentinites from these settings are expected to be formed in different conditions (e.g. temperature of serpentinization, pH of the serpentinizing fluid etc.) and thus to provide a meaningful database to understand the fate of sulfur during seafloor serpentinization. XANES spectra of serpentinite powders show that the sulfur budget of the studied samples is dominated by sulfate bearing phases ( $S^{6+}/\sum S = 0.6-1$ ). However, sulfate micro-phases, such as barite and anhydrite, are absent. X-ray fluorescence mapping reveal large area of  $400 \times 400 \mu m$  with homogeneous S concentrations which is consistent with a structural incorporation of S in serpentine minerals. Indeed, XANES analyses of mesh, bastite and antigorite veins in thin sections and of serpentine separated grains show the presence of sulfate ions structurally incorporated into the cavities of serpentine minerals. Mesh and bastite textures could display variable S concentrations, ranging from 140 to 1350 ppm while antigorite veins only incorporate a little amount of sulfur ( $< 60$  ppm). In sulfide free samples, a positive correlation between F or Cl and S is also observed which is consistent with the absence of sulfate accessory phases at micro- or nano-scale, as these phases are F or Cl free.

## MULTIPLE SULFUR ISOTOPE COMPOSITIONS OF ABYSSAL SERPENTINITES: INSIGHTS INTO SERPENTINIZATION PROCESSES

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### Multi-sulfur isotope compositions, redox conditions, serpentinization processes

Sulfur (S) is one of the most important elements on Earth, being present in all major reservoirs. Its speciation depends on the conditions prevailing in the reservoirs and its isotopic composition reflects the chemical reactions (biotic and/or abiotic) occurring within the reservoir or between two, or more, of them. Some reservoirs (mantle and ocean) are characterized by very homogenous S speciation and isotope compositions. In contrast, in the oceanic lithosphere, a number of processes (reduction, oxidation, leaching, ...) can occur during fluid-rock interactions leading to small-scale and local variations in the chemical conditions and consequently to different S oxidation states and species that affect element and isotope fractionation. However, it is sometimes difficult to decipher what process influenced the S isotope compositions of S-bearing phases in the rocks, as different processes may yield to similar isotopic signature. Multiple S-isotope compositions reveal thus to be a powerful tool in determining the different processes involved in S-bearing phases formation.

Serpentinized peridotites from two high-temperature hydrothermal systems, Ashadze and Logatchev, located along the Mid-Atlantic Ridge, have been investigated for their sulfide mineralogy, S content and multiple S-isotope compositions of their S-bearing phases. Sulfide minerals in serpentinites are primarily pentlandite, pyrrhotite, heazlewoodite, millerite and awaruite, suggesting that reducing conditions predominate in the basement of these hydrothermal systems. Nevertheless, chemical extractions on 21 samples indicate that sulfide-S contents are low compare to sulfate-S contents ( $SO_4/S_{tot}$ : 0.57-1). Only  $d^{34}S$  values of extracted sulfates were analyzed and range from 9.3 to 30.9‰ suggesting other processes than direct precipitation of seawater sulfate in the rocks. Multi-S ( $^{33}S$ ,  $^{34}S$ ,  $^{36}S$ ) isotope compositions of sulfates show linear trends with slopes of 0.507 and 1.96, respectively, that differ significantly from the mass-dependent fractionation lines. Correlation between negative  $D^{36}S$  values and positive  $D^{33}S$  values would suggest that oxidation of sulfides to sulfates in an open system would be the predominant process to explain the multiple S-isotope compositions of the sulfates in serpentinites of both hydrothermal systems. In situ multi-S ( $^{33}S$ ,  $^{34}S$ ) isotope compositions of sulfides give  $d^{34}S$  values ranging from -8.1 to 3.6‰ suggesting that reduction, thermochemical or bacterial, and/or oxidation processes affected the S-isotope composition of these sulfides.

## IRON ISOTOPES COMPOSITION OF THE OCEANIC LITHOSPHERE DURING FLUID-ROCK INTERACTIONS

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### Serpentinization, iron isotopes

Fluid-rock interactions at mid-oceanic ridges, due to seawater infiltration, lead to major changes in the chemical composition and redox conditions of seawater (becoming hydrothermal fluids), and mafic (basalts and gabbros) to ultramafic rocks (mantle peridotites) that compose the oceanic lithosphere.

Iron is one of the major elements that are affected by fluid-rock interaction processes. Present in very small amounts in the ocean (ppm), it is a good tracer of the hydrothermal activity (Johnson and Beard, 2006). The iron isotope composition of a system strongly depends on the redox conditions and the type of reactions that affect it, e.g. oxidation fractionates preferentially the heavy Fe isotopes (Johnson et al, 2002). Therefore, understanding the behavior of iron isotopes during alteration of the oceanic lithosphere, and more precisely during serpentinization of mantle peridotites, would be a key in reconstructing the redox conditions during oceanic rocks formation and subsequently the behavior of iron in subduction zone (Debret et al., 2016).

The South West Indian Ridge (SWIR) is one of the slowest ridges on Earth (4mm/yr). Its magmatic activity is nearly inexistent, which allows the study of serpentinization processes without a magmatic influence (Cannat et al., 2008). A selection of 19 samples coming from the SMOOTHSEAFLOOR campaign (2010) was characterized petrographically and geochemically. The petrographic and bulk-rock chemical data indicate that most of these rocks are serpentinized harzburgites, a few are serpentinized dunites. Primary minerals were partially or totally replaced by mesh and bastite serpentine, along with magnetite and clays. Sulfides, mainly present as pentlandite and millerite, hematite, metallic iron, and carbonates complete the secondary mineral assemblages.

Bulk rock iron isotopes compositions reveal that most of the serpentinites belong to the range of abyssal peridotites, as defined by Craddock et al. (2013). However, some of them show a stronger enrichment in <sup>56</sup>Fe, with  $\delta^{56}\text{Fe}$  values up to 0.21‰. Those serpentinite samples underwent the strongest alteration, according to their  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$  ratio. This would be consistent with the study of Rouxel et al. (2003) reporting an enrichment of the oceanic crust in heavy Fe isotopes.

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**SERPENTINE IN ULTRAMAFIC ROCKS FROM THE ISUA SUPRACRUSTAL BELT,  
 A PROXY FOR ARCHAEOAN SEAWATER CHEMISTRY?**

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**Halogens, Noble gases, Archaean seawater, Isua Supracrustal Belt (ISB)**

Ancient alteration minerals formed by reaction between Archaean seawater and the oceanic lithosphere represent a potentially valuable proxy for constraining the composition of Earth's early surface reservoirs. In this context, serpentinites from the Isua Supracrustal Belt (ISB) have been suggested to record the D/H and <sup>16</sup>O/<sup>18</sup>O ratios of Eoarchaeon seawater (~3.7 Ga; Pope et al., 2012) and trapped ancient atmospheric noble gases have been reported in fluid inclusions hosted in hydrothermal quartz from the North Pole locality in the Pilbara Block (~3.5 Ga; Pujol et al, 2013). Recent work has revealed that serpentinites incorporate high concentrations of atmospheric noble gases and halogens (Kendrick et al., 2011). Therefore Isua serpentinites have the potential of recording Eoarchean noble gas signatures, a key parameter for refining early Earth geodynamic models and the origin of the Earth's atmosphere.

To this end, 3.7 Ga serpentinites and associated lithologies were collected from the ISB locality best preserving Archaean seawater oxygen and hydrogen isotope signatures. The samples were irradiated and analyzed for noble gases to enable determination of heavy halogens, K and Ca (extended <sup>40</sup>Ar-<sup>39</sup>Ar methodology; see Kendrick, 2012). It was not possible to obtain age information, however, the measurement of K allows the data to be corrected for in situ production of radiogenic <sup>40</sup>Ar and the initial <sup>40</sup>Ar/<sup>36</sup>Ar and halogen characteristics of the rocks provide information about the alteration fluids.

The results indicate the presence of secondary fluids overprinting the serpentinites. Excess <sup>40</sup>Ar is present in all samples and an Archaean paleoatmospheric component could not be isolated. The <sup>40</sup>Ar/<sup>36</sup>Ar of the serpentinites ranges from ~1700 to 8000, and is higher than the predicted Archaean value of 143±24 (Pujol et al., 2013) and the modern atmospheric ratio of 296. Excess <sup>40</sup>Ar in the metamorphic fluid could have been acquired by fluid interaction with tonalitic gneisses that surround the ISB and could be associated with the ca. 3.6 Ga regional metamorphic event accompanied by intrusions of granites and pegmatites (Nutman et al., 2009). We note a strong Cl depletion which appears to be correlated to the degree of carbonation of the serpentinites, with a talc and magnesite bearing schist having the lowest Cl, Br and I concentrations of respectively 5 ppm, 145 ppb and 18 ppb. The spread in noble gas and halogen concentrations and relative abundance ratios seems to be related to variously overprinting original seawater signatures related to serpentinisation by CO<sub>2</sub> bearing fluids. Heavy mineral separations from the most hydrated and carbonated sample yielded 4 small zircons with a SHRIMP U/Pb mean age of 3699±15 Ma that is likely related to magmatic emplacement rather than later fluids. Additional halogen measurements from Eoarchaeon ISB cherts and carbonates are being used to constrain the origin and significance of the serpentinite compositions.

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**DEHYDRATION OF SERPENTINITE VEINS:  
MICROSTRUCTURES, CPO, AND EMBRITTLEMENT**

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**Deserpentinisation, Embrittlement, EBSD**

Prograde olivine veins that formed by dehydration of serpentinite veins in dunites from the Leka Ophiolite Complex in the Central Norwegian Caledonides exhibit an unusual, brick-like microstructure. The olivine has high forsterite contents and contains abundant magnetite inclusions. The vein centres, surrounding sharp slip surfaces, experienced a grain size reduction caused by dehydration embrittlement. Electron-backscatter diffraction mapping reveals that the vein olivine has the same crystallographic-preferred orientation (CPO) as the olivine in the porphyroclastic host rock; however the misorientations are weaker and less crystallographically controlled.

We propose that prograde olivine grew epitaxially on relics of mantle olivine and thereby inherited its CPO. Growth towards pre-existing microfractures along which serpentinisation had occurred led to straight grain boundaries and the brick-like microstructure in the veins. When dehydration embrittlement induced slip, a strong strain localisation on discrete fault planes prevented a weakening or distortion of the CPO during grain size reduction.

Comparison with other examples of olivine formed by deserpentinisation, which is often fine-grained and may deform by stable rather than unstable sliding, demonstrates that the amount and distribution of serpentine are key factors determining the morphology, crystallographic orientation, and rheology of prograde olivine.



**SERPENTINIZATION ON MARS & IN OMAN:  
NEW INSIGHTS AND NEW TECHNOLOGIES FOR EXPLORATION**

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**Serpentinization, Carbonation, Microimaging Spectroscopy, Deep UV Raman, Samail Ophiolite**

Serpentine occurs on Mars in rocks associated with small exposures within olivine-carbonate units, in crater walls and ejecta, and in outcrops lacking coherent stratigraphy but associated with Fe/Mg smectites, chlorites, and other secondary minerals [Ehlmann et al., 2010; Michalski et al., 2013; Bultel et al., 2015; Viviano-Beck et al., in prep.]. As on Earth, the existence of Mg-serpentine suggests its formation from waters that were reducing, high pH, and relatively low aSiO<sub>2</sub>. The context of all detections from Mars orbit so far is consistent with initial formation in the subsurface by groundwater/hydrothermal activity and later exhumation by erosion or impact. Even in olivine-rich terrains, serpentine is relatively rare, most likely because the rocks are not ultramafic (and thus the favored secondary alteration products are chlorites or Fe/Mg smectites) or because, once formed, serpentine at the surface is weathered and overprinted (thus forming Fe/Mg smectites, the most common alteration mineral on Mars). To date, serpentine has not been detected in situ by landed rover missions, and, lacking petrologic context for the orbital detections, the conditions leading to the occurrence of serpentine is necessarily speculative. Nevertheless, there is a candidate site under consideration for the Mars 2020 rover mission at which serpentine was detected in the olivine-carbonate unit (Northeast Syrtis).

For Mars 2020 and landed missions of the future, new technologies are under development for in situ petrology to assess the texture, mineral assemblages, and presence/absence of organic matter in Martian rocks. We have trialed some of these methods in rocks from the Samail ophiolite [Leask & Ehlmann, 2016ab] and one sample from the deep ocean crust [Menez et al., 2012]. Field-based imaging spectroscopy was used to map target outcrops at cm-to-m scale, tracing changes in the mineralogy of the protolith and the extent and nature of secondary carbonation and serpentinization. Subsequent microimaging spectroscopy allowed non-destructive, semi-quantitative estimation of modal mineralogy at sub-mm scale, finding pyroxene clasts partially altered to serpentine, textures indicating multiple episodes of aqueous alteration and autobrecciation, and carbonates with solid solution variability [Leask et al., 2016ab]. Similar work in Quebec mines has yielded similar data along with variation in the redox of serpentines [Greenberger et al., 2015]. We are presently investigating some of these samples with SHERLOC, a deep UV raman and fluorescence spectrometer, which will be on the Mars 2020 rover, to look for associated organics.

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## CO-REGISTERED FE REDOX AND RAMAN IMAGING TO TRACE LOW-TEMPERATURE SERPENTINIZATION REACTION PATHWAYS

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### Iron, Redox, Oman, XRF, Raman

Low temperature serpentinization reactions have the capacity to generate hydrogen that may support subsurface lithoautotrophic microbial ecosystems. Hydrogen is produced by the oxidation of Fe(II) to Fe(III) by reaction with water under highly reducing conditions. However, the reaction pathways that facilitate the release of Fe(II) to solution and sequester Fe(III) in mineral phases at low temperature are poorly understood. We employ several complementary and spatially co-registered microscale imaging techniques to quantify Fe oxidation state and elucidate iron mineral speciation in serpentinite rocks with complex alteration histories.

We have developed an approach to quantitatively image the Fe(III)/Fe(Total) ratio within rocks that contain multiple generations of minerals produced during water/rock interaction. Synchrotron-based micro X-ray Fluorescence multiple energy mapping (e.g. Mayhew *et al.* 2011) has been optimized for the pre-edge region of the Fe K-edge and carefully calibrated to a set of well-characterized standards (e.g. Andreani *et al.*, 2013) to estimate the Fe(III)/Fe(Total) ratio for every pixel. Iron element distribution maps derived from micro-XRF mapping reveal the mineral phases that contribute to the overall iron budget. Hyperspectral Raman imaging of the same region enables identification of distinct mineral phases even when minerals may be intimately intergrown. Minor spectral differences in the Raman maps reflect variation in chemical composition and crystallinity between distinct generations of serpentine and hydroxide minerals.

The sequential application of these techniques to a single region of interest generates spatially co-registered datasets that reveal the complex variation of Fe-oxidation with mineral speciation and composition. Fe(II)/Fe(III) ratio maps can be placed into the context of total Fe concentration and mineralogy to determine the key mineral sources of Fe(II) and sinks for Fe(III), facilitating interpretation of reactions that may be important at low temperature. This technique has been applied to studying serpentinite rocks from the Samail Ophiolite in Oman which contain abundant Fe(II)-bearing brucite, usually intimately intergrown with serpentine containing both Fe(II) and Fe(III). Microscale Fe-oxidation state mapping suggests that the oxidation of brucite may be recorded by the presence Fe(III)-bearing hydrotalcite-group minerals such as pyroaurite and iowaite, prior to conversion to magnetite and Fe(III)-bearing serpentine. Quantitative imaging therefore allows us to explore whether brucite may represent an important reservoir for Fe(II), and whether brucite is destabilized at low temperatures by silica- and bicarbonate- bearing groundwater, potentially fueling hydrogen production.

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## CHRYSOTILE AND POLYGONAL SERPENTINE IN SERPENTINITES FROM KUROSEGAWA BELT KYUSHU JAPAN

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### Chrysotile, polygonal serpentine, Kurosegawa belt

Serpentine minerals are 1: 1 type phyllosilicate with ideal composition  $Mg_3Si_2O_5(OH)_4$ . They can be classified into three types, antigorite, lizardite, and chrysotile. Chrysotile takes a nanotube like structure and is divided into clinochrysotile (chrysotile- $2M_{c1}$ ) and orthochrysotile (chrysotile- $2Or_{c1}$ ) by the  $\beta$  angle. In addition there is a multi-angular column shaped serpentine called polygonal serpentine (e.g. Baronnet and Devouard, 2005; Mugnaioli et al., 2007). In Whittaker and Zussman (1956), it is noted that pure orthochrysotile is very rare compared to pure clinochrysotile, though minor orthochrysotile is included in many fibrous serpentine specimens. However, pure orthochrysotile is confirmed by powder X-ray diffraction (XRD) analyses in serpentinites from Kurosegawa belt, which were composed of polygonal serpentine in transmission electron microscope (TEM) observation (Inoo and Uehara, 2009). In this study, we researched the occurrence and distribution of chrysotile and polygonal serpentine in serpentinites from Kurosegawa belt, Kyushu, Japan, in order to reconsider the relationships of chrysotile and polygonal serpentine.

The samples were analyzed by powder XRD and TEM. Since chrysotile and polygonal serpentine show similar XRD pattern, they were distinguished by selected area electron diffraction (SAED) pattern of the grinded sample. The result of powder XRD is noted as clinochrysotile or orthochrysotile for convenience.

The serpentinites of the Kurosegawa belt in Kyushu are composed of various serpentine species. Chrysotile and polygonal serpentine are often seen in veins, and sometimes makes up most part of the rock. In powder XRD observation, the middle area is rich in clinochrysotile, while other areas include orthochrysotile. The middle-west area (Fukami, Nekotani, Shimotake) is particularly rich in orthochrysotile.

In TEM observation, clinochrysotile rich sample determined by XRD was mostly clinochrysotile with diameter below 100 nm, often seen as bundles of fibers orientated in similar directions. Orthochrysotile rich sample determined by XRD was mostly polygonal serpentine ( $\beta = 90$ ) with various diameters from 100 nm to 400 nm, accompanied by minor orthochrysotile and/or clinochrysotile with diameters below 100 nm. In the thin section from Shimotake, fibers were oriented in various directions and 15 sectored polygonal serpentine with deformed center were common. The mixture of clinochrysotile and orthochrysotile determined by XRD included polygonal serpentine ( $\beta = 90, 93$ ), clinochrysotile and orthochrysotile.

The variation of chrysotile and polygonal serpentine showed no correlation to the distribution of antigorite and lizardite, which corresponds to alteration temperature. In addition, blue schists are seen at Shimotake, which is extremely polygonal serpentine ( $\beta = 90$ ) rich among the Kyushu Kurosegawa belt, so the variation of the forming species may have some relation with pressure or shear stress.

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## HYDROTHERMAL FLUXES IN THE OCEANIC MANTLE LITHOSPHERE: EXPERIMENTAL STUDY OF THE SERPENTINIZATION REACTION AND CO<sub>2</sub> EXCHANGES

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### Serpentinization, X- ray microtomography, percolation experiments

Serpentinization is the main hydrothermal process driving the alteration of the mantle lithosphere by seawater at ridges. It consists in the alteration of olivine to serpentine and is associated to processes such as oxidation as well as carbonation when CO<sub>2</sub> is present. The sustainability and efficiency of the reaction requires penetration and renewal of fluids at the mineral-fluid interface yet the secondary low density minerals can fill the porous network clogging efficiently flow paths. This study aims at better understanding the coupled hydrodynamic and chemical processes driving the earliest stages of alteration of the ultramafic basement, when seawater-derived hydrothermal fluids penetrate and interact with exposed mantle rocks at slow spreading ridges. We investigate the structural changes of the rock in relation to dissolution-precipitation rates using an experimental approach. Reactive percolation experiments were performed using the ICARE Lab 3 bench (Géosciences Montpellier) that allows measuring continuously permeability changes during experiments and sampling the outlet fluids passing through the sample. We analyzed the reacted samples before and after the experiments using a combination of a geochemical (SEM, EPMA, ICPMS) and High Resolution X-Ray microtomography (HR  $\mu$ tomography; ID19 ESRF Grenoble) approaches.

Two series of experiments were carried out at 190°C, 25 MPa, XCO<sub>2</sub> of 5.24 mmol/kg and constant Darcy's velocity of  $\sim 2$  mm/min. Natural seawater was injected into samples of pressed powdered San Carlos olivine (Fo90; grains 100-150  $\mu$ m). The first set of experiments was realized in Titanium capsules of 2 mm diameter and 6 mm length and the samples analyzed at 0.65  $\mu$ m resolution using HR  $\mu$ tomography. The second sequence of experiments was performed in steel capsules of 7 mm diameter and 18 mm length. They were used for petrological and geochemical analysis. The alkalinity and pH of outlet fluids were analyzed as well as their cationic composition (ICP-MS) for mass balance calculations.

Comparison of  $\mu$ tomography images of reacted and unreacted samples show evidences of olivine dissolution and secondary minerals precipitation during the 14 days long experiments. The dissolution is mainly localized in the grain borders and the precipitation is located in fractures and sometimes in grains borders. Precipitation appears dominant in segmented images. Chemical analyses in the outlet fluids show that Mg, Si and HCO<sub>3</sub> are trapped in the reacted samples indicating also that precipitation was the dominant process in our experiments. Preliminary mass balance calculations, carried out assuming that no olivine dissolution occurred, indicate that secondary minerals (serpentine, brucite, magnesite, magnetite and anhydrite) represent at least 6 wt.% of the total mass of the reacted sample. These results are discussed in terms of methodology, texture (microporosity ...) and processes (localization of precipitation and dissolution).

## OLIVINE GROWTH DURING SERPENTINIZATION OF DULUTH COMPLEX PERIDOTITE

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### **Mg-depletion, Mg-fayalite, Fe-rich phyllosilicates**

Major Mg-depletion accompanying the serpentinization of peridotite (olivine  $Fa_{40}$ ) in the Duluth mafic complex, Minnesota USA, produced veinlets containing (along with magnetite) a sequence of phyllosilicates ranging from lizardite, chrysotile, and clinochlore, to Mg-hisingerite, ferrosaponite, and chamosite. At the same time reaction progress across the olivine-serpentine isobaric T- $X_{Fe}$  phase-loop was reversed, with the production of magnesian fayalite ( $Fa_{50-80}$ ). Chlorite and serpentine mirror the bimodal compositional frequency of observed olivine compositions, suggesting a measure of local Fe/Mg exchange equilibrium. The metamorphic olivine grew in the serpentine veinlets as small idiomorphic crystals attached to igneous olivine, and as up to 20  $\mu$ m-wide veinlets cross-cutting igneous olivine, in both cases with substantial increases in the tephroite component. Measured phyllosilicate compositions (EMPA and TEM-EDX) are predominantly physical mixtures. CaO is progressively enriched up to 1.5 wt.% in hisingerite-serpentine mixtures, and small amounts of Na and K are unevenly present in the ferrosaponite. Traces of talc, various sulfides, andradite, and ilvaite were found - but no brucite, carbonate, NiFe-alloy, quartz, or goethite. The removal of Mg is inferred to have taken place initially at low  $fO_2$  and temperature roughly 300°C, under the action of an infiltrating acidic, aqueous fluid. This fluid was likely influenced by nearby concentrations of CuNi-sulfides, or alternatively it was derived from underlying graphitic, sulfidic metapelites. Growth of the hisingerite and some of the ferrosaponite (and its partial oxidation) are inferred to have taken place at a later stage under cooler and more oxidizing conditions. Similar MgFe-phyllosilicates and ferroan olivine are found in terrestrial ore deposits, on the ancient (Noachian) cratered surface of Mars, and in Martian meteorites (nakhlites). Other layered ultramafic-mafic intrusions, zoned mafic intrusions, and ophiolites with CuNi-sulfide concentrations may conceivably be found locally to have undergone the same style of serpentinization reported here accompanied by Mg-depletion.

## THERMODYNAMIC PROPERTIES OF H<sub>2</sub>-RICH SERPENTINIZING FLUIDS: QUANTIFYING H<sub>2</sub> PRODUCTION AND REDOX STATE

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### H<sub>2</sub>-rich fluids, experimental serpentinization, redox conditions

Serpentinization involves complex H<sub>2</sub>-rich fluid mixtures whose thermodynamic properties are poorly known. One parameter that needs to be better constrained is  $\gamma_{\text{H}_{2,\text{aq}}}$ . Knowledge of  $\gamma_{\text{H}_{2,\text{aq}}}$  is necessary to model water-rock interactions involving hydrogen-rich fluids, relate hydrogen fluid concentration ( $m\text{H}_{2,\text{aq}}$ ) and H<sub>2</sub> fugacity ( $f\text{H}_2$ ) and evaluate redox changes during serpentinization. In this study, the theoretical basis for estimating  $\gamma_{\text{H}_{2,\text{aq}}}$  has been examined and results are compared with the rare determinations available (*Ding and Seyfried*, 1990). New  $\gamma_{\text{H}_{2,\text{aq}}}$  data have been obtained at 50 MPa, 250 and 300°C, by measuring simultaneously  $m\text{H}_{2,\text{aq}}$  and  $f\text{H}_2$  in H<sub>2</sub>O-H<sub>2</sub> fluid mixtures. The experiments were performed in large-volume Dickson-Seyfried bombs allowing periodic sampling of the fluid and analysis of dissolved H<sub>2</sub> ( $m\text{H}_{2,\text{aq}}$  determined by gas chromatography). The same bomb was fitted with a Au<sub>20</sub>Pd<sub>80</sub> (wt.%) H<sub>2</sub> permeable membrane ( $f\text{H}_2$  read manometrically). Knowing the equilibrium constant of the reaction between H<sub>2, aq</sub> and H<sub>2, g</sub> (from SUPCRT92) allows  $\gamma_{\text{H}_{2,\text{aq}}}$  to be determined from the experimental results.  $\gamma_{\text{H}_{2,\text{aq}}}$  results are very close to 1 (1.11±0.08 at 250°C and 0.99±0.08 at 300°C), in agreement with the theoretical value for pure aqueous fluid, and confirming the validity of our experimental setup.

However, for these results to be applied to natural serpentinization environments, it is necessary to take into account the influence of NaCl on  $\gamma_{\text{H}_{2,\text{aq}}}$ . In the absence of direct measurements,  $\gamma_{\text{H}_{2,\text{aq}}}$  has been evaluated for NaCl-bearing hydrogen-rich fluids by using serpentinization experiments where both  $m\text{H}_{2,\text{aq}}$  and  $f\text{H}_2$  have been measured. These experiments were carried out at 50 MPa in flexible Ti or Au/Ti cells loaded with crushed (<60µm) Vourinos harzburgite plus artificial seawater (demineralized water + 3.2 wt.% NaCl) so as to give water/rock mass ratios of ~1.8. Except for the experiment performed at 350°C, extensive mineralogical transformations were recorded at 250 and 300°C. Newly formed phase include serpentine (>60 vol%), magnetite and brucite, consistent with a serpentinization process. Awaruite was observed in one run, indicating extremely reducing conditions.  $m\text{H}_{2,\text{aq}}$  measurements reach a maximum at 300°C (59, 141 and 13 mmol/kg<sub>water</sub> at 250, 300 and 350°C respectively).  $f\text{H}_2$  measurements reach 3.7 and 2.2 MPa at 250 and 300°C respectively, corresponding to  $f\text{O}_2$  values of NNO-5.6 and NNO-4.4.  $\gamma_{\text{H}_{2,\text{aq}}}$  values derived from these serpentinization experiments are < 1. This is unexpected given the salting out effect that should take place in presence of NaCl. We attribute this mismatch between measured and expected  $\gamma_{\text{H}_{2,\text{aq}}}$  to a systematic H<sub>2</sub> loss in the hot part of the  $f\text{H}_2$  reading device, leading to a significant  $f\text{H}_2$  underestimation. This implies that the  $f\text{O}_2$  calculated above are overestimated. There is still a need for systematic  $\gamma_{\text{H}_{2,\text{aq}}}$  measurements in NaCl-bearing hydrogen-rich fluids.

Ding, K. & Seyfried, Jr., W. E. (1990). Activity coefficients of H<sub>2</sub>, H<sub>2</sub>S in NaCl solutions at 300–425 °C, 300–500 bar with application to ridge crest hydrothermal systems. EOS, *Transactions American Geophysical Union*, 71:1680.



## **SUBSURFACE MODELS OF SERPENTINITE / PERIDOTITE BODIES, ONSHORE AND OFFSHORE NORWAY**

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### **Geophysics, subsurface models, Norway**

Buried ultramafic rock bodies in crustal settings can be detected and a simplified model of its geometry can be derived utilizing geophysical data, here with focus on gravity and magnetic data. This requires the knowledge of densities and magnetic attributes of ultramafic rocks as well as of its host rocks. At outcrops, the buried part of the ultramafic rocks can be derived to a reasonable detail as such models can be well constrained by rock parameters of the outcrop and local geological information.

At offshore locations, modelling and parameter characterization has higher uncertainties, especially where the ultramafic body is located in the deep crust below sedimentary basins. One problem is the decaying gravity and magnetic anomaly with increasing depths, another problem, the lack of direct measurements of rock parameters. A common approach is to use parameters from data tables, but classifications in there are generally simplified. A better way is to utilize onshore analogs which reflect the assumed tectonic setting and as such provide a clue to the expected ultramafic rock type and its geophysical parameters. Furthermore, it needs to be considered that ultramafic rocks with a moderate to high degree of serpentinization overlap in geophysical parameters with other rock types. Support for a distinction between ultramafic rocks and other rocks can be found by classifying the tectonic setting in order to gain the probability for the occurrence of ultramafic rocks. Finally, in deep crustal locations, temperature–pressure conditions need to be consulted with respect to stability and phase transitions in the serpentinite-peridotite phase diagrams.

Geophysical data and subsurface models for onshore and offshore locations are presented: (1) an exhumed mantle fragment outcropping in the Western Gneiss Region (Otrøya), (2) a lower crustal body below the East Shetland Basin, North Sea, interpreted as partly serpentinized rock in an ophiolitic setting (Fichler et al., 2011), which is compared with respective outcrops, (3) a basement high in the southwestern Barents Sea (Veslemøy High), originally interpreted as hyperextended mantle (Barrere et al., 2009), but now also discussed in relation to adjacent outcrops of the Seiland Igneous Province.

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**SERPENTINIZATION AND LIFE:  
DRILLING THE ATLANTIS MASSIF (IODP EXPEDITION 357)**

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**Atlantis Massif, IODP, subsurface biosphere**

Expedition 357 “Atlantis Massif Serpentinization and Life” was the first Mission Specific Platform (MSP) expedition implemented by the ECORD Science Operator in the current phase of the International Ocean Discovery Program (IODP). An east-west transect across the southern wall of the Atlantis Massif was cored to study the links between serpentinization processes and microbial activity in the shallow subsurface of highly altered ultramafic and mafic sequences that have been uplifted to the seafloor along a major detachment fault zone. A coring and sampling strategy was developed that used two seabed rock drills: the BGS Seafloor Rockdrill 2 (RD2) and the MARUM Meeresboden-Bohrgerät (MeBo). New technologies were also developed and successfully applied for the first time: (1) an in-situ sensor package and water sampling system on each seabed drill to measure real-time variations in dissolved methane, oxygen, pH, oxidation reduction potential, temperature, and conductivity during drilling and take water samples after drilling; (2) a borehole plug system to seal the boreholes and which was successfully deployed at two sites to allow access for future sampling; and (3) delivery of chemical tracers into the drilling fluids for contamination testing.

Seventeen holes were drilled at nine sites across Atlantis Massif, recovering more than 57 m of core, with borehole penetration ranging from 1.3 to 16.4 meters below seafloor and core recoveries as high as 75% of total penetration. The cores show highly heterogeneous lithologies, bulk rock compositions, types of alteration and degrees of deformation. Ultramafic rocks are dominated by harzburgites with intervals of dunite and minor pyroxenite veins, and with gabbroic rocks occurring as melt impregnations and veins. Dolerite dikes and basaltic rocks represent the latest stage of magmatic activity. Overall, the ultramafic rocks revealed a high degree of serpentinization, as well as metasomatic talc-amphibole-chlorite overprinting and local rodingitization. Metasomatism postdates an early phase of serpentinization but predates late-stage intrusion and alteration of dolerite dikes and the extrusion of basalt.

This keynote presentation will provide an overview of the drilling strategy and preliminary results of Expedition 357 and will highlight the role of serpentinization in driving hydrothermal systems, in sustaining microbial communities, and in sequestering carbon in a region of active serpentinization and low temperature hydrothermal alteration. Sampling during the offshore phase specifically targeted obtaining contaminant-free microbiological samples, which will be analyzed in various laboratories to investigate the extent and activity of the subsurface biosphere and will allow us to assess how abiotic and biotic processes change with aging of the lithosphere and with variations in rock type.

## OXYGEN AND NEODYMIUM ISOTOPIC EVOLUTION OF CONTINENTAL SERPENTINIZATION AND MAGNESITE MINERALIZATION

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### continental serpentinization, oxygen and neodymium isotopes, cryptocrystalline magnesite

Serpentinization and extensive cryptocrystalline magnesite vein complexes, hosted in harzburgite of the Del Puerto ophiolite, California, constrain geochemical pathways for the interaction of serpentinizing and mineralizing solutions in the subsurface. As water-dominated systems, continental serpentinization of harzburgite and cryptocrystalline magnesite vein mineralization constitute records of temperatures of formation, source of the fluids, and extent of fluid-rock interaction. Cryptocrystalline magnesite also serves as a natural analogue to carbon storage in ultramafic rocks. In this study, we present oxygen and neodymium data to evaluate (1) continental harzburgite serpentinization; (2) cryptocrystalline magnesite mineralization in serpentinized harzburgite; and (3) late silica veining, shearing, and overprinting. Oxygen-isotope thermometry of cogenetic magnetite-serpentinite pairs yields a range of serpentinization temperature between 176°C to 59°C. These temperatures allow calculation of the  $\delta^{18}\text{O}$  composition of serpentinizing fluids at  $-3.6\text{‰}$ , which coincides with average composition of thermal and mineral waters issuing in the California Coast Ranges. In contrast, the  $\delta^{18}\text{O}$  composition of the fluid precipitating the secondary silica veins is  $-6.9\text{‰}$ , consistent with the compositions of modern streams and springs near the Del Puerto ophiolite. Neodymium isotope compositions of harzburgite ( $\epsilon_{\text{Nd}} = +12.91$ ) and serpentinite ( $\epsilon_{\text{Nd}} = -20.52$ ) are correlative with representative worldwide values for peridotite and serpentinite, respectively. The highly developed negative  $\epsilon_{\text{Nd}}$  value of serpentine results from the long-lived interaction with crustal fluids that modify the initial  $\epsilon_{\text{Nd}}$  composition of harzburgite after emplacement of the ophiolite complex. Average neodymium isotope compositions of cryptocrystalline magnesite ( $\epsilon_{\text{Nd}} = -3.9$ ) and secondary silica ( $\epsilon_{\text{Nd}} = -5.4$ ) indicate mineralization from fluids hosted in the neighboring Franciscan Complex (sediments and metasediments). Mass-balance calculations suggest that formation of cryptocrystalline magnesite is a sensitive function of the degree of serpentinization if the serpentinized component has a Nd concentration enrichment factor  $\sim 10^2$  with respect to the harzburgite. Our modeling also predicts a minimum water-rock interaction ratio ( $w/r$ ) between  $2.85 \times 10^{-1}$  to  $\sim 1.2 \times 10^0$ , based on  $\delta^{18}\text{O}$  compositions, and maximum  $w/r$  ratios two orders of magnitude greater ( $\sim 1 \times 10^2$ ) on the basis of  $\epsilon_{\text{Nd}}$  values. For cryptocrystalline magnesite,  $w/r$  ratios are  $1 \times 10^4$ . Such large  $w/r$  ratios indicate that large volumes of water, relative to the mass of the harzburgite, are required to induce serpentinization and subsequent cryptocrystalline magnesite mineralization in continental settings.

## SEISMIC POTENTIAL OF ANTIGORITE-RICH SERPENTINITES, AN EXPERIMENTAL POINT OF VIEW

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### Keywords: Deformation, High-pressure, Intermediate-depth earthquakes

The origin of intermediate-depth earthquakes, which occur at depths of 60-300 km along subducting slabs, remains somehow enigmatic. In the pressure, temperature and strain rate conditions involved, rocks should indeed deform in a ductile fashion. One, or more, mechanism is therefore responsible for mechanical instabilities. Dehydration embrittlement, due to serpentine breakdown, was long considered a good candidate (Dobson et al., 2002) and may still explain seismicity at shallow depths. However, in recent years, a few high pressure experimental studies have challenged this classic theory, by showing that deformation and faulting of antigorite-rich serpentinites, related to dehydration, occurs in a stable and aseismic way (Chernak and Hirth, 2011; Gasc et al., 2011).

In order to assess the seismic potential serpentinites we have performed a series of high pressure deformation experiments on natural (i.e., cored) and synthetic (i.e., sintered) samples, during which micro-seismicity of the samples (i.e., cracks and faulting) was monitored by recording Acoustic Emissions (AE's). Deformation was carried out at pressures of 1-5 GPa, using a Deformation-DIA device, and over a wide range of temperatures, both within and outside antigorite's stability field.

The results show that, below ~400°C, serpentine deformation involves semi-brittle mechanisms that are aseismic, even in cases where strain localization is observed. At high temperature (i.e., above 600°C), despite our attempts at reproducing dehydration embrittlement with fast strain rates and reaction kinetics, joint deformation and dehydration leads to ductile and distributed deformation, without generation of AE's. However, our data evidence a brittle temperature window centered at ca. 500°C. In this latter case, AE's are consistently collected upon deformation and faulting is evidenced on the recovered samples, where extremely sharp strain localization is observed. This brittle field may therefore be a source of seismicity in subducting slabs at mantle pressures. However, analysis of the acoustic signal shows that it is –relatively– orders of magnitude weaker than its real-earth counterparts, which implies that other mechanisms must be responsible for larger intermediate-depth earthquakes. In fact, results on sintered samples, composed of antigorite and olivine mixtures, show that mechanical instabilities develop upon antigorite dehydration, with the appropriate antigorite content, thus suggesting that the largest intermediate depth earthquakes occur in partly hydrated peridotites, capable of sustaining larger bulk strengths.

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## ALPINE SERPENTINITE GEOCHEMISTRY AS KEY TO DEFINE TIMING OF OCEANIC LITHOSPHERE ACCRETION TO THE SUBDUCTION PLATE INTERFACE

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### HP serpentinite, fluid-rock interaction, subduction zone geodynamics

Isotopic (Pb, Sr and B) and trace element (B, Be, As, Sb, U, Th) signatures of serpentinites are useful geochemical tools to assess element exchange and fluid-rock interactions in subduction zone settings (Scambelluri and Tonarini, 2012; Scambelluri et al., 2014; Cannaò et al., 2015). They help to unravel geological history, timing of accretion and tectonic evolution of subduction serpentinites and associated meta-oceanic crust. Sedimentary-derived fluid influx within HP plate interface environments strongly enriches serpentinites in As, Sb, Be, B, U and Th and resets their B, Sr and Pb isotopic compositions. This HP metasomatic signature is preserved during exhumation and/or released at higher PT through de-serpentinization, fueling partial melting in the sub-arc mantle and recycling such fingerprint into arc magmas.

This study focuses on the subduction recrystallization, geochemical diversity and fluid-rock interaction recorded by ophiolitic high- to ultra-high pressure (HP, UHP) Alpine serpentinites from the subducting oceanic plate (Cignana Unit, Zermatt-Saas Complex, Monviso and Lanzo Ultramafic Massifs). The As and Sb compositions of the HP-UHP Alpine ophiolitic rocks reveal the interaction between serpentinite and crust-derived fluids during their emplacement along the plate interface. This enables to define a hypothetical architecture of the Alpine subduction interface, considering large ultramafic slices. In this scenario, the Lanzo peridotite and serpentinite retain an As-Sb composition comparable to DM and PM: i.e. they behaved as relatively closed systems during subduction, with little exchange with sediment-derived fluids. Lanzo thus belonged to sections of the subducting plate, afar from the plate interface. Serpentinites from the Lago di Cignana Unit and Monviso and Voltri (Cannaò et al., 2015) are richer in As and Sb, showing moderate to strong interaction with sediment- and crust-derived fluids during subduction (i.e. they behaved as open systems). These serpentinite slices accreted at the plate interface and exchanged with slab-derived fluids at different depths during Alpine subduction: Voltri accreted at shallower conditions (50-60 km; Cannaò et al., 2016) than Monviso Unit (around 80 km depth) and Lago di Cignana (about 100 km depth), and exchanged with sedimentary and crustal systems during the entire burial history. Their relatively lower density might act as buoyancy force, triggering the exhumation of much denser lithologies (eclogite and peridotite).

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Scambelluri, M. & Tonarini, S. (2012). Boron isotope evidence for shallow fluid transfer across subduction zones by serpentinitized mantle. *Geology*, 40(10), 907-910.

Scambelluri, M., Pettke, T., Rampone, E., Godard, M., & Reusser, E. (2014). Petrology and trace element budgets of high-pressure peridotites indicate subduction dehydration of serpentinitized mantle (Cima di Gagnone, Central Alps, Switzerland). *Journal of Petrology*, 55(3), 459-498.



## **NEW CALEDONIA: AN OPHIOLITIC COMPLEX BECOMING INDUSTRIALIZED**

Habault, C.

ERAMET New Caledonia

The presentation discusses the emergence of New Caledonia as a player in the international mining and metallurgical sector. Its industrial development is based on the exploitation of oxidized nickel found in the weathered profiles of more or less serpentinized ophiolitic structures. Various aspects of the industry are presented from the point of view of sustainable development, with examples, both from the mining and the metallurgical processing angles. The issue of Corporate Social Responsibility is also discussed, as well as a research and development project based on the development of some original, shared industry-wide initiatives. New Caledonia an example to follow or not?

## HIGH-PRESSURE DEFORMATION OF SERPENTINE + OLIVINE AGGREGATES

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### **subduction, high-pressure, deformation**

Serpentinization is expected to occur when fluids are released from the dehydrating subducting slabs and migrate into shear zones and the mantle wedge formed of peridotite. At shallow depths (15-30km) a few percent volume serpentine can lower the viscosity of peridotites by almost an order of magnitude (Escartin, Hirth and Evans, 2001). However, the deformation mechanisms are not easily extrapolable to deeper contexts. The rheology of a rock with two phases of contrasted mechanical properties is highly non-linear with composition and cannot be modelled from its end-members. Here we investigate the rheology of serpentine + olivine « synthetic » peridotites with varying serpentine content (5 to 50%) at high pressure (2-3 GPa, ca. 60-90 km depth), using the D-DIA large volume press and synchrotron powder X-ray diffraction and imaging. The results will provide insights on the conditions under which serpentinized peridotites evolve in a regime dominated by the rheology of the strongest phase (olivine) or the weakest phase (antigorite).

Escartin, J., Hirth, G., and Evans, B.W (2001) Strength of slightly serpentinized peridotites: Implications for the tectonics of oceanic lithosphere, *Geology*, 29,1023-1026.

**NEOPROTEROZOIC AIT AHMANE SERPENTINITES (BOU AZZER, MOROCCO): PROTOLITH, SERPENTINIZATION AND POLYPHASED HYDROTHERMAL HISTORY.**

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**Ophiolite, Neoproterozoic, Serpentinite, Chemistry, Hydrothermalism, Magnetite**

Ophiolitic units are the only remains of ancient oceanic lithosphere (> 200 Ma). Widely investigated in the Phanerozoic land, their Precambrian counterparts are less documented. Specifically, ultramafic units of these sequences tell us about oceanic lithospheric mantle composition and allow us to study geochemical processes induced by their hydration (serpentinization), as well as their exhumation.

We present here a study combining field observations, magnetic, petrographic and geochemical analysis of Ait Ahmane serpentinites (Bou Azzer Neoproterozoic ophiolite, Morocco) in order to assess: protolith, exhumation modalities and hydrothermal history of these mantle rocks. Identification (Raman spectroscopy, XRD) and major elements *in situ* chemistry (electronic microprobe) of mineral phases, were combined with micro-textural relationships observations and whole rock geochemical analysis (major and trace). Magnetic experiments allow the characterization of iron oxide related to serpentinization and late hydrothermal processes which locally affected the unit.

The precursor of Ait Ahmane serpentinites are spinel-bearing harzburgites associated with rare dunitic lenses, both fully serpentinized. They generally exhibit a typical pseudomorphic texture, which probably results of a static serpentinization. Very high Cr# values (0.65-0.77) and low Mg# (0.33-0.65) in chromites, low whole rock incompatible major elements concentrations (Al<sub>2</sub>O<sub>3</sub>: 0.20-1.28 wt. % and Ti: 3-38 ppm) and very low REE suggest a highly refractory protolith, typical of a supra-subduction context. We highlight two different mantle protoliths from the west and the east of the unit. Difference of HREE pattern could be explained by higher fertility and pyroxene abundance in sample from the west. This tendency appears to be in agreement with the other chemical features such as a higher Ti and Al content. In addition, some samples exhibit a strong LREE enrichment (La/Yb to 175.79), correlated to a positive peak for Eu (Eu/Eu<sub>N</sub> until 27.43), which seems to be the signature of a subsequent hydrothermal event. More locally, another hydrothermal event is responsible for the development of massive pure magnetite veins (up to 5 cm thick) and changes in magnetite composition and size within host serpentinite. The same event is also associated with a low temperature (< 350 °C) chromite alteration into ferritchromite and into Cr-magnetite, which is usually attributed to amphibolite facies metamorphism.

## **METABOLIC POTENTIAL AND ACTIVITY IN FLUIDS OF THE COAST RANGE OPHIOLITE MICROBIAL OBSERVATORY, CALIFORNIA, USA**

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### **Hydrogen, Carbon Monoxide**

Metabolic potential and activity associated with hydrogen and carbon monoxide were characterized in fluids sampled from the Coast Range Ophiolite Microbial Observatory (CROMO). CROMO consists of two clusters of science-dedicated wells drilled to varying depths up to 35m in the actively serpentinizing, Jurassic-age Coast Range Ophiolite of Northern California, USA, along with a suite of pre-existing monitoring wells at the same site. Consistent with the fluid chemistry observed in other serpentinizing systems, CROMO fluids are highly alkaline, with pH up to 12.5, high in methane, with concentrations up to 1600 micromolar, and low in dissolved inorganic carbon (DIC), with concentrations of 10's to 100's of micromolar. CROMO is conspicuous for fluid H<sub>2</sub> concentrations that are consistently sub-micromolar, orders of magnitude lower than is typical of other systems. However, higher H<sub>2</sub> concentrations (10's -100's of micromolar) at an earlier stage of fluid chemical evolution are predicted by, or consistent with: thermodynamic models for fluid chemistry based on parent rock composition equivalent to local peridotite and with water:rock ratio constrained by observed pH; the presence of magnetite at several wt% in CROMO drill cores; and concentrations of formate and carbon monoxide that would require elevated H<sub>2</sub> if formed in equilibrium with H<sub>2</sub> and DIC.

Calculated Gibbs energy changes for reaction of H<sub>2</sub> and CO in each of several metabolisms, across the range of fluid composition encompassed by the CROMO wells, range from bioenergetically feasible (capable of driving ATP synthesis) to thermodynamically unfavorable. Active consumption relative to killed controls was observed for both CO and H<sub>2</sub> during incubation of fluids from the pre-existing monitoring wells; in incubations of freshly cored solids, consumption was only observed in one sample set (corresponding to the lowest pH) out of three. The specific metabolisms by which H<sub>2</sub> and CO are consumed remain to be determined.

## FLUID INDUCED METAMORPHISM OF STRESSED ROCKS

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### Volatilization, fragmentation, localization

Significant volumes of the Earth's lithosphere (continental and oceanic) does not contain free fluids. When subject to the changing temperature and pressure conditions at plate boundaries, these rocks do not react until exposed to externally derived fluids. Introduction of external fluids is often associated with fracturing and seismic activity, both at shallow and deeper parts of the Earth's crust.

Fluid driven metamorphism takes place far from equilibrium through a complex coupling between fluid migration, chemical reactions, and deformation processes. This *disequilibrium metamorphism* is characterized by fast reaction rates, dissipation of large amounts of energy as heat and work, and the generation of a range of emergent pore structures and fracture patterns that often control transport properties and thus further reaction progress.

Fluid consuming metamorphism leads to mechanical weakening due to grain size reduction, the formation of sheet silicates, and local heat production. Shear zone development in the ductile parts of the lithosphere is often associated with fluid introduction and may be controlled by the availability of fluids. Fault-controlled migration of fluids from the brittle crust, to the underlying ductile region may provide a spatial and temporal link between localized strain and seismic activity in the upper crust and shear zone controlled deformation below. In a similar way, channelized fluid migration from areas undergoing prograde metamorphism (f.ex. in the lower plate of a subduction zone) may control the distribution of retrograde metamorphism and strain localization in the upper plate.

Jamtveit, B., Austrheim, H., and Putnis, A., (2016), Disequilibrium metamorphism of stressed lithosphere. *Earth-Science Reviews*, 154, 1-13



**MID-OCEAN RIDGE SERPENTINITE IN THE PUERTO RICO TRENCH: FROM SLOW SEAFLOOR SPREADING TO SUBDUCTION**

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**keywords: Atlantic, serpentinite, subduction**

Serpentinite is believed to be one of the main carriers of water and other volatiles into subduction zones, but direct evidence for serpentinite subduction has been elusive. The Antilles island arc is one of only two subduction zones worldwide that recycles slow-spreading oceanic lithosphere where descending serpentinite is directly accessible on the seafloor. Here we examined serpentinitized peridotites from the North Wall of the Puerto Rico Trench to assess their formation and alteration history and discuss geological ramifications resulting from their emplacement and subduction. Lithospheric accretion and serpentinitization occurred, as indicated by U-Pb geochronology of hydrothermally altered zircon, at the Cretaceous Mid-Atlantic Ridge. Serpentinized peridotites recorded multifaceted igneous and high- to low-temperature hydrothermal processes that involved extensive chemical, physical, and mineralogical modifications of their peridotite precursors. The cumulative effects of these processes produced highly magnetic, porous, and oxidized serpentinites that are enriched in volatiles and fluid mobile elements with strong implications for the magnetic structure of the seafloor in the Cretaceous Quiet Zone, gravity anomalies in the Puerto Rico Trench, and element cycling between the oceanic lithosphere, seawater, and the Antilles subduction zone.

## METAMORPHIC EVOLUTION AND HYDRATION-DEHYDRATION REACTIONS OF A SERPENTINITE-RODINGITE SUITE DURING SUBDUCTION (CERRO DEL ALMIREZ MASSIF, SOUTHERN SPAIN)

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### Metarodingite, antigorite dehydration, subduction setting

Rodingites are Ca-, Al-enriched and Si-undersaturated rocks; they usually form after basaltic precursors due to seafloor metasomatism and commonly occur associated with serpentinites in exhumed terrains that experienced subduction and HP-metamorphism. However, the response of rodingites to devolatilization and geochemical partition during subduction is not well constrained. In the Cerro del Almirez ultramafic massif (S. Spain) metarodingites constitute about 2% of the total volume of exposed rocks. This is the only locality known so far where the arrested dehydration front due to antigorite breakdown at HP conditions (releasing up to ~ 9 wt % H<sub>2</sub>O) has been preserved (Padrón-Navarta et al., 2011). Since the work by Trommsdorff et al. (1998) these outcrops have revealed as a unique setting to investigate the prograde metamorphic evolution from Atg-serpentinite to Chl-harzburgite and its various petrological, geochemical, and petrophysical implications.

In Cerro del Almirez, metarodingite bodies and their associated blackwalls are enclosed in both Atg-serpentinite and Chl-harzburgite. They occur as boudinaged layers, 1 to 42 m in length and 30 cm to 1.8 m in thickness. During subduction they underwent a complex tectono-metamorphic evolution (including interaction with fluids released from dehydration of hosting serpentinite) that resulted in four different metarodingite types. *Type I grossular-metarodingite* mainly occurs in Atg-serpentinite and consists of grossular-andradite-rich garnet + chlorite + diopside + titanite + magnetite. It behaved as an essentially brittle rock during subduction. *Type II epidote-metarodingite* displays the progressive growth of epidote and diopside and the breakdown of garnet. Thermodynamic modelling indicates that this transformation took place at  $P > 1,1$  GPa,  $T = 480-520$  °C, and decreasing  $\mu\text{CaO}$ . It was probably enhanced by H<sub>2</sub>O release due to brucite breakdown in host serpentinite. Type II occurs incipiently within Atg-serpentinite and it is widely developed in the Chl-harzburgite domain. Fluids released by Atg dehydration ( $T = 550-610$  °C) in open system conditions (Marchesi et al., 2013) allowed some Na to enter the metarodingites and pargasite-rich amphibole to grow. Subsequent equilibrium during prograde metamorphism ( $P > 1,5$  GPa,  $T > 550$  °C) gave place to *Type III amphibole-metarodingite* (amphibole + epidote + chlorite + diopside + titanite + magnetite), which is very common in the Chl-harzburgite domain and shows a very penetrative foliation. In some small, strongly deformed boudins within Chl-harzburgite *Type IV almandine-metarodingite* occurs. It consists of newly formed, almandine-rich garnet + amphibole + epidote + chlorite ± diopside + rutile + magnetite and probably corresponds to the peak metamorphic conditions ( $P \approx 2$  GPa,  $T > 580$  °C).

These data reveal the significance of the Cerro del Almirez serpentinite-rodingite suite as a proxy of the petrological evolution of a mafic-ultramafic sequence during hydration and dehydration in subduction settings.

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Padrón-Navarta, J. A., López Sánchez-Vizcaíno, V., Garrido, C. J., Gómez-Pugnaire, M. T. (2011). Metamorphic record of high-pressure dehydration of antigorite serpentinite to chlorite harzburgite in a subduction setting (Cerro del Almirez, Nevado-Filábride Complex, Southern Spain). *Journal of Petrology*, 52, 2047-2078.

Trommsdorff, V., López Sánchez-Vizcaíno, V., Gómez-Pugnaire, M. T., Müntener, O. (1998). High pressure breakdown of antigorite to spinifex-textured olivine and orthopyroxene, SE Spain. *Contributions to Mineralogy and Petrology*, 132, 292-302.

## AB-INITIO CHRYSOTILE FORMATION: INSIGHTS INTO THE STRUCTURE OF PROTO-SERPENTINE

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### Proto-serpentine, pair distribution function, chrysotile, stacking, simulation

Any poorly crystalline serpentine-type mineral with a lack of recognizable textural or diffraction features for typical serpentine varieties (i.e. chrysotile, lizardite, antigorite) is usually referenced as proto-serpentine (e.g. Andreani et al., 2008; Godard et al., 2013). The formation of the so-called proto-serpentine seems ubiquitous in serpentinization reactions.

It is related to dissolution-precipitation of strongly reactive particles prior to true serpentine formation (e.g. in veins where both chrysotile and proto-serpentine are described). However, the structural characteristics of proto-serpentine and its relation with serpentine crystalline varieties remain unclear.

In this study a model describing the transformation from proto-serpentine to chrysotile is presented based on experimental chrysotile synthesis using thermogravimetric analyses, transmission electron microscopy and high-energy X-ray diffraction with pair distribution function analyses. The combination of the high resolution TEM and high-energy X-ray diffraction enables to resolve the local order of neo-formed particles and their structuration processes occurring during pure chrysotile formation (i.e. during the first three hours of reaction). The formation of individual nanotubes is preceded by the formation of small nanocrystals that already show a chrysotile short-range order, forming porous anastomosing features of hydrophilic crystallites mixed with brucite. This is followed by a hierarchical aggregation of particles into a fiber-like structure. These flake-like particles subsequently stack forming concentric layers with the chrysotile structure. Finally, the individualization of chrysotile nanotubes with a homogeneous distribution of diameter and lengths (several hundreds of nanometer in length) is observed. The competitive precipitation of brucite and transient serpentine during incipient serpentinization (Lafay et al., 2013) reaction indicates that both dissolution-precipitation and serpentine-particle aggregation processes operate to form individual chrysotile.

This study sheds light into serpentine mineralization processes and sets a first milestone towards the identification of the factors controlling polymorph selection mechanisms.

Andreani, M., Grauby, O., Baronnet, A., Muñoz, M., 2008. Occurrence, composition and growth of polyhedral serpentine. *Eur. J. Mineral.* 20, 159–171.

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## SERPENTINIZATION-DERIVED CLATHRATE RESERVOIRS OF EARLY MARS

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### Martian crust, Martian dynamo, Martian water, Martian atmosphere

Methane is a key molecule to understand the habitability of Mars due to its possible biological origin and short atmospheric lifetime. Recent methane detections on Mars present a large variability that is probably due to relatively localized sources and sink processes yet unknown.

One of the main ways to produce methane abiotically is through serpentinization, a metamorphic process by which low-silica mafic rocks are hydrothermally altered to store water, produce magnetite and release dihydrogen. While this process may still be occurring today at depth, it must have been more frequent on early Mars for which conditions included higher rates of volcanic activity and impact cratering together with liquid water on the surface. This could have proven a major process to trap a large fraction of the water of the planet during the Noachian in altered minerals at depth and at the same time release a significant amount of methane in the atmosphere (Chassefière et al., 2013). In this study, we determine how much methane could have been produced by early Mars serpentinization processes that could also explain the observed martian remanent magnetic field.

Under the assumption of a cold early Mars environment, when a water cryosphere should have started forming in the subsurface of the planet, it is likely that large amounts of methane clathrate reservoirs formed during the early episodes of alteration of the martian crust. The cryosphere could have trapped such methane as clathrates in stable form at depth. The extent and spatial distribution of these methane reservoirs have been calculated with respect to the current magnetization distribution and other factors. The maximum storage capacity of such a clathrate cryosphere is about  $2.1 \times 10^{19} - 2.2 \times 10^{20}$  moles of  $\text{CH}_4$ , which can explain sporadic releases of methane that have been observed on the surface of the planet during the past decade ( $\approx 1.2 \times 10^9$  moles, Mumma et al., 2009). This amount of trapped methane is sufficient for similarly sized releases to have happened yearly during the history of the planet. While the stability of such reservoirs depends on many factors that are poorly constrained, it is possible that they have remained trapped at depth until the present day. It is also possible that major and sudden geological events (such as the Tharsis bulge, the Hellas impact formation or the martian polar wander, Bouley et al., 2016) could have destabilized methane clathrates and injected in the atmosphere a quantity of gas ( $\text{CH}_4$ , or subsequently oxidized  $\text{H}_2$ ) sufficient to alter the thermal state of the planet and generate a long-lived global warm episode for Mars climate.

Due to the possible implications of methane detection for life and its influence on the atmospheric and climate processes on the planet, confirming the sporadic release of methane on Mars and the global distribution of its sources is one of the major goals of the current and next space missions to Mars. Current and future missions (MSL, MAVEN, TGO, ExoMars and Mars Rover 2020) will provide invaluable understanding of the volatile reservoirs of Mars, their origins and their sinks, allowing us to assess this model in the coming years.

## EXPEDITION 357 SENSOR PACKAGE DATA AND H<sub>2</sub> AND CH<sub>4</sub> CONCENTRATIONS IN PRE-AND POST-DRILLING SAMPLES

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### Serpentinization, Atlantis Massif, IODP

On Expedition 357 we collected water column fluids prior to drilling using the ship's CTD/Niskin bottle rosette and also collected post-drilling bottom water fluids using Niskin bottles mounted on the rock drills. These water samples were all analyzed for H<sub>2</sub> and CH<sub>4</sub> concentrations. In parallel, a suite of in situ sensors was deployed on the rock drills to quantify dissolved oxygen, methane, temperature, pH, and oxidation-reduction potential (ORP).

The variability in temperature, pH, CH<sub>4</sub>, ORP and, in some instances, dissolved O<sub>2</sub> detected by the rock drill sensors was monitored in real-time during drilling. Typically the pH value increased downhole and significant downhole CH<sub>4</sub> peaks were common at most sites. ORP minima were very common and were associated with at least two causal mechanisms: a) associated with specific horizons during continuous drilling of a specific core; b) caused by the shutting off of flushing water, which reduced the dilution of formation fluid as core barrels were changed. Temperature was variable (typically by a few tenths of a degree but up to 1°C at some sites) but difficult to interpret due to the potential for heating by the drill. Background values were in the order of 0.1 to 58 nM for CH<sub>4</sub>; 7.8 for pH; and about 340 mV for ORP. Background temperatures were variable with depth and ranged from 5 to 10°C.

In this report we will present detailed sensor data for specific drillholes and compare the pre-drilling gas concentrations found in the ship-based rosette samples with the post-drilling water samples mounted on the drills.



## CPO DEVELOPMENTS OF SERPENTINITE AT HPHT: IMPLICATION FOR SEISMIC ANISOTROPY

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### HP-HT shear experiments, antigorite, fabrics, seismic anisotropy

Antigorite, the high P/T polytype of serpentine, is considered to be a significant component of the mantle wedge and the subducting lithosphere mantle in subduction zone. Its crystallographic preferred orientation (CPO) may play an important role in trench parallel anisotropy. However, there is a significant discrepancy in the CPO development among natural serpentinite and experimental samples. Toward a better understanding the fabric development of antigorite, we have conducted systematic shear experiments on a hot-pressed serpentinite at temperatures of 350 to 600 °C, pressures of 1.0 to 3.0 GPa, and shear strain rates of  $3.8 \times 10^{-3}$  to  $2.4 \times 10^{-4} \text{ s}^{-1}$  by using a 5GPa deformation apparatus. The serpentinite was hot-pressed from a powdered serpentinitized peridotite by using a 1000-ton multi-anvil press at first. The CPOs of antigorite are characterized by the (001) nearly parallel to the foliation plane and forming a girdle with multiple high concentrations in the foliation plane at 350-500 °C, while the [010] axes parallel to the lineation at 500-600 °C. These results suggest a transition of dominant slip direction in antigorite from [hk0] to [010] with increasing temperature or the increasing plasticity of antigorite as temperature increasing. In contrast to antigorite, the coexisting olivine develops random fabrics, confirming a much greater strength of olivine. The deformation of serpentinite can explain not only the trench-parallel seismic wave polarization but also the shear wave delay time in steeply subduction zones with contribution from serpentinite layer above subducting crust and serpentinitized peridotite in subducting lithosphere mantle, while olivine contributes little to the anisotropy. We propose that the observed seismic anisotropy in the subduction zones are caused by the antigorite CPO rather than by the B-type olivine CPO.

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Proctor, B., Hirth, G., 2016. “Ductile to brittle” transition in thermally stable antigorite gouge at mantle pressures. *J. Geophys. Res. Solid Earth* 121, 1–12.

## SULFIDIZATION OF SERPENTINITE: AN EXPERIMENTAL APPROACH

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### Sulfidization, H<sub>2</sub>S, hydrothermal experiment

Infiltration of hydrothermal fluids within mantle rocks results in the formation of serpentine minerals. But often, the hydration of oceanic material does not end there. Serpentinite continues to be subjected to hydrothermal alteration, which allows different mineral assemblages to form. Some of these later-stage reactions come with the development of Fe-Ni-As-S mineralization. In fact, serpentinites are frequently sulfidized although the initial serpentinization has been shown to come with a desulfidation of the rock (Alt and Shanks, 1998). One setting in which sulfidation can be expected is hydrothermal upflow zones, in which serpentinites are fluxed by large quantities of hot, H<sub>2</sub>S bearing fluids. These fluids trigger replacement reactions during which the serpentinite is mineralized by sulfides.

To evaluate these sulfidization reactions, we have conducted a batch experiment that placed serpentinite powder in contact with an H<sub>2</sub>S saturated solution. No iron was added to the system with this fluid. This mixture was heated to 250 °C at 400 bars and kept under these conditions for 8 weeks. During the run, fluid and gas samples were taken to monitor the ongoing sulfide forming reactions. Preliminary results show that the solid reaction product consists of serpentinite with dissolution textures, as well as newly grown pyrite crystals along with analcime. Increasing hydrogen release reflects the progressing reaction of H<sub>2</sub>S with magnetite where sulfur is captured as pyrite. Under these conditions, it is thus possible to have pyrite formation in serpentinite rock.

Remaining questions about the stability field of sulphides will be addressed using similar experiments at different PT-conditions as well as geochemical modeling. With this, we hope to shed light on the formation of sulfide-bearing serpentinites.

Alt, J.C. & Shanks, W.C. (1998). Sulfur in serpentinized oceanic peridotites: Serpentinization processes and microbial sulfate reduction. *Journal of Geophysical Research* 103, 9917-9929.

## BORON ISOTOPIC DISCRIMINATION FOR SUBDUCTION-RELATED SERPENTINITES

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### Serpentinite mélange, ophiolite, boron isotope discrimination

Serpentinites are key features in subduction and suture zones. They most commonly originate by hydration of peridotite by two different processes: (i) by a seawater source reacting with peridotite beneath oceanic crust and (ii) by reaction of peridotite at the base of the mantle-wedge with fluids released from the slab during subduction.

The Guatemala Suture Zone (GSZ), Guatemala, is a region that contains two distinct suture-related serpentinite mélanges (North Motagua Mélange (NMM) and South Motagua Mélange (SMM)) straddling the Motagua Fault system, as well as an ophiolitic complex paired with the northern mélange. In the GSZ, the serpentinite matrix of the mélanges formed by subduction-fluid hydration of deep mantle wedge. Finding serpentinite from both exhumed subduction channel mélange and ophiolite is not uncommon in paleo-suture zones, but recognizing them and their tectonic origin can be difficult.

A new method of discrimination has been developed based on *in situ* measurement of boron isotopes by LA-MC-ICP-MS in serpentine from both mélanges (6 samples) and ophiolite (4 samples), as well as in mica and pyroxene from the metamorphic and vein-rock blocks (15 samples) embedded within the mélanges.

Metamorphic and vein samples have very negative  $\delta^{11}\text{B}$ , as low as  $-15.3\text{‰}$ , in the same range as the serpentine from the mélanges (down to  $-14.4\text{‰}$ ). Besides being the most negative  $\delta^{11}\text{B}$  values ever measured in serpentinite, comparable values for minerals precipitated in veins and serpentine argues for a single subduction-sourced fluid. In contrast, serpentine samples from ophiolite have positive  $\delta^{11}\text{B}$ , in the range 0 to  $+18.0\text{‰}$ , consistent with hydration by seawater-derived fluid.

As the GSZ displays two different mélanges whose serpentinite originates from deep subduction, we hypothesize that the negative signature of exhumed mélange serpentine is indeed the norm and that the B isotopic signature should be a useful tool to discriminate the tectonic origin of serpentinite in paleo-suture zones.

## THE OMAN DRILLING PROJECT

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### Serpentinisation, Carbonation, Microbial Ecosystems

The Oman ophiolite, a block of oceanic crust and upper mantle that was thrust onto the Arabian continent ~100 million years ago, is an excellent field laboratory to explore rock forming processes that occurred near the surface down to 20 km depth in the Earth's interior. The chemical potential energy, resulting from the exposure of these rocks to surface conditions, drives heat generation, rapid reactions, expansion and cracking.

The Oman Drilling Project (OmanDP) will address long-standing questions regarding mantle melting, melt transport and crystallization of lavas at ocean spreading ridges to form ocean crust, characterize the nature and extent of water-rock interactions between oceans and oceanic crust, determine the extent of CO<sub>2</sub> and H<sub>2</sub>O uptake via weathering to form serpentine and carbonates, explore reaction-driven cracking mechanism as well as serpentinite-hosted microbial ecosystems. We will address these objectives via observations on core, geophysical logging, fluid and microbiological sampling, hydrological measurements and seismic monitoring in a series of newly drilled boreholes. We selected several drill sites in the Samail and Wadi Tayin massifs of the Oman ophiolite targeting the sheeted dike-gabbro transition, the mid- and lower crust, the crust-mantle boundary, the basal thrust as well as the active low-temperature serpentinization zone in the mantle peridotite. Recent surveys showed that active low-temperature serpentinization and carbonation of the upper mantle rocks is an ongoing process. Dissolved hydrogen and methane concentrations in fluid samples collected in existing in 300 m deep boreholes are up to 1.3 and 8 mmol/l, respectively [1]. Related to the near surface alteration of mantle rocks, a multi-boreholes test site will be established in the mantle peridotite of the Wadi Tayin massif that will facilitate in-situ studies of water-rock-microbe interactions.

Societally relevant aspects of the OmanDP include the involvement and training of university students, including numerous students from Sultan Qaboos University and the German University of Technology in Oman. Studies of the natural mineral carbonation at the multi-borehole test site in the mantle peridotite will contribute to design engineered systems for geological CO<sub>2</sub> capture and storage. Furthermore, studies of alteration of mantle rocks will further our understanding of reaction-driven cracking mechanisms, which could enhance geothermal power generation and extraction of unconventional hydrocarbon resources.

Technical details, scheduling of drilling activities and potential opportunities will be discussed.

[1] Paukert, A. PhD Thesis, Columbia University, New York, 2014.

## IRON AND MINERALOGICAL TRANSFORMATIONS IN SERPENTINITES FROM LOW TEMPERATURE REACTION SYSTEMS

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### iron, redox, Oman, Atlantis Massif

Iron redox reactions are a key component of the dynamic chemistry and potential habitability of low temperature serpentinizing systems. Water/rock reactions control fluid chemistry and the formation of secondary mineral phases and the oxidation of Fe(II) in (ultra)mafic minerals may reduce water to H<sub>2</sub> gas. Yet, relatively little is known about the speciation and partitioning of Fe into the diversity of secondary mineral phases that can form during low temperature serpentinization (<150°C).

Multiple complementary techniques are necessary to identify and characterize reactive Fe-bearing phases and thus unravel the dynamic history of Fe transformations during water/rock reactions. Detailed microscale geochemical studies of serpentinites from the Oman ophiolite and the Atlantis Massif (AM) allows us to assess the origin and fate of Fe in actively (or very recently) reacting rocks from distinct low temperature terrestrial and marine serpentinizing systems. The rocks cover gradients in extent of alteration (e.g. degree of serpentinization) and substrate lithology (gabbros, peridotites, serpentinites) allowing for characterization of the diversity of reactive minerals and alteration phases. QEMSCAN and Raman spectroscopy were used to identify and map the distribution of component minerals. Synchrotron radiation x-ray absorption spectroscopy was employed to identify and assess the oxidation state of Fe while wavelength dispersive spectroscopy was used to quantify Fe.

Partially serpentinized Oman rocks, considered the 'protoliths' of modern day low temperature alteration, possess a variety of FeII-bearing minerals, such as relict primary phases (olivine, chromite, and pyroxene), as well as secondary minerals (serpentine and brucite). All of these may act as reactive phases during low temperature alteration. Serpentine in protoliths is relatively Fe-rich and variably intergrown with Fe-brucite on the microscale. In the completely serpentinized Oman rocks, Fe-brucite is not present but FeIII-oxides are detected. At the bulk scale, Fe in the highly altered rocks is more oxidized than Fe in the protoliths. At the microscale, Fe in serpentine in the highly reacted rocks is more oxidized than in the protoliths. The notable mineralogical and chemical differences between the protoliths and the completely reacted serpentinites require extensive oxidation of Fe associated with modern day processes. In the absence of oxygen or nitrate, the mechanisms of alteration have the potential to generate H<sub>2</sub> such as that measured in hyperalkaline subsurface and spring waters in Oman. Similar characterization of variably altered AM rocks is in-progress. Some samples possess relict primary, as well as secondary, Fe-bearing phases while others are completely altered and contain only serpentine and magnetite. The oxidation state of Fe in these samples is being quantified and comparisons of the variety of Fe-bearing reaction products and the extent of oxidation will be made between these two unique systems.



## EXPERIMENTAL ADVENTURES IN THE LAND OF THE SERPENTINE

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### Experimental serpentinization, hydrogen generation, iron partitioning

Numerous experimental studies of serpentinization have been conducted over the years. In spite of these efforts, however, many fundamental aspects of serpentinization remain poorly understood, such as how rates of reaction and the composition of products vary as a function of environmental parameters like temperature and rock composition. Because experimental studies have been performed using many different methodologies, it is problematic to resolve these issues by comparing results from published work. For instance, reported rates of H<sub>2</sub> production in experimental serpentinization studies vary by several orders of magnitude at the same temperature, for reasons that are not yet clear.

To better understand how serpentinization reactions proceed under different reaction conditions, I have been working with several colleagues to conduct a series of laboratory experiments to examine how reaction rates and composition of products change as variables such as temperature, rock composition, and pH are systematically varied. The results have often been confounding, since seemingly minor changes in experimental conditions can produce very different outcomes. Nevertheless, some trends have emerged (e.g., McCollom et al., 2016), including: (1) in agreement with Malvoisin et al. (2012), reaction rates for serpentinization of olivine are 50-80 times slower than older studies indicated, (2) contrary to previous reports, orthopyroxene reacts much faster than olivine when both are included in experiments, (3) brucite becomes increasingly enriched in Fe with decreasing temperature, but its composition does not change with increasing H<sub>2</sub> or increasing extent of reaction as equilibrium models predict, and (4) dissolved SiO<sub>2</sub> concentrations in the experiments appear to be controlled by equilibrium between olivine and brucite, which seems to be consistent with some measurements from natural systems. At the conference, I will discuss the latest findings from these studies, including some curious results that continue to defy rational understanding.

Malvoisin, B., Brunet, F., Carlut, J., Rouméjon, S., & Cannat, M. (2012) Serpentinization of oceanic peridotites: 2. Kinetics and processes of San Carlos olivine hydrothermal alteration. *Journal of Geophysical Research* 117, doi:10.1029/2011JB008842.

McCollom, T. M., Klein, F., Robbins, M., Moskowitz, B., Berquó, T. S., Jöns, N., Bach, W., and Templeton, A. (2016) Temperature trends for reaction rates, hydrogen generation, and partitioning of iron during experimental serpentinization of olivine. *Geochimica et Cosmochimica Acta* 181, 175-200.

## ORGANIC CARBON DRIVES TRANSITION METAL DISTRIBUTION AND SECONDARY MINERALIZATION IN THE HYDRATED MANTLE-DERIVED OCEANIC CRUST

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### Organics, transition metal complexation and mobility, organomineralization, polyhedral and polygonal serpentine, supergene ore formation, mineral storage

Serpentinization is known to provide sustainable amounts of energy in the form of molecular hydrogen along with a suite of organic compounds of low molecular weights (as short chain alkanes and carboxylic acids), overall sustaining the development of chemolithotrophic microbial ecosystems within the mantle-derived crust. Those have a cryptoendolithic life style being responsible of the production of extracellular polymeric substances which allow structuring the community on the rock in the form of biofilm, along with the formation of biomass and metabolic organic byproducts (Ménez et al., 2012). In accordance, as recently evidenced, organic compounds can be diverse and widespread in the shallow mantle-derived crust where they undergo hydrothermal degradation and remobilization through fluid circulations (Pasini et al., 2013). Here we show that this organic carbon is directly involved in the dynamics of serpentinization. Notably, fine scale investigations of these niches using Scanning and Transmission Electron Microscopy along with Scanning Transmission X-ray Microscopy allowed to demonstrate that organic films generated at the mineral surface as a consequence of rock colonization or surface catalyzed organic synthesis influences the nature and the structure of serpentinization products along with transition metal (Mn, Fe, Co, Ni) mobility as the reaction progresses (Pasini et al., 2016). This likely constitutes an efficient but yet poorly considered mechanism in active serpentinizing systems with consequences on metal flux from oceanic hydrothermal systems to the ocean, and hence on crust and ocean habitability, up to ore formation associated with the alteration of ultramafic complexes in ophiolitic systems.

Ménez, B., Pasini, V., Brunelli, D., 2012. Life in the hydrated suboceanic mantle. *Nature Geoscience* 5, 133-137.

Pasini, V., Brunelli, D., Dumas, P., Sandt C., Frederick J., Benzerara K., Bernard S, Ménez B., 2013. Low temperature hydrothermal oil and associated biological precursors in serpentinites from Mid-Ocean Ridge. *Lithos* 178, 84-95.

Pasini V., Ménez B., Guyot F., Benzerara K., Bernard S., Brunelli D. Organic carbon drives transition metal distribution and secondary mineralization in the hydrated mantle-derived oceanic crust. *Earth and Planetary Science Letters*, to be submitted.

## CONSEQUENCES OF FE AND S REDUCTION DURING SERPENTINITE DEHYDRATION: EXPERIMENTAL STUDY

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Dehydration of serpentinites produces a large amount of H<sub>2</sub>O at elevated P-T conditions relevant for subduction settings. Our experimental results identified that this aqueous fluid has a different redox capacity at intermediate and high P-T conditions due to different degree of Fe and S reduction.

The progress of the redox reactions during serpentinite dehydration was constrained by experimental approach. The experiments were performed in piston-cylinder apparatus. Three serpentinites compositions varied in terms of bulk Fe, Fe<sup>3+</sup> and S contents were used. Intrinsic oxygen fugacity (fO<sub>2</sub>) of the experimental setup was stable at fO<sub>2</sub> ~QFM-2, close to conditions of subduction settings. Experimental results demonstrated decrease of initial high bulk Fe<sup>3+</sup>/Fe<sub>total</sub> ratios (0.9) of serpentinites down to ~0.2 in anhydrous high temperature assemblages through magnetite and Fe<sup>3+</sup>-bearing antigorite breakdown. Serpentinites without magnetite are shown to drastically reduce their Fe<sup>3+</sup>/Fe<sub>total</sub> at 650°C. Magnetite is occurred to be crucial for production of highly oxidized fluids and volatile sulfur species which can be transported from the subducting slab to the mantle wedge. The presence of pyrite, which transforms to pyrrhotite below 450°C, imposes a release of 25 % of initial sulfur, most-likely in H<sub>2</sub>S form.

The experimental approach with detailed characterization of mineral assemblages and bulk Fe and S speciation allowed to estimate quantitatively the amount of released H<sub>2</sub>O and redox potential of the released fluid at different steps of dehydration process. The extrapolation of experimental results to natural settings was accomplished with the help of thermodynamic modeling. We suggest that the presence of reduced species (e.g., sulfur and carbon) in subducting slab may drive elemental reduction in serpentinites. The results show that the fluid released at depths ~70 km within flat subduction geotherm is about 15 times more oxidized in comparison with the fluid formed at deeper levels (~120 km) of subduction. The demonstrated great oxidizing power of serpentinites could explain why mantle wedge peridotites and arc magmas are more oxidized compared to the upper mantle in other geological settings.

## SECONDARY OLIVINE IN OCEAN FLOOR SERPENTINES FROM THE MID-ATLANTIC RIDGE (13°30N)

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### **Ocean-floor serpentinite, secondary olivine, detachment fault**

Ocean floor detachment faults commonly expose serpentized peridotites resulting from the exhumation of mantle rocks altered during interaction with seawater. During the ODEMAR Cruise (Pourquoi pas, Nov-Dec 2013), we collected in situ a suite of ultramafic samples from the 13°30 detachment surface. Most of the serpentized ultramafic rocks display the usual serpentine and magnetite bearing mesh texture after olivine and bastite after orthopyroxenes. However, we have identified an occurrence of secondary olivine in a restricted location of this detachment. Some samples show secondary olivine in olivine pseudomorphs, forming small rounded grains that are occasionally aligned, and in some cases defining polygonal patterns. In all cases secondary olivines are associated with serpentine + talc. When secondary olivine occurs in orthopyroxene, it forms elongated grains that mimic the cleavage direction, and in association with talc + chlorite + serpentine. In both cases, small magnetite grains may be observed as inclusions in the secondary olivine. All secondary olivines are enriched in magnesium (Mg#94-98) compared with residual mantle olivine (Mg#90-92). We discuss the conditions of formation of these secondary olivines and the implications for the thermal regime of this detachment fault.

## EXPERIMENTAL AND THERMODYNAMIC CONSTRAINTS ON THE FORMATION OF CONDENSED CARBON FROM H<sub>2</sub>- and CO<sub>2</sub>-RICH HYDROTHERMAL FLUIDS

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### Abiotic compounds, carbonaceous material, thermodynamic modeling

Recent studies have identified macromolecular carbonaceous deposits in serpentinites recovered from the seafloor (Ménez et al., 2012; Pasini et al., 2013) but whether these deposits have a biogenic or an abiotic origin is still unclear. Laboratory experiments were carried out with synthetic siderite (FeCO<sub>3</sub>) and deionized water in the 200-300°C range and at 50 MPa to investigate the processes governing the speciation of carbon in H<sub>2</sub>- and CO<sub>2</sub>-rich hydrothermal fluids (Milesi et al., 2015). While the generation of CH<sub>4</sub> is kinetically hindered, thermodynamic calculations suggest that the H<sub>2</sub> and CO<sub>2</sub> produced by the transformation of siderite into magnetite achieve equilibrium with a solid carbon phase with thermodynamic properties close to those of graphite. This was confirmed by transmission electron microscopy observations of carbonaceous material coating the grains of magnetite, which may act as catalyst for the reduction of CO<sub>2</sub>. Additional thermodynamic calculations were performed to examine the potential for abiotic condensed carbonaceous material to be produced in the more general context of serpentinization of ultrabasic rocks under hydrothermal conditions. Calculation of reaction pathways during serpentinization of olivine showed that fluid compositions should equilibrate with condensed carbonaceous material (represented in the calculations by either graphite or anthracene), which regulates the H<sub>2</sub> and CO<sub>2</sub> activities. Fluids produced in serpentinization experiments as well as fluids sampled from ultramafic-hosted deep-sea hydrothermal systems at Lost City and Rainbow are shown to be consistent with this model. The calculations suggest that carbonaceous material should be a major product of the reduction of CO<sub>2</sub> in hydrothermal systems, which would have significant implications for the cycling of organic carbon in the oceanic crust by creating a pool of relatively immobile reduced carbon, which may be used by microorganisms as a source of energy. Alternatively, the carbonaceous material formed abiotically may react with water under different temperature-pressure-redox conditions to produce low-molecular-weight abiotic organic compounds.

Ménez B., Pasini V. and Brunelli D. (2012) Life in the hydrated suboceanic mantle. *Nat. Geosci.* **5**(2), 133-137.

Pasini V., Brunelli D., Dumas P., Sandt C., Frederick J., Benzerara K., Bernard S. and Ménez B. (2013) Low temperature hydrothermal oil and associated biological precursors in serpentinites from Mid-Ocean Ridge. *Lithos*, **178**, 84-95.

Milesi V., Guyot F., Brunet F., Richard L., Recham N., Benedetti M. and Prinzhofer A. (2015) Formation of CO<sub>2</sub>, H<sub>2</sub> and condensed carbon from siderite dissolution in the 200–300°C range and at 50MPa. *Geochim. Cosmochim. Ac.* **154**, 201-211.



## STRENGTH AND DEFORMATION RATE OF PLATE BOUNDARIES

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### Localization, Plate Boundaries, Oceanic lithosphere

Geodetic and moment release data have been used to compile global maps of lithospheric strain rate. Plate tectonics is clearly evident on these maps, which highlight the contrast between plate boundaries and plate interiors. The contrast in strain rate between the two can be up to six orders of magnitude, with continental plate boundaries and oceanic diffuse plate boundaries typically deforming at a factor of one thousand higher rate than plate interior. We develop rheological models that can explain this distribution of strain rate based on concepts of shear zone localization and structure evolution, which includes serpentinization.

The development of ductile shear zones can be understood as the effect of weakening a rock by changing its structure, either by reducing grain size, changing the mineral assemblage, or forming interconnected layers. If stress is externally controlled and therefore kept constant, such transformations result in an increased strain rate that is expressed as a combination of acceleration and narrowing of the deforming zone.

A similar concept can be applied to plate boundaries. Globally, stress is dominated by the current plate configuration, mainly by the negative buoyancy of slabs (slab pull) and the progressive thickening of the oceanic lithosphere (ridge push). Therefore, the stress integrated over the thickness of plate can be considered as an externally imposed variable. We calculate the strain rate for which the integrated strength of the lithosphere matches that stress. Then, we consider changes in rock structure and their effects on rheology, computing a new relation between strain rate and integrated stress.

When the grain size of an oceanic lithosphere changes from an initial value (e.g., 1 cm) to whichever value corresponds to a piezometric relation, the strain rate increases by about a factor of one thousand. This effect is sufficient to explain the formation of diffuse plate boundaries. Effects of similar magnitude are seen when considering the continental lithosphere. An additional process must be called for to explain the generation of narrow plate boundaries. The thinness of the lithosphere at mid-ocean ridges can concentrate stress and increase strain rate by another three orders of magnitude, but this concept does not work well for transform zones and cannot explain the formation of the plate boundary, only its maintenance.

We propose here that weakening due to hydration of the oceanic lithosphere, especially serpentinization combined with fabric development, reduces strength sufficiently to facilitate the formation of plate boundaries. Active serpentinization in diffuse plate boundaries, especially in the Central Indian Basin, may hint that this region is in the process of localizing and becoming a narrow plate boundary.

**NICKEL SPECIATION AND IRON REDOX DURING  
THE WEATHERING OF THE NEW CALEDONIA OPHIOLITE**

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**Nickel, Iron, XANES, Weathering, New Caledonia**

We investigate the mineralogy and crystal chemistry of the saprolite rocks of the Koniambo massif (New Caledonia). We sampled a boulder rock (~20 cm in diameter) in the saprolite facies to understand the first stages of bedrock weathering (Ulrich et al., 2014). A polished cross-section of the boulder reveals a radial weathering profile. “Fresh” serpentized-harzburgite is localized in the center (Zone 1), while a gradually increasing weathering is observed from the center to the edge (Zone 2 to 3) of the boulder. Large-scale  $\mu$ XRF maps performed on the polished surface reveal a dense network of Ni-rich mineral veins in the external part of the boulder. Thin sections corresponding to the different weathering Zones were characterized by optical microscope, electron microprobe (BSE, micro-analyses, X-ray maps), and Raman spectroscopy. In addition, Fe and Ni-K edge XANES spectra were collected at the BM23 beamline of the ESRF to constrain, respectively, the oxidation state and the speciation of these two cations.

In Zone 1, lizardite – most likely related to the oceanic hydrothermal alteration – is observed, including ~0.2 to 0.4 wt% of NiO and a ferric-to-total iron ratio (i.e.,  $XFe^{III}$ ) of ~0.5. In Zone 2, oceanic lizardite is still observed, together with partially recrystallized/neofomed lizardite enriched up to ~1.5 wt% of NiO;  $XFe^{III}$  increases up to 0.6-0.7. Zone 3 shows a dense network of phyllosilicate veins, mainly composed of three different types of lizardite with various chemical composition, i.e., 0.8 to 5 wt% NiO, and 0.4 to 2 wt%  $Al_2O_3$ . Petrological observations show a reactivation of the lizardite network through the precipitation of highly concentrated Ni-talc-like (kerolite) in the central part of the veins (Cathelineau et al., 2015, 2016). A first generation concentrates nickel up to ~20 wt% NiO, which appears to be subsequently replaced by a kerolite vein at ~36 wt% NiO; both minerals are highly depleted in iron (0.4 and 0.1 wt%, respectively).  $XFe^{III}$  ranges from 0.8 to 1 in those veins, showing a clear correlation between the occurrence of Ni-bearing phases and the  $XFe^{III}$  ratio in neofomed phyllosilicates.

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## RATES OF FORE-ARC MANTLE SERPENTINIZATION AND THEIR IMPLICATIONS FOR THE UPWELLING CONDITION OF SLAB-DERIVED FLUID: AN EXPERIMENTAL STUDY

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### Fore-arc mantle, slab-derived fluid, antigorite

Seismic observations of subduction zones where slab dehydration in fore-arcs is considerable (i.e., relatively hot subduction zones) have suggested extensive serpentinization of the fore-arc mantle wedge (e.g., Bostock et al., 2002). Geodynamic modellings indicated that the fore-arc mantle should be stagnant and thus be cold enough to react with water to form serpentine minerals (Wada et al., 2008). On the hand, recent geochemical and isotopic studies of fore-arc hot spring water have revealed that slab-derived fluid upwells directly from the dehydrating slab through the mantle wedge without causing significant reaction with country rocks or mantle melting in hot subduction zones (e.g., Morikawa et al., 2016). To correlate these geophysical and geochemical observations and to obtain a complete understanding of fluid circulation in fore-arc regions, reaction-transport modeling based on the peridotite hydration rate is crucial.

In order to constrain the hydration rates of fore-arc peridotites, series of hydration experiments were conducted at 400–580°C and 1.3 and 1.8 GPa, where antigorite is expected to form as a stable serpentine phase. Crushed powders of olivine ± orthopyroxene and orthopyroxene + clinopyroxene were reacted with 15 wt% distilled water for 4–19 days. The synthesized serpentine varieties were identified to be lizardite and aluminous lizardite (Al-lizardite) in all experimental conditions except those of 1.8 GPa and 580°C in the olivine + orthopyroxene system, in which antigorite was formed. In the olivine + orthopyroxene system, the reactions were interface controlled except for the reaction at 400°C, which was transport controlled. The corresponding reaction rates were  $7.0 \times 10^{-12}$ – $1.5 \times 10^{-11}$  m s<sup>-1</sup> at 500–580°C and  $7.5 \times 10^{-16}$  m<sup>2</sup> s<sup>-1</sup> at 400°C for the interface- and transport-controlled reactions, respectively. Based on a simple reaction-transport model with these hydration rates, we infer that leakage of the slab-derived fluid through a water-unsaturated fore-arc mantle is permitted only when focused flow occurs with a spacing larger than 77–229 km in hot subduction zones such as Nankai and Cascadia. In contrast, the necessary spacing is only 2.3–4.6 m in intermediate-temperature subduction zones such as Kyushu and Costa Rica. These calculations suggest that fluid leakage in hot subduction zones may occur after the fore-arc mantle is completely hydrated, whereas in intermediate-temperature subduction zones, leakage through a water-unsaturated fore-arc mantle may be facilitated.

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**STRUCTURAL, MINERALOGICAL AND GEOCHEMICAL EVIDENCES OF MULTIPLE CO-GENERATIONS OF SERPENTINE AND CARBONATE FROM COMPLETELY ALTERED HARZBURGITE BASEMENT (WADI DIMA, OMAN OPHIOLITE).**

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**Serpentinization, Carbonatization, Oman ophiolite**

The mantle section of the Oman ophiolite records multiple stages of hydrothermal alteration (serpentinization, carbonatization and redox reactions) from the ocean ridge to the ophiolite system. Hydrothermal alteration contributes to global geochemical cycles of volatile elements, in particular for CO<sub>2</sub>. In order to investigate the links between serpentinization and carbonatization, we performed an integrated structural, petrological and geochemical study of a suite of five oriented cores of completely serpentinized harzburgites, sampled in the Wadi Dima area (Southern Massif of Oman ophiolite). We used a multi-method approach coupling electron microprobe, electron backscattered diffraction, Raman spectrometry, and X-ray microtomography to characterize the samples from the µm- to the cm-scale.

The studied harzburgite samples are completely serpentinized, dominantly by mesh textured lizardite. They are crosscut by abundant carbonate veins which represent up to 20% of the sample. The most abundant type of carbonate veins is large (> 5 mm width) sub-vertical veins that are oriented NE-SW and NW-SE (type A). They are composed of well developed calcite crystals that are locally replaced by small grains of dolomite and calcite. In one sample (*15WadiDima44*), we observed crack-seal structures. The second type of carbonate veins (type B) correspond to thin veins (< 1 mm) composed of well-developed calcite. Type B veins are perpendicular to type A veins and seem to merge with calcite minerals infilling type A veins. In the serpentinized harzburgite matrix, we distinguished two zones. The first zone borders type A carbonate veins, displays a mesh texture with lizardite veins (Mg# 92-94, CaO 0.02-0.04 wt%) inclosing Fe-rich chrysotile (+/- lizardite) cores (Mg# 74-83, CaO 0.02-0.1 wt%). In the second zone, > 1 cm from type A carbonate veins, mesh texture serpentine becomes Ca-enriched with lizardite veins (Mg# 86-93, CaO 0.1-0.2 wt%); and chrysotile (+/- lizardite) cores (Mg# 89, CaO: 0.12 wt%). Locally, serpentine cores are partially to completely replaced by Mg-bearing calcite.

We propose that lizardite veins formed at the onset of serpentinization at ridges, growing along cracks after primary olivine and pyroxenes (stage S1). S1 type lizardite is typically associated with relicts of olivine or to lizardite cores in partially serpentinized peridotites in Oman. Generation of chrysotile-dominated cores after relicts of olivine or lizardite cores (stage S2) due to interaction with seawater- or sediment-derived hydrothermal fluids during aging of oceanic lithosphere and/or obduction. Stage 3 produced carbonatization of the serpentinized peridotite and generation of carbonate veins. Carbonatization is associated to ductile deformation and dynamic recrystallization of calcite (> 150 °C). The carbonatization process probably continues today. Its relation with on-going serpentinization is discussed.

**THE HIGH-PRESSURE ANTIGORITE DEHYDRATION:  
 A REVIEW OF THE UNIQUE RECORD OF CERRO DEL ALMIREZ  
 (BETIC CORDILLERA, SE SPAIN)**

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**Fluid release, natural laboratory, subduction zones**

The occurrence of serpentinite bodies in structurally deep units of mountain belts (crystalline basements s.l.) has been noticed since the first efforts of regional mapping (e.g. Von Drasche 1879), captivating the attention of early 20<sup>th</sup> century geologists (e.g. Staub, 1922) but also of pioneering experimental petrologists (Bowen and Tuttle, 1949, Raleigh and Paterson, 1965). In the Alpine orogen serpentinite and associated ultramafic rocks record a complex exhumation and subduction history that in places resulted in the partial or complete dehydration of antigorite (the stable serpentine variety at high pressure and high temperature). A classical example is found in the Malenco serpentinite (N Italy, Trommsdorff and Evans, 1972) affected by regional and contact metamorphism where serpentinite dehydrated first to the low pressure assemblage talc + olivine +/- chlorite. At higher temperature this assemblage is replaced by olivine + enstatite +/- chlorite. At higher pressure (> 1.2 GPa) antigorite dehydrates directly to olivine + enstatite +/- chlorite. This reaction was experimentally constrained by Ulmer and Trommsdorff (1992) and it has profound implications for our understanding of subduction zones. Although this landmark paper bloomed the current interest of serpentinite in our community, a natural equivalent of the high pressure antigorite dehydration reaction was not found until the reinterpretation made by Trommsdorff and coworkers in 1998 of the significance of the Cerro del Almirez outcrop in the Betic cordillera, SE Spain (first described by Jansen in 1936 as of magmatic origin). Since then, this unique has been (and it is still) intensively investigated. This contribution will review the main findings since 1998 and delineate future challenges to be addressed.

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## THE FATE OF CARBON DURING EXPERIMENTAL SERPENTINIZATION OF PERIDOTITE

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### Carbon, Hydrogen, Hydrocarbons

Serpentinization of peridotite is a widespread process with key emerging societal and environmental implications, such as the production of hydrogen as a source of carbon-free energy. In the presence of CO<sub>2</sub>, hydrogen may also be converted into methane and more complex hydrocarbons via Fischer-Tropsch-Type (FTT) synthesis. These reactions control part of the fluxes and global budget of carbon within the Earth. But they are still little known. Up to now, most of the experiments were carried out in simplified aqueous systems focusing either on the gaseous phase or the liquid one. Our approach was to develop an experimental protocol for quantifying carbon speciation and balance during serpentinization in both liquid-solid and liquid-solid-gas systems by coupling solid, liquid and gas analyses. We also assessed the problem of C contamination during analyses by running blanks in parallel to serpentinization experiments. Ten experiments were conducted on olivine powders (Fo<sub>91</sub>; 50-150 μm) in both single-phase fluid (gas) and two-phase fluid (gas and liquid) environments under typical conditions of hydrothermal vents (250°C; 15 MPa). The experimental fluid was a MilliQ water enriched in NaCl (0.55 m – seawater salinity), CO<sub>2</sub> (0.1 m NaHCO<sub>3</sub>) and Al (0.1 m AlCl<sub>3</sub>). The advantage of using Al is twofold: characterizing its effect on the kinetics of serpentinization as was observed at 200-300°C and 200 MPa (Andreani et al., 2013) and simulating complex natural systems like troctolites.

Our results show no major effects of Al on the kinetics of serpentinization in these low P conditions; only ~3 % of serpentine was formed in all experiments. Serpentine has a typical lizardite structure and is generally associated with magnetite. Raman analyses also revealed the formation of hematite and C-rich phases with an organic signature along dissolved olivine surfaces. According to bulk rock analyses, total amount of CO<sub>2</sub> trapped in reacted olivine powders is on average higher in the single-phase fluid system (0.11 - 0.15 wt. % including 0.02 wt. % of organic C) than in the two-phase fluid one (0 - 0.17 wt. % including 0.01 wt. % of organic C). Regarding the fluids, μGC analyses showed an efficient and increasing production of H<sub>2</sub> and CH<sub>4</sub> in the serpentinization experiments compared to the blanks: up to 3 mmol/Kg of H<sub>2</sub> and 0.3 mmol/Kg of CH<sub>4</sub> in both systems. GC-MS analyses moreover identified the formation of heavier hydrocarbons (up to C<sub>5</sub>) in the two-phase fluid experiments. These results suggest that the nature and reactivity of redox and FTT processes during serpentinization depend on environmental conditions. A two-phase fluid system favors the production of heavy hydrocarbons while a single-phase fluid environment tends to promote the fixation of solid carbon at olivine surfaces.

Andreani M., Daniel I., Pollet-Villard M. (2013). Aluminum speeds up the hydrothermal alteration of olivine. *American Mineralogist*, 98, 1738-1744.

## POLYPHASED BRECCIATION SYN- TO POST-TECTONIC VERSUS CONTINUOUS CARBONATION ILLUSTRATED BY THE IBERIA-NEWFOUNDLAND MARGINS BASEMENT

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### Brecciation, ophicarbonates, replacement, stable isotopes

While increasingly studied, the relationship between carbonation and brecciation during and after exhumation of (ultra) mafic rocks to the seafloor remains fuzzy. Different types of breccias were described in the IODP cores Sites 1068, 1070 from Iberia margin and Site 1277 from Newfoundland margin over 18 to 58m-long (Whitmarsh et al, 1998; Tucholke et al, 2004). Here, we distinguish three types of breccias according to their formation setting, i.e. 1) tectonic breccias; 2) hydrothermal breccias and 3) sedimentary breccias. The aim is to characterize the setting (i.e. syn-tectonic and/or post-tectonic) of brecciation and carbonation. For this we combine the study of specific features of each type of breccias textures to the textures and temperature of carbonate formation. We differentiate carbonate replacing serpentinite from the carbonate growing in a sedimentary environment.

The combination of microprobe, SEM and cathodoluminescence was cogent to observe the contacts between serpentine and carbonates and to understand mineral growth. Moreover, the analyses of  $\delta^{18}\text{O}$  for carbonates was performed using conventional bulk techniques for veins and matrix, as well as SwissSIMS in-situ facility in Lausanne for carbonate replacing serpentinites.

We propose that carbonate replacing serpentine initiates in tectonic breccias and is characterized by carbonate growth in the mesh core as well as veining surrounding serpentinite clasts. In hydrothermal breccias, carbonate is growing in a vein setting, and in sedimentary breccias, carbonate is either replacing serpentinite, or growing as a fine-grained matrix. Cathodoluminescence tell us about the redox conditions of the fluids responsible for carbonate grain growth. Preliminary results on  $\delta^{18}\text{O}$  from ophicarbonates replacing serpentine give us a higher temperature than for the sedimentary carbonates. In Site 1070 serpentinite, no replacement features were observed in mesh cores or carbonate veins do not surround serpentinite clasts, thus we interpret that carbonation is only post-tectonic in this localized area (Site 1070), whereas carbonation starts while the detachment fault is still active in Sites 1068 and 1277. Ultimately, we use equilibrium thermodynamic modeling to calculate the stability field and composition of carbonates as a function of fluid/rock ratio and temperature.

Tucholke, B.E., Sibuet, J.-C., Klaus, A., et al., (2004). Proceedings of the Ocean Drilling Program, Initial Reports Volume 210.

Whitmarsh, R. B., Beslier, M. O., & Wallace, P. J. (1998). Proceedings of the Ocean Drilling Program, Initial Reports Volume 173, p. 493.

**$\delta^{18}\text{O}$  ISOTOPIC ANALYSIS WITH SWISSSIMS TO ILLUSTRATE SYN- TO POST-TECTONIC CARBONATION IN THE IBERIA-NEWFOUNDLAND MARGINS BASEMENT**

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**Brecciation, ophicarbonates, replacement, stable isotopes, SwissSIMS**

In this poster we detail the three types of breccias presented in the oral presentation. These breccias are distinguished according to their formation setting, i.e. 1) tectonic breccias; 2) hydrothermal breccias and 3) sedimentary breccias. The aim is to characterize the setting (i.e. syn-tectonic and/or post-tectonic) of brecciation and carbonation. Different types of breccias were described in the IODP cores Sites 1068, 1070 from Iberia margin and Site 1277 from Newfoundland margin over 18 to 58m-long (Whitmarsh et al, 1998; Tucholke et al, 2004).

Here we describe the methodology used to understand the carbonate growth. We combine cathodoluminescence to  $\delta^{18}\text{O}$  analyses with the SwissSIMS in-situ facility in Lausanne. Cathodoluminescence tells us about the redox conditions of the fluids responsible for carbonate grain growth. Preliminary results on  $\delta^{18}\text{O}$  from ophicarbonates replacing serpentine give us a higher temperature than for the sedimentary carbonates. In Site 1070 serpentinite, no replacement features were observed in mesh cores or carbonate veins do not surround serpentine clasts, thus we interpret that carbonation is only post-tectonic in this localized area (Site 1070), whereas carbonation starts while the detachment fault is still active in Sites 1068 and 1277.

## D/H DIFFUSION IN SERPENTINE

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### Diffusion, isotopes, fluid-rock interactions

Interactions between aqueous fluids and ultrabasic rocks are essential processes in a broad range of contexts including hydrothermal alteration on the parent body of carbonaceous chondrites, at mid-oceanic ridge, and in subduction zones. Tracking these processes and understanding reaction kinetics requires the knowledge of the diffusion of water in rocks, and of isotopes in major minerals forming under such conditions, such as serpentines. We present a study of D-H interdiffusion in antigorite, an abundant variety of serpentine. For that purpose, two types of exchange experiments were conducted. High-temperature (HT) experiments were performed in a belt apparatus at 540°C and 3.0 GPa on natural antigorite powders and interstitial D<sub>2</sub>O. A low-temperature (LT) experiment was performed in diamond anvil cell at 350°C and 2.5 GPa on an antigorite single-crystal loaded with pure D<sub>2</sub>O. D/(D+H) ratios were mapped using Raman spectroscopy for the HT experiment and from nano-SIMS for the LT experiment. As antigorite is a phyllosilicate, diffusion coefficients were obtained for crystallographic directions parallel and perpendicular to the antigorite layers (perpendicular and parallel to the *c*\*-axis, respectively). The equations of D/H interdiffusion coefficients were determined to be  $D_{H-D} \text{ (m}^2\cdot\text{s}^{-1}\text{)} = 5.04 \times 10^{-5} \exp(-170(\pm 53) \text{ (kJ}\cdot\text{mol}^{-1}\text{)} / RT)$  and  $D_{H-D} \text{ (m}^2\cdot\text{s}^{-1}\text{)} = 1.52 \times 10^{-7} \exp(-157(\pm 32) \text{ (kJ}\cdot\text{mol}^{-1}\text{)} / RT)$  perpendicular and along the *c*\*-axis, respectively, and  $D_{H-D} \text{ (m}^2\cdot\text{s}^{-1}\text{)} = 7.29 \times 10^{-6} \exp(-166(\pm 14) \text{ (kJ}\cdot\text{mol}^{-1}\text{)} / RT)$  for the bulk diffusivity. These results are similar to those obtained on chlorite, in consistency with the similar crystallographic structures and atomic bonds in the two minerals. Assuming D/H inter-diffusion coefficients for antigorite are the same for all serpentine species, closure temperature and diffusion durations are calculated in the case of hydrothermal fields and in CI and CM chondrites. Closure temperatures lie below 300°C for terrestrial hydrothermal alteration and depend on serpentine variety with different typical grain sizes. They lie below 100°C for carbonaceous chondrites, indicating that D/H isotopic exchange may have persisted down to very low temperatures on their parent bodies. D/H isotopic difference associated with diffusion may occur according to grain size heterogeneities.

## A QUANTITATIVE APPROACH OF SEAWATER STORAGE AND ELEMENT TRANSFER RELATED TO MANTLE SERPENTINIZATION IN MAGMA-POOR RIFTED MARGINS:

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### Serpentinization, water storing, element transfer, OCT

Magma-poor rifted margins can consist of hundreds of km long and up to 180 km wide Zones of Exhumed Continental Mantle (ZECM). In these zones the serpentinization of mantle rocks can extend down to 5-6 km, as observed in refraction seismic data. The formation of such high volumes of serpentinized rocks, by the seawater intrusion and circulation through the exhumation process, has the potential to change the seawater chemistry, sustain the evolution of primitive life, control the depositional environments, and form weak zones preferentially used during the formation of distal rifted margin and their reactivation during the onset of subduction.

Based on geological observations, geophysical and geochemical data from and fossil ZECM a first-order quantification shows that approximately  $0.380 \text{ km}^3$  of water per  $\text{km}^2$  can be stored in the mantle. This estimation of the amount of mantle hydration was done using the interpreted IAM-9 (Iberia Margin) reflection and refraction seismic data. We postulate that the serpentinization starts at km 270 and extends to km 30, i.e., from the mantle underlying the hyperextended crust to the end of the J-anomaly. ODP drilling record shows that basalt and gabbro are rare or absent. The correlations between  $V_p$ , density and serpentinization degrees (and their equivalents in wt.% of water) can be done. Then, a first order calculation allows to quantify the amount of absorbed water in the ZECM: the average wt.% of water ranges from 5% in the Coupled Domain, 8% in the ZECM, and 9% in the Embryonic Oceanic Crust. These values establish that about  $17,142 \text{ km}^3$  of water was absorbed in the  $45,006 \text{ km}^2$  of serpentinized mantle (Pinto et al. submitted).

On other hand, the mass budget and element transfer during serpentinization was established using a simple mass balance calculation based on whole rock geochemical data from an exhumed mantle domain from the Alps, which includes weak ( $\leq 10\%$  serpentinization), moderate and completely ( $> 60\%$ ) serpentinized samples (Pinto et al. 2015). The mantle serpentinization reactions can induce a significant loss of Si, Mg, Fe, Mn, Ca, Ni and Cr, and their transfer to the marine and sedimentary environments. Especially during the formation of embryonic oceans, when basins are often restricted and seaways are not yet connected, massive serpentinization of mantle rocks during their exhumation may result in a major transfer of elements between the main Earth reservoirs, such as the mantle and seawater.

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**PROBING THE BIOLOGICAL vs ABIOTIC ORIGIN OF ORGANIC CARBON WITHIN SERPENTINITES USING CHEMOMETRICALLY-ASSISTED FOURIER TRANSFORM INFRARED MICROSCOPY**

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**Deep carbon cycle, deep life, abiotic organic molecules, carbon speciation, multiset analysis, Multivariate Curve Resolution**

The recognized capability of serpentinization to generate abiotic organic compounds and to sustain an intraterrestrial life raise questions about the distribution of biotic/abiotic organic carbon vs inorganic ones at depth and how it impacts the global carbon cycle. It is then mandatory to increase our knowledge on the nature and extent of carbon reservoirs at depth. It implies to be able to characterize organic molecules within hydrated oceanic rocks and to determine their biological or abiotic origin. But, this might be hampered by their scarceness and heterogeneous distribution in serpentinites. We then developed a combination of hyperspectral techniques to track organic molecules at the pore level in oceanic rocks using, among them, Synchrotron-based Fourier Transform Infrared microscopy (Sr-FTIR).

Sr-FTIR hyperspectral images, with 108 to 360 individual spectra/image, were acquired on natural serpentinized peridotites containing organic carbon (IODP exp. 304/305; Blackman et al. 2006). Due to the complexity of these geobiological samples, including numerous mineral and organic phases with a high spatial variability, the acquired data were multicomponent spectra. In order to extract pure organic and mineral components and to precisely determine their relative spatial distribution, we applied a chemometric approach. We analyzed each individual map as well as multiple combinations of these maps (multiset analysis) using Principal Component Analyses (PCA) and Multivariate Curve Resolution (MCR) routines from Matlab software (de Juan et al. 2004, Felten et al. 2015, Piqueras et al. 2015).

PCA analyses of individual maps allowed correlating some mineral phases between each other and with organic ones but were strongly influenced by the dominant species of each individual map. They provided only 3 informative principal components (PC), which precluded a precise characterization of all the phases of the system that were much more numerous. Conversely, combining hyperspectral maps together (multiset analysis), each of them being representative of different organic/mineral assemblages, increased the efficiency and reliability of the extraction of pure components. The variance was then expressed into 6 PC. MCR analyses provided robust resolved FTIR spectral signatures of 8 pure components of the system either of mineral (olivine, serpentine, Fe-rich serpentine, clays) or biological/abiotic organic origin. The subsequent reconstruction of the distribution of these pure components gave us a fine representation of the spatial relationships between minerals, organic phases and reactive interfaces (Pisapia et al. *subm*). Consequently, in order to track biological or abiotic organic molecules in rocks and to be able to distinguish the process from which they derive, an appropriate experimental strategy looking for several distinct representative areas rather than to focus on organic-rich areas, and hence multiset data analysis, is highly recommended.

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## ABIOGENIC METHANE PRODUCTION DURING MANTLE PERIDOTITE ALTERATION AT NEAR AMBIENT CONDITIONS

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### serpentinization, abiogenic methane, catalysis,

The occurrence of abiogenic hydrocarbons, particularly methane (CH<sub>4</sub>), has been recognized in a variety of geological settings on Earth. These settings include seafloor hydrothermal systems, fracture networks in crystalline rocks from continental and oceanic crust, volcanic gases, and gas seeps from serpentinized rocks (e.g., Sherwood Lollar, 2006). Recent investigations also suggest the presence and production of abiogenic CH<sub>4</sub> on other rocky planets such as Mars (e.g., Mumma et al. 2009). Understanding the origin and mechanisms of abiogenic hydrocarbon formation has significant implications for a range of topics, encompassing the global carbon cycle, the origin of life, the distribution of life within the deep subsurface, and as a potential contributor to hydrocarbon reservoirs. Particularly mantle peridotite hydration, i.e. serpentinization, has been invoked to play a key role in the synthesis of abiogenic CH<sub>4</sub>. Although CH<sub>4</sub> synthesis is known to occur in the presence of metal alloys or chromite during serpentinization at T>200 °C, little is known about the potential for massive CH<sub>4</sub> catalysis at low-temperatures, within the temperature limits of life. Here, we present the results of our investigations into catalysis of massive, low-temperature (~50 °C) production of, primarily, abiogenic CH<sub>4</sub> at the Chimaera site, Turkey (Etiope et al., 2011). The original CH<sub>4</sub> reservoir is estimated to be thousands to millions of cubic meters making it the Earth's largest onshore abiogenic CH<sub>4</sub> seep. Carbon required for CH<sub>4</sub> synthesis is provided through nearby limestone dissolution and a hydrogeological aquifer system that is connected to the peridotite body (Etiope et al., 2011). Hydrogen is generated through massive Fe-oxidation during peridotite alteration. The combination of bulk-rock Fe<sup>3+</sup> and serpentine mineral chemistry analysis with saturation remanent magnetization analysis implies that at Chimera oxidation (Fe<sup>3+</sup> content up to 85%) and H<sub>2</sub>-production occurred with negligible magnetite production (0.5-1%) and incorporation of Fe<sup>3+</sup> into serpentine, suggesting low temperature serpentinization (e.g., Klein et al. 2013). This is supported by clumped isotopes thermometry of carbonated serpentinites directly associated to the CH<sub>4</sub> seeps, showing that carbonate formation temperatures are equivalent to previously determined CH<sub>4</sub> formation temperatures. As the serpentinites are particularly enriched in altered chromite and lack Ni-Fe alloys, we argue that CH<sub>4</sub> catalysis occurs within the mesoporous network of a nanocrystalline spinel phase, a product of chromite alteration. Nanotomography combined with transmission electron microscopy shows that the spinel pore network has a strong preferred pore wall orientation and high surface area aiding catalytic reactions. We conclude that although CH<sub>4</sub> formation is kinetically hindered over carbonate precipitation, environments such as the one investigated here can sustain large fluxes of abiogenic CH<sub>4</sub> over geological timescales.

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## SERPENTINIZATION AND CL-RICH FLUIDS IN SUBDUCTION ZONES

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### **Subduction, mantle wedge, fluids**

In the forearc region, aqueous fluids are released from the subducting slab at a rate depending on its thermal state. Escaping fluids tend to rise vertically unless they meet permeability barriers such as the deformed plate interface or the Moho of the overriding plate. Channeling of fluids along the plate interface and Moho may result in fluid overpressure in the oceanic crust, precipitation of quartz from fluids and low Poisson ratio areas associated with tremors. Above the subducting plate, the forearc mantle wedge is the place of intense reactions between dehydration fluids from the subducting slab and ultramafic rocks leading to extensive serpentinization. The plate interface is mechanically decoupled, most likely in relation to serpentinization, thereby isolating the forearc mantle wedge from convection as a cold, potentially serpentinized and buoyant, body. Geophysical studies are unique probes to the interactions between fluids and rocks in the forearc mantle, and experimental constrains on rock properties allow inferring fluid migration and fluid/rock reactions from geophysical data. Seismic velocities reveal high degree of serpentinization of the forearc mantle in hot subduction zones, and little serpentinization in the coldest subduction zones because the warmer the subduction zone, the higher the amount of water released by dehydration of hydrothermally altered oceanic lithosphere. Interpretation of seismic data from petrophysical constrain is limited by complex effects due to anisotropy that need to be assessed both in the analysis and interpretation of seismic data. Electrical conductivity increases with increasing fluid content and temperature of the subduction. However the forearc mantle of Northern Cascadia, the hottest subduction zone where extensive serpentinization was first demonstrated, shows only modest electrical conductivity. Electrical conductivity may vary not only with the thermal state of the subduction zone, but also with time for a given thermal state through variations of fluid salinity. High-Cl fluids produced by serpentinization can mix with the source rocks of the volcanic arc and explain geochemical signatures of primitive magma inclusions. Signature of deep high-Cl fluids was also identified in forearc hot springs. These observations suggest the existence of fluid circulations between the forearc mantle and the hot spring hydrothermal system or the volcanic arc. Such circulations are also evidenced by recent magnetotelluric profiles.

## HYDROTHERMAL ALTERATION OF PERIDOTITES EXHUMED ON THE SOUTHERN WALL OF THE ATLANTIS MASSIF

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### Atlantis Massif, ocean drilling, serpentinization sequences

Peridotites are commonly exhumed and altered along detachment faults at slow-spreading ridges. This is the case at the Atlantis Massif (Mid-Atlantic Ridge, 30°N), where serpentinized and metasomatised harzburgites and dunites, associated with gabbros and dolerites, have recently been drilled by the IODP Expedition 357 (Dec. 2015, RSS James Cook). The recovered peridotites belong to nine shallow (max. 16.4 meters) holes spread among three sites forming an east-west transect on the southern wall of the massif, in the vicinity of the Lost City hydrothermal field. This spreading-parallel transect allows examination of small-scale (100 m to km) alteration heterogeneities in the crust, linked to hydrothermal alteration, as a function of lithosphere aging and initial depth.

This petrological study primarily focuses on the serpentinization history, with a characterization of textures and mineralogical assemblages, and in situ major and trace elements chemistry. It involves a set of 30 samples selected to cover the diversity of serpentinization textures found in the holes.

All sites exhibit high to complete serpentinization (90-100%) that overprints primary mantle textures. However, the sequence of serpentinization textures varies between sites and holes and typically includes lizardite-dominated mesh texture after olivine, recrystallization textures into chrysotile-polygonal serpentine or antigorite, and a set of veins (e.g., fibrous, banded). Most of these textures are associated with magnetite crystallization. Pyroxenes show diverse alteration to serpentine, talc, tremolite, or chlorite. In addition, some holes present further metasomatism leading to the progressive replacement of serpentine by talc ( $\pm$  chlorite, amphibole), and/or later carbonate veins.

This presentation will provide a detailed description of these textural sequences in order to estimate the conditions of alteration and their scales of heterogeneity. The results will be discussed in the light of major and trace elements systematics that give indications on chemical transfers within the hydrothermal system.

## INVESTIGATIONS OF METHANE, SULFUR, AND IRON IN THE SERPENTINITE SUBSURFACE USING DEPTH-RESOLVED BIOGEOCHEMICAL ANALYSES, STABLE ISOTOPE GEOCHEMISTRY, AND MICROCOSM APPROACHES

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### Microcosms, Methane, Biogeochemistry

Serpentinizing systems are considered to be an analogue for geologic processes throughout the Solar System, in locations such as Mars, Europa, and Enceladus. Characterizing the unique geomicrobiology and of these systems has potential to yield insight into the potential for life on those worlds. The more we can learn from accessible analogue sites on Earth, the more focused and streamlined searches can become in resource-limited extraterrestrial locations. Because methane is widespread within the serpentine subsurface, understanding its origins and fate can provide essential information about carbon cycling, redox reactions, and microbial activity. To this end, we conducted a detailed investigation of biological methane oxidation within the serpentine groundwater at the Coast Range Ophiolite Microbial Observatory (CROMO), to constrain how microbial community composition and activity is linked to methane, sulfur, and iron availability with depth.

Depth profiles of methane, methane stable isotopes, oxygen, iron, sulfur, pH, and microbial community composition (16S rRNA analysis) were determined in the water column occupying a purpose-drilled borehole (CSW1,1) at CROMO. Samples were collected at depths where dissolved oxygen concentrations were 100%, 50%, 15%, and 0% of air saturation. In parallel, microcosm incubations were conducted to quantify rates of methane consumption. From the 15% O<sub>2</sub> air saturation point and the anoxic well bottom, groundwater was pumped directly into bottles for laboratory incubation. All bottles were inoculated with 50cc of 20% <sup>13</sup>CH<sub>4</sub>: 80% <sup>12</sup>CH<sub>4</sub> gas, with parallel experiments run following the addition of iron-hydroxide or thiosulfate respectively. Changes in fluid chemical composition were monitored by colorimetric methods (HS<sup>-</sup>, ferrous and total iron), ICP-MS (total sulfur, iron), and gas chromatography (methane). The evolution of <sup>13</sup>C labeled CO<sub>2</sub> -- the presumable product of methane oxidation -- was quantified using membrane-inlet mass spectrometry (MIMS) and, as an independent control, isotope ratio mass spectrometry (IRMS). The results of these in-progress microcosms and geochemical analyses will be presented.



## CARBONATION OF SUBDUCTION-ZONE SERPENTINITE AND IMPLICATIONS FOR THE DEEP CARBON CYCLING

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### Serpentinite, carbon, subduction

Much of the long-term carbon cycle in solid earth occurs in subduction zones, where devolatilization, partial melting of carbonated rocks, and dissolution of carbonate minerals lead to the return of CO<sub>2</sub> to the atmosphere via volcanic degassing. Release of COH fluids from hydrous and carbonate minerals influences C recycling and magmatism at subduction zones. Contradictory interpretations exist on the retention/storage of C in subducting plates and in the forearc to subarc mantle. Several lines of evidence indicate mobility of C, of uncertain magnitude, in forearcs. A poorly constrained fraction of the 40–115Mt/yr of C initially subducted is released into fluids (by decarbonation and/or carbonate dissolution) and 18–43Mt/yr is returned at arc volcanoes. Current estimates suggest the amount of C released into subduction fluids is greater than that degassed at arc volcanoes: the imbalance could reflect C subduction into the deeper mantle, beyond subarc regions, or storage of C in forearc/subarc reservoirs.

We examine the fate of C in subduction-zone ultramafic rocks via study of fluid–rock evolution of marble and variably carbonated serpentinite in the Ligurian Alps. Based on petrography, major and trace element concentrations, and carbonate C and O isotope compositions, we demonstrate that serpentinite dehydration at 2–2.5GPa, 550°C released aqueous fluids triggering breakdown of dolomite in nearby marbles, thus releasing C into fluids. Carbonate + olivine veins document flow of COH fluids and that the interaction of these COH fluids with serpentinite led to the formation of high-*P* carbonated ultramafic-rock domains (high-*P* ophicarbonates). We estimate that this could result in the retention of ~0.5–2.0Mt C/yr in such rocks along subduction interfaces. As another means of C storage, 1 to 3 km-thick layers of serpentinitized forearc mantle wedge containing 50 modal % dolomite could sequester 1.62 to 4.85Mt C/yr.

We stress that lithologically complex interfaces could contain sites of both C release and C addition, further confounding estimates of net C loss at forearc and subarc depths. Sites of C retention, also including carbonate veins and graphite as reduced carbonate, could influence the transfer of slab C to at least the depths beneath volcanic fronts.

## GLOBAL METABOLOMICS AS A MEANS OF LINKING MICROBIAL ACTIVITIES AND THEIR BIOGEOCHEMICAL CONSEQUENCES IN SERPENTINIZING SYSTEMS

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### Metabolomics, transcriptomics, biogeochemistry

Environmental metabolomics is an emerging approach used to study ecosystem properties, yet to date this technique has mostly been applied to soils and plant-associated habitats. Through bioinformatic comparisons to genomic and transcriptomic data sets, metabolomics can be used to study microbial adaptations and responses to varying environmental conditions. Since the techniques are highly parallel to organic geochemistry approaches, metabolomics can also provide insight into biogeochemical processes, such as carbon turnover. These analyses are a reflection of metabolic potential and intersection with other organisms and environmental components. Here, we use an untargeted metabolomics approach to characterize both intracellular and aqueous metabolites from environmental biomass samples obtained from an actively serpentinizing habitat, in order to describe overlapping biogenic and abiogenic processes impacting carbon cycling in serpentinizing rocks.

We applied untargeted metabolomics techniques to environmental biomass samples taken from the Coast Range Ophiolite Microbial Observatory (CROMO), a subsurface observatory consisting of a series of eight wells drilled into an actively serpentinizing ophiolite in the California Coast Range. Cellular biomass from groundwater (~4 L) was collected on combusted glass fiber filters using a peristaltic pump, and immediately frozen in liquid nitrogen. Metabolites were extracted from frozen cells using cold 40:40:20 acetonitrile:methanol:0.1 M formic acid. Total organic carbon in the filtrate was measured using a Shimadzu TOC-L analyzer. Dissolved organic carbon from the filtrate was trapped using Solid Phase Extraction (SPE) Bond Elut PPL (Agilent) cartridges and eluted in pure methanol. All extracts were dried down via vacuum centrifugation, resuspended in 95:5 water:acetonitrile, and analyzed via quadrupole time-of-flight liquid chromatography tandem mass spectrometry (QToF-LC/MS/MS) on a Waters Xevo G2-XS UPLC/MS/MS instrument. Sample splits were also analyzed using NMR and FT-ICR-MS through an ongoing collaboration with the Environmental Molecular Sciences Laboratory (EMSL) for analysis of continental serpentinites. Direct cell counts were obtained using DAPI staining.

Biomass was also collected (~2 L per well) using Sterivex filter units (EMD Millipore) and total RNA was extracted, reverse transcribed, and sequenced to produce a metatranscriptome of each well. Metabolomes and metatranscriptomes were imported into Progenesis Q1 software for statistical analysis and correlation, and metabolic networks constructed using the Genome-Linked Application for Metabolic Maps (GLAMM), a web interface tool. Further multivariate statistical analyses and quality control was performed using EZInfo. All metabolomics data is currently being combined into a boutique database that can be repeatedly mined as more data is obtained and metabolic networks are constructed from this environment.

## EVIDENCE OF NON-EQUILIBRIUM REACTIONS DURING SERPENTINIZATION OF DUNITES (OMAN OPHIOLITE)

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### Serpentinization, microtomography, Liesegang banding

Serpentinization is the main alteration process affecting the mantle lithosphere. It encompasses a suite of a water-rock reactions producing hydrous minerals (serpentine, brucite, ...) and oxides at the expense of olivine ( $Mg_{1.8}Fe_{0.2}SiO_4$ ), the main mineral in the mantle. These reactions modify not only the composition and mineralogy of the mantle but also its texture and microstructure from the microscale to that of an outcrop. These changes will in turn modify the physical and rheological properties of the serpentinizing mantle. In order to better constrain the textural and structural changes associated to serpentinization, we studied a serpentinized dunite sampled in the Batin area (Wadi Tayin massif, Oman Ophiolite) using a dual approach combining high resolution X-ray microtomography (ID19, ESRF, Grenoble, France) and petro-geochemical analyses (EPMA, Montpellier).

X-ray microtomography images were acquired at two resolutions (voxel 0.65 & 0.16  $\mu m$ ) on dunite minicores (diameter 1.7mm, length 5mm). The 0.65  $\mu m$  and 0.16  $\mu m$  tomography images were registered to find a common coordinate frame. After this step the techniques of image processing (contrast enhancement, segmentation) were applied to the images in order to visualize structures of interest. They reveal a complex structure of the sample, which contains mm-wide magnetite-rich serpentine veins cross-cutting a mesh texture serpentinized background. The serpentinized background contains a network of smaller serpentine veins, associated with fractures, partially filled with magnetite, surrounding patches showing Liesegang rings-type textures. Liesegang rings-type textures appear associated with the replacement of the olivine. Their diameter varies between 0.4mm and 0.035mm.

X-ray microtomography images show only the X-ray absorption coefficient and, to investigate the possible compositional origin of its variations, EPMA mapping (semi-quantitative analyses) was performed on thin-sections. Mapping reveal a sequence of Fe, Ni, Ca poor and Mg rich rings (low absorption) alternating with Fe, Ni, Ca rich and Mg poor rings (high absorption). On the outward of the Liesegang band structure we observe iron rich zones associated with several magnetite oxides.

Such structure could be common for the serpentinization process, or it could be dependent on the environmental conditions (flow rate, redox condition, etc). A reactive diffusion model is envisaged to explain the formation of these structures in serpentinized dunites.

## QUANTIFYING ENERGY YIELDS FOR METHANOGENS IN SERPENTINIZING SYSTEMS

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### Bioenergy, Methanogenesis, Modeling

Geological settings dominated by water-to-rock reactions are natural targets for geobiological investigations decoupled from surface processes. The geochemical diversity that characterizes such sites provides abundant energy to support subsurface microbial life. Hydrogen oxidizers are of particular interest because H<sub>2</sub>-based metabolisms are widespread and deeply rooted throughout the phylogenetic tree of life, implying they may have emerged extremely early in the evolution, and possibly even the origin of life on Earth and potentially any other rocky body bearing liquid water. Initial work on lithogenic H<sub>2</sub> production has focused on ultramafic serpentinization, as it is occurring on Earth, is known to have occurred on Mars, and is likely occurring on icy satellites such as Europa.

Serpentinization is modeled using EQ3/6 with the thermodynamic databases of McCollom and Bach, 2009, whereby ultramafic harzburgite rocks are reacted with oxygen- and sulfate- depleted seawater. Reaction kinetics are not explicitly considered, but comparable effects of partial reaction are approximated by assuming post-reaction dilution of equilibrated fluids. The output of EQ3/6 serves as the input to a single-cell bioenergetic model, which calculates energy yields based on spherically-symmetrical diffusion of substrates to a cell followed by reaction at the diffusion-limited rate. Membrane selectivity for substrate transport is explicitly considered. Methanogenesis is the metabolism of focus.

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McCollom, T. & Bach, W. (2009). Thermodynamic constraints on hydrogen generation during serpentinization of ultramafic rocks. *Geochimica et Cosmochimica Acta* 73, 856-875.

## HIGH PRESSURE DESERPENTINIZATION: MODELING THE EVOLVING FLUID CHEMISTRY DURING ANTIGORITE BREAKDOWN

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### Antigorite, Fluids, Pressure

The dehydration of serpentinite minerals in the ultramafic parts of subducting slabs provides abundant water that may contribute to the oxidation of the overlying mantle wedges (Kerrick & Connolly, 1998; Evans, 2012). However, the chemistry of the water is poorly understood. Traditional metamorphic models adopt a COH fluid chemistry in which only a few neutral aqueous species such as H<sub>2</sub>O, CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>, and CO are considered. Aqueous ions and silicate rock components are not considered. The simplistic chemistry of the COH model is inconsistent with experimental studies of mineral solubilities (Manning, 2013), fluid inclusion evidence (Scambelluri & Philippot, 2001), and petrographic, trace element, and isotopic evidence (Scambelluri et al., 2004; Debret et al., 2015, 2016). Furthermore, it is not possible using the COH fluid model to chemically couple the fluid and rock taking into account all the major and trace components expressed as aqueous ionic species, metal complexes, and aqueous organic species. As a consequence, our understanding of fluid-rock interactions involving subduction-zone fluids is severely hampered.

The recently developed Deep Earth Water model enables computation of the equilibrium constants for all kinds of aqueous species, including ions, complexes, and organic species at pressures up to 6.0 GPa and 1,200 °C (Facq et al., 2014; Sverjensky et al., 2014). In turn, this enables quantitative modeling of the chemistry of fluid-rock interactions for subduction-zone conditions that can yield insight into many problems of geologic interest. As one such application, the fluid-rock interactions involving antigorite breakdown, i.e. deserpentinization, were calculated at 2.0 GPa and 550 to 680°C. The minerals formed and the evolution of the oxidation state to highly oxidizing conditions during the transformation of antigorite to olivine closely approximate geologic observations (Debret et al., 2015).

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**NEW INSIGHTS INTO THE SUBSURFACE MICROBIAL BIOSPHERE AND ASSOCIATED BIOGEOCHEMICAL ACTIVITY IN THE OMAN OPHIOLITE**

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**geomicrobiology, peridotite, subsurface**

Oman contains numerous peridotite aquifers, which store and transmit fluids continuously modified by water/rock interaction. Hydrological, geochemical and modeling investigations have inferred the reaction pathways occurring in the subsurface, by comparison to the fluid chemistries, dissolved gases and mineral precipitates observed in wadi waters and hyperalkaline seeps. However, the nature of the subsurface biosphere(s) hosted within fractured peridotite is largely unknown. It is timely to assess what types of microbial organisms are present and functionally active within the fluids, how microbial activity affects the rates and pathways of the mineral hydration and carbonation reactions, and whether biological processes are actively cycling C, Fe, N and S.

We have accessed alkaline and hyperalkaline fluids through existing groundwater monitoring wells in the Samail ophiolite. Abundant biomass can be recovered from the fluids. 16S rRNA amplicon sequencing of DNA reveals the presence of methanogens (e.g. *Methanobacterium*), methane oxidizers (e.g. *Methanococcus*, NC10), and organisms involved in N and S cycling (e.g. *Thermodesulfobrio*, *Sulfuritalea*, *Nitrosphaera*). Organisms with enigmatic metabolisms are pervasively distributed in the subsurface fluids, such as Candidate division OP1, *Meiothermus*, and *Cupriavidus*. We also detect organisms common to terrestrial serpentinizing systems, such as *Hydrogenophaga*, *Clostridia*, and Candidate division OD1. We will present a statistical analysis of how the biological diversity is distributed across gradients in pH, dissolved gas (H<sub>2</sub>, CH<sub>4</sub>) and oxidant (nitrate, sulfate, CO<sub>2</sub>) concentrations, within a geological and hydrological context.

To gain insights into spatial variability in the modern water/rock reactions, we have analyzed the mineralogy of drill cuttings. We utilize microscale Raman and x-ray spectroscopic analyses of the changes in mineralogy and Fe speciation associated with progressive stages of low-temperature serpentinization. Spectroscopic analysis of rocks in contact with deep subsurface fluids indicates that the freshest rocks are ~50% serpentinized, and still contain relict olivine and pyroxene, with abundant Fe(III)-rich serpentine and Fe(II)-bearing brucite. More highly altered rocks near the surface are almost fully serpentinized and exhibit a greater degree of Fe-oxidation, with Fe(III)-serpentine intermixed with Fe(III)-oxides and magnetite.

Serpentine Days will be a great opportunity to discuss the possible feedbacks between peridotite-hosted biological activity and the mineralogical, geochemical and hydrological properties of an “actively serpentinizing system”. Due to the upcoming Oman Drilling Project, it will also be worthwhile to present as much data as possible that may help numerous investigators design studies to explore the connections the hydrology of the peridotite catchments, the reaction pathways, and the distribution and function of subsurface microbial life.

## HYDROTALCITE GROUP MINERALS IN SERPENTINITE FROM FURUYASHIKI, FUKUOKA PREFECTURE, KYUSHU, JAPAN

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### Stichtite, Hydrotalcite Group, Furuyashiki

Stichtite, a rare hydrated carbonate-hydroxide of Mg and Cr, is isostructural with other members of the hydrotalcite group, which have the general formula  $Mg_6R_2(OH)_{16}CO_3 \cdot 4H_2O$ , where  $R^{3+} = Fe, Cr, \text{ or } Al$  (Mills *et al.*, 2012). Stichtite and other hydrotalcite group minerals were found in a dolomite vein in serpentinite body from Furuyashiki, Iizuka, Fukuoka Prefecture, Japan. The serpentinite belongs to the Sangun metamorphic rocks. The Sangun metamorphic belt is one of the high pressure type metamorphic belts in Japan. Sangun metamorphic rocks consist of several metamorphic belts with different metamorphic ages, including the Sangun-Renge belt (ca. 300 Ma), Suo belt (ca. 220 Ma), and Chizu belt (ca. 180 Ma) (Shibata and Nishimura, 1989). The Sangun-Renge belt in the Fukuoka area in northern Kyushu, is one of the largest mass of Paleozoic metamorphic rocks in Japan. The area mainly consists of greenschist, metabasite, and serpentinite. Main serpentine minerals are lizardite and/or antigorite in the Fukuoka area (Uehara & Shirozu, 1985; Uehara, 1987).

Specimens used in this study were purple stichtites, brown and white pyroaurites in serpentinites from Furuyashiki. Stichtites from Dundas, Tasmania, Australia and Barberton, Kaapsoop, South Africa were also investigated for comparison. These specimens were analyzed by X-ray diffractometer (XRD), scanning electron microscope with energy dispersive X-ray spectrometer and transmission electron microscope (a JEOL JEM-ARM200F STEM/TEM at the Ultramicroscopy Research Center in Kyushu University). Stichtite from Furuyashiki occurs around chromite in small serpentinite block, which is contained in dolomite veins. Brown pyroaurite occurs as a platy crystal in dolomite veins and white pyroaurite occurs as a plate filling a dolomite druse.

Stichtite from Furuyashiki showed pure  $3R$  polytype XRD pattern, while Dundas and Barberton specimens had mainly  $3R$  polytype with a small amount of  $2H$  polytype (formerly called barbertonite). Unit-cell parameters of  $3R$  stichtite were  $a = 6.19 \text{ \AA}$  and  $c = 47.03 \text{ \AA}$  (Furuyashiki),  $a = 6.19 \text{ \AA}$  and  $c = 47.07 \text{ \AA}$  (Dundas),  $a = 6.204 \text{ \AA}$  and  $c = 47.15 \text{ \AA}$  (Barberton). Brown and white pyroaurite from Furuyashiki were also  $3R$  polytype. Chemical composition of stichtite were  $Mg_{6.07}(Cr_{1.55}Fe_{0.35}Al_{0.01})Si_{0.02}Ca_{0.01}Ni_{0.01}(OH)_{16}[(CO_3)_{0.98}S_{0.02}] \cdot 4H_2O$  (Furuyashiki),  $Mg_{6.07}(Cr_{1.19}Fe_{0.61}Al_{0.07})Si_{0.06}(OH)_{16}CO_3 \cdot 4H_2O$  (Dundas) and  $Mg_{6.05}(Fe_{0.89}Cr_{0.74}Al_{0.19})Si_{0.10}Ni_{0.01}(OH)_{16}[(CO_3)_{0.95}Cl_{0.04}Br_{0.02}S_{0.02}] \cdot 4H_2O$  (Barberton). A unique reaction zone was found in grain boundaries between stichtite and chromite of Furuyashiki specimens, which is composed of nano-size spherical chromite in host stichtite. It was not observed in previous stichtite from the other localities (Ashwal & Cairncross, 1997; Theiss, *et al.*, 2013). The occurrence of spherical nano-size chromite suggests that original chromite in serpentinite once dissolved by  $CO_2$  fluid, and secondary chromite recrystallized using excess chrome component.

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## GEOCHEMISTRY OF THE NEW CALEDONIA SERPENTINITES: EVIDENCES FOR MULTIPLE SERPENTINIZATION EVENTS AT VARIOUS DEPTHS

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### Serpentine, New Caledonia ophiolite, Traces and Fluid-mobile elements, Oxygen and Hydrogen isotopes

Studies of serpentine minerals around the world have shown that different varieties can coexist depending on external conditions such as temperature, pressure and chemical exchanges. Identifying serpentine variety can thus provide significant constraints on the geodynamic environment at the time of formation. The New Caledonia (NC) ophiolite (Southwest Pacific) is one of the world's, mostly composed of harzburgites and minor lherzolites where serpentinization is ubiquitous (typically > 50%). The base of the ophiolite is made of a thick serpentinite sole that recorded multiple serpentinization events. This study aims at deciphering the nature and the origin of fluids involved in serpentinization processes from the characterization of serpentine geochemistry. Concentration of major and trace elements was determined in situ for primary minerals and the different varieties of serpentine, and the behavior of fluid mobile element (FME; As, Sb, B, Li, Cs, Pb, U, Ba, Sr) was characterized. In addition, stable isotope oxygen and hydrogen ratios were measured on separated mineral fractions in order to identify the origin of the fluids responsible for the hydration of the NC ophiolite.

Our results show that lizardite is the main mineral species that representing over 80% of the serpentine minerals in the ophiolite. In the lower part of the ophiolite, lizardite is crosscut by multiple serpentine veins ordered as follow: lizardite 1 → lizardite 2 → antigorite → chrysotile → polygonal serpentine. From the trace elements analysis, we demonstrate that the transition from primary minerals to lizardite 1 occurs almost isochemically. The transition from lizardite 1 to 2 is characterized by a great enrichment in FME and an increase of  $Fe^{3+}/Fe_T$  ratio. Stable isotope results show that each serpentine variety is characterized by different values of  $\delta^{18}O$  ranging from 1.9-14‰. In contrast, a narrow range is observed for  $\delta D$  (88-106‰).

Stable isotope results were then modeled based of Monte-Carlo simulations. Results show that fluids in equilibrium with NC serpentines define a linear trend that extends from the meteoric water line to an area defined between 3‰ and 8‰ in  $\delta^{18}O$  and -80‰ and -60‰ in  $\delta D$  in which most of the results plot. These compositions are consistent with fluids derived from the dehydration of the hydrated-basaltic basement (i.e. the altered oceanic crust) during the subduction in the South Loyalty Basin at temperatures between 250°C and 400°C. No evidence of sedimentary contribution was observed, suggesting that the serpentinization of the NC ophiolite was complete within few million years after the initiation of the subduction. Low  $\delta^{18}O$  values indicate that the latest generation of serpentine may derive from the circulation of meteoric fluids at low temperature (<150°C), suggesting that the latest steps of serpentinization started from the beginning of the ophiolite obduction.

**ORIGIN OF SAPPHIRINE-BEARING ROCKS IN CONTACT WITH LHERZOLITE BODIES (ETANG DE LERS AREA, CENTRAL PYRÉNEES) : EVOLUTION OF METAMORPHIC EVAPORITIC SEDIMENTS ALONG A CRUST-MANTLE DETACHMENT.**

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**Lherzolites, Pyrenees, HT metamorphism, meta-evaporites, subcontinental mantle exhumation.**

In order to decipher the mode of exhumation of the Pyrenean lherzolites and the mechanisms of extreme thinning of the continental crust, it is necessary to obtain consistent information from the direct geological environment of mantle bodies. Our field investigations conducted since ten years along the North Pyrenean Zone led us to the conclusion that, despite they are famous among Earth scientists, the lherzolite bodies of Étang de Lers and Freychinède forest still lack detailed geological mapping. Therefore, we achieved a study of the metasedimentary terranes in direct contact with the lherzolites of the inverted Aulus Basin of Albian-Cenomanian age, completed by the optical observation and microprobe analysis of more than 50 thin sections. This allows us providing robust constraints on the lithology of the units progressively exhumed during the successive stages of mantle unroofing. We show that various polymictic breccias, microbreccias and sandstones are exposed in the immediate vicinity of the mantle bodies and associated meta-ophites. Among these detrital sediments, the famous sapphirine-bearing sandstones (Monchoux 1970, 1972) are located on the northern edge of the Lers lherzolite. Here, we describe a progressive transition from the lherzolite body towards the surrounding massive limestones. This transition consists of breccias and sandstones, whose nature varies according to the distance to the lherzolite. The mm-sized clasts are mainly composed of Al and Mg bearing minerals, such as sapphirine, phlogopite and anthophyllite associated with kornéropine and (metamorphic) Al-spinels in a carbonate cement. By place, the polymineral clasts have been deposited along with the monomineral debris, often defining a clear grain-size sorting. In addition, minor isolated clasts originating from the disaggregation of various rock types are observed in the sapphirine-bearing sandstones suite. We recognized : lherzolite, micaschists, quartzite, alkaline gabbro, meta-ophite, metaevaporite and marble debris. Sandstones composed of alternating beds of minerals deriving from these rock-types are also exposed close to the mantle body. All the sources of these detrital elements can be identified in the Aulus Basin, apart from the sapphirine-bearing rocks protolith which remains enigmatic. Microprobe analyses allow to estimate an average composition of this protolith. We found that the best candidate is a mix of evaporitic clays and dolomite, typical of the Late Trias sediments, that evolved under the HT-LP conditions of the Pyrenean metamorphism. The presence of evaporitic inclusions (Cl-apatite) in the sapphirine crystals, revealed by MEB analysis, strongly supports this hypothesis. Earlier observations of anhydrite enclosed in metamorphic enstatite also confirms these conclusions (Foucard, 1997). Finally, we propose that the sapphirine-bearing and associated sedimentary rocks originated from the transformation of sediments of Triassic and Lower Jurassic age during the Cretaceous metamorphism event, in relation with mantle exhumation. Metasomatism and cataclasis of the Mesozoic pre-rift cover occurred along the extensional detachment fault which was progressively exposing the lherzolites to the seafloor. The cataclastic debris were abandoned on the unroofed detachment surface and rapidly reworked through sedimentary processes.

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## ALTERATION CONDITION OF CM CHONDRITES: AN EXPERIMENTAL APPROACH

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### CM chondrite, experiment, tochilinite/cronstedtite

Asteroidal parent bodies represent the source of unequilibrated meteorites (i.e., chondrites) in the solar system. Among chondrites, CM carbonaceous chondrites recorded intense episodes of hydrothermal alteration that have modified their primitive petrography. A large variety of secondary phases are present in CMs, including carbonates and Fe-Ni sulfides (Zolensky *et al.*, 1997; Brearley, 2006). However, the most characteristic secondary phases in CM chondrites are tochilinite ( $6\text{Fe}_{0.9}\text{S}\cdot 5(\text{Mg}, \text{Fe}^{++})(\text{OH})_2$ ) - cronstedtite ( $\text{Fe}^{2+}_2\text{Fe}^{3+}(\text{Fe}^{3+}\text{Si})\text{O}_5(\text{OH})_4$ ) associations (also referred as TCI), which occur as complex intergrowths dispersed throughout the chondrules and the matrix (Rubin *et al.*, 2007). These secondary phases are likely to have formed during hydrothermal alteration processes, but their stability fields are still poorly constrained.

To fill this gap, we performed 3 sets of anoxic hydrothermal experiments at 80°C containing glass powder with composition close to the primitive chondrite matrix (Leroux *et al.*, 2015), metal iron and forsterite with a salty solution ( $I = 0.07\text{m}$  NaCl,  $\text{MgCl}_2$  and  $\text{CaCl}_2$ ) during 2 months. The starting products were assembled into Parr non-stirred pressure vessel made of Teflon in inert argon atmosphere at 20ppm of  $\text{O}_2$ . The water/rock ratio is set to 10, and we played on pH (neutral to alkaline) and sulphide (as  $\text{Na}_2\text{S}$ ) concentrations.

In neutral environment, petrographic observations show that the samples are composed of micrometric pyramidal crystals of Fe-rich silicates. SAED Pattern indicates that these phases have parameter  $c = 7\text{Å}$  like T-O phyllosilicate. The chemical compositions are close to the cronstedtite composition. So, the average structure formula were calculated by adjusting the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio (Pignatelli *et al.*, 2013):  $(\text{Fe}^{2+}_2\text{Fe}^{3+}_{0.9}\text{Mg}_{0.1})(\text{Si}_{1.1}\text{Fe}^{3+}_{0.7}\text{Al}_{0.2})\text{O}_5(\text{OH})_4$ . In sulphide-rich environment, TEM observations reveal the presence of nanoscale acicular Fe and S-rich phases around iron metal beads. HRTEM images indicate that these acicular crystals are heterogeneous in crystallinity, but are essentially composed of a 5.4 Å D-spacing phase. The SAED pattern highlights the characteristic d-spacing of some hkl ferrotouchilinite plans. The Fe/S atom ratio is in agreement with ferrotouchilinite described by Pekov *et al.*, (2012).

Our experiments confirmed that TCI in CM chondrites are formed by low-temperature hydrothermal alteration under reducing conditions. The formation of experimental TCI is strongly pH dependent and requires probably 2 steps of aqueous alteration under different microenvironments. Thus, the precipitation of cronstedtite is favored by the dissolution of the Si-rich glass and a high quantity of iron metal (30%) in neutral solution while tochilinite precipitation requires the presence of iron metal and sulphur in alkaline solution. Future works are ongoing to constrain the stability fields of cronstedtite and tochilinite at 50 and 150°C during long-term hydrothermal experiments.

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**MASSIVE PRODUCTION OF ABIOTIC METHANE DURING SUBDUCTION EVIDENCED IN METAMORPHOSED OPHICARBONATES FROM THE ITALIAN ALPS**

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**Abiotic CH<sub>4</sub>, ophicarbonates, subduction**

Alteration of ultramafic rocks plays a major role in the production of hydrocarbons and organic compounds via abiotic processes on Earth and beyond. This process contributes to the redistribution of C between solid and fluid reservoirs over geological cycles. Abiotic methanogenesis has been widely documented at shallow crustal levels, whereas little natural evidence exists at greater depths. We provide proof of intense deep abiotic methanogenesis during high-pressure alteration of ophicarbonates in the Italian Alps. Protracted ( $\geq 0.5$ -1Ma) production of CH<sub>4</sub> occurred from at least  $\sim 40$  km depth, and then even increased during decompression up to  $\sim 15$ -20km depth. Textural, mineralogical and petrological evidence, including abundant CH<sub>4</sub>-H<sub>2</sub> fluid inclusions, shows that saturation of CH<sub>4</sub> triggered precipitation of graphite and replacement of the precursor serpentinite. Although previous studies proposed that ophicarbonates contribute little to the deep C cycle at forearc depths, this study provides a clear natural evidence of massive abiotic methanogenesis from these rocks, with strong implications for deep C mobility. Moreover, as shown for other fluid-precipitated graphite, the massive graphite precipitation exerts a negative feedback on C fluxes from the deep Earth to shallower reservoirs, and a strong redox potential in mantle rocks. This study also provides new views on the genesis of extra-terrestrial methane and condensed organic C compounds in ultramafic rocks.

## HALOGEN RATIO AND IN-SITU OXYGEN ISOTOPE RECORDS WITHIN THE ATLANTIS MASSIF: CONSTRAINING SERPENTINIZATION AND HYDROTHERMAL CIRCULATION

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### Oxygen isotopes, halogens, serpentinization

The large-scale geochemical characteristics of altered oceanic crust have been extensively studied, particularly by bulk analytical techniques and often within the scope of constraining global geochemical fluxes and subduction inputs. The micro- to local scale stable isotopic and elemental heterogeneity and the geochemical evolution of seafloor alteration systems (in both time and temperature) are not as well constrained. Additionally, the halogen budgets and systematics of altered oceanic crust (and particularly serpentinites) are poorly constrained due to the lack of reliable iodine, bromine and chlorine data obtained by techniques with sufficiently low detection limits.

Here we present preliminary results from an investigation of halogen (Cl, Br, I) and noble gas abundances and in-situ oxygen isotope compositions of serpentinites collected from the Atlantis Massif as part of IODP Expedition 357. The novel combination of halogen, noble gas and in-situ oxygen isotope analyses allows greater discrimination of process and source/compositional effects. The evolution of the hydrothermal system is presented in the context of the exhumation and cooling of the system through the use of zonation and overprinting textures observed. Samples of variably altered and veined serpentinized harzburgites and serpentinized dunites were collected from multiple sites across the massif. A small number of partially serpentinized harzburgites preserve fractured/veined olivines; orthopyroxene is often partially preserved but typically pseudomorphically replaced by bastites (containing either serpentine or talc). Multiple generations of crosscutting fine sub-parallel serpentine veins and associated alteration channels crosscut early semi-brittle/brittle deformation of large olivine grains. Serpentinite (both veining and mesh texture) is locally overprinted by talc- and amphibole-bearing assemblages as either veining or alteration adjacent to shear zones.

In-situ oxygen isotope analysis by SHRIMP has been conducted on serpentine and olivine where present. Analysis of serpentines provides information to constrain the temperature of serpentinization and the composition of subsequent generations of fluid infiltration (e.g. early fine veins, mesh core-rim relationships, larger/banded serpentine veins). In-situ oxygen data also allow assessment of local oxygen isotopic homogeneity for the interpretation of bulk rock isotope measurements (e.g. Boschi et al, 2006). Halogens were measured in small rock chips using the neutron-irradiation noble gas method (Kendrick, 2012). These data contribute additional information on fluid sources and evolution during serpentinization and improve estimates of halogen budgets in altered oceanic crust and lithosphere. This study enhances the understanding of ultramafic-hosted hydrothermal systems associated with detachment faults and provides a stronger geochemical framework for the comparison to similar modern and relict ophiolitic analogues.

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## CARBON CYCLING IN SERPENTINIZING SPRINGS OF THE ZAMBALES OPHIOLITE RANGE

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### Metagenomics, Zambales ophiolite, methane cycling

Serpentinizing fluid springs originating in the Zambales Ophiolite Range (Luzon, the Philippines) were investigated to determine microbial community composition and putative function via metagenomic analysis. Assessment of taxonomic biodiversity and metabolic capacity was contextualized with regards to the fluid and solid geochemistry of these ecosystems. Field observations of pH, temperature, and dissolved oxygen indicated that spring fluids were highly alkaline (pH 10-11 at 33-34°C) and hypoxic. Fluids collected from the springs for dissolved organic and inorganic carbon yielded very low concentrations (less than 0.5 mM in both cases). The spring fluids were actively bubbling at the source pools; approximately 207.0 micromoles of hydrogen gas and 187.2 micromoles of methane (Cardace et al., 2015)

Amplicon sequencing of the small subunit rRNA gene indicated that microbial communities were dominated by heterotrophic and lithotrophic microorganisms. Shotgun metagenomic analysis of fluid and sediments provided evidence of the metabolic capacity for methanogenesis, suggesting that some of the methane present in these serpentinizing fluids may be microbial in origin. Archaea from the classes Methanobacteria and Methanomicrobia were detected in spring fluids and sediments. Key enzymes involved in methanogenesis, including methyl coenzyme M reductase (MRI, encoded by *mcrBDCGA*), and formylmethanofuran dehydrogenase (FWD, encoded by *fwdHFGDACB*) were detected. Relative abundance of these enzymes increased in pools near the spring source, where fluids approached anoxic conditions.

The phyla Firmicutes, Bacteroidetes, and Proteobacteria were dominant in both metagenome and amplicon sequence data. Anaerobic Firmicutes from the class Clostridia were abundant in the fluids and sediment of these source pools; the sulfate-reducing *Dethiobacter* and *Desulfotomaculum* comprised the majority of taxa from this lineage. A large percentage of taxa were associated with the phylum Proteobacteria, including: methanotrophic Alphaproteobacteria and Gammaproteobacteria, and sulfate-reducing Deltaproteobacteria, and Betaproteobacterial hydrogen-oxidizing *Hydrogenophaga*. The carbon cycling regime at Manleluag is likely reliant on methanogenesis, acetogenesis, sulfate reduction, hydrogen oxidation, and methane oxidation.

Given the presence of key methanogenesis genes and taxa, it is possible that some of the dissolved methane in these seeps is microbial in origin. Disentangling the thermogenic/microbial and/or abiotic formation of methane in this system will require more sophisticated analytical techniques. Future field expedition will focus on the collection of methane gas from the Zambales system for clumped isotopologue analysis, to be carried out in the Ono lab at the Massachusetts Institute of Technology.

Cardace, D., Meyer-Dombard, D.R., Woycheese, K.M., Arcilla, C.A. (2015). Feasible metabolisms in high pH springs of the Philippines. *Front. Microbiol.* 6:10.

## STRESS CONTROL ON WEATHERING IN THE FERAGEN ULTRAMAFIC BODY

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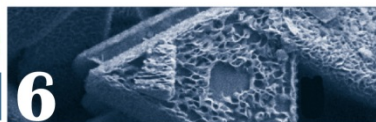
### Serpentinized dunite, stress, fracturing, weathering

Tectonically exposed upper-mantle peridotite or dunite can enhance in situ carbonation processes during weathering and retrograde metamorphism (Kelemen et al., 2008). The reaction-induced volume changes can drive fracturing which enables sustained fluid-rock interaction and accelerate weathering (Malthe-Sørenssen et al., 2006, Jamtveit et al., 2008, J F. Rudge, 2010, Beinlich and Austrheim, 2012).

The Feragen Ultramafic Body, Norway (FUB) has been studied in some detail. The surface stress is controlled by topography, post glacial rebound, and the tectonic stress from the Mid-Atlantic ridge. The associated strain is represented by intensive surface fracturing in the study area (Keiding et al., 2015). The widely distributed fractures accelerate the weathering process by bringing in more fluid. Serpentinization of the dunite led to the production of brucite (cf. Bucher et al, 2015), and the dissolution of brucite is the critical reaction during subsequent weathering of the dunite. There is a significant compositional change from the serpentinized dunite to the weathered part. Decreasing MgO and the compensated increase of SiO<sub>2</sub> reflects the brucite dissolution. There is an approximately 30% increase of porosity from the fresh dunite to the weathered zone.

In this study, we first modelled the stress state at FUB using COMSOL and then compare it to the fracture distribution in the field. Then get the weathering rate controlled by the reactive surface area made available through this fracturing. A late stage of fracturing caused by stresses associated with near-surface carbonation and freeze-thaw effects, adds to the reactive surface area.

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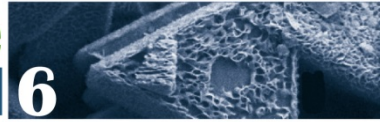
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