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- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF

Experiment title:
Tracking biotic and abiotic processes at play within the serpentinizing ocean crust by characterizing the distribution of metals and metalloids associated to organic remnants

Experiment number:
ES-421

Beamline:
ID16B-NA

Date of experiment:
from: 04/05/2016 to: 09/05/2016

Date of report:

Received at ESRF:

Shifts:
15

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Introduction: Serpentinization of the ultramafic rocks composing the oceanic crust, i.e. its hydration by large-scale seawater circulation, represents the most powerful chemical reactor on Earth since plate tectonics arose, billions of years ago. The serpentinization reaction produces highly-reduced fluids enriched in H_2 promoting abiotic carbon reduction resulting in the production of diverse organic compounds of likely prebiotic interest[1,2]. In addition, the produced H_2 together with the abiotic organic compounds are able to sustain deep chemolithotrophic ecosystems. The serpentinizing lithosphere is thus a vast reservoir where biotic and abiotic organic compounds are mixed and where abiotic and biotic processes compete. The mechanisms and products of both processes are still little known but could have a non-negligible impact in our way to consider the deep carbon cycle along with the emergence of life on Earth[3,4]. Metals are essential players in the formation of organic compounds in these systems as they can act as catalysts of the slow carbon reduction reactions[5,6], promoting abiotic production of organic compounds. They are also essential bio-nutrients for deep ecosystems that can gain energy from their oxidation or reduction or use them to build up their enzymatic co-factors for their activities[7]. Understanding the processes controlling metal distribution within the serpentinizing lithosphere, could give essential keys to distinguish between abiotic and biotic formation of organic material.
The aim of this proposal was to recognize specific association between metals, minerals and organic compounds to track abiotic and biotic processes responsible for endogenic organic carbon accumulation and preservation within carefully selected samples of serpentinites from the South West Indian and Mid Atlantic ridges as well as from the Apennines (Italy). Pre-experiment analysis[8,9,10,11] of these samples showed that carbon occurrences appear heterogeneously distributed in micrometric aggregates within the serpentine mesh or associated with specific mineral phases, notably Fe-Mg-Cr spinels and Ca-Fe hydro-garnets of 10 to 40 µm. Associations between metals and organic material were rarely evidenced in such context, mainly due to their low concentrations within the organic aggregates and the detection limits of conventional techniques (e.g. EMPA ~30 ppm *vs.* SR-XRF ~ppm). However, they are excellent targets to characterize the metabolisms present in the deep ecosystems (primordial and modern), the role of abiotic processes in the distribution of the main nutrients (C, H_2, metals), and finally the contribution of each process to the Earth's C-budget.
Data collection: The ID16B-NA hard X-ray nanoprobe station was used at 17.5 keV excitation energy (pink beam). Beamtime was fully utilized and no beam interruption or technical difficulties were encountered. Around 60 draft scanning (1×1 µm acquisition steps, 0.1 s/px down to 0.1 ms/px) was carried out on zones of interest of 100 x100 µm in size, identified within 5 different free-standing thin section of serpentinites from the South West Indian and Mid Atlantic ridges, as well as from Appenines ophiolites. This was followed by ~30 high resolution mapping (100×100 nm or 300×300 nm acquisition steps, 1s/px) of areas selected from the

draft maps. This analytical procedure has permitted to carefully describe the distribution of metals in association with minerals and endogenic organic carbon accumulations evidenced in pre-experiment analyses. **Results:** All data acquired during experiment ES-421 were processed with PyMCA and Matlab allowing to evidence in the samples Si, Ca, V, Ti, Cr, Fe, Mn, Ni, Cu, Zn distribution. The most significant result of this study is that all the different samples present **similar metal distribution patterns**, suggesting that the processes controlling the elemental distribution in these samples are **commonly spread throughout the serpentinizing lithosphere**. Cr >> Mn, Ti > Zn, Ni, V, and Cu were found in association with specific mineralogic phases and organic material (Fig.). The results and their interpretation reported here are still preliminary and need to be considered with caution. Once confirmed by suplementary analyses (underway), they will be integrated to different publications that are in preparation.

Trace metal within hydrogarnet could sustain the abiotic production of CM: The X-ray fluorescence mapping showed the presence of V, Ti and Cr in lower abundance compared to major elements such as Fe and Ca (Fig). Ti is generally concentrated in the core of the hydrogarnets while V is more abundant at the border, suggesting that during the growth of the hydrogarnet the global environmental conditions shifted toward more oxidized conditions[12]. Although the occurrence of CM in these hydrogarnets was attributed to remnants of deep ecosystems microorganisms thriving on the garnet forming elements, the presence of metals suggest that a fraction of this CM could have an abiotic origin. Hydrogarnet formation is associated with the production of H_2 that could favor the abiotic reduction of carbon. The presence of Cr within these garnets could have enhanced this reaction as it is an efficient catalyzer[11,13,14].

Mobility of theorically immobile metals is controlled by the solubilization (±oxidation) of CM by the hydrothermal fluids: The preliminary study[10] has shown that the serpentine to which are associated the garnet contain a significant amount of organic matter. These organic compounds seem to migrate progressively toward the late veins. Groundmass serpentine shows a non-uniform low enrichment in Fe, Mn, Cr and Ni (Fig), suggesting different degree of serpentinization, marked with a more or less important impoverishment in Fe and other trace metals linked to the progress of the serpentinization reaction. The serpentine are also cross cut by late serpentine veins, showing an enrichment in Cr, Mn and Zn. Some veins do not display a Cr enrichment, suggesting different phases of vein implacement that all contain various organic compounds as shown by FTIR microscopy. Finally, larger veins show a metal enrichment at their border, especially in Cr associated to CM. Cr ions have a low solubility in reducing conditions[15] and should be theorically immobile. However, its is clearly mobilized in the studied samples. Cr easily forms organometallic compounds that can later be easily transferred to the veins by the fluids and transported within the lithosphere[16].

Potential influence of biologic processes on the metal distribution patterns: Fe-oxides associated to hydrogarnets contain abundant Zn, Cu and Mn concentrations. The oxides are thought to be formed when the garnet is dissolved either by the deep ecosystems or by the circulation of hydrothermal fluids[9]. The metal enrichment of these oxides could correspond to passive adsorption on the Fe-oxides of metals carried by the hydrothermal fluids. It could also reflect their local enrichment in organic compounds on which thrive the microbial community. The occurrence of Ni small hot spots (1-3 µm, Fig), specifically associated to CM, suggest that Ni could have been concentrated by biological activity. Indeed, Ni is a bioessential metal for the deep ecosystem community as it is a cofactor of hydrogenase enzymes involved in methanogenesis, a microbial metabolisms frequently evidenced in such a context[17].

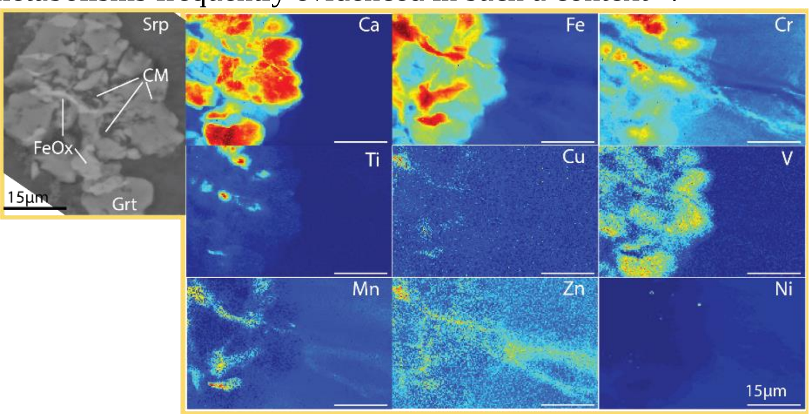

Figure: SEM image of a garnet (Grt) and the corresponding SR-XRF imaging. These maps show the different metal patterns observed throughout the different samples studied during experiment ES-421. (i) Metals are mobilized within veins and their mobility is enhanced when associated to carbonaceous material (CM). (ii) Metals are concentrated within Fe-Oxides (FeOx) resulting from the dissolution of garnet by microorganism community. (iii) Ni small hotspots coupled to CM could highlight the presence of methanogens.

References: [1] McCollom T.M. (2013) In *Carbon in Earth, Rev. Mineral. Geochem.* 75, 467-494 [2] Schrenk M.O. et al. (2013) In *Carbon in Earth, Rev. Mineral. Geochem.* 75, 575-606; [3] Lang S.Q. et al (2010) *Geochim. Cosmochim. Acta* 74(3), 941-952; [4] Lang S.Q. et al (2012) *Geochim. Cosmochim. Acta* 92, 82-99; [5] McCollom T.M. et al. (1999) *Orig Life Evol Biosph* 29, 153–166 [6] Martinez A. et al (2003) *J. Catal.* 220, 486–499 15 [7] Gadd (2010), *Microbiology* 156, 609-943 [8] Pasini (2013) PhD thesis, UNIMORE/IPGP [9] Ménez B et al (2012). *Nat. Geosc.* 5 (2), 133-137. [10] Pasini et al. (2013) *Lithos* 178, 84-95 [11] Sforna et al. In Prep [12] Canil D. (2002) *Earth Planet Sc Lett* 195, 75-90 [13] Plümper O. et al. (2014) *Geochim. Cosmochim. Acta* 141, 454-471 [14] Foustoukos D. I. & Seyfried W. E (2004) *Science* 304, 1002-1005 [15] Klein-BenDavid O. et al (2011) *Lithos* 125, 122-130 [16] Puzon G.J. et al (2008) *Chemosphere* 70, 2054-2059 [17] Ragsdale S. W. (2009) *J Biol Chem*, 284, 18571-18575.