


Experiment Report Form

	Experiment title: <i>Micro-XANES mapping of Fe in serpentinites from Rainbow hydrothermal field.</i>	Experiment number: HS-3593
	Beamline: ID24	Date of experiment: from: 02/07/2008 to: 08/07/2008
Shifts: 18	Local contact(s): Manuel Muñoz	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Applicants : *Muriel ANDREANI, LGL, ENS-UCB Lyon 1 *Clément MARCAILLOU, ISTERre, UJF Grenoble Additionnal experimentalists : *Adelie DELACOUR, GET, Toulouse *Lyderic France, CRPG, Nancy		

Report:

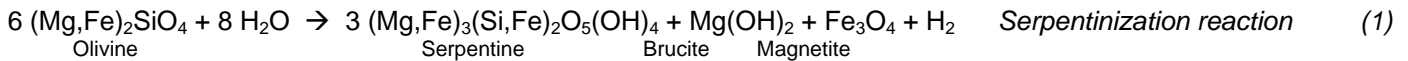
We have encountered numerous technical difficulties during the experiments, as reported in the experimental feedback form sent back just after the experiment. In particular, the exploitation of μ XANES mapping have not been optimum and we finally had to focus on the ponctual analyses we performed during the second half of the session (about 320 spectra acquired manually, including doublons).

However, the use of the μ XANES method it-self at the iron K-edge on natural serpentine minerals, prepared on rock thin sections, was successfull, even for sample with low amount of iron (down to 1,4 wt% FeO). Because of the micrometric heterogeneity of natural rock samples, the selection of valuable spectra among the 320 we managed to acquire were fastidious and several spectra had to be removed because of local signal « pollution » by micrometric iron oxydes. But we finally gathered a pertinent set of data, that is still unique for natural samples. Data from the Rainbow site, initially central in this study, were not good enough but we got excellent data from 3 other oceanic sites in Atlantic (MARK, Ashadze, Lodgatchev) and one on land (Pindos ophiolite, Greece).

The interpretation of data required additional analyses using other complementary techniques like whole rock chemical data by ICPMS, ponctual analyses by electron microprobe, SEM imaging for phases quantification on thin sections. This has delayed our work because of the time necessary to get the required financement

and then to realize the analyses. Financement of this project was obtained in summer 2009 thanks the CNRS PIE program (Programme Interdisciplinaire Energie : projet Hy-GEO¹, principal investigator : M. Andreani).

A set of 23 analyses calibrated on 6 standards have been selected and scientifically exploited. An example of 4 serpentine spectra from MARK site is given on Fig. 1. Each analysis is correlated to a peculiar location of the serpentine within the rock thin section and this is used to interpret the results in term of natural processes. In particular, serpentine analyses have been realized on rock samples that display various degree of alteration (i.e. serpentinization, see equation below) in order to correlate the evolution of Fe redox state and speciation with the reaction advancement and H₂ production.



Using the method of Wilke et al. (2001), we have calculated the Fe³⁺/Fe^{Tot} ratio of the serpentine minerals and have estimated the amount of Fe³⁺ in tetrahedral sites thanks to the pre-edge centroid position and the integrated pre-edge area, respectively (Fig. 2).

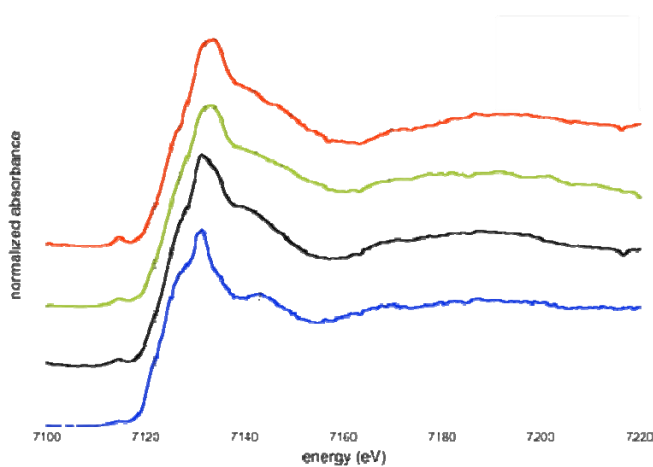


Figure 1 : Normalized Fe K-edge spectra of serpentine minerals located in various optical texture in the rock thin section (MARK site, 23°N, Atlantic).

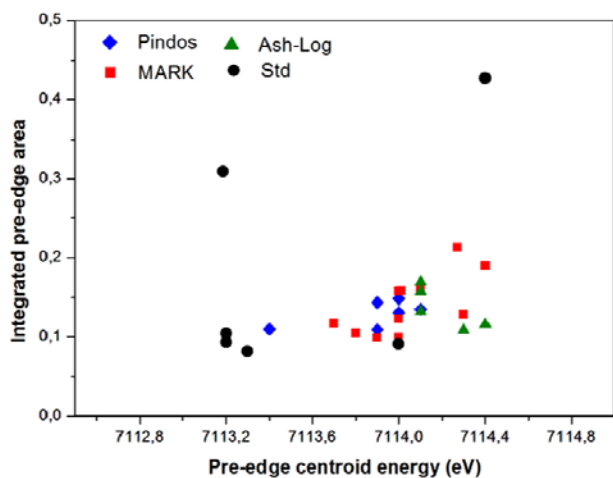


Figure 2 : Colour dots show the results obtained on serpentine from the different natural sites and the black ones are the standards used for calibration.

The results show that Fe³⁺ is abundant in serpentine formed at mid-ocean ridges and can represent up to 100% of the total iron in the structure. Most of the sample showing more than 60% of serpentinization tend to the general value of 62% of Fe³⁺, which is close to the one of magnetite (66%). Whole rock chemical analyses, in addition to petrographic and mineralogical characterization of the samples allowed us to establish that the evolution of Fe³⁺ in serpentine with the degree of serpentinization, follows a power law whose curvature parameter depends on the amount of associated magnetite. Fe³⁺ is more rapidly incorporated in serpentine mineral if magnetite is not present, and then tends to the value of 62% whatever the amount of iron in the mineral (Fig. 3).

This clearly demonstrates the involvement of serpentine formation on the H₂ production (cf. reaction 1) and our general law can now be used to estimated it at various natural sites. We have estimated that at least 10% of the H₂ produced is related to serpentine (MARK samples) and that this value easily attain 30% (Pindos samples) or even 70% locally in some samples from Logatchev. Thus the evaluation of the natural production of H₂ during serpentinization is site-dependent and must now take into account the Fe(III) incorporated in serpentine and not only the one contained in magnetite. This also opens new perspective on the role of serpentine minerals on the redox state in subduction zones where the oceanic crust is recycled in the earth mantle.

From a crystallographic point of view, it is worth noting that the morphology of the serpentine XANES spectra evolves with the amount of Fe³⁺ in the structure (Fig. 1 : Fe³⁺ increases from bottom to top in MARK

samples). This reveals an evolution of the local iron environment in the serpentine structure. Our present-day data do not show an obvious correlation between the tetrahedrally-coordinated Fe³⁺ and the amount of total Fe or Fe³⁺. But XANES with pre-edge region study is not the most appropriate method to investigate such a question. Additional specific investigation (e.g. using EXAFS) are required to further our understanding on the local iron environment in variably oxidized serpentine minerals.

This work has been presented in an international congress and an article is in preparation.

Andreani M., Munoz M., Marcaillou C., Delacour A., France L., Iron speciation as a function of serpentinization degree in natural serpentinites. (*in prep for Earth & Planetary Science Letters*)

Andreani M., Munoz M., Delacour A., Marcaillou C., Godard M., France L., Serpentinization at oceanic hydrothermal sites with emphasis on iron incorporation in serpentine. *International Clay Conference, Italy, June 2009.*

¹Hy-GEO project (CNRS PIE 2009/10) : « Characterisation of hydrogen production processes during the hydrothermal alteration of ferro-magnesian rocks » (P.I. : M. Andreani)

Wilke et al., 2001. Oxidation state and coordination of Fe in minerals : an Fe K-XANES spectroscopic study. *American Mineralogist*, 86, 714-730.

