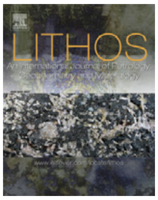
Lithos 178 (2013) 70–83

Contents lists available at ScienceDirect

Lithos

journal homepage: www.elsevier.com/locate/lithos



μXANES study of iron redox state in serpentine during oceanic serpentinization

M. Andreani [a,*], M. Muñoz [b,c], C. Marcaillou [b], A. Delacour [d,e]

[a] Laboratoire de Géologie de Lyon, UMR 5276, ENS-Université Lyon 1, France
[b] Institut des Sciences de la Terre, Université Grenoble 1, France
[c] European Synchrotron Radiation Facility, Grenoble, France
[d] Géosciences Environnement Toulouse, Université Toulouse 3, France
[e] Laboratoire Magmas et Volcans, UMR 6524, Université St Etienne, France

ARTICLE INFO

Article history:
Received 28 August 2012
Accepted 11 April 2013
Available online 20 April 2013

Keywords:
Serpentine
Iron
Redox
Hydrogen
W/R
Mid-ocean ridge

ABSTRACT

Serpentinization of ultramafic rocks at mid-ocean ridges generates significant amounts of H_2, CH_4, and supports specific biological communities. The abiotic H_2 production is attributed to the reduction of H_2O during serpentinization, which balances oxidation of ferrous iron contained in primary minerals (mainly olivines and pyroxenes) to ferric iron contained in secondary minerals (mainly serpentines and magnetite). Magnetite has thus far been considered as the sole Fe^{3+}-carrier for estimating bulk H_2 production, notably because the valence of iron in serpentine minerals and its relationship with both magnetite abundance and serpentinization degree are usually not determined. We show that the serpentine contribution to the Fe and Fe^{3+} budget has a significant effect on H_2 production. We performed μ-XANES analysis at the Fe *K*-edge on thin sections of peridotites with various degrees of serpentinization from ODP Leg 153 (MARK region, 23°N). Fe^{3+}/Fe^{Tot} in oceanic serpentines is highly variable (from ~0.2 to 1) at the thin section scale, and it is related non-linearly to the local degree of serpentinization. A typical value of 0.7 is observed above 60% serpentinization. The highest values of Fe^{3+}/Fe^{Tot} observed within or close to late veins suggest that the Fe^{3+}/Fe^{Tot} in serpentine record the local water–rock (W/R) ratio, as previously proposed from thermodynamic modeling. We estimate that the (W/R) ratio increased from ~0.6 to 25 during serpentinization at MARK, and locally reached ~100 in veins. Mass balance calculations combining all mineral and bulk rock analyses provide the distribution of Fe and Fe^{3+} as serpentinization progresses. Serpentine dominates the Fe^{3+} budget of the rock over magnetite during the first 75% of serpentinization, contributing up to 80% of the total Fe^{3+}. At later stages, serpentine contribution to the Fe^{3+} budget decreases down to ~20%, while magnetite formation exponentially increases. Iron transfer from serpentine to magnetite balances the bulk Fe^{3+} content of the rock that increases almost linearly with the advance of the reaction. Formation of serpentine accounts for the majority of Fe^{3+} and H_2 production at early stages of serpentinization at a depth >2 km at MARK where the concentration of H_2 can reach more than 100 mM according to the low W/R. H_2 production values and depths can vary from one site to another, depending on the evolution of the temperature, W/R ratio, inlet fluid composition, and favored formation of serpentine vs. magnetite. At MARK, Fe^{3+} in serpentine represents 15–27% of the total Fe contained in a rock serpentinized to more than 80%, and accounts for 25% of the total H_2 production that is estimated at 325–335 mmol/kg of rock. The absence of magnetite does not necessarily mean a negligible H_2 production, even at low T conditions (<150–200°C) under which the Fe- and Fe^{3+}-richest serpentines have been observed. Serpentine minerals are important Fe^{3+}-carrier in the altered ocean lithosphere, and may affect mantle redox state while dehydrating at depth in subduction zones.

1. Introduction

Serpentinization is a hydration and redox reaction that transforms mantle-forming minerals (olivine and pyroxenes) into hydrous phyllosilicates (serpentine +/— brucite), iron oxides and hydrogen. In the oceanic lithosphere, serpentinization has been widely documented at slow- and ultraslow-spreading ridges where partially to fully serpentinized mantle peridotites represent up to 50% of the lithologies along some ridge segments (Cannat et al., 1995a; Escartin et al., 2008; Lagabrielle et al., 1998; Smith et al., 2006). Oceanic serpentinization is locally associated with active hydrothermal vents known to release significant amounts of abiotic H_2, CH_4, and possibly other complex carbon molecules (Charlou et al., 2002; Holm and Charlou, 2001; Lang et al., 2010; Proskurowski et al., 2008).

Production of large amounts of H_2 during serpentinization has raised an increasing interest in the last decade as it is a source of energy that could be optimized and industrially exploited, and it constitutes a

---

[*] Corresponding author.

E-mail addresses: muriel.andreani@univ-lyon1.fr (M. Andreani), manuel.munoz@ujf-grenoble.fr (M. Muñoz), adelie.delacour@univ-st-etienne.fr (A. Delacour).

0024-4937/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.lithos.2013.04.008

metabolic substrate for microorganisms that develop away from photosynthetic energy supply (Schrenk et al., 2011; Takai et al., 2004). Numerous experimental studies have demonstrated the efficient production of H_2 by bulk rock serpentinization of olivine or peridotites between 200–400 °C and 300–500 bars (Allen and Seyfried, 2003; Berndt et al., 1996; Malvoisin et al., 2012; Marcaillou et al., 2011; McCollom and Seewald, 2001; Seyfried et al., 2007). Thermodynamic calculations suggest that H_2 production is most favored at 200–315 °C for a pressure of 350 bar (McCollom and Bach, 2009).

The abiotic production of hydrogen is attributed to the reduction of H_2O during oxidation of the ferrous component of primary minerals. The 1:1 linear correlation between hydrogen production and the total amount of ferric iron in product minerals has also been verified experimentally (Marcaillou et al., 2011). The raw amount of hydrogen formed is thus directly linked to the amount and oxidation state of iron incorporated into product minerals, mainly magnetite and serpentine. Usually, magnetite is assumed to be the only Fe^{3+}-carrier considered for relating the bulk H_2 production to mineralogical changes in natural, experimental or theoretical systems (Cannat et al., 2010; Malvoisin et al., 2012; McCollom and Bach, 2009). Actually, the serpentinization reaction is often further simplified in the literature by considering that serpentine contains no iron. When iron in serpentine is taken into account, it is usually assumed to be ferrous (Cannat et al., 2010; Malvoisin et al, 2012; McCollom and Bach, 2009; Sleep et al., 2004). Hence, the ferric component of serpentine is neglected, although several authors have demonstrated that a significant amount of ferric iron can be incorporated in the serpentine structure, with a Fe^{3+}/Fe^{Tot} ranging between ~0 and 1 in both natural (Andreani et al., 2008; Fuchs et al., 1998; Klein et al., 2009; O'Hanley and Dyar, 1993) and experimental samples (Marcaillou et al., 2011; Seyfried et al., 2007). Trivalent cation is incorporated into the trioctahedral serpentine structure by a ferri-Tschermack's substitution (toward a cronstedtite end-member) or by an octahedral-vacancy model (Evans, 2008; Wiks and Plant, 1979). In any case, serpentine can play an important role in Fe^{3+} storage that has been disregarded when estimating H_2 production.

Klein et al. (2009) have considered the possible Fe^{3+} uptake in serpentine in reaction path modeling of serpentinization. In their equilibrium model, the temperature (T), water–rock ratio (W/R), and initial modal rock composition control hydrogen production via iron speciation and iron partitioning between secondary phases. However, natural serpentinizing systems are kinetically controlled and opened to external fluid inputs. In addition, T and W/R may vary with time and space, depending on the geological setting, and lead to variable H_2 fluxes.

Understanding of the serpentinization dynamics at natural sites requires the knowledge of iron content and redox state in natural serpentine minerals, and its relationship with both magnetite abundance, serpentinization degree, and the regional setting. We performed µ-XANES analyses at the iron *K*-edge (ID24 beamline, ESRF; France) for determining the redox state of serpentine minerals selected from serpentinized peridotites drilled during ODP Leg 153, at 23°N along the Mid-Atlantic Ridge. This site is well characterized, notably for the temperature (Agrinier and Cannat, 1997) and depth of serpentinization (Canales et al., 2000), and its petrographic and tectonic evolution (Andreani et al., 2007). Combined with bulk rock analyses and magnetite content (Oufi et al., 2002), we built a model of the evolution of iron speciation and hydrogen production associated with serpentinization of oceanic peridotite.

2. Geological setting

Serpentinites were sampled in the cores recovered from Holes 920 B (126.4 m.b.s.f., meter below sea floor) and D (200.8 m.b.s.f.). These holes were drilled during ODP Leg 153 within the western fault scarp bounding the Mid-Atlantic Ridge valley at 23°20.31′N, 30 km south of its intersection with the Kane transform fault (MARK area). The full-spreading rate in this area is ~2.7 cm/years, and the drilled serpentinites are part of a <1 m.y. old oceanic crust exposed under the footwall of a major detachment fault (Cannat et al., 1995b). Interpretation of the seismic velocity structure at ODP Site 920 shows a continuous velocity gradient that increases to reach mantle velocities (~8 km/s) at ~3–4 km b.s.f., suggesting a progressive decrease of serpentinization with depth (Canales et al., 2000) and a serpentinite-dominated lithology below Site 920.

Holes 920 B and D have predominantly recovered partially to fully serpentinized harzburgites with an average mode of 82% olivine, 15% orthopyroxene, 2% clinopyroxene and 1% of spinel (Cannat et al., 1995b). The degree of serpentinization along both holes is estimated between 50% and 100% from mean relic mineral abundances at the thin section scale. No periodicity or gradient of serpentinization with depth is observed along the alteration profiles in these holes. The

Table 1
Bulk rock (BR) characteristics of the selected MARK samples.

		L7	L9	L11	L24
Selected samples, ODP		153-920B-3R1 87–92 cm	153-920D-5R2 2–9 cm	153-920D-14R2 91–94 cm	153-920D-14R3 19–23 cm
Given name		MARK7	MARK9	MARK11	MARK24
Depth (mbsf)		24	38	116	117
Density		2.65	2.66	2.88	2.83
Porosity		0.10	0.10	0.02	0.04
BR serpentinization degree1	%	83.4	81.0	54.1	59.9
BR serpentinization degree2	%	86.8	84.5	57.2	63.1
BR chemical analyses					
SiO_2	wt	37.90	38.59	41.02	39.32
Al_2O_3	wt	0.95	1.29	1.30	1.20
Fe_2O_3Tot	wt	7.77	7.28	8.38	8.53
MnO	wt	0.14	0.09	0.13	0.12
MgO	wt	38.26	38.85	39.47	40.69
CaO	wt	0.33	< L.D.	1.90	1.35
Na_2O	wt	< L.D.	< L.D.	< L.D.	0.00
K_2O	wt	< L.D.	< L.D.	< L.D.	0.02
TiO_2	wt	0.01	0.02	0.02	0.01
P_2O_5	wt	< L.D.	< L.D.	< L.D.	0.00
LOI	wt	13.79	13.32	7.72	9.22
Tot	wt	99.14	99.44	99.93	100.46
FeO (Fe^{2+} titration)	wt	2.19	2.21	4.96	4.43
Fe^{3+}/Fe^{Tot}		0.69	0.66	0.34	0.42