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Serpentinization, iron oxidation, and aqueous conditions in an ophiolite: Implications for hydrogen production and habitability on Mars

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ABSTRACT

Molecular hydrogen produced through iron oxidation during formation of serpentine and magnetite can sustain terrestrial subsurface ecosystems. The Fe^{3+} in serpentine partitions into octahedral and tetrahedral sites differently as serpentinization proceeds, and tetrahedral Fe^{3+} is present toward the end of serpentinization. We map Fe oxidation states in a serpentinite to determine the degree to which serpentinization progressed and where hydrogen production has been maximized to assess habitability at an abandoned chrysotile mine in Norbestos, Quebec, in association with the Canadian Space Agency's Mars Methane Analogue Mission. We also analyzed stable isotopes of carbon and oxygen in carbonates to constrain the conditions of water–rock interaction during serpentinization. Iron oxidation and coordination was determined through field imaging of rock walls with a visible hyperspectral imager (420–720 nm), and samples collected from imaged rocks and elsewhere in the mine were imaged in the laboratory (420–1100 nm). Sample chemistry, mineralogy, and oxidation state were determined with laboratory measurements of visible through mid-infrared reflectance spectra, major element chemistry, mineralogy, and Mössbauer spectroscopy. Mapping with hyperspectral imaging of outcrops and hand samples shows that tetrahedral Fe^{3+} is common in serpentinites at this site, and results are confirmed through other measurements. Major element chemistry and mineralogy are consistent with serpentine plus minor carbonate. Carbonate samples show an exceptional range in $\delta^{13}C$ (-13.14 to $+16.12$‰ VPDB) and $\delta^{18}O$ (-15.48 to -3.20‰ VPDB) that vary with location in the mine. Carbonates south of a shear zone ($\delta^{13}C$ more positive) likely formed during periods of serpentinization in a carbon-limited reservoir closed to carbon addition but open to methane escape. Carbonates in a shear zone ($\delta^{13}C$ more negative) probably formed later at low temperatures through CO_2-metasomatism or atmospheric weathering, and isotopic trends are consistent with kinetic fractionation. The extensive presence of tetrahedral Fe^{3+} in serpentine shows the system liberally produced H_2 while the isotope systematics have implications for preservation of indicators of the aqueous conditions that formed serpentinites on Mars and their habitability.

1. Introduction

Evidence of atmospheric methane on Mars and localized, episodic release of methane detected by the Mars Science Laboratory *Curiosity* rover have generated significant interest because methane can be produced though biological processes (e.g., Formisano et al., 2004; Krasnopolsky et al., 2004; Oze and Sharma, 2005; Mumma et al., 2009; Webster et al., 2014). One plausible source of this methane could be serpentinization, where olivine and pyroxene are hydrated at elevated temperatures, producing molecular hydrogen that can be oxidized biotically or abiotically to methane (e.g., Horita and Berndt, 1999; Sleep et al., 2004; Oze and Sharma, 2005; Schulte et al., 2006). Further connecting

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methane and serpentinization, atmospheric methane on Mars may be spatially associated with serpentine-bearing deposits identified from orbit (Wray and Ehlmann, 2011). Serpentinization has even been proposed to explain the martian crustal dichotomy and magnetic anomalies (Quesnel et al., 2009) and loss of surface water after the Noachian period (Chassefière et al., 2013). The presence of serpentine and carbonate on the Martian surface detected through orbital (e.g., Bandfield et al., 2003; Ehlmann et al., 2008, 2009, 2010) and surface (Boynton et al., 2009; Morris et al., 2010) investigations is important in assessing martian subsurface habitability.

Previous work has shown that H_2 produced during serpentinization can support microbial communities that use H_2 to produce CH_4 (e.g., Schulte et al., 2006; Cardace and Hoehler, 2009; McCollom and Seewald, 2013). Microbes on Earth live off H_2 and CH_4 produced via serpentinization of peridotite on the seafloor Lost City hydrothermal field (Kelley et al., 2001, 2005), and CH_4 fluxes have been detected at locations of continental serpentinization (e.g., Etiope et al., 2012; Cardace et al., 2013; Szponar et al., 2013). The gaseous and mineral products of serpentinization may have been important in the origin of life on Earth and other planets (Russell et al., 1989; Sleep et al., 2004; McCollom and Seewald, 2013; Schrenk et al., 2013 and references therein). The serpentinization reaction is exothermic and, once initiated, may heat fluids enough to allow serpentinization to continue in the absence of an external heat source (Lowell and Rona, 2002; Emmanuel and Berkowitz, 2006). The goals of this paper are to characterize conditions of water–rock interactions and formation of biologically important byproducts (e.g., H_2, CH_4) in a terrestrial serpentinizing system in order to better understand the habitability of such systems elsewhere in the solar system and the signatures of serpentinizing conditions that might be preserved in the geologic record. To do this, we use hyperspectral imaging of outcrops and samples to map Fe oxidation state and coordination environments as proxies for degrees of serpentinization and H_2 generation and isotopic analyses to understand fluid chemistries and alteration environments.

1.1. Serpentinization

H_2 production via serpentinization accompanies Fe oxidation in both magnetite and serpentine (O'Hanley and Dyar, 1993, 1998; Seyfried Jr. et al., 2007; Marcaillou et al., 2011; Neubeck et al., 2011; Andreani et al., 2013; Mayhew et al., 2013; Stander et al., 2013; Klein et al., 2014). Andreani et al. (2013) found that most Fe^{3+} was in serpentine in rocks that had been up to 75% serpentinized, after which serpentine became more Mg-rich with more Fe^{3+} in magnetite. They estimate that Fe oxidation within serpentine accounts for 80% of the total H_2 produced in 50% serpentinized rocks and 22–40% of the H_2 in 90% serpentinized rocks, with the remaining H_2 from Fe^{2+} oxidation that goes into magnetite (Andreani et al., 2013). At temperatures <150–200 °C, thermodynamics does not favor magnetite formation, and Fe oxidation in serpentine may produce all of the H_2 (Andreani et al., 2013; Klein et al., 2014). During serpentinization, Fe^{3+} is produced and goes into both tetrahedral and octahedral sites in serpentine, and Fe^{3+} content increases in octahedral sites before tetrahedral sites (Marcaillou et al., 2011), as shown in Fig. 1a. Fe^{3+} in serpentine may stabilize the crystal structure, and coupled substitution of Fe^{3+} for Si^{4+} in tetrahedral sites and Fe^{3+} for Mg^{2+} in octahedral sites is one method of charge-balancing the structures (O'Hanley and Dyar, 1993; Evans et al., 2013). Fe^{3+} substitution in tetrahedral sites is favored in low Si environments such as where the protolith is ultramafic (O'Hanley and Dyar, 1993; Evans et al., 2013). Additionally, during advanced serpentinization as indicated by bulk rock water contents >10 wt%, enough Fe^{3+} can be produced that Fe^{3+}/Fe^{2+} ratios exceed 2, the ratio in magnetite, and the excess Fe^{3+} goes into serpentine (Evans et al., 2013). Throughout this Fe^{3+} production and substitution into the serpentine structure, first in octahedral and then in both octahedral and tetrahedral sites, H_2 is produced (Marcaillou et al., 2011). Tetrahedral Fe^{3+} can be identified with visible and near infrared spectroscopy by a spin forbidden electronic transition near 450 nm as shown in Fig. 1b (e.g., Burns, 1993; Dyar, 2002; Cloutis et al., 2011b). Building on these results by Marcaillou et al. (2011) and others, we argue that remote sensing can determine locations where the highest total H_2 has been produced by identifying tetrahedrally-coordinated Fe^{3+} in serpentine.

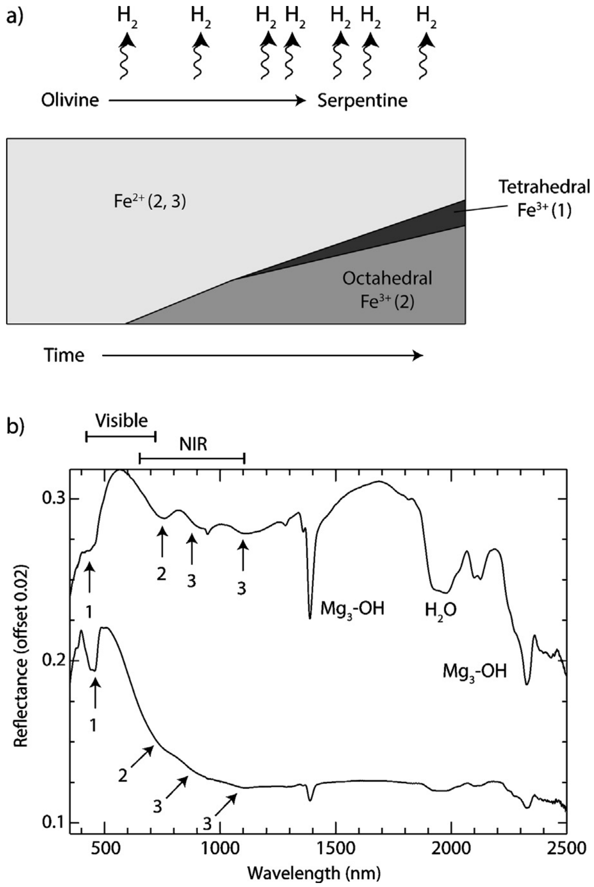

Fig. 1. a. Diagram showing relative proportions of Fe^{2+} and tetrahedral and octahedral Fe^{3+} in serpentine with time during serpentinization determined experimentally by Marcaillou et al. (2011). H_2 is produced during this process. Numbers correspond with absorption features in b. b. Reflectance spectra of two points on the surfaces of samples with arrows showing locations of absorption features in serpentines. 1: Spin-forbidden electronic transition of tetrahedrally-coordinated Fe^{3+}. 2: Fe^{2+}/Fe^{3+} intervalence charge transfer. 3: Electronic transition of octahedrally-coordinated Fe^{2+}. Also shown is the wavelength coverage of the visible imager (labeled visible) and NIR imager (labeled NIR). Band assignments are from Bishop et al. (2002, 2008), Burns (1993), Cloutis et al. (2011a, 2011b), Dyar (2002), King and Clark (1989), and Post and Borer (2000).

2. Field site

Field investigations were conducted at an abandoned open-pit chrysotile asbestos mine in Norbestos, Quebec, located at 45.82°N, 71.84°W in association with the 2012 deployment of the Canadian Space Agency's Mars Methane Analogue Mission (M3) (Cloutis et al., 2011c, 2013). M3 utilized a micro-rover to search for methane and explore the site geology in order to characterize the biological potential (Cloutis et al., 2013). Results of the 2011 M3 deployment at nearby Jeffrey Mine in Asbestos, Quebec, located ~10 km southwest of the Norbestos mine (Cloutis et al., 2012) include de-