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

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\textbf{A B S T R A C T}

Molecular hydrogen produced through iron oxidation during formation of serpentine and magnetite can sustain terrestrial subsurface ecosystems. The Fe\textsuperscript{3+} in serpentine partitions into octahedral and tetrahedral sites differently as serpentinization proceeds, and tetrahedral Fe\textsuperscript{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\textsuperscript{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 δ\textsuperscript{13}C (−13.14 to +16.12‰, VPDB) and δ\textsuperscript{18}O (−15.48 to −3.20‰, VPDB) that vary with location in the mine. Carbonates south of a shear zone (δ\textsuperscript{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 (δ\textsuperscript{13}C more negative) probably formed later at low temperatures through CO\textsubscript{2}-metasomatism or atmospheric weathering, and isotopic trends are consistent with kinetic fractionation. The extensive presence of tetrahedral Fe\textsuperscript{3+} in serpentine shows the system liberally produced H\textsubscript{2} while the isotope systematics have implications for preservation of indicators of the aqueous conditions that formed serpentinites on Mars and their habitability.

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1. Introduction

Evidence of atmospheric methane on Mars and localized, episodic release of methane detected by the Mars Science Lab-
methane and serpentinization, atmospheric methane on Mars may be spatially associated with serpentine-bearing deposits identified from orbit (Wray and Ehlimann, 2011). Serpentinization has even been proposed to explain the martian crustal dichotomy and magnetic anomalies (Quensel et al., 2009) and loss of surface water after the Noachian period (Chasséfère et al., 2013). The presence of serpentine and carbonate on the Martian surface detected through orbital (e.g., Bandfield et al., 2003; Ehlimann 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 H₂ produced during serpentinization can support microbial communities that use H₂ to produce CH₄ (e.g., Schulte et al., 2006; Cardace et al., 2013; McCollom and Seewald, 2013). Microbes on Earth live off H₂ and CH₄ produced via serpentinization of peridotite on the seafloor LOST CITY hydrothermal field (Kelley et al., 2001, 2005), and CH₄ fluxes have been detected at locations of continental serpentinization (e.g., Etope 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., H₂, CH₄) 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 H₂ generation and isotopic analyses to understand fluid chemistries and alteration environments.

1. Serpentinization

H₂ 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 Fe³⁺ was in serpentine in rocks that had been up to 75% serpentinized, after which serpentine became more Mg-rich with more Fe⁺ in magnetite. They estimate that Fe oxidation within serpentine accounts for 80% of the total H₂ produced in 50% serpentinized rocks and 22–40% of the H₂ in 90% serpentinized rocks, with the remaining H₂ from Fe²⁺ 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 H₂ (Andreani et al., 2013; Klein et al., 2014). During serpentinization, Fe³⁺ is produced and goes into both tetrahedral and octahedral sites in serpentine, and Fe³⁺ content increases in octahedral sites before tetrahedral sites (Marcaillou et al., 2011), as shown in Fig. 1a. Fe³⁺ in serpentine may stabilize the crystal structure, and coupled substitution of Fe³⁺ for Si⁴⁺ in tetrahedral sites and Fe³⁺ for Mg²⁺ in octahedral sites is one method of charge-balancing the structures (O’Hanley and Dyar, 1993; Evans et al., 2013). Fe³⁺ 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

![Diagram of Fe oxidation in serpentine](image)
tection of methane and modeling of its source and dispersal (Olsen et al., 2012) and discrimination of peridotite and slate units using an electromagnetic induction sounder (Boivin et al., 2013).

The geologic history of the Asbestos Ophiolite Complex, in which the Jeffrey and Norbestos mines are located, has been described previously (e.g., Riordon, 1973; Laurent, 1975; Laurent and Hebert, 1979; O’Hanley, 1987, 1996; Pinet and Tremblay, 1995). The Norbestos mine is part of the Nicolet deposit described by Riordon (1973) where serpentinized Early Ordovician peridotites are in contact with Cambrian slates. The Jeffrey Mine and Norbestos sites are in the ophiolite belt of the Quebec Appalachians obducted during the Taconic orogeny (Pinet and Tremblay, 1995; Schroetter et al., 2006). Dating of the nearby Thetford Mines ophiolite determined a 479 +3/−2 Ma crystallization age (Dunning and Pedersen, 1988), and the ophiolite was emplaced onto the continent 477 ± 5 Ma (Whitehead et al., 1995). The ophiolite was serpentinized twice: first in an oceanic environment and then again after obduction (Laurent and Hebert, 1979), although it has been suggested that these events may not be distinct and the first may grade into the second because the ophiolite was emplaced onto the continent shortly after crystallization (O’Hanley, 1987). Laurent (1975) notes the presence of low temperature alteration near faults attributed to hydrothermal metasomatism after emplacement onto the continent. The deposit was later deformed during the Acadian orogeny (Pinet and Tremblay, 1995 and references therein). The protolith for the serpentinite studied here was harzburgite (Riordon, 1973). Most mineable chrysoilite deposits formed in harzburgite, which was not fully serpentinized during the first serpentinization event, allowing chrysoilite vein formation during the second period of serpentinization (Laurent and Hebert, 1979). Today, the main rock type present is serpentine with minor carbonate.

3. Methods

Points across all rock sample surfaces were measured with an ASD (Analytical Spectral Devices, Boulder, Colorado) FieldSpec 3 spectrometer (350–2500 nm, spectral resolution 3 nm at 700 nm and 10 nm at 1400 and 2100 nm) at Brown University using an external light source and bare fiber optic cable and were made relative to Spectralon® (Labsphere, North Sutton, New Hampshire) and corrected for the absolute reflectance properties of Spectralon®. Measurements at these wavelengths show diagnostic absorption features due to electronic transitions and charge transfers of transition metal cations (e.g., Burns, 1993) and vibrational absorption features from OH, H2O, and metal–OH overtones and combination tones (e.g., Clark et al., 1990; Bishop et al., 2002).

Descriptions of all samples analyzed further and analyses done on each are given in Table 1, and all data not online or in the text are available upon request. Six serpentine and carbonate samples were ground with a mortar and pestle and sieved to form <45, 45–75, 75–125, and >125 μm particle size separates. The 45–75 μm separates were measured in the Keck/NASA Reflectance Experiment Laboratory (RELAB) at Brown University on a Nicolet Nexus 870 Fourier Transform Infrared (FTIR) spectrometer relative to a gold standard (Peters, 1983). Spectra at this wavelength range show fundamental vibrational absorption features and their combinations and overtones (e.g., Farmer, 1974; Strens, 1974). Wavelengths longer than 2500 nm permit identification of carbonates in mixtures with serpentine because the carbonate and serpentine absorption features do not overlap as they do at wavelengths <2500 nm (e.g., Hunt and Salisbury, 1971; Gaffey, 1987; King and Clark, 1989). These data will be available through the RELAB online database in accordance with their release procedures (http://www.planetary.brown.edu/relab/).

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Description</th>
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<th>Raman</th>
<th>Stable isotopes</th>
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</tr>
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<td>Nor3-1-4</td>
<td>Serpentine with carbonate blebs from shear zone</td>
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<td>Serpentine from shear zone with carbonate coatings</td>
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<td>Nor3-2</td>
<td>Vein of fine white powder or dark serpentine, float</td>
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<tr>
<td>Nor3-4</td>
<td>Vein of bendable serpentine and hydromagnesite from shear zone</td>
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<td>Nor3-9b</td>
<td>Green and dark blue serpentinite with rare carbonate coatings from shear zone</td>
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<tr>
<td>Nor5-2</td>
<td>Serpentinite with carbonate from shear zone</td>
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</tbody>
</table>

Table 1. Samples, descriptions, and analyses done. Reflectance spectra (ASD) and hyperspectral images were obtained of all samples.

a Numbered samples from each single hand sample that were analyzed. Note that carbonate samples were often thin coatings on serpentinite rock.

b Sample was ground and sieved to <45, 45–75, 75–125, and >125 μm separates.
Bulk major element chemistry (Al, Ca, Cr, Fe, K, Mg, Mn, Na, P, Ni, Si, and Ti) was measured on five ground samples (Table 1) with three runs in triplicate using Inductively Coupled Plasma–Atomic Emission Spectrometry (ICP–AES) after a flux fusion sample preparation using methods modified from Murray et al. (2000) at Brown University’s Environmental Chemistry Facility. Seven National Institute of Standards and Technology and U.S. Geological Survey standard reference materials were run (MAG-1, BIR-1, BCR-2, BHVO-2, NIST2711, NIST1646a, and SGR-1). Blanks were run every 6 samples. For the flux fusion preparation, 40 mg of each sample were mixed with 160 mg lithium metaborate flux and fused at 1050°C for 10 min. The molten flux and samples were then poured into 10% HNO₃, agitated for at least 30 min, filtered through 0.45 μm filters, and diluted to achieve ~4000× dilutions. Major element concentrations were then measured on a JY2000 UltraTrace ICP–AES using peak wavelengths given in Murray et al. (2000), and actual concentrations were calculated through linear regressions of standards with known concentrations to account for losses during the flux fusion process after correcting for ICP–AES drift and subtracting blanks. Carbon content was determined on the same five samples with three in triplicate using a CE Instruments Model NC2100 Elemental Analyzer. Samples were dried overnight at 60°C, and 8–10 mg of each were weighed into tin capsules. Concentrations were determined from regressions using acetonilide, cyclohexane, pine (SRM 1575), and Montana soil (SRM 2711) standards.

Minerals of Nor3-1 (coating), Nor3-6, Nor4-9, Nor4-12 (green), Nor4-12 (red), and Nor4-13 (<125 μm particle size separates) were determined using an inXitu Terra (#213) X-ray diffractometer (XRD) with a Co source at the University of Rhode Island, summing 250 exposures over 2500 s after drying samples at 50°C for 7 h. Two-dimensional images were converted to conventional one-dimensional XRD patterns, with a 2θ range of 5.0 to 54.9°. Peak positions of XRD patterns were compared with known library minerals using the database within XPowder. Minerals of carbonate samples Nor3-7, Nor3-8 (thinner), Nor4-2 (bottom), Nor4-7_1, and Nor5-1_2 (outside) were determined through powder XRD at Indiana University (Bloomington, Indiana) using a Bruker D8 Advance instrument with Cu radiation and a Si001 point detector. Data were measured from 2 to 70° 2θ overnight (count times per 0.02° step of 8 to 15 s), using samples mounted as slurry on “zero-background” quartz plates. Data analysis used Bruker AXS EVA and Topas software.

Mössbauer spectra were acquired for ~125 μm separates of three samples (Nor4-9, Nor4-12_green, Nor4-13) to determine the fraction of Fe in different oxidation states and coordination environments using a source of ~40 mCi ⁵⁷Co in Rh on a S20 Co. model WT302 spectrometer (Mount Holyoke College). Data were collected at 295 K over a ±4 mm/s velocity range and at 4 K over a ±10 mm/s velocity range in 2048 channels. Spectra were corrected for nonlinearity via interpolation to a linear velocity scale, which is defined by the spectrum of the 25 μm Fe foil used for calibration. All data were corrected to remove the fraction of the baseline due to Compton scattering of 122 keV gamma rays by electrons inside the detector. Mössbauer data were posted on www.mtholyoke.edu/courses/mdl40/database/. Spectra were fit using the Mextisd program, which uses a line-shape-independent model for fitting spectra and solves the full hyperfine-interaction Hamiltonian, producing a distribution of values for the hyperfine field and using quadrupole shift, center shift, and line width as adjustable parameters. It does not assume any particular distribution shape. The area of the peaks that make up each doublet or sextet is proportional to the percentage of Fe in that site. If known, correction for the mineral-specific recoil-free fraction can be applied for optimum accuracy, but f has not yet been determined for serpentine minerals. Errors (accuracy) of peak areas are roughly ±3% absolute, on Mössbauer parameters are ±0.03 mm/s, and on Bhf ~ ±0.2 T for individual sextets or doublets.

Samples of carbonates precipitated on serpentinite (Table 1) were identified by reaction with dilute HCl, scraped off with a metal spatula, and ground for isotope analyses. Carbon and oxygen stable isotopes were analyzed by a Gas Bench II coupled with Delta Plus XP IRMS at the Stable Isotope Research Facility at Indiana University with 16 samples run in triplicate and one in duplicate. Standardization to the VPDB international scale was performed using NBS-19 and two internal carbonate reference materials, LC-1 and CM-A. Carbonate contents (as calcite) for each sample were calculated using the CO₂ yields assuming all carbonate present is calcite.

Rock samples were imaged at the University of Winnipeg with two Channel Systems hyperspectral imagers: a visible imager (1.3 megapixel sensor, 420–720 nm, 10 nm spectral resolution, 5 nm sampling interval) and a near-infrared (NIR) imager (1.3 megapixel sensor, 650–1100 nm, 10 nm spectral resolution; two images interleaved to achieve 5 nm sampling). Spatial resolutions depend on distances from imager to sample, but typical resolutions at the observing distances were sub-mm. Exposure times varied with wavelength and were adjusted to maximize signal to noise through the imagers’ autoexpose feature. Images were calibrated to reflectance (R) using the following equation:

$$ R = \frac{S_t - S_d}{S_t - S_{	ext{dark}}} \times R_5, $$

(1)

where $S_t$ is the target sample image, $S_d$ is the dark image, $S_5$ is the Spectralon® image, $t_5$ are the target sample image exposure times, $t_{	ext{dark}}$ are the Spectralon® image exposure times, and $R_5$ is the reflectance spectrum of Spectralon®. Dark values were independent of exposure times, while tests of the imagers showed that signals where the sensor received light scaled linearly with exposure time. Since Spectralon® is not a perfect reflector (e.g., 100% reflectance), images were corrected for the absolute spectrum of Spectralon® using RELAB spectrum HL-JFM-012 of SRT-99-050 resampled to the wavelengths sampled by the imagers.

Hyperspectral images were collected in the field of rock outcrops on mine walls and samples collected around the mine with the same visible imager used in the laboratory. Images were calibrated through a dark object subtraction (Chavez Jr., 1996 and references therein) and ratio to in-scene calibration target (white poster board) with the following equation:

$$ R = \frac{S_t - D}{C - D} \times R_p, $$

(2)

where $D$ is the average dark spectrum, $C$ is the average calibration target spectrum, and $R_p$ is the reflectance spectrum of the calibration target. All values except $R_p$ are in digital number. These methods are similar to those of Clark et al. (2002) for AVIRIS data calibration. There is good agreement between field and laboratory imaging (Fig. S1).

Images were analyzed with parameters to map various spectral features (e.g., Clark and Roush, 1984; Pelkey et al., 2007) with formulas and interpretations in Table 2. Images were resampled to Pancam and Mastcam bandpasses using transmission profiles given by Bell et al. (2003, 2012) to compare these hyperspectral measurements with multispectral systems on the Opportunity and Curiosity rovers currently operating on the surface of Mars. This was done by assuming that the bandpass shape for these hyperspectral imagers is a sinc²(x) function as has been reported for acousto-optic tunable filter systems (Georgiev et al., 2002) with full width at half maximum equal to the 10 nm spectral resolution.
## 4. Results

Laboratory measurements (spectroscopy, chemistry, and mineralogy) show samples dominated by serpentine with minor carbonate and magnetite that differ in the iron oxidation states and coordination environments within serpentine. These results scale to the outcrop. The samples also differ with location within the mine in the stable isotopic signatures of thin carbonate precipitates.

ASD spectra of samples are generally consistent with serpentine with some variations (Fig. 1b). FTIR spectra of select samples further resolve absorption features near 1390 and between 2000 and 2600 nm into several sharp bands (Fig. 2). In one piece of sample Nor4-9, which is serpentine with no discernible carbonate, narrow absorption features at 1382, 1388, 1390, and 1392 nm are due to the first Mg$_2$–OH stretching overtone, consistent with published serpentine spectra (e.g., King and Clark, 1989; Clark et al., 1990; Bishop et al., 2008). The presence of multiple absorption features may result from OH coordinated by multiple cations (Mustard, 1992) or differences in vibrational frequencies of inner and outer OH groups (e.g., King and Clark, 1989). An asymmetric Mg$_2$–OH combination tone near 2320–2330 nm is seen in most ASD spectra (e.g., Clark et al., 1990; Post and Borer, 2000; Bishop et al., 2008) and is further resolved into distinct features at 2326 and 2337 nm in FTIR data. Most spectra also have vibrational absorption features at 2100 and 2130 nm typical of serpentine (e.g., Hunt and Evarts, 1981; King and Clark, 1989; Ehlmann et al., 2009) but not formally assigned to specific molecular vibrations. While H$_2$O is not present in ideal serpentine mineral structures, spectra of all serpentine samples measured here have broad OH stretch and H–O–H bend combination bands near 1900 nm (e.g., Clark et al., 1990). This absorption feature commonly seen in serpentine (e.g., Hunt and Evarts, 1981) may be due to adsorbed water, a H$_2$O-bearing phase such as another phyllosilicate mixed with serpentine, or trace water incorporated into the serpentine structure. In FTIR data (Fig. 2), an absorption feature near 2500 nm in a few spectra is due to a C–O combination often used to distinguish carbonates (Hunt and Salisbury, 1971). Additional features at 3350–3500 and 3800–4000 nm are diagnostic of carbonates (e.g., Schroeder et al., 1962).

The visible and near infrared wavelengths of ASD spectra (Fig. 1b) provide insight into Fe oxidation states within serpentine or other Fe-bearing minerals. In some spectra, a spin-forbidden electronic transition of tetrahedrally-coordinated Fe$^{3+}$ in serpentine is seen near 450 nm (e.g., Burns, 1993; Dyar, 2002; Cloutis et al., 2011b). A Fe$^{2+}$/Fe$^{3+}$ intervalence charge transfer at 700–750 nm and octahedral Fe$^{2+}$ electronic transitions within serpentine at 900–940 and 1100–1200 nm also are seen (e.g., Clark et al., 1990; Cloutis et al., 2011a, 2011b). The charge transfer and Fe$^{2+}$ electronic transitions are present in most spectra but vary in strength and spectral contrast, and overall slopes of spectra differ. These variations may be due to textures, coatings, the presence of magnetite, or oxidation state or coordination (Singer and Roush, 1983; Fischer and Pieters, 1993; Cloutis et al., 2011a). Minor magnetite in rocks disproportionately reduces reflectance and lowers spectral contrast (Hunt and Evarts, 1981). Red slopes are likely due to Fe$^{3+}$ in phases other than serpentine and formation of ferric oxides such as hematite, goethite, and ferrhydrite (e.g., Hunt and Ashley, 1979; Cloutis et al., 2011a).

Other sample analyses are consistent with mineralologies dominated by serpentine. Major element chemistries of samples without significant carbonate fractions are mostly Fe, Mg, and Si, consistent with the ultramafic protolith (Table 3). The chemistry of sample Nor4-9, which is typical of serpentinites at this site, is similar in composition to other reported serpentinites in Canada (e.g.,

<table>
<thead>
<tr>
<th>Spectral parameter</th>
<th>Formula$^a$</th>
<th>Red slope</th>
<th>Blue slope</th>
<th>Green peak</th>
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<td>BD1240</td>
<td>$1 - \frac{\text{reflectance at wavelength} \times 10^{-2}}{\text{reflectance at wavelength}}$</td>
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<td>BD1075</td>
<td>$1 - \frac{\text{reflectance at wavelength} \times 10^{-2}}{\text{reflectance at wavelength}}$</td>
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</table>

$^a$ Red = reflectance at wavelength \# nm
Wares and Martin, 1980; O’Hanley and Wicks, 1995), and mineralogy (Table 3) determined by XRD shows antigorite, lizardite, and magnetite, consistent with other analyses. Other samples also contain calcite (Nor4-12_red, Nor4-12_green, Nor4-13), hydromagnesite and magnesite (Nor3-1, Nor3-6), brucite (Nor3-6), and ferric oxides (Nor4-12_red). Note that XRD did not identify chrysotile in these samples because chrysotile veins were intentionally avoided when grinding the rocks. Carbonate samples that were analyzed contain calcite (Nor4-2, Nor5-1_2 outside), hydromagnesite and dolomite/ankerite (Nor3-7, Nor3-8 thinner), and pyroauroite (Nor3-7, Nor3-8 thinner, Nor4-7_1, Nor5-1_2 outside) as well as serpentine and, for some, talc or smectite.

Mössbauer spectra provide insights into the iron oxidation state and coordination, and fits are given in Table S1. These spectra can have multiple interpretations because tetrahedral and octahedral Fe$^{2+}$ peaks are close together, but despite these limitations are consistent with interpretations from visible-NIR spectroscopy of tetrahedral and octahedral Fe$^{2+}$ in Nor4-9 and Nor4-12_green and only octahedral Fe$^{3+}$ in Nor4-13. In the parameters for fits of Mössbauer spectra, tetrahedral Fe$^{2+}$ has an isomer shift $<0.25$, and octahedral Fe$^{3+}$ has an isomer shift of 0.25–0.50 (Dyar et al., 2006).

Carbon stable isotope measurements show a range of nearly 30‰ ($\delta^{13}$C), extending from $-13.14$ to $+16.12$‰ VPDB (Fig. 3; Table S2). Standard deviations where enough material was present to run replicates are $<0.62$‰, with most $<0.3$‰. While carbonate morphologies show no discernible correlation with isotope values, spatial distributions within the mine suggest that carbonates formed under different conditions and from different carbon reservoirs. With one exception, samples with $\delta^{13}$C values lower than $+2$‰ were collected within a shear zone that ran through the mine. Samples with $\delta^{13}$C values higher than 0‰ are from massive serpentinites located $\sim$100–200 m south of the shear zone.

Oxygen isotopic values ($\delta^{18}$O) are $-15.48$ to $-3.20$‰ VPDB with a reproducibility of 0.24‰ based on the standards, while larger standard deviations in some samples result from sample heterogeneity. Generally, samples with the most negative and most positive $\delta^{13}$C values have the most negative $\delta^{18}$O values (Fig. 3). Carbonate contents were calculated with an error of $\pm10$%, range from 9.6% to pure carbonate, and do not correlate with $\delta^{13}$C or $\delta^{18}$O.

Hyperspectral imaging maps different oxidation states within samples at high spatial resolutions. In the laboratory image of sample Nor4-9 (Fig. 4), a spatial resolution $<100$ μm/pixel was
achieved. Laboratory measurements were done under controlled lighting conditions with little to no contribution from atmospheric scattering. Absorption features due to tetrahedral Fe$^{3+}$, Fe$^{2+}$/Fe$^{3+}$ charge transfers, octahedral Fe$^{2+}$, H$_2$O/OH, and slopes from Fe$^{3+}$ were all mapped (Fig. 4, S4c), and the sample surface shows high variability despite the entire sample being serpentinite. Locations highlighted by the BD450 parameter generally also have high green peak parameter values and appear white or magenta in Fig. 4c (scatterplot in Fig. 4d). This correlation is expected because the peak at green wavelengths occurs due to absorptions from tetrahedral Fe$^{3+}$ at shorter wavelengths and an Fe$^{2+}$/Fe$^{3+}$ charge transfer at longer wavelengths (e.g., Burns, 1993; Dyar, 2002; Cloutis et al., 2011a, 2011b). Tetrahedral Fe$^{3+}$ has also been shown to correlate with octahedral Fe$^{3+}$ in lizardite (O’Hanley and Dyar, 1993). Spectra with the highest values for the green peak parameter have the deepest absorptions on either side of the peak, both of which require Fe$^{3+}$. Spectra with blue slopes differ texturally from other parts of the sample, there may be thin coatings transparent at longer wavelengths that contribute to the spectrum at shorter wavelengths, or the texture at the surface may be smooth, resulting in the surface scattering light differently at different wavelengths (Singer and Roush, 1983; Fischer and Pieters, 1993). Magnetite can also cause the spectrum to have a blue slope (Fischer and Pieters, 1993; Cloutis et al., 2011a). Redder parts of samples highlighted by the red slope parameter likely have Fe$^{3+}$-oxides present and have undergone oxidation unrelated to serpentinization (e.g., Hunt and Ashley, 1979; Cloutis et al., 2011a).

Other samples show similar results to Nor4-9, with red slope, green peak, and blue slope spectral parameters mapping discrete areas and correlations between the green peak and BD450 parameters. Samples Nor4-13 (Fig. S2) and Nor4-14 (Fig. S3) were collected from an imaged rock wall of the mine (Fig. 5) and show similar trends in laboratory imaging, although the 450 nm band depth is generally weaker or absent in Nor4-13 spectra. Nor4-13 is mostly serpentine with some calcite, and the green peak spectral parameter dominates most of the sample’s surface in laboratory and field images (Figs. 5, S2). ASD spectra of the ground portion of Nor4-13 and Mössbauer spectra indicate no tetrahedral Fe$^{3+}$ present, although laboratory imaging shows that small areas of the sample contain tetrahedral Fe$^{3+}$ in serpentine. At the outcrop-scale (Fig. 5), imaging highlights spectra of the sample’s surface overall as being dominated by the green peak, as in laboratory data. Sample Nor4-14 (Fig. S3) from elsewhere within the same outcrop.
image has red coatings on half its surface and green serpentine on the other half. Both the laboratory (Fig. S3) and field imaging data (Fig. 5) show these trends, and laboratory data show a correlation between the 450 nm band depth and the green peak parameter.

NIR images show spatial correlations between Fe$^{3+}$ and the degree of hydration (Fig. S4). While work by O’Hanley and Dyar (1998) shows that octahedral Fe$^{3+}$ substitutions can be charge-balanced by H$^+$ vacancies, predicting a negative correlation between these spectral features, the substitutions in samples analyzed here of Fe$^{3+}$ for Si$^{4+}$ in tetrahedral sites require a different process to charge balance the structure. Two possibilities are coupled substitutions of Fe$^{3+}$ into the tetrahedral and octahedral sheets with no change in H$^+$ content (Evans et al., 2013; O’Hanley and Dyar, 1993) or additions of H$^+$ into the structure, either of which could explain the spectral observations here. These results are consistent with other work showing that advanced serpentinization produces serpentines with both high H$_2$O and high Fe$^{3+}$ contents (Evans et al., 2013).

In field imaging data (Fig. 5), tetrahedral Fe$^{3+}$ is better inferred using the green peak parameter and visually inspecting spectra rather than mapping directly via the BD450 parameter. The imager’s spectral performance degrades at the long and short wavelength ends of the detector, particularly at the shortest wave-lengths. This effect is present in both laboratory and field data, but the shortest wavelengths are further complicated by downwelling atmospheric scattering in the field, which adds to the spectra and contributes most in blue wavelengths where the 450 nm feature occurs, lowering the imaging system’s signal-to-noise. For these reasons, it is difficult to use the BD450 parameter in field data. However, as already shown, laboratory data of samples including some from within field images show good correlations between BD450 and the green peak (Figs. 4, S2–3), and the green peak can therefore be used as an indirect indicator of oxidation state and possible tetrahedral Fe$^{3+}$. Inspecting averages as small as 5–10 pixels (∼11–24 cm in Fig. 5) confirms the presence of the 450 nm feature above the level of noise.

Using laboratory data as confirmation, spectral units are mapped across the outcrop wall (Fig. 5). Variability is seen at this scale, with discrete redder, greener, and bluer units that represent formation of Fe$^{3+}$-oxides, Fe$^{3+}$ oxidation within serpentine, and the presence of magnetite or a textural property of the serpentine, respectively. Limited yellow or cyan areas may be due to sub-pixel mixing where multiple materials are present within a single pixel or spectra of one material exhibiting properties mapped by multiple spectral parameters. Overall, the wall is dominated by the green peak, and the results and interpretations are consistent with the known serpentine lithology.

5. Discussion

The results of hyperspectral imaging and stable isotope analyses characterize conditions of water–rock interactions and habitability during serpentinization. We infer extents of serpentinization and relative amounts of biologically-important H$_2$ produced with spectroscopey from Fe oxidation states and coordination environments in serpentine (e.g., Marcaillou et al., 2011; Evans et al., 2013). At this site, much of the protolith has been extensively serpentinized at elevated temperatures, with high H$_2$ production based on the presence of tetrahedral Fe$^{3+}$. The nature of the system (e.g., open/closed, fluid chemistry and source, timing) is further illuminated from stable isotope analyses of carbonates, and signatures from the production and removal of CH$_4$ formed as a byproduct of serpentinization are present. These complementary analyses

Fig. 5. a. Approximate true color image of rock wall of mine from the visible hyperspectral imager. Red: 660 nm, green: 530 nm, blue: 450 nm. Locations where samples Nor4-13 and Nor4-14 (Figs. S2 and S3) were collected are shown. b. Spectral parameter map of wall of mine. Red: red slope, green: green peak, blue: blue slope. Vegetation and the calibration target have been masked. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)
Table 3

| Sample name | Mineralogy | Al2O3 | CaO | Cr2O3 | Fe2O3 | K2O | MgO | Na2O | MgO | FeO | Ni | SiO2 | TiO2 | C  
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<tbody>
<tr>
<td>Nor3-6c</td>
<td>serpentine, magnetite, hydromagnesite, magnesite, brucite</td>
<td>0.33</td>
<td>0.03</td>
<td>0.14</td>
<td>0.08</td>
<td>0.0</td>
<td>0.18</td>
<td>0.04</td>
<td>0.04</td>
<td>0.04</td>
<td>0.01</td>
<td>0.27</td>
<td>0.01</td>
<td>0.11</td>
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<tr>
<td>Nor3-7a,c</td>
<td>serpentine, talc, pyroaurite, hydromagnesite, dolomite/ankerite</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.0</td>
<td>0.10</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.34</td>
<td>0.01</td>
<td>0.17</td>
</tr>
<tr>
<td>Nor3-8</td>
<td>serpentine, talc, pyroaurite, hydromagnesite, dolomite/ankerite</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.0</td>
<td>0.10</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.34</td>
<td>0.01</td>
<td>0.17</td>
</tr>
<tr>
<td>Nor4-7_1a,c</td>
<td>pyroaurite/sjogrenite, serpentine, smectite</td>
<td>0.06</td>
<td>0.05</td>
<td>0.04</td>
<td>0.05</td>
<td>0.0</td>
<td>0.10</td>
<td>0.02</td>
<td>0.02</td>
<td>0.02</td>
<td>0.01</td>
<td>0.34</td>
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Field and laboratory hyperspectral imaging shows differences in Fe oxidation state and coordination environments within this serpentinite deposit. These results are consistent with laboratory measurements of individual samples by O’Hanley and Dyar (1993, 1998) finding different Fe oxidation states and coordination among samples from the same localities. The identification of tetrahedrally-coordinated Fe3+ directly through a 450 nm spin-forbidden electronic transition and indirectly through a peak near 580 nm related to both octahedral and tetrahedral Fe3+ generally correlates with the 450 nm absorption feature indicates that the sample or outcrop has undergone advanced serpentinitization where there has been the highest cumulative H2 production. In a planetary mission searching for habitable environments, biomarkers, and evidence of past life in a serpentinite terrain, areas with tetrahedral Fe3+ are important candidates for additional in situ analyses because the H2 produced could have been an energy source for microbes (e.g., Schulte et al., 2006). Calculating total volumes of H2 produced requires quantification of Fe3+ content and is beyond the scope of this work but has been done for other serpentinites by Stander et al. (2013). While primary olivine and pyroxene were not found in these samples, previous work has shown that visible-NIR spectroscopy can be used to distinguish lower degrees of serpentinitization in samples with low magnetite contents (Hunt and Evarts, 1981). It is unclear whether CO2-metasomatism or atmospheric weathering could change the Fe oxidation state within serpentine. We feel that these processes are unlikely to introduce new tetrahedral Fe3+ since Fe2+ within serpentinite should only be in octahedral sites, but a complete discussion of this question is beyond the scope of this work. We do note that low temperature weathering of serpentinite can generate H2 and CH4 (Okland et al., 2012).

Our data resampled to the bandpasses of multispectral imaging systems such as Pancam and Mastcam on current Mars rovers (Bell et al., 2003, 2006, 2012) show variability within images (Fig. 6), but precise mineralogical or oxidative differences causing spectral variability cannot be determined. Fig. 6 shows that neither multispectral system is capable of identifying tetrahedrally-coordinated Fe3+ because neither samples short enough wavelengths nor has sufficient bands between ~400 and 480 nm. Hyperspectral systems that sample such short wavelengths not only show the presence of a feature at 450 nm but also have sufficient bands covering the feature to provide confidence that the feature exists above the level of noise. Chemcam on Curiosity should be able to identify this feature in passive reflectance mode, if it is present (Johnson et al., 2014). Also notable in the resampled multispectral data is that band centers and shapes for the same spectrum sampled with different bandpasses appear differently depending on the wavelengths of the multispectral bands. The loss of critical information in multispectral systems was also seen by Cousins et al. (2010, 2012), who tried to design a multispectral imaging system that could identify the diversity of minerals potentially present on Mars. Swaze et al. (2003) noted that minerals with distinct absorption features can appear the same if the sampling interval of a spectrometer is too broad. Expanding the wavelength range of this hyperspectral system into the infrared would allow for more sophisticated analyses of astrobiological potential, could distinguish serpentine from other green-colored minerals, show where other interesting minerals may be present, and allow for remote identification of the mineral assemblages.

Stable isotopic measurements further illuminate the serpentinitization conditions. Present conditions are not possible with spectroscopy alone. These measurements show a wide range of carbon and oxygen isotope ratios within carbonate coatings on serpentinites col-
lected around the mine and show two distinct trends in isotopic compositions reflecting different alteration scenarios within and outside the shear zone (Fig. 3). Carbonate samples from the wall imaged ~100–200 m south of the shear zone (Fig. 5) likely precipitated during serpentinization in a relatively closed system with a deep groundwater source similar to that described by Neal and Stanger (1985) and Mervine et al. (2014) to explain observations of the Semail ophiolite in Oman. This model is supported in our investigations by high δ13C values likely resulting from reaction of H2 from serpentinization with CO2 to produce CH4 enriched in 13C (Ohmoto, 1972), leaving the remaining carbon reservoir enriched in 13C if the system was closed to carbon addition but open to CH4 escape. In this scenario, the carbonates formed when the fluids became saturated in Ca2+ removed from the ophiolite and the pH rose during serpentinization (Neal and Stanger, 1985). While the ophiolite likely had low overall Ca content, harzburgites in nearby Thetford Mines, Quebec, contain up to 6% clinopyroxene, and orthopyroxenes there have up to 1.8 wt% CaO (Pagé et al., 2008). The presence of Ca from primary mineralogies released by weathering combined with the absence of Ca in typical serpentinization products (i.e., serpentine, magnetite, brucite) could have allowed Ca2+ to build up in the fluids until the system saturated and calcite precipitated (Neal and Stanger, 1985). The carbonates with the highest 13C proportion probably formed last from the most evolved fluids under the most water-limited conditions as volume expansion during serpentinization reduced fluid flow (O’Hanley, 1992 and references therein). The carbonate mineralogies determined with XRD from this portion of the mine are dominated by calcite with less magnesite and/or pyroaurite. This scenario for evolving conditions during serpentinization is shown conceptually in Fig. 7. We note that these data cannot distinguish carbonate formed during serpentinization in oceanic versus continental environments because environmental conditions leading to these high δ13C values required little or no input from the ocean or atmosphere above. Even in oceanic environments with significant calcite precipitation near the seafloor, less calcite is seen at depth (Schwarzenbach et al., 2013).

The isotopic trend for shear zone samples matches the overall trends and ranges in isotopic compositions previously reported for carbonates in ophiolites in Oman and elsewhere attributed to kinematic fractionation (e.g., Clark Jr. et al., 1992; Kelemen et al., 2011; Mervine et al., 2014). Radiocarbon dates of carbonate veins in Oman reported by Kelemen et al. (2011) and Mervine et al. (2014) range from 4 to 36 ka, showing that carbonates there formed recently, and stable isotope analyses of monomineralic carbonate samples show that carbonates formed at temperatures <60°C and are not associated with the serpentinization (Mervine et al., 2014). Similarly, carbonates in the shear zone in Norbestos likely formed after serpentinization ended, overprinting most isotopic signatures of the original serpentinizing fluids, although one sample has high 13C and may be related to these primary serpentinizing fluids. Carbonate mineralogies of analyzed shear zone samples are hydromagnesite and pyroaurite with dolomite/ankerite and/or magnesite. Magnesite often forms in serpentinites through CO2-metasomatism (Klein and Garrido, 2011; Klein and McCollom, 2013), and hydromagnesite can be a product of atmospheric weathering (e.g., Power et al., 2009). These mineralogies support our interpretation that these carbonates formed through later processes after serpentinization ceased. Carbonate in one shear zone sample with the most negative δ13C measured, Nor4-2 (bottom), is calcite, suggesting that there is not a perfect correlation between mineralogy and stable isotopes.

Although no biological isotopic fractionations have been found in these data, isotopic signatures of samples from the imaged wall south of the shear zone suggest that some carbonates present formed during serpentinization events in close association with methane production. The methane could have formed biotically or abiotically through CO2 reduction by H2 (e.g., Horita and Berndt, 1995; Oze and Sharma, 2005; Schulte et al., 2006), which, along with the CH4, is important in microbial metabolisms (e.g., Schulte et al., 2006; Cardace and Hoehler, 2009; McCollom and Seewald, 2013). Signatures of carbonates formed through CH4 oxidation by microbes were not found, but those signatures were also absent in nearby ophicalcites in Quebec with deposits thought to be fossilized microbial communities that are the same age as the Norbestos serpentinites (Lavoie and Chi, 2010). In fact, the samples here have a broader δ13C range than the samples analyzed at that site by Lavoie and Chi (2010). Thus, in the ancient serpentinite deposit in Norbestos there is still an isotopic signature of the original serpentinization event and the gases produced as
Fig. 2. Conceptual figure showing fluid flow, hydrogen and methane production, and carbonate formation with different C isotope ratios during early (left) and late (right) stages of serpentinization in the subsurface out of contact with the overlying atmosphere or ocean. This figure describes formation of carbonates with the isotopic signatures of samples from outside the shear zone, and oceanic and continental serpentinization events cannot be distinguished. Rectangles are carbonate veins, and ovals are carbonate coatings. Large, light blue arrows are fluid flow paths. In the right panel, the fluid flow path is wavy to signify decreased water/rock ratios and decreased permeability in the serpentinite, likely due to volume expansion (O’Hanley, 1992 and references therein). As serpentinization proceeded and the system evolved, available carbon decreased, water–rock ratios decreased, and \(^{13}\)C values became heavier. Throughout this process, \(H_2\) and \(CH_4\) were produced, and these gases could have been important energy sources for microbes (e.g., Schulte et al., 2006; Cardace and Hoehler, 2005; McCollom and Seewald, 2013). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

6. Conclusion

In serpentinite terrains, Fe oxidation within serpentinite, in addition to magnetite production, produces \(H_2\) that microbes can use as an energy source, and tetrahedrally-coordinated \(Fe^{3+}\) in serpentinite is produced at the end stages of serpentinization (Marcaille et al., 2011). Therefore, identification of tetrahedral \(Fe^{3+}\) in serpentinite through diagnostic absorptions at visible wavelengths indicates maximum \(H_2\) production during serpentinization and the highest astrobiological potential. In the Norbestos serpentinite studied here, tetrahedral \(Fe^{3+}\) is common, suggesting high \(H_2\) production during serpentinization. Analyses of carbon and oxygen stable isotopes in carbonates precipitated on serpentinite show that some carbonates likely formed during the original serpentinization events when \(H_2\) and \(CH_4\) were produced and illuminate aqueous conditions of alteration at elevated temperatures and low water/rock ratios in a carbon-limited system. The retention of signatures of serpentinization and methane production is promising for the detection of ancient biosignatures in similar environments on Mars, if they were ever present.

7. Author contributions

RNG, JFM, EAC, and LMP designed the research; RNG, PM, KT, PES, MDD, and DLB did the measurements; RNG, JFM, EAC, LMP, and PES analyzed the data; RNG, JFM, and MDD wrote the paper; all authors provided comments on the paper and approved the final version.

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Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2015.02.002.


