1 **Conditions of Stichtite ($\text{Mg}_6\text{Cr}_2(\text{OH})_{16}[\text{CO}_3] \cdot 4\text{H}_2\text{O}$) formation and its Geochemical**
2 **and Isotope Record of Early Phanerozoic Serpentinizing Environments**

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ABSTRACT

Stichtite is a magnesium-chromium hydroxycarbonate mineral found in association with early Phanerozoic chromite-rich serpentinite rocks of Tasmania, Australia and Tehuiztingo, Mexico. Elemental analysis of stichtite shows a range of compositions within the Cr-Fe-Al hydrotalcite group, with compositional trends associated with each discrete serpentinite host body. Elemental and textural analysis of stichtite-associated chromite indicates that stichtite forms in fore-arc setting rocks through interaction of chromite and methane-rich serpentinizing fluids. The degree to which chromite is replaced by stichtite is inferred to correlate with the length of time that the host rocks spent within the “stichtite window.” Carbon stable-isotope analyses of stichtite suggest carbon sourcing from marine kerogen with a minor marine carbonate component in some samples. The carbon and hydrogen stable isotope profile of stichtite ranges from the field of methane from active serpentinizing zones, to organic thermogenic methane. The association of the stichtite 2H polytype (nee barbertonite) with aragonite ± antigorite suggests this is a higher pressure/temperature polytype of stichtite. Reaction completion textures, isotopic values, and qualitative mineral thermobarometric indicators indicate that stichtite forms during serpentinization of fore-arc setting rocks in a methane/H₂-rich environment within fluid conduits, ranging from near the surface to depths where pressure is up to 1.2 to 0.8 GPa and temperature is up to ~300°C. These unique chemical, isotopic, and textural properties of stichtite from distinct serpentinite bodies likely record the duration of serpentinization at specific thermobarometric conditions, and provide a window into the conditions associated with a potentially habitable environment on early Earth and other bodies of the solar system.

248 Words;

Key Words: stichtite, serpentinite, carbon isotope, hydrogen isotope, methane

1. INTRODUCTION

The alteration of low-silica ultramafic rocks by water-rock reactions, commonly referred to as serpentinization, produces a unique environment with high pH and abundant electron donors such as hydrogen gas and methane (e.g., Proskurowski et al., 2008; McCollom and Seewald, 2013). While there are many challenges for life within serpentinizing fluids (e.g., Tiago et al, 2004; Brazelton et al., 2010), life proliferates with great diversity where they mix with ambient waters such as the biofilms of the shallow subsurface and surface at Lost City (e.g., Schrenk et al, 2004), and the anaerobes and methanogenic archaea of deep hydrothermal mixing zones (e.g., Moser et al, 2005; Itävaara et al., 2011). Both the deep and shallow serpentinizing environments provide ideal conditions for early life; nutrient-rich, warm, and protected from many potentially sterilizing events by a deep oceanic blanket.

Considerable work has been done in attempts to characterize conditions which occur during active modern serpentinization (e.g., Etiope and Sherwood Lollar, 2013; Evans et al., 2013). Much of the recent work has focused on using this knowledge to understand the possible sources of methane on Mars, due to potential implications for biosignatures (e.g., Parnell et al., 2010; Etiope et al., 2013; McCollom and Seewald, 2013). What is lacking is an understanding of what these conditions may have been in the past, and how to recognize their isotopic and geochemical record in deep Earth time. Geochemical results from recent work on active serpentinizing systems (Mottl et al., 2003; Klein et al., 2015) suggest conditions similar to those indicated by our results for hydrotalcite minerals from Phanerozoic serpentinites. We propose that hydrotalcite minerals which formed in the past during serpentinization preserve a geochemical

record of the fluids and possibly biosignatures associated with these fossil hydrothermal systems. This bears directly upon understanding conditions and possible biosignatures from fossil serpentinizing systems on early Earth and early Mars.

Stichtite ($\text{Mg}_6\text{Cr}_2(\text{OH})_{16}[\text{CO}_3]\cdot 4\text{H}_2\text{O}$) is a relatively rare magnesium-chromium hydroxycarbonate mineral of the rhombohedral hydrotalcite group. End members of the hydrotalcite group include stichtite (Cr), pyroaurite (Fe), and hydrotalcite (Al). Minerals of the hydrotalcite group have unique properties and chemical engineering applications by virtue of their ability to store molecules within the hydrated interlayer between their brucite-like layers (e.g., Del Hoyo, 2007). Examples include delivery of pharmaceuticals (e.g., Tronto et al., 2001), incorporation of biocatalysts (Rahman et al., 2004; 2005), and storage of peptides and amino acids (e.g., Newman et al., 2002; Kottegoda and Jones, 2005; Gerstel et al., 2006). Such properties should be of keen interest to astrobiologists and those examining potential early Earth biomarkers.

Stichtite is purple to pink in color and has a waxy to pearly luster. It has never been reported as macroscopic crystals, but occurs as fine platy to acicular aggregates of crystallites typically less than 2mm in the longest dimension. Stichtite 2H (formerly known as Barbertonite) is a hexagonal polytype of stichtite (Mills et al., 2011; 2012). Stichtite 2H is found in some localities as intimate syngenetic intergrowths with aragonite, suggesting possible formation at higher pressures. Stichtite is known to form during the period of active serpentinization, as demonstrated by cross-cutting relations and intergrown textures (Varadarajan, 1966; Melchiorre and Lopez, 2011). Stichtite has been shown to form at the expense of brucite and Cr spinel in the south Iberia Abyssal Plain (Klein et al., 2015), presumably with the reaction $\text{MgCr}_2\text{O}_4 + 5 \text{Mg}(\text{OH})_2 + \text{CH}_4 + 2$

$O_2 + 5 H_2O = Mg_6Cr_2(OH)_{16}[CO_3] \cdot 4H_2O$. This reaction involves methane, which is known to be produced during serpentinization. Conversely, stichtite may form by the reaction of DIC and hydrogen gas (Mottl et al., 2003) with brucite and Cr spinel by the reaction $MgCr_2O_4 + 5 Mg(OH)_2 + CO_3 + H_2 + 6 H_2O = Mg_6Cr_2(OH)_{16}[CO_3] \cdot 4H_2O$. Hydrogen is also a product of serpentinization, and in the high pH conditions of these fluids DIC should speciate as CO_3 .

Stichtite of broadly similar age occurs in relative abundance in western Tasmania, Australia, and to a lesser degree near Tehuitzingo, Mexico (Figure 1a, b). In both cases, the stichtite is hosted by serpentinized rocks. There are seven main Tasmanian localities (Burrett and Martin, 1989; Bottrill and Graham, 2006). The type locality for stichtite, and the most extensive deposit, is located at Stichtite Hill. Stichtite also occurs at an adit above the Red Lead Mine, the Kapitani prospect, outcrops near the Adelaide Mine, adjoining the West Comet Mine, Tunnel Hill, and Nevada Creek (Figure 1c). A reported trace occurrence of stichtite at Birches Inlet, on the Macquarie peninsula, was not accessible at the time of field work and there are questions regarding authenticity of the few samples available through other sources. All Tasmania localities, with the exception of Birches Inlet, are located within the greater Dundas mining district. For brevity in the following sections, all Tasmania, Australia localities will be referred to by just their specific locality name (e.g., Tunnel Hill), while the Tehuitzingo, Mexico locality will be referred to simply as "Mexico."

1.1 Geology and Mineralogy

1.1.1 Tasmania Localities

The mineral that was later to be known as stichtite was first noted at the Dundas mining district in 1891 (Petterd, 1896), though it was another 23 years before it was properly described as a new species for the type locality at Stichtite Hill (Twelvetrees, 1914).

The stichtite occurrences of Tasmania are hosted by serpentinitized mid-Cambrian ultramafic rocks known as the Dundas ultramafic complex (Brown, 1986; Burrett and Martin, 1989). This unit consists of variably serpentinitized ultramafics, gabbros, and basaltic volcanic rocks. Three types of serpentinite are recognized in these rocks (Rubenach, 1974). Black serpentinites are unsheared, often contain abundant fine-grained magnetite, and are dominantly lizardite, which has replaced olivine bearing ultramafic rocks. Green serpentinites are lizardite-chrysotile mixtures with localized deformation. Sheared contact serpentinites consist mainly of chrysotile and rare antigorite, and may have formed during tectonic emplacement. These serpentinite bodies lie within Middle to Late Cambrian strata. Stichtite mineralization occurs mainly within massive chromite-rich green serpentinite, and rarely within its border zones with black serpentinite (Bottrill and Graham, 2006). Stichtite has a strong association with zones of brecciated serpentinite (Bottrill and Graham, 2006).

The stichtite locality at Tunnel Hill, situated near the local topographic high of Serpentine Hill, is an exception to the occurrences described above. At this site, the serpentinite consists of a complex of fault-disrupted blocks of ultramafic gabbroic rocks exposed through a fault window between an area of Eocambrian basic volcanoclastic

rocks to the northwest, and fossiliferous Middle to Late Cambrian strata to the southeast (Figure 1c; Brown et al., 1988). The ultramafic gabbroic rocks include an orthopyroxene-rich layered sequence, and a later olivine-rich layered sequence. Both are in turn intruded by a two-pyroxene gabbro (Brown et al., 1988). The stichtite at Tunnel Hill occurs within the green serpentinite of the olivine-rich sequence.

The chromites found in association with all of the Tasmanian stichtite localities contain 200 to 1400 ppb Platinum Group Elements (PGE), with enrichment in the Iridium subgroup elements Ir, Os, and Ru (Brown et al., 1988). PGEs have well-known catalytic properties, including facilitation of reactions with methane and hydrogen gas, and the fixation of carbon (e.g., Rostrupnielsen and Hansen, 1993; Deutschmann et al., 2000).

1.1.2 Mexico Locality

Stichtite was reported to occur in serpentinitized rocks near Tehuitzingo, Mexico by Proenza et al. (2004). The stichtite occurs as fine needles around magnetite and chromite grains within a sequence of eclogitized and serpentinitized mafic and ultramafic rocks interlayered with pelitic and siliceous metasedimentary rocks known collectively as the Xayacatlán Formation (e.g., Carballido-Sánchez and Delgado-Argote, 1989; González-Mancera, 2001). The Xayacatlán Formation was emplaced along the Iapetus suture during the Late Ordovician-Early Silurian collision between eastern Laurentia and Oaxaquia (Ortega-Gutiérrez et al., 1995, 1999). Chromite found in association with the stichtite contains 100 to 300 ppb Platinum Group Elements (PGE), with enrichment in the Iridium subgroup elements Ir, Os, and Ru (Proenza et al., 2004). Mineralogy and

PGE patterns suggest that these rocks have not been altered by metamorphism following their high-pressure formation (Proenza et al., 2004).

2. METHODS

2.1 Sample preparation and characterization

Whole-rock samples containing abundant stichtite were collected from each of the sites described above. Samples for scanning electron microscope (SEM), electron microprobe (probe), and secondary ion mass spectrometry (SIMS) analyses were placed into 1-inch round silicone molds, embedded in a low-volatile epoxy, ground flat, and polished, with the final polish using 0.2 μ grit, and employing the standard methodology of microanalysis laboratories around the world (e.g., Goldstein et al., 2003; Reed, 2005). Samples for traditional stable isotope analyses were crushed and hand-picked to produce a stichtite concentrate which was crushed to <0.25mm. The concentrate was then processed with a Frantz magnetic separator to remove chromite and serpentinite impurities, then crushed to pass through a 100-mesh screen (<0.147mm). Resulting powders were scanned by x-ray diffraction (XRD) to check purity.

Samples were also characterized based upon chromite-stichtite reaction progress. A Dino-Lite digital microscope was used to capture reflected-light images of chromite-stichtite assemblages from polished slabs. These images were quantified using shape digitalization in drafting software to produce a reaction progress ratio, where 0 is pure chromite and 100 is pure stichtite.

2.2 Geochemical analyses

Backscatter electron images and element analyses were generated using a JEOL JXA-8500F electron microprobe at the Department of Geology and Geophysics, University of Hawai'i, Mānoa, and a CAMECA SX100 electron microprobe at the University of Arizona Lunar and Planetary Laboratory. The microprobes are equipped with five tunable wavelength dispersive spectrometers. Operating conditions were 40° takeoff angle, and beam energy of 15 keV. The beam current was 20 nA, and the beam diameter was 1 µm. Counting time was 60 s. Off-peak counting time was 20 s, using the LINEAR off-peak correction method. Well-characterized natural and synthetic minerals were used for in-house standards. Detection limits were better than 0.02 wt.% for all elements. Analytical sensitivity (at the 99% confidence level) ranged from 0.263% relative for Si Ka to 2.795% relative for S Ka. The matrix correction method was ZAF/Phi–Rho–Z calculations with an Armstrong/Love Scott algorithm (Armstrong, 1988). The Fe₂O₃ content of chromite was calculated stoichiometrically (e.g. Bliss and MacLean, 1975; Dick and Bullen, 1984). It is acknowledged that errors associated with other elements may propagate into these estimates (Wood and Virgo, 1989), which may be significant when dealing with small variations in ferric iron content (Barnes and Roeder, 2001). However, this effect should be insignificant in our samples because of the high Fe₂O₃ values and large scale of the variations observed.

2.3 Isotope analyses

2.3.1 Traditional isotope analyses

Traditional stable-isotope analysis was performed on pure stichtite mineral separates. Measurements of stichtite $\delta^{13}\text{C}$ were performed by the standard method of reaction with 100% orthophosphoric acid (H_3PO_4) at 25 °C to release CO_2 gas (e.g., McCrea, 1950; Walters et al., 1972). The resulting CO_2 gas was purified, and then analyzed by continuous flow methods on an isotope ratio mass spectrometer (Spötl and Vennemann, 2003). Detailed descriptions of sample preparation, analysis techniques, data correction, and data reporting notation are outlined by Melchiorre et al. (1999) and Melchiorre et al. (2000). Carbon analyses are reported in the usual manner as per mil deviations from the VPDB standard. The precision of the $\delta^{13}\text{C}$ value is $\pm 0.09\text{‰}$ for carbon isotopes. Precision is based upon analysis of internal laboratory standards calibrated to the VPDB scale, and duplicate analyses performed for all unknown samples.

Stichtite was also analyzed for δD using standard pyrolysis methods. Samples were pre-heated overnight under vacuum at ~ 70 °C. This pre-heating was essential, due to the way stichtite decomposes at increasing temperature, to drive off water of hydration (Bouzaid and Frost, 2007). These waters of hydration are most likely readily exchanged on the surface of the sample with atmospheric water. For measurement of δD values the sample was placed under vacuum at ~ 80 °C for three hours and then pyrolyzed with the resulting gas analyzed by standard mass spectrometry. Results are reported in the usual per mil deviation from the VSMOW standard, and precision of the δ value is $\pm 1\text{‰}$.

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222 **2.3.2 Stable isotope analysis by SIMS**

223 A state-of-the-art Cameca ims 1280 ionmicroprobe at the W.M. Keck Cosmochemistry
224 Laboratory, University of Hawai'i, Mānoa, was used for detailed measurements of
225 carbon and hydrogen isotope ratios for stichtite. The ims 1280 features high sensitivity
226 at high mass resolving power, a multicollector permitting measurements of up to five
227 masses simultaneously, and the ability to perform both raster ion imaging and direct ion
228 imaging. The ims 1280 has a solid-state imaging detector called SCAPS for quantitative
229 direct ion imaging (Nagashima et al., 2001; Yurimoto et al., 2003). A detailed description
230 of the ims 1280 is given by Valley and Kita (2009). Detailed operational parameters,
231 analysis techniques, and data correction methods are summarized in Melchiorre et al.
232 (2014).

233 We corrected the measured C isotope data for instrumental effects using the UWC-3
234 calcite ($-0.91 \pm 0.08\text{‰}$; Kozdon et al., 2009) following standard methods. Carbon data
235 are reported in delta notation relative to VPDB. Our hydrogen standard for these
236 measurements was a house standard chrysotile mineral specimen from the Mariana
237 forearc with a δD value of -84.0‰ relative to VSMOW. While this is not a good matrix
238 match to carbonates, it permits a first-order correction for matrix effects. Both C and H
239 correction methodologies were determined to be effective, based upon comparison of
240 multiple isotope analysis techniques for stichtite (Melchiorre et al., 2014). Random
241 uncertainties for our $\delta^{13}\text{C}$ and δD measurements, are $\pm 3\text{‰}$ and $\pm 30\text{‰}$ respectively (2σ),
242 consistent with SIMS values reported for other minerals (e.g., Hallis et al., 2015).

243

244 3. RESULTS

245 Stichtite was sampled from seven localities in Tasmania, Australia, and one locality in
246 Tehuiztingo, Mexico. In the following results and discussion sections, we will under
247 some contexts refer to Tasmania stichtite localities, grouped by the belt of serpentinite
248 in which they are hosted (Figure 1c). These three groupings are 1) Stichtite Hill
249 serpentinite (Stichtite Hill and Red Lead localities), 2) Tunnel/Serpentine Hill
250 serpentinite (Tunnel Hill locality), and 3) Nevada Creek serpentinite (north: Nevada
251 Creek Locality; south: Kapitani, Adelaide, and West Comet localities).

252 Samples from the Tunnel Hill locality consist of massive stichtite with magnetite,
253 ferritchromite, and rare chromite. Stichtite Hill and Red Lead Mine samples are
254 dominantly stichtite pseudomorphs after chromite, with brecciated chromite cores
255 (Figure 2a). The Red Lead samples have a much lower stichtite abundance, but where
256 present it has a similar texture as those from Stichtite Hill. Some Stichtite Hill samples
257 are massive stichtite similar to Tunnel Hill samples. Samples from Tehuiztingo, Mexico
258 and Nevada Creek, Australia have a unique appearance due to the darker purple color
259 of the stichtite 2H (nee barbertonite) and white aragonite in the serpentinite. Antigorite is
260 occasionally associated with serpentinite samples from Nevada Creek and Tehuiztingo,
261 Mexico. Samples from the Kapatani, Adelaide, and West Comet localities were typically
262 stichtite replacement of small <5mm chromite grains within serpentinite. In these
263 samples, remnant chromite was rare.

Optical examination of chromite-stichtite assemblages from polished slabs revealed a wide range of reaction completion. We define the reaction-progress ratio as the percentage of original chromite that has been replaced by stichtite (e.g., pure chromite = 0%, pure stichtite = 100%). The reaction-progress ratios for stichtite show unique textures for specific serpentinite belts (Figures. 3, 4). Reaction completion ranged from as low as 31% at the Red Lead locality to near 100% at the Kapitani and West Comet localities (Figures 3 and 4; Table 1). In samples with complete or near-complete stichtite replacement of chromite, magnetite and ferritchromite was commonly present. The stichtites from the Stichtite Hill serpentinite belt (Stichtite Hill and Red Lead localities) have low reaction progress, averaging 64% at Stichtite Hill, and 43% at Red Lead. Both of these localities have distinctive angular and ordered chromite breccia textures (Figure 4). Further north, in the Nevada Creek serpentinite belt, the reaction progress values are substantially higher for both the northern and southern localities, averaging in the mid to upper 90% range. Similarly, the Tunnel Hill locality in the Tunnel/Serpentine Hill belt has reaction completion averaging 91%. The stichtite localities of the Nevada Creek and Tunnel Hill serpentinite belts all have a distinctive texture of rounded and typically disordered remnant magnetite, ferritchromite, and chromite. Stichtite from the Mexico locality has an average reaction progress of 86%, based upon measurements of chromite and magnetite inclusions >0.1 mm. However there is a significant volume of very fine-grained magnetite/ ferritchromite inclusions within the stichtite that is very difficult to quantify, though limited probe work suggests the majority of these fine grains are ferritchromite, which counted as an alteration product would increase the reaction progress values by up to an additional 12%.

Chromian clinocllore was a rare to locally common intergrowth with some stichtite samples. Pyroaurite-hydrotalcite from the Tunnel Hill and Stichtite Hill localities was also confirmed by textural relations to replace stichtite in association with magnetite, where Fe-rich, presumably retrograde, fluids intersect earlier stichtite (Figure 2b). The magnetite in these veins often forms in a distinctive oriented fibrous habit (Figure 2c). A final stage of alteration was observed within pyroaurite-hydrotalcite masses, where late-stage stichtite halos have formed around remnants of chromite grains, replacing pyroaurite-hydrotalcite (Figure 2d).

The results of geochemical analyses of the stichtite are presented in graphical form in figure 5, and with a summary table of geochemical data (Table 2). Mineralogically, these correspond to a range of compositions from near end-member stichtite to iron- and aluminum-rich stichtite, and define unique populations (Figure 5). The results of chemical analyses of pyroaurite-hydrotalcite masses are also presented in figure 5.

The first stichtite geochemical grouping is the Tunnel/Serpentine Hill serpentinite belt samples, forming a trend of decreasing Cr with a fairly constant Fe:Al ratio of 1:4. The lowest Cr levels approach, but do not cross into the hydrotalcite field. The “Dundas” stichtite samples reported in Ashwall and Cairncross (1997) plot neatly within the Tunnel Hill field, which is consistent with known commercial availability of Tasmanian stichtite at the time of that study. The second population is the Stichtite Hill serpentinite belt, which forms a trend of decreasing Cr with a fairly constant Fe:Al ratio of 5:2. The lowest Cr levels approach, but do not cross into the pyroaurite field. The stichtite samples from the Red Lead Mine plot along the Stichtite Hill compositional trend. The third population consists of the Nevada Creek serpentinite belt localities, which forms a

trend of decreasing Cr with a fairly constant Fe:Al ratio of 20:1. The lowest Cr levels approach, but do not cross into the pyroaurite field. Of note is that the composition of the Kapitani stichtites plot along the Nevada Creek trend. This should be expected, as both localities occur within the same serpentinite belt. However, these deposits are 3 km apart and have different mineralogies and appearance. Stichtite samples from Tehuiztingo, Mexico plot within the Nevada Creek trend

A suite of chromite grains was analyzed to generate Cr# [=Cr / (Cr+Al) atomic ratio] and Mg# [=Mg / (Mg+Fe²⁺) atomic ratio] data (Figure 6). Populations of chromite include chromite cores within pseudomorphs of stichtite after chromite, chromite within serpentinite from rocks immediately adjoining stichtite-bearing localities, and highly-altered chromite-ferritchromite within remobilized stichtite veins. Geochemical data from other workers for chromite from the same localities were also plotted. With the exception of the most altered chromite, virtually all samples plot within the field of fore-arc peridotites with a Cr# between 0.4 and 0.9, and a Mg# between 0.35 and 0.65 (Figure 6). The altered chromite samples occur within highly fractured zones of obvious fluid flow, and their chemistry is assumed to reflect conditions of peak serpentinization with high fluid flow, rather than protolith origin.

Carbon and hydrogen isotope values for stichtite were measured using both SIMS and traditional/pyrolysis methods (Tables 1 and 2). Stichtite samples analyzed with SIMS by Melchiorre et al. (2014) were found to have isotopic variation within samples, but not along individual crystals. As the isotope values for stichtite from specific localities are quite similar for both methods (Tables 1 and 2), we assume that the analyses performed by traditional pyrolysis methods have produced effective weighted isotopic averaging of

the samples. Carbon and hydrogen stable isotope characterization by standard isotope analysis methods show that samples have $\delta^{13}\text{C}$ values between -8.9‰ and -29.4‰ (Table 3). The δD measurements range between -89‰ and -149‰ (Table 3). Carbon and hydrogen stable-isotope characterization by SIMS shows that samples have $\delta^{13}\text{C}$ values between -10.4‰ and -18.3‰, while δD measurements range between -73‰ and -162‰ (Table 3).

4. DISCUSSION

4.1 Mineralogical and geochemical interpretation

The mineralogy of samples from most locations in this study is nearly identical, with key differences at two sites. Typically, serpentinite is dominated by lizardite and chrysotile, with abundant chromite grains. Where present, stichtite occurs as either massive veins with inclusions of magnetite, ferritchromite, and chromite; or as discrete pseudomorphs after chromite and containing a chromite core or chromite breccia. Samples from Tehuitzingo, Mexico and Nevada Creek, Tasmania are different in that they contain the stichtite 2H polytype (nee barbertonite) and aragonite $\pm$ antigorite.

Stichtite mineralization is known to form during the serpentinization process (e.g., Varadarajan, 1966; Melchiorre and Lopez, 2011). Some workers have interpreted sequences of serpentine crystallization and recrystallization as a record of progressive exhumation of peridotite and the exposure to increasing hydrothermal fluid circulation (Dilek et al., 1997; Andreani et al., 2007). Using a similar interpretation of relationships

in our samples, we suggest that stichtite formation occurred during the period of mid to late retrograde serpentinization.

The abundance of Cr, Fe, and Al in the hydrotalcite samples from this study define unique populations (Figure 5) which suggests that the control on stichtite mineralogy was of larger scale, uniquely associated with each belt of serpentinite. The stichtite samples from Tehuiztingo, Mexico plot within the Nevada Creek trend. Given their continental-scale geographic separation, and age difference, it is speculated that this apparently fortuitous compositional similarity results from an environmental-control overlap during formation of the stichtite. This is supported by the mineralogy, with both localities reporting the stichtite 2H polytype (nee barbertonite) and aragonite. With unique compositional fields for Tasmanian stichtite associated with each of the three main serpentinite bodies, and a possible environmental control dictating compositional similarities between the Nevada Creek and Tehuiztingo, Mexico stichtites, we suggest that stichtite compositional trends reflect a combination of reactant host rock chemistry, P-T conditions, and serpentinizing fluid chemistry unique to each serpentinite belt.

The pyroaurite at these locations also serve as an indicator of past conditions during waning stages of serpentinization. An examination of iron stability diagrams (e.g., Garrels and Christ, 1965) reveals that it is only at lower temperatures and pH that iron should be available as a dominant cation for formation of pyroaurite. These are the conditions that would be expected during the late stages of serpentinization, or in the distal regions of alteration effected by dilution. Indeed, these same associations are observed in Oman (Taylor et al., 1991), where pyroaurite alteration is associated with 25-45°C serpentinization fluids (Streit et al., 2012).

The reaction-progress ratios for stichtite show unique textures for specific serpentinite belts (Figures. 3, 4). We define the reaction-progress ratio as the percentage of original chromite that has been replaced by stichtite (e.g., pure chromite = 0%, pure stichtite = 100%). Observations of serpentinite characteristics from each locality also support the notion of stichtite reaction-progress ratio. For example, increasing degree of serpentine alteration as recorded in geochemistry and mesh/hourglass textures at specific sites (Rubenach, 1974; Varne and Brown, 1978; Brown et al., 1988; González-Mancera, 2001; Proenza et al., 2004; Bottrill and Graham, 2006; González-Mancera et al., 2009) correlates with our observations of increasing replacement of chromite by stichtite.

The chromite breccia textures associated with infilling stichtite mineralization at Stichtite Hill and the Red Lead Mine are very similar to textures in other serpentinites where fractures in chromite are intruded by clinocllore, lizardite, and other serpentine minerals. Some workers have proposed that this texture represents an artifact of lattice exsolution along the {111} crystallographic planes during oxidation (Haggerty, 1991). Others hypothesized that it might represent mineralization along octahedral spinel partings of chromite (Deer et al., 1992; Saumur and Hattori, 2013). Regardless of the exact mechanism, it is likely that the stichtite mineralization occurs in similar fashion.

The reaction progress, by which chromite is altered to stichtite, is most likely controlled by a combination of the availability of reactants and favorable P-T conditions. Combined, we refer to these conditions as the “stichtite window.” The duration of time that a chromite-rich host spends in the stichtite window is presumed to dictate the degree of reaction completion. Localities such as those in the Stichtite Hill serpentinite

are inferred to have spent less time in the stichtite window than localities of the Nevada Creek, Tunnel Hill, and Mexico serpentinites.

4.2 Serpentinization setting

4.2.1 Chromite geochemistry

As stichtite mineralization requires specific conditions within the “stichtite window,” there is a need to quantify these conditions. A lack of appropriate thermodynamic data dictates an empirical approach using general geological settings. Many workers have used the chemistry of chromite within mafic rocks and serpentinite to determine the geologic settings of formation (e.g., Dick and Bullen, 1984; Dick, 1989; Tamura and Arai, 2006; Hirauchi et al., 2008). One of the most common techniques is to use a major element discrimination plot of Cr# [=Cr / (Cr+Al) atomic ratio] vs Mg# [=Mg / (Mg+Fe²⁺) atomic ratio].

We interpret this chromite data (Figure 6) as an indication that the rocks at these localities originated in a fore-arc environment. One explanation is that stichtite and serpentine minerals formed during serpentinization within the fore-arc environment. However, it is also possible that the stichtite and serpentine minerals formed during later retrograde serpentinization as an overprint in rocks with an earlier fore-arc signature. Regardless of whether stichtite formed during active fore-arc serpentinization, the association of coeval stichtite-serpentine mineralization with serpentinization of rocks with a fore-arc history is clear at these localities.

422 There are some significant chemical trends for the chromites at these localities. For the
423 Stichtite Hill, Tunnel Hill, and Mexico localities the stichtite chromite cores have a higher
424 Cr# than chromite without stichtite alteration (Figure 6). Typically, the Cr# of chromite is
425 a good indicator of the degree of partial melting (e.g., Evans and Frost, 1975). We
426 consider it unlikely that localized zones of partial melting were preferentially mineralized
427 by stichtite, given the associated mineral thermal stabilities. This suggests that stichtite
428 formed after the peak P-T conditions of fore-arc serpentinization, or that the processes
429 associated with stichtite formation are responsible for altering the chemistry of the
430 chromite. Localized zones of high fluid flow with unique chemistry could have produced
431 the observed trend towards elevated Cr#. Significantly, the chromite from each locality
432 forms a distinct compositional field, suggesting unique thermal-fluid history for each of
433 the stichtite-bearing serpentinite belts.

434 Given that a lower Mg# at a given Cr# is interpreted as lower temperature equilibration
435 (e.g., Evans and Frost, 1975), it is also possible to perform qualitative thermometry for
436 each of the sites. The Tunnel Hill samples have the most elevated Mg# at constant Cr#,
437 while the Stichtite Hill samples have lower Mg# values (Figure 6). This suggests that
438 thermal equilibration was at higher temperatures at Tunnel Hill, and lower temperatures
439 at Stichtite Hill. The inferred higher temperatures correlate with greater reaction
440 progress at these sites. Chromite data for the Mexico locality span a relatively wide
441 range of Mg# at constant Cr#, suggesting a range of intermediate equilibration
442 temperatures or possibly slow retrograde thermal equilibration.

443 Chromite from the Nevada Creek and Kapitani deposits, as well as chromite from
444 remobilized stichtite veins at Stichtite Hill and Tunnel Hill have irregular borders and a

corroded appearance. In these localities, chromite-magnetite composite grains are observed, and fine-grained magnetite is quite common. The majority of these altered chromite grains was determined to be ferritchromite, based upon their Cr# and Mg# values relative to the ferritchromite composition field reported from other localities (e.g. Evans and Frost, 1975; Barnes and Roeder, 2001). Ferritchromite is reported for the Mexico locality (Proenza et al., 2004), and was abundant in our samples. Typically, ferritchromite is rarely observed in forearc settings outside of highly metamorphosed rocks (e.g., Saumur et al., 2011), suggesting special conditions in which stichtite and ferritchromite could form. The wide range of ferritchromite compositions associated with stichtite indicates the ferritchromite did not reach compositional maturity, and like the stichtite reaction-progress values provides a record of incomplete and frozen reactions. The absence or rarity of high-temperature minerals such as antigorite, cummingtonite, and talc in the serpentinites with ferritchromite-bearing stichtite also supports the case for immature ferritchromite.

4.2.2 Qualitative mineral thermobarometry

The stability relationships of serpentine minerals have been used to estimate characteristics of serpentinizing fluid such as temperature (Wicks & Whittaker, 1977; Evans, 2004), and water–rock ratios (Evans, 2004). In addition, the occurrence and abundance of brucite, magnetite, and talc have been used to estimate temperature, pH, silica activity, and redox conditions during serpentinization (e.g. Bach et al., 2004; Bach et al., 2006; Klein et al., 2014). Thus precedence is clearly set for the interpretation of serpentinizing conditions using mineralogical indicators.

The serpentinite at all stichtite localities in this paper, except Mexico, is dominated by lizardite. This mineral is stable at temperatures up to ~300°C, but the lizardite readily alters to antigorite at higher temperatures (Evans, 2004; Schwartz et al., 2013). Aside from Nevada Creek, where minor antigorite was noted, antigorite was not detected in the Tasmania samples, and there is no textural evidence for retrograde replacement of antigorite by lizardite. Quite the contrary, the lizardite in Tasmania stichtite-bearing serpentinites typically exhibits mesh, hourglass and bastitic pseudomorphic textures after primary olivine and orthopyroxene, which is typical of low-temperature serpentinitization (O'Hanley, 1996). Replacement of lizardite by chrysotile does occur in some veins hosting stichtite masses. This style of replacement is interpreted as representing lizardite replacement of olivine and/or pyroxene, followed by a later period of dissolution of lizardite at higher fluid-rock ratios to produce a supersaturated fluid, consistent with localized fluid flow and concentration along major structures (e.g., Boudier, 1971; O'Hanley, 1991; Grauby et al., 1998; Normand et al., 2002).

Similarly, stichtite has an upper limit of stability at 294°C (Bouzaid and Frost, 2007). Stichtite undergoes dehydration at 52°C, but one of the unique properties of the hydrotalcite minerals is that they have a strong memory effect, by which they may reform (DelHoyo, 2007). Above 294°C this memory effect is eliminated by dehydroxylation. This provides additional support for a thermal history that did not exceed ~300°C.

The Mexico locality contains mineralogical evidence of a higher-temperature/pressure history than the Tasmania localities. The Tehuitzingo serpentinite contains abundant antigorite and is associated with eclogites which record pressures of up to 1.2 GPa

(~45 km depth) and at least 400°C (Proenza et al., 2004). As antigorite forms from lizardite at temperatures above 320°C but becomes unstable above 640°C (Evans et al., 2013), the abundance of antigorite and non-pseudomorphic textures in the serpentinite suggest a high-pressure, low-temperature environment of serpentinization. Stichtite would be thermally unstable in this environment, however the effects of pressure on stability of stichtite are unknown. It is hypothesized that the environment of serpentinization and stichtite mineralization at the Mexico locality was at the low end of antigorite stability, with stichtite formation during the retrograde stage.

The Nevada Creek and Mexico localities also are noted for the occurrence of intimate aragonite-antigorite-stichtite assemblages (e.g., González-Mancera et al., 2003; Bottrill and Graham, 2006; Bottrill and Baker, 2008), which is typically interpreted as a higher-pressure phase. Assuming a temperature of serpentinization that was in the low range of antigorite stability, aragonite would be stable at pressures exceeding 0.8 GPa (e.g., Boettcher and Wyllie, 1968; Johannes and Puhon, 1971). This would be broadly consistent with the 1.2 GPa reported for the rocks associated with the Mexico serpentinite-stichtite locality.

Both the Nevada Creek and Mexico stichtite localities have inferred depths and temperatures of formation which are consistent with the 150-250°C, 0.8 GPa, 27 km depth calculated for the origin of Mariana forearc serpentinization based upon fluid chemistry (Mottl et al., 2003) using established steady state models (Peacock, 1996; Kincaid and Sacks, 1997). It is noteworthy that the unique mineralogy of stichtite+stichtite_{2H}+aragonite±antigorite is inferred to form under the same conditions associated with zones of active modern serpentinization. This similarity spans different

geographic regions, separated temporally by 550 Ma, and determined by different methodologies. Future experimental work should attempt to directly link the synthesis of stichtite with these conditions, and determine specific thermodynamic values for stichtite. For the Nevada Creek and Mexico localities, the association of stichtite 2H (nee barbertonite) with aragonite suggests that stichtite 2H may be a high-pressure polytype. It is not likely that the transition to stichtite 2H occurs solely along a thermal boundary, as no such effect was observed during thermal decomposition experiments (Bouzaid and Frost, 2007).

4.3 Isotopic evidence for origins of C and H in stichtite

4.3.1 Carbon isotope record

There is a long history of carbon isotope values being used to infer the possible origins of carbon within carbonate minerals, and their possible environment of formation (e.g., Degens and Epstein, 1964; Allan and Matthews, 1982; Deitrich et al., 1983; Melchiorre and Williams, 2001; Melchiorre and Enders, 2003). This utility is facilitated by the minimal effects of temperature on carbon isotope fractionation for carbonate minerals (e.g., Baertschi, 1957; Vogel, 1959; Emrich et al., 1970; Romanek et al., 1992; Melchiorre et al., 1999; 2000). We assume that the temperature dependence of carbon isotope fractionation behavior for stichtite will be similar to other carbonate minerals.

Regardless of whether stichtite forms during serpentinization directly within the marine forearc environment, or during later serpentinization of obducted marine fore-arc rocks,

the main sources of carbon derived from these rocks should remain constant. There are three obvious potential sources of this carbon: marine carbonates, marine kerogen, and reduction of dissolved carbonate by H_2 (Mottl et al., 2003). In Figure 7, the accepted ranges of $\delta^{13}C$ values for marine carbonate (Prokoph et al., 2008) and marine kerogen (Eigenbrode and Freeman, 2006) are plotted over time from the Cambrian to present. The $\delta^{13}C$ values of stichtite from Tasmania and Mexico are also plotted, over a range of time corresponding to the range of uncertainty associated with the age of the host serpentinite. The stichtite $\delta^{13}C$ values do not overlap with marine carbonate values at the time of their formation, or at any other time in this portion of the geological record. With the exception of stichtite from the Red Lead locality, they do correlate with the $\delta^{13}C$ values of marine kerogen. This suggests a biological origin for the carbon within stichtite, though the process which liberated the carbon from the marine kerogen was most likely abiogenic thermogenesis. Stichtite samples from the Red Lead locality may represent a mixing of carbon from marine carbonate and kerogen sources.

It is also possible that some of the heavier $\delta^{13}C$ stichtite samples such as those from the Red Lead mine may record mixing of atmospheric CO_2 ($\delta^{13}C$ averaging -8‰), with a fluid containing a lighter carbon source, such as that proposed by theoretical modeling for some Type I serpentinizing fluids (e.g., Paukert et al., 2012). However, this mechanism alone would not adequately explain stichtite with $\delta^{13}C$ values that are above -20‰.

It is also possible that this isotopic signal could be an artifact of abiogenic fractionation processes such as substrate depletion and oxidation acting upon thermogenic carbon-based gas from a marine kerogen source. Indeed, the heavy $\delta^{13}C$ values of methane (-

11±5‰) and the high methane to ethane ratios of emissions from the Mariana fore-arc were used to suggest an abiogenic origin (Mottl et al., 2003). Gases from the Zambeles ophiolite resemble those of the Mariana forearc, and Abrajano et al. (1988) proposed an abiogenic origin. Given that the $\delta^{13}\text{C}$ values of DIC in the deep upwelling solutions of the Mariana fore-arc (-16‰; Mottl et al., 2003) overlap with those of methane and stichtite, it may not be possible to discriminate between these two potential abiogenic sources using carbon isotopes alone.

4.3.2 Carbon and hydrogen isotope record and methane

Stichtite mineralization is known to form during the serpentinization process (e.g., Varadarajan, 1966; Melchiorre and Lopez, 2011). Serpentinization is well known for production of H_2 and CH_4 gas (e.g., Evans et al., 2013; McCollom and Seewald, 2013). Given these associations, it is hypothesized that stichtite may receive carbon and hydrogen from serpentinization-generated methane- or H_2 -rich fluids. Specifically, hydrogen gas produced by serpentinization may react with marine carbonate and/or kerogen to produce methane. Methane may also be generated by reaction of hydrogen gas with inorganic carbon (McCollom and Seewald, 2007), and reduction of dissolved carbonate by H_2 (Mottl et al., 2003). The use of combined C and H isotope values for stichtite is used in this study to examine these possible sources of methane (Figure 8).

Kinetic fractionations associated with formation of H_2 and methane are higher than equilibrium exchange values, and subsequent isotopic exchange with water only occurs at extreme geothermal temperatures (e.g., Bottinga, 1969; Clark and Fritz, 1997). This

permits interpretation of hydrogen isotope values of methane and hydrogen gas to determine potential origins, regardless of their interactions with water. In fact, standard plots of $\delta^{13}\text{C} - \delta\text{D}$ for methane gas have long been used to infer sources of methane, and fields defining these sources are well established (e.g., Whiticar et al., 1986; Schoell, 1988; Whiticar, 1999). Similarly, the field of isotopic compositions of methane from zones of active serpentinization (Figure 8) may be plotted for Lost City (Proskurowski et al., 2008), Oman (Fritz et al., 1992), Zambales (Abrajano et al., 1988), Chimera (Hosgörmöz, 2007), and the East Pacific Rise (Welhan, 1988). It bears repeating here that abiogenic methane refers to gas produced by abiogenic means. Yet this does not preclude production of abiogenic methane from an organic carbon source. It must also be noted that the relatively low temperatures of stichtite stability suggest minimal hydrogen isotope exchange between hydrogen-based gases and water.

The $\delta^{13}\text{C}$ and δD values for stichtite plot within three main fields: Organic thermogenic (4 samples), Geothermal/hydrothermal (8 samples), and Serpentinization methane (9 samples). The field of stichtite values show variation in isotope values that are consistent with fractionation caused by substrate depletion of the source, and/or methane oxidation (Figure 8). This would suggest that stichtite from different localities formed from methane with different histories of oxidation and sourcing/depletion. This is consistent with mineralogical and textural observations that the stichtite-bearing Tasmanian serpentinite belts and Mexico serpentinite have distinct P-T histories.

The isotopic similarity of many of the stichtite samples to modern methane from serpentinizing zones at non-stichtite bearing localities is not a surprising result, given that stichtite is known to form during serpentinization. Workers at Lost City

(Proskurowski et al., 2008), Oman (Fritz et al., 1992), Zambales (Abrajano et al., 1988), Chimera (e.g., Hosgörmez, 2007), and the East Pacific Rise (Welhan, 1988) have presented evidence that methane from seeps at these localities is an abiogenic product of Fischer-Tropsch type reactions, or that the methane results from abiogenic thermogenesis acting upon an organic substrate, suggesting an abiogenic origin for C and H in these stichtite samples. Isotopic behavior of both carbon and hydrogen during stichtite formation should be well understood, as many workers have repeatedly demonstrated for other divalent cation carbonates (e.g., Freidman and O'Neil, 1977; Carothers et al., 1988; Melchiorre et al., 2001) and hydrated divalent cation carbonates and other hydrated minerals (e.g., Suzuoki and Epstein, 1976; Melchiorre et al., 1999; Melchiorre et al., 2000), based upon the relatively temperature-insensitive nature of well-defined fractionation curves (e.g., Bottinga, 1968). Post-depositional isotopic exchange is probably minimal, based upon radio-isotope tracer studies of similar systems (DeGraaf et al., 1996).

4.4 Proposed origins of stichtite with implications for early Earth and Mars

Each stichtite-bearing serpentinite body examined in this study has a unique reaction-progress ratio and chemistry (Figures 3, 4, and 5), suggesting that different degrees of fluid flow or the duration of reaction times were associated with each serpentinite host unit. Furthermore, the subtle variations in these parameters for stichtite within individual serpentinite bodies may serve as indicators of P, T, and fluid flow gradients within these bodies during serpentinitization.

Measured carbon-isotope values of stichtite were found to be consistent with mixing between a marine-kerogen carbon source and/or an H₂-reduced dissolved carbonate carbon source, with a minor contribution from marine carbonate. In addition, the carbon isotope ratios of stichtite are consistent with those of other carbonate minerals which are known to form within serpentinizing environments (e.g., Perry and Tan, 1972; Zeddef et al., 2000). Similarly, hydrogen isotope values for stichtite were observed to be consistent with measured hydrogen isotope ratios for methane gas from serpentinizing environments (e.g., Abrajano et al., 1988; Welhan, 1988; Ripley et al., 1993; Proskurowski et al., 2008). Combined, the C and H stable isotope values of stichtite support formation within a serpentinizing environment from abiogenic thermogenic methane sourced from a marine kerogen substrate.

When variation in reaction progress ratios and chemistry is viewed through the lens of isotope geochemistry, a more complete picture is derived for how and why stichtite forms. Correlation between the $\delta^{13}\text{C}$ value of stichtite and the corresponding average reaction-progress ratio was noted (Figure 10). The average reaction-progress ratio (% stichtite replacement of chromite within a pseudomorph) for each sample site was used in generating this figure as it was not directly measured prior to destructive isotope analyses on each unique sample. Reaction completion is interpreted to represent a proxy for the duration of time which the samples spent within the “stichtite window.” It is assumed that the duration within the “stichtite window” increases with the depth to which the serpentinization has occurred, based upon mineralogical indicators of P and T. For example, the presence of aragonite in association with stichtite at the Nevada Creek and Tehuitzingo, Mexico localities suggests elevated pressures during

serpentinization and stichtite mineralization. Similarly, the presence of minor antigorite and ferritchromite within zones dominated by remobilized veins of stichtite indicate sectors of localized higher-temperature conditions.

The correlation between the $\delta^{13}\text{C}$ value and reaction completion, with additional constraints from associated mineralogy, suggests that the stichtite from the deepest and most complete reactions received carbon from a marine kerogen source, while stichtite with the most shallow and incomplete reactions received carbon from a mixture of marine kerogen and carbonate sources. This would be consistent with a serpentinization model in which the most deeply circulating hydrothermal fluids are stripped of marine carbonate, while shallower fluids retain more, (e.g., Alt and Teagle, 1999; Proskurowski et al., 2004; Proskurowski et al., 2008).

The chemistry of Cr-spinel associated with stichtite also provides a window into conditions of formation. It has been shown that stichtite from the localities examined in this study forms exclusively within serpentinized fore-arc rocks (Figure 6). While not part of the present study, a new stichtite locality reported for an abyssal plain appears to dispute the notion that all stichtite forms within the fore-arc (Klein et al., 2015). Future work is planned at additional localities to examine the geochemistry of stichtite and the type of associated serpentinizing environment to evaluate the range of conditions under which stichtite may form.

Other workers have determined that chemical zoning in Cr-spinel from the fore-arc environment represents 'immature' ferritchromite which formed in short-lived thermal events (Saumur and Hattori, 2013). Such events are likely of too short a timescale to

669 produce extensive ferritchromite, or significant quantities of high-temperature minerals.
670 These transient conditions would be consistent with our observations of incomplete
671 alteration of chromite to ferritchromite for all localities in this study, and may explain
672 secondary pyroaurite/hydrotalcite mineralization zones in association with fibrous
673 magnetite. This type of high temperature alteration is considered rare in forearc
674 serpentinites (Saumur and Hattori, 2013).

675 The rocks within each of the serpentinizing environments in this study experienced
676 hydration and formation of serpentine and magnetite at the expense of chromite and
677 mafic silicates, as outlined in section 1.1 and the references therein. Localized pipes or
678 fracture zones within these serpentizing rocks facilitated collection and migration of
679 serpentinizing fluids and their reaction products such as H_2 . It should be noted that
680 stichtite is found in the margins and tapering ends of serpentinite bodies (Figure 1),
681 where fluid conduits and enhanced permeability are expected. The association of these
682 zones of enhanced brecciation with stichtite have been noted by other workers (e.g.,
683 Bottrill and Graham, 2006). Abiological thermogenic breakdown of marine kerogen in
684 the presence of H_2 -rich fluids produced CH_4 . When these warm fluids with elevated
685 pressure and methane/ H_2 concentration came in contact with chromite, it created
686 conditions ideal for the growth of stichtite. The varying reaction progress ratios between
687 the chromite reactant and stichtite product suggests that these conditions were
688 transitory which likely reflects a shift in fluid pathways, or a termination of
689 serpentinization due to changing P-T conditions. It is presumed that such conditions
690 may exist at depth under modern methane-rich springs of fore-arc serpentinizing
691 systems (Figure 10).

This work bears directly upon studies of early Earth and Mars. Methane was first detected on Mars in 2004 by the Mars Express mission (Formisano et al., 2004), followed by Earth ground-based observations of methane on Mars (Krasnopolski et al., 2004). Variable methane concentrations on Mars were documented for durations of weeks and months (e.g., Mumma et al., 2009; Webster et al., 2015). However, the source of this methane remained controversial (e.g., Boston et al., 1992; Etiope and Sherwood-Lollar, 2013; Yung and Chen, 2015). What is clear is that rates of UV and oxidant destruction of methane on Mars requires modern methane emissions to match observations. On Earth, the majority of methane is biological in origin, with only a few percent contribution by inorganic sources such as geological activity. However, the geological settings that produce abiological H₂ and/or methane, such as hydrothermal and volcanic systems, also provide habitable environments for extremophile microorganisms. By direct analog, methane on Mars may indicate the presence of life, or at least the presence of potentially habitable methane-rich environments.

Recognizing and understanding the fossil chemical- and isotopic-fingerprint of gases and fluids from serpentinizing environments at various points in Earth history has great significance for interpreting emissions from serpentinizing environments on Mars. While study of modern methane production from active serpentinization on Earth is an important task, it may not be directly applicable to the Martian environment. Perhaps the best window into conditions on Mars may be found in studies of conditions recorded by stichtite, which likely forms in deep-Earth time during serpentinization (e.g., Varadarajan, 1966; Melchiorre and Lopez, 2011), when our biological systems were more primitive (e.g., Lyons et al., 2014).

715

716 4. CONCLUSIONS

717 Stichtite from early Phanerozoic chromite-rich serpentinite rocks of Tasmania and
718 Mexico have reaction completion textures, isotopic values, element abundances, and
719 qualitative mineral thermobarometric indicators that indicate that stichtite forms in fore-
720 arc rocks at a range of depths in a methane/H₂-rich environment within fluid conduits,
721 ranging from near the surface to depths where pressure is up to 1.2 to 0.8 GPa and
722 temperature is up to ~300°C. These properties of stichtite are unique for each stichtite-
723 hosting serpentinite body, and likely record the duration of serpentinization at specific
724 thermobarometric conditions. As future work refines and quantifies our understanding of
725 exact conditions under which stichtite forms, this mineral may prove a useful tool in
726 understanding the dynamics of serpentinization. For example, isotopic, chemical, and
727 polytype trends within the Nevada Creek serpentinite body suggest that rocks of the
728 northeast (Nevada Creek) end of this unit was subjected to higher pressures and
729 temperatures than those in the southwest (Kapitani) end of the same unit.

730 Significantly, light stable isotope values are consistent with stichtite recording the
731 presence of methane or H₂ gas that was likely generated by abiological thermogenesis of
732 a marine kerogen biological substrate. Such a record over a broader range of geological
733 time will provide a window into the conditions associated with a potentially habitable
734 environment over a range of early Earth history, with implications for understanding
735 similar methane-producing terrains on Mars.

736

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FIGURE AND TABLE CAPTIONS

Figure 1. Sample location maps, showing the locations of a). Tehuiztingo, Mexico, and b). Tasmania, Australia stichtite occurrences (black squares). A detailed sample map, showing the location of specific stichtite occurrences c). within the Dundas mineral field (Tasmania), and their relationship to geology and specific serpentinized rock belts.

Figure 2. Stichtite textural associations. a) single euhedral crystal of chromite (grey metallic) showing pseudomorphous replacement by stichtite (purple) in a serpentinite matrix. b) stichtite (purple) alteration to pyroaurite (pinkish-orange) c) fibrous oriented magnetite d) stichtite alteration to pyroaurite, with secondary regrowth of stichtite mantling chromite grains.

Figure 3. Reaction progress percentages for all localities. Vertical divisions separate stichtite samples by their common serpentinite host unit. Box shows 50% data distribution (line shows mean), error bars show 95% confidence, and circles show outliers.

1296 Figure 4. Representative examples of reaction progress textures for stichtite from a)
1297 Stichtite Hill, b) Red Lead Mine, c) Tunnel Hill, d) Kapitani Prospect, e) West Comet
1298 Mine f) Adelaide Mine, g) Nevada Creek, and h) Tehuitzingo, Mexico.

1299 Figure 5. Ternary plot of hydrotalcite end member compositions, showing elemental
1300 data for samples from this study. Ellipse fields enclose stichtite samples associated with
1301 specific serpentinite host bodies.

1302 Figure 6. Plot of Cr# vs Mg# for chromite grains from stichtite localities, showing fields
1303 of origin from Dick and Bullen (1984) and Tamura and Arai (2006). Grey arrow shows
1304 vector of inferred low-temperature alteration of chromite to ferritchromite and magnetite.

1305 Figure 7. The $\delta^{13}\text{C}$ values of stichtite from Tasmania and Mexico shown in comparison
1306 to the accepted ranges of $\delta^{13}\text{C}$ values for marine carbonate (Prokoph et al., 2008) and
1307 marine kerogen (Eigenbrode and Freeman, 2006), plotted over time from the Cambrian
1308 to present. Tasmania and Mexico samples are plotted over a range of time
1309 corresponding to the range of uncertainty associated with the age of the host
1310 serpentinite.

1311 Figure 8. Plot of $\delta^{13}\text{C}$ vs δD for stichtite samples in this study. The fields showing major
1312 types of methane and their origins are from Whiticar et al. (1986), Schoell (1988), and
1313 Whiticar (1999). The combined field of isotopic composition of methane from
1314 serpentinizing vents are for Lost City (Proskurowski et al., 2008), Oman (Fritz et al.,
1315 1992), Zambales (Abrajano et al., 1988), Chimera (Hosgörmez, 2007), and East Pacific
1316 Rise (Welhan, 1988). Black arrows show the vector for substrate depletion and methane
1317 oxidation.

1318 Figure 9. Plot of $\delta^{13}\text{C}$ vs reaction completion %. Black arrows from the Mexico samples
1319 show the expected shift in reaction completion percentages expected when accounting
1320 for the fine-grained ferritchromite/magnetite component.

1321 Figure 10. Idealized cross section through a serpentinizing fluid conduit, showing
1322 reaction boundaries for calcite/aragonite and lizardite-chrysotile/antigorite transitions.
1323 Black axis shows approximate reaction completion percentages. Blue arrows show

1324 inferred carbon sources and mixing. Positions of stichtite sample localities reflect
1325 relative depths, consistent with chemical, isotopic, and mineralogical evidence.

1326

1327 Table 1. Stichtite-chromite reaction progress ratios.

1328

1329 Table 2. Summary geochemical data for stichtite.

1330

1331 Table 3. Stable isotope data for stichtite.

1332

1333

Table 1

Stichtite Hill	Red Lead	Tunnel Hill	Kapitani	Adelaide	West Comet	Nevada Creek	Mexico
Reaction	Reaction	Reaction	Reaction	Reaction	Reaction	Reaction	Reaction
Progress (%)	Progress (%)	Progress (%)	Progress (%)	Progress (%)	Progress (%)	Progress (%)	Progress (%)*
66	31	97	98.5	95	98	94	85
64	34	93	96	92	99	93	82
54	45	90	97	94	98	88	90
71	35	95	90	97		92	81
65	36	95	92	94		94	97
62	41	88	96	94		95	85
60	47	84	99			93	92
52	47	91	93			90	88
63	49	93	96			93	83
77	50	87	95			91	83
65	52	92	89			93	79
68	55	94	98			96	84
70	39	82	97			92	87
66	42	89	99			93	83
57			96				84
AVE: 64	AVE: 43	AVE: 91	AVE: 95	AVE: 94	AVE: 98	AVE: 93	AVE: 86

*Estimates for the Mexico samples are a lower limit, due to an abundance of fine-grained ferritchromite/magnetite. Actual values may be up to 12% higher.

Table 2. Average Geochemical Values for Stichtite Samples in this Study

SAMPLE	N	Cr (wt%)	Cr stdev (wt%)	Fe (wt%)	Fe stdev (wt%)	Al (wt%)
Tunnel Hill, Tasmania, Australia	6	11.99	1.83	1.65	0.72	4.57
Stichtite Hill, Tasmania, Australia	16	11.95	0.79	5.01	1.13	2.54
Nevada Creek, Tasmania, Australia	8	8.45	0.61	3.93	0.55	0.32
Kapitani, Tasmania, Australia	6	10.85	1.58	5.89	0.58	1.15
Tehuiztingo, Mexico	7	10.46	0.64	5.74	0.40	0.11

Table 3

Table 3: Conventional and SIMS carbon and hydrogen isotope data for stichtite.

Location	Analysis Type	$\delta^{13}\text{C}$ (VPDB)	δD (VSMOW)
Stichtite Hill, Australia	Conventional	-15.5	-96
Stichtite Hill, Australia	Conventional	-17.2	-116
Stichtite Hill, Australia	Conventional	-14.0	-133
Stichtite Hill, Australia	SIMS	-14.3	-119
Stichtite Hill, Australia	SIMS	-16.2	-87
Stichtite Hill, Australia	SIMS	-16.1	-133
Stichtite Hill, Australia	SIMS	-16.9	-162
Stichtite Hill, Australia	SIMS	-12.5	-144
Red Lead Mine, Australia	Conventional	-11.5	-89
Red Lead Mine, Australia	Conventional	-8.9	-121
Red Lead Mine, Australia	SIMS	-10.9	-73
Tunnel Hill, Australia	Conventional	-20.5	-131
Tunnel Hill, Australia	Conventional	-19.5	-122
Tunnel Hill, Australia	Conventional	-20.4	-141
Tunnel Hill, Australia	SIMS	-18.3	-149
Tunnel Hill, Australia	SIMS	-18.2	-109
Nevada Creek, Australia	Conventional	-21.5	-101
Nevada Creek, Australia	Conventional	-26.1	-142
Tehuiztingo, Mexico	Conventional	-26.4	-127
Tehuiztingo, Mexico	Conventional	-25.3	-149
Tehuiztingo, Mexico	Conventional	-29.4	-119

Figure 1

Figure 1

Figure 2

Figure 2

Figure 3

Figure 3

Figure 4

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