



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 and isotope record of early Phanerozoic serpentizing 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 serpentizing 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 serpentizing zones, to organic thermogenic methane. The association of the stichtite 2H polytype (nee barbertonite) with aragonite \pm 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 serpentization of fore-arc setting rocks in a methane/H₂-rich environment within fluid conduits, ranging from low temperatures and pressures near the surface, to depths where pressure is up to 0.8–1.2 GPa and temperature is up to \sim 300 °C. These unique chemical, isotopic, and textural properties of stichtite from distinct serpentinite bodies likely record the duration of serpentization 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.

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1. INTRODUCTION

The alteration of low-silica ultramafic rocks by water–rock reactions, commonly referred to as serpentization, 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 ser-

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pentinizing 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](#); [McCullom 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 ($\text{Mg}_6\text{Cr}_2(\text{OH})_{16}[\text{CO}_3]_4\text{H}_2\text{O}$) 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 2 mm 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 $\text{MgCr}_2\text{O}_4 + 5 \text{Mg}(\text{OH})_2 + \text{CH}_4 + 2 \text{O}_2 + 5 \text{H}_2\text{O} = \text{Mg}_6\text{Cr}_2(\text{OH})_{16}[\text{CO}_3]_4\text{H}_2\text{O}$. 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 $\text{MgCr}_2\text{O}_4 + 5 \text{Mg}(\text{OH})_2 + \text{CO}_3 + \text{H}_2 + 6 \text{H}_2\text{O} = \text{Mg}_6\text{Cr}_2(\text{OH})_{16}[\text{CO}_3]_4\text{H}_2\text{O}$. 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 Tehuizingo, Mexico ([Fig. 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 ([Fig. 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 Tehuizingo, 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 serpentinized mid-Cambrian ultramafic rocks known as the Dundas ultramafic complex ([Brown, 1986](#); [Burrett and Martin, 1989](#)). This unit consists of variably serpentinized ultramafics, gabbros, and basaltic volcanic rocks. Three types of serpentinite are recognized in these rocks ([Rubenach, 1974](#)). Black serpentinites are unshredded, 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](#)).

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