ABSTRACT: Stichtite is a naturally occurring layered double hydroxide (LDH) with the ideal chemical formula \( \text{Mg}_6\text{Cr}_2\text{CO}_3(\text{OH})_{16}\cdot4\text{H}_2\text{O} \). It has received less attention in the literature than other LDHs and is often described as a rare mineral; however, abundant deposits of the mineral do exist. In this article we aim to review a number of significant publications concerning the mineral stichtite, including papers covering the discovery, geological origin, synthesis and characterization of stichtite. Characterization techniques reviewed include powder X-ray diffraction (XRD), infrared spectroscopy (IR), near infrared spectroscopy (NIR), Raman spectroscopy (Raman), thermogravimetry (TG) and electron microprobe analysis.

KEYWORDS: stichtite, layered double hydroxide, anionic clays, hydrotalcite, synthesis, X-ray powder diffraction, thermal analysis, IR spectroscopy, near-IR spectroscopy, Raman spectroscopy, electron microprobe analysis.

The mineral stichtite is a chromium-substituted layered double hydroxide (LDH) which occurs in nature. Unlike many other LDHs, little has been published on stichtite. One of the reasons for this oversight may be the perceived rarity of stichtite, which is known to exist only in a limited number of locations around the world. One of these locations is Tasmania, Australia, where the mineral was first discovered and where significant deposits may still be found. Layered double hydroxides (which are also known as anionic clays or hydrotalcites) are a group of layered clay minerals that are described by the general formula:

\[
[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2]^{x^+}[A^{n-}]_n\cdot m\text{H}_2\text{O} \tag{1}
\]

where \( M^{2+} \) and \( M^{3+} \) are the divalent and trivalent layer cations respectively, \( 0.2 < x < 0.33 \) and \( A^{n-} \) is the exchangeable anion which is often (but not always) carbonate (Labajos & Rives, 1996; Rives, 2001, 2002; Frost et al., 2007, 2009). The ideal chemical formula of stichtite is \( \text{Mg}_6\text{Cr}_2\text{CO}_3(\text{OH})_{16}\cdot4\text{H}_2\text{O} \). When compared with hydrotalcite (\( \text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot4\text{H}_2\text{O} \)), the most commonly studied LDH, \( \text{Al}^{3+} \) is substituted with \( \text{Cr}^{3+} \) in the same way as \( \text{Fe}^{3+} \) substitutes for \( \text{Al}^{3+} \) in pyroaurite (\( \text{Mg}_6\text{Fe}_2\text{CO}_3(\text{OH})_{16}\cdot4\text{H}_2\text{O} \)). Samples of naturally occurring stichtite often exhibit varying degrees of partial substitution of \( \text{Cr}^{3+} \) in the cation layers for \( \text{Al}^{3+} \) or \( \text{Fe}^{3+} \) (Ashwal & Cairncross, 1997).

Stichtite is an interesting and potentially underutilized resource as evident by the limited number of publications available in the literature. Currently stichtite is primarily valued only for its intense purple to pink colour (which depends on impurities present) resulting in its popularity as a semi-precious stone and as a curiosity in mineral collections. The only practical application of stichtite is as a minor source of metallic chromium. This paper aims to provide a comprehensive review of the published literature on the mineral and make recommendations for possible future work.

DISCOVERY AND EARLY INVESTIGATIONS (1891–1933)

Stichtite was first discovered in western Tasmania, Australia, in 1891; however, it was mistakenly identified as kämmererite (a purple form of chlorite) at the time by Stitt and Cullingsworth.
This mistake occurred because of the remarkable similarity of the two minerals and the absence of any chemical analysis. In 1910 Wesley, the chief chemist at the Mount Lyell Mining and Railway Company, Tasmania, Australia, conducted the first wet chemical analysis on a sample of stichtite and determined that the mineral was not a silicate, as expected, but a new uncatalogued mineral. Wesley estimated the empirical formula of the new mineral as (CrFe$_2$)O$_3$.6MgO.CO$_2$.13H$_2$O. Stichtite was named after Robert Carl Sticht, the general manager of the Mount Lyell Mining and Railway Company, in appreciation for his assistance in the preparation of the ‘Catalogue of the Minerals of Tasmania’. It was in this publication by Petterd that stichtite was first reported (Petterd, 1910; Twelvetrees, 1914). Petterd was the first to identify the similarity of stichtite to pyroaurite, the iron substituted LDH described earlier. Samples of stichtite were sent to the Mineralogic-Petrological Institute in Zurich where Hezner (Twelvetrees, 1914) carried out further chemical analysis and confirmed that the sample was indeed a new mineral. In a paper published in 1912, Hezner suggested stichtite may be a chrome-brugnatellite with the formula: 2MgCO$_3$.5Mg(OH)$_2$.2Cr(OH)$_3$.4H$_2$O. Himmelbauer (Twelvetrees, 1914) found that stichtite had a hardness of 1.75 (1 1/4, between gypsum and rock salt), a relative density of 2.161 (by the fluid method), and a refractive index of 1.542 (immersion method). Himmelbauer also reported the similarity of stichtite to hydrotalcite and pyroaurite in 1913 (Twelvetrees, 1914). The results described above were translated, compiled and re-published with the author’s permission by Twelvetrees for the Tasmanian Department of Mines (Twelvetrees, 1914). By 1933 stichtite had been identified at three other locations, Black Lake, Quebec, Canada (1918), the Barberton district, Transvaal, South Africa (1922) and the Shetland Islands, Scotland (Read, 1933; Mondal & Baidya, 1996; Ashwal & Cairncross, 1997).

**GEOLOGICAL ORIGIN OF STICHTITE**

Ashwal and Cairncross performed analysis of stichtite from various sources in an attempt to understand better the mechanisms of stichtite formation (see electron microprobe analysis section below) (Ashwal & Cairncross, 1997). It was clear to Ashwal & Cairncross that serpentinite must be the source of Mg$^{2+}$ as stichtite is always found intergrown with serpentinite. It is likely that the trivalent cations such as Cr$^{3+}$ (as well as, to a lesser extent, Al$^{3+}$ and Fe$^{3+}$) originate from chromite (FeCr$_2$O$_4$) as it is present in almost all known cases (Ashwal & Cairncross, 1997). No individual reaction could be proposed to adequately explain stichtite formation; however, stichtite could have formed as a product of the breakdown of serpentinite and chromate by one of two mechanisms (Ashwal & Cairncross, 1997):

\[
\begin{align*}
2 \text{serpentinite} + \text{chromite} + 8\text{H}_2\text{O} + \text{CO}_2 & \rightarrow \text{stichtite} + 4\text{quartz} + \text{FeO} \\
3 \text{serpentinite} + \text{chromite} + 7\text{H}_2\text{O} + \text{CO}_2 & \rightarrow \text{stichtite} + \text{talc} + 4\text{quartz} + \text{FeO}
\end{align*}
\]

The main problem with the proposed mechanisms is the absence of quartz, talc or FeO in direct association with known stichtite deposits. Ashwal & Cairncross suggested this may be explained by the dissolution and re-deposition of silica by aqueous and carbonic fluids. FeO may be partially oxidized and form magnetite or removed from solution. The observation that stichtite usually occurs as veins in serpentinite deposits provides some evidence to support this mechanism (Ashwal & Cairncross, 1997). Another possibility is that stichtite may be formed from magnesite or brucite. These equations do not require the removal of silicates as it would have occurred during the original formation of the magnesite or brucite (Ashwal & Cairncross, 1997).

\[
\begin{align*}
6 \text{magnesite} + \text{chromite} + 12\text{H}_2\text{O} & \rightarrow \text{stichtite} + 5\text{CO}_2 + \text{FeO} \\
6 \text{brucite} + \text{chromite} + 6\text{H}_2\text{O} + \text{CO}_2 & \rightarrow \text{stichtite} + \text{FeO}
\end{align*}
\]

The presence of small amounts of magnesite associated with some stichtite deposits provides evidence to support this mechanism (Ashwal & Cairncross, 1997). Though the exact mechanism of stichtite formation is still unclear, the absence of silicates associated with stichtite-bearing rocks and the overall rarity of the mineral suggests that a unique combination of conditions must exist for its formation.

**SYNTHESIS OF STICHTITE**

As previously mentioned, it is difficult to obtain pure stichtite from natural sources as the material is often intermixed with serpentinites as well as other LDHs including hydrotalcite, pyroaurite, iowaite.
the expected range for an LDH type structure. Next, and 7.37 Å respectively. These values were within
Distances of the pink and green samples as 7.76 Å to the ideal formula of stichtite given earlier.

This method required the preparation of two solutions, solution 1 contained NaOH and Na$_2$CO$_3$ (both 2 M). Solution 2 contained Mg$^{2+}$ (0.75 M) as Mg(NO$_3$)$_2·6$H$_2$O and Cr$^{3+}$ (0.25 M) as CrCl$_3·9$H$_2$O. Precipitation of stichtite occurred when solution 2 was slowly added to solution 1 at a rate of 40mL min$^{-1}$ under a nitrogen atmosphere and with constant stirring. The resulting precipitate was collected, washed with boiled ultrapure water and dried. (Frost & Erickson, 2004; Bouzaid & Frost, 2007). Frost and Erickson determined the formula of the synthetic stichtite prepared by this method was Mg$_{5.78}$Cr$_{2.09}$CO$_3$(OH)$_{16}·4$H$_2$O, which is very similar to the ideal formula of stichtite given earlier.

**POWDER X-RAY DIFFRACTION OF STICHTITE**

Powder X-ray diffraction (XRD) is a powerful technique that is often used to study crystalline minerals. Powder XRD of the mineral stichtite was investigated by Bookin et al. (1993) and Mills et al. (2011). Bookin et al. investigated a naturally occurring stichtite collected from the Terectin Ridge (Altai Mountains). The stichtite sample consisted of a mixture of pink and green grains which could be separated with the aid of a binocular microscope. Samples of both the pink and green grains were collected for powder XRD analysis. Tatarinov et al. (1985), who originally studied the sample noted that the pink grains, when exposed to X-rays or visible light appeared to undergo a photochemical reaction causing them to change to a green colour. Bookin et al. exposed some of the pink grains to light over the period of one week to determine if this would be any effect on the powder XRD pattern of the material.

Bookin et al. (1993) reported the interlayer distances of the pink and green samples as 7.76 Å and 7.37 Å respectively. These values were within the expected range for an LDH type structure. Next, the peak positions in the powder XRD pattern of pink stichtite was investigated. The positions of all reflections in the pattern corresponded to a three-layer rhombohedral cell, which is typical of most carbonate-bearing LDHs (Bookin et al., 1993). To confirm their observations, they attempted to simulate the powder XRD pattern of stichtite using the well established structure of hydrotalcite ($3R_1$) as a basis for their model. Good agreement between the major peaks in the model and the actual powder XRD patterns confirmed that the pink grains of stichtite were isostructural with hydrotalcite ($3R_1$) (Bookin et al., 1993).

Samples of the green grains did not appear to exhibit the same crystal structure as the pink stichtite grains, and did not correspond to the $3R_1$ structure expected for carbonate-bearing LDHs. The reflection positions in the pattern corresponded to a one-layer hexagonal cell (1H) in which $a = 5.3$ Å and $c = 7.36$ Å (Bookin et al., 1993). A sample of the pink grains exposed to light appeared to contain a combination of both structures. Bookin et al. were able to conclude that the green material was the product of stichtite decomposition and proposed a mechanism to describe this decomposition. It is likely that the green grains described in the paper are a mineral commonly known as barbertonite (Mills et al., 2011).

Mills et al. (2011) recently re-examined the crystal structure of stichtite and the associated mineral barbertonite using samples of stichtite collected from Stichtite Hill, Tasmania, and barbertonite from Barberton, South Africa. They again showed that the powder XRD pattern of stichtite was dominated by the $3R_1$ polytype common to most LDHs; however, peaks corresponding to the $2H_1$ polytype and lizardite (Mg$_3$Si$_2$O$_5$(OH)$_4$) were also observed. The final composition of the sample was Mg$_{6.12}$Cr$_{1.88}$(OH)$_{16}$(CO$_3$)$_{0.94}·4$H$_2$O, which is close to the ideal formula (Mills et al., 2011).

Barbertonite is a mineral with the same ideal chemical formula as stichtite and is described as the hexagonal polymorph of stichtite. It was first reported by Fondel (1940) as occurring in Barberton, South Africa. Powder XRD of barbertonite showed a material consisting of a mixture of the $2H_1$, and to a lesser extent the $3R_1$ polytype. Mills et al. (2011) suggested that stichtite and barbertonite are polymorphs, and as such recommended that barbertonite should be denoted as stichtite-2H in accordance with Nickel & Grice, 1998.
VIBRATIONAL SPECTROSCOPY OF STICHTITE

Frost and Erickson investigated samples of synthetic stichtite prepared by the co-precipitation method using infrared (IR), Raman and Near-IR spectroscopy (Frost & Erickson, 2004, 2005). Numerous bands were identified in the IR spectrum (Frost & Erickson, 2004). A weak band at 1076 cm\(^{-1}\) that was only observed with 50 times expansion of the spectrum was attributed to the forbidden carbonate symmetric stretching mode. The band at 1644 cm\(^{-1}\) was attributed to the HOH water bending mode. Next, two bands at 1457 and 1381 cm\(^{-1}\) could be attributed to \(v_1\), CO\(_3\) antisymmetric stretching modes. Bands at 744 and 685 cm\(^{-1}\) were assigned to the \(v_4\) carbonate bending mode indicating that two carbonate species must exist in the interlayer (strongly and a weakly hydrogen bonded). Bands at 909 and 861 cm\(^{-1}\) may be attributed to MOH bending modes (where \(M\) is Cr or Mg). The hydroxyl stretching region IR spectrum was found to result from a complex combination of units including: Mg\(_2\)OH, Mg\(_2\)CrOH, MgCr\(_2\)OH and Cr\(_3\)OH (Frost & Erickson, 2004). Three bands at 3618, 3529 and 3430 cm\(^{-1}\) could be assigned to the Mg\(_2\)OH, Mg\(_2\)CrOH and Cr\(_3\)OH OH stretching bands respectively. Two remaining bands at 3220 and 2960 cm\(^{-1}\) were assigned to water OH stretching (Frost & Erickson, 2004).

Frost and Erickson also carried out Raman microprobe spectroscopy on the same sample of stichtite (Frost & Erickson, 2004). Two intense overlapping bands were observed at 1087 and 1067 cm\(^{-1}\). These bands were assigned to the \(v_1\) symmetric carbonate stretching mode. Again two types of carbonate are observed. The band at 1087 cm\(^{-1}\) could be attributed to the strongly hydrogen bonded carbonate. The ratio of the intensities of the two peaks was calculated to be 2.5:1. This corresponds well to the ratio of 2.3:1 obtained from the corresponding \(v_4\) bending mode peaks at 539 and 531 cm\(^{-1}\). The band at 453 cm\(^{-1}\) was assigned to the CrO stretching mode while the large number of bands between 200 and 366 cm\(^{-1}\) could only be attributed to lattice modes (Frost & Erickson, 2004).

Mills et al. more recently investigated a naturally occurring stichtite using Raman spectroscopy (Mills et al., 2011). Firstly, no H\(_2\)O bending bands were observed in the Raman spectrum of natural stichtite. They reported that the \(v_3\) antisymmetric stretching mode was present at 1343 cm\(^{-1}\). The observed value of the \(v_3\) peak is much lower than a typically expected value of approximately 1400 cm\(^{-1}\). It was proposed that the \(v_3\) peak may be due to the presence of barbertonite impurities in the natural sample (Mills et al., 2011).

All carbonate modes in the naturally occurring stichtite were found to be Raman active; this contrasts with the results of Frost and Erickson described earlier. The \(v_1\) symmetric carbonate stretching mode was observed at 1055 cm\(^{-1}\). Asymmetry of this peak suggested the presence of additional unresolved bands. The \(v_2\) carbonate stretching mode was present at 680 cm\(^{-1}\); however, it was extremely weak. The bands at 672 and 534 cm\(^{-1}\) were assigned to the \(v_4\) carbonate stretching and \(v_2\) carbonate bending modes respectively (Mills et al., 2011). Bands at 2632 and 2621 cm\(^{-1}\) were attributed to Mg-OH and Cr-OH vibrations. It was proposed that these bands may be useful for the identification of stichtite. Finally, an additional band at 428 cm\(^{-1}\) could only be attributed to lattice modes (Mills et al., 2011).

Layered double hydroxides are well suited to study by near-IR spectroscopy (NIR) due to the presence of the hydroxyl surface and interlayer water. Frost and Erickson investigated synthetic stichtite using NIR spectroscopy and found that the three distinct spectral regions could be observed in the NIR spectra of stichtite (Frost & Erickson, 2005). The high wavenumber region (6400–7400 cm\(^{-1}\)) was attributed to the first overtone of the fundamental hydroxyl stretching mode. This region contained a broad profile with inflections at 7200 and 6800 cm\(^{-1}\). Bands were observed at 7246, 7151, 7069, 7017, 6890 and 6633 cm\(^{-1}\) and were attributed to the combination of OH stretching vibrations observed in the mid-IR region of the spectrum due to the complexity and distribution of the MOH bonds across the LDH. No bands could be attributed to specific vibrations in this spectral region (Frost & Erickson, 2005).

The second spectral region (4800–5400 cm\(^{-1}\)) contained the combination modes of the fundamentals of water. Bands were observed at 4460, 4411 and 4366 cm\(^{-1}\) and attributed to OH combination bands. The third region (4000–4800 cm\(^{-1}\)) was attributed to the combination of MOH stretching and deformation modes. Finally, NIR spectra of three different LDH materials (stichtite, iowaite and desautelsite,
Mg₆Mn₂CO₃(OH)₁₆·₄H₂O) were compared. It was found that the minerals could be distinguished by their NIR spectra alone. This demonstrates the power of NIR spectroscopy as a tool for identifying and studying LDHs (Frost & Erickson, 2005).

### THERMAL DECOMPOSITION OF STICHTITE

To our knowledge, thermal decomposition of natural stichtite has never been reported in the literature. Bouzaid & Frost (2007) used thermogravimetry coupled with evolved gas mass spectrometry to determine the mechanism of thermal decomposition of a sample of synthetic stichtite. Decomposition was found to occur through a mechanism similar to those of most other LDH materials. The first step involved the removal of weakly adsorbed and interlayer water at approximately 52°C. Evolved gas mass spectrometry confirmed the release of H₂O, OH and O in this temperature region. The theoretical mass loss of water determined from the ideal formula of stichtite was 11.0%; however, the mass loss in this temperature region was found to be considerably greater with a value of 24.9%. It was proposed that stichtite like some other LDHs (such as honessite, Ni₆Fe₂SO₄(OH)₁₆·₄H₂O and hydrohonessite, Ni₆Fe₂SO₄(OH)₁₆·₇H₂O) may contain more than four water molecules per formula unit. Using the mass loss of 24.9% it was predicted that nine moles of water per formula unit must be present instead of four (Bouzaid & Frost, 2007). They proposed a mechanism for the thermal decomposition of synthetic stichtite. The first step of the decomposition mechanism can be described by Equation 4 (Bouzaid & Frost, 2007):

\[
\text{Mg}_6\text{Cr}_2\text{CO}_3\text{(OH)}_{16} \cdot 4\text{H}_2\text{O} \rightarrow \text{Mg}_6\text{Cr}_2\text{CO}_3\text{(OH)}_{16} + 4\text{H}_2\text{O}
\]  

(4)

The next two steps in the thermal decomposition of stichtite appear to occur almost simultaneously at approximately 294°C. This temperature region corresponded to the dehydroxylation and decarbonation of the stichtite. The ion current curves clearly show the loss of H₂O, OH and CO₂ in this temperature region. Ion current curves also show that dehydroxylation occurred at a slightly lower temperature than decarbonation. Equations 5–8 describe the steps that occur in this temperature region during thermal decomposition (Bouzaid & Frost, 2007):

\[
\begin{align*}
\text{Mg}_6\text{Cr}_2\text{CO}_3\text{(OH)}_{16} & \rightarrow (\text{MgO})_6\text{Cr}_2\text{CO}_3 + 8\text{H}_2\text{O} \quad (5) \\
(\text{MgO})_6\text{Cr}_2\text{CO}_3 & \rightarrow 6\text{MgO} + \text{Cr}_2\text{O}_3 + \text{CO}_2 \quad (6) \\
\text{MgO} + \text{CO}_2 & \rightarrow \text{MgCO}_3 \quad (7) \\
\text{Cr}_2\text{O}_3 + \text{CO}_2 & \rightarrow \text{Cr}_2\text{CO}_3 \quad (8)
\end{align*}
\]

Finally the ion current curves revealed the loss of CO₂ and O₂ at 545 and 675°C. These mass losses were described by the following equations (Bouzaid & Frost, 2007):

\[
\begin{align*}
\text{MgCO}_3 & \rightarrow \text{MgO} + \text{CO}_2 \quad (9) \\
\text{Cr}_2\text{CO}_3 & \rightarrow 2\text{Cr}_2\text{O}_3 + \text{CO}_2 \quad (10)
\end{align*}
\]

### ELECTRON MICROPROBE ANALYSIS OF STICHTITE

In an attempt to understand the mineralogy and origin of stichtite better, Ashwal & Cairncross (1997) carried out electron probe microanalyses on samples of stichtite collected from various locations around the world. It was hoped that this technique would reduce interference caused by the numerous impurities present in natural stichtite. Several unexpected difficulties were encountered and overcome before this technique could be successfully applied. As previously mentioned, stichtite is usually intergrown with serpentinite, making it difficult to obtain pure samples. In some specimens the stichtite and serpentinite were too tightly intergrown to be resolved even with electron probe microanalysis using a highly focused electron beam (1–2 µm). A reasonable analysis was obtained by examining spots of the specimens with minimal intrusion of silicates using a rapid energy dispersive analysis technique (Ashwal & Cairncross, 1997). A second difficulty is that stichtite volatilises under the normal operating conditions of the electron microprobe used to perform the analyses. To counter this problem, they reduced the beam current to 10 nA (usually operated at 15 kV and 15 nA).

The electron microprobe analysis was carried out on samples collected from the widest range of stichtite-bearing localities possible. The formulae calculated from all analyses corresponded well to the ideal formula of stichtite. The results obtained using electron microprobe analysis techniques were much closer to the ideal formula than many results previously reported in the literature. A small but consistent excess of divalent cations and a similar small deficiency of trivalent cations in the layers of the LDH suggested that minor substitution of Cr³⁺...
with Mg$^{2+}$ or possible multivalency of ions of Mn or Ni present as impurities occur in stichtite. Further analysis revealed that the impurities often found in a sample of stichtite depend heavily on the location from which the sample was collected. For example, samples collected from Morocco or India contained more Fe$^{3+}$ when compared to samples collected from Russia which contain higher levels of Al$^{3+}$. The purest stichtites compared to samples collected from Russia which it is formed.

likely depending on the geology of the locality in which it is formed. Further analysis revealed that that the impurities or Ni present as impurities occur in stichtite. They were obtained from the Black Lake area in Quebec (Cr > 98 mol.%) with all other samples investigated containing more than 15 mol.% hydrotalcite or pyroaurite (Ashwal & Cairncross, 1997). They concluded that the composition of natural stichtites is variable with the exact chemical composition likely depending on the geology of the locality in which it is formed.

CONCLUSIONS

There have been a number of publications on the characterization of natural and synthetic stichtites; however, there is still much work to be done as the authors were not able to find any publications concerning applications of stichtite in the literature. Many other LDHs have been investigated for many potential applications such as adsorbents, catalysts and polymer additives. It is therefore reasonable to expect that stichtite may prove useful for a wide range of applications in the future.

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