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Magnesite everywhere: Formation of carbonates in the alkaline lakes and playas of the Cariboo Plateau, British Columbia, Canada



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ABSTRACT

The Cariboo Plateau in central British Columbia, Canada, hosts the largest aerial extent of low temperature lacustrine magnesite in the world. Magnesite was the most abundant carbonate mineral in 21 of 33 sampled alkaline lakes and 20 of 22 sampled playas. Calcite, hydromagnesite and very high magnesium calcite (VHMC, also called disordered dolomite) were also found in closed basin alkaline lakes on the plateau. Carbonate mineralogy was strongly associated with lake water geochemistry, particularly total alkalinity. VHMC was the dominant carbonate mineral in lakes with the highest alkalinities (>1000 mEq/kg), magnesite was the dominant carbonate mineral in lakes with the highest alkalinities (>1000 mEq/kg) and hydromagnesite with minor amounts of magnesite was the phase assemblage in lakes with lower relative alkalinities (<110 mEq/ kg). The geochemical trends for the activity of CO_3^{2-} , Ca^{2+} and Mg^{2+} suggest that these constituents in all Cariboo water bodies are controlled by the precipitation of Ca- and/or Mg-carbonate minerals. We hypothesize that carbonates present in the lakes likely formed via non-classical crystallization pathways based on the relationship between aqueous geochemistry and mineralogy and the chemical composition of the Ca-bearing magnesites. Non-classical crystallization offers new models for thinking about magnesite formation in lacustrine environments.

1. Introduction

The formation of magnesite (MgCO₃) at low temperature is poorly understood as it is relatively rare in Holocene environments and difficult to synthesize in low temperature (< 60 °C) laboratory experiments. Understanding the geochemical controls for magnesite precipitation is important because 1) of its role as a natural carbon sink; 2) promoting crystallization of magnesite can be used to trap and store CO₂ using enhanced mineral carbonation; and 3) magnesite deposits preserved in the geologic past are important sources of mined magnesium. Mineral carbonation technologies aim to lock away anthropogenic CO₂ by enhanced chemical weathering of mafic and ultramafic rocks and mineral wastes, such as mine tailings, by releasing Ca and Mg into solution while generating alkalinity followed by carbonate precipitation (EFI, 2020; Kelemen et al., 2019; Power et al., 2013a; Sandalow et al., 2021). Magnesite is considered one of the ideal mineral traps for CO₂ as it is the most stable Mg-carbonate phase and the carbonate phase most resistant to chemical weathering (Power et al., 2013b).

Several processes limit the formation of magnesite. Many natural waters are supersaturated with respect to magnesite, but it does not precipitate. Similar kinetic limitations on the formation of Ca-Mg carbonates, such as very high magnesium calcite (VHMC, also called disordered or poorly-ordered dolomite) and dolomite [both of which are CaMg(CO₃)₂], are the cause of the "dolomite problem" (Santos et al., 2023). In particular, the strong hydration of Mg ions in solution kinetically limits the precipitation and growth of magnesite (Königsberger et al., 1999; Lippmann, 1973; Pokrovsky et al., 1999; Saldi et al., 2009). As a result, low temperature laboratory synthesis experiments often precipitate metastable hydrated Mg-carbonates, such as hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O], rather than magnesite (Hänchen et al., 2008; Montes-Hernandez and Renard, F.O, 2016). Following Ostwald's step rule, these metastable hydrated Mg-carbonates are kinetically favoured (Chaka, 2018). As a result of the difficulty in synthesizing magnesite in laboratory experiments, the synthesis of

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magnesite at ambient temperature has been labelled "virtually impossible" with the mineral "unable to precipitate" (Hänchen et al., 2008; Saldi et al., 2009).

More recently, a few laboratory experiments have synthesized low temperature magnesite, generally with very small amounts of material produced. The direct low temperature precipitation of magnesite from artificial seawater has been facilitated by the presence of polystyrene microspheres possessing a high carboxyl group site density (Power et al., 2017). Magnesite has also been formed in a cyanobacterial bioreactor system aimed at inducing carbonate mineral precipitation from a magnesium-rich leachate (McCutcheon et al., 2019) and during the degradation of microbial mats from Lake Las Eras, Central Spain (Sanz-Montero et al., 2019). The carboxyl functional groups on cell walls and extracellular polymeric substances (EPS) are hypothesized to structure and dehydrate Mg ions, thereby promoting magnesite precipitation (Power et al., 2017). The growth of cyanobacteria can also locally increase pH, which promotes carbonate precipitation (Dupraz et al., 2009). Magnesite precipitation via an amorphous magnesium carbonate intermediate has also been observed within thin water films during carbonation of forsterite (Mg_2SiO_4) with supercritical CO₂ (Mergelsberg et al., 2020).

The precipitation of low temperature magnesite in modern natural environments is poorly understood, with only a few localities that are well documented. Holocene magnesite sediments occur in closed basin, alkaline lakes and playas, such as in the Cariboo Plateau, central British Columbia, Canada (Renaut, 1993), Milne Lake, South Australia (Raudsepp et al., 2022; Warren, 1988), the Atlin playa system, northern British Columbia, Canada (Power et al., 2019; Power et al., 2014), and in a palaeoshoreline of Lake Afourgagh, Morocco (Détriché et al., 2013). Magnesite also occurs in Mg-SO₄ rich lakes and playas, such as the Basque Lakes, British Columbia (Nesbitt, 1990), Hot Lake, Washington (Zachara et al., 2016) and it occurs at depth in the sediment in Freefight Lake, Saskatchewan (Last, 1993) and in lakes of the Los Monegros region (Mees et al., 2011; Mur and Urpinell, 1987) and Gallocanta Lake (Corzo et al., 2005; Luzón et al., 2009), Spain.

While most studies have focused on (bio)geochemical processes that control magnesite formation, Raudsepp et al. (2022) also examined crystallization pathways of magnesite in lake sediments. Due to the slow kinetics of classical magnesite precipitation, non-classical crystallization pathways, such as via a highly soluble amorphous precursor, may be preferred (Raudsepp et al., 2023; Raudsepp et al., 2022). In this case, the high solubility of the amorphous carbonate phase may also limit the formation of magnesite (Raudsepp et al., 2022). The most comprehensive study of primary magnesite precipitation and the spatial, temporal and geochemical relationships to other hydrated Mg-carbonate minerals is of the wetlands and playa system at Atlin (Power et al., 2019; Power et al., 2014; Power et al., 2009; Power et al., 2007). Here, magnesite precipitates within magnesite-hydromagnesite mounds due to the capillary action of Mg-rich groundwater, derived from weathering of a nearby ophiolite complex, and CO₂ degassing (Power et al., 2019; Power et al., 2014). Magnesite is hypothesized to precipitate directly from the groundwater at Atlin, rather than via a hydromagnesite-to-magnesite transformation (Mavromatis et al., 2021; Power et al., 2019).

In contrast, the surface water geochemistry of lakes on the Cariboo Plateau is consistent with models of closed basin lakes with restricted outflow and high evaporation on a basalt bedrock (Renaut, 1990). These closed basin lakes have become alkaline (Na-HCO₃-CO₃) due to evaporation of inlet waters that have [alkalinity] $> 2[Ca^{2+}+Mg^{2+}]$ and precipitation of carbonate minerals, which removes most of the aqueous Ca and Mg and enriches the alkalinity (Eugster and Hardie, 1978; Pecoraino et al., 2015; Tosca and Tutolo, 2023b). In natural waters, alkalinity is defined as the sum of titratable bases and is usually dominated by the aqueous carbonate species HCO_3^- and CO_3^{2-} (Tosca and Tutolo, 2023a). For example, seawater has an alkalinity of 2.3 mEq/kg and most natural lakes and rivers have alkalinities between 0.1 and 5 mEq/kg (Mattson, 2009; Wolf-Gladrow et al., 2007), however, enrichment of aqueous

chemical species by evaporation and subsequent mineral precipitation can result in much higher alkalinities in closed basin lakes (Tosca and Tutolo, 2023b) An initial geochemical survey of lakes on the Cariboo Plateau showed a wide range in salinities (Renaut, 1990), however, this aqueous geochemistry has not previously been systematically connected to the carbonate mineralogy occurring within the lakes.

The occurrence of low temperature magnesite and hydromagnesite on the Cariboo Plateau has mostly been studied with a sedimentological approach. Original mapping of the carbonate mineral resources in the Cariboo Plateau was conducted by geologic surveys in the early 20th century (Cummings, 1940; Grant, 1987; Reinecke, 1920). In the 1980s and 1990s, Renaut and colleagues examined several of the lakes and playas in the region in greater detail, undertaking studies of the formation of Na-carbonates and VHMC (described as protodolomite) at Last Chance Lake, the distribution of magnesite and hydromagnesite around Milk and Alberta Lakes, and the formation of magnesite in a Mg-Na-SO₄ pond near the town of Clinton, British Columbia (Renaut, 1990; Renaut, 1993; Renaut, 1994; Renaut and Long, 1987; Renaut and Long, 1989). The sediment at the center of Milk Lake is primarily magnesite, whereas, cores of the western mudflats and shoreline sediments contain magnesite and hydromagnesite at the surface with calcite, Mg-calcite and/or aragonite below a depth of 30 cm (Renaut, 1993). The sediment in nearby Alberta Lake is primarily hydromagnesite. While the occurrence of other carbonate lakes and playas in the region has been noted, neither their mineralogy nor aqueous geochemistry has been studied in detail. The present study conducts a regional survey of the mineralogy and aqueous geochemistry of lakes in the Cariboo Plateau to determine the geochemical controls on the formation of magnesite.

2. Study location

The lakes and playas that were sampled are located approx. 30 km north of Clinton, British Columbia in the Cariboo Plateau with an elevation of 1050-1250 m above sea level (Renaut, 1990). Sampling focused on the carbonate lakes and playas occurring within the Meadow-Milk-Alberta glacial outwash valley, however, several other lakes on the Cariboo Plateau outside this outwash valley were also sampled (Fig. 1). To the west of the Cariboo Plateau is the Marble Range, with an elevation of up to 2200 m. The local bedrock geology of the plateau is composed of Miocene-Pliocene basalt (Mathews, 1989) covered by a Quaternary till sheet and glaciofluvial sand and gravel outwash (Margold et al., 2013). The area was covered by the Cordilleran Ice Sheet during the last glacial period, with deglaciation occurring at approx. 10,000 ky BP (Clague, 1981). Deglaciation created an undulating terrain on the plateau and surface drainage is usually absent (Valentine and Schori, 1980). Most of the lakes sampled in the present study occur in a single continuous glaciofluvial outwash channel, composed of till, gravel and sand. Most lakes are closed, shallow basin systems and thus the lake hydrology is greatly affected by climate, particularly the balance between precipitation and evaporation. The local climate is semiarid with an annual precipitation of 300-400 mm/y and moisture deficit of 300-400 mm/y (Valentine and Schori, 1980). Lakes are frozen from November to late March, with the wettest time in the spring and early summer, and they become progressively more saline due to greater evaporation compared to precipitation through the late summer and autumn. During the summer, benthic cyanobacterial mats may cover the entire bottom of a shallow lake, such as documented at Goodenough Lake (Brady et al., 2013; Schultze-Lam et al., 1996).

2.1. Methods

Field sampling was conducted in late June 2018, mid-August 2020 and late September 2021 (Fig. 2). Sediment cores from the dry playa next to Milk Lake were obtained with an Edelman auger. Sediment cores taken within Milk Lake and Last Chance Lake were obtained with a 10cm diameter push corer and cores were subsampled at intervals of 2.5 to



Fig. 1. A) Location of study within British Columbia (modified from Renaut, 1994). B) Sampling locations and primary carbonate mineralogy in the Cariboo Plateau. Two samples were also taken north of area shown here. Relative mineral abundances and GPS coordinates of all samples are available in Table S2.



Fig. 2. A) Photo overlooking Milk Lake from moraine on the west side of lake (June 2022). B) Cyanobacterial mats and basaltic erratics at edge of Milk Lake (June 2018). C) Dried magnesite playa located in between Milk and Meadow Lakes (Sept. 2021). D) Na-carbonate crust (white) at the edge of Liberty Lake with VHMC in the sediment (Sept. 2021). E) Photo overlooking Alberta Lake from top of esker (June 2018). F) Raised polygon sediment in hydromagnesite-magnesite playa (21CX2–1) located north of Oriole Pond (Sept. 2021).

5 cm. All other surficial lake and playa sediments were sampled to a depth of 10 cm with a soil probe. Conductivity and pH were measured in the field with a Thermo Scientific Orion Star portable meter (calibrated daily with NIST-traceable standards). Lake water was filtered through a 0.45 μ m filter and stored at 4 °C. The alkalinity of lake water was measured by titration of 0.1 M HCl on a ThermoScientific T910 Orion Star pH titrator. Anions and nutrients (SO₄^{2–}, Cl[–], PO₄^{3–}, NH₄⁴, NO₃[–], and NO₂[–]) were measured using colourimetry on a ThermoFisher Gallery Beermaster Plus at the Natural Resources Analytical Laboratory (University of Alberta) after appropriate dilutions with MilliQ water. Samples were acidified with HNO₃ and cations were measured on a Thermo

iCAP6300 Duo inductively coupled plasma-optical emission spectrometer (ICP-OES; ThermoFisher), also at the Natural Resources Analytical Laboratory.

Sediment was air dried at room temperature, ground in a tungsten carbide ring mill for 1 min, micronized in a McCrone Mill with 100% ethanol for 3 min and then air dried at room temperature. Samples were analyzed on a Rigaku Ultima IV X-ray diffractometer (XRD) with a Co source (38 kV and 38 mA) or a Bruker D8 Advance powder XRD with a LYNXEYE-XE-T position sensitive detector and a Co source (35 kV and 40 mA). Both instruments were operated with a step size of 0.02° 20 and scan speed of 1 to 1.2 s/step between 5 and 80° 20. Relative mineral

abundances were determined by Rietveld refinements (Bish and Howard, 1988; Hill and Howard, 1987; Rietveld, 1969) with XRD data using TOPAS 5 (Bruker). A structural model for VHMC was made by combining the crystal structure and space group of calcite with the stoichiometry and unit cell parameters of ideal dolomite. Crystallite (LVol-IB) size was determined by refining the Lorentzian and Gaussian integral breath values using the Double-Voight method (Balzar, 1999; Balzar et al., 2004) but microstrain was not refined. The molar proportion of Ca to Mg in calcite group minerals (including calcite, VHMC and magnesite) was calculated from the $d_{104}\ peak$ position using the equation $N_{MgCO3} = 100 - [d_{104} \times 333.33) - 911.99]$, which was derived by Lumsden (1979). Although small abundances of structurally disordered phyllosilicate minerals were sometimes observed in XRD patterns, these phases were not included in refinements (Fig. S3). As such, quantitative phase analysis results reflect only the highly crystalline fraction of the solids and they do not include amorphous materials or clay minerals.

In the field, cyanobacterial mat samples for electron microscopy were fixed in 2.5% glutaraldehyde and stored at 4 °C. Before imaging, mat samples were sequentially dehydrated with 25, 50, 75, and 3 × 100% ethanol at 15 min/step. Samples were then critical point dried with liquid CO₂ in a Bal-tech critical point drier (CPD030). Select sediment samples were treated with 30% H₂O₂ to remove organics, which allowed better visualization of the mineral morphology. Carbonate morphology in H₂O₂-treated samples did not differ from that in untreated samples. All samples were mounted on carbon sticky tape and coated with approx. 5 nm of gold in a Nanotek SEMprep 2 sputter coater. Imaging was completed on a Zeiss Sigma Field Emission scanning electron microscope (SEM) in secondary electron mode at a voltage of 3.0 kV and elemental analysis was completed with a Bruker energy dispersive X-ray spectroscopy (EDS) at voltage of 15.0 kV.

For particle size analysis, an aliquot (approx. 0.5 g) of each sample was added to a 15 mL Falcon tube with sodium hexametaphosphate (30 g/L), shaken by hand, vortex mixed and then analyzed using a Horiba LA-950 V2 laser scattering particle size distribution analyzer (PSA). A separate aliquot was used for Brunauer–Emmett–Teller (BET) specific surface areas. Samples were degassed overnight (200 °C) on a Smart VacPrepTM 067 (Micromeritics, Norcross, GA, USA). BET analysis was performed at -196.15 °C on the Micromeritics TriStar II Plus adsorption unit (Micromeritics, Norcross, GA, USA) with the N₂ adsorption method. Isotherms were acquired using a p/p° range of 0.01–0.90. All data processing was conducted using MicroActive Interactive software (Micromeritics, Norcross, GA, USA).

The saturation indices (SI) of waters with respect to minerals were calculated with the extended Debye-Huckel equation and phreeqc database in Phreeqc v3.4 (Parkhurst and Appelo, 2013). Solubility product constants (Ksp) for brucite, disordered dolomite (VHMC), hydromagnesite, magnesite and nesquehonite were transferred from the wateq4f database. The solubility product constants of dypingite and monohydrocalcite were added from the experimental work of Harrison et al. (2019) and Kralj and Brečević (1995), respectively. Solubility product constants for amorphous calcium carbonate (ACC) and amorphous magnesium carbonate (AMC) were determined experimentally by Purgstaller et al. (2019). A solubility product for an amorphous calcium magnesium carbonate (ACMC) with a 50:50 ratio of Ca to Mg was calculated from the published equation of Purgstaller et al. (2021). For consistency between log K_{sp} of amorphous and crystalline phases, only log K_{sp} values determined by dissolution of the solid have been included. A less soluble log K_{sp} value of -7.5 for ACC, as determined after precipitation of the solid from solution, has been reported by Gebauer et al. (2008) and Kellermeier et al. (2014). However, it is expected that ACC should be more soluble than the crystalline phases (monohydrocalcite; log K_{sp} value of -7.2). The molalities and log activities of aqueous species (free ion and aqueous complexes) were modelled in Phreeqc using the standard stability constants (K) in the phreeqc database.

3. Results

3.1. Aqueous geochemistry

None of the sampled water bodies had surficial water inlets or outlets. When sampled in September 2021 during approximately the driest time of year, lakes in the Cariboo Plateau ranged in temperature from 9.4 to 20.4 °C, in pH from 9.24 to 10.50, electrical conductivity from 1.3 to 107 mS/cm, alkalinity from 19 to 2046 mEq/kg, Ca concentrations from 0.03 to 0.27 mM and Mg concentrations from 0.40 to 11.59 mM (Table S1). In contrast, groundwater sampled from two domestic wells close to Meadow Lake had a circumneutral pH (7.88-8.20), lower electrical conductivity (0.7 mS/cm), lower alkalinity (8 mEq/kg) and higher Ca concentration (0.67-0.78 mM). All lakes had a Mg/Ca ratio over 5 and two lakes (Meadow Lake and 21AT1-1) had a Mg/Ca ratio over 100. Most lakes contained <20 mM SO₄²⁻, although Liberty, Snow White and Last Chance Lakes contained higher sulfate concentrations (54 to 385 mM). All aqueous samples were supersaturated relative to aragonite, calcite, VHMC, dolomite, and magnesite and most waters were supersaturated relative to hydromagnesite and dypingite (Table S1). All waters, except one sample (21CX7-1), were undersaturated relative to brucite. Based on alkalinity and pH, lakes were near to equilibrium with the modern atmosphere (pCO₂ of $10^{-3.4}$ atm) (Table S1). All aqueous samples were undersaturated relative to all amorphous Ca-Mg carbonate phases.

3.2. Mineralogy

Magnesite was the most common mineral present in carbonate lakes and playas in the Meadow–Milk–Alberta glacial outwash valley (Fig. 1 and Table S2). Magnesite was the most abundant carbonate mineral in 21 of 33 lake samples and 20 of 22 playa samples (Table S2). The average d_{104} magnesite peak position was 2.765 \pm 0.008 Å, which corresponds to an average Ca concentration in the magnesite of 10.0 \pm 2.5 mol%. Magnesite crystals observed with SEM are small, generally <1 µm, with some larger crystals on the micrometre scale (Fig. 3). Magnesite grains were generally single, euhedral rhombohedra or aggregates of very small, <100 nm rhombohedra having a step-like morphology. Cyanobacterial mats collected from magnesite-rich lakes (Milk and Snow White Lakes) had some magnesite grains attached to cyanobacterial and algal cell surfaces and some magnesite grains within the EPS (Fig. 4).

Sediment cores collected within Milk Lake had a relatively high proportion of magnesite to clays and detrital minerals (quartz, plagioclase, pyroxene; Fig. S4 and Table S2). The small grain size of magnesite is confirmed by PSA of the sediment from Milk Lake containing 70 wt% magnesite, in which 76% of the sediment has a grain size of <500 nm (Fig. S5). The measured BET surface area of sediment from the top and bottom of the Milk Lake core are $44.4 \text{ m}^2/\text{g}$ (18Milk1–12) and $41.4 \text{ m}^2/\text{g}$ (18MILK1–1), respectively. In cores taken from the playa, magnesite was present to a depth of at least 125 cm, with the abundance of carbonate minerals decreasing at depth. With an abundance of 3 to 5 wt%, VHMC was also present in the Milk Lake sediment core below ~20 cm, as well as in 16 of the 55 surficial samples containing magnesite (Table S2). In general, the relative proportion of carbonate minerals to detrital minerals depended on the proximity to till slopes and the amount of carbonate precipitation.

Hydromagnesite was present in the shoreline sediment of some larger lakes, including Alberta and Meadow Lakes, deeper lakes adjacent to or connected to Alberta Lake, such as Pollard and Moloney Lakes, and in a carbonate playa to the northwest of Oriole Pond. Most of these hydromagnesite-rich carbonate sediments also contained magnesite at abundances between 5 and 25 wt%. Hydromagnesite plates in the lakes were small, generally $<5 \mu$ m (Fig. 3E). Hydromagnesite (Fig. 3F). Cyanobacterial mats collected from Alberta Lake had both



Fig. 3. Scanning electron microscope (SEM) images of (A) magnesite (Mgs) with a grain size of $<1 \mu$ m in the sediment from Milk Lake and (B) Milk Lake sediment at depth (15–17.5 cm). (C) Magnesite with a larger grain size and step morphology from Oriole Pond. (D) Rhombs of VHMC in the sediment of Last Chance Lake. (E) Hydromagnesite (Hmgs) plates and small magnesite rhombs from Alberta Lake. (F) Hydromagnesite and magnesite from the playa north of Oriole Pond (21CX2–1). Note magnesite occurring in between hydromagnesite plates. Sediment in images A, B and D were treated with 30% H₂O₂ and air dried before imaging to remove the abundant organics present in the samples.

hydromagnesite and magnesite grains attached to the surfaces of cyanobacterial cells and EPS (Fig. 4C and D).

Of the lakes that were sampled, those with the highest alkalinities (Last Chance, Margaret and Liberty Lakes), all fell outside the Meadow-Milk-Alberta glacial outwash valley and none of them contained magnesite (Fig. 1). The sediments from these lakes were mostly detrital material and VHMC was the primary carbonate mineral. VHMC was also the only carbonate phase present in one of the playas (21 MW11-1) to the west of Meadow Lake. At Last Chance Lake, centimetre thick crusts of Na-carbonates {natron (Na₂CO₃·10H₂O), trona [Na₃H(CO₃)₂·2H₂O]} were observed during sampling in September 2021 after extensive evaporation produced spotted brine pools. Smaller Na-carbonate crusts were observed on the mudflats of Margaret Lake and Liberty Lake. Grains of VHMC were larger than magnesite grains but still generally <1 µm. VHMC from Last Chance Lake occurs as euhedral rhombohedra, ranging in size from 100 nm to several micrometers (Fig. 3D). Based on its d_{104} peak position the average composition of VHMC was 49.3 ± 2.4 mol% Mg.

3.3. Relationship between carbonate mineralogy and aqueous geochemistry

Trends in lake geochemistry with regards to the primary carbonate mineralogy were also observed (Fig. 5). The three sampled lakes that contain VHMC had an alkalinity over 1000 mEq/kg, Mg concentrations <2 mM and lower Mg/Ca ratios (\leq 15) than other sampled Cariboo Plateau lakes. Lakes containing magnesite had a range of alkalinities, between 70 and 800 mEq/kg, except for Oriole Pond with an alkalinity of 40 mEq/kg and an unnamed lake (21 MW7–1) with an alkalinity of 1600 mEq/kg. Lakes containing magnesite had a Mg concentrations of <6 mM, except for Oriole Pond (10 mM) and a range in Mg/Ca ratios from 6 to 115 (Fig. 5). Lakes containing hydromagnesite, calcite or no carbonate minerals had alkalinities <110 mEq/kg and a slightly lower pH compared to lakes containing magnesite and VHMC. Lakes

containing hydromagnesite or no carbonate minerals also had a higher Mg concentration, over 5 mM. The two sampled lakes with the lowest salinities (Rivers Lake and Watson Lake) did not contain any carbonate minerals. A lake at the east end of the glacial outwash valley (21CX8–1) did, however, contain calcite.

>50% of Mg_(aq) is present as MgCO_(aq) complexes in most of the samples from the Cariboo Plateau lakes (Fig. 5F), however, only the activity of the free ion (i.e., a_{Mg2+}) is considered in the SI calculation of amorphous and crystalline phases. When the log of a_{Ca2+} , a_{Mg2+} , a_{CO32-} was determined with Phreeqc and plotted in a Ca-carbonate and a Mg-carbonate solubility diagram, almost all the lakes fell on a trend line, even lakes where carbonate minerals were not detected in sediments (Fig. 6). The aqueous geochemistry of Cariboo lake waters was close to the equilibrium line of monohydrocalcite (CaCO₃·H₂O) for Ca-carbonates (Fig. 6). Data for the two well waters did not plot close to trendlines observed for lake waters.

4. Discussion

4.1. Formation of magnesite

The lakes of the Cariboo Plateau are unique amongst alkaline Holocene magnesite-forming lakes globally. The Cariboo Plateau is the only known location in which magnesite forms as the sole carbonate phase in alkaline lake sediments. Other well-studied, modern alkaline lakes where magnesite precipitates instead produce assemblages of carbonate minerals, such as the co-occurrence of magnesite and VHMC in Milne Lake in South Australia (Raudsepp et al., 2022; Warren, 1988) and the co-occurrence of hydromagnesite and magnesite in the Atlin playa in northern British Columbia (Power et al., 2019; Power et al., 2014).

Renaut (1993) hypothesized that carbonate minerals in Cariboo Plateau lake sediments, including magnesite, precipitated as primary precipitates from surface water. The present study supports this



Fig. 4. Scanning electron microscope (SEM) images of carbonate minerals and cyanobacteria. (A) Cyanobacterial (cyano) and heterotrophic (het) cells, extracellular polymeric substances (EPS) and magnesite (Mgs) on the surface of a large algal filament in a pelagic microbial mat from Milk Lake. (B) EPS and Mg-silicates on a filamentous cyanobacterium in a benthic microbial mat from Last Chance Lake. (C) Magnesite and hydromagnesite associated with a filamentous cyanobacterium in a benthic microbial mat from Alberta Lake. (D) Close up of magnesite and hydromagnesite on cell surface from Alberta Lake.

hypothesis with several lines of evidence pointing to the direct precipitation of magnesite, rather than a transformation from a crystalline, metastable Mg-carbonate phase, such as dypingite or hydromagnesite, to magnesite. While magnesite and hydromagnesite do co-occur in two of the lake samples (lobe of Pigeon Lake and east lobe of Milk Lake) and one playa, magnesite was the only carbonate phase in 28 of 55 lake and playa samples and more often magnesite co-occurs with a small amount of VHMC (16 of 55 samples). In addition, there is a strong association between lake water geochemistry and mineralogy, with hydromagnesite only being found in low alkalinity lakes. Finally, all of the Cariboo magnesite contained ~10 mol% Ca. Ca is easily incorporated into the crystal structure of magnesite. In contrast, Ca is excluded from the crystal structures of all hydrated Mg-carbonates (lansfordite, nesquehonite, dypingite, hydromagnesite) that can be metastable crystalline precursors of magnesite. Thus, the relatively high concentration of Ca in magnesite supports the hypothesis of direct precipitation, rather than a crystalline-to-crystalline mineral transformation. This is similar to magnesite in Milne Lake, which also contains ~10 mol% Ca (Raudsepp et al., 2022). Magnesite in the Atlin playa (Power et al., 2019) and Milne Lake (Raudsepp et al., 2022), as well as magnesite formed in wellcharacterized bioreactors (McCutcheon et al., 2019) are also hypothesized to form directly from solution or from an amorphous-to-crystalline pathway. It has been demonstrated that there is complete solid solution of amorphous Ca and Mg carbonates based on laboratory experiments (Purgstaller et al., 2019: Radha et al., 2012).

Precipitation of carbonates in Cariboo Plateau alkaline lakes occurs in the overlying surface water (Renaut, 1993), which is similar to other alkaline lakes including in the Coorong Lakes, South Australia (Rosen et al., 1989), Lake Hayward, Western Australia (Rosen et al., 1995) and Deep Spring Lake, California (Meister et al., 2011). In general, the precipitation of carbonate minerals in the surface water of alkaline lakes is thought to be caused by seasonal evapoconcentration and/or blooms of photosynthesizing microorganisms. Although, in high alkalinity lakes and playas, the contribution of microbial metabolic processes to carbonate mineral precipitation is diminished (discussed in section 4.4) (Meister et al., 2011). Magnesite is also known to form from groundwater in playas as a result of capillary action in a groundmass of hydromagnesite (Power et al., 2019; Power et al., 2014). The aqueous geochemistry and mineralogy of most lakes in the Cariboo Plateau are consistent with the precipitation of carbonate minerals in the overlying surface water. However, the spatial relationship between magnesite and hydromagnesite (Fig. 3F) at one playa north of Oriole Pond (21CX2-1), suggests that magnesite growth occurred after hydromagnesite formation in that instance, similar to what is observed at Atlin, where carbonate precipitation is controlled by evaporation and capillary action (Power et al., 2019).

In general, Cariboo magnesite lakes have higher alkalinity and pH values and lower Ca and Mg concentrations than other well studied sites where magnesite forms at low temperatures. The small grain size and smooth, euhedral surfaces of Cariboo magnesite and VHMC are likely due to the limited availability of Ca and Mg compared to CO_3^{2-} in solution. In contrast, magnesite and VHMC particles from Milne Lake are several micrometers in size (Raudsepp et al., 2022) and some Atlin magnesite particles are over 10 µm (Power et al., 2019). Both Milne Lake



Fig. 5. (A-D) Conductivity, alkalinity, pH Mg, molar ratio of Mg/Ca and primary carbonate mineralogy of Cariboo lakes and two well waters sampled mid-September 2021. Proportion of (E) the concentration of free $Mg^{2+}_{(aq)}$ and (F) MgCO[°]_(aq) as modelled with distribution of species in Phreeqc. Only the activity of the free $Mg^{2+}_{(aq)}$ is considered in mineral SI calculations.

and Atlin magnesite have a more complex morphology characterized by stepped surfaces. The small grain size of Milk Lake magnesite, in addition to clays in the sediment, results in a much higher BET surface area, 44.4 m^2/g , for the top of a core with 70 wt% magnesite. In comparison a sample from Atlin with 96 wt% magnesite had a BET surface area of 5.9 m^2/g (Power et al., 2019). In terms of aqueous geochemistry, Milne Lake had an alkalinity of 6.12 mEq/kg, pH of 8.68, 0.92 mM Ca and 29.2 mM Mg when sampled in the spring (Raudsepp et al., 2022). At Atlin, the interstitial water of two hydromagnesite-magnesite mounds sampled in mid-summer had an alkalinity of 98-110 mEq/kg, pH of 8.14-8.17, 0.01-0.03 mM Ca and 69-78 mM Mg (Power et al., 2019). In general, the surface waters in the Atlin playa and wetlands had lower alkalinities and Mg concentrations than this interstitial mound water (Power et al., 2014; Power et al., 2009). In contrast, Cariboo lakes containing magnesite had alkalinities of 40 to 1607 mEq/kg, pH of 9.58-10.50, 0.03-0.15 mM Ca, and 0.40-10.15 mM Mg.

4.2. Formation of hydromagnesite

Hydromagnesite is a less common primary carbonate mineral in Cariboo Plateau lake sediments. Hydromagnesite occurs at the shorelines of larger, less saline lakes, such as Meadow and Alberta Lakes. Hydromagnesite also forms in Pollard and Moloney Lakes, which are located close to Alberta Lake and appear to be relatively deep based on Google Earth imagery (Fig. S1). Some of the basins connected to Alberta Lake in September 2021, such as Slime Lake, may be isolated basins in years with less rainfall or groundwater inflow. The occurrence of hydromagnesite in the playa north of Oriole Pond (21CX2–1) appears to be unique amongst the sampled playas. As this playa is in close proximity to Meadow Lake, the local groundwater may be less saline and less alkaline, thus favouring the precipitation of hydromagnesite in addition to magnesite. Hydromagnesite plates from this playa are slightly larger in size than the lacustrine hydromagnesite found elsewhere in the Cariboo Plateau (Fig. 3F). Similar to the hydromagnesite-magnesite playa at



Fig. 6. Mineral stability relationships for (A) Ca-CO₃ phases and (B) Mg-CO₃ phases. Water were collected from lakes on the Cariboo Plateau, BC in mid-September 2021 and the activities were modelled in Phreeqc using the phreeqc database. Solubility constants for calcite, aragonite, vaterite, magnesite, hydromagnesite and nesquehonite are from the phreeqc or wateq4f databases. Solubility constant for monohydrocalcite is from Kralj and Brečević (1995), dypingite is from Harrison et al. (2019) and that of AMC is calculated from Purgstaller et al. (2019). The double dashed line shows the difference in ACC K_{sp} reported by Brečević and Nielsen (1989), ACC (B), and calculated from Purgstaller et al. (2019), ACC (P).

Atlin, grains of magnesite grow between oriented plates of hydromagnesite, although the grain size of both minerals is smaller than at Atlin (Power et al., 2019).

4.3. Formation of VHMC

The formation of only VHMC rather than magnesite in the highest alkalinity lakes is likely controlled by the relatively low Mg/Ca ratios of their surface waters. Eugster and Hardie (1978) suggested that VHMC precipitates out of solution before magnesite during brine evolution. However, lakes on the Cariboo Plateau demonstrate that ambient temperature precipitation of magnesite is possible and that as lakes become increasingly enriched in Na-HCO3-CO3, magnesite may precipitate before VHMC. Compared to magnesite, quite a few morphologies have been described for VHMC or protodolomite, including dumbbells, spherical aggregates and euhedral rhombs [reviewed in supplementary information of Raudsepp et al., 2022]. Interestingly, the simple rhombohedral morphology of VHMC in the Cariboo lakes is most similar to VHMC particles from other lakes with high alkalinity and low cation concentrations, such as Deep Spring Lake (1 mM Mg and 0.3 mM Ca) (Meister et al., 2011). In contrast, the dumbbell morphology of VHMC is associated with generation of alkalinity by microbial metabolic processes resulting in microbially mediated carbonate precipitation (Warthmann et al., 2000). Although seasonal formation of Na-carbonates in these lakes influences water chemistry, it remains unclear whether Na-carbonate precipitation plays a role in the formation of VHMC.

4.4. Role of cyanobacterial growth in carbonate precipitation

Photosynthesis by cyanobacteria may be an important driver for carbonate precipitation (Dupraz et al., 2009; McCutcheon et al., 2019; Power et al., 2007). Previous researchers have noted that while there is extensive cyanobacterial growth in Cariboo Plateau lakes, the structures of microbial mats are not preserved by the carbonates, i.e. mats are not preserved as microbialites or stromatolites (Brady et al., 2013; Schultze-Lam et al., 1996). Photosynthetic growth results in undersaturation of aqueous CO₂ and a ¹³C-enriched dissolved inorganic carbon (DIC) pool (Brady et al., 2013). In many inland lakes, cyanobacterial growth is limited by the availability of phosphate, however, in hypersaline lakes phosphate is not limiting, resulting in higher biological activity than in other types of lakes (Haines et al., 2023; Hupfer and Lewandowski, 2008; Smolders and Roelofs, 1993; Wetzel, 2001).

The relative importance of cyanobacteria in the precipitation of carbonate minerals appears to differ depending on the alkalinity of a lake. Benthic cyanobacterial mats collected in June from the highly alkaline Last Chance Lake are almost completely free of VHMC grains, instead cyanobacterial filaments are covered in clay minerals (Fig. 4B). Cyanobacterial mats from Milk Lake did contain some grains of magnesite but some areas of the mat had surprisingly few magnesite grains considering that the sediment of Milk Lake is up to 70 wt% magnesite. Few carbonate minerals were also observed on cyanobacterial mats from Snow White Lake and an unnamed lake (21 MW8-1), which were collected in September after the summer growth period. In contrast, hydromagnesite and magnesite grains were closely associated with EPS and cyanobacterial surfaces in mats collected from Alberta Lake where alkalinity is lower. In general, this suggests that as lake alkalinity increases, and the Ca and Mg concentration decreases, cation availability rather than alkalinity generation becomes more important for carbonate precipitation. In moderately alkaline lakes, such as Pyramid Lake, Nevada, USA, cyanobacteria have been hypothesized to be important for locally concentrating cations and promoting passive biogenic calcite precipitation (Arp et al., 1999). Adsorption of Mg onto carboxyl groups on microbial cell walls and EPS are also hypothesized to help dehydrate the Mg and facilitate precipitation of anhydrous Mg-carbonates (Kenward et al., 2013; Power et al., 2017; Roberts et al., 2013). However, as alkalinity increases and Ca and Mg concentrations decrease, the relative importance of microbial processes decreases

compared to evapoconcentration and the rate of cation input into a lake. Because pH is well buffered by the high alkalinity, cyanobacterial photosynthesis only induces a minor rise in carbonate precipitation in these systems, and thus, carbonate minerals do not precipitate preferentially on cells (Arp et al., 2001).

4.5. Aqueous geochemistry and non-classical crystallization of carbonate minerals

Alkalinity is the primary geochemical control on which carbonate minerals occur in Cariboo Plateau lake sediments. Generally, lakes with the highest alkalinity (over 1000 mEq/kg) contain VHMC, lakes in the middle range of alkalinity (70 to 800 mEq/kg) contain magnesite and lakes with the lowest alkalinity (< 110 mEq/kg) have hydromagnesite as the dominant carbonate mineral with minor amounts of magnesite. Most previous studies comparing lake water geochemistry and primary carbonate mineralogy have studied the geochemical parameters that separate Ca-carbonate minerals from Mg-carbonate minerals. For example, a relationship between alkalinity and the primary carbonate mineral within microbialites was noted in a series of Mexican alkaline lakes, which ranged in alkalinity (1 to 50 mEq/kg) and contained Mgcalcite, aragonite, monohydrocalcite and/or hydromagnesite (Zeven et al., 2021). In a review of closed basin lakes containing microbialites (alkalinity <155 mEq/kg), Mg/Ca ratio was also found to influence formation of either Ca-carbonate or Mg-carbonate minerals (Chagas et al., 2016). The present study covers a much larger range in alkalinities than these previous studies.

It is important to evaluate crystallization pathway (classical, nonclassical or both) in carbonate environments as the crystallization pathway may control the relative importance of kinetic and equilibrium geochemistry (Raudsepp et al., 2022). While thermodynamically favourable, crystallization via a classical pathway has a higher activation energy barrier and thus can have kinetic limitations (De Yoreo et al., 2015; Radha and Navrotsky, 2013). In contrast, non-classical pathways have lower activation energies but phases such as amorphous carbonates are highly soluble compared to their crystalline counterparts (De Yoreo et al., 2015; Gebauer et al., 2008; Purgstaller et al., 2019; Radha and Navrotsky, 2013) and thus natural waters may have an equilibrium limitation to non-classical pathways (Raudsepp et al., 2022). Growing evidence suggests that anhydrous Mg-carbonate minerals are more likely to form via non-classical crystallization and growth, likely through an amorphous precursor. This is best shown for the formation of

Three potential models for carbonate formation

1. Carbonates crystallize via classical nucleation directly from solution. Arrows shows magnitude of supersaturation of lakes for magnesite (yellow) and hydromagnesite (green) relative to equilibrium.

2. Carbonates crystallize via the phase (shaded box) that the waters are at equilibrium with (e.g. nesquehonite $K_{sp} \pm 0.25$) and then transform to magnesite or hydromagnesite.

3. Carbonates crystallize via an amorphous precursor or prenucleation cluster (non-classical pathways). Heterogenous nucleation on organic and inorganic surfaces, evapoconcentration and MgCO₃° complexes help precipitatation of AMC (dark blue arrow). During amorphous-to-crystalline transformation, precipitation of additional carbonates may draw down cations and anions from solution (light blue arrows). Formation of magnesite over hydromagensite may be influenced by hydration of MgCO₃° complexes. VHMC, as demonstrated in numerous laboratory studies (Long et al., 2011; Ohde and Kitano, 1978; Oomori et al., 1983; Rodriguez-Blanco et al., 2015). Low temperature formation of magnesite from an amorphous precursor has also been demonstrated in thin water films (Mergelsberg et al., 2020). Raudsepp et al. (2022) used the crystallographic alignment of VHMC and magnesite nanocrystals in the sediments from the Coorong lakes to demonstrate that they formed via non-classical growth and likely via an amorphous precursor. Here we take a geochemical approach to examining crystallization pathways in the Cariboo lakes. This approach is most practical given that diagenesis and recrystallization are common in carbonate sediments and because (at present) distinct crystal morphologies have not been directly linked with non-classical crystallization.

Trends in the solubility diagrams of $\log(a_{C032-})$ versus $\log(a_{Ca2+})$ or $\log(a_{Mg2+})$ (Fig. 6) show that formation of Ca and Mg carbonates is controlling the water chemistry of all surface water bodies in the Cariboo Plateau. The trendline for $\log(a_{C032-})$ versus $\log(a_{Ca2+})$ data for the 33 alkaline lakes sampled in the present study is very similar to that for 24 globally distributed alkaline lakes plotted by Fukushi and Matsumiya (2018) and for the 10 Mexican alkaline lakes sampled by Zeyen et al. (2021). We explore three hypotheses for mineralogical pathways that could produce the $\log(a_{C032-})$ and $\log(a_{Ca2+})$ or $\log(a_{Mg2+})$ solubility trendlines for the Cariboo Plateau (Fig. 7) and more broadly for alkaline lakes.

The first hypothesis is that carbonates crystallize via classical nucleation directly from solution. In classical crystallization, an activation energy barrier to nucleation can be overcome by critical supersaturation of the aqueous solution. In the Cariboo Plateau, all of the lakes are supersaturated relative to calcite, aragonite, magnesite and hydromagnesite but the magnitude of carbonate supersaturation (as determined by SI) does not distinguish which minerals are actually precipitating in the lakes. Rather, all of the lakes, independent of primary carbonate mineralogies, fall on a single trendline for $log(a_{CO32-})$ versus $log(a_{Ca2+})$ or $log(a_{Mg2+})$. As discussed above,

kinetics limits classical crystallization in natural waters, whereas undersaturation of waters relative to the amorphous precursor limits non-classical crystallization. While it is possible that critical supersaturation of each of the individual Ca and Mg carbonate minerals could produce a single trendline for $\log(a_{CO32-})$ versus $\log(a_{Ca2+})$ or $\log(a_{Mg2+})$ in alkaline lakes, a single trendline is more consistent with a single equilibrium process controlling aqueous geochemistry (Fig. 7).



Fig. 7. Conceptual models for how mineralization pathways could produce aqueous geochemistry observed in Cariboo Plateau lakes.

As proposed by Fukushi and Matsumiya (2018), the second hypothesis is that stable carbonate minerals form via a metastable, precursor phase (either crystalline or amorphous) and that alkaline lakes are at equilibrium with that metastable precursor. For Ca-carbonates, Fukushi and Matsumiya (2018) argued that monohydrocalcite is the critical precursor phase. For Mg-carbonates, Fukushi and Matsumiya (2018) hypothesized that the aqueous geochemistry of alkaline lakes is close to the K_{sp} of one or more amorphous magnesium carbonates (which they described as AMC1 and AMC2). This is a novel and useful idea, however, the study had several issues that should be considered; for instance, it did not include the extensive research on amorphous carbonates that had already been conducted [e.g. Radha et al., 2012].

In particular, in the experimental study of Fukushi and Matsumiya (2018), solutions of CaCl₂, MgCl₂ and Na₂CO₃ are combined to form an amorphous carbonate and then a mixed phase assemblage of monohydrocalcite and AMC1 or AMC2. However, the elemental compositions of the amorphous phases were not characterized and based on the reported experimental methods in Fukushi and Matsumiya (2018), it is impossible for the phases labelled AMC1 and AMC2 to be pure amorphous magnesium carbonates; they must be amorphous calcium magnesium carbonates (ACMC) containing a significant proportion of Ca. It is unclear why AMC was not synthesized from only MgCl₂ and Na₂CO₃. The reported "log K_{sp} values" of AMC1 and AMC2 (-5.2 and - 5.59) is much less soluble than the well-characterized AMC reported by Purgstaller et al. (2019) [log(IAP) of -4.42], but is consistent with an ACMC. In addition, ion activity products were calculated from experiments after the formation of monohydrocalcite, which is known to contain Mg, and the alkalinity was not measured in the study but inferred from cation charge imbalance, which propagates errors and makes [CO₃²⁻] dependent on [Ca], [Mg] and pH. Finally, the proposed "log K_{sp} values" reported Fukushi and Matsumiya (2018) for AMC1 (-5.2) and AMC2 (-5.59) are the same as or similar to the reported log K_{sp} values for nesquehonite (between -4.96 and -5.59) (Harrison et al., 2019). As amorphous carbonates quickly transform into nesquehonite in laboratory experiments, it is highly unlikely that there is a true AMC that is less soluble than nesquehonite. Given it is not possible to determine a log K_{sp} from mixed phase assemblages, where two or more phases contain the same chemical species, we have not included reported data from Fukushi and Matsumiya (2018) in Figs. 6 or 7.

As noted by Zeyen et al. (2021), another challenge to the second model is that monohydrocalcite often forms via an amorphous precursor in laboratory experiments, including in the study by Fukushi and Matsumiya (2018). Finally, while monohydrocalcite was hypothesized to be the controlling phase in the aqueous geochemistry of alkaline lakes, it is only reported in 2 of 24 listed alkaline lakes (Fukushi and Matsumiya, 2018). In the Cariboo Plateau, formation via nesquehonite, the phase with which many of the lake waters are close to equilibrium (Fig. 7), cannot explain the observed trend between alkalinity and carbonate mineralogy, i.e. magnesite versus hydromagnesite. The incorporation of \sim 10 mol% Ca (as determined by the d₁₀₄ peak position in XRD patterns and observed in qualitative SEM-EDS data) also provides evidence against a crystalline-to-crystalline transformation to produce sedimentary magnesite (discussed above). If a crystalline-to-crystalline transformation did occur, Ca would need to be incorporated from the aqueous solution during the dissolution-reprecipitation process. In the Cariboo Plateau, the Ca concentration in all lakes was <0.28 mM and Mg/Ca ratios ranged from 3.7 to 114.2, making this scenario unlikely.

The third hypothesis is that carbonate minerals in the lakes formed via an amorphous carbonate precursor and then crystallized directly into the carbonate phases observed in the sediments of the Cariboo Plateau. As the bulk lake waters are undersaturated with respect to ACC, ACMC and AMC, additional (bio)geochemical processes are required in this scenario to increase the concentration of cations and anions to reach equilibrium with ACMC or AMC. The formation of magnesite through an amorphous precursor was hypothesized for Milne Lake, even though the SI values of the lake water were undersaturated relative to magnesite at

the time, because water sampling was done at a relatively wet time of year (Raudsepp et al., 2022). Evaporation is known to increase the SI values of minerals in lakes; however, lakes in the Cariboo Plateau were sampled in autumn at approximately the driest time of year. There may be some additional mechanism of concentrating lake water on the Cariboo Plateau, for instance during periods of ice formation and freeze out, similar to what has been reported by Renaut and Long (1987) for the formation of natron in Last Chance Lake. In marine environments, the degradation of EPS is hypothesized to release cations and promote formation of amorphous carbonates (Petrash et al., 2017). In more detailed work completed on alkaline lakes in Mexico, Zeyen et al. (2021) noted that formation of carbonate minerals via amorphous precursors may occur due to heterogeneous nucleation, such as the concentration of ions by organic functional groups on cell walls and extracellular polymeric substances (EPS), which allows for nucleation of these phases even when bulk waters are undersaturated. The stabilization of amorphous carbonates within the cells of cyanobacteria is well documented [reviewed in Cosmidis and Benzerara, 2022 and Dong et al., 2022], however, additional work needs to be completed on the role of cell walls and EPS on the formation and stabilization of amorphous carbonates in natural environments.

In this third model, lake waters become undersaturated with respect to amorphous carbonate phases when the amorphous-to-crystalline transformation results in re-equilibration of the water, i.e. the amorphous-to-crystalline transformation draws down Ca or Mg and alkalinity. This is supported by laboratory work examining the amorphous-to-crystalline transformation in carbonate phases, in which Ca and/or Mg and alkalinity are removed from the aqueous phase during crystallization and crystal growth (Purgstaller et al., 2021). After the amorphous-to-crystalline transformation the remaining water is always undersaturated with respect to the amorphous phase or phases that initially precipitated.

The difference between the minerals that precipitate from natural waters and those predicted from K_{sp} values may also be due to the difficulty in determining K_{sp} for highly reactive amorphous phases. For example, different Ksp values have been determined for ACC after synthesis (e.g. (Gebauer et al., 2008) compared with after dissolution of ACC in solutions with a lower ionic strength (e.g. (Brečević and Nielsen, 1989: Purgstaller et al., 2019; Purgstaller et al., 2021). For simplicity's sake, we have compared Cariboo lake waters to conditions that form end-member amorphous carbonates (Fig. 6), however, ACMC phases span the complete solid solution between ACC and AMC (Purgstaller et al., 2019). Amorphous carbonates that form in waters containing Ca and Mg incorporate both elements (Blue and Dove, 2015; Purgstaller et al., 2019; Radha et al., 2012). For the Cariboo Plateau lakes, if ACMC phases formed they would likely be dominated by Mg given the high Mg/Ca ratios of the waters. Additional experimental work is required to confirm the solubility of amorphous carbonates and determine how the amorphous-to-crystalline transformation changes the aqueous geochemistry of the surrounding water.

Finally, the definition of the saturation index (SI) may not be able to fully account for non-classical pathways. In classical nucleation theory, nucleation of a crystal is hypothesized to occur in a supersaturated solution due to spontaneous concentration of individual monomers in solution to form a nucleus of critical size [reviewed by Lutsko, 2017]. Classical growth occurs by monomer-by-monomer addition onto crystal surfaces (Lutsko, 2017). In non-classical nucleation, the formation and growth of aqueous complexes in solution, named prenucleation clusters, leads to their agglomeration into large enough clusters to result in a separate liquid or amorphous phase (Gebauer et al., 2008; Kellermeier et al., 2016). Mineral growth can also occur non-classically, which includes the addition of larger aqueous complexes, amorphous solids or crystalline nanoparticles to the mineral surface (De Yoreo et al., 2015). For example, Mills et al. (2022) recently demonstrated that during the growth of calcite in a solution containing Mn or Mg both classical and non-classical growth mechanisms occur. In their calcite growth experiment, free ions of Ca are incorporated in the calcite (classical growth), whereas the Mn and some portion of the Mg is incorporated via non-monomer species, such as ion pairs or larger polynuclear clusters (non-classical growth) (Mills et al., 2022).

Because the alkaline lakes of the Cariboo Plateau have a very high alkalinity, the complexation of Mg becomes important, following the equation:

$$\left[\mathrm{Mg}^{2+}\right] + \left[\mathrm{CO_{3}}^{2-}\right] \leftrightarrow \left[\mathrm{Mg}\mathrm{CO_{3}^{\circ}}_{(aq)}\right] \qquad \qquad log~(\mathrm{K}) = 2.98$$

As a result, >50% of total Mg in solution is held as $MgCO^{}_{(gaq)}$ in the higher alkalinity lakes where VHMC, magnesite and hydromagnesite + magnesite precipitate (Fig. 5F). However, the calculation of all mineral SI only considers free ions in solution. Given that the presence of aqueous complexes, including $MgCO^{}_{(gaq)}$, are important for mineral nucleation and growth in non-classical pathways, the calculated SI values likely underestimate the true potential for precipitation of amorphous solids (ACMC) or carbonate minerals.

Emerging ideas from the field of non-classical crystallization may also help us understand why the mineralogy of Cariboo lakes is so explicitly controlled by alkalinity rather than SI. In particular, the formation of magnesite appears to require a relatively high CO_3^{2-} concentration, but not so high that all of the Ca and Mg have been stripped from solution. It is well established that the high hydration of Mg in solution limits the reactivity of Mg and its ability to precipitate or attach to mineral surfaces (Di Tommaso and de Leeuw, 2010; Lippmann, 1973; Sayles and Fyfe, 1973). However, recent computational modelling by Aufort et al. (2022) suggests that the presence of carbonate ions results in the dehydration of Mg and formation of Mg-CO₃ ion pairs. This suggests that the CO_3^{2-} concentration may influence the amount of water in Mg-carbonate complexes, which in turn may influence the formation of anhydrous Mg-carbonates (magnesite, VHMC) over hydrous Mg-carbonates (e.g. hydromagnesite). Additional experimental work is required to verify how CO_3^{2-} concentration changes the hydration state of aqueous Mg-carbonate complexes and subsequent Mg-carbonate crystallization.

Understanding formation of carbonate sediments via non-classical pathways also challenges traditional estimates of the magnesite growth rate based on higher temperature classical growth experiments. For example, based on the classical growth rate of magnesite at 100 °C (Saldi et al., 2009) estimated that it would take 340,000 years to precipitate 1 mm of magnesite at ambient temperature. This is at odds with observations from natural, ambient temperature magnesite lakes and playas. At the Atlin playa, the sediment accumulation rate (hydromagnesite and magnesite) is estimated to be 0.3 to 0.4 mm/yr and the rate constant of magnesite growth is estimated to be 10^{-17} and 10^{-16} mol/cm²/s (Power et al., 2019). The sediment accumulation rate at Milne Lake (up to 62 wt% magnesite) is approximately 0.1 mm/yr (Raudsepp et al., 2022). Radiocarbon dating has not been conducted on the sediment of the Cariboo Plateau but at least 100 cm of magnesite containing sediment has been deposited in center of Milk Lake (Renaut, 1993) since deglaciation, approx. 10,000 ky BP, resulting in a deposition rate of at least 0.1 mm/yr. Thus, if magnesite is forming via non-classical pathways, the growth of magnesite may be more dependent on the concentration of $MgCO_{\mbox{(}aq)}^{^{\!\!\circ}}$ complexes or how often AMC saturation is reached in the lake, rather than the slow kinetics extrapolated from higher temperature classical growth experiments.

4.6. Conclusions

The closed basin lakes and playas in the Meadow–Milk–Alberta glacial outwash channel on the Cariboo Plateau, British Columbia, constitute one of the world's largest aerial extents of low temperature Holocene magnesite. The direct formation of magnesite without cooccurring minerals demonstrates that magnesite preserved in the geologic record did not necessarily form through a metastable, crystalline hydrated Mg-carbonate, such as hydromagnesite. In the Cariboo Plateau, hydromagnesite (with minor magnesite) precipitates in lakes with the lowest alkalinity, magnesite precipitates in lakes in the middle range of alkalinity and VHMC precipitates in the three lakes with the highest alkalinity. New models for crystallization pathways, including larger Mg-CO₃ complexes in aqueous solutions and formation through amorphous precursors, may help explain what exactly controls the formation of magnesite or hydromagnesite in a low temperature environment and may explain the relatively rapid formation of Mg-carbonates in the Cariboo Plateau.

Authorship statement

M.J.R. and S.W. designed the study. All authors conducted fieldwork in the Cariboo Plateau and survived the mosquitoes. M.J.R conducted the laboratory work, analyzed the data and wrote manuscript. All authors edited and approved the manuscript.

CRediT authorship contribution statement

Maija J. Raudsepp: Conceptualization, Formal analysis, Investigation, Methodology, Visualization, Writing – original draft, Writing – review & editing. Sasha Wilson: Conceptualization, Funding acquisition, Investigation, Supervision, Writing – review & editing. Nina Zeyen: Investigation, Writing – review & editing. Maria L. Arizaleta: Investigation. Ian M. Power: Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data available in supplementary information and will be made available on request

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2024.121951.

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