Non-classical crystallization of very high magnesium calcite and magnesite in the Coorong Lakes, Australia

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ABSTRACT

The Coorong Lakes, South Australia, are one of the models for unravelling the ‘Dolomite Problem’. Critically, today only a few modern environments remain where large quantities of very high magnesium calcite (VHMC; Ca$_{0.5}$Mg$_{0.5}$CO$_3$; also described as protodolomite or disordered dolomite) and magnesite (MgCO$_3$) precipitate. Previously conducted laboratory studies demonstrate that carbonate minerals can precipitate via classical and non-classical crystallization pathways. This study uses the preserved crystal sizes, morphologies and microstructures of Ca–Mg carbonates in the Coorong Lakes (Milne Lake, Pellet Lake and North Stromatolite Lake) to evaluate which crystallization pathway most likely occurred. In the fine-grained sediments of these lakes, very high magnesium calcite and magnesite occur as aggregate particles of nanocrystals (<100 nm). Rietveld refinements using X-ray diffraction data give modelled $L_{\text{vol}}$–IB crystallite size values of <120 nm for all carbonates. Transmission electron microscopy shows that, within VHMC and magnesite particles, nanocrystals have an almost identical orientation of their crystal lattice fringes. This is morphologically similar to Ca–Mg carbonates formed via an amorphous carbonate precursor in non-classical crystallization laboratory experiments. Precipitation of carbonate minerals via an amorphous-to-crystalline pathway requires the water to be supersaturated relative to both crystalline and amorphous phases. In the Coorong Lakes, surface water likely only becomes supersaturated relative to amorphous carbonate phases in the late summer after extensive evaporation. Observations suggest that VHMC and dolomite do not directly precipitate from bulk modern seawater, despite oversaturation relative to the crystalline phases, because seawater is undersaturated with respect to amorphous calcium magnesium carbonate, thus limiting the precipitation through a non-classical crystallization pathway.

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Keywords Aragonite, dolomite, lacustrine carbonates, magnesite, non-classical crystallization, very high magnesium calcite.

INTRODUCTION

Dolomite \([\text{CaMg(CO}_3\text{)}_2]\) is one of the most common sedimentary carbonate minerals in the rock record. Much of this dolomite, particularly in the Phanerozoic, formed through dolomitization, which is large-scale pseudomorphic replacement of a Ca-carbonate within limestone by dolomite during diagenesis, usually due to interaction with Mg-rich water at elevated temperatures (ca 50 to 80°C; Warren, 2000; Machel, 2004). However, some dolomite beds in the geological record have no evidence for secondary fluid flow and are hypothesized to have formed as a primary precipitate, or at least as a Ca–Mg carbonate with an approximate 1 : 1 Ca to Mg ratio that has since recrystallized into dolomite (Warren, 2000). In particular, primary dolomite is hypothesized to have precipitated in the Precambrian (Tucker, 1982), perhaps from aragonite–dolomite seas (Hood et al., 2011; Hood & Wallace, 2012) and in the Triassic in the Dolomites of Northern Italy (Preto et al., 2015; Meister & Frisia, 2019).

Understanding the formation of low-temperature dolomite has been challenging as there are relatively few modern environments where geochemical conditions allow for direct precipitation of dolomite or its cation-disordered polymorph, very high magnesium calcite (VHMC; \(\text{Ca}_{0.5}\text{Mg}_{0.5}\text{CO}_3\); also referred to as disordered dolomite and protodolomite) from the water column. Saline and hypersaline closed basin lakes are one type of environment in which Holocene VHMC/protodolomite, or dolomite formation has been studied extensively (e.g. Von der Borch, 1965; Rosen et al., 1988, 1989; Warren, 1988; Last, 1990; Meister et al., 2011; Fussmann et al., 2020).

The discrepancy between: (i) abundant dolomite in the geological past; and (ii) the very limited modern environments where VHMC or dolomite form is often called the ‘Dolomite Problem’ (Arvidson & Mackenzie, 1999; Holland & Zimmermann, 2000). More specifically, even though modern seawater is supersaturated relative to both dolomite and VHMC, neither of these phases precipitate directly without the influence of a geochemical and/or biogeochemical process that further increases the saturation state. Thus, the direct precipitation of these Ca–Mg carbonate minerals, as well as replacement of calcite or aragonite with dolomite at low-temperature (<40°C), is hypothesized to be limited by kinetics and, more specifically, the slow kinetics of \(\text{Mg}^{2+}_{\text{aq}}\) dehydration (Land, 1998; Arvidson & Mackenzie, 1999). The leading hypothesis to explain kinetic limitations on the precipitation and growth of Mg-bearing carbonates is that the double layer hydration of the aqueous \(\text{Mg}^{2+}\) cation limits its ability to participate in reactions (Lippmann, 1973; Sayles & Fyfe, 1973). In addition, once attached to the surface of a crystal, \(\text{Mg}^{2+}\) is difficult to dehydrate, which is thought to inhibit further crystal growth (Lippmann, 1973). Various abiotic and biotic mechanisms have been proposed to overcome these kinetic limitations. The first mechanism requires that Ca–Mg carbonate mineral supersaturation be increased by evapo-concentration (Rosen et al., 1989) or microbial metabolic processes that increase alkalinity or local pH, such as photosynthesis and dissimilatory sulphate reduction (Dupraz et al., 2009). The second mechanism requires dehydration and ordering of \(\text{Mg}^{2+}\) during bonding to carboxyl groups on microbial cell walls and organic matter (Van Lith et al., 2003; Kenward et al., 2013; Roberts et al., 2013; Bontognali et al., 2014). Microbes may play a further role in the formation of Ca–Mg carbonates by generating alkalinity and ordering of \(\text{Mg}^{2+}\) on cell walls.

Very high magnesium calcite is the metastable polymorph of dolomite. The structure of dolomite consists of ordered, alternating planes of \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) bonded together by carbonate groups. VHMC, whilst stoichiometrically identical, lacks this ordering of cations into distinct planes; instead, \(\text{Ca}^{2+}\) and \(\text{Mg}^{2+}\) are found together in the same planes, in a state referred to as cation disorder (reviewed in Gregg et al., 2015). The nomenclature proposed by Gregg et al. (2015) for VHMC follows the 50% rule for complete solid solutions without structural ordering established by the International Mineralogical Association (Nickel, 1992). VHMC crystallizes in the space group \(R3\bar{c}\), whereas cation ordering in dolomite results in a lower symmetry space group, \(R\bar{3}\), which can be identified from X-ray diffraction (XRD) patterns by the
presence of 101, 015 and 021 superstructure or supercell peaks, which have also been referred to as ‘ordering’ peaks (Reeder & Wenk, 1979; Reeder, 2000; Gregg et al., 2015). It should be noted that there is some variability in the degree of cation ordering in different samples of dolomite (Goldsmith et al., 1958; Kaczmarek & Sibley, 2007; Kell-Duivestein et al., 2019). Where the authors of previous studies have specified or described the relative extent of cation ordering, this study has prefixed the name dolomite with descriptors such as disordered, poorly ordered, weakly ordered, moderately ordered, or highly ordered, accordingly. Note that, because powder XRD, the analytical technique most used to identify these minerals, is a bulk method, ‘the degree of ordering’ (as measured by relative peak intensity) might sometimes reflect a measure of the relative proportion of VHMC and dolomite crystals within a sample or domains within a single crystal. Discrete domains of VHMC and dolomite have previously been observed within single crystals, for example, as observed by transmission electron microscopy (TEM) in Holocene Manito Lake stromatolites (Fang & Xu, 2019), and mixtures of structurally distinct crystals of VHMC and dolomite have also been reported, for example, such as sediment containing detrital dolomite grains (Last, 1990). However, powder XRD cannot distinguish between these scenarios and only measures long-range ordering within a bulk sample.

Although sedimentary magnesite (MgCO₃) is less common than dolomite, there is also a ‘Magnesite Problem’, in which metastable hydrated Mg-carbonate minerals [for example, hydromagnesite [Mg₅(CO₃)₄(OH)₂·4H₂O]] form more readily than the stable magnesite, even if the parent water is supersaturated with respect to magnesite. Naturally occurring low-temperature magnesite has been documented in a handful of lacustrine and playa systems; Milne Lake in the Coorong Lakes and Lagoon system, South Australia (Warren, 1988, 1990), at Atlin, British Columbia (Power et al., 2014, 2019), the Cariboo Plateau, British Columbia (Renaut, 1993) and in Freefight Lake, Saskatchewan (Last, 1993) in Canada; in Gallocanta Lake (Luzón et al., 2009) and the Los Monegros region (Mur & Urpinell, 1987; Mees et al., 2011) in Spain and in Lake Afouragh, Morocco (Détriché et al., 2013). Similar to the crystallization of low-temperature VHMC in laboratory experiments (Kenward et al., 2013; Roberts et al., 2013), the crystallization of magnesite can be facilitated by the presence of surfaces possessing carboxyl functional groups, such as the cell walls of cyanobacteria (Power et al., 2017; McCutcheon et al., 2019).

Several laboratory studies have been conducted to examine the geochemical conditions and mineralization pathways required to produce VHMC and dolomite. Each of these can be grouped broadly into one of three categories: (i) high temperature (>60°C) replacement of calcite or aragonite with dolomite (dolomitization; e.g. Goldsmith et al., 1958; Goldsmith & Heard, 1961; Kaczmarek & Sibley, 2011, 2014); (ii) high temperature (>60°C) crystallization of VHMC or dolomite after a precursor amorphous Ca–Mg carbonate (ACMC; e.g. Graf & Goldsmith, 1956; Rodríguez-Blanco et al., 2015); or (iii) low-temperature formation (<60°C) of VHMC or weakly ordered dolomite, including biologically-influenced precipitation (e.g. Vasconcelos et al., 1995; Kenward et al., 2009, 2013; Roberts et al., 2013; Daye et al., 2019). Not all of these studies describe crystallization pathways in detail, however, the crystallization of VHMC from an amorphous carbonate precursor, which is now described as a non-classical crystallization pathway, is common in low-temperature abiogenic experiments (e.g. Ohde & Kitano, 1978; Oomori & Banfield, 1998; Colfen & Antonietti, 2008; De Yoreo et al., 2015). During aggregation, and prior
to attachment, nanocrystals of the same mineral may also orient themselves such that there is a continuity of crystal planes at the boundary between the nanocrystals, resulting in degrees of oriented attachment from poorly oriented (containing defects) to well-oriented (Penn & Banfield, 1998; Banfield et al., 2000; De Yoreo et al., 2015). Alternatively, amorphous carbonate nanoparticles have been observed to attach to crystalline nanoparticles and then use the pre-existing crystal as a template during crystallization (Nielsen et al., 2014b; De Yoreo et al., 2015). Particle-based crystallization mechanisms may lead to mesocrystal formation (Cölfen & Antonietti, 2005, 2008). A mesocrystal is formed when there is a high degree of crystallographic alignment of individual nanocrystals, such that X-rays scattered from the aggregate appear as if they are from a single crystal (Cölfen & Antonietti, 2005, 2008). Finally, nanocrystal aggregates or mesocrystals may recrystallize into a single crystal through Ostwald ripening (De Yoreo et al., 2015). In this way, it is important to note that classical and non-classical crystallization are not mutually exclusive processes. For instance, a crystal may grow ion-by-ion (i.e. classically) from solution following non-classical crystallization from an amorphous precursor and subsequent nanoparticle aggregation. The non-classical framework serves only to consolidate the range of pathways and steps by which crystals may form and grow, including the classical concept of monomer-by-monomer crystallization.

Quite a few laboratory studies have examined the complete solid solution from amorphous calcium carbonate (ACC) to amorphous magnesium carbonate (AMC) and the various intermediate amorphous calcium magnesium carbonates (ACMC) with varying Ca : Mg ratios (e.g. Radha et al., 2012; Blue & Dove, 2015; Purgstaller et al., 2019). AMC are much more soluble than their crystalline counterparts, and thus are short-lived metastable phases, with a live time of hours in an aqueous solution (Brečević & Nielsen, 1989; Gebauer et al., 2008; Purgstaller et al., 2019). In a laboratory study, Rodriguez-Blanco et al. (2015) demonstrated that when heated, AMC with 40 mol.% MgCO₃ crystallizes as either VHMC (at 60 and 100°C) or dolomite (>140°C) and suggested that non-classical crystallization occurs in the formation of natural Ca–Mg carbonates. More specifically, Wang et al. (2012) noted a morphological similarity between VHMC from the Coorong Lakes and VHMC produced via ACMC in laboratory experiments. However, a more detailed analysis of the morphology and microstructure of the VHMC and other carbonate minerals formed in the Coorong Lakes relative to crystallization pathways has not previously been completed.

In a review paper, Jones (2017) suggests that most of the hot spring calcite and aragonite precipitated via non-classical crystallization, and that scanning electron microscope (SEM) images indicate that these carbonates are mesocrystals. Imaging with high resolution transmission electron microscope (TEM) is better technique for observing the size, morphology and crystallographic orientation of nanocrystals. Its utility is demonstrated by Frisia et al. (2018) where TEM data is used to hypothesize that dolomite nanocrystals in the Triassic Travenanzes Formation (northern Italy) formed by non-classical crystallization and that these nanocrystals are preserved due to a close association with inorganic Si-rich and organic colloids. Further work by Meister & Frisia (2019) expanded on the non-classical crystallization model of Triassic dolomite in northern Italy and hypothesized that aggregation of primary Triassic dolomite nanocrystals in the Dolomia Principale may have been induced by pH fluctuations. Oriented attachment of Mg-calcite nanocrystals associated with smectite has also been described in Lake Balaton, Hungary (Nyirő-Kósa et al., 2018).

Generally, the presence of nanocrystalline carbonates in environmental samples has been distinguished by SEM and TEM. Nanocrystals can be described equivalently as ‘crystallites’ [reviewed in Ingham (2015) and Jones (2017)]. When mineral samples are analyzed with XRD, small crystallites create peak broadening due to disruptions to the long-range order of the crystal structure. Crystallite size can be calculated from peak broadening, for instance with the Scherrer equation, particularly for nanocrystals between 5 nm and 100 nm (Ingham, 2015).

The present study takes a nano-scale perspective to determine the crystal size, morphology and microstructure of naturally occurring Ca–Mg carbonate minerals from the Coorong Lakes using SEM, TEM and XRD data. Crystal size, crystal structure and microstructure, and lake water geochemistry are evaluated within the context of crystallization pathways (i.e. classical and non-classical nucleation and growth). In the present study, the geochemical and sedimentological formation conditions of the carbonate minerals (for example, groundwater mixing, evaporation,
biogenically influenced or mediated) were not evaluated; however, the work of previous researchers on these formation conditions will be framed in the context of crystallization pathways.

**Study location**

The Coorong Lakes, near Salt Creek, South Australia (Fig. 1), have long been studied as a sedimentological model for the formation of Ca–Mg carbonates (described as ‘protodolomite’ or ‘poorly ordered dolomite’; Von der Borch, 1965; Rosen et al., 1988, 1989; Warren, 1988, 1990; Wright & Wacey, 2005; Wacey et al., 2007). The Coorong Lakes have a Mediterranean-like climate with cool wet winters and hot dry summers, an average maximum annual rainfall of 400 mm and a mean annual air temperature of 13.5°C (Warren, 1988). The water temperature ranges from 10 to 28°C (Warren, 1988). The carbonate-forming lakes are divided from the Coorong Lagoon by a beach dune ridge. Halite Lake, Dolomite Lake, Pellet Lake and North Stromatolite Lake had a marine connection to the lagoon during the mid-Holocene, whereas Milne Lake did not have a marine connection (Warren, 1988). Subsequently, the lakes have been isolated and have evolved unique surface water geochemistry and distinct mineral assemblages consisting almost entirely of Ca-carbonate and Mg-carbonate phases, including what has previously been described as poorly ordered dolomite, magnesite, hydromagnesite and aragonite (Warren, 1988; Rosen et al., 1989). Based on δ13C and δ18O values, and the dolomite unit cell parameters, two types of dolomites are present in the Coorong. Magnesium-rich ‘type A dolomites’ are usually evaporitic and form massive carbonate units in the centres of the lakes, whereas the calcium-rich ‘type B dolomites’ form at lake margins and in basal units, likely associated with groundwater inflow (Warren, 1988; Rosen et al., 1989). Type A dolomite occurs with, or is stratigraphically associated with, magnesite or hydromagnesite (Rosen et al., 1989). Wright & Wacey (2005) also demonstrated that sulphate reducing bacteria (SRB) from the sediment of the Coorong Lakes can induce biogenic precipitation of poorly ordered dolomite in laboratory experiments.

**METHODS**

**Sampling procedures**

Sediments were collected using a 10 cm diameter push corer in early October 2016. Sediments were retrieved from Milne Lake (54H 0378062 5999780) to a depth of 50 cm, from Pellet Lake (54H 0378863 5997481) to depth of 63 cm and from North Stromatolite Lake (54H 0379691 5996541) to a depth of 93 cm. These depths reflect the maximum extent to which the corer could be pushed at a given location. Cores were divided into 2.5 or 5.0 cm slices and then centrifuged at 1880 relative centrifugal force (RCF) for 30 min to separate sediments and pore water. Surface water samples were filtered (<0.45 μm) and stored at 4°C.

**Aqueous geochemical analyses**

Aqueous pH, Eh and electrical conductivity were measured in the field using a Thermo Scientific Orion 5 Star pH–Eh–conductivity meter (Thermo Fisher Scientific, Waltham, MA, USA). Aqueous sulphide [methylene blue; Cline (1969)] and
alkalinity (Sarazin et al., 1999) were also measured in the field using a portable Hach spectrophotometer (error of ±5%; Hach Company, Loveland, CO, USA). Major cation concentrations (Li, Na, Mg, Ca and Sr) were measured using inductively coupled plasma mass spectrometry (ICP-MS; Thermo Finnigan X Series II Quadrupole; Thermo Fisher Scientific). Major anion concentrations (F, Cl, Br, SO₄²⁻ and NO₃⁻) were measured using a Thermo Fisher Ion Chromatograph (Thermo Fisher Scientific) with appropriate dilutions to solutions with very high concentrations.

The saturation indices (SI) of crystalline Ca and Mg carbonates in the surface water were calculated in PHEEQC v.3.3 (Parkhurst & Appelo, 2013) using the phreeqc.dat database, the extended Debye–Hückel equation and a temperature of 25°C. Ksp values for disordered dolomite (VHMC), magnesite and hydromagnesite were taken from the wateq4f.dat database. SI of amorphous carbonates for surface waters were calculated with modelled ion activities and the solubility product constants (Ksp) for ACC (10⁻⁶.19), ACMC with 53 mol.% MgCO₃ (10⁻⁵.44) and AMC (10⁻⁴.41) that were determined experimentally by Purgstaller et al. (2019). These experiments were conducted at 25°C and ionic strength of 0.17 ± 0.02 M (Purgstaller et al., 2019).

**Powder X-ray diffraction and Rietveld refinement**

Air-dried sediment samples were washed with MilliQ water to remove halite and then disaggregated in a tungsten carbide ring mill for 1 min. A ca 2 g aliquot of each sample of dried was further ground under 100% ethanol in a McCrone micronizing mill (McCrone Group, Westmont, IL, USA) using agate pellets for 5 min. Micronized aliquots were air dried and analyzed on a Rigaku Ultima IV powder X-ray diffractometer (Rigaku, Tokyo, Japan). This XRD is equipped with a Cu source that was operated at 38 kV and 38 mA. X-ray diffractometer patterns were collected from 5° to 80° using a step size of 0.02° 2θ at a rate of 2° 2θ/min. Rietveld refinements (Rietveld, 1969; Hill & Howard, 1987; Bish & Howard, 1999; Balzar et al., 2004). A structural model of VHMC was produced using the crystal structure and space group of calcite and the unit cell parameters and stoichiometry of ideal dolomite. A circles function was applied to phases with strongly anisotropic Bragg peaks. The fractional occupancies of Ca and Mg were allowed to vary between 0.3 and 0.7 provided Ca + Mg = 1. Crystallite size was permitted to refine without constraint and microstrain was not refined. Using the equation N_MgCO_3 = 100 - (|d_{104} × 333.33| - 911.99) derived by Lumsden (1979), the relative amount of Ca and Mg in the structure of calcite–VHMC–magnesite minerals was calculated from the d₁₀₄ peak position.

**Electron microscopy**

Scanning electron microscopy (SEM) samples were coated with ca 10 nm of Au in a sputter coater and imaged on a Zeiss Sigma 300 Variable Pressure Field Emission SEM (Carl Zeiss AG, Jena, Germany) with a Bruker energy-dispersive X-ray spectrometer (EDS; Bruker Corporation). A voltage of 3.0 kV was used for secondary electron (SE) imaging and EDS analysis was done at 15 kV. TEM samples were mounted on lacy carbon formvar 300 mesh Cu grids. Low-resolution images were captured with a Philips/FEI (Morgagni) TEM operated at 80 kV (Philips, Amsterdam, The Netherlands). High resolution images were obtained with a JEOL JEM-ARM200CF high resolution scanning/transmission electron microscope (HR S/TEM; JEOL Limited, Tokyo, Japan) at 200 kV with a 40 μm aperture to reduce beam interaction with the sample (see Fig. S5 which includes Figs S1 to S7; Tables S1 to S3). Obtaining completely focused images and crystal lattice fringes in HRTEM was challenging due to the thickness of the particles, as such all high-resolution images were taken at particle edges. Images were analyzed with the GATAN MICROGRAPH (v. 3.22) software and TEM microscopy suite in Fiji ImageJ (Schindelin et al., 2012). Mineral identification using characteristic d-spacings was completed by measuring fast Fourier transform (FFT) diffractograms of crystal lattice fringes in HRTEM images.

**Radiocarbon analysis**

Radiocarbon data were obtained on a single stage accelerator mass spectrometer (SSAMS) at the Research School of Earth Sciences at The Australian National University (Canberra, Australia).
and using the Libby half-life of 5568 years (Fallon et al., 2010). Calibrated radiocarbon dates were calculated using Oxcal 4.4.2 (Ramsey, 2020) using SHCal20 Southern Hemisphere calibration (Hogg et al., 2020). All reported radiocarbon ages are for carbonate minerals rather than organic matter in the sediments; thus, they represent a maximum age of the sediment.

RESULTS

Surface water chemistry

At the time of sampling (October 2016), the surface water in all three lakes had a pH in the range of 8.68 to 10.02, an alkalinity between 7.66 to 11.9 mM (as HCO$_3^-$) and a Mg/Ca ratio between 32 and 63 (Table 1). In all three lakes, surface waters were oversaturated with respect to aragonite, calcite, VHMC (disordered dolomite), dolomite (ordered) and magnesite (Table 2). Pellet Lake and North Stromatolite Lake surface waters were also oversaturated with respect to hydromagnesite (Table 2). All three lakes were undersaturated relative to all phases of ACMC (0 to 100 mol.% Mg) with SI values between $-1.14$ and $-1.96$. At the time of sampling, the surface lake water was slightly less undersaturated with respect to ACMC (53 mol.% Mg) compared to ACC (0 mol.% Mg).

Table 1. Aqueous geochemistry of Milne Lake, Pellet Lake and North Stromatolite Lake in the Coorong Lakes region of South Australia (sampled October, 2016).

|                | Milne Lake | Pellet Lake | North Stromatolite Lake |
|----------------|------------|------------|-------------------------|
| Temperature (°C) | 20.3       | 13.5       | 19.8                    |
| Electrical conductivity (mS) | 45.4       | 97.5       | 58.4                    |
| pH              | 8.68       | 10.0       | 8.98                    |
| Alkalinity (mM) | 6.12       | 9.08       | 7.90                    |
| Cation concentration (mM) |           |            |                         |
| Ca$^{2+}$      | 0.92       | 1.40       | 0.78                    |
| K$^+$          | 7.34       | 14.3       | 5.56                    |
| Mg$^{2+}$      | 29.2       | 60.8       | 49.2                    |
| Na$^+$         | 436        | 1117       | 546                     |
| Sr$^{2+}$      | 0.26       | 0.25       | 0.04                    |
| Anion concentration (mM) |           |            |                         |
| Br$^-$         | 0.37       | 0.80       | 0.52                    |
| Cl$^-$         | 418        | 1115       | 561                     |
| F$^-$          | 0.02       | 0.07       | 0.03                    |
| NO$_3^-$       | 0.18       | 0.09       | 0.58                    |
| SO$_4^{2-}$    | 13.9       | 34.2       | 26.3                    |
| Mg/Ca ratio    | 32         | 43         | 63                      |

Table 2. Saturation indices of amorphous and crystalline Ca-Mg carbonates phases calculated in Phreeqc v3.3 with the Phreeqc.dat database using the extended Debye–Hückel equation and a model temperature of 25°C. $K_{sp}$ values for ACC, ACMC (53 mol% Mg) and AMC are from Purgstaller et al. (2019). Lake water was sampled in early October, 2016.

| Phase               | Milne Lake | Pellet Lake | North Stromatolite Lake | Sea water* |
|---------------------|------------|------------|-------------------------|------------|
| Ionic strength      | 0.49       | 1.21       | 0.67                    | 0.67       |
| ACC                 | $-1.72$    | $-1.23$    | $-1.62$                 | $-1.51$    |
| ACMC (53 mol% Mg)   | $-1.72$    | $-1.14$    | $-1.47$                 | $-1.90$    |
| AMC                 | $-1.96$    | $-1.30$    | $-1.55$                 | $-2.52$    |
| Aragonite           | 0.41       | 0.90       | 0.52                    | 0.63       |
| Calcite             | 0.57       | 1.05       | 0.66                    | 0.77       |
| Ca$_{0.5}$Mg$_{0.5}$CO$_3$ | 1.05       | 1.62       | 1.30                    | 0.87       |
| Magnesite           | 1.65       | 2.31       | 2.06                    | 1.07       |
| Hydromagnesite      | $-1.56$    | 4.02       | 0.85                    | $-4.45$    |
| Dolomite            | 2.79       | 3.94       | 3.30                    | 2.43       |
| VHMC (disordered)   | 2.24       | 3.39       | 2.75                    | 1.88       |

* Using modern seawater composition from Millero (2006).

† SI calculated with the form Ca$_{0.5}$Mg$_{0.5}$CO$_3$ ↔ 0.5Ca + 0.5Mg + CO$_3$ to equivalently compared the ACC-AMC solid solution to the calcite-magnesite solid solution. $K_{sp}$ is from disordered dolomite.
46 mol.% and 50 mol.% Mg and magnesite from Milne Lake contains ca 11.5 mol.% Ca (Table S2). Poorly crystalline Mg-silicate clays were also observed with SEM and TEM.

X-ray diffraction peaks of all carbonate phases in the Coorong Lakes are broad and all L_{vol−}IB values refined for carbonate minerals are in the range of 10 to 120 nm (Table S2). In comparison, all L_{vol−}IB values refined for detrital quartz in the sediments are over 1 μm. Magnesite and VHMC generally have the smallest refined L_{vol−}IB values, with an average of ca 15 nm (Table S2). Calcite and hydromagnesite have larger refined L_{vol−}IB values, between 25 nm and 85 nm; aragonite has the largest refined L_{vol−}IB values, between 80 nm and 120 nm.

**Carbonate mineral morphology and microstructure**

Scanning electron microscopy analysis shows that particle morphologies of specific mineral
species are generally similar between lakes. VHMC particles have a size range of 0.05 to 4 µm and the particles consist of aggregates of multiple nanometre sized crystals. They typically have a botryoidal or blocky appearance, with a high surface area and roughness (Fig. 3A to C). In the surface sediment of Milne (Fig. 3A) and Pellet Lake (Fig. 3C) well-developed, distinct faces within VHMC particles could not be resolved with the SEM. At depth in the Milne and Pellet Lake cores, nanocrystals with well-developed, distinct faces (up to 150 nm) within VHMC particles could be resolved by SEM (Fig. S4A). VHMC particles were difficult to image using SEM, except at the lowest beam voltages (<5 kV) owing to their high surface area.

Magnesite particles are less than 2 µm in length and have the morphology of blocky aggregates with well-developed 104 faces ca 10 to 500 nm in size when observed with SEM (Fig. 3B). Hydromagnesite occurs as single platy crystals or books of plates, generally with a plate width of several hundred nanometres, but almost all less than 2 µm, in the longest dimension (Fig. 3C). Aragonite has a tabular to acicular morphology and are usually several micrometres long (Fig. S4B and C).

Due to preferential orientation of the particles during settling on the TEM grid, the {104} planes were most commonly observed in high-resolution and low-resolution TEM. Low-resolution TEM shows that the VHMC and

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Fig. 3. Scanning (A) to (C) and transmission electron (D) to (F) micrographs of sediment from the Coorong Lakes, South Australia containing very high magnesium calcite and magnesite. (A) Surface (0 to 2.5 cm; 16ML2-20) sediment from Milne Lake containing a mixture of very high magnesium calcite (VHMC) and magnesite (Mgs). (B) Sediment from depth (27.5 to 30.0 cm; 16ML2-9) in Milne Lake showing botryoidal morphology of VHMC and blocky morphology of magnesite. (C) Surface (0 to 2.5 cm; 16PL1-18) sediment from Pellet Lake containing VHMC and hydromagnesite (Hydromgs). (D) TEM image of Milne Lake surface sediment (16ML2-20) showing some VHMC particles that lack distinct crystal faces (arrow). (E) At a depth of ca 30 cm (16ML2-9) well-developed crystal faces are observed for almost all VHMC and magnesite particles. Organics are also present in the sediment. (F) TEM image of Pellet Lake surface sediment (16PL1-18) containing VHMC, hydromagnesite and Mg-silicate clays.
Magnesite aggregates observed in SEM are composed of many smaller crystals in the size range of 10 to 100 nm, with most crystals less than 70 nm (Fig. 3D to F). Botryoidal VHMC particles were observed in the surface sediment of Milne (Fig. 3D) and Pellet Lake (Fig. 3F) but were rarely observed at depth. High-resolution TEM showed that some of the botryoidal VHMC particles from the surface sediment did not have any distinct planar faces (Fig. 4A and D), whereas other botryoidal VHMC particles contained some euhedral nanocrystals with distinct planar crystal faces, including some <10 nm nanocrystals (Fig. 4C and F). High-resolution TEM data complements the observations from SEM and low-resolution TEM that the morphology of VHMC at depth in the sediments was of crystal aggregates composed of more euhedral nanocrystals. For example, in Milne Lake sediment from a depth of ca 48 cm, well-defined crystal faces were observed for almost all nanocrystals within the crystal aggregates (Fig. 4B and E).

Fig. 4. High resolution TEM micrographs of sediment from Milne and Pellet lakes in the Coorong, South Australia. (A) VHMC and magnesite from the surface sediment of Milne Lake (0 to 2.5 cm; 16ML2-20). Box shows location of (D). (B) VHMC from the bottom of the Milne Lake core (47.5 to 49 cm; 16ML2-1) showing well-defined planar crystal surfaces. Box shows location of (E). (C) VHMC from the surface of Pellet Lake (0 to 2.5 cm; 16PL1-18). Box shows location of (F). (D) Higher resolution image of (A) showing a continuous crystal lattice fringe and FFT diffractograms of the magnesite and VHMC particles. Boundary between magnesite and VHMC marked with yellow dashed line. Both particles show the [104] crystal lattice fringe. As measured from the FFT, magnesite has a d_{104} value of 2.78 Å and VHMC has a d_{104} value of 2.89 Å, both of which are consistent with the d_{104} values of VHMC and magnesite as determined by XRD. Both minerals show the [104] crystal lattice fringe due to preferential orientation during settling on the grid. Triple lines trace three crystal lattice fringes, showing orientation of the [104] lattice fringe in the VHMC (top left particle) and magnesite (bottom left particle). (E) Higher resolution image of (B) showing a continuous [104] crystal lattice fringe in a VHMC particle from the bottom of the core. (F) Higher resolution image of (E) showing a continuous [104] crystal lattice fringe of VHMC and ca 10 nm nanocrystals in the aggregate (arrow). All units in FFT are in angstroms. Images (B), (C), (E) and (F) are of larger particles and therefore exhibit edge effects in the images. For abbreviations, see Fig. 3.

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Regardless of crystal shape, VHMC and magnesite nanocrystals from both the surface sediment and at depth had continuous crystal lattice fringes within the particle aggregate (Fig. 4D to F). For example, crystal lattice fringes of the [104] plane observed for the VHMC particle in Fig. 4B has almost exactly the same orientation along its entire length. Nanocrystals within the VHMC or magnesite particle aggregates are nearly perfectly oriented in most (Fig. 4D to F) but not all particles (Fig. S5). This is exemplified by: (i) the continuity of their crystal lattice fringes; and (ii) their FFT diffraction patterns, which show single crystal diffraction rather than the multiple spots or rings. Even for carbonates dated to ca 6700 cal yr BP, VHMC nanocrystals were almost all less than 100 nm in size in the longest dimension (Fig. 4B and E). Crystal lattice fringes were not observed for Mg-silicate clay particles, but the sheet structure was observed.

DISCUSSION

Mineralogy and stoichiometry

The present study has the same mineral assemblages in each of the three Coorong Lakes samples as reported in previous research (Rosen et al., 1988, 1989; Warren, 1988). The average refined c axis and a axis lengths for the unit cell of VHMC are 16.09 Å and 4.81 Å in Pellet Lake and 16.07 Å and 4.81 Å in Milne Lake, which are consistent with the average unit cell dimensions for type A ‘poorly ordered’ dolomite previously reported for samples from these two lakes (Rosen et al., 1988, 1989).

Carbonate mineral morphology and microstructure

The particle morphology of Coorong VHMC particles observed in SEM is consistent with previously published SEM images and morphological description of Coorong carbonates (Rosen et al., 1988). Several studies describe carbonate particles within the Coorong Lakes sediments as ‘spherical’ or ‘sub-spherical’ (Borch & Jones, 1976; Wright & Wacey, 2005). However, this morphology was only observed under a high electron beam voltage (<10 kV) and when samples were carbon coated. Thus, it is likely to be an artefact caused by particle charging under the electron beam due to the very high surface area of these grains. A dumbbell morphology, which is commonly associated with biologically induced precipitation of VHMC (Warthmann et al., 2000; Sánchez-Romá et al., 2011), was not observed in the Coorong sediments. The morphology of Milne Lake magnesite particles resembles that of magnesite produced in abiotic (Power et al., 2017) and microbial (McCutcheon et al., 2019) mineral precipitation experiments in the laboratory, as well as magnesite previously observed in other carbonate lake sediments (Power et al., 2019). Milne Lake magnesite particles are slightly smaller than: (i) particles of low-temperature magnesite produced abiotically in the laboratory (Power et al., 2017); and (ii) magnesite found in a hydromagnesite/magnesite playa near Atlin, British Columbia, Canada (Power et al., 2019). They are similar in size to polycrystalline magnesite particles produced in a cyanobacteria-dominated bioreactor that was built using a photosynthetic microbial consortium cultured from the playa at Atlin (McCutcheon et al., 2019). In addition, Coorong hydromagnesite occurs as single small platy crystals (this study), whereas Atlin hydromagnesite occurs as larger single plates or as rosettes (Power et al., 2014, 2019).

Rosen et al. (1989) used TEM to observe a range of microstructures in weakly ordered dolomite from the Coorong: “from heterogenous, with closely spaced, random defects, to relatively featureless and homogenous crystals”. In particular, that study described the microstructure of most type A dolomite as heterogenous with a large number and high density of ‘defects’ (Rosen et al., 1988, 1989). Particles of type A dolomite diffracted as single crystals with TEM selected area electron diffraction (Rosen et al., 1988). Combined high-resolution and low-resolution TEM images from this study show that these ‘defects’ described by Rosen et al. (1988) are likely the edges of nanoparticles, in the range of 10 to 100 nm. Particularly at depths below 30 cm in the sediment, particles of VHMC are clearly composed of many euhedral nanocrystals (Figs 3E and 4B). Continuity of crystal lattice fringes and single points in FFT diffraction patterns demonstrate that the nanocrystals within the particle have almost perfect crystallographic alignment (mechanisms to produce crystallographic alignment of nanoparticles is discussed below).

For the Coorong Lakes, VHMC and magnesite crystallite sizes, as determined by Rietveld refinement of peak width in XRD patterns (Lvol–IB), were smaller (ca 15 nm) than the size of nanocrystals measured in TEM (generally 10 to 70 nm). Rietveld refinements provide a measure
of crystallite size using the double-Voigt approach, which can account for the effect of crystallite size and strain on peak broadening but does not account for compositional variation (Balzar, 1999). Compositional variation, i.e. multiple populations of the same mineral each with a range of stoichiometries, does result in peak broadening and currently is attributed to crystallite size and strain within the double-Voigt approach and all other methods of estimating crystallite size from XRD. In the Coorong Lakes, VHMC and magnesite within any given sample likely have a range in the Ca/Mg ratio, which contributes to peak broadening. The \( L_{\text{vol}}^{\text{IB}} \) values for aragonite and hydromagnesite are between 25 nm and 120 nm (Table S2), which is likely due in part to their crystal structures being unable to accommodate as much magnesium and calcium substitution, respectively, as members of the calcite–VHMC–magnesite mineral series. Thus, XRD is useful for indicating that VHMC and magnesite particles are polycrystalline and composed of nanocrystals; however, TEM is a better technique for determining the nanocrystal size.

**Relationship between size, microstructure and crystallization pathways**

Theoretically, nanocrystals of carbonate minerals could be formed by either classical or non-classical crystallization. Carbonate crystallization pathways depend on both the thermodynamics and kinetics of the nucleation and growth of the solid phase \( (\Delta G_{\text{nucleation}} + \Delta G_{\text{growth}}) \) and phase transformations \( (\Delta G_{\text{transform}}) \), all of which depend on the bulk free energies and the surface energies of the solid phases [reviewed in Radha & Navrotsky (2013)].

In classical nucleation theory, a nucleus above a critical size must form from solution for growth of a crystal to occur (see review in Lutsko, 2017). Nuclei below the critical size are unstable and will dissolve back into solution. As such, oversaturation of a solution increases the probability that nuclei above the critical size will form. Within the classical framework, after nucleation, crystals grow by monomer-by-monomer attachment, with different crystal morphologies being controlled by the relative growth rates onto crystallographic axes, growth front nucleation and the supersaturation of the aqueous solution [reviewed in Andreassen & Lewis, 2017]. At low supersaturation, crystals grow with the terrace, ledge, kink model, whereas as at higher supersaturations, dendritic or spherulitic growth will occur (Andreassen & Lewis, 2017). Ostwald ripening, which is the growth of larger crystals at the expense of the dissolution of smaller crystals, may also occur as part of this process. In this context, oversaturation relative to crystalline phases in the Coorong Lakes could increase the likelihood of crystallization through a classical pathway. However, considering the results of this study within the classical crystallization model, it is unclear what would stop crystal growth completely or change the growth kinetics to produce the sub-100 nm crystals of VHMC and magnesite – especially when the surrounding waters are still supersaturated relative to the crystalline phases.

Non-classical crystallization is an extension to the classical theory that addresses complexity in the free energy landscape and the influence of dynamics in the nucleation and growth of solid phases that form crystals (De Yoreo et al., 2015). In this way, it can provide an explanation for the formation of crystalline phases whose crystallization is thermodynamically favoured but kinetically inhibited. Three components of non-classical crystallization have important implications for mineral formation and growth: (i) prenucleation clusters; (ii) liquid–condensed or amorphous mineral precursors; and (iii) growth by particle attachment (reviewed in Radha & Navrotsky, 2013; Van Driessche et al., 2016). Laboratory experiments have shown that crystallization of carbonate minerals via non-classical mechanisms, such as the formation of prenucleation clusters (Gebauer et al., 2008; Gebauer & Cölfen, 2011; Kellermeier et al., 2016) and the development of liquid, amorphous and other nanophase precursors, can be thermodynamically favourable (Navrotsky, 2004; Raiteri & Gale, 2010; Radha & Navrotsky, 2013). Prenucleation clusters, which are stable multi-ion associations in a solution, have been proposed as an alternative nucleation mechanism for mineral precipitates, with the aggregation of prenucleation clusters resulting in nucleation of amorphous nanoparticles (Gebauer et al., 2010; Gebauer & Cölfen, 2011; Kellermeier et al., 2016).

Multi-step pathways, including an amorphousto-crystalline transition, are commonly followed to produce crystalline carbonate minerals because either: (i) the formation of the stable phase has kinetic limitations (e.g. Habraken et al., 2013); or (ii) at the nanometre scale, the increasing importance of surface energy relative
to bulk energy can produce an inversion of phase stability with decreasing size (Navrotsky, 2004). For a particle with a length of 10 nm, ca. 16% of the particle’s atoms are on the surface, and this percentage increases as the particle size decreases (Waychunas & Zhang, 2008). In general, while thermodynamically stable phases have lower bulk free energies, metastable phases generally have lower surface energies (Navrotsky, 2004). This concept is supported by molecular dynamics simulations that show that ACC is more stable than calcite below a diameter of 4 nm, likely due to its structurally bound water (Raiteri & Gale, 2010). In this way, non-classical crystallization follows the familiar Ostwald’s step rule, whereby the phase that is initially formed is not most thermodynamically stable but the phase that is more kinetically probable due to its lower activation energy.

Once an amorphous carbonate has formed from a solution, there is a very small energy barrier to growth allowing ACC nanoparticles to grow from several nanometres to hundreds or thousands of nanometres at a faster rate than crystalline Ca-carbonate phases (Raiteri & Gale, 2010). Resulting amorphous carbonates can be up to several micrometres in diameter. For example, synthesized ACMC with between 25 mol.% and 70 mol.% Mg has particle diameters between 0.1 µm and 2 µm, with an average of 1 µm (Blue & Dove, 2015) and naturally occurring ACMC with approximately 50 mol.% Mg formed in fish guts has a particle diameter of 200 to 500 nm (Foran et al., 2013).

The transformation of amorphous carbonate phases to crystalline phases can be a solid-state transformation (Ihli et al., 2014) but it is usually a dissolution–precipitation reaction (Nielsen et al., 2014b; Fernandez-Martinez et al., 2017). Crystallization of amorphous carbonates can produce either much smaller nanocrystals or slightly smaller nanocrystals (Rodriguez-Blanco et al., 2008, 2015). For example, TEM beam induced crystallization of ACC particles with an average diameter of ca. 125 nm produced CaCO₃ nanocrystals in the size range of 5 to 10 nm (Rodriguez-Blanco et al., 2008). After incubation at 60°C, VHMC with an average length of ca. 35 nm (refined crystallite size of 23 ± 5 nm from XRD) crystallized from an ACMC (39 mol.% Mg) with an average length of ca. 45 nm (Rodriguez-Blanco et al., 2015). In comparison, VHMC and magnesite nanocrystals from the top 2.5 cm of Milne Lake ranged from 15 to 100 nm and were typically less than 50 nm.

In this way, the presence of nanocrystals in the Coorong VHMC and magnesite maybe a signature of an amorphous-to-crystalline transition. However, without directly observing transformation of an amorphous carbonate phase, such as with in situ TEM, it is not conclusive evidence. Interestingly, in early research on the Coorong, Borch & Jones (1976) hypothesized that the disordered dolomite in the Coorong crystallized from an amorphous carbonate gel. This hypothesis was based on morphological similarity of the Coorong carbonates to synthesized disordered dolomite that was produced by Müller & Fischbeck (1973) from an amorphous carbonate gel (Borch & Jones, 1976).

A challenge to using crystal size as a signature of an amorphous-to-crystalline transition is that further Ostwald ripening can result in large single crystals that appear similar to crystals produced from a classical pathway (De Yoreo et al., 2015). Nanocrystals produced by an amorphous-to-crystalline transformation may also grow by additional particle attachment or by classical ion-by-ion addition (De Yoreo et al., 2015). Kim et al. (2014) also noted that overgrowths on single crystals may resemble mesocrystals in SEM, highlighting the importance of using HRTEM or XRD to describe the microstructure (for example, strain and crystallite/nanocrystal size) of carbonate minerals. The presence of botryoidal VHMC without well-defined crystal faces at the top of the sediments from Milne and Pellet lakes and the notable absence of this morphology at depth suggests that the VHMC is recrystallizing during early diagenesis. As a small nanocrystal size is maintained during recrystallization, further growth appears kinetically limited.

Research by Rodriguez-Blanco et al. (2015) hypothesized that spherical or dumbbell morphologies of biogenic VHMC are formed by non-classical crystallization, thus becoming one of the first studies to explicitly connect Ca–Mg carbonate nanocrystals to an amorphous–crystalline transformation. In a review of environments with Holocene VHMC or dolomites, including lacustrine, sabkha, lagoon and tidal environments, many more examples of crystal aggregates in published SEM micrographs were found as part of this study (see Table S1; Figs S6 and S7). For example, Wenk et al. (1993) and Frisia (1994) describe Holocene, low-temperature poorly ordered dolomite from an Abu Dhabi sabkha that has a mosaic of 5 to 20 nm crystals in TEM micrographs. These nanocrystals have since been interpreted to be the signatures of
non-classical crystallization by Frisia et al. (2018) and Meister & Frisia (2019). The prevalence of VHMC or dolomite aggregates containing sub-micron sized crystals in a variety of Holocene marine and terrestrial environments suggests that similar crystallization pathways, perhaps non-classical crystallization via an amorphous precursor, could potentially occur in these settings. Further research is required to examine crystallization pathways in these environments.

High-resolution TEM of Coorong VHMC and magnesite demonstrates that particles are composed of nanocrystals with almost identically aligned crystal lattice fringes and with continuity for more than 100 nm (Fig. 4), thus particles are mesocrystals and are highly likely to have formed via particle attachment. In in situ TEM experiments, the formation of nanoparticles with aligned lattice fringes has been observed to occur by: (i) oriented attachment, which is the rotation of crystalline nanocrystals; or (ii) the templating of an amorphous particle onto a pre-existing crystalline phase (Nielsen et al., 2014b). In general, the process of oriented attachment or rotation of nanocrystals has more frequently been observed in metals and oxides, and may be size dependent (e.g. Penn & Banfield, 1998; Banfield et al., 2000; Nielsen et al., 2014b; Zhang et al., 2014). Nielsen et al. (2014b) noted that true oriented attachment of the calcium carbonate nanocrystals during an in situ TEM experiment were likely rare.

Several mechanisms have been proposed for natural environments where crystallographic alignment of nanoparticles has been observed in Ca–Mg carbonates. In the suspended sediment of Lake Balaton, a shallow Mg-rich lake in Hungary, Nyirő-Kósa et al. (2018) hypothesized that oriented attachment of Mg-calcite to produce mesocrystals was facilitated by negatively charged smectite particles, which locally enrich cations and could serve as a nucleation point. Frisia et al. (2018) hypothesized that colloidal silica and organics in the sediment preserved dolomite nanocrystals in the Triassic Travennazes Formation (Northern Italy) and prevented their prefect-oriented attachment. In the Dolomia Principale, which post-dates the Travennazes Formation, Meister & Frisia (2019) hypothesized that imperfect oriented attachment of dolomite nanocrystals occurred due to pH fluctuations that changed the carbonate surface charge potential, because these rocks contain much less clay. As organics, Mg-silicate clays, pH fluctuations and annual cycles of wetting and drying all occur in the Coorong Lakes, all of these mechanisms could play a role in promoting oriented attachment of nanocrystals. Alternatively, if an amorphous-to-crystalline transformation is occurring in the Coorong Lakes, templating of amorphous carbonate nanoparticles to pre-existing crystals is a mechanism that does not require movement or rotation of nanocrystals to produce crystallographic alignment.

The amorphous-to-crystalline transformation of carbonates in laboratory experiments is now a well-studied field in non-classical crystallization; however, connecting this process to field-based geological research has remained challenging because the amorphous phase is highly transient. Once a solution is supersaturated relative to an amorphous carbonate phase (for example, ACMC), the stable phase (for example, dolomite) and all the related metastable crystalline phases are also supersaturated; thus multiple pathways of mineral transformation could occur in the same solution, dependent on the kinetics of the reactions (Nielsen et al., 2014a,b). The nanometre-sized crystals and crystallographic alignment into mesocrystals by VHMC and magnesite in the Coorong Lakes suggests that non-classical nucleation and growth pathways occurred. While nanocrystals of aragonite and hydromagnesite were not observed in the Coorong sediment, it is conceivable that these two crystalline phases could have also formed via non-classical crystallization mechanisms.

**Aqueous geochemistry and non-classical crystallization of Ca–Mg carbonates in natural environments**

Numerous studies of Ca–Mg carbonate formation have noted that VHMC, ordered dolomite and magnesite do not crystallize readily despite extreme oversaturation in naturally occurring waters and laboratory experiments (Land, 1998; Arvidson & Mackenzie, 1999; Petrash et al., 2017). Where extreme oversaturation exists and Mg-bearing carbonate minerals do crystallize, determining the exact mechanisms of crystallization has been challenging. If a non-classical amorphous-to-crystalline pathway occurred in the Coorong Lakes, water SI relative to the amorphous precursors, ACMC (for VHMC and dolomite) and AMC (for magnesite), may be important geochemical controls for the precipitation of these minerals.
The $K_{sp}$ values for ACMC with a range of mol.% Mg have been experimentally derived by Purgstaller et al. (2019). Amorphous carbonate phases are much more soluble than their crystalline counterparts and the difference in solubility between the amorphous and crystalline phases increases with increasing mol.% Mg. Of relevance here, ACMC (53 mol.% Mg) is approximately 600 times more soluble than equivalent crystalline $Ca_0.5Mg_0.5CO_3$. Thus, when the ion activity product (IAP) is calculated with equivalent reactions and the SI value of crystalline $Ca_0.5Mg_0.5CO_3$ is 2.77, the water is at equilibrium with ACMC (53 mol.% Mg; $SI_{ACMC} = 0$). Currently, only one study, that of Purgstaller et al. (2019), has calculated the solubility product constants for ACMC; however, $K_{sp}$ values for ACC, the calcium endmember, have been determined in several studies. For ACC, Gebauer et al. (2008) report lower solubility products of $10^{-7.4}$ and $10^{-7.5}$, whereas Brečević & Nielsen (1989) reports a higher solubility product of $10^{-6.4}$, similar to the study by Purgstaller et al. (2019), which reports a solubility product of $10^{-6.19}$. Thus, additional research is required to confirm the $K_{sp}$ of ACMC, particularly as the amount of $H_2O$ incorporated into the structure may affect its solubility.

Here it is proposed that evaluating the saturation states for crystalline carbonate phases and their amorphous precursors may help in determining which crystallization pathway has been taken. Under a classical crystallization model, and with the relatively high SI for the crystalline phases in Coorong Lake water, the precipitation of specific carbonates, or the lack thereof, can be explained by kinetic limitations. Under a non-classical crystallization model, the formation of carbonates is instead limited by the equilibrium geochemistry of the amorphous phases. Unfortunately, the ephemeral Coorong Lakes were sampled during spring in Australia, which is a relatively wet time of year for coastal South Australia; however, it is very likely that the lakes reach equilibrium with respect to amorphous phases in the late summer and autumn. During summer, these lakes become more saline, and the alkalinity and Mg$^{2+}$ concentrations increase until the surface water is completely evaporated (Wright & Wacey, 2005). Notably, an evaporitic model for poorly ordered type A dolomite in the Coorong is proposed by Rosen et al. (1989) based on carbonate $δ^{13}C$ and $δ^{18}O$ isotopic values. Monthly sampling and isotopic analysis of the water and carbonate sediments by Rosen et al. (1995) in Lake Hayward, Western Australia, which is a similar closed-basin carbonate lacustrine system, found that the highest bicarbonate concentration and carbonate precipitation occurs during the late summer and autumn. Carbonate precipitation may also have been enhanced by late summer increases in photosynthetic activity, which can also increase the pH (Rosen et al., 1995). There may also be an increase in alkalinity or pH in the pore water, which can help to drive oversaturation, if disimulatory sulphate reduction is ongoing in the sediment (Wright & Wacey, 2005). For example, laboratory incubations of sulphate reducing micro-organisms from the Coorong Lakes result in additional Ca–Mg carbonate precipitation (Wright & Wacey, 2005).

Currently, the oceans are undersaturated with respect to ACMC (53 mol.% Mg; ACMC SI of $-1.90$) compared to the equivalent crystalline phase ($Ca_0.5Mg_0.5CO_3$ SI of 0.87; Table 2). If non-classical crystallization pathways are important in marine environments, as proposed by Rodriguez-Blanco et al. (2015), the undersaturation of ACMC in seawater may also explain why VHMC does not currently form in bulk ocean water but does form in select coastal environments with high alkalinity, such as hypersaline lagoons, the sulphate reduction zone of sediments and in photosynthetic microbial mats. Geochemical processes that generate alkalinity or increase the pH in these environments, including evapo-concentration and microbial metabolic processes, such as photosynthesis and sulphate reduction, will increase the SI for ACMC. Interestingly, in the experiment by Rodriguez-Blanco et al. (2015), after the precipitation of ACMC, the remaining solution was oversaturated with respect to dolomite with an SI of 3.00. Currently, most Holocene dolomite or VHMC forming environments have dolomite SI values of over three (Table S1). At present there is an equilibrium barrier for the formation of amorphous carbonates in seawater through an amorphous phase (SI = $-1.90$). However, the oceans during the Cryogenian may have had higher alkalinites and Mg/Ca ratios, making direct precipitation of dolomite crusts possible during early diagenesis (Hood et al., 2011; Hood & Wallace, 2012). Thus, for periods of the geological record where dolomite or VHMC appears to precipitate directly from the oceans, it can be hypothesized that the oceans were near equilibrium with respect to ACMC (ca 50 mol.% Mg), which potentially explains this aspect of the ‘Dolomite Problem’ and may give predictive

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power for understanding when direct dolomite precipitation occurs.

Interestingly, at the time of sampling all Coorong Lakes in the present study, the SI of ACMC (53 mol.% Mg) is equivalent to or higher than the Ca and Mg endmember phases (ACC and AMC; Table 2). If an amorphous-to-crystalline pathway is occurring to precipitate the Coorong carbonates, the chemical composition of the initial ACMC, which is a product of the water chemistry, may also contribute to producing the distinct mineral assemblages observed between lakes. For instance, when Radha et al. (2012) heated synthetic ACMC with >50 mol.% Mg it produced Mg-calcite and periclase (a decomposition product of hydrated Mg-carbonates or magnesite; e.g. Morgan et al., 2015), suggesting that at least two crystalline Mg-bearing carbonate phases were initially generated at a lower temperature. ACMC with >50 mol.% Mg may be the origin of the multi-phase carbonate mineral assemblages occurring in the Coorong, resulting in mixtures of VHMC and either magnesite in Milne Lake or hydromagnesite in Pellet Lake. The formation of multiple carbonate phases from ACMC has also been observed by Montes-Hernandez et al. (2020) and Rodriguez-Blanco et al. (2015) with both groups observing precipitation of monohydrocalcite (CaCO$_3$/C$_1$H$_2$O) and nesquehonite (MgCO$_3$/C$_3$H$_2$O). One difficulty in interpreting laboratory non-classical crystallization experiments in the context of natural environments, such as the Coorong Lakes, is that solutions used in the preparation of ACMC in the laboratory usually have very high CO$_3^{2-}$ concentrations and much lower Mg/Ca ratios (reviewed by Blue et al., 2017). These synthetic solutions are useful for promoting the rapid formation of ACMC; however, future experiments could emulate lake and pore water conditions in natural sedimentary environments.

**IMPLICATIONS AND CONCLUSIONS**

For over 50 years, the Coorong Lakes have been used as a sedimentological model for low-temperature dolomite formation, with a focus on *formational* conditions rather than *crystallization* mechanisms. Recent advances in understanding
nucleation and growth of crystals from the fields of physical chemistry and mineralogical crystallography demonstrate that carbonates can crystallize via classical and non-classical pathways. The present study demonstrates that very high magnesium calcite (VHMC) and magnesite particles in the Coorong Lakes were built by the particle attachment resulting in mesocrystals. Aqueous geochemical modelling suggests it is possible that these carbonate nanoparticles formed via an amorphous precursor. In the Coorong, nanocrystals are preserved in the top 1 m of sediment for up to 6000 years.

A summary model for crystallization pathways of Ca–Mg carbonate minerals is presented in Fig. 5, based on the results of the present and previous studies. This model provides a framework for investigating equilibrium and kinetic limitations on the formation of carbonate minerals in natural environments. Identifying the initial mineral formation pathway may also be important to understanding the partitioning of elements and equilibrium isotopic fractionation between the minerals and the aqueous phase. These geochemical signatures are widely used as proxies for reconstructing past environments, and a growing body of work indicates that they are sensitive to crystallization pathways and to phase transitions (e.g., Frisia et al., 2018). For example, initial work suggests that the formation of calcite from amorphous calcium carbonate (ACC) enhances Sr uptake (Littlewood et al., 2017) and biomineralization of aragonite from ACC in mollusc shells enhances incorporation of Mn (Soldati et al., 2016). Further work is also required to determine whether the high surface area of carbonate nanocrystals increases the adsorption of ions to mineral surfaces, thus increasing the total trace metal inventory that is preserved in the rock record.

Interestingly, several Proterozoic dolomites have also been described as containing crystals that are from ten to hundreds of nanometres in size (Sánchez-Román et al., 2008; Schinteie, 2011), indicating that Mg-bearing carbonate nanocrystals can be preserved for hundreds of millions of years. The presence of nanocrystals has also been hypothesized as a potential tool to differentiate between primary low-temperature dolomite and dolomitized rocks in the geological record (Meister & Frisia, 2019).

The occurrence of VHMC and magnesite as nanocrystal aggregates in the Coorong Lakes suggests that non-classical crystallization mechanisms may be important and perhaps geologically common. An assessment of crystallization pathways (Fig. 5), which is a potential geochemical control on elemental distribution and mineralization, may be a useful tool for examining Holocene carbonate environments and the ‘Dolomite Problem’ in the geological record.

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CONFLICT OF INTEREST

All authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

Raudsepp, Morgan and Wilson designed the study. Raudsepp conducted the electron
microscopy, XRD, geochemical modelling and wrote the manuscript. Wilson participated in fieldwork and contributed to data interpretation and writing. Patel contributed to data interpretation and manuscript review. Morgan organized the fieldwork, conducted pore water analysis and contributed to manuscript review. Johnston and Gagen assisted with field-work sample collection, pore water analysis and manuscript review. Fallon conducted radiocarbon dating.

DATA AVAILABILITY STATEMENT

Data available in article Supplementary Material.

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Supporting Information

Additional information may be found in the online version of this article:

Fig S1. Google Earth© image of Coorong Lakes field site.

Fig S2. Example of Rietveld refinement plot (Diffrac. TOPAS v5) showing the refined abundances of minerals at the top of Milne Lake (0 to 2.5 cm; 16ML2-20).

Fig S3. The XRD pattern of acid treated 16PL1-18 sample and a crushed hand specimen rhomb of dolomite compared to ideal dolomite and VHMC XRD patterns were modelled in CrystalDiffract v.6 based on the unit cell of these two minerals and with different crystallite sizes.

Fig S4. Scanning electron microscope (A) and (B) and low-resolution transmission electron microscope (C) and (D) images of VHMC, hydromagnesite and aragonite from the Coorong Lakes, South Australia.

Fig S5. (A) and (B) High resolution transmission electron microscope images of VHMC from Pellet Lake (0 to 2.5 cm; 16PL1-18), with an example of misaligned crystal lattice fringes.

Fig S6. Examples of VHMC rhombs and aggregates from lacustrine and terrestrial environments.

Fig S7. Examples of VHMC from sabkhas, hypersaline lagoons and tidal environments.

Table S1. Morphology of Holocene dolomites/VHMC and corresponding surface water and/or pore water geochemistry.

Table S2. Rietveld refinements of X-ray diffraction patterns from Coorong Lakes, Australia.

Table S3. Calibrated radiocarbon ages of carbonate sediment from Coorong Lakes, Australia.