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Ian J. Kelleher^a; Simon A. T. Redfern^a

^a Department of Earth Sciences, University of Cambridge, Cambridge, UK

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HYDROUS CALCIUM MAGNESIUM CARBONATE, A POSSIBLE PRECURSOR TO THE FORMATION OF SEDIMENTARY DOLOMITE

IAN J. KELLEHER and SIMON A.T. REDFERN*

*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2
3EQ, UK*

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Material of composition $\text{Ca}_{1.056}\text{Mg}_{0.944}(\text{SO}_4)_{0.035}(\text{CO}_3)_{1.965}\cdot 0.26\text{H}_2\text{O}$ has been synthesised from solutions of $\text{Ca}(\text{NO}_3)_2$, MgSO_4 and Na_2CO_3 . X-ray diffraction and infrared spectroscopy show this to be identical to “protodolomite” found in nature, and that the structure is related to dolomite but is hydrous, retaining water to beyond 200°C on heating. This hydrous magnesium calcium carbonate grows as spherules, with a distinct core–rim structure apparent in optical microscopy. It seems likely that in low-temperature environments (around 80°C) a dolomite crystal grows in nature via this or a similar hydrous intermediate phase, which may hold the solution to the “dolomite problem”.

Keywords: Hydrous calcium magnesium carbonate; Sedimentary dolomite; Protodolomite

INTRODUCTION

Dolomite, calcium magnesium carbonate ($\text{CaMg}(\text{CO}_3)_2$), is a common mineral of considerable economic importance that forms in a wide variety of geological environments. It occurs most frequently as a sedimentary mineral, precipitating from aqueous solution in a diverse range of settings; it invariably undergoes extensive diagenetic evolution after precipitation [1]. Dolomite commonly forms during hydrothermal mineralisation; in particular it forms in association with

*Corresponding author. Tel.: +44-1223-333475. Fax: +44-1223-333450. E-mail: satr@cam.ac.uk.

Mississippi Valley type ore deposits. Mineralisation occurs from highly saline solutions at relatively low temperatures (60–250°C) [2]. In metamorphic regimes, dolomite forms both as a distinct phase and by exsolution from magnesian calcites [3]. Dolomite is even known to form from late stage fluids associated with igneous intrusions. However, the most unusual reported occurrence of dolomite is as a urolith, discovered in the urinary tract of a Dalmatian hound [4].

Much attention has recently been focussed on the so-called “dolomite problem”. The precise mechanism of dolomite formation in the sedimentary environment is still not known, with many observed trends not following thermodynamic predictions. Large amounts of dolomite have precipitated over the past geological history of the Earth; by comparison, relatively little is forming now [1].

Solving the dolomite problem depends upon understanding the formation of dolomite at Earth-surface conditions. This is complicated by the fact that dolomite rarely appears to form in its thermodynamically ideal state, but rather as a metastable phase about which little is known. This material, often referred to as “protodolomite” appears to be structurally and compositionally similar to ideal dolomite [5–13]. However, the exact relationship between protodolomite and dolomite is not known as the material has never been adequately characterized. This paper investigates “protodolomite” in more detail. It describes the synthesis and characterization of a hydrous calcium magnesium carbonate phase that is similar to dolomite in composition and crystal structure, and which may act as a precursor to material which more closely resembles ideal dolomite. It also presents the first evidence that hydrous calcium magnesium carbonate phases may exist. We postulate that this may be an important precursor to dolomite formation. Its existence is important also in forming an overall picture of the nature of carbonate surfaces, since it is likely that the growth of dolomite in nature is dependent upon the interactions between Mg^{2+} , Ca^{2+} , CO_3^{2-} and water at the crystal surface. Our results suggest that this may lead to alternative metastable growth phases, and it is the thermodynamic and kinetic stability of these with respect to dolomite *sensu stricto* that may be most important in determining dolomite occurrence in nature.

DOLOMITE MINERALOGY

The structural geochemistry of dolomite has been thoroughly reviewed by Reeder [14]. Its crystal structure consists of alternating layers of cations (Ca^{2+} and Mg^{2+}) and planar carbonate groups. Although a limited solution between Ca and Mg

exists at elevated temperatures, below approximately 300°C the solid solubility of calcite and magnesite in dolomite are both very low, and the stoichiometric Ca/Mg ratio of unity is closely maintained. At higher temperatures, dolomite undergoes a cation disordering transition, transforming to the disordered phase at temperatures between 1000 and 1100°C. Below this temperature, Ca and Mg cations are ordered onto crystallographically distinct sites. Thus, the thermodynamically ideal structure of dolomite at Earth-surface conditions comprises a layer of calcium cations, followed by a layer of carbonate groups, then a layer of magnesium cations, then another layer of carbonate groups, and so on.

Sedimentary dolomite, however, rarely adheres to this crystallographic ideal. It often has an excess of Ca (up to 10 mol.% CaCO_3) and is almost never fully ordered. In fact, it often has a very low degree of metal cation order. The primary reasons for this may be summarized as a kinetic difficulty in forming such a highly ordered crystal structure at low temperatures of formation [12]. This particular problem may be related to the difference in hydration energy of a calcite (CaCO_3) surface and a magnesite (MgCO_3) surface at low temperatures [12,15].

Ancient dolomites tend to have structures closer to thermodynamic equilibrium phase than their recent counterparts, in terms of both ordering and composition. Petrological studies suggest that this occurs over geological time through episodes of dissolution—re-precipitation [12]. This represents dolomite formation via Ostwald Ripening, whereby the thermodynamic equilibrium state is reached via a succession of metastable precursors [16]. That is, in order to overcome a large energy barrier to the formation of a certain phase, it forms instead through a series of intermediary steps, each with a much smaller energy barrier to overcome. In dolomite, intermediaries with imperfect composition and ordering are well documented [5–13]. Given the difficulty in dehydrating Mg ions at low temperatures, it is perhaps not unreasonable to suggest that a hydrous intermediary may be another such step, under certain formation conditions. That is, the existence of a hydrous calcium magnesium carbonate phase may not be unreasonable. Such a phase has not been documented before, although many hydrous calcium carbonates and hydrous magnesium carbonates are known to exist.

SYNTHESIS OF PROTODOLOMITE

Calcium magnesium carbonate samples were synthesized by a method derived from earlier researchers [5–7]. Molar solutions of $\text{Ca}(\text{NO}_3)_2$, MgSO_4 and

Na_2CO_3 were prepared, and added directly to the reaction vessel to give a sample mixture with the following ionic concentrations: Ca^{2+} , 0.23 M; Mg^{2+} , 0.28 M; Na^+ , 0.98 M; NO_3^- , 0.46 M; SO_4^{2-} , 0.28 M; CO_3^{2-} , 0.49 M. This mixture is supersaturated with respect to dolomite. It has a Ca/Mg ratio of 0.82, and a salinity of 123‰. Such a solution is geologically plausible, as seen in Fig. 1. The sulphate content is rather high for a natural system, although not implausible: dolomite is found in Deep Springs Lake, CA, where brines have a sulphate concentration of 0.31–0.63 M, for example [17]. The reaction vessel itself was a pyrex tube approximately 2×10 cm, sealed with a teflon-lined screw cap, heated in an oil bath.

The three aqueous solutions were put into the reaction vessel in quick succession, with either $\text{Ca}(\text{NO}_3)_2$ or MgSO_4 first, but Na_2CO_3 always last. The reaction vessels were then sealed, shaken vigorously by hand for 5 min and immediately put into the heated oil bath. The reaction vessels were kept vertical in the oil bath. A white precipitate formed within a minute of mixing the three solutions together. This precipitate was analysed using X-ray diffraction to

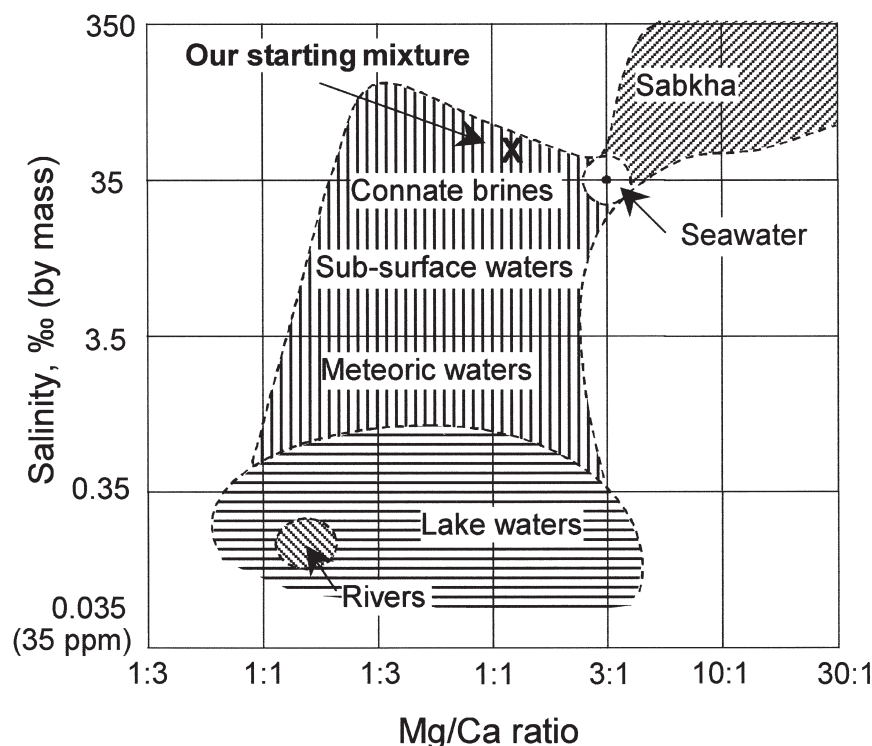


FIGURE 1 Ranges of Mg/Ca ratio and salinity of solutions found in natural sedimentary environments, after Folk and Land [25].

determine its composition. The resulting trace was very difficult to analyse since it consisted of weak, broad peaks on an intense, noisy background, reflecting that the precipitate was either poorly crystalline, or that the particle size was very small, or both. However, weak reflections that could be attributed to calcium carbonate (calcite) and calcium sulphate (gypsum) were observed. No peaks corresponding to dolomite could be identified.

The reaction vessels were vigorously shaken for approximately 2 min every 12 h during syntheses. At the end of a synthesis period, the reaction vessels were removed from the oil bath and immediately quenched by slowly rotating them under flowing cold water for 5 min. At this point all the reaction vessels contained an amount of fine-grained white powder at the bottom. Samples appeared homogeneous and identical to each other. The grains were not cemented together on a scale discernible to the naked eye. There was neither a crust on the surface of the powder nor the sides of the reaction vessel. A colourless liquid filled the rest of the reaction vessel.

The solution was decanted off and the powder scraped out. The bulk of the powder was washed and dried by suction filtration using absolute alcohol; this process was repeated five times, and produced a sample that was dry without heating. The remaining powder was further cleaned by ultrasound in absolute alcohol. After each ultrasound treatment, the absolute alcohol solvent was removed by careful pipetting; the powder left at this point was washed by suction filtration with fresh absolute alcohol. More fresh absolute alcohol was then added to the powder, and the ultrasound treatments repeated five times. Following this, the powder was rinsed through five times by suction filtration with absolute alcohol; this process also dried the sample.

Syntheses were performed at 40, 61 and 81°C, $\pm 1^\circ\text{C}$. Syntheses were run for 1, 3, 11, and 23 days, and timed so that samples were removed at the exact time of day they were put on; all durations are exact to within ± 10 min. The reaction that took place may be summarized as:



The results described here are from the samples heated at 81°C, since these were phase pure as determined by microscopy and X-ray diffraction (XRD). Samples synthesised for 1, 3 and 23 days at this temperature will hereafter be referred to as pds1, pds3 and pds23.

SAMPLE CHARACTERISATION

Samples were characterised by XRD, SEM, EMPA, FTIR spectroscopy, optical microscopy and TGA (thermogravimetric analysis). The XRD trace of sample

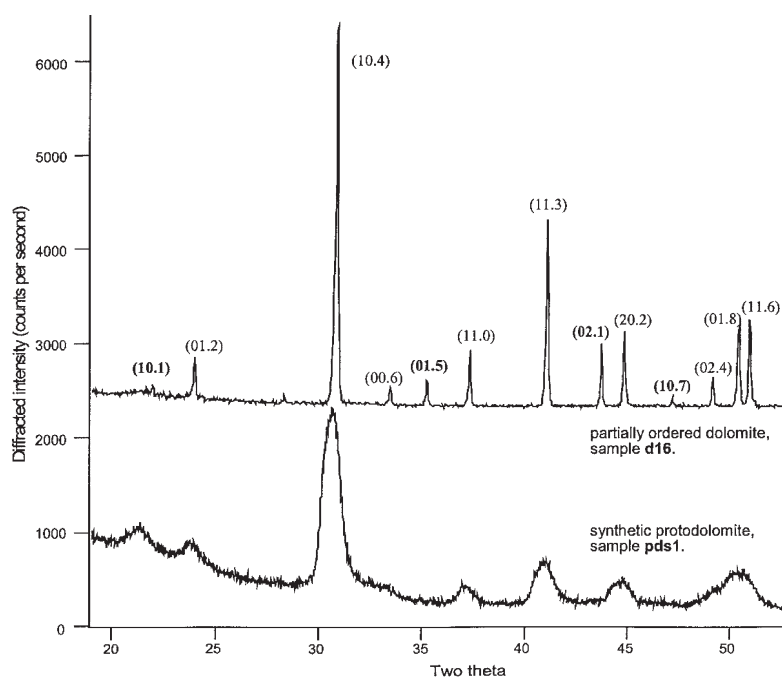


FIGURE 2 Comparison of the X-ray powder diffraction patterns of a synthetic protodolomite, pds1, and a partially ordered dolomite. Diffraction patterns were recorded using a Guinier diffractometer with $\text{CuK}\alpha_1$ radiation. Reflections from the dolomite have been indexed, and ordering superlattice reflections are shown in bold type.

pds1, synthesized for 1 day at 81°C , is shown in Fig. 2, along with the trace from a partially ordered dolomite for comparison. The similarity between the traces suggests that the crystal structure of the synthetic material is similar to that of dolomite. The lack of “superlattice” reflections, however, suggests that it is poorly ordered. The reflections from pds1 occur at slightly lower 2θ values than dolomite, suggesting it has an expanded lattice. This is more apparent from Table I,

TABLE I A comparison of the XRD data from sample pds1 fitted to a hexagonal unit cell to values for dolomite (from [14])

	Sample pds1	Ordered dolomite [Ca _{1.00}][Mg _{1.00}](CO ₃) ₂		Disordered dolomite [Ca _{0.88} Mg _{0.12}][Mg _{0.88} - Ca _{0.12}](CO ₃) ₂	
		25°C	81°C	25°C	81°C
a (Å)	4.820 ± 0.005	4.804	4.805	4.805	4.806
c (Å)	16.05 ± 0.03	16.006	16.026	16.022	16.042
Volume (Å ³)	322.8 ± 1.4	319.90	320.44	320.36	320.89

which compares a unit cell fit of the XRD data from pds1 to values for dolomite. It suggests that poor cation ordering alone cannot account for the expanded lattice observed. Residuals for individual peaks in the unit cell fit were large; the XRD data did not fit the hexagonal unit cell very well, suggesting that the structure of pds1 is strained somehow with respect to dolomite, possibly of lower symmetry, although the width of the diffraction maxima preclude further determination at present. Graf *et al.* [4] made similar observations on similar material to sample pds1. By comparing their observed diffraction pattern to theoretically calculated ones for modified dolomite-like structures, they concluded that the structure could consist of different stacking arrangements of Ca-filled and Mg-filled cation planes; or it could contain H₂O molecules, OH¹⁻ ions or both. The latter explanation was dismissed since no hydrous calcium magnesium carbonate phase was known to exist. The former explanation, however, relies on forming a highly ordered crystal structure, which seems unlikely in view of kinetic difficulties at the low temperatures of formation, as discussed above.

The characteristic appearance of the XRD trace of pds1 is usually the only evidence used to characterize a material as “protodolomite” in the literature. Some studies have used the broad, smeared nature of the reflections to suggest that the material could be poorly crystalline [9]. The FTIR and optical microscopy data presented later in this paper lead us to question this suggestion, however. An alternative explanation is that it reflects small particle size. Analysis of reflection widths, based on the Scherrer formula, from pds1 gives an approximate particle size of $90 \pm 20 \text{ \AA}$. As such, the material may be termed nanocrystalline. Its physical properties will inevitably differ to those of the bulk material, and since the ratio of surface to bulk will be greater it is anticipated that the reactivity and stability of this phase may be dominated by the physico-chemical characteristics of the surface. For example, the thermal decomposition of the protodolomite synthesised in this study occurs at 320°C, while in bulk material this occurs at around 600°C [18]. Presumably, this is due to the difference in surface area of bulk and fine-grained material. It is clear that care must be used when applying data obtained from experiments performed on bulk material to protodolomite.

Further structural and compositional information may be obtained from FTIR spectra, as shown in Fig. 3, which shows a comparison between the spectra from sample pds1 to that of well-ordered dolomite spar. The CO₃ vibrational modes are similar in both spectra, suggesting that our synthetic material has a structure similar to that of dolomite. However, the spectra of pds1 contains additional modes. A broad band of from 3100 to 3700 cm⁻¹ can be interpreted as two H₂O stretching modes at 3337 and 3472 cm⁻¹. A corresponding H₂O bending mode is present as a small shoulder on the ν_3 mode at approximately 1460 cm⁻¹. More

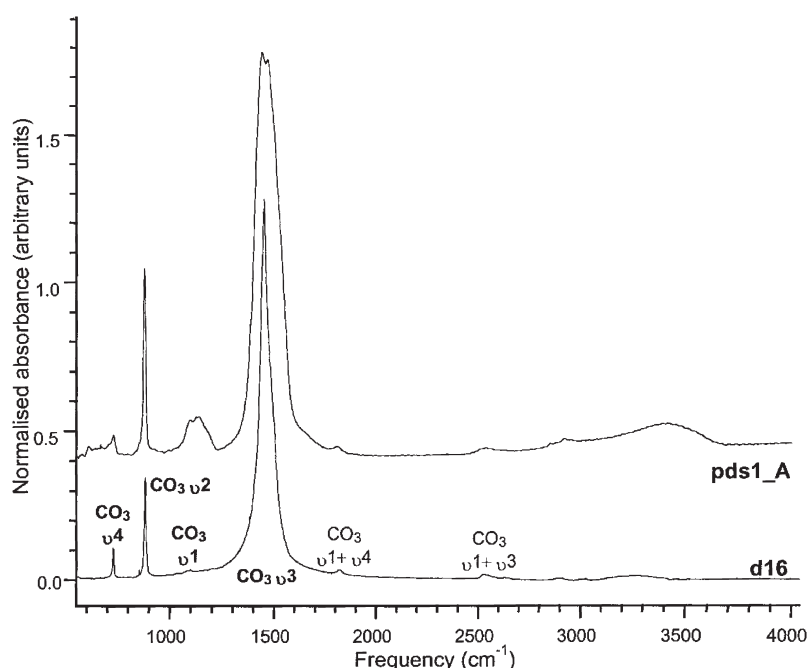


FIGURE 3 FTIR spectra of the same samples as shown in Fig. 2. The absorbance of each was normalised using the intense band at 1400 cm^{-1} .

difficult to interpret is the area of intensity from 1050 to 1200 cm^{-1} . This may include the carbonate ν_1 , symmetrical stretch mode, which, whilst theoretically being IR-inactive, is often present in spectra of dolomite. This is probably due to a slight asymmetry of the CO_3 groups caused by cation ordering between Ca and Mg and the size difference between Ca and Mg. It may also include SO_4 modes (EMPA analysis indicates the presence of 3.5% of SO_4 per formula unit within this sample). The frequencies of these modes do not correspond to any known sulphate compound, suggesting that sulphate ions are incorporated in the “dolomite” lattice of pds1 rather than as a separate phase. However, the role of sulphate in the formation of dolomitic material is unclear.

Free water molecules have a stretching mode at 3756 cm^{-1} . However, when H_2O molecules are bonded, this frequency will decrease; the shorter the bond, the lower the frequency. The modes in pds1 at 3337 and 3472 cm^{-1} would correspond to $\text{O} \cdots \text{H}-\text{O}-\text{H}$ bond lengths of 2.79 and $2.93 \pm 0.05\text{ \AA}$ respectively according to the calibration of White [19,20]. This suggests that water or hydroxyl molecules could be bonded in the structure of pds1 rather than just present as surface water. Further evidence for this comes from an in-situ heated

FTIR experiment, the results of which are shown in Fig. 4, which shows that the OH stretching band is still present at temperatures as high as 371°C. These results suggest that the synthetic material is hydrogenous, containing water or hydroxyls within the lattice or at defects.

Combining results from EMPA and weight loss on heating suggests our sample has a water content of 2.5 ± 0.7 wt%, and a chemical formula $\text{Ca}_{1.056}\text{Mg}_{0.944}(\text{SO}_4)_{0.035}(\text{CO}_3)_{1.965} \cdot 0.26\text{H}_2\text{O}$. It is slightly calcium rich, with a Ca/Mg ratio of 1.12. It may be that sulphate plays an important role in the formation of the first carbonate to precipitate, but this not yet clear.

Scanning electron microscopy (SEM) was used to investigate the microstructure of our synthetic protodolomites. In SEM, a specimen is bombarded with a very fine probe of electrons at accelerating voltages up to 30 kV. Micrographs of sample pds1 are shown in Fig. 5 and show that it exists as fairly uniform spheres, 15–30 μm in diameter. The size distribution is very uniform; most spheres are about 22 μm in diameter. A closer examination of the spheres suggests that they are an aggregation of sub-micron sized anhedral particles, rather than each sphere being a single crystal. The particles appear to be

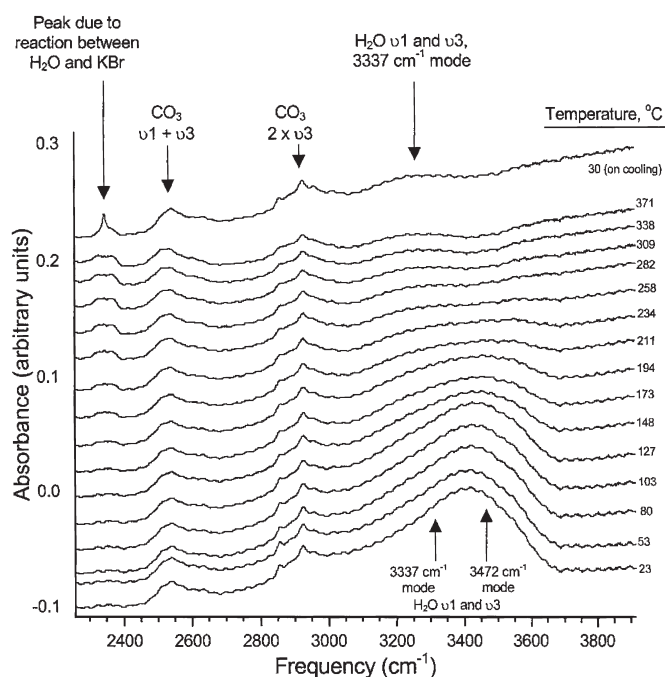


FIGURE 4 The change in intensity of the OH stretching mode of water is seen in these FTIR spectra taken from pds1 on heating from 23 to 371°C.

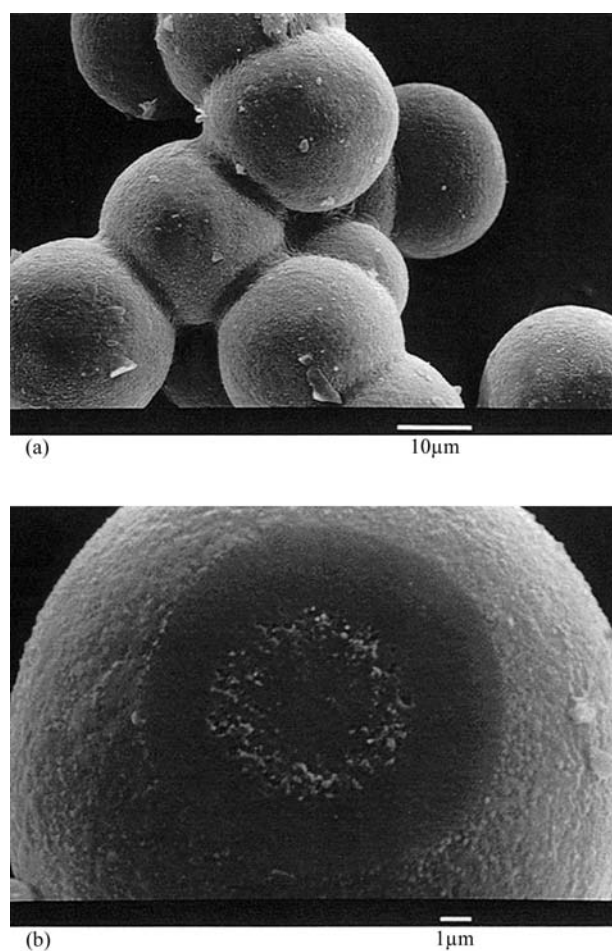


FIGURE 5 SEM micrographs of sample pds1, showing spheroidal particles.

arranged randomly within a sphere. Micrographs of samples pds3 and pds23 are shown in Fig. 6, and show a distinct overgrowth of euhedral micron-sized crystals on the rims of the spheres seen in sample pds1. The texture shown by sample pds23 suggests that the euhedral phase forms by dissolution and reprecipitation of the anhedral phase.

Samples for optical microscopy were prepared by putting small droplets of optically transparent epoxy, normally used for mounting thin sections, onto microscope slides. Small amounts of our fine, powdered synthetic protodolomite material were sprinkled onto the droplets of epoxy, which were left to harden. The slides were cut, ground and carefully polished in the same way as thin

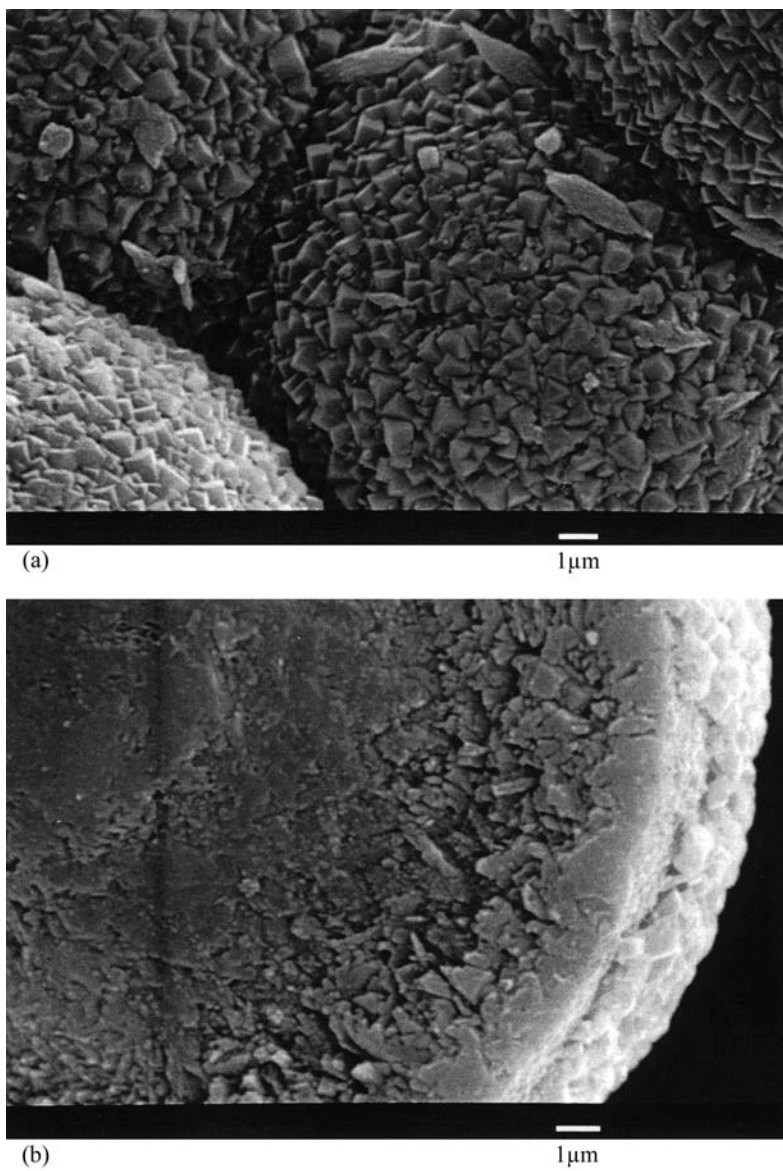


FIGURE 6 SEM micrographs of (a) sample pds3, showing the growth of euhedral crystals upon the spheroidal particles, (b) pds23, where the relationship between the overlying euhedral crust and the underlying spheroidal grain suggests that the euhedral component forms by dissolution and reprecipitation of the anhedral spheroidal particle.

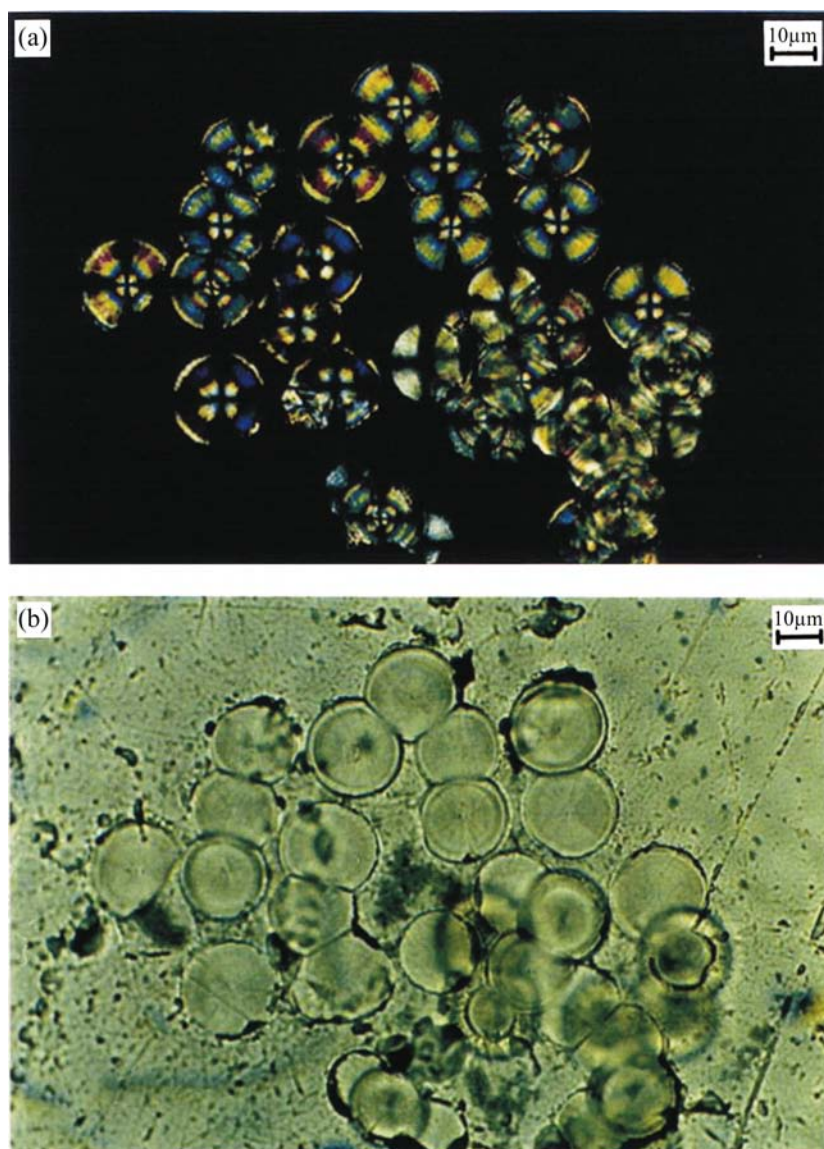


FIGURE 7 Optical micrographs of sample pds3. Both figures show the same view: (a) is imaged through crossed polarisers, while (b) is imaged in plane polarised light. These images show that the orientation of the optical indicatrix of the material in the core and rims of the spherules differ.

sections. The slides were viewed with objective lenses of up to one hundred times magnification. Optical micrographs of sample pds3 are shown in Fig. 7(a) and (b). Both micrographs show the same view; Fig. 7(a) is imaged through crossed-polarisers, Fig. 7(b) is viewed in normal light. All the particles appear to be circular; from this we have inferred that the material probably exists as spherical particles approximately $20 \pm 5 \mu\text{m}$ in diameter. There appear to be two distinct phases, one in the cores of spheres, one on their rims. The relationship between the two phases appears very similar to that observed in our SEM analyses of the same material (shown in Fig. 6). We will refer to the two phases as the “core” phase and the “rim” phase.

Fig. 7(a), sample pds3 viewed under crossed-polarisers, suggests that both the “core” phase and “rim” phase are crystalline, since both are birefringent. All the particles in the core phase appear to be oriented with their optic axis (the [00.1] direction) parallel to radii, as indicated by the cross-shaped extinction pattern that the material shows under crossed-polarisers. The euhedral crystals in the “rim” phase appear to be oriented identically, as shown by the fact that the extinction pattern appears to be continuous through the core–rim boundary. A quartz wedge was used to determine the order of the interference colours in the two phases. The rim phase typically showed high second order and third order interference colours. The core phase typically showed first to low second order interference colours. That is, lower order interference colours were observed in the cores of the spheres, despite them being much thicker than the rims. We infer from this that the rim phase has a significantly higher birefringence than the core phase. There is a significant difference between the birefringence of the two phases on the either side of the boundary between them; this suggests that the observed difference in birefringence is not just due to orientation. The birefringence of the rim phase appears to be similar to that of dolomite.

DISCUSSION

Evidence suggests that hydrous calcium magnesium carbonate phases can exist. Such material is structurally and compositionally similar to dolomite, and has a low degree of cation ordering. It is metastable with respect to dolomite of composition $\text{CaMg}(\text{CO}_3)_2$ and complete cation ordering. Episodes of dissolution–reprecipitation may transform it into material which more closely resembles this thermodynamically ideal state; thus, we have the model of dolomite growth via Ostwald Ripening. The formation, early in the diagenetic history, of a hydrous calcium–magnesium carbonate phase may be a kinetic answer to the problem of dehydrating magnesium ions at low temperatures of

formation. Nucleation of the initial carbonate phase is the key kinetic step in the formation of dolomite [21,22].

One obvious question is, do hydrous calcium magnesium carbonate compounds occur in nature? Such compounds would be hard to distinguish from “normal” anhydrous dolomite, particularly with the routine methods of carbonate analysis, so the possibility does exist. The fact that a hydrous phase may only exist for a very short time in the diagenetic history of a dolomite’s formation, perhaps measurable in days, increases the possibility that they may have previously been overlooked. However, whilst the evidence from the textures of natural samples looks promising [11], this must remain speculation until further work, including a more detailed analysis of the chemistry involved in the formation of the hydrous phase, is carried out. For instance, the importance, and possible role, of sulphate ions in this process is not known. The literature on dolomite formation contains many references to the effects of sulphate; some say it increases the rate of dolomite formation, some say it decreases it. A closer reading, however, suggests that sulphate may increase the rate of nucleation [8,20] but decreases the rate of crystal growth [23]. Such changes would be amenable to further study by AFM, which could diagnose the dependence of morphology on changes in the sulphate content. Further investigation of the roles of sulphate is, however, a future challenge.

It is possible that hydration may be even more significant in natural material. For instance, sample pds1 was synthesized at 81°C and contains 2.5 wt.% H₂O. One might expect that at lower temperatures of formation, closer to the conditions where dolomite is forming in sedimentary environments, the water content might be higher.

The properties of hydrous calcium magnesium carbonate are likely to differ significantly from the anhydrous material. In particular, the enthalpy of formation, free energy, and solubility will be different. This is important when we consider that most of the models for dolomite solubility, and reactivity, are based on values obtained from analyses of anhydrous material, often ignoring cation ordering. Since sedimentary dolomite invariably precipitates as a metastable phase, the models are inherently inaccurate. This emphasises the lack of energetic data that exists for the dolomite system. It is clear from simple entropy considerations that changes in cation ordering (as well as changes in Ca/Mg ratios) have a significant effect on the free energy of dolomite. The influence of changes in cation ordering on the kinetics of dissolution and precipitation of dolomite has never been properly quantified, however. There is a similar need for a study of the effects of hydration, based on thorough thermodynamic data.

The nanocrystalline nature of the material we have synthesised also has implications that need to be considered in more detail. For instance,

nanocrystalline materials are likely to have different solubility rates than their bulk counterparts, and may undergo different reactions. It is likely that nanocrystalline dolomite does exist in nature, since the indicative XRD trace, shown in Fig. 2, is very similar to that commonly used as the diagnostic characteristic of material described as “protodolomite” in the literature.

The formation of a hydrous calcium magnesium carbonate is likely to be energetically easier than the anhydrous analogue, since it lessens the problem of dehydrating, in particular, magnesium ions. That is, there is likely to be a smaller kinetic barrier to the formation of the hydrous compound. However, the hydrous compound will only form under certain chemical conditions (for example, there are likely to be limits for temperature, pH, $[\text{Ca}^{2+}]/[\text{Mg}^{2+}]$, salinity, $[\text{SO}_4^{2-}]$ to name but a few). The possibility exists, therefore, that certain natural conditions may allow dolomite formation to occur through this energetically easier route. That is, small changes in natural conditions could cause large changes in the rate of dolomite formation.

Since natural dolomite formation is dominated by metastable and largely uncharacterised phases, the term “protodolomite” should perhaps be avoided. Currently, it is a very loosely defined term, often applied to material on the basis of very little analysis; its use is misleading at best. One solution is to use the name dolomite for all material with the approximate composition $\text{CaMg}(\text{CO}_3)_2$, and the general crystal structure as shown by XRD analysis, but supplementing this with thorough characterization of metastable proto-phases, primarily in terms of composition (Ca/Mg ratio and H_2O content) and cation ordering.

CONCLUSIONS

The existence of a hydrous calcium magnesium carbonate phase raises more questions than it answers. The chemical conditions necessary for its formation need to be better constrained, and this may be one route towards considering its possible occurrence in nature. If this proves to be the case, it represents another, and perhaps energetically easier, route by which dolomite may form. Thus, under certain chemical conditions, the possibility exists for accelerated rates of dolomite formation.

The thermodynamics and kinetics of water content and the incorporation of hydrogen into dolomite during its growth need to be understood in much more detail if we are to have reliable models for natural dolomite formation. To this end, the recent work of de Leeuw and Parker [24], in exploring hydrated surfaces and low-temperature hydrous carbonates such as ikaite by computational

methods, would appear to be a useful approach to shedding further light on the dolomite problem.

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