

Deposition, Diagenesis and Practical Applications of Limestones, Dolostones and Associated Deposits

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By

Colin J.R. Braithwaite

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CHAPTER 0

WHY STUDY CARBONATE DEPOSITS?

James Lee Wilson, in his book *Carbonate facies in Geologic History* published in 1975, observed, “since 1950 geologists have learned more about the origin and lithification of carbonate sediments than in all the previous years of the history of science”. He was right, but we have not stopped. **Carbonate rocks, limestones and dolostones**, represent only about 15% of those currently forming continental areas, but have a disproportionate economic significance. They provide the reservoirs for about 50% of the World’s **oil reserves** and locally host a variety of **deposits**, including **lead-zinc-barite-fluorite** and **copper ores**, bauxite and **phosphorites**. Limestones are fundamental ingredients in the manufacture of **cement**, required to make concrete, and provide both **building stones** (dimension stones and cladding) and **aggregates**. Their use in the construction of iconic buildings, like the Palace of Westminster, housing the United Kingdom Parliament, and many of the architectural wonders of the world, including St. Peters church in Rome, the Taj Mahal in India and the Great Pyramid at Giza in Egypt are testament to their structural and aesthetic value. Carbonate rocks also give rise to some of our most startling landscapes, in distinctive **karst scenery**, like that in the Guangxi Province in China, and in countries flanking the eastern shores of the Adriatic Sea. As a result, they have the distinction of generating some of the most intractable **hydrogeological** and **foundation problems** for engineers. The carbonate sediments from which these rocks originate dominate present-day tropical coastal and shelf environments, and locally form significant proportions of shelf sediments in temperate seas. Their environmental importance reflects the intrinsic biodiversity of sediments and structures like coral reefs, that support important fisheries and act as natural sea defences. Carbonate deposits underpin the foundations for a wide range of coastal works and offshore structures in what are today rapidly developing communities.

Introduction

The geological background to carbonate deposits includes an examination of their compositions, origins, and distributions. Descriptions of the general characteristics of the most common carbonate minerals include their chemistry and structural features, together with guides for their identification. The varied modern environments in which carbonate deposits form, offer conceptual models of such systems for the geologist and earth scientist, and a predictive framework for the subsurface geometry of hydrocarbon reservoirs, hydrological systems, and engineering works occupied by them. Depositing environments include tidal margins, shallow lagoons, coral reefs, continental shelves, and the deep oceans, in the marine realm, together with cave, stream and lake deposits, and calcretes in land-based systems.

Descriptions of the changes that occur in carbonate sediments after burial, and ultimately lead to the formation of limestones and dolostones, provide an understanding of the processes of compaction, the growth and characteristics of cements, and the roles played by dissolution and recrystallization, with the concomitant evolution of porosity and strength. Dolostones result largely from the alteration of limestones, and the section devoted to them reflects their importance as host rocks for both hydrocarbons and mineral deposits, but also sheds light on the issues of migration of the fluids involved in diagenetic changes. Schematic classifications simplify the description of carbonate deposits and of porosity. They provide information for earth scientists but also a reference framework for others unfamiliar with terms but who need to understand and evaluate reports provided by geoscientists.

The geomorphology and hydrology of karst regions reflect the peculiarities of landforms developed on rocks that are relatively soluble, but also bear on economic issues. Methods of exploitation depend both on the natural characteristics of the rocks and on their intended use. Discussion of the mechanical properties of carbonate sediments, limestones and dolostones underline the difficulties of predicting strength and permeability and the potential hazards associated with construction in landscapes where carbonate rocks dominate. Case histories and examples demonstrate the part they play in hydrocarbon and mineral deposits. Locally, features of the rocks themselves such as their fossil content, have become issues for conservation and the subject of legislation.

Acknowledgements

This work grew from a project initiated by the International Society for Soil Mechanics and Geotechnical Engineering (ISSMGE) led by Peter Fookes, and I am grateful for the constructive advice offered during initial production. The intention was to provide a review of the characteristics of carbonate rocks and sediments for geotechnical engineers but, because of their economic importance in the petroleum and minerals industries, there was also a need to incorporate undergraduate geologists and earth scientists, and non-specialists. Thus, the original objectives have been significantly enlarged and updated here.

My interest in limestones was first aroused by Robin Bathurst, and I owe much to encouragement from him and from Wally Pitcher. Following research on Devonian carbonates, James Taylor provided an opportunity to study present-day carbonate environments on Mahé in the Seychelles, and fieldwork has since taken me to Aldabra, Australia, The Bahamas, Florida, Kenya, Mauritius, Sudan, and Tobago. I have worked with students on limestones in Iraq, in Ireland, Libya, Norway, Saudi Arabia and the UK, on projects related to the hydrocarbons, minerals, and civil engineering industries. My work has been supported by the UK Natural Environment Research Council, The Royal Society of London, The Carnegie Trust for the Universities of Scotland, the European Community, The Royal Academy of Engineering, and The Leverhulme Trust. Over the years, I have benefitted from collaboration with many people, but mention John Taylor, Lucien Montaggioni, and Gilbert Camoin in particular.

SECTION 1

MINERALOGIES AND CHARACTERISTICS OF CARBONATE SEDIMENTS

CHAPTER 1

MINERALOGY OF CARBONATE SEDIMENTS AND ROCKS

Introduction

Carbonate sediments, and the rocks derived from them, differ from other sedimentary deposits. Unlike typical silicate mineral and rock grains, that form the sediment released by land-surface weathering and erosion, and are transported to the site of deposition, most carbonate grains, and thus sediments and rocks, originate within the basin of deposition and many show little influence of transport.

There are approximately 150 carbonate minerals, many of which have several varieties, but only six are common in natural environments. Their descriptions provide details of chemical compositions and information on mineral structures relevant to their behaviour, together with physical properties and practical field guides to identification. A brief section describes the use of isotopes and their value in determining conditions of formation, rates of accumulation, and the age of deposits.

Six carbonate minerals are present in recent sedimentary deposits, and in the rocks formed by processes following burial, that are grouped under the term 'diagenesis'.

Calcite	CaCO_3
Dolomite	$\text{CaMg}(\text{CO}_3)_2$
Aragonite	CaCO_3
Siderite	FeCO_3
Magnesite	MgCO_3
Ankerite	$\text{Ca}(\text{MgFeMn})(\text{CO}_3)_2$

Calcite and dolomite are the most abundant carbonate minerals, and together represent around 90% of natural occurrences. Although aragonite is common in many present-day environments, it is metastable, and is typically lost from rocks with increasing age. Two other metastable

carbonates, ikaite and vaterite, both polymorphs of calcite, are rare but are of local importance. Detailed descriptions of these minerals and of their physical and chemical properties are available in Chang *et al.*, 1998.

Carbonate Minerals

Calcite CaCO_3

Physical properties: Calcite commonly forms trigonal prismatic crystals with either low-angle rhombohedral (nail-head) or scalenohedral (dogtooth) terminations, but there are over 300 variations in morphology that include both fibres and powders. Twinning, in which two or more crystals of slightly differing orientation share structural elements, is common. Calcite crystals are typically colourless and transparent or white, but there are also yellow, blue, red, and brown varieties. There is a perfect cleavage, a natural planar separation within the crystal, reflecting the distribution of relatively weak bonds in the atomic structure. These define three intersecting planes, forming characteristic rhombohedral fragments when the crystal breaks. Hardness is 3.0 on Mohs' scale, and specific gravity is typically 2.72, ranging up to 2.94, depending upon added elements. However, because a large proportion of carbonates in present sedimentary environments are a result of organic activity, reflected in skeletal growth and external biochemical processes, fresh grains commonly do not show these structurally defined features. Calcite has high refractive indices, with a wide disparity between high and low values (1.658–1.486), commonly illustrated by the double image of features viewed through transparent crystals or cleavage rhombs. But as a result, in thin-section under the microscope, calcite has a high birefringence and, using crossed polars, produces pale high-order interference colours, although these may not be obvious in sections thicker than the standard 30 μm .

Practical identification: The simplest means of identifying calcite in the field is to use a few drops of dilute (10%) hydrochloric acid that typically produce a vigorous effervescence. Staining with Alizarin Red-S dye (0.1 g in 100 ml of 0.2% HCl) will differentiate calcite and dolomite. Both calcite and aragonite turn red in this solution, whereas dolomite remains colourless, largely because it reacts more slowly. The addition of potassium ferricyanide to the solution will turn ferroan calcite (in which iron replaces some calcium in the structure) purple. Dickson (1966), Friedman (1959), and Milliman (1974) describe a variety of other staining techniques,

including Clayton Yellow (also referred to as Titan Yellow), that preferentially stains high-magnesium calcite, common among organic skeletal varieties. This requires a solution of 0.5 g of stain, 0.8 g of NaOH and 2 g of EDTA (ethylenediaminetetraacetic acid) in 500 ml of water. Etch the sample in dilute acetic acid for 30 sec and blot away the excess acid before immersing it in the EDTA solution for 30 min. Magnesium calcite will turn bright yellow.

Many calcites are fluorescent, with colours varying with impurities and with the wavelength of the ultraviolet light between pink and blue. They are commonly also optically luminescent (cathodoluminescent), typically with red-orange shades that also vary with differences in composition.

Mineralogy: Calcite and dolomite both have rhombohedral unit cells, the basic building blocks of the atomic structure of their crystals but are described, as a matter of convenience, in terms of hexagonal crystal symmetry. In calcite, the long axes of crystals connect the acute angles of the rhombohedra and lie at right angles to the common and widely recognized rhombs formed by cleavage of the calcite crystal (Fig. 1.1). The carbonate (CO_3) group is the fundamental structural unit that appears in a wide variety of carbonate minerals, consisting of a central carbon and three oxygen atoms that form the vertices of an equilateral triangle. In calcite, the triangles are perpendicular to the three-fold (long) axis of the crystal, forming separate layers in which, although the carbonate units all point in the same direction, they face in opposite directions in alternate layers. Layers of calcium (Ca) atoms alternate with the carbonate layers along the c-axis of the crystal.

The carbonate (CO_3) group is the fundamental structural unit that appears in a wide variety of carbonate minerals, consisting of a central carbon and three oxygen atoms that form the vertices of an equilateral triangle. In calcite, the triangles are perpendicular to the three-fold (long) axis of the crystal, forming separate layers in which, although the carbonate units all point in the same direction, they face in opposite directions in alternate layers. Layers of calcium (Ca) atoms alternate with the carbonate layers along the c-axis of the crystal. Because the bonds between the carbon and oxygen atoms are four times stronger than those between oxygen and calcium, the directions taken by the cleavage planes within the crystals break very few of the Ca-O bonds and none of the C-O bonds.

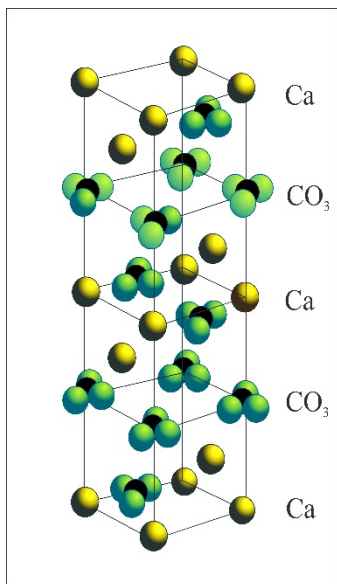


Fig. 1.1. Schematic illustration of the hexagonal unit cell of calcite showing how the independent Ca atoms, and CO_3 groups form alternate layers (after Lippman, 1973).

Relatively pure calcite, CaCO_3 , lacking other ions, is the dominant form generated in limestones after prolonged **diagenesis**, the process in which minerals in a rock equilibrate with the ambient physicochemical groundwater environment, and in which less-stable polymorphs (like aragonite) are progressively replaced (Chapter 11). Many organisms use calcite as a skeletal mineral (Chapter 2) and it forms the carbonate cement commonly found in freshwater environments, including soils, precipitation in caves and around both cool-water and thermal springs (Chapter 7).

Small amounts of magnesium (up to 20 mol %) may be included within the calcite structure, substituting for the calcium (Ca) ions. Such **high-magnesium (high-Mg) calcite** is common in the skeletal remains of a variety of marine organisms, but particularly red calcareous algae, foraminifera, bryozoans, echinoderms, and barnacles (Chapter 2). High-magnesium calcite may also crystallize directly from seawater, forming marine cement (Chapter 10). The substitution of Mg for Ca within the atomic structure is possible because the Mg atoms are smaller, but the distortions in structure that result mean that high-magnesium calcites are less stable (and therefore more soluble) than those containing only calcium.

There is a temperature dependent trend of decreasing Mg content in biogenic (organically formed) calcites from the tropics to the poles but there are additional factors. The magnesium concentration depends on the level of saturation of the seawater with respect to magnesium (Mackenzie *et al.*, 1983) and the rate of change varies between different organisms. In red calcareous algae magnesium may range from 5–30 mol percent MgCO_3 over a temperature range of 30°C . In most organisms, higher temperatures result in skeletons with higher Mg contents. Without additional magnesium, calcite is **low-magnesium** (or **low-Mg**) **calcite**. Various other divalent cations may substitute for Ca in the calcite structure, including Fe, Mn, Zn, Co, and Ni. Total substitution by iron forms the mineral **siderite**, a common component of carbonate nodules in sediments.

Dolomite $\text{CaMg}(\text{CO}_3)_2$

Introduction: Until recently, geologists used the name 'dolomite' for both the mineral and rocks consisting mostly of the dolomite mineral. This can be misleading, and many workers now prefer to use the term 'dolostone' for the rock, to avoid confusion. The rock 'dolomite' was first described in the mountains of Northern Italy by Déodat de Dolomieu and named after him by Nicolas de Saussure in 1792. In translation 'dolomie' became 'dolomite', with the traditional 'ite' suffix for minerals and, but for common usage, this would have had precedence. Dolomite/dolostone typically forms as a replacement of limestone and varied views of its origins are discussed in Chapter 12.

Physical properties: Unlike calcite, dolomite crystals are trigonal and typically form rhombohedra. However, those growing at higher temperatures commonly have curved crystal faces. In thin section, under the microscope, such crystals are referred to as **baroque or saddle dolomite** and show a sweeping extinction reflecting distortions of the atomic structure. As in calcite, simple twins are present, and there is again a perfect rhombohedral cleavage. Pure dolomite is typically white or colourless but, in the natural world, crystals are commonly yellow or brown, reflecting the incorporation of iron, and there are rare pink varieties. Hardness is 3.5–4.0 on Mohs' scale, with a specific gravity of 2.86 for typical dolomite, ranging up to 3.10 for **ankerite** in which iron replaces some of the magnesium.

Practical identification: Physical properties are not usually enough to separate dolomite from calcite, particularly if the two minerals occur as

interlocking crystalline masses. However, dilute acids (e.g., 10% HCl) produce a vigorous effervescence with calcite but have little immediate visible effect on dolomite, and this offers a useful means of differentiation in the field. As described above, calcite rapidly accepts organic stains such as Alizarin Red-S, whereas dolomite appears to be unaffected. By contrast, dolomite turns orange-red when boiled in an alkaline solution (30% sodium hydroxide, NaOH) with Titan Yellow or one of several other organic stains, whereas calcite is unaffected (Friedman, 1959). In a solution of potassium ferricyanide in dilute (hydrochloric) acid, ferroan varieties of both dolomite and ankerite stain bright blue. More precise identification relies on X-ray diffraction of powdered samples, and comparisons of the intensities, or ratios of selected X-ray reflections, with standard calibration curves providing estimates of the relative proportions of calcite and dolomite in bulk samples (Tennant and Berger, 1957). Dolomite replacing limestone may form structureless sucrosic (sugary) masses, but selective fine-grained growth may mimic the forms of original features such as fossils or ooids, or larger scale depositional structures such as cross bedding, in precise detail. Coarser crystals may retain staining or trails of inclusions that also replicate the structures of the grains replaced (Chapter 12).

Mineralogy: The structure of dolomite (the mineral) is, in some respects, like that of calcite. However, because of differences in their atomic radii, the two cations, Ca and Mg, form separate alternating layers and are not typically mixed. Layers of carbonate ions interleave with the cation layers (Fig. 1.2). This regular alternation is one of the key reasons why, although on grounds of solubility dolomite should be the first mineral to crystallize from evaporating seawater, it is relatively difficult for the cations to segregate in the precise manner required to form an organized structure. Thus, rapidly grown crystals are commonly disordered, forming so-called proto- or calcian-dolomites, and may contain an excess of calcium, only later recrystallizing to give a more ordered structure.

An additional difficulty occurs because of the greater affinity of the magnesium ions for water, such that the adsorption of magnesium to crystal surfaces inhibits further growth by preventing the attachment of other ions.

It is therefore kinetically easier for dolomite to replace calcite than for it to form by an independent process of crystallization. For these reasons, together with the widespread petrographic evidence of replacement, all large-scale dolomite bodies appear to have formed by the replacement

of existing limestones. There is, however, local evidence of direct precipitation, including reports of microbial activity in some examples. There is also clear evidence of local replacement of dolomite by calcite.

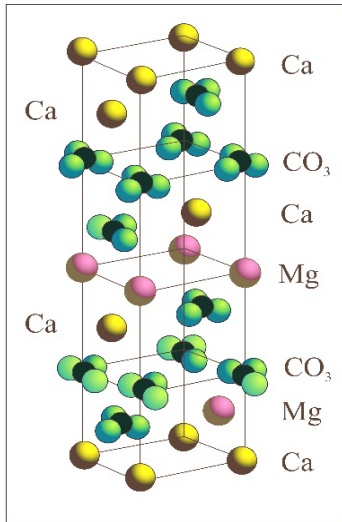


Fig. 1.2. Schematic illustration of the hexagonal unit cell of dolomite showing how the layers of Ca and Mg atoms alternate with each other and with CO_3 layers (after Reeder 1983).

As noted, the ionic radius of the Mg ion is smaller than that of Ca, resulting in a shorter bond length of the MgO ion. The effect of this is to force a slight rotation of the carbonate units in the dolomite structure relative to those in calcite. As a result, the structure of dolomite is denser than that of calcite. Some workers have argued that where dolomite replaces calcite the resulting decrease in volume (13%), is responsible for the higher porosity of the dolostones relative to their precursor limestones. However, changes in the characteristics of the bulk rock depend more on the mass balance of the replacement reaction than on the fact of replacement and such figures can be grossly misleading. **Ankerite**, $\text{Ca}(\text{MgFe})(\text{CO}_3)_2$, has the same structure as dolomite but in this Fe-ions are thought to substitute largely for Mg. The mineral is a **ferroan dolomite** where $\text{Mg} > \text{Fe}$ and is **ankerite** where $\text{Fe} > \text{Mg}$.

Aragonite CaCO_3

Physical properties: Aragonite crystals are typically orthorhombic and prismatic or acicular, but repeated **twinning** may result in pseudo-

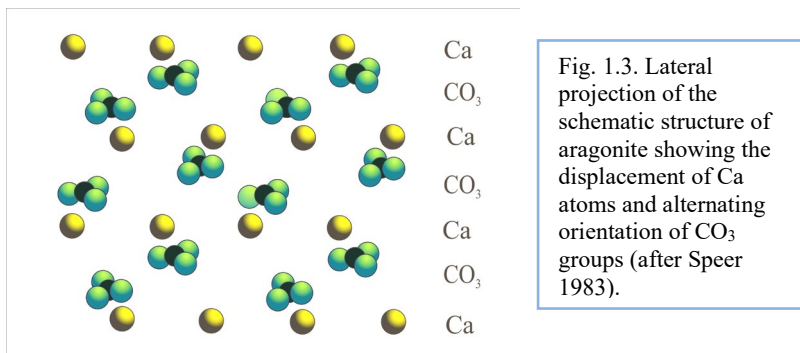
hexagonal forms. Crystals may be transparent, white, yellowish or, rarely, greenish, or violet. Unlike calcite, there is only one poor cleavage. Hardness is 3.5–4.0 on Mohs' scale and specific gravity is 2.95. However, most of the aragonite in surface sediments is of biological origin and, like the calcite formed in this way, does not show all the physical properties of the pure mineral. Like high-Mg calcite, aragonite can precipitate directly from seawater and is widespread in present-day tropical shallow seas. It also forms in high pressure, low temperature, metamorphic rocks associated with subduction zones (blueschist facies). Experiments show that in these, it crystallizes at pressures of 5–10 kbar and temperatures of 400–700°C, but pressure is the key and, as it falls, aragonite converts spontaneously to calcite above ~400°C. Because the structure of aragonite is denser than that of calcite, volume-for-volume replacement by calcite results in a net export of material, equivalent to about 8% of the original aragonite volume, as calcium carbonate-rich fluid, providing an important source for the growth of carbonate cements elsewhere in the rock volume.

Practical identification: It is not easy to differentiate aragonite and calcite but staining again provides a useful aid. Two methods are available. The sample may be boiled for 20 minutes in Meigen's Solution, a 1.0 N solution of $\text{Co}(\text{NO}_3)_2$. Aragonite turns purple, whereas calcite should remain colourless, although high-magnesium calcite sometimes also stains. An alternative, Feigl's solution, 7.1 g of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 2–3 g of AgSO_4 , 100 ml of distilled water and a few drops of 1 % NaOH solution, produces a dense black precipitate on aragonite. However, this may take up to half an hour to form, the solution is difficult to prepare and store, and the opaque precipitate hinders observations in thin sections.

Aragonite and calcite may also be differentiated using X-ray diffraction. Comparative measurements of peak heights are the simplest method, but calcite from different sources commonly shows different peak heights and a more accurate method is to measure peak intensity. Unfortunately, as noted by Milliman (1974), even this method may be compromised by errors that affect the quality of results.

Mineralogy: Although aragonite has essentially the same chemical composition as calcite, it differs structurally, and crystals have an orthorhombic symmetry (Speer, 1983). The calcium ions form layers parallel to the basal plane of the crystals, with alternate atoms displaced fractionally above or below the layer. The carbonate ions form similar distinct layers, with groups alternating in orientation, like calcite, and displaced above and below the layers to give a regular corrugation (Fig.

1.3). There are relatively few substitutions, but in typical marine aragonite up to about 8,500 ppm strontium (Sr) may replace Ca ions and typical Sr values are 3 to 5 times higher in aragonite than in most calcite. Although less common in nature, complete substitution within the aragonite structure forms the minerals strontianite (SrCO_3), witherite (BaCO_3) and cerussite (PbCO_3). Calcite crystals that have replaced aragonite sometimes preserve microcrystals of strontianite.



Many invertebrate organisms use aragonite as a skeletal material, particularly bivalves and corals in present-day seas, and it is common also as marine cement and forming ooids, crystallizing directly from seawater (Chapter 3). However, although it is the least stable of common carbonate minerals it has also been widely reported from fresh-water deposits in caves (speleothems, Chapter 7) and hot springs.

Siderite FeCO_3

Siderite is isostructural with calcite, but pure FeCO_3 is rare in nature, because of the common substitution of Fe^{2+} by ions such as Mg^{2+} and Mn^{2+} . Siderite occurs in sedimentary sequences both as interbedded “clay ironstones”, and as “septarian” nodules. Crystals are rhombohedral, but typically show curved or striated faces, like those of baroque dolomite. They range in colour from yellow to dark brown or black, the latter commonly reflecting the incorporation of manganese. Hardness is 3.75–4.25 on Mohs’ scale, with a specific gravity of 3.96. However, neither of these properties is easy to determine in fine-grained varieties forming nodules. Crystalline siderite, filling veins, and sometimes referred to as chalybeate, are associated with some mineral springs. Siderite formation in sediments is typically a reflection of reducing conditions in which sulphide activity is relatively low and carbonate activity high. It is

commonly found in non-marine or brackish-water environments, like those represented in the Upper Carboniferous rocks of Europe and North America. Because siderite contains up to 48% iron, in the past it locally formed an important iron ore.

Magnesite MgCO_3

Magnesite typically occurs as fine-grained white powdery masses, commonly as an alteration product of magnesium-rich metamorphic or igneous rocks, but also as a sediment associated with the hydrated form hydromagnesite $\text{Mg}_4(\text{CO}_3)_3(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ and other carbonates. Magnesite and hydromagnesite are found in recent sediments of glacial Lake Bonneville, Utah (Graf *et al.*, 1961), in the Coorong, South Australia (von der Borch, 1965), and in Salda Lake in Turkey (Braithwaite and Zedef, 1996, see Chapter 7), where precipitation has been attributed to the biochemical activities of diatoms and cyanobacteria.

Magnesite has a calcite-type structure and there is a complete solid solution series between magnesite, MgCO_3 , and siderite, FeCO_3 . Magnesite has a hardness of 3.5–4.5 on Mohs' scale, and specific gravity of 3.0–3.2. When viewed in thin section on a microscope, under crossed polars, it appears like other carbonates. Birefringence is high, with crystal colours typically a pale pearly grey (high-order white). In the field, it can resemble dolomite, as it is only slightly soluble in dilute HCl, but Stevens and Carron (1948) suggested using an "abrasion pH" to differentiate the two minerals. A series of indicator papers measure this and magnesite has a reported abrasion pH of 10–11, whereas dolomite is 9–10 and calcite 8.

Ankerite $\text{Ca}(\text{MgFeMn})(\text{CO}_3)_2$

Ankerite is isostructural with dolomite with only slight changes in interatomic distances. It typically occurs in sedimentary rocks, commonly as burial cement, and in hydrothermal deposits, but it is also present in some metamorphic and igneous rocks. Members of the dolomite-ankerite series and siderite are abundant in low-grade iron-rich metamorphic rocks. The optical and physical properties of ankerite show continuous gradation with those of dolomite, darker colours reflecting higher iron contents. Crystals are rhombohedral, commonly with curved faces, like baroque dolomite, varying in colour from white to brown, reflecting higher iron contents. Stalactitic, granular, and massive earthy varieties are also common. Specific gravity rises from 2.93 to 3.1 in the most Fe-rich variants. Hardness is 3.5–4 on Mohs' scale. A technique to

differentiate ankerite from other carbonates again involves the use of Alizarin Red-S stain, first in acid and then in alkaline solutions (Warne, 1962).

Ikaite ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) and Vaterite (CaCO_3)

At low temperatures ($<3^\circ\text{C}$) and elevated pressures (2–3 bars), the hydrated carbonate **ikaite** ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) may form instead of calcite. Precipitation appears to require a reduction of $p\text{CO}_2$ of the brine by photosynthesis or CO_2 degassing, or both (Papadimitriou *et al.* 2013). First described from the Ika Fjord in Greenland, from which it takes its name (Pauly, 1963; Buchardt *et al.*, 1997), the mineral is metastable and rapidly decomposes on exposure. Rarely, replacements by porous calcite preserve (pseudomorph) the original monoclinic crystal structure (Bischoff *et al.* 1993); with examples in Quaternary deposits from the Clyde and Tyne estuaries in Britain (Shearman and Smith, 1985), and in Mono Lake in California (Council and Bennett, 1993). There are also reports of ikaite pseudomorphs in Neoproterozoic metamorphic rocks in Scotland (Dempster and Jess, 2015).

Vaterite (CaCO_3) is chemically like calcite and aragonite but has a distinctive (hexagonal) crystal structure. Like aragonite and ikaite, it is metastable at normal surface temperatures and pressures. More soluble than either calcite or aragonite, when exposed to water at temperatures below 60°C , it recrystallizes spontaneously to calcite, or to aragonite where temperatures are higher. For this reason, it is very rare in nature, but it is nevertheless the initial phase secreted to repair damage to the aragonitic shells of some bivalves and gastropods and forms in snail eggshells. It occurs in human gallstones, in fish otoliths, and in spicules of the solitary sea squirt *Herdmania* that, remarkably, provides the only source forming crystals large enough for their structure to be determined (Kabalah-Amitai *et al.* 2013). Wightman *et al.* (2018) recorded it in the leaves of saxifrage plants. Vaterite is also recorded forming in the early stages of curing of Portland cement, where its replacement by calcite is an important stage in hardening. It has also been recorded in a few ancient mortars.

Isotopes and the Geochemistry of Carbonates

Carbonates, and particularly calcite and aragonite, are notoriously soluble in the natural environment. Their behaviour is, however, counter-intuitive in that, in contrast to most other minerals, solubility apparently

decreases with increasing temperature. In deionized water their solubility is quite low, comparable with that of quartz (Ford and Williams, 1989a), and their apparently *increased* solubility in natural waters is largely due to the presence of dissolved carbon dioxide (CO₂) and dilute organic acids. This explains their anomalous behaviour relative to temperature, as reflecting a progressive degassing, and the evasion of CO₂ from the water as the temperature rises, increasing alkalinity. Nevertheless, there is increasing evidence that sulphuric acid and a variety of reactions involving oxidation-reduction (of ferric iron), salt and evaporite-derived solutions, may also play a role in natural systems (Chapter 7). Although dolomite is appreciably less soluble than calcite, the differences in weathering rates are only obvious where the two occur together in a single outcrop. The relative functional solubility of all carbonate rocks results in distinctive weathering and landforms (karst topography, Chapters 13 and 14) that have important implications for groundwater movements and foundations.

Isotopes in Carbonates. Four groups of **isotopes** are important in carbonates, those of carbon, oxygen, strontium, and uranium/thorium. Of the three carbon isotopes, **radiogenic carbon** (¹⁴C) forms continuously in the upper atmosphere as nitrogen nuclei are bombarded by cosmic rays. It mixes throughout the atmosphere and the waters of the oceans to be assimilated into the organic matter and skeletal deposits of all living things, together with inorganic precipitates. Over time, it decays to ordinary nitrogen, reaching half of its original volume, its ‘half-life’, in $5,730 \pm 40$ yrs. Thus, within limits of about 50,000 yrs, analyses of these materials using mass spectrometry can determine their age. However, radiocarbon dates are commonly reported using older estimates of the half-life, of 5,568 yrs, described as “conventional radiocarbon ages”. In unaltered deposits, up to about 30,000 yrs old, radiocarbon offers a valuable means of determining the ages of shells, bones, wood, travertines, and speleothems (Chapter 7) anything that contains carbon, and carbonates have a particular role in this. Fragments of only a few milligrams can provide reliable ages and constraints on times of deposition, rates of accumulation of sediments, and the return periods of events such as storms, linked to characteristic deposits. Dates are important in mapping climatic variation, but also in areas where the stabilities of bottom sediments or slopes are at issue. However, the ages provided by this method are predicated on the assumption that the original ¹⁴C content of the material was the same as that of similar present-day examples and, critically, that the sample analysed has not been diagenetically altered.