Feature

Carbonate concretions—explained

Carbonate concretions are common features of sedimentary rocks of all geological ages. They are most obvious in sandstones and mudstones as ovoid bodies of rock that protrude from natural outcrops: clearly harder or better cemented than their host rocks. Many people are excited by finding fossils in the centre of mudstone-hosted concretions (Fig. 1) but spend little time wondering why the fossils are so well preserved. While the study of concretions has benefitted from the use of advanced analytical equipment, simple observations in the field can also help to answer many questions. For example, in cliff sections, original sedimentary beds and sedimentary structures can be traced right through concretions (Fig. 2): so it can be deduced that the concretion clearly formed after these depositional structures were laid down. In this article we explain how and where concretions form and discuss the evidence, ranging from outcrop data to sophisticated laboratory analyses, which can be used to determine their origins. The roles of microbes, decaying carcasses, compaction and groundwaters are highlighted. Concretions not only preserve fossils but can also subdivide oil, gas and water reservoirs into separate compartments.

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What do we see?

If we divert our attention from the spectacular fossils (Fig. 1), concretions are simply patches of cemented sediment. The mineral cement between the grains is different, or more abundant, from that in the host sediment (which may not be cemented at all). As the preferentially cemented patches form more resistant bodies they commonly 'weather out' as prominent features at outcrop (Fig. 2). The cement crystals forming the concretions are often too small to see in the field: they fill the pore spaces between the grains and are commonly, therefore, smaller than the grains in the rock. Sometimes, however, individual crystals envelope dozens or hundreds of grains (so called 'poikilitopic' growth) and a recently broken surface of a concretion will 'twinkle' as sunlight catches the cleavage faces of the larger fractured crystals.

Calcium carbonate (calcite) is the most common cement but iron carbonate, (siderite) is particularly common in non-marine sediments (Fig. 3). Magnesium rich and mixed phases (such as dolomite or ankerite) and more exotic minerals can also occur. Sometimes, as in the famous Liassic concretions at Charmouth in Dorset, UK, different minerals form concentric growth zones around a central core (Fig. 4.). Pyrite, or 'fools' gold', is associated with many carbonate concretions in marine mudstones. It can occur entirely replacing the shells of marine fossils, often in exquisite detail, or less dramatically as tiny crystals spread throughout the concretion or even as a gold-coloured band within, or as a

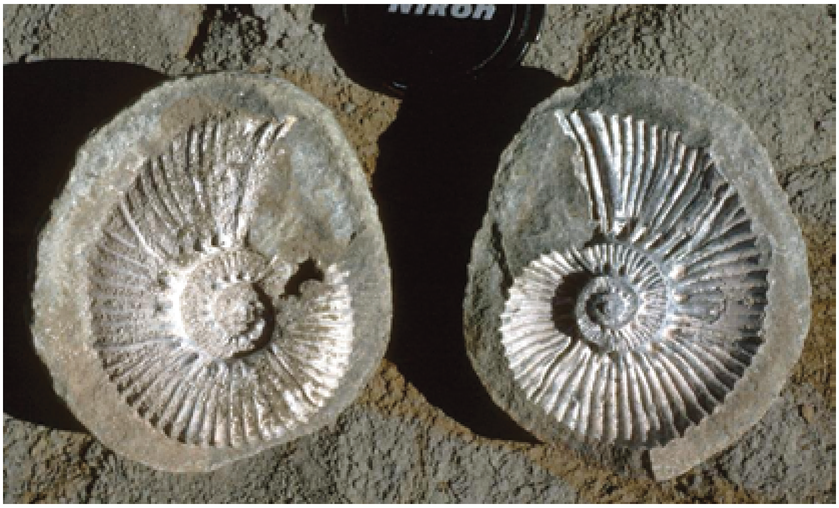

Fig. 1. An early diagenetic carbonate concretion split in half to reveal an ammonite retaining its original aragonite shell, from the Maastrichtian of Antarctica. Image courtesy of Alistair Crame (British Antarctic Survey, NERC). Lens cap is 6 cm.

Fig. 2. Calcite cemented concretion standing proud from the otherwise poorly cemented sandstones. Large spherical concretions commonly occur in sandstones, where the porosity and permeability are equal in all directions. Jurassic, Bencliffe Grit, Osmington Mills, Dorset. Vertical thickness is 80 cm.

rind at the edge of the concretion. Many mudstone examples also contain enigmatic networks of fractures, sometimes called 'septarian' cracks, which are broadest near the centre of the concretion and taper towards the margins. These are often filled with a succession of coarse crystal deposits (Fig. 5). Multiple generations of banded carbonates are often inter-layered with other minerals including pyrite, sphalerite, barite and galena.

Concretions range in size from a few centimetres to several metres in diameter: the smaller (cm-scale bodies) are commonly described as nodules. In their simplest form both the large and small forms are commonly oval in vertical cross section (particularly when they have formed in mudstones) and more or less circular when viewed on a bedding plane. They typically occur in particular levels in the sediment, rather than dispersed throughout the whole unit. More complex shapes may occur and even continuous layers can form when adjacent ovoid concretions have continued to grow laterally until they merge (Fig. 6) to form strange lumps or even laterally continuous sheet-like bodies.

Fig. 3. 'Early diagenetic' concretion in Carboniferous mudstones, Newgale, Pembrokeshire. The iron-rich concretion has formed prior to significant compaction so that the enhanced compaction of the surrounding mudstone leads to the lamination 'wrapping around' the concretion. Vertical thickness is 25 cm.

How and where do they form? The use of field observations

Simple field data, described above, provide us with clues that can help us to constrain how and where a particular concretion formed. The occurrence of fossils and sedimentary structures inside concretions (Figs 1, 2, 5) indicates that they formed after the deposition of the sediment. Concretions, therefore, are always 'diagenetic' phenomena. Diagenesis, however, can start very soon after deposition, immediately below the sea or lake floor, and continue to depths of several kilometres. Whilst the story of concretions is mostly concerned with very early diagenesis, some also include later minerals deposited at much greater depth by hot basinal brines.

Timing—in relation to compaction

When sediments are first deposited they contain a lot of water between the grains. As a deposit is buried by more and more sediment, the water is simply squeezed out: during this stage of physical compaction the grains are packed closer together, and platy minerals (like the tiny clay particles that make up most muds) tend to rotate from a random arrangement towards a horizontal orientation. Several important effects occur: the porosity (void space) of the sediment obviously decreases and it becomes easier for water to move horizontally through the rock rather than vertically. In more technical language the 'permeability becomes more anisotropic'. During initial compaction, original sedimentary layers will tend to get thinner as the water disappears. Muds which can initially be deposited as 'gloop', with as much as 80 percent water, will compact more than coarser grain-supported sandstones or limestones. Muds compact enormously so the porosity, and consequently the water content, decreases, more or less exponentially. Porosity in muds decreases from around 80 percent on deposition to less than 10 percent at depth; whereas sands will go from a maximum porosity of just over 40 percent to around 25 percent.

As noted above, the formation of a concretion involves cementation of the grains in the sediment.

Fig. 4. Concentrically zoned carbonate concretion, Lias: Lower Jurassic, mudstones Charmouth Dorset. The different weathering colours of the concretion body reflect differences in the chemical composition of the concretion cements. Septarian fractures (lined with dark brown calcite) cut the core of the concretion. Hammer is 30 cm.

During this process, the mineral precipitates from the pore water and simply takes the place of the water in the rock. If a cement forms early in the compaction history, before much burial, the grains will be relatively widely spaced and the cement will occupy a large volume of the concretion (Figs 1, 7a). On the other hand if the minerals don't form until later in the burial history then the space available for cement will be much reduced (Figs 2, 3, 7a,). Under the microscope we can therefore use the amount of cement to give us an indication of the amount of porosity available when cementation took place and thus give us an indication of the timing of mineral precipitation relative to the compaction history. The very common observation that the amount of cement in the middle of a concretion is often more than that towards its edges has been used to provide evidence that concretions grow outwards from a central nucleus and continue to form whilst the host sediment compacts (Fig. 7a).

In the field we can use these ideas to get a preliminary idea of when a concretion formed: at least in relation to the overall compaction history of the sediment (Fig. 8). 'Early diagenetic' (or pre-compaction) concretions form solid 'lumps' in a compacting sediment that shield their contents. Fossils inside them are not crushed (Fig. 1) and sedimentary structures are well preserved. Moreover sedimentary layers that can be traced through the concretion are thicker inside the concretion than outside. Similarly, layers above and below in the surrounding sediment wrap around the outside of the concretion demonstrating that compaction continued after the 'lump' had formed (Fig. 8a,b). 'Late diagenetic' concretions, on the other hand, form after the sediment has compacted—fossils are less well preserved and the difference in spacing between layers inside and outside the concretion and the degree of deformation of layers around the concretion are much reduced (Fig. 8c,d). Figure 8 demonstrates, in cartoon form, the differences that can be expected in concretions that grew before, during and after sediment compaction. It should be noted that the timing is relative to compaction—and that it may be difficult to decide on an origin in sediments that have not been buried enough for compaction to have occurred.

Shapes—and permeability anisotropy

Concretions in sandstones and 'grainy' limestones such as oolitic deposits tend to be 'rounder'—or, strictly, more spherical, than those in mudstones which are commonly ovoid or disk shaped and form much flatter structures parallel to the bedding. From the ideas presented above we can understand this difference simply in terms of the ability of the concretion to grow within sediments with different fabrics. In a pure, clean sand, consisting of spherical, or at least more or less equant grains, the properties of the sediment, including the permeability, will be similar in all directions. Once a concretion has nucleated in such a deposit it will be likely to grow outwards in all directions (Fig. 6). However in a mud, with its mixture of platy clay minerals and equant, silt-sized grains, it will be much easier for crystals to grow (and for new material for crystal growth to be provided by the pore water—see below) in directions which parallel the clay fabric rather than across the fabric. The clays tend to lie horizontally so that

Fig. 5. Slabbed concretion formed in intensely bioturbated silty mudstones (with a large bored oyster shell at the centre). Septarian fractures filled with brown and white calcite crystals radiate out from the centre of the concretion. Note how the fractures taper out towards the edge of the concretion. Nothe Clay, Dorset. Concretion is 20 cm across.

Fig. 6. Concretion formed from the lateral and vertical amalgamation of four smaller concretions. Planar bedding can be traced through the concretion. External layers only show limited bending around the concretion. Middle Jurassic sandstones, Eigg. (Lens cap for scale).

lateral, horizontal, growth of the concretion is easier than vertical growth (Fig. 3). Sometimes, odd shaped concretions form in sandstones where there is a primary bed-scale, permeability fabric; again controlled by the distribution of clays. This is illustrated by the rather odd concretions from the Jurassic of Skye, near Elgol (Fig. 9) where inclined concretions in a tidal sand body follow the, originally permeable, sandstone layers between clay 'drapes'. These thin mud layers evidently acted as partial barriers to the cementing fluids.

Decreasing cement content from core to edge of concretions and concentric bands of different mineral composition support the idea that concretions grow outwards by the concentric addition of material from a central nucleus—and many appear to form in this way (Figs 4, 7a). However, detailed examination of the distribution of different minerals within the concretion (using back-scatter scanning electron microscopy to examine polished thin sections) has led to the discovery of both early and late mineral phases, even in the cores of concretions. This has led to suggestions that at least some concretions form as a more diffuse patch of slightly cemented sediment—leaving pore space that can be in-filled by later mineral phases. This alternative model (Fig. 7b) has important implications for the origin of septarian cracks in mudstone-hosted concretions as will be discussed below.

Source of minerals—chemical considerations

For a concretion to form at a particular point in a pile of sediment a number of things have to happen. Notably, from a chemical point of view, the water has to be 'super-saturated' with respect to the mineral that will start to precipitate (i.e. contain a super-abundance of cations, like calcium and magnesium and an anion, in this case carbonate (CO^{3+}), in solution). To form as a specific concretionary 'lump', rather than as individual crystals dispersed randomly throughout the

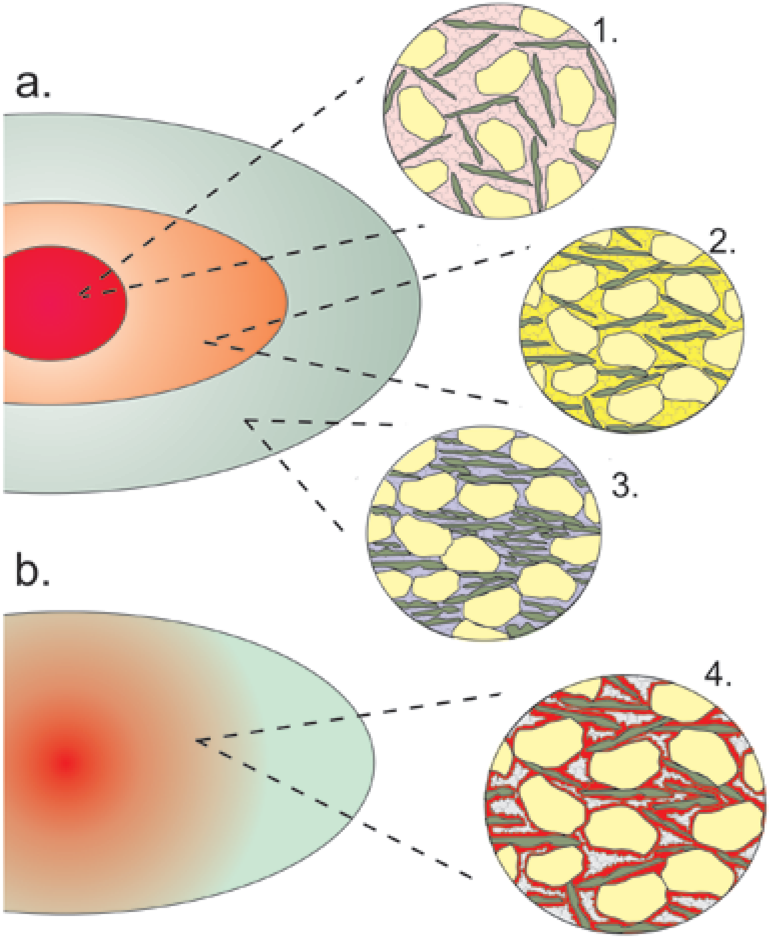

Fig. 7. Diagram illustrating two different models for concretion growth (**a.** and **b.**). The cartoons on the right (1–4) illustrate differences in microfabric which can be seen in thin section (rounded grains represent silt-sized quartz or feldspar and elongate, dark green, grains represent clays). **a.** Simple concentric growth where the concretion has grown in discrete stages (differently coloured 'cements') from the centre outwards. The different orientation and distribution of the grains in 1, 2 and 3 demonstrate that the concretion grew at three discrete times during compaction. Note that there is much more carbonate (pink) between the grains in the early zone (1) than (blue) in the zone which formed after compaction. The second concretion (**b.** 4) has a mixed fabric resulting from incomplete cementation by a first generation of carbonate (red) and later cementation by a second generation (blue). The body of the concretion will have a mixed fingerprint with samples containing both cement types.

sediment, it also requires a preferred nucleation site to act as the main growing point for the concretion. This site needs to continue as the preferred point for crystal growth during the formation of the whole concretion. We can picture the idea of a nucleation site by analogy with the old demonstration of crystal growth in a school laboratory. A bright blue copper sulphate solution in a beaker will only start to precipitate solid material when a nucleus, in the form of a seed crystal, often suspended on a string, is dangled into the solution. In the case of concretion growth in sediments, the 'nucleus' may be provided by mineral grains, a calcite shell or collections of shells. Decaying organisms can provide a supply of carbon atoms.

The chemical aspects of concretion growth have been debated for many decades and there are many papers on the subject. A number of early concepts have been overturned by advances in theory and by data from new sources. For example, the occurrences of well preserved fossils in the centres of concretions originally lead to the idea that the carbon for the carbonate could simply be sourced by carbon from the decay of the soft tissues of the animal in the centre. Such ideas are readily discounted by simply working out that the amounts of carbon from a single organism are simply not sufficient to account for the amount of carbon in the concretion itself. In a similar way it is not possible to grow a concretion of any size without renewing the sources of cations and anions. Even the most super-saturated solutions cannot contain enough ions to form significant mineral deposits—so the ions have to be renewed and transported to the site of concretion growth either by diffusion (static water with the movement of ions along a concentration gradient from their source) or flow (movement of ions in moving groundwaters). It has been suggested that as many as 10 000 pore volumes of water are needed for complete cementation to occur. Diffusion is also problematic as a mechanism as it can be a very slow way to transport ions over long distances.

Shallow marine sandstones—spherical concretions, cemented sheets and reservoirs divided

Large spherical concretions or carbonate-cemented sheets are common in shallow marine sandstones. Examples at outcrop can be found in the Jurassic of the UK at Filey in Yorkshire and the Bridport Sands and Bencliffe Grit in Dorset (Fig. 2) or in the Bearreraig Sandstone in the Inner Hebrides (Fig. 6). Internationally, the famous Moeraki Boulders of New Zealand feature on postcards and on the web.

These bodies are important to understand as they form tight zones of low porosity and permeability in subsurface reservoir rocks including the Rannoch Formation in the Brent Group and the Fulmar Sands of the North Sea. The sheet-like cemented sandstones in the cliff sections of the Bridport Sands (Fig. 10) persist into the subsurface and are reported to compartmentalise one of the reservoir units in the UK's largest onshore oil field into alternating, thin porous reservoirs and non-porous intervals. Each layer has to be treated separately by engineers considering secondary recovery strategies to get the oil out.

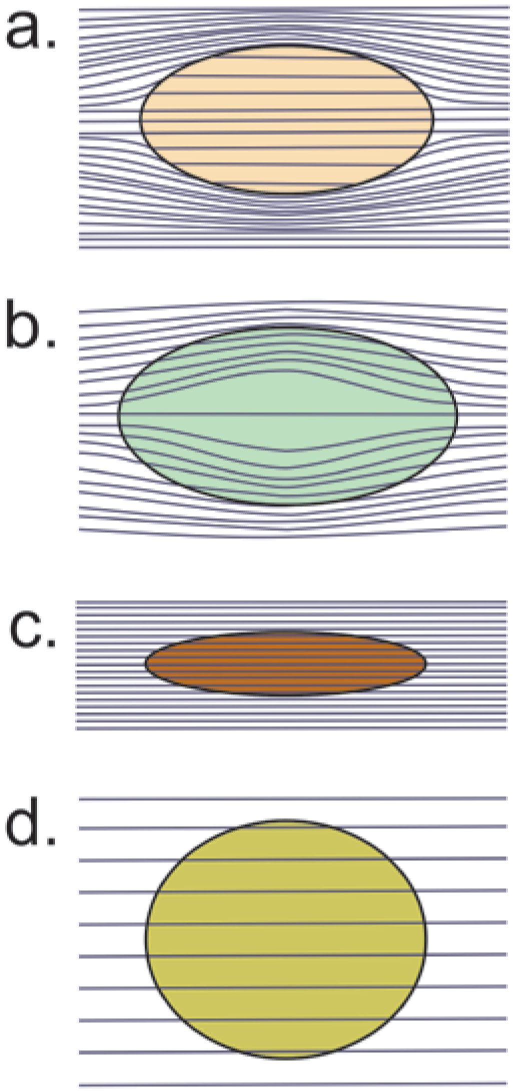

Fig. 8. Diagram showing how field observations can allow us to work out the timing of concretion growth relative to sediment compaction. Ellipses represent the outer margin of the concretion. In all cases the layers were initially planar horizontal bedding or lamination and can be traced through and around the concretions: **a.** early diagenetic concretion formed before compaction. **b.** early diagenetic concretion which continued to grow during compaction (layers are deformed inside and outside the concretion); **c.** and **d.** represent concretions that formed after compaction. Ovoid concretions (**c.**) are more common in mudstones whilst more spherical bodies (**d.**) occur in sandstones. This reflects the differences in horizontal and vertical permeability in the different sediment types.

Sandstone concretions rarely contain exceptional fossils, they tend to be cemented by relatively large sparry calcite crystals typically occupying 20–30 percent of the rock, so the simple model described above, where cement volume equates to porosity at the time of cementation, would suggest that they are likely to have formed after at least some compaction. The precise depth of formation can be difficult to determine purely from the carbonate abundance. The presence of carbonate shells within the sands and the occurrence of 'aggressive' carbonate cements that have replaced feldspar grains can both lead to an over estimation of the original void space. These concretions are mostly thought to form in relatively shallow groundwater systems during the first few hundred metres of burial. Oxygen isotopic evidence points to the involvement of relatively fresh waters that most likely flowed through the sediments. The nuclei for concretion growth are likely to be provided by concentrations of shelly material in the original sediment or perhaps around concentrations of organic material in burrows. Dissolution of unstable shells made of aragonite (which is a much more soluble calcium carbonate mineral) and re-precipitation as calcite (the less soluble polymorph) in the concretion provides the most likely solution to the origin of the ions. The chemical composition of the cements changes very little from core to margin suggesting that they grew under relatively uniform groundwater conditions.

Such calcite cemented sandstones are commonly encountered in boreholes drilled either for water or hydrocarbon extraction. It is not easy to tell whether the borehole has crossed a localised individual round concretion which poses little problem for resource extraction, or the much more divisive cemented horizons that may cause production problems, necessitating expensive water and gas injection schemes. The answer for the engineers may rely on a geological understanding of the local controls on concretion nucleation. Commonly the cemented beds are most likely to represent sedimentary units which originally contained more shell material than those between them or were originally more porous and permeable.

Mudstone concretions—bugs, armaments, 'bonking wenches', depth zones, enigmatic cracks and source rocks

Carbonate concretions are common in both marine and non-marine mudstones where they tend to be associated with dark grey or black sediments (Figs 3, 4). They are generally concentrated in particular layers in the succession rather than randomly dispersed through the rocks. Typically made up of very finely crystalline carbonate, most show the classic evidence of a very early, pre-compactional origin: uncrushed fossils (Fig. 1), carbonate content in excess of 40 percent and up to 70 percent of the rock, and distortion of overlying and underlying layers (Fig. 8a). Good examples in the UK occur in the marine Jurassic mudstones of Dorset, Yorkshire and the Inner Hebrides as well as in the Carboniferous fresh to brackish mudstones of the Yoredale cycles and the Westphalian Coal Measures of Northern England.

Anyone who has stepped or fallen into recently deposited mud in a pond or estuary will know that it can be a very smelly experience! Muds and mudstones are not simply accumulations of minerals. They also often contain a few percent of organic matter derived from animals, plants, algae and bacteria living above and within the sediment. The organic matter does not only control the resulting colour of many mudstones, or indeed their potential as hydrocarbon source rocks, it also controls the distribution and origin of the carbonate concretions.

Organic matter is reactive stuff! As soon as an organism dies, organic compounds are subject to attack by oxygen in the environment; or by microbes in the sediment. The processes of decay start to destroy the

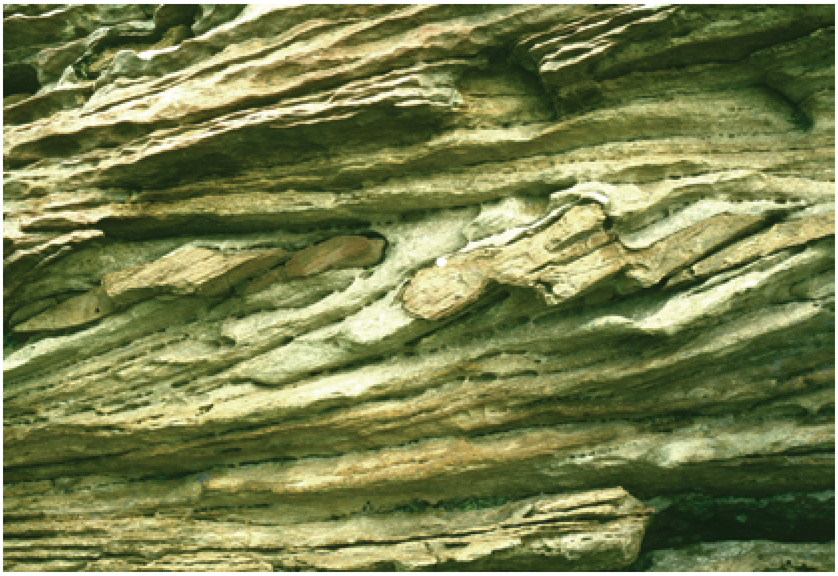

Fig. 9. Concretions developing parallel to the cross bedding in a tidal sand body. Mud drapes on the foresets caused a heterogeneity in the porosity–permeability characteristics and the concretion formed in the best-connected sandstones, Middle Jurassic, Bearreraig Sandstone, Elgol, Skye. (Cliff section is about 1 m high)

Fig. 10. The Jurassic Bridport Sandstones on the Dorset coast comprise laterally persistent concretionary sheets with poorly cemented sands in between. These sheets can impede fluid migration in oilfields in the subsurface. Overall these striking cliffs are also unstable, and sadly, in July 2012, a rockfall just along the coast from this locality, led to the death of a tourist walking at the foot of the cliff.

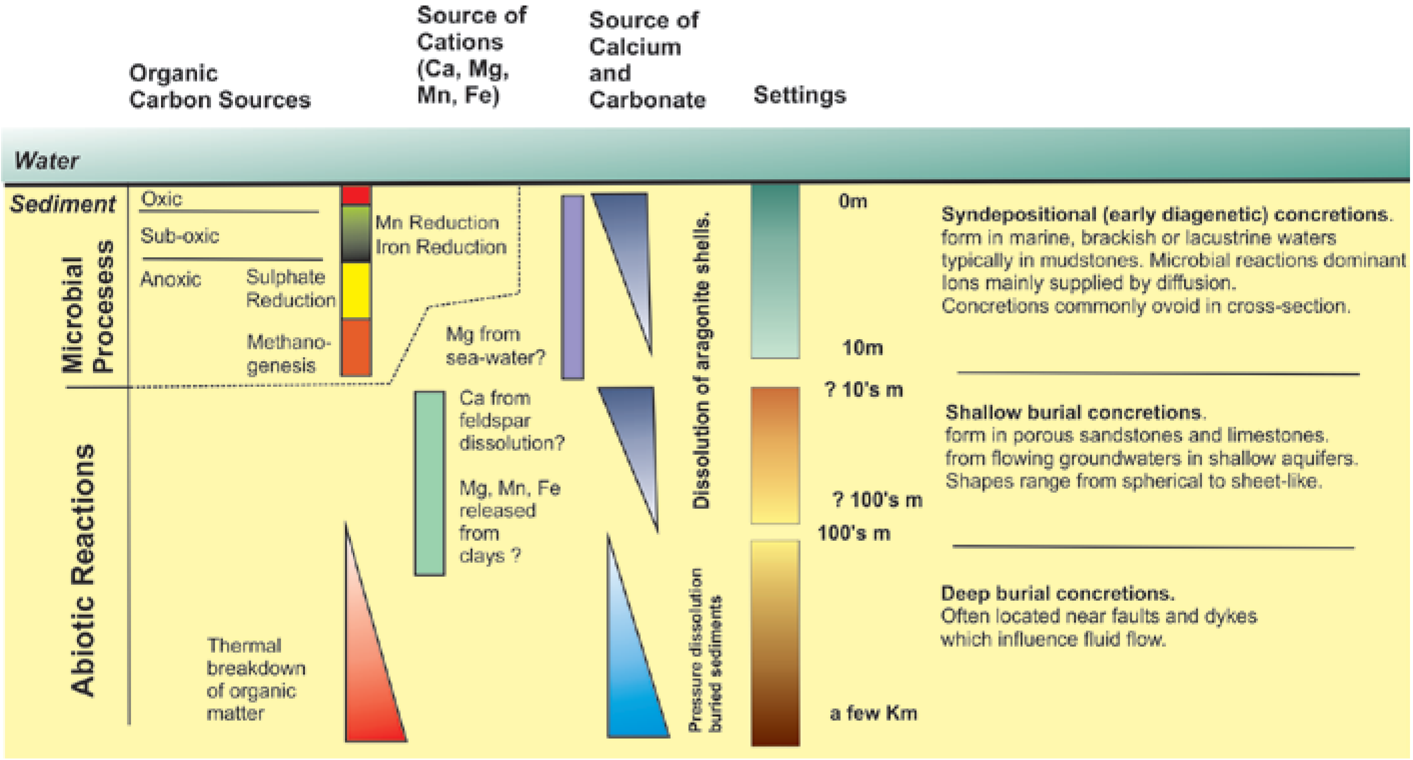

Fig. 11. Cartoon showing the different sources of carbon and metal cations in different burial settings.

complex molecules originally created by living things. They break them down into much more simple compounds like carbon dioxide and methane which can form the building blocks of carbonate concretions. In the air, or if the water column is oxygen-rich, these decay products are lost and are recycled into the environment. Within the sediment, however, the carbon may be fixed into mineral matter and a concretion can start to form (Fig. 11). For this to happen the geochemical conditions have to be right: production of carbon dioxide on its own will generate carbonic acid and calcite will tend to dissolve rather than precipitate. Other reactions are needed to control the alkalinity.

The geochemistry of pore-waters in recently deposited mud is extraordinarily complex and governed by the interplay of reactions involving organic matter, living microbial communities, minerals and the amorphous oxides and hydroxides absorbed and adsorbed on to the surface of clay minerals. Even if this mixture is reasonably stable in the water overlying the sediment it can become highly reactive in the microenvironments created by decay. Micro-biologists and geo-microbiologists have come to recognise that organic decay reactions and porewater geochemistry change more or less systematically in the first few metres below the sediment-water interface (Fig. 11). Reactions are controlled by successive consortia of microbes which utilise different components of the sediment/organics/elemental soup in their metabolism. For example, below oxygen-rich waters the top few centimetres of the sediment contain oxygen, and decay processes are very similar to those in air; the free oxygen is consumed in the production of carbon dioxide from the reduced carbon characteristic of organic matter. Below this we enter sub-oxic conditions (Fig. 11) where microbial communities selectively utilise the organic food and oxidise it to carbon dioxide successively using nitrate from the pore water, followed by amorphous manganese and iron oxides and hydroxides, which occur largely on the clays. As the oxygen becomes further depleted, conditions become anoxic, and in the case of seawater the bugs now utilize the stronger bonds in the sulphate ions dissolved in the water. The combination of iron and sulphate reduction leads to the happy coincidence of a source of iron and a source of carbon—leading, commonly via some intermediaries, to the precipitation of pyrite. In non-marine waters and in marine conditions below the peak of sulphate reducing bacteria, methane-producing bacteria continue the work of decay and liberating carbon now in the form of methane.

About 30 years ago Charles Curtis, Max Coleman, Rob Raiswell and John Hudson were amongst the first geologists to realise that the products of these decay reactions could be detected in the minerals in mudstone concretions. They published a series of case studies and modelling exercises to demonstrate how the products could be detected. Although the details are complex, and knowledge of both the microbiology and geochemistry has become increasingly sophisticated over the intervening years, the fundamentals remain relatively straightforward, relying on the presence of chemical fingerprints created by the decay processes. Evidence for the origin of a particular concretion, or indeed zone within a concretion, is provided both by the trace metals and the carbon incorporated in the concretionary carbonate cement. So, for example, the presence of manganese (detected by chemical analysis and also because it causes calcite to luminesce brightly under an electron beam) is indicative of the activity of manganese-reducing bacteria. Iron, detected in calcite by simple staining techniques as well as more complex instrumental methods, is more complex. It is only incorporated in calcite alongside the similarly-sized calcium ions in its reduced (Fe^{2+}) state. Iron tends to be absent in oxic carbonates and present in deeper-formed minerals as long as iron reduction persists and as long as pyrite formation hasn't 'gobbled up' all of the available iron. Useful chemical signals in the concretion carbonate are detected by measuring the changes in carbon isotope ratios. Carbon from organic matter (slightly enriched in the lighter ^{12}C) has a very different isotopic signature from carbon in sea water or shells, so the products of microbial decay can be detected relatively easily. Methane has a very characteristic carbon signature as does the subsidiary carbon dioxide liberated alongside it.

Overall, a basic understanding of processes and products enable us to understand why different types of concretion are found in different types of sediment. For example the early-formed central parts of concretions in marine Jurassic mudstones tend to be composed of iron-poor calcite often with pyrite. They formed under the influence of both iron reduction and sulphate reduction. Later zones are often iron-rich, if iron reduction continued, and they sometimes have the very negative isotopic signatures characteristic of methane production. In Westphalian coal measures the so-called concretions known as 'coal balls' have carbon isotope signatures that again link their origin to methane production in environments similar to those in a stagnant pond. Here the concretions are composed of siderite rather than calcite. This is partly because of the reduced availability of calcium but largely because in freshwater intense iron reduction takes place without the co-occurrence of sulphate reduction, so there is no competition with pyrite formation for the iron. Concretions in such environments can house fantastic fossil assemblages. For example, the Coseley Fauna from the West Midlands in the UK and the Mazon Creek assemblage from the USA are examples of conservation lagerstätten and occur in very early diagenetic concretions. The remarkable fossils include animals and plants, and even the soft tissues and wing structures of insects can be preserved in fine detail. The concretions that trapped them must have started to form in anoxic ponds within hours or days after the creatures died. The sediments outside the concretions contain many fewer fossils indicating that any animal remains were lost to decay. As described in a previous *Geology Today* article by Nudds and Selden (*Geology Today*, 2008, v.24, pp.153–158) conservation deposits provide a unique window into evolution and the composition of entire ecosystems.

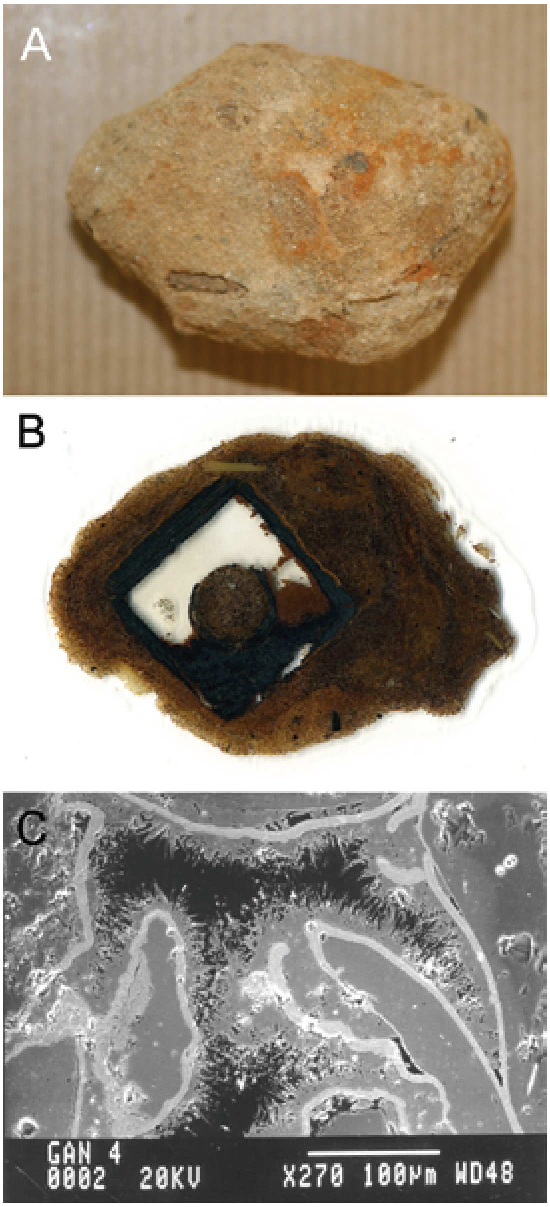

Fig. 12. Iron-rich concretions from modern intertidal sediments, Cornwall, UK. **a.** Siderite concretion, which when slabbed, **b.** reveals that it is nucleated around a fragment of discarded metal waste. Concretion is 5 cm across. **c.** Under scanning electron microscopy these concretions can be seen to have multiple generations of mineral cements, in this case pyrite (bright phase) post-dated by calcite.

In economically hard times in the past, the Coseley fauna in the Carboniferous Coal Measures was a source for income for its exceptional fossils. The local women could sometimes make better money selling fossils than the miners could selling poor quality coal. They were apparently known at the time as 'bonking wenches' due to their activity splitting concretions and evidently before later evolution of the language!

Concretions and layers

If the processes described above are so common why don't we find concretions in every bed of mudstone? Rob Raiswell and others have suggested that the occurrence of concretions in separate layers reflect changes in the rate of sediment accumulation. It is argued that under conditions of continuous sedimentation the geochemical zones conducive to carbonate formation will simply migrate upwards through the sediment as it accumulates and that any precipitates will either be dispersed through the mud or will perhaps be dissolved again as conditions change during burial. The occurrence of nodular limestones, formed where individual concretions start to grow and then join together to make beds of secondary carbonate, suggest that the concretions first nucleate at a horizon in the sediment and subsequently grow laterally. Raiswell has suggested that this indicates that beds of concretions formed in response to hiatuses in deposition and that concretions are only successfully preserved where there is sufficient time to enable ions to diffuse through the sediment and to grow stable carbonate bodies. If this model is correct then a bed of concretions should be mirrored by a hiatal surface a few metres higher in the sedimentary sequence and this can be observed in a number of instances. Evidence for the very early formation of concretions in sediments prone to pauses in sedimentation and short-term erosion comes from the discovery of concretions with top surfaces covered in oysters or bored into by bivalves. They were evidently exhumed and sat on the sea floor for some time.

Septarian cracks

The origins of the large, often spar-filled, cracks that occur in networks within mudstone-hosted concretions (Fig. 5) have been the subject of much discussion. Examples are found in large Lias and Kimmeridge deposits in Dorset (Lower and Upper Jurassic, respectively) and in Jurassic mudstones from northern Skye. The cracks are more abundant in the central parts of the concretion and taper out towards the outer margins, which they seldom reach. They all have the characteristics of brittle failure. Isolated individual angular lumps of dark grey coloured cemented mudstone sit in a white maze of sparry calcite and can, by eye, be fitted back together. They evidently indicate some kind of *in situ* brecciation. Early accounts likened their formation to mudcracks, but failed to explain why they are only found in the middle of very solid concretions. Models for crack formation suggested 'overpressuring'—episodes where the fluid pressure in the mudstones built up sufficiently during periods of rapid burial to crack the concretions apart. However, neither of these ideas had a solution to the 'space problem'. How are large angular voids accounting for as much as 30–40 percent of the concretion created in the midst of a supposedly solid sedimentary body? The discovery that some concretions form by the infill of later generations of carbonate in a partially cemented framework (Fig. 7b) might help to explain the phenomena of septarian concretions, if the fracturing took place whilst the concretion was brittle and only partly cemented.

Discoveries of gelatinous microbial material in modern sediments might also provide a partial solution. If the growing concretion initially incorporated such material (known technically as 'extracellular polymeric substances' or EPS) in its core it might be mobilised into discrete veins and patches as the later compaction and fracturing occurred. Subsequent removal of the EPS, perhaps by further microbial decay, could then create the void space for cementation. We are still left, however, with the problem of how to pass enough water through the middle of the apparently solid body to fill the fractures with calcite.

Areas for further study

Although concretions are common in sedimentary rocks, equivalents are relatively rare in modern sediments. Microbial reactions are present and modern precipitates have been found where there is a really reactive source of metals. A notable example was the occurrence of a rather amorphous, rounded nodule in the marshy sediments of the Wash in Eastern England. Its finders were a little perturbed to discover that the nucleation point of the nodule, and probable source of some of the iron, was an unexploded hand grenade that had landed in the marsh earlier last century. Further, less dangerous and more typical, modern analogues would be very useful. Figure 12 illustrates an example from modern intertidal sediments in Cornwall where the provenance of the iron-rich core was probably much more mundane.

The links between microbial processes and some types of concretion seem to be proven. Recent studies have tried to examine the organic matter trapped within concretions to confirm more precisely which processes were responsible for their formation. The measurement of organic molecular biomarkers can, in theory, be used to identify the specific microbial communities that produced the conditions for the concretions to form. In this context concretions may also provide a window into the early modification of the organic matter in hydrocarbon source-rocks. Precise interpretation is difficult, because studies of modern sediments have demonstrated that the different consortia of bacteria often fail to exist in well-ordered depth-related zones, but rather overlap in a more complex pattern of co-existing micro-environments.

Ideas about concretions forming during periods of reduced sedimentation are leading some people to suggest that barrier forming concretions in reservoirs may be, in part, predictable. Attempts to determine whether there are any links between positions of concretionary horizons and their sequence stratigraphic context are beginning to throw light on this.

In summary whilst the study of concretions has advanced our understanding enormously over the last few decades there is still much to be learnt about these enigmatic diagenetic structures which are so common throughout the geological record.

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Suggestions for further reading

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