Sedimentology and stratigraphy

Hydrocarbon source rocks and ocean anoxia events (*January 2002*)

Much of the world's oil resources formed by maturation and migration of hydrocarbons from organic-rich, marine mudrocks, which seem to have formed episodically during Earth history. A widely accepted view is that such source rocks' content of organic matter fell to the ocean floor as the remains of tiny organism. That they were not oxidized by bacterial action seems to suggest that the periods when source rocks accumulated were characterized by low oxygen levels in bottom waters. Each major source rock has been linked to such ocean-anoxia events, and to periods when deep-ocean circulation effectively stopped, so cutting off oxygen supplies to deep levels. However, studies of modern deposition of organic matter in marine sediments at continental margins reveals that discrete particles of organic matter are far outweighed by biological molecules that coat the surfaces of minerals, particularly those of clay minerals. The amount of organic carbon in modern sediments depends largely on its content of clay minerals derived from intense chemical weathering of continental rocks. Such coatings are protected from normal processes of decay, so that the adsorbed organic carbon compounds can be buried, more or less intact

It should be possible to check whether ancient source rocks are similar to modern carbon-rich sediments by seeking a strong correlation between clay content and organic content - mudrocks also contain fine silt particles made of non absorbent quartz. It seems that in at least one Cretaceous source rock in the US Mid-West such a correlation is clear (Kennedy, M.J., Pevear, D.R. and Hill, R.J. 2002. Mineral surface control of organic carbon in black shale. *Science*, v. **295**, p. 657-660; DOI: 10.1126/science.1066611). This suggests that oil-shale deposition is as much related to the intensity of continental weathering of silicates as it is to ocean-water chemistry. Since clays, especially the sponge-like smectites, adsorb organic molecules from solution in seawater, they draw on a vast pool of material, so that enhanced biological productivity need not be linked to oil-shale formation either. The fact that most organic material in such rocks is structureless kerogen, rather than identifiable particles, also supports this alternative hypothesis.

Both petroleum geologists and palaeoclimatologists have assumed a source rock - ocean anoxia connection in both exploration strategies and assessment of past climate shifts. So Martin Kennedy *et al*.'s painstaking findings are sure to cause a major stir. However, what cannot be avoided is that increased chemical weathering of the continents is likely to accompany globally warm conditions, and they in turn sponsor growth in planktonic productivity. Likewise, global warmth does not favour the formation of dense, cold and therefore oxygenated sea-surface water, which sinks to aerate deep oceans when the planet is cool.

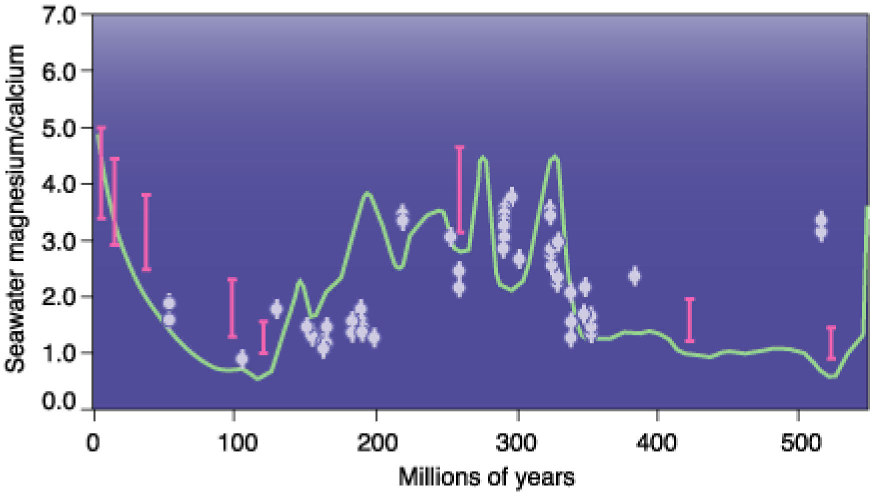
Biofilms and BIFs (August 2002*)*

Biomineralization is a growing topic that ranges from life's influence on the production of economic deposits of metal ores to even the suspicion that it might play a role in Alzheimer's syndrome. The most common, and enduring evidence of the influence of micro-organisms in making rocks are stromatolites made of carbonates that blue-green bacteria have secreted, perhaps from as early as 3500 Ma ago. Something similar, though it involves eukaryotic algae, is the formation of tufa or travertine where springs emerge from limestones. Many a child, including my young self, consigned a cuddly toy to "petrifying" springs, such as Mother Shipton's Well in Knaresborough, Yorkshire. Few retrieved them, which is why there aren't many lithified Teddies around.. Another childhood memory, which bears on biomineralization, is of a spring surrounded by orange and brown slime that we supposed was so deadly that only bathing in helicopter fuel would ward off a dreadful end brought on by the faintest splash of the loathsome gunk. It is a great surprise to learn that such ochreous springs, common where coal mines drain to the surface, might hold a key to the formation of Precambrian banded iron formations (BIFs) (Brake, S.S. *et al*. 2002. Eukaryotic stromatolite builders in acid mine drainage: implications for Precambrian iron formations and oxygenation of the atmosphere. *Geology*, v. **30**, p. 599-602; doi: 10.1130/0091-7613(2002)030<0599:ESBIAM>2.0.CO;2).

Groundwater that has passed through iron-sulphide bearing rocks, becomes both acid and charged with iron-2 after oxidation of pyrite. It is high acidity and low Eh that dissolves toxic heavy metals and arsenic, rather than their iron content, that make springs of such waters so hazardous to small boys bent on careers as hydraulic engineers (check their shins and fingers for the lingering water blisters that are a sure sign of the onset of arsenic poisoning). It seems that *Euglena*, a common "animalcule" in such springs that is easily seen with a cheap microscope, is an ochre (iron-3 hydroxides and sulphates) forming agent. It is an acid-tolerant, oxygenic photosynthesizer that builds slimy mats. Given time and substantial supplies of dissolved iron, *Euglena* actually builds hard structures reminiscent of stromatolites. Brake and colleagues from Indiana State and Kansas universities, and the Colorado School of Mines, studied *Euglena* from coal-mine drainages under lab conditions, and provide details of their metabolism. The modern iron-stromatolites are so like some variants of BIFs from the Archaean and Palaeoproterozoic, when they were at their acme, that the authors suspect their origins in biofilms formed by prokaryotic organisms with similar metabolism to the more complex *Euglena*. Until their work, most geologists regarded BIFs as products of inorganic precipitation of iron-3 compounds and silica when iron-2 rich seawater met oxygen produced by photosynthesizing cyanobacteria. Indeed they speculate that the biofilm makers could have been early eukaryotes, despite the first unambiguous evidence for nucleus-bearing organisms being no older than 2100 Ma. If they are correct, then such communities would have needed free oxygen, and would themselves have contributed to oxygen build-up in the early atmosphere.

Changing composition of seawater (*November 2002*)

Using carbonate sediments and fossil shells to assess how the composition of seawater has changed is a long-standing technique in sedimentary geochemistry. Isotopes of strontium and oxygen have provided revolutionising windows on the pace of continental weathering and fluctuations in sea-surface temperature and continental ice cover for over 30 years. The magnesium to calcium ratio in fossil shells has given insights into deep-water temperatures for the Cenozoic, more recently. However, tracking changes in the bulk composition of seawater through time, through analyses of carbonates, is plagued by the continual chemical interaction between rocks and the waters with which they are in contact. The Mg/Ca ratio of sea water is a potential proxy for the amount of hydrothermal activity on the sea floor, and thus the rate of sea-floor spreading. This is not because oceanic basalts are magnesium rich compared with continental crust that provides much of the dissolved matter that enters the oceans, but because hydrothermal reactions tend to mop up dissolved magnesium and release calcium.. Unfortunately, magnesium also easily replaces calcium in carbonates during diagenetic processes, particularly dolomitisation. There are two means of overcoming this hindrance, by analysing seawater trapped as fluid inclusions in evaporite minerals and the shells of echinoderms that still contain minute structures formed in life and are unlikely to have been altered (Dickson, J.A.D. 2002. Fossil echinoderms as monitor of the Mg/Ca ratio of Phanerozoic oceans. *Science*, v. **298**, p. 1222-1224; DOI: 10.1126/science.1075882). Early results seem to match a prediction that while supercontinents existed, the length of mid-ocean ridges and therefore ocean floor hydrothermal activity were at a minimum. Around the Precambrian boundary and during the Carboniferous to Jurassic periods, Mg/Ca was high at the time of the Vendian and Pangaea supercontinents. During major bouts of continental break up - the Lower Palaeozoic and Mesozoic - the ratio is low. Oddly, the ratio has risen to unprecedented high levels during the Cenozoic Era, when clearly there is high hydrothermal activity.



Variations in the Mg/Ca ratio of seawater during the Phanerozoic (Credit: Dickson 2002; Fig. 3)

Despite the fact that the Mg-Ca record of the oceans is limited to just a few short time spans in the 545 Ma record of the Phanerozoic, plenty of geochemists and palaeobiologists are speculating about the possible consequences for evolution of changes in the bulk composition of seawater. There have been major swings in the proportion of calcite to dolomite in carbonate sediments throughout geological time (see *Bacteria and dolomites*, January 2001). Discussion now centres on the possible effect of changing Mg/Ca ratios on the waxing and waning of important carbonate secreting organisms, ranging from corals and molluscs that build reefs to the minute coccoliths that formed the Cretaceous Chalk. Perhaps different groups responded differently to changing water composition, and maybe the Cambrian Explosion of shelly faunas was triggered somehow by a critical shift in the ratio.

See also: Kerr, R.A. 2002. Inconstant ancient seas and life's path. *Science*, v. **298**, p. 1165-1166; DOI: 10.1126/science.298.5596.1165.

Deep carbon cycling, and gold mineralization (*November 2002*)

One of the more speculative aspects of the carbon cycle concerns the fate of carbonate sediments that descend subduction zones. One popular hypothesis, with an acronym that is likely to amuse colloquially inclined, British readers (the BLAG model named after its three originators Berner, Lasaga and Garrels) avows that such carbonates contribute to CO_2 emissions from volcanoes above subduction zones by reacting with silica. The presence in blueschists of abundant aragonite associated with silica suggests that if that does happen, not all carbonate is consumed and a great deal enters very long-term storage in the mantle. Indeed, aragonite-magnesite associations are stable to pressures that are equivalent to depths of 240 km. Rocks formed under exceptionally high-pressure conditions, which might shed further light on the deep part of the carbon cycle, are exceptionally rare. One such occurrence is the Kokchetav massif of Kazakhstan, in which dolomitic marbles accompany eclogites. Notable for the occurrence of metamorphic diamonds, Kokchetav rocks probably equilibrated deeper than 250 km, so the carbonates are particularly interesting. Yongfeng Zhu and Yoshihide Ogasawara of Beijing University in China and Waseda University in Japan have found evidence for dissociation of dolomite in them (Zhu, Y. & Ogasawara, Y. 2002. Carbon recycled into deep Earth: Evidence from dolomite dissociation in subduction-zone rocks. *Geology*, v. **30**, p. 947-950; 10.1130/0091-7613(2002)030<0947:CRIDEE>2.0.CO;2) during reactions that generate garnet and clinochlore. The mineral textures reveal equilibria that involve the production of carbon and oxygen, rather than CO_2, so it is quite possible that reflux of CO_2 from subduction zones to the atmosphere may not be as significant as the "BLAGgers" suppose.

Interestingly, the same issue of *Geology* includes a paper on the geochemical conditions under which gold and copper enter subduction-zone magmas to source major ore deposits (Mungall, J.E. 2002. Roasting the mantle: Slab melting and the genesis of major Au and Au-rich Cu deposits. *Geology*, v. **30**, p.915-918; DOI: 10.1130/0091-7613(2002)030<0915:RTMSMA>2.0.CO;2). Mungall focuses on the inability of chalcophile metals to enter magmas when sulphides are stable in the mantle. Under those condition Au and Cu tend to enter sulphide melts whose density and immiscibility separate them from silicate melts. Oxidation of sulphur is needed to overcome this tendency, and that requires high oxygen fugacity at the depths involved, suggested by him to accompany abundant iron-3 in the subducted materials. That may be so, but release of molecular oxygen by high-pressure carbonate dissociation, as described by Zhu and Ogasawara, seems an even more likely means of freeing chalcophile metals to magmas.