

## Authigenic minerals from the continental margins

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Authigenic minerals are widespread and diverse in the oceans. Some are confined to shallow continental margins while others form in deep sea. Authigenic minerals in shallow continental margins include authigenic green clays, phosphorites, dolomites and barites.

### Authigenic Green Clays

Authigenic marine green clays in shallow marine environment usually form within the granular substrates such as faecal pellets, foraminiferal chambers or within the cracks of mineral grains and are also referred to as granular green clays. In contrast with the detrital clays, which form as fine-grained clay sized materials, authigenic clays are iron-rich and thus can be separated by Iso-dynamic separator. They are light green to dark green in colour, with usual surface cracks indicative of degree of evolution of green clay within the substrate (Fig 1). There are variety of granular green clays which are similar in colour and morphology but differ in their mineral composition. It is necessary to identify the specific green clay minerals as they reflect distinct environments of sedimentation.



Fig. 1. Green grains of different colours

### Verdine Facies

One such newly distinguished authigenic green clay facies is the verdine facies. It develops at the continent-ocean boundary near the abundant source of iron at depths between 5 m and 60 m. One mineral in this facies has recently been designated as odinite. It is a ferric-magnesium dioctahedral-trioctahedral 1:1 clay mineral which was initially named 7A° phyllite V (Odin, 1985). Another authigenic clay co-existing with odinite is phyllite C, which has an intermediate structure between

chlorite and smectite (Odin, 1988). The presence of Verdine facies is now known from 15 locations in the present oceans (Odin, 1988; Rao et al., 1993, 1995; Thamban et al., 2001). Of these 15 locations 10 are from the Atlantic, three from the Indian (including the eastern and western margin of India) and two from the western Pacific Oceans. Except for the verdine facies from the Miocene sediments of the Niger delta, all other occurrences are from recent marine sediments <15 kaBP (Odin, 1988). They form in an overall oxidizing environment, but sub-oxic conditions necessary for their formation are maintained within the granular substrates.

### Glaucy facies

Glaucy is another green grain facies develops in the open ocean, farther from continental input and in areas of low sedimentation under sub-oxic conditions and at relatively large depths (>60 m to <1000 m). Several workers have used the term 'glaucy' in a broader manner to represent the glaucy facies rather than the mineral itself. It has two mineral phases: Glaucy smectite first forms *de novo*, then recrystallizes to glaucy mica with an increasing potassium content in the interlayers (Odin and Matter, 1981). Glaucy mica is the recommended term for glaucy. In younger and present day forming glaucy should contain glaucy smectite rather than glaucy mica which needs more time ( $10^5$ -  $10^6$  years) to form (Odin and Letolle, 1980). The glaucy minerals forms early in the sediments close to the sediment-water interface (sub-oxic environment) fed by the partial reduction of inherited ferric iron.

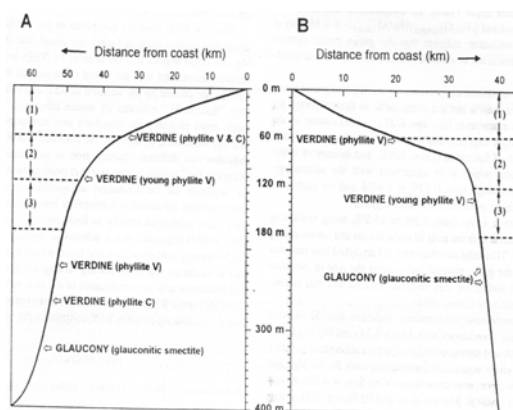


Fig. 2. Verdine and glaucy distribution on the Southwestern (A) and Northeastern (B) margin of India

As the verdine facies commonly grades into deeper water glaucony facies, studies on verdine and glaucony facies are useful in interpreting the palaeogeography of the continental margins. Part of the lecture covers the substrates for authigenic green grains, minerals present and distribution of verdine and glaucony facies on the eastern and western margins of India (Fig. 2) and their palaeogeographic significance. Text book examples from the Atlantic Ocean are also presented.

## Phosphorites

Phosphorite is defined as a rock that contains higher phosphate (>18% P<sub>2</sub>O<sub>5</sub>) content. There are mainly 3 types of primary deposits of phosphate: Igneous deposits, Guano deposits and Sedimentary deposits

Igneous phosphate deposits are geographically fairly widespread and range in age from Precambrian to Tertiary. They are associated with alkaline intrusive plutonic rock, generally Nepheline syenites, or carbonates, or alkaline ultra basic complexes occurring mainly in plug like bodies and ring complexes. Igneous phosphate deposits constitute about 16% of the World production (Notholt, 1979). The Guano-derived phosphate deposits are divided into cave deposits and Insular Guano deposits. The cave deposits constitutes about a few thousand tons, whereas Insular Guano deposits constitute about 2% of the World production (Cook, 1984). Insular phosphate deposits are formed directly or indirectly by the accumulation of bird droppings. Sedimentary phosphate deposits are by far the most important of the world's resources of phosphate rock. They currently provide about 82% of the total world phosphate production and 95% or more of the world's phosphate reserves (Cook, 1984). The major part of world's production comes from the sedimentary deposits. Phosphorites occur on every continent and range in age from Precambrian to Recent, though almost all the commercially exploited deposits are of Phanerozoic age.

Sedimentary phosphorites occur more commonly as beds ranging in thickness for a few centimeters to tens of meters and are composed of grains of cryptocrystalline carbonate fluorapatite or collophane. Phosphorite nodules, mud stone phosphorites and stratiform to columnar phosphorite deposits have also been reported in different parts of the world. Except a few phosphorites that have formed in lacustrine environments such as that of the Green River formation (Cook, 1984) and Glenn's Ferry formation (Cook, 1984), the overwhelming majority formed under marine conditions. Many contain marine fossils and other evidence of marine origin. Stromatolitic phosphorites where the algal laminae are composed of collophane

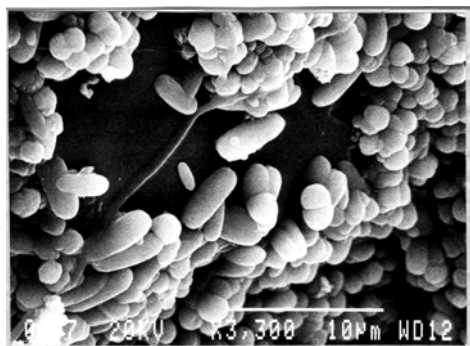
have also been described. This type of phosphorites is especially common in the Precambrian age.

Several aspects of phosphorite deposits (size, grade and facies association) have been investigated by researchers from all over the world and found that the ancient phosphorite deposits distinctly differ from the Quaternary and modern phosphorites occurring in the present day oceans. Ancient deposits are larger in size, are mostly granular (pellets and ooids) and contain high concentrations of phosphate. Stromatolitic phosphorites are most common in ancient deposits. Ancient phosphorites exhibit evidence on the role of extensive reworking and benthic microbial activity in their formation. Stromatolitic phosphorites were reported even during the Eocene. On the other hand, Quaternary and modern phosphorite deposits are smaller in size and occur as scattered nodules and pellets at the sediment-water interface and at near boundary of the oxygen minimum zone (OMZ) (Burnett, 1977; Baturin, 1982). The sources of modern phosphorites have been presumed to be sedimented plankton organic matter, fish debris, and iron-redox phosphate pump.

Several workers investigated the genesis of sedimentary phosphorites occurring from Precambrian to Recent and proposed different mechanisms for their formation. The most popular among them are (a) diagenetic precipitation of phosphate from pore waters, (b) replacement of carbonate by phosphate and (c) precipitation of phosphate by microbial activity and bacteria (Baturin, 1982). It is also suggested that more than one mechanism operates in the formation of every phosphorite deposits. By identifying the dominant mechanism one can able to decipher climatic conditions, bottom water conditions and role of oceanic processes such as coastal or equatorial upwelling in controlling the phosphorite formation.

Part of the lecture covers the detailed investigations made on the genesis of apatite in phosphorites sampled from the continental margins and seamounts. It has been shown that the Quaternary phosphorites on the continental margin off Chennai are similar to that of phosphate stromatolites and thus form a Quaternary/modern analogs of ancient phosphorites (Rao et al., 2000). Based on petrography, mineralogy elemental geochemistry, radiogenic (Sr, Nd, U) and stable (O, C, S) isotope chemistry of the phosphorites it is suggested that the environment of phosphatization remained similar during ancient and Quaternary times. Distinct compositional differences between the phosphorites off Chennai and other offshore phosphorites arised because the sources of phosphate and associated constituents were different.

Investigations on the Pleistocene high-grade phosphorites, Holocene phosphatized limestones and glaucony-phosphate sediments of the western continental margin of India showed that phosphate occurred as apatite microparticles that resembled fossilized phosphate bacteria and/or microbial filaments (Fig. 3). This established the prominence of micro-environments and microbial communities in phosphogenesis and in the intergrowth of glaucony-phosphate during early diagenesis (Rao et al., 1993; Rao et al., 2000)



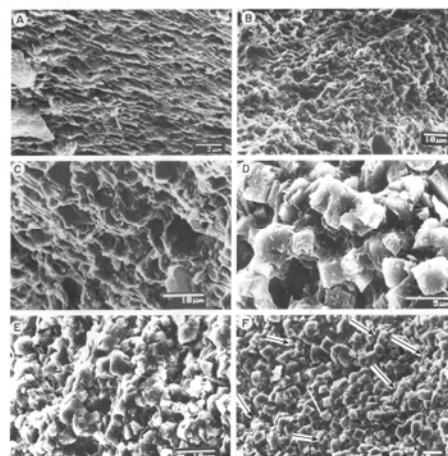
**Fig. 3.** Phosphatized bacteria in the phosphorites off western India

Phosphorites from Seamounts of the Pacific and Indian Oceans demonstrated the influence of microbial activity on their formation. Elemental sulfur, which exclusively forms by microbial processes, was reported in phosphorites of the Error Seamount. These results established that all the phosphorites on flat-topped seamounts were not guano-derived nature as has been believed so far and, some are microbial in origin (Rao et al., 1992). Comparing the composition of phosphorites formed in different environmental settings the physico-chemical factors responsible for their genesis and sedimentary processes that govern each deposit were identified.

### Dolomites

Dolomite is a magnesium-rich carbonate. It is found in far greater abundance in Earth's early history than during Quaternary/modern times, in which its occurrence is small and disparate. Although numerous models have been proposed for dolomite formation (Machel and Mountjoy, 1986; Hardie, 1987), the explanation for its unequal distribution through time still remains an enigma – known as the 'dolomite problem'. Modern dolomite occurs in a wide variety of settings from lacustrine to subtidal to deep sea environments. Most of the hydrological models proposed for the formation of shallow-water dolomites involve pumping of large volumes of normal sea water or brines through the

sediments (Melim and Scholle, 2002), or its production in a mixing zone of marine and meteoric waters (Badiozamani, 1973; Humphrey, 2000). These models however do not convincingly explain how dolomite precipitation has overcome the kinetic inhibiting factors, such as high hydration energy of  $Mg^{2+}$  (Lippmann, 1973), the extremely low activity of  $CO_3^{2-}$  anions (Garrels and Thompson, 1962) and the presence of even very low concentrations of sulphate (Baker and Kastner, 1981). The organogenic model for deep-sea dolomites in organic-rich sediments proposes dolomite precipitation by simultaneous increase in carbonate alkalinity and decrease in sulphate concentrations to near zero by sulphate-reducing bacterial degradation of organic matter (Compton, 1988). This model however, has not been invoked for the origin of massive dolomites in ancient Precambrian and Phanerozoic carbonate platforms. Modern primary or penecontemporaneous dolomites occur in several lacustrine and shallow-marine regions and are associated with organic-rich sediments or with buried algal mats that occur at the same level. Although dolomite was produced in laboratory experiments using sulphate-reducing bacteria, the microbial link in dolomite formation was first documented by Vasconcelos et al., (1995) and Vasconcelos and McKenzie (1997). In this lecture the investigations carried out on the dolomites occurring on the carbonate platform of the western margin of India (Rao et al., 2003) are presented and suggested dolomitization occurred under anoxic conditions by benthic microbial communities (Fig. 4).



**Fig. 4.** Dolomitized microbial mats and dolomites associated with microbial filaments.

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