4 Sedimentary phosphate deposits

4.1 Introduction

Sedimentary phosphate deposits or phosphorites contain few percents of calcium phosphate in form of grains of apatite, bone fragments or coprolites, and constitute important natural resources. They are the major component of phosphorus fertilizers, and are widely used in chemical industry. Moreover, phosphorites contain relatively high amounts of useful elements such as U, F and V.

Phosphorus is one of the essential elements for life and is present in all living matter. It constitutes only a minor portion of plant and animal soft parts, but phosphate is the major component of all vertebrate skeletons (bones), teeth and some invertebrate hard parts.

Sedimentary phosphates occur in three forms:
1- Nodular and bedded phosphorites.
2- Bioclastic and pebble-bed phosphorites.
3- Oceanic-island phosphorites or guano.

4.2 Mineralogy

The most common sedimentary phosphate minerals are different varieties of apatite. The apatite in igneous rocks is mainly fluorapatite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$, but in sedimentary apatite phosphate might be replaced by carbonate or sulphate, Ca might be replaced by Na, Mg, Sr, U and rare earths, fluorine may be replaced by hydroxyl or chlorine ions. Therefore, sedimentary phosphates are carbonate hydroxyl fluorapatites, which can be represented by the formula: $\text{Ca}_{10}(\text{PO}_4,\text{CO}_3)_6\text{F}_{2-3}$.

There are two specific sedimentary apatite minerals, best identified by X-ray diffraction and chemical analysis, which are francolite and dahllite. Francolite contains more than 1% F and large amount of carbonate, whereas dahllite is a carbonate hydroxyl apatite and contains less than 1% F. Both of the minerals are anisotropic.

The term cellophane is applied to sedimentary apatite of cryptocrystalline, isotropic form for which the precise composition is variable.

4.3 Nodular and bedded phosphorites

4.3.1 Recent-sub-Recent occurrences

Marine phosphate deposits on the sea-floor have been recorded on the continental shelf and slope off many continents (Fig. 4.1), particularly the western coasts of North and South America, the eastern coast of USA and the shelves off northwest Africa and Japan.
Phosphate nodules and crusts generally occur at depths from 60 to 300 m. The nodules have several centimeters diameter but may reach a meter or more across. They range in shape from slabs to spherical nodules and irregular masses. The internal structure of the nodules varies from homogeneous to concentrically laminated and conglomeratic, and may contain pellets and coated grains (oooids). Vertebrate skeletal debris, especially of fish, and coprolite are commonly associated.

4.3.2 Origin of marine phosphorites
In the marine environment, phosphate is a primary nutrient so that it is a control of organic productivity.
In seawater, it is present mainly as dissolved “orthophosphate” and particulate phosphate contained within or adsorbed onto organic detritus.

In the ocean, most organic productivity utilizes dissolved orthophosphate that takes place in the upper levels (photic zone) through phytoplankton growth. Following are details of this marine origin of phosphorites.

The dissolved orthophosphate is concentrated into the sediment through upwelling mechanism. Here cold waters containing nutrients rise from the ocean depths towards the surface (Fig. 4.2).
Fig. 4.2: Model for formation of marine phosphorites.

Upwelling currents lead to high organic productivities and phytoplankton growth in surface waters, which in turn results in organic-rich (and so phosphate-enriched) sediments and oxygen-deficient waters overlying the sea floor.

Mass mortalities of fish occasionally take place in areas of upwelling, particularly through poisoning by phytoplankton blooms. More organic matter, with its combined phosphorus, and skeletal phosphate (bones) are thus contributed to the sea floor during these events.

Upwelling is a feature of mid-latitude continental margins and it is controlled by the predominant high-pressure atmospheric systems. There are five major zones of coastal upwelling, mainly located on the western side of the landmass.

The sea floor where phosphorites are being deposited is at depths of a few hundred meters, and this commonly is within the oxygen minimum zone. Oxygen-depleted waters permit the deposition of organic matter, and its contained phosphate is released by bacterial reduction.

Low sedimentation rates are required for phosphogenesis, which is reflected in the associated sediments of being organic-rich mudrocks, cherts, pelagic limestone, hardgrounds and glauconite.

Ancient phosphates occur in the outer shelf locations at times of relative sea-level rise and highstand, with sediment starvation in deeper water.

Preset data indicates that phosphorites do not precipitate directly from sea water as some type of colloid, but they are formed within the surface sediments mainly by replacement and impregnation of non-phosphatic grains.

The bacterial decay of organic matter in the sediment liberates phosphate that is precipitated in the pellets and coprolites, and replaces siliceous and calcareous skeleton and lime mud, eventually giving rise to nodular masses of phosphorites.
The role of phytoplankton is crucial in transporting the phosphate from upwelling currents and near-surface waters to the sea floor. Microorganisms such as bacteria and fungi, and microbes are important in the process of concentrating phosphate.

A further important stage in the formation of extensive marine phosphorites is reworking. Ocean currents and severe storms remove much of the fine, unphosphatized sediment from the sea floor, leaving a concentrate of nodules, pellets and coprolites in various stages of induration and phosphate impregnation, which are then further phosphatized.

4.3.3 Ancient phosphorite sequences
Phosphate deposits related to upwelling and high organic productivity are known from the Precambrian onwards. In fact, there are a number of phosphogenic episodes of global extent, principally in the late Precambrian to Cambrian, Permian, late Cretaceous to early Tertiary, and Miocene-Pliocene.

Extensive and valuable phosphate deposits occur in the Upper Cretaceous to Lower Tertiary of North Africa and the Middle East, from Morocco and Arabian Sahara eastward to Iraq and Turkey, including Jordan. These bioclastic and pelleted phosphorites accumulated on the continental margin along the southern side of the Tethys Seaway and are related to upwelling currents.

Most of the phosphorites deposits of the geological record formed when sea-level was relatively high or were associated with short-lived transgressions. During these times, shallow, fertile, shelf seas promoted phytoplankton blooms, which led to poorly oxygenated shallow sea floors where organic matter (with its PO₄³⁻) could accumulate. There is also a correlation of phosphogenesis with warm climate because this climate induces an increase in the phosphorus flux to the ocean from increased chemical weathering on land, and it leads to prevalence of oxygen-depleted waters due to reduced oxygen solubility.

4.4 Bioclastic and pebble-bed phosphorites
Vertebrate skeletal fragments are concentrated locally to form bone beds, commonly with fish scales and coprolites (spherical to elongate faecal pellets). These phosphatic constituents are concentrated by current- and wave-reworking of sediments and winnowing of finer materials, so that coarser phosphatic grains are left over as lag deposits. This is achieved in transgressive and regressive shelf and shore zones and fluvial and intertidal currents, and also associated with upwelling phosphatic deposits.

In thin section, skeletal phosphate is distinguished by its light yellow to brown color and presence of a microstructure of regularly arranged canals (canaliculi) and growth lines. Bone phosphate is usually isotropic, or anisotropic with weak, irregular, patchy or undulose extinction (Fig. 4.3).
The coprolites may be homogeneous or may show some concentric laminations, and may contain broken shell fragments and quartz silt, depending on what the organism had eaten. Since the coprolites are usually composed of cellophane they are isotropic (Fig. 4.4a, b).

Fig. 4.4a: Photomicrograph showing a phosphorite consisting of coprolites (elongate, oval shape) having a brown color as those in upper part, and bone fragments having gray color or colorless as the one at middle right part and in middle bottom part. Cement between grains is quartz, plane polarized light.
Fig. 4.4b: Same as 4.4a but under cross-polarized light. Note that the coprolites are isotropic, totally in extinction, whereas the bone fragments are anisotropic showing a weak birefringence. The quartz cement consists of fine crystals (microquartz) having first order interference color.

During diagenesis, bone fragments in bioclastic phosphorites are further enriched in phosphate through cementation by collophane and formation of phosphate nodules by nucleation around grains.

Diagenetic phosphate can be precipitated within limestone, mudrocks and sandstones in the form of nodules, cements or replacements of calcareous skeletal grains.

**4.5 Guano and ocean-island phosphorites**

The excrements of birds mainly, and less commonly excrements of bats, may form thick phosphate deposits called guano which might be of economic significance. Thick accumulations of bird guano are found on some small islands in the eastern Pacific, and along the Pacific coast of South America.

Geologically, guano itself is not significant, but downward percolation of solutions derived from leaching guano may cause phosphatization of underlying carbonate sediments and rocks, and this has happened extensively on some islands, thus they are called ocean-island phosphorites.