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Mineralogy

Phosphorite is defined as a marine sedimentary rock with $\geq 18\%$ P_2O_5 (Slansky 1979, 1989), so by definition, phosphate minerals are its major constituents. In practice, francolite, a carbonate-fluorapatite with $>1\%$ F and appreciable amounts of CO_2 (Sandell et al. 1939; McConnell 1973), is essentially the only phosphate mineral occurring in phosphorites unaltered by metamorphism or weathering.

Francolites are structurally and chemically complex (Gruner & McConnell 1937; Borneman-Starinkevich & Belov 1940, 1953; Altschuler et al. 1952; Smith & Lehr 1966; Lehr et al. 1968; McClellan & Lehr 1969; McArthur 1978a, 1985, 1990; McClellan 1980; Kolodny 1981; Nathan 1984; McClellan & Van Kauwenbergh 1990). The group may be represented by the general formula: $Ca_{10-a-b}Na_aMg_b(PO_4)_{6-x}(CO_3)_{x-y-z}(CO_3 \cdot F)_y(SO_4)_zF_2$. However, other substitutions (Tab. 1) occur in all of the apatite sites (the two Ca sites, the PO_4 site and the F site). Not all substituents have the same valency as the original ion (e.g. Na^+ substituting for Ca^{2+} ; CO_3^{2-} or SO_4^{2-} for PO_4^{3-}), and coupled substitutions (e.g. $NaCO_3^-$ for $CaPO_4^-$ or $CO_3 \cdot F^{3-}$ for PO_4^{3-}) are generally proposed to maintain charge balance. Calcium deficiency has also been suggested (Gulbrandsen et al. 1966; Bonel et al. 1973) as an additional means of accomplishing the balance of charge. The substitution of CO_3^{2-} in apatites and the replacement of F by hydroxyl ions has been discussed by Vignoles et al. (1982). McArthur (1990) speculated that francolite may form with a Na/OH ratio of 1, with $1/2$ of the OH being replaced by H_2O , and suggested that in unweathered francolites half of the F^- atoms in the structural site are replaced by OH^- . High F contents are then caused by different degrees of coupled substitution of $CO_3 \cdot F^{3-}$ for PO_4^{3-} . However, such a high level of hydroxyl substitution has yet to be proven analytically. Finally, there are other substitutions which do not change the charge balance, such as Mg^{2+} and Sr^{2+} for Ca^{2+} , which nevertheless have considerable crystallographic and geochemical importance.

Minerals such as quartz (e.g. North Carolina, Florida phosphorites of the SE United States) and calcite (Tethyan deposits of North Africa) are major components in most phosphorite deposits. Silica also commonly occurs as opal-CT and chalcedony, forming

Tab. 1. Possible substitutions in the francolite structure

Constituent ion	Substituting ion
Ca^{2+}	Na⁺ , K^+ , Ag^+ Mg²⁺ , Sr²⁺ , Ba^{2+} , Cd^{2+} , Mn^{2+} , Zn^{2+} Bi^{3+} , Sc^{3+} , Y^{3+} , REE^{3+} U^{4+}
PO_4^{3-}	CO₃²⁻ , SO₄²⁻ , CrO_4^{2-} CO₃ · F³⁻ , $CO_3 \cdot OH^{3-}$, AsO_4^{3-} , VO_4^{3-} SiO_4^{4-}
F^-	OH^- , Cl^- , Br^- O^{2-}

REE = rare-earth elements; compositionally significant substitutions are indicated in bold

porcelanites and cherts which together with organic matter and phosphorite, constitute the so-called P-C-Si trilogy (Bentor 1980). Many other phases occur in phosphorites, notably dolomite, glauconite, sulphides (pyrite), sulphates (gypsum), clinoptilolite, clay minerals (illite, kaolinite, palygorskite, smectites) and organic matter. Clearly, the proportions, distributions, grain sizes and textural characteristics of such accessory phases have important implications for the extraction and beneficiation of a deposit.

Chemistry

Francolite chemistry may be affected by a number of factors, including: (1) kinetic effects due to the rate of formation; (2) thermodynamic factors; (3) precipitation from solutions of different composition due to secular variation in seawater or evolving porewater chemistry; (4) mechanism of formation, such as differences resulting from precipitation directly from solution or via dissolution and replacement of a pre-existing mineral (most commonly calcite), or bacterially mediated versus 'inorganic' precipitation; (5) post-precipitation burial diagenetic or metamorphic alteration; (6) weathering. The relative importance of these factors is still not well-constrained, but their significance will become apparent in the ensuing discussion.

Over the last decade, new information concerning the geochemical processes which lead to francolite precipitation and the formation of phosphorites has been derived from three main sources: (1) pore-water and solid-phase geochemical studies of sediments from modern phosphogenic areas, particularly the Mexican, Peru and East Australian shelves (Froelich et al. 1983; Jahnke et al. 1983; Glenn et al. 1988, 1994a; Van Cappellen & Berner 1988; Glenn 1990a; Heggie et al. 1990; O'Brien et al. 1990); (2) oxygen, carbon and sulphur stable-isotope studies of modern and ancient phosphorites (see Kolodny & Luz 1992a for a recent review); (3) geochemical and mineralogical data, and modelling of inorganic and bacterially-mediated apatite precipitation under experimental conditions (Lucas & Prévôt 1981, 1984, 1985; Jahnke 1984; Prévôt & Lucas 1986; Van Cappellen & Berner 1988, 1991; Prévôt et al. 1989).

Major elements

The major-element geochemistry of unaltered francolites display surprisingly little variation; unweathered Cenozoic francolites (McArthur 1978a, 1980, 1985, pers. comm. 1994) contain 32% P_2O_5 , 52% CaO , 4% F , and typically include (%): 1.2 ± 0.2 Na; 0.25 ± 0.02 Sr; 0.36 ± 0.03 Mg; 6.3 ± 0.3 CO_2 ; 2.7 ± 0.3 SO_4 . In general, the level of substitution shown by the mineral decreases progressively with increasing age, burial diagenesis and/or weathering, which promote a transition towards unsubstituted fluorapatite [$Ca_{10}(PO_4)_6F_2$] compositions. With the onset of greenschist facies metamorphism, hydroxyfluorapatites may develop (Da Rocha Araujo et al. 1992; Girard et al. 1993). Subsequently, under extreme weathering conditions, Fe- and Al-phosphate minerals such as crandallite, millisite, wavellite and strengite commonly form (Zanin 1968; Altschuler 1973; Lucas et al. 1980; Schwab & Oliveira 1981; Flicoteaux 1982; Flicoteaux & Lucas 1984; Bonnot-Courtois & Flicoteaux 1989).

The major-element chemistry of phosphorites reflects both the composition of francolite and that of accessory minerals. Consequently, SiO_2 for example, is highest in quartz-