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PHOSPHATE IN ANGRA DOS REIS: STRUCTURE AND COMPOSITION OF THE $Ca_3(PO_4)_2$ MINERALS

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Extraterrestrial calcium phosphates ("whitlockites") have the anhydrous β-$Ca_3(PO_4)_2$ structure, which is different from that of hydrous terrestrial whitlockite. This has been confirmed by X-ray refinement of the structure of a phosphate from the achondrite Angra dos Reis. In the β-$Ca_3(PO_4)_2$ structure, there is one crystallographic site, Ca(IIA), which is half-occupied by calcium, and which seems to have an energetically unfavorable configuration; natural phosphates with this configuration (including Angra dos Reis) have composition $Ca_{19}(Mg,Fe)_2(PO_4)_{14}$. Stability of the structure is probably increased by substitution of Na for Ca in Ca(IIA) giving composition $Ca_{18}(Mg,Fe)_2Na_2(PO_4)_{14}$, which occurs in chondrites; by vacancy of Ca(IIA), with rare earths and yttrium substituting for calcium in other sites for charge balance, giving composition $Ca_{16}(Y,RE)_2(Mg,Fe)_2(PO_4)_{14}$, found in lunar rocks; or by replacing Ca with hydrogen, giving composition $Ca_{18}(Mg,Fe)_2H_2(PO_4)_{14}$, which is terrestrial whitlockite. Lack of the favorable substitutions of Na, (Y, RE) or H in Angra dos Reis phosphate implies that these elements were relatively scarce in its environment of formation.

1. Introduction

Minerals with the approximate composition $Ca_3(PO_4)_2$ occur as accessories in many meteorites, most lunar rocks, and some terrestrial rocks. There has been some confusion recently about the nomenclature of these minerals [1]. Calcium phosphate was originally described from meteorites by Merrill and the name merrillite was applied by Wherry [2] in 1917. Whitlockite was subsequently described, as $Ca_3(PO_4)_2$, from a terrestrial occurrence by Frondel [3], and later Fuchs [4] concluded on the basis of X-ray powder data that the meteoritic material was identical to whitlockite. The name whitlockite has been used subsequently on lunar and meteoritic problems.

However, more recent evaluation by Keppler [5] showed that terrestrial whitlockite is hydrous and has composition close to $Ca_{18}X_2H_2(PO_4)_{14}$, where X is Mg, Fe, Mn, etc., rather than pure $Ca_3(PO_4)_2$. Moreover, X-ray structural analyses of both natural and synthetic whitlockite [6–8] have shown that its structure is somewhat different from that of synthetic β-$Ca_3(PO_4)_2$, since one of the tetrahedral PO_4 groups is inverted. Gopal and Calvo [6] predicted that the meteoritic mineral should have structure essentially the same as that of β-$Ca_3(PO_4)_2$, which was confirmed by X-ray refinement on a crystal from the chondrite Estacado by Prewitt and Rothbard [9].

The $Ca_3(PO_4)_2$ minerals are of cosmogenic and petrologic importance because they often contain relatively large amounts of some geochemically important "incompatible" trace elements, such as rare earths, uranium and thorium. Griffin et al. [10] noted what appeared to be a geochemical anomaly; in a terrestrial occurrence which they examined, apatite contained greater quantities of rare earths than coexisting whitlockite, whereas the reverse is the rule in lunar rocks.

As a contribution to the knowledge of this mineral group, as well as to the knowledge of the origin of the meteorite itself, the structure of calcium phosphate from the unique achondrite Angra dos Reis has been refined by X-ray diffraction. An attempt is made to synthesize the available data and give some explanations for the compositions of the various members of the $Ca_3(PO_4)_2$ mineral group in terms of crystal structure.

2. Experimental

The crystal examined was an irregular fragment of 0.14 mm in largest dimension. Molybdenum K_α radiation was used for all X-ray work. Precession photographs showed extinctions consistent with space group $R3c$-C_{3v}^6, in common with all members of the $Ca_3(PO_4)_2$ mineral group. Least-squares refinement of 20 two-theta values measured on the Picker FACS-1 single-crystal diffractometer yielded hexagonal cell dimensions $a = 10.362(1)$, $c = 37.106(5)$ Å. A two-theta scan technique was used to collect 2401 intensity data, 1972 of which had intensities greater than 3-sigma above background and were included in the least-squares refinement, except for the four most intense reflections, which were excluded on account of suspected secondary extinction. The program RFINE, written by L.W. Finger, was used for refinement. Data were corrected for Lorentz and polarization factors, and weighted by the reciprocal of the counting error. A primary extinction correction was included in the refinement, but the data were not corrected for absorption, which should be negligible ($\mu = 28.5$ cm^{-1}). Starting parameters were obtained from the work on heated whitlockite by Gopal and Calvo [6]. The composition was assumed to be as given by ADORABLES [11], but the minor amounts of rare earths, sodium, etc., were neglected, and the occupancies of the cation sites Mg and Ca(IIA) were refined, as Fe versus Mg and total Ca respectively. The refinement converged after 15 cycles, the last 8 with complete anisotropic thermal parameters, to a weighted R value of 0.041 (unweighted $R = 0.055$).

TABLE 1

Fractional atomic positional parameters and equivalent isotropic temperature factors, Angra dos Reis phosphate

	x	y	z	B (Å)
*Mg	0.0	0.0	0.0	0.49(5)
Ca(IB)	0.2700(2)	0.1241(2)	0.1753(1)	1.20(2)
*Ca(IIA)	0.0	0.0	0.3141(2)	1.5(1)
Ca(IIB1)	0.2725(1)	0.1308(2)	0.0681(1)	0.60(2)
Ca(IIB2)	0.1261(2)	0.2830(2)	0.4359(1)	0.65(2)
*P(A)	0.0	0.0	0.2348(1)	0.77(4)
P(B1)	0.3125(2)	0.1744(2)	0.3658(1)	0.66(3)
P(B2)	0.1821(2)	0.3222(2)	0.1358(1)	0.53(3)
*O(IA)	0.0	0.0	0.1935(2)	1.7(2)
O(IB1)	0.2612(7)	0.1788(6)	0.3268(2)	1.74(9)
O(IB2)	0.1517(6)	0.2886(6)	0.1764(1)	1.11(7)
O(IIA)	0.1422(6)	0.1381(5)	0.2484(2)	1.71(8)
O(IIB1)	0.2417(7)	0.0145(6)	0.3798(2)	1.52(9)
O(IIB2)	0.2887(6)	0.2686(5)	0.1237(2)	1.00(7)
O(IIB3)	0.2764(6)	0.2772(6)	0.3885(2)	0.95(7)
O(IIB4)	0.0322(6)	0.2453(6)	0.1161(2)	1.29(8)
O(IIB5)	0.0920(7)	0.1798(5)	0.0353(2)	1.11(7)
O(IIB6)	0.1761(5)	0.0994(5)	0.4622(1)	0.77(6)

One standard deviation is given in parentheses in terms of the last significant figure. All atoms in general position 18 *b* of space group $R3c$-C_{3v}^6, except those marked with *, which are in 6 *a*. Refined occupancies: Mg site, 0.78(1) Mg, 0.22 Fe; Ca(IIA) site, 0.55(1) Ca, 0.45 vacancy.

TABLE 2

Average cation-oxygen distances (in Å), Angra dos Reis phosphate

Mg	– (6) 2.097	Ca(IIB2)	– (8) 2.476
Ca(IB)	– (8) 2.513	P(A)	– (4) 1.537
Ca(IIA)	– (6) 2.641	P(B1)	– (4) 1.550
Ca(IIB7)	– (8) 2.484	P(B2)	– (4) 1.535

Number of oxygen atoms given in parentheses.

Difference Fourier maps showed very few areas with difference electron density greater than 1.0 e/cm^3. In particular, no evidence was found on the maps for an inverted P(A) phosphate group, (that is, with an orientation as in terrestrial whitlockite) nor was hydrogen detected. Hydrogen probably would not have been detectable on the maps even if present, since it is apparently disordered in terrestrial whitlockite [8]. The final parameters obtained are given in Table 1, and the average cation-oxygen distances are given in Table 2. Complete anisotropic temperature factors, bond lengths and angles, and observed and calculated structure factors may be obtained from the author.

3. Results and discussion

The results obtained for Angra dos Reis phosphate are in accord with those previously obtained by Prewitt and Rothbard [9] on Estacado phosphate and confirm the prediction of Gopal and Calvo [6]; meteoritic phosphates of this type have the β-$Ca_3(PO_4)_2$ structure, and not that of terrestrial whitlockite, and they evidently contain no hydrogen.

The structure of the crystal from Angra dos Reis will not be described in complete detail here; it is similar to that of β-$Ca_3(PO_4)_2$ which has been described by Dickens et al. [12]. The structure of terrestrial whitlockite has been described by Calvo and Gopal [8]. Only those aspects of the structures of the $Ca_3(PO_4)_2$ minerals which are directly relevant to the variations in composition will be discussed here.

Most of the calcium sites in the β-$Ca_3(PO_4)_2$ structure have essentially normal configuration. The sites Ca(IB), Ca(IIB1) and Ca(IIB2) are all eight-coordinated and lie in general positions. However, the sites which are denoted here Mg and Ca(IIA) are both six-coordinated and lie on three-fold symmetry axes, with one-third the multiplicity of the other sites. As is often the case in complex structures, slight structural misfit is concentrated at positions of relatively high symmetry. The "Mg" site is evidently constrained by the overall structure to be six-coordinated and slightly smaller than normal for calcium sites. Thus the presence of Mg or Fe^{2+} in this site stabilizes the compound with respect to pure $Ca_3(PO_4)_2$ [12]. Substitution of smaller cations into the other Ca sites appears to be relatively limited, so that the normal amount of $Mg + Fe^{2+}$ ($+Mn^{2+}$, etc.) is one atom per seven PO_4 units; any amount less than this would probably indicate an environment of formation very poor in these cations.

The differences between β-$Ca_3(PO_4)_2$ and terrestrial whitlockite appear around the Ca(IIA) site and the P(A) phosphate group (Fig. 1). In β-$Ca_3(PO_4)_2$, the Ca(IIA) site shares a face with the P(A) phosphate tetrahedron. Stoichiometry requires that the Ca(IIA) site be only half-occupied in β-$Ca_3(PO_4)_2$; the same is true of the phosphate crystal from Angra dos Reis (Table 1). In terrestrial whitlockite, the P(A) phosphate group is inverted, as the O(IA) atom is relocated above the phosphorus, and the Ca atoms in the Ca(IIA) site are evidently replaced by twice as many hydrogen atoms. These hydrogens are presumably located on the O(IA) atom, which acts as donor for hydrogen bonds to the O(IB1) atoms. Since there can only be one hydrogen per O(IA) atom, the hydrogen bonding to the O(IB1) atoms must be randomized in space and/or time [8].

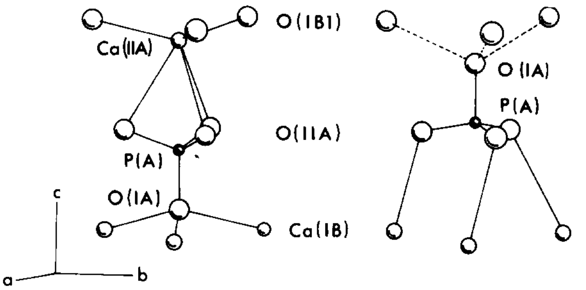

Fig. 1. Comparison of part of the structure of Angra dos Reis phosphate (β-$Ca_3(PO)_2$ structure), left, and terrestrial whitlockite. In Angra dos Reis, Ca(IIA) is only about half occupied. In terrestrial whitlockite, the O(IA) atom is shifted in such a way that the P(A) phosphate group is inverted. Possible hydrogen bonds linking O(IIA) to O(IB1) are shown by dashed lines; for a given O(IA) atom, only one such bond can exist.

It appears that all extra-terrestrial phosphates of this type have the β-$Ca_3(PO_4)$ structure, which is significantly different in having a phosphate group inverted from its configuration in terrestrial whitlockite. Thus the extraterrestrial $Ca_3(PO_4)_2$ minerals can be distinguished from terrestrial whitlockite on the basis of occurrence, crystal structure and composition (lack of hydrogen). In accordance with the conclusions of previous workers [1,8,9] it is suggested that the name merrillite be used for anhydrous phosphates with the β-$Ca_3(PO_4)$ structure. The name whitlockite could be retained for the hydrous terrestrial mineral. A recommendation to this effect has been submitted to the IMA commission on New Minerals and Mineral Names.

The Ca(IIA) site in β-$Ca_3(PO_4)_2$ has a number of features which should tend to destabilize the structure. First, the sharing of a polyhedral face with the P(A) tetrahedron must be unfavorable, according to Pauling's third rule for complex ionic crystals. The fact that the three Ca(IIA)–O(IB1) bonds are much shorter than the three Ca(IIA)–O(IIA) bonds (2.442 vs. 2.838 Å) is no doubt a reflection of direct cation-cation repulsion, even though the phosphorus-oxygen bonds must be largely covalent. Second, quite aside from the distortion caused by this repulsion, the Ca(IIA) site has a peculiar shape; the two sets of three oxygen atoms related by the three-fold axis are rotated away from a regular octahedron so that the polyhedron approaches the shape of a distorted trigonal prism. Third, the half-occupancy of this site must introduce at least some local distortions.

It is suggested that this peculiar site is the key to the understanding of much of the compositional variation in the $Ca_3(PO_4)_2$ minerals. In particular, it appears that the various compositions represent substitutions which modify the Ca(IIA) site in such a way as to stabilize the structure with respect to pure β-$Ca_3(PO_4)_2$ or $Ca_{19}Mg_2(PO_4)_{14}$.

The most favorable substitution is evidently that found in whitlockite, in which the inversion of the PO_4 group eliminates the Ca(IIA) site. This inversion presumably can occur only when hydrogen is present to bond the O(IA) atom to the O(IB1) atoms, since no other cation can perform the particular role it plays here. In most merrillites, as in ordinary chondrites and some achondrites, sodium apparently substitutes for Ca in Ca(IIA) [8]. The lower ionic charge of sodium should reduce the direct repulsion against the P(A) phosphorus atom, and also allows the cation site to be fully occupied. This is evidently the configuration found in the crystal from Estacado which was refined by Prewitt and Rothbard [9]. An alternative to filling the Ca(IIA) site with a univalent cation is vacancy or near vacancy of the site, which is possible if large trivalent cations such as yttrium or rare earths substitute for calcium in the three eight-coordinated sites. This appears to be the case in many specimens from lunar rocks, although the vacancy of the Ca(IIA) site and the location of the rare earth ions should be confirmed by actual structure refinement.

In summary, the suggested end-member compositions, and their typical occurrences, are as follows:

(1) Ca-merrillite: $Ca_{19}(Mg,Fe)_2(PO_4)_{14}$	Angra dos Reis
(2) Na-merrillite: $Ca_{18}(Mg,Fe)_2Na_2(PO_4)_{14}$	chondrites
(3) RE-merrillite: $Ca_{16}(Y,RE)_2(Mg,Fe)_2(PO_4)_{14}$	Moon
(4) whitlockite: $Ca_{18}(Mg,Fe)_2H_2(PO_4)_{14}$	Earth

Of course, there is at least partial solid solution among these end-members. Gopal and Calvo [6] showed that one specimen of whitlockite consists of about 4/5 of end-member (4) and 1/5 of end-member (1). Some analyses of merrillite are plotted in Fig. 2. Fig. 2 does not represent all published analyses; in some cases, either sodium or rare earths were not determined. Rare earths are probably low in most meteorites, however, and the analyses of Fuchs [13] suggest that there may be a fairly complete range between end-members (1) and (2). Stony-irons as well as achondrites seem to approach end-member (1). Thus differentiation of the parent body may be associated with a departure from end-member (2), although initial parent-body composition probably also has an effect.

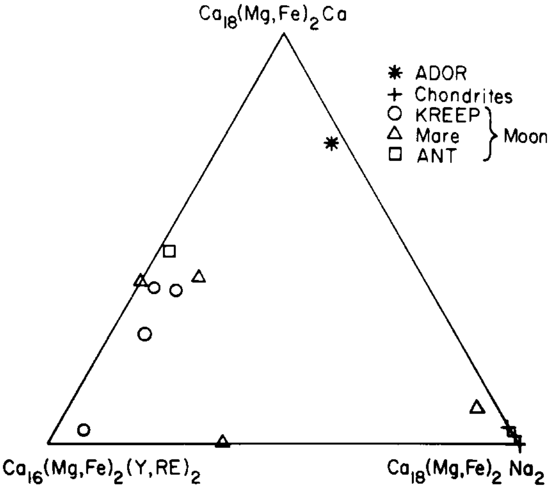

Fig. 2. Compositions of extraterrestrial $Ca_3(PO_4)_2$ minerals.

From the fact that it contains little sodium or rare earths, it would seem that the crystal from Angra dos Reis formed in an environment which was relatively poor in these elements, as well as hydrogen. The meteorite itself is enriched by factors of 10 to 15 over chondrites in rare earths [14], but most of these are contained in the abundant fassaitic pyroxene [11]. Phosphates normally crystallize late in the sequence of igneous rocks, and when the major minerals are plagioclase, olivine and low-calcium pyroxene, as in most lunar rocks and other achondrites, the rare earth elements build up to high concentrations in the liquid. Partial melts from such materials also should contain high RE, and thus most lunar rocks are enriched by factors of 10 or more over chondrites. On the other hand, crystallization of the unusual high-calcium pyroxene of Angra dos Reis probably kept the rare earths at relatively low levels in the liquid, as the solid/liquid RE partition coefficients for high-calcium pyroxenes tend to be much higher than for the other minerals mentioned above. Sodium is very low in Angra dos

Reis as a whole, contents of ~0.04% Na_2O having been reported [15,16]. The composition of the merrillite thus is consistent with low initial Na, and chondritic or greater initial RE abundances, in line with other evidence that the parent body was refractory in composition.

Granted that the substitution of hydrogen as in end-member (4) is much more favorable than the other substitutions, then the observations of Griffin et al. [10] concerning relative enrichments of rare earths in terrestrial and lunar apatites and "whitlockites" are not surprising. Since hydrogen is already present to stabilize the structure of terrestrial whitlockite, it is much less receptive to rare earths than the lunar merrillite. As would also be expected, sodium contents of terrestrial whitlockites also tend to be low, compared especially with chondritic merrillites.

The composition of phosphate thus may give some information about the abundance of certain components in the environment of formation. It should be a particularly sensitive indicator of the presence of water. However, the concept of distribution coefficients for the elements concerned appears to be essentially inapplicable to the $Ca_3(PO_4)_2$ minerals, because the substitutions of most of these elements are controlled by structural factors, and the uptake of some ions is dependent on the presence of others; in particular, the distribution coefficients for rare earths, yttrium and sodium will be strongly dependent on the presence of hydrogen, and there may be interdependencies among those for sodium, yttrium and rare earths as well. The total amount of iron and magnesium versus calcium is essentially fixed by the structure, although there appears to be no reason why the relative amounts of iron versus magnesium should not directly reflect those in the environment (as well as possible effects of temperature), as in many other minerals. In this connection, for example, merrillite from the achondrite Shergotty has distinctively high iron content [13].

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