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Structure and chemistry of phosphate minerals*

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ABSTRACT

For complex rocks in which the structure of minerals, rather than their chemical composition, changes with progressive evolution of the system, it makes sense to try and monitor such an evolving system through the progressive change in the crystal structures of the constituent phases. In effect, the paragenetic sequences of minerals in such complex environments should be related to the crystal structures of the constituent minerals. In order to consider variations in structure topology, we need to organize crystal structures into hierarchical schemes, using the hypothesis that structures may be hierarchically ordered according to the polymerization of the coordination polyhedra with higher bond-strengths. Structural units are organized according to the mode of polymerization: unconnected polyhedra, clusters, chains, sheets and frameworks.

The bond-valence structure of (OH) and (H_2O) shows that on one side, (OH) and H_2O are strong Lewis bases; on the other side, they are weak Lewis acids. As a result, a very important role of both (OH) and (H_2O) is to prevent polymerization of the structural unit in specific directions. Thus, the dimensionality of the structural unit is controlled primarily by the amount and role of hydrogen in the structure. The way in which we have formulated these ideas also allows development of a predictive framework within which specific aspects of the chemistry and structure of phosphates can be considered.

This approach to mineral structure, applied via the idea of a structural unit, can play a major role in developing structural hierarchies in order to bring about some sort of order to the plethora of hydroxy-hydrated-phosphate structures. Furthermore, by combining the idea of binary structural representation with bond-valence theory, we see the eventual possibility of predicting stoichiometry and structural characteristics of these minerals, particularly those in complex low-temperature hydrothermal environments.

KEYWORDS: phosphate minerals, bond-valence structure, Lewis acids, Lewis bases.

Introduction

THE rock-forming minerals are an extremely small subset of the mineral kingdom. Nevertheless, they have had the lion's share of scientific attention, particularly with regard to their role in petrologic and geochemical processes. The structures of these minerals have one common characteristic: they are stable over a wide range of pressure, temperature and/or chemical composition, one of the principal reasons why they are rock-forming. They are stable over wide ranges of temperature and pressure for reasons listed in Fig. 1*a*.

The rest of the mineral kingdom is usually thought of as being composed of rare minerals that are not important in geological processes. Of course, this is not the case. Although the exotic oxysalts may not be as common as the rock-forming minerals, their very existence is a challenge to our understanding of geochemical processes. In addition, such minerals are important in many geological environments (Fig. 1*b*). It is just that many of their occurrences are not fashionable to work on at the present time, as they tend to be resistant to conventional approaches based on equilibrium thermodynamics. In this class, we have such examples as highly fractionated pegmatites, the more chemically complex saline lakes, weathered zones over orebodies, etc. Not only do such environments contain a large number of complicated minerals,

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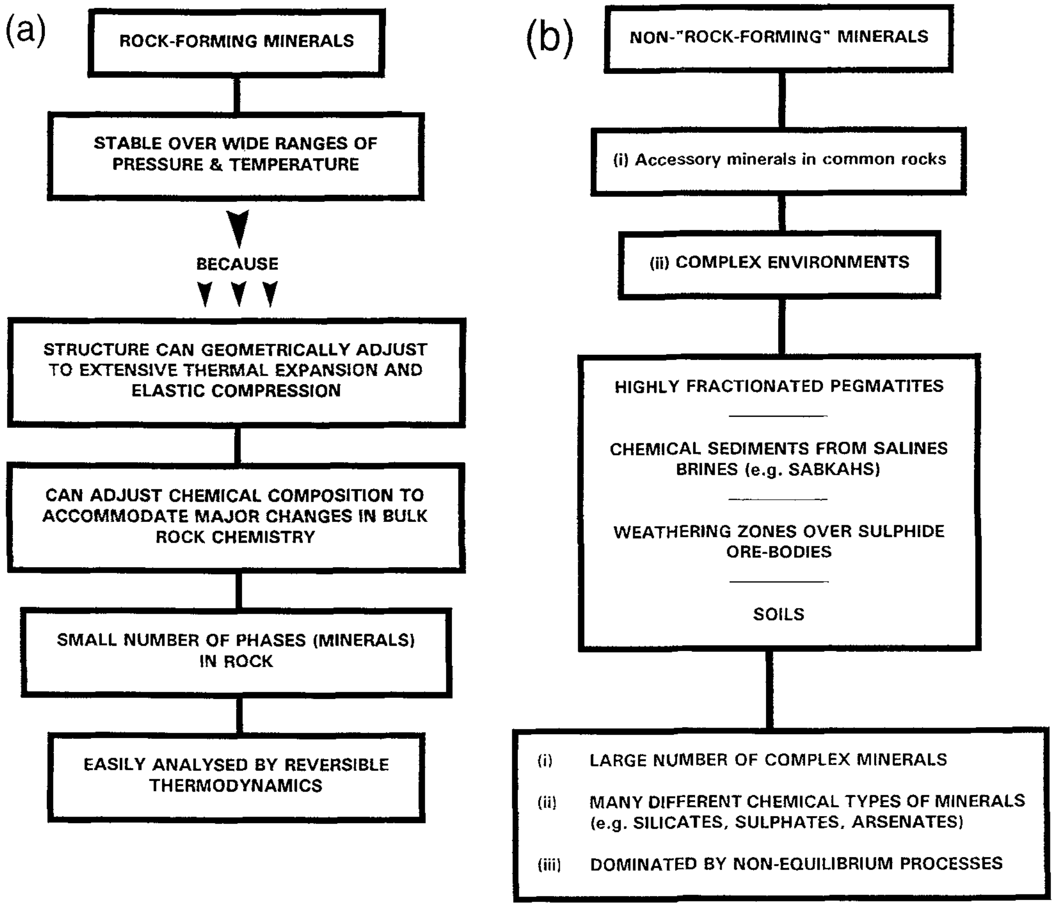


FIG. 1. (*a*) The behaviour of rock-forming minerals as a function of temperature, pressure and composition; (*b*) the behaviour of non-rock-forming minerals as a function of temperature, pressure and composition.

but they often contain minerals of several different chemical types (e.g. phosphates, silicates, oxides, sulphates, sulphides and sulphosalts); such systems tend to resist the conventional approach to petrologic interpretation.

In this regard, it is useful to contrast the mineralogy of such environments with that observed in common rocks such as granites, basalts, limestones or amphibolites. Common rocks consist of a small number of rock-forming minerals that adjust their chemistry and structural state in response to changing conditions. Thus we can follow petrologic history (Fig. 2*a*) through changes in mineral chemistry as a function of progressive crystallization.

The non-rock-forming, or exotic, minerals occur as accessory minerals in common rocks, or as constituents of what we can call complex environments, represented by such rock-types as highly fractionated pegmatites, sabkahs, weathering zones over sulphide ore-bodies, etc. These are characterized by a large number of complex minerals, and the presence of many different types of minerals. Their formation is dominated by non-equilibrium precesses. These rocks consist of large numbers of minerals that adjust their structure; i.e. break down to form new minerals, in response to even small changes in ambient conditions. Thus for complex rocks, in which structure rather than chemistry changes with

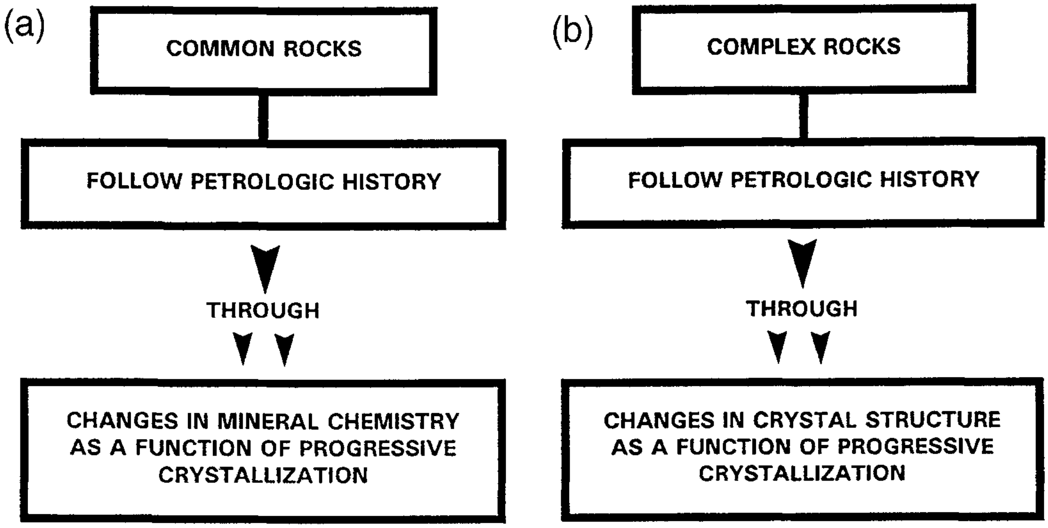


FIG. 2. (*a*) The role of rock-forming minerals in petrology; (*b*) the suggested role of non-rock-forming minerals in petrology.

progressive evolution of the system, it makes sense to try and monitor such an evolving system through the progressive change in crystal structure (Fig. 2*b*). In effect, the paragenetic sequences of minerals in such environments should be related to the crystal structures of the constituent minerals.

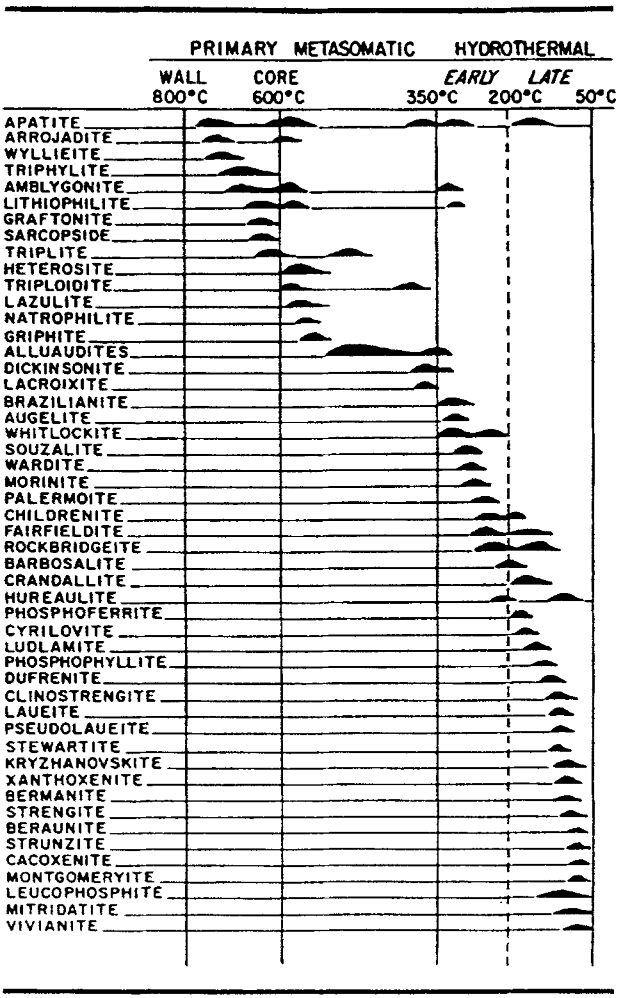
Pegmatitic phosphates

There are several hundred accredited phosphate minerals, and their most common occurrence is in highly fractionated granitic pegmatites. Thus I will concentrate primarily on this specific environment. Fisher (1958) described the phosphates as "mineralogical step-children" and as "a pain in the neck"; however, he also arranged the phosphates in a paragenetic sequence for pegmatites, and the scheme shown in Fig. 3 essentially encapsulates his findings. Fisher emphasized the correlation between position in the paragenetic sequence and the amount of H_2O in the mineral formula.

Moore (1973) attached temperature estimates to this diagram, varying from about 750°C for the primary phosphates such as triphylite and amblygonite, to about 100°C for mitridatite and vivianite. The broken line at 200°C indicates approximately where H_2O groups are stable as ligands to the transition metals.

Pegmatite phosphates are usually confined to well-zoned and very coarse granitic pegmatites where the primary phosphate phases crystallized toward, or in the core of, the pegmatite (Fig. 4). Phosphates generally occur as pods in the core. Their complexity arises from the fact that, after consolidation, the primary phosphates stew in residual aqueous fluids. This results in a large number of oxidation and exchange reactions, generating a series of phosphate minerals of increasing structural and chemical complexity with decreasing temperature.

Figure 5 shows a selection of minerals and reactions that can take place. With amblygonite-montebrasite as the primary phosphate, there is no possibility of oxidation, and hence we just get cation and anion exchange with the fluid (Moore, 1973). Removal of Li and addition of other alkali and alkaline-earth cations produce such aluminophosphates as lacroixite [$NaAl(PO_4)F$], morinite [$NaCa_2Al_2(PO_4)_2(F,OH)_5(H_2O)_2$], bertossaite [$(Li,Na)_2CaAl_4(PO_4)_2(OH,F)_4$] and the ubiquitous apatite. With triphylite-lithiophilite as the primary phosphate, we now have the possibility of oxidation of both Fe and Mn, as well as the



PARAGENETIC SEQUENCE IN PEGMATITIC PHOSPHATES

After DJ Fisher & PB Moore

FIG. 3. Generalized paragenetic sequence of phosphate minerals in pegmatites (from Moore, 1973).

same cation- and anion-exchange reactions as operative for amblygonite-montebrasite. Cation exchange with little or no oxidation gives rise to some extremely complicated minerals such as triploidite-wolfeite [$(Mn^{2+},Fe^{2+},Mg,Ca)_2(PO_4)(F,OH)$], griphite [$Na_4Ca_6(Mn,Fe^{2+},Mg)_{19}Li_2Al_8(PO_4)_{24}(F,OH)_8$] and whitlockite [$Ca_9(Mg,Fe^{2+})(PO_4)_6(PO_3OH)$] in the metasomatic zone and a large family of hydrothermally reworked phosphates (Fig. 5). Cation exchange with oxidation produces such minerals as ferrisicklerite-sicklerite [$Li(Fe^{3+},Mn^{3+})PO_4$], heterosite-purpurite [$(Fe^{3+},Mn^{3+})PO_4$] and the minerals of the alluaudite group, which, in turn, produce a plethora of structurally and chemically complex phosphate minerals (Fig. 5). Thus we have a rich hierarchy of secondary phosphates developed. It is the complexity of these parageneses that challenge our understanding of geochemical processes.

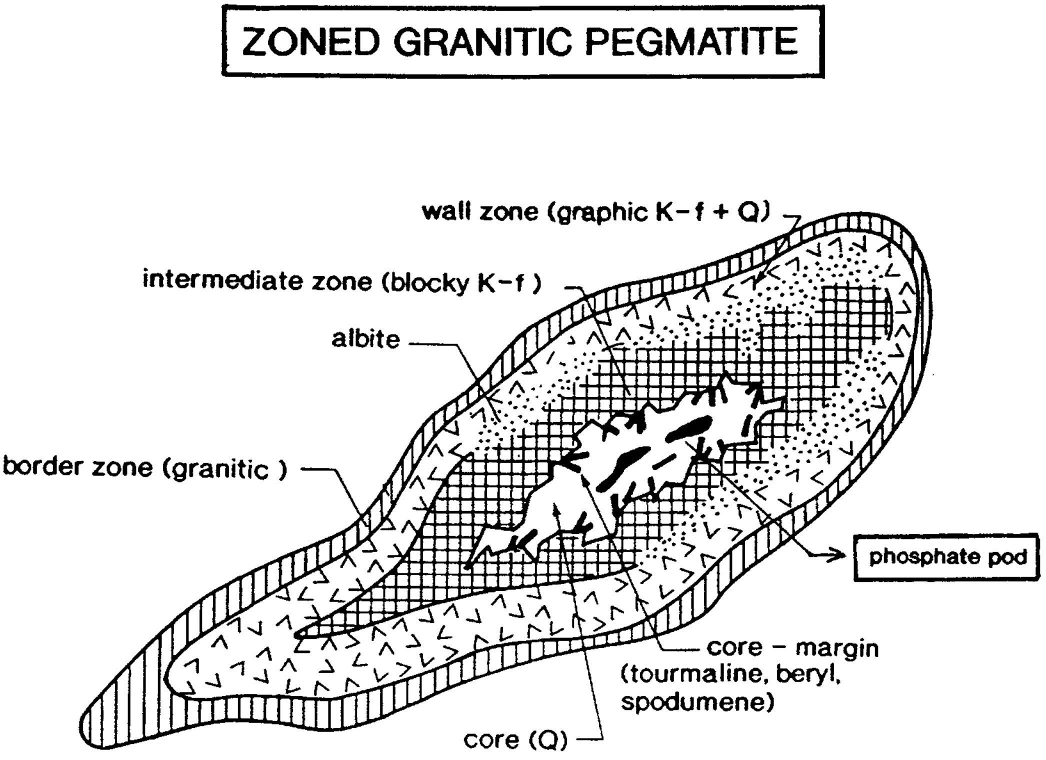


FIG. 4. The generalized structure of a zoned granitic pegmatite (from Černý, 1982).

Bond-valence theory

Crystal structures are often extremely complicated objects, and it is not intuitively obvious how to compare different structures in a quantitative manner. This is particularly the case for the exotic phosphates with their exotic atomic arrangements and complex networks of hydrogen-bonding. Molecular-orbital theory is useful for making 'in principle' arguments that provide the theoretical underpinnings for what we may want to do, but they are not, as yet, very useful in considering complex crystal structures. We need a simple 'back-of-the-envelope'-type approach for these structures, and we find this in bond-valence theory (Brown, 1981, 1992) which treats the crystal as a Lewis-Acid...Lewis-Base network. I should stress that this is not an ionic model. We take the valence electrons of the cation and use them to form chemical bonds with the surrounding anions. Despite the vocabulary used by Pauling (1929, 1960), this is a molecular-orbital model. Pauling's bond-strength is defined as the cation- valence/cation-coordination number, and Pauling's second rule states that the sum of the bond strengths around an anion is approximately equal to the magnitude of the valence of that anion (Pauling, 1929).

Many people have recognized an inverse relation between the sum of the bond strengths around anions and the variation of bond lengths in crystals. Most useful is the relationship of Brown and Shannon (1973) who called the strength of a bond the bond-valence s, and express it as

$$s = \left(\frac{r}{R}\right)^{-n} \qquad (1)$$

where R is the observed bond-length and r and n are empirical constants derived from a large number of well-refined crystal structures.

Characteristic bond-valence

If we examine the bond-valences around a specific cation in a wide range of crystal structures, we find that the values lie within

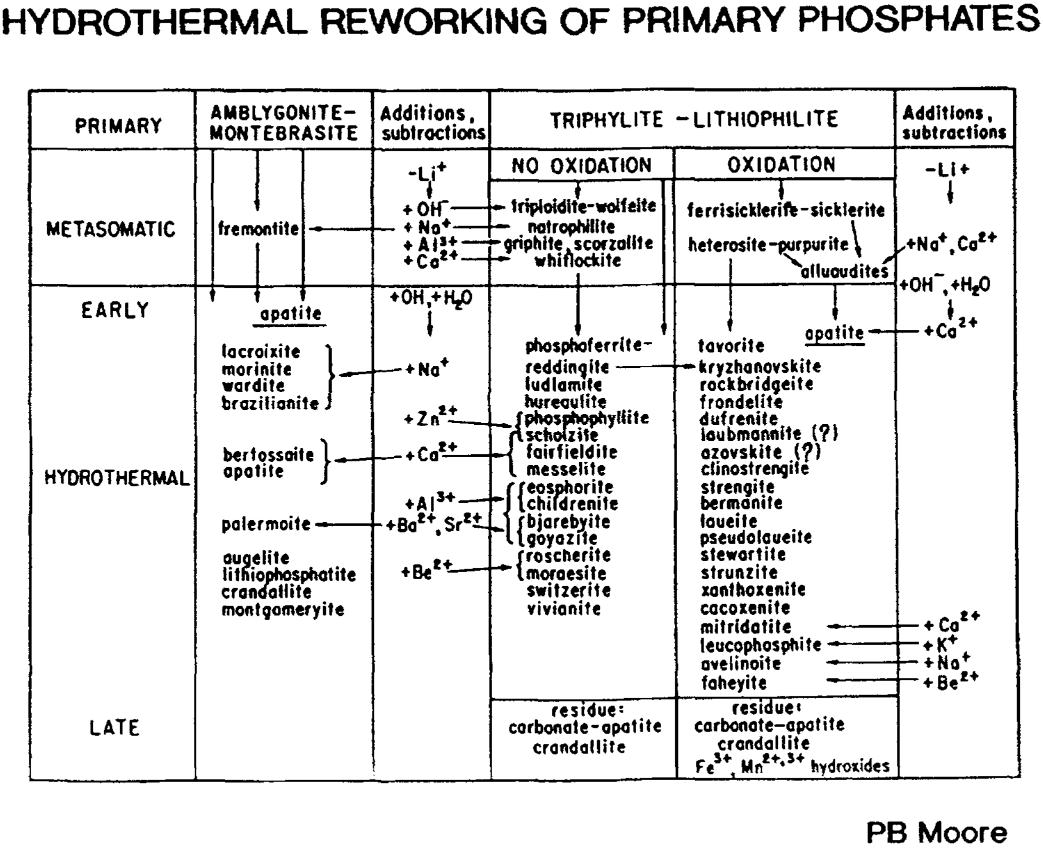


FIG. 5. Hydrothermal reworking of primary pegmatitic phosphates (from Moore, 1973).

~20% of the mean value. This mean value is characteristic of that particular cation (Fig. 6). Phosphorus, P^{5+}, is always in tetrahedral coordination in minerals; the mean bond-valence is thus equal to the Pauling bond-strength of 1.25 *vu* (valence units). For ferrous iron, Fe^{2+}, the observed coordination numbers vary from [4] to [8], with [4] and [5] more common than [7] or [8]; averaging over a large number of crystal structures gives the mean bond-valence 0.40 *vu*.

As mean bond-valence correlates with ionic size and charge, it should vary systematically throughout the periodic table, and this is indeed the case.

Lewis-acid and Lewis-base strengths

Characteristic bond-valence also correlates well with electronegativity (Fig. 7). Now electronegativity is a measure of electrophilic strength, and its correlation with the characteristic bond-valence indicates that the latter is a measure of the Lewis-Acid strength of the cation. Thus we can define the Lewis-acid strength of a cation as the average bond-valence to that cation. We can define the Lewis-base strength of an anion in the same way.

These definitions of Lewis acid and base strengths lead to a specific criterion for chemical bonding, the valence-matching principle: the Lewis-acid strength of the cation must closely match the Lewis-base strength of the anion (Fig. 8). If they don't match, a structure is not stable or does not form. This is essentially the chemical analogue of the handshaking principle in combinatorial mathematics.

This definition of Lewis basicity is not very useful for simple anions, as they show too great a

CHARACTERISTIC BOND-VALENCES

PHOSPHORUS: Always [4]-coordinated.

∴ bond-valence = 5/4 = 1.25 v.u. ± small amount

∴ characteristic bond-valence for P ≈ 1.25 v.u.

FERROUS Fe: Coordination number varies from [4] to [8]; most often [6].

The average value over all known Fe^{2+} structures = 0.40 v.u.

∴ characteristic bond-valence for Fe^{2+} ≈ 0.40 v.u.

These characteristic bond-valences vary smoothly through the periodic table, and are a function of covalency.

FIG. 6. Explanation of characteristic bond-valence of cations.

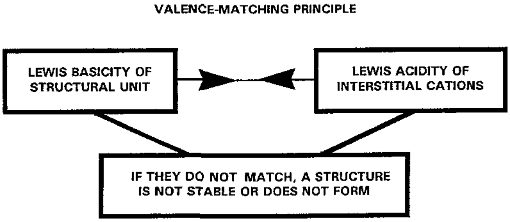


FIG. 8. Graphical explanation of the valence-matching principle.

variation in anion bond-valence for the mean value to have any predictive worth. Thus in apatite (Fig. 9), the anion bond-valences vary between 0.27 and 1.25 *vu*. The mean value is 0.50 *vu* [(0.27 × 3 + 1.25)/4], but this does not predict the individual values very well at all. However, the situation changes if we consider complex oxyanions, such as the $(PO_4)^{3-}$ oxyanion (Fig. 9). Each oxygen receives 1.25 *vu* from the central P, and needs an additional 0.75 *vu* from three additional bonds, giving a basicity of 0.25 *vu* for the $(PO_4)^{3-}$ group. Thus the base strength of the oxyanion is 0.25 *vu*, and the acid strength of the

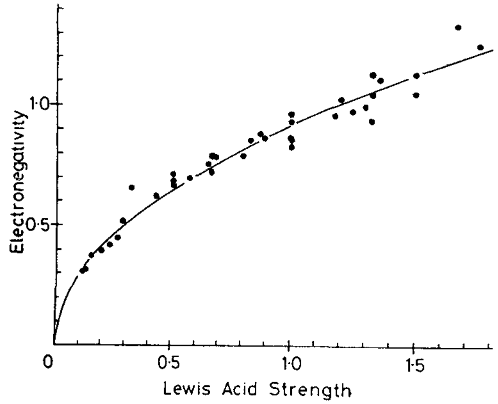


FIG. 7. Electronegativity as a function of Lewis acid strength for simple cations (from Brown, 1992).

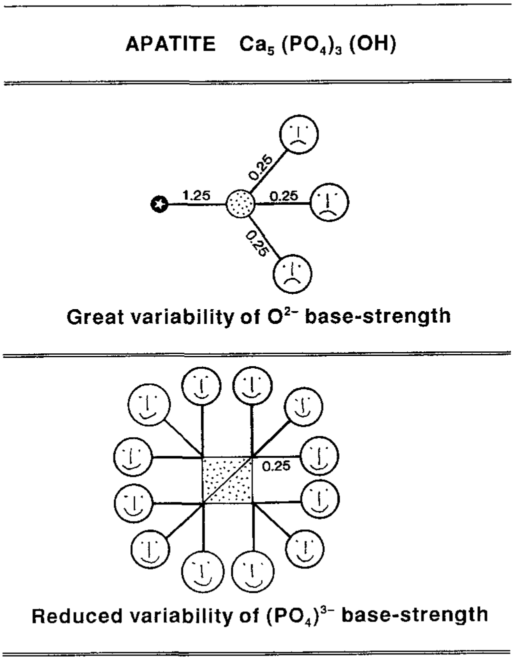


FIG. 9. The Lewis base strength for both simple $[O^{2-}]$ and complex $[(PO_4)^{3-}]$ anions in apatite; the starred circle is S, the dotted sphere is O, the dotted tetrahedron is the $(PO_4)^{3-}$ oxyanion, and the sad/happy faces are Na; the bond-valence values are shown in valence units.

Ca is 0.27 *vu*; these match up, and apatite is a stable mineral.

The important point to make here is that this analysis is *a priori*. Unlike Pauling's rules and the Brown-Shannon bond-valence curves, we do not need to have a stable arrangement formed before we can examine it; with these ideas on Lewis acid/base strength, we have predictive power.

Binary structural representation

Hawthorne (1983) has proposed that crystal structures may be hierarchically ordered according to the polymerization of the coordination polyhedra with higher bond-strengths. We can summarize the basis of this hierarchical organization of structure in the following way (Fig. 10): higher bond-valence polyhedra link to form a strongly-bonded cluster of coordination polyhedra that constitutes the fundamental building block of the mineral. This cluster is repeated, often polymerized, to form the structural unit, a complex anionic array whose excess charge is balanced by the presence of large low-valence interstitial cations.

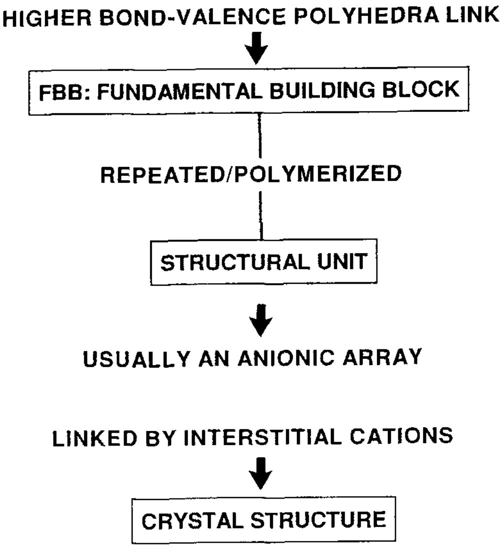


FIG. 10. Conceptual formation of a crystal structure; this idea is the basis of organizing crystal structures hierarchically according to the polymerization of coordination polyhedra of higher bond-strengths.

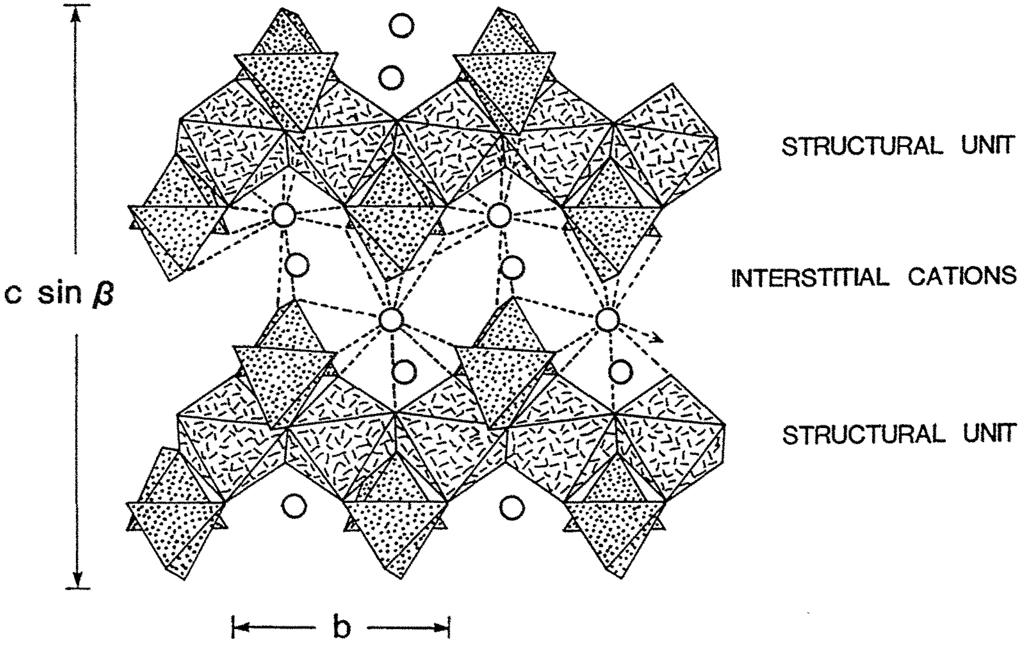


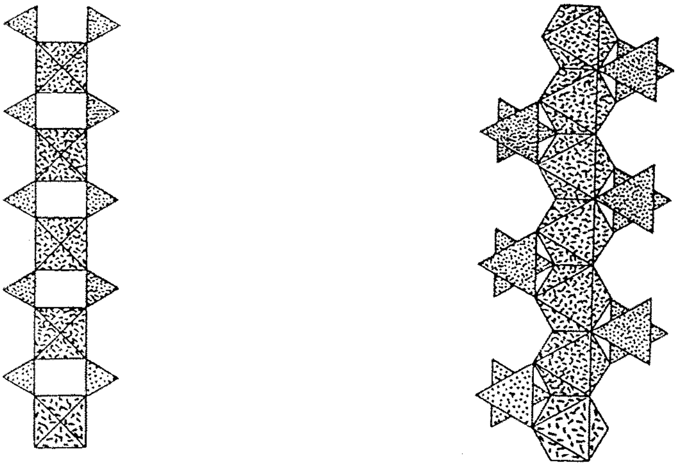
FIG. 11. The crystal structure of goedkenite portrayed to emphasize the binary representation as a structural unit and interstitial cations; (PO_4) tetrahedra are dotted, $(Al\phi_6)$ octahedra are dashed, Sr is shown as unshaded circles.

Consider the mineral goedkenite, a Sr-Al-hydroxy-phosphate shown in Fig. 11. Al is [6]-coordinated, forming the octahedra shaded with dashes. These octahedra share *trans* edges to form chains extending along the *b*-axis, and these chains are decorated by (PO_4) tetrahedra in a staggered fashion along their length. These decorated chains are cross-linked into a three-dimensional structure by [9]-coordinated Sr cations.

If we consider the structural unit (shown shaded in Fig. 11) as a very complex anion, we can calculate its Lewis base strength and relate this, *via* the valence-matching principle, to the Lewis acidity of the interstitial cations. In this way, we have reduced even the most complex structure to a quantitative binary representation. It is this simple representation that allows us to look at many complex mineralogical questions.

Interstitial-cation chemistry

First, let us look at what controls the nature of the interstitial cation chemistry in minerals. As an example, we will consider the two structural units shown in Fig. 12. The first consists of octahedra linked by corner-sharing with pairs of tetrahedra; the general stoichiometry of this arrangement can be written as $[M(TO_4)_2\phi_2]$ where M = octahedrally coordinated cation, T = tetrahedrally coordinated cation, and ϕ is an unspecified anion. Phosphate and arsenate minerals with this type of structural unit are listed in Fig. 12; when the interstitial cation is divalent, it is always Ca. The second structural unit consists of octahedra linked by sharing *trans* edges to form an $[M\phi_4]$ chain that is flanked by pairs of tetrahedra that link by corner-sharing to adjacent octahedra; the general stoichiometry of this arrangement can be



Brandtite	$Ca_2[Mn(AsO_4)_2(H_2O)_2]$
Krohnkite	$Na_2[Cu(SO_4)_2(H_2O)_2]$
Roselite	$Ca_2[Co(AsO_4)_2(H_2O)_2]$
Cassidyite	$Ca_2[Ni(PO_4)_2(H_2O)_2]$
Collinsite	$Ca_2[Mg(PO_4)_2(H_2O)_2]$
Gaitite	$Ca_2[Zn(AsO_4)_2(H_2O)_2]$
Roselite-beta	$Ca_2[Co(AsO_4)_2(H_2O)_2]$
Talmessite	$Ca_2[Mg(AsO_4)_2(H_2O)_2]$
Fairfieldite	$Ca_2[Mn(PO_4)_2(H_2O)_2]$
Messelite	$Ca_2[Fe^{2+}(PO_4)_2(H_2O)_2]$

Yftisite	$Y_4[Ti(SiO_4)_2O](F,OH)_6$
Arsenbrackebuschite	$Pb_2[Fe^{2+}(AsO_4)_2(H_2O)]$
Arsentsumebite	$Pb_2[Cu(SO_4)(AsO_4)(OH)]$
Brackebuschite	$Pb_2[Mn(VO_4)_2(H_2O)]$
Gamagarite	$Ba_2[(Fe^{3+},Mn)(VO_4)_2(OH,H_2O)]$
Goedkenite	$Sr_2[Al(PO_4)_2(OH)]$
Tsumebite	$Pb_2[Cu(PO_4)(SO_4)(OH)]$
Fornacite	$Pb_2[Cu(AsO_4)(CrO_4)(OH)]$
Molybdofornacite	$Pb_2[Cu(AsO_4)(MoO_4)(OH)]$
Tornebohmite	$*(RE)_2[Al(SiO_4)_2(OH)]$
Vauquelinite	$Pb_2[Cu(PO_4)(CrO_4)(OH)]$

FIG 12. The structural units $[M(TO_4)_2\phi_2]$ and $[M(TO_4)_2\phi]$, and the phosphate, arsenate and vanadate minerals based on these structural units; note the difference in interstitial-cation type between the two groups of minerals.

written as $[M(TO_4)_2\phi]$. Phosphate, arsenate and vanadate minerals with this type of structural unit are listed in Fig. 12; the interstitial cation is Pb^{2+} or Sr in these minerals. For both structural units of Fig. 12, the electroneutrality principle requires only that the interstitial cation(s) be a single divalent cation or two monovalent cations. However, only divalent interstitial cations occur, and there is complete chemical ordering: only Ca occurs with the $[M(TO_4)_2\phi_2]$ structural unit and only Pb^{2+} or Sr occurs with the $[M(TO_4)_2\phi]$ structural unit. Both structural units show a wide range in chemistry, and these minerals are not restricted to any particular paragenesis, so why is there such an extreme ordering of the interstitial cations? There must be another mechanism, in addition to the electroneutrality principle, controlling this aspect of structural chemistry. We find the answer in the valence-matching principle.

Consider first the structural unit $[M(TO_4)\phi_2$ such as occurs in the mineral collinsite, $Ca_2[Mg(PO_4)_2(H_2O)_2]$. There are eight O-anions and two H_2O groups in the structural unit. For an anion coordination number of [4] for O and three for (H_2O) of the structural unit (Hawthorne, 1994), the anions of the structural unit require thirty-eight bonds to them from their coordinating cations. The number of cation-oxygen bonds implicit in the formula $[Mg(PO_4)_2(H_2O)_2]$ is twenty-two, six Mgφ bonds, two times four P–O bonds and two times four H–O bonds. The difference between the number of bonds required (38) and the number of bonds implicit in the coordination polyhedra of the $[Mg(PO_4)_2(H_2O)_2]$ structural unit (22) must be made up by bonds to the interstitial cations. This difference is sixteen. As the structural unit has a charge of 4^- and requires sixteen bonds to fulfil its anion-coordination requirements, the Lewis basicity of the structural unit is 4/16 = 0.25 *vu*. This matches closely with the Lewis acidity of Ca at 0.27 *vu*; this satisfies the valence-matching principle and stable structures will form. Although Pb^{2+}, Sr and Na_2 or K_2 satisfy the electroneutrality requirement, their Lewis acidities (Pb^{2+} = 0.20 *vu*, Sr = 0.20 *vu*, Na = 0.17 *vu*, K = 0.13 *vu*) do not match the Lewis basicity of the $[M^{2+}({}^{5+}TO_4)\phi_2]$ structural unit and stable structures do not form.

Consider next the structural unit $[M(TO_4)_2\phi]$, such as occurs in vauquelinite, $Pb_2[Cu(PO_4)(CrO_4)(OH)]$. The Lewis basicity of the structural unit is 4/(3616) = 0.20 *vu*. This matches closely with the Lewis acidities of Pb^{2+} and Sr, and stable structures are formed with these species as interstitial cations (Fig. 12). Thus it is the matching of the acid and base strengths of the interstitial cations and the structural unit that accounts for such contrasting interstitial-cation chemistry in the minerals with different structural units.

Water of hydration in minerals

Next, let us look at the role of H_2O in minerals, and ask the question "Why are some minerals hydrated whereas others are not, and what controls the degree of hydration?"

Figure 13 shows the bond-valence structure around an H_2O group. A cation bonds to the O-anion with a particular bond-valence. The remaining bond-valence requirements of the O-anion are satisfied by the associated H-atoms, and the bond-valence requirements of the H-atoms are met by H-bonds with adjacent anions. Note that the valences of the H-bonds are exactly half that of the M–O bond. The H_2O group is acting as a bond-valence transformer, causing one bond to be split into two weaker bonds.

Consider the mineral metavauxite, $Fe^{2+}[Al(PO_4)(OH)(H_2O)]_2(H_2O)_6$ (Fig. 14); the

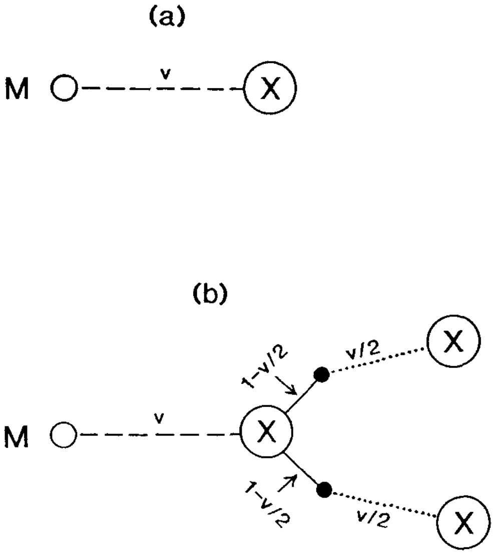
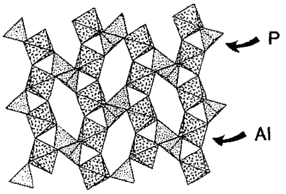


FIG. 13. The bond-valence structure around (*a*) an anion (X) bonded to a cation (with a bond valence *v*); (*b*) an (H_2O) group consisting of an oxygen (X) and two H-atoms (small black circles).

WATER OF HYDRATION

METAVAUXITE

$Fe^{2+}[Al(PO_4)(OH)(H_2O)]_2(H_2O)_6$



Module basicity = 0.17 *vu*. Excess charge = –2 *vu*.

Lewis acidity of Fe^{2+} = 0.33

Anion coordination of Fe^{2+} = $(H_2O)_6$

Effective coordination of Fe (*i.e.*, number of bonds to structural unit per Fe^{2+} cation) = 6 x 2 = [12]

Effective Lewis acidity = charge/number of bonds = 2/12 = 0.17 *vu*

FIG. 14. Examination of the (bond-) valence-matching principle in metavauxite; the valence-matching principle is satisfied when the structural unit (module) Lewis basicity (0.17 *vu*) matches with the Lewis acidity (0.17 *vu*) of the complex cation $[Fe^{2+}(H_2O)_6]^{2+}$.

structural unit, shown in square brackets, has a Lewis basicity of 0.18 *vu*. By the valence-matching principle, we would expect an interstitial cation with a Lewis acidity of 0.18 *vu*. But Fe^{2+} is the interstitial cation, and [6]-coordinated Fe^{2+} has a Lewis acidity of 0.33 *vu*. However, each Fe^{2+} is coordinated by six (H_2O) groups. Thus the average valence of a bond between interstitial Fe^{2+} and the structural unit is 2, the valence of Fe^{2+}, divided by (6 × 2), the number of bonds between the complex cation $[Fe^{2+}(H_2O)_6]^{2+}$ and the structural unit, which is 0.17 *vu*. The Lewis basicity, 0.18 *vu*, of the structural unit matches the Lewis acidity of the interstitial complex cation $[Fe^{2+}(H_2O)_6]^{2+}$ in agreement with the valence-matching principle, and metavauxite is a stable mineral.

Thus water of hydration occurs in crystals to moderate the Lewis acidity of the interstitial cation, and match it with the Lewis basicity of the structural unit. This idea is fairly successful in predicting the degree of hydration in complex phosphates.

Structural hierarchy in phosphate minerals

The utility of organizing crystal structures into hierarchical sequences has long been recognized. Bragg (1930) classified the silicate minerals according to the way in which the (SiO_4) tetrahedra polymerize, and this scheme was generalized to polymerized tetrahedral structures by Zoltai (1960) and Liebau (1985). Further developments along similar lines were the classifications of the aluminium hexafluoride minerals (Pabst, 1950; Hawthorne, 1984) and the borate minerals (Christ, 1960; Christ and Clark, 1977). Such an approach to hierarchical organization is of little use in such chemical groups as the phosphates or the sulphates, in which the principal oxyanion does not self-polymerize because of the constraint of the valence-sum rule (Hawthorne, 1983). Moore (1984) developed a classification of phosphate minerals, based on the polymerization of divalent and trivalent metal octahedra. However, all these hierarchical schemes focus on specific chemical classes of compounds, and are not easily adapted to other classes.

We can approach this general problem within the framework of bond-valence theory. First let us consider the cations in a structure. The cation bond-valence requirements are satisfied by the formation of anion coordination polyhedra around them. Thus we can think of a structure as an array of complex anions that polymerize in order to satisfy their (simple) anion bond-valence requirements according to the valence-sum rule. Let the bond-valences in an array of coordination polyhedra be represented by s_0^i $(i = 1,n)$ where $s_0^i > s_0^{i+1}$. The valence-sum rule indicates that polymerization can occur when

$$s_0^1 + s_0^i < |V_{\text{anion}}| \qquad (2)$$

and the valence-sum rule is most easily satisfied when

$$s_0^1 + s_0^i = |V_{\text{anion}}| \qquad (3)$$

This suggests that the most important polymerizations involve those coordination polyhedra with higher bond-valences, subject to the constraint of equation (3), as these linkages most easily satisfy the valence-sum rule (under the constraint of maximum volume).

Dimensional polymerization

Families of structures can be developed based on different structural units built from the same fundamental building block. Structural units can be arranged according to the mode of polymerization: (a) unconnected polyhedra; (b) finite clusters; (c) chains; (d) sheets; (e) frameworks. Most work has focused on structures with tetrahedra (i.e. phosphates) and octahedra as principal coordination components of the structural unit, although there has been some notable work (Moore, 1981) on structures with higher coordination numbers. The following outline is not, of course, comprehensive, but should be representative of the structural diversity of phosphates and give a flavour of the hierarchical nature of their atomic arrangements.

Unconnected-polyhedra minerals

In minerals of this type, the PO_4 group and intermediate-coordination complex-cations [e.g. $\{Mg(H_2O)_6\}$, $\{NH_4\}$] are linked together solely by hydrogen bonding. Inspection of Table 1 shows that most of these minerals are somewhat unusual: acid-phosphate groups are common, and some minerals have NH_4 as the interstitial complex cation. The PO_4 group has a Lewis basicity of 0.25 *vu*, and must link to a cation of matching Lewis basicity. The only cations that satisfy this criterion are Ca and NH_4, hence the presence of apatite and struvite in this group. This is also the reason why apatite is such a common mineral: Ca is an extremely common component of many geochemical environments, and easily satisfies the valence-matching principle with PO_4. In the absence of Ca, the PO_4 group has two options: (1) it can link to H to form an acid phosphate group with a Lewis basicity of 0.18 *vu*, in which case it can bond to hydrated complex cations such as $\{Mg(H_2O)_6\}$ with a Lewis acidity of 0.17 *vu* (as in phosphorroesslerite, Table 1): (2) it can link to a strong Lewis acid and form a polymerized structural unit with a lower Lewis basicity. This reasoning accounts for the fact that most phosphate minerals have complex structures and chemical compositions.

Monetite is an extremely interesting mineral with regard to the valence-matching principle. Should the formula be written as $CaH(PO_4)$ or $Ca(PO_3OH)$? Consider the first option: the Lewis basicity of the structural unit is 0.25 *vu*, and the Lewis acidity of the interstitial cation is $(0.28 + 0.50)/2 = 0.39$ *vu*; note that in this formulation, there must be a symmetrical H-bond and the Lewis acidity of H is 0.50 *vu*. Consider the second option: the Lewis acidity of the structural unit is 0.22 *vu* and the Lewis acidity of the interstitial cation is 0.27 *vu*; note that in this formulation, the H-bonding is asymmetric. In monetite, the H atom seems to occupy a centre of symmetry; i.e. one H atom occurs between two O atoms related by a centre of symmetry. However, the agreement with the valence-matching principle essentially rules out the first possibility but allows the second possibility. The agreement for the second option suggests that the H atom is dynamically disordered in monetite, such that the H atom spends most of the time in a PO_3OH configuration and only a small part of the time in a symmetrical configuration.

Nahpoite and dorfmanite both have a Lewis basicity of 0.25 *vu* or 0.22 *vu*, depending on whether they are formulated as normal phosphates or acid phosphates. As normal phosphates, they

TABLE 1. $MT\phi_n$ and $MT_2\phi_n$ minerals based on isolated $M\phi_6$ octahedra and $T\phi_4$ tetrahedra

Mineral	Formula	Space group	Ref.
Apatite	$Ca_5[PO_4]_3(OH,F)$	$P6_3/m$	(1)
Phosphorroesslerite	$[Mg(H_2O)_6][PO_3(OH)](H_2O)$	$C2/c$	–
Struvite	$(NH_4)[Mg(H_2O)_6][PO_4]$	$Pmn2_1$	(2)
Monetite*	$CaH[PO_4]$	$P\bar{1}$	(3)
Nahpoite	$Na_2H[PO_4]$	$P2_1/m$	–
Dorfmanite	$Na_2H[PO_4](H_2O)_2$	–	–
Stercorite*	$Na(NH_4)H[PO_4](H_2O)_4$	$P\bar{1}$	(4)

References: (1) Sudarsanan and Young (1969); (2) Abbona *et al.* (1984); (3) Catti *et al.* (1977); (4) Ferraris and Franchini-Angela (1974)

TABLE 2. $MT\phi_n$ and $MT_2\phi_n$ minerals based on isolated $[M(T\phi_4)\phi_n]$ and $[(M(T\phi_4)_2\phi_n)_m]$ clusters.

Mineral	Formula	Space group	Ref.
Anapaite	$Ca_2[Fe^{2+}(PO_4)_2(H_2O)_4]$	$P\bar{1}$	(1)
Schertelite	$(NH_4)_2[Mg(PO_3OH)_2(H_2O)_4]$	$Pbca$	(2)
Morinite	$Ca_2Na[Al_2(PO_4)_2F_4(OH)(H_2O)_2]$	$P2_1/m$	(3)

References: (1) Catti *et al.* (1979); (2) Khan and Baur (1972); Hawthorne (1979)

have Lewis acidities of 0.28 and 0.25 *vu*, respectively, whereas as acid phosphates, they have Lewis acidities of 0.17 *vu* and 0.13 *vu*, respectively. Agreement with the valence-matching principle is closer for the normal phosphate model in both cases, suggesting that nahpoite and dorfmanite are not acid phosphates.

Stercorite is the most complicated example of an isolated phosphate structure that we will consider here. Written as a normal phosphate, the additional bonds needed by the structural unit are 16 − 4 = 12 and the charge on the structural unit is 3^-; thus the Lewis basicity is 3/12 = 0.25 *vu* and the Lewis acidity is 0.27 *vu*. Written as an acid phosphate, the additional bonds needed by the structural unit are 15 − 6 = 9 and the charge on the structural unit is 2^-; thus the Lewis basicity is 2/9 = 0.22 *vu* and the Lewis acidity is 0.18 *vu*. Either formulation seems reasonable, but requires the presence of NH_4 to achieve a sufficiently high Lewis acidity.

Finite-cluster minerals

Selected minerals from this class are given in Table 2, and the corresponding structures are shown in Fig. 15. Anapaite and schertelite are based on the simple $[M(T\phi_4)_2\phi_4]$cluster in which two (PO_4) tetrahedra link to the *cis* vertices of an $(M\phi_6)$ octahedron. In anapaite (Fig. 15*a*), the clusters are arranged at the vertices of a centered orthorhombic plane lattice and are linked together by Ca and by H-bonds. In schertelite (Fig. 15*b*), as in anapaite, the clusters are arranged at the vertices of a centered orthorhobmic plane lattice, and are linked together by H-bonds from the complex cation (NH_4). Morinite (Fig. 15*c*) is based on the $[M_2(T\phi_4)_2\phi_7]$ cluster in which two $(Al\phi_6)$ octahedra link through a common vertex and (PO_4) tetrahedra bridge between each octahedron. These clusters are arranged at the vertices of a centered orthorhombic plane lattice, and are linked by interstitial Ca and Na, and by H-bonds.

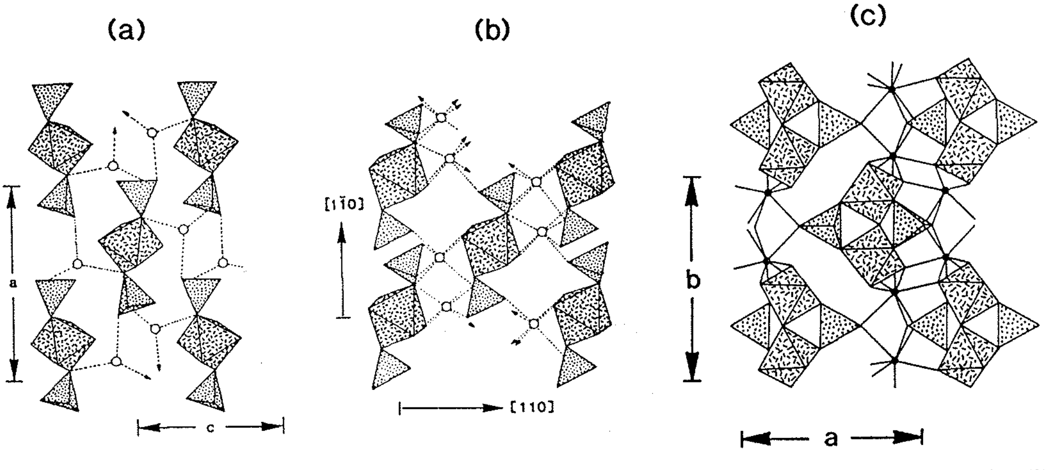


Fig. 15. Structural arrangements in selected phosphate minerals based on finite polyhedral clusters: (*a*) anapaite; (*b*) schertelite; (*c*) morinite; phosphate tetrahedra are dot-shaded, octahedra are dash-shaded.

The structural unit of anapaite has a Lewis basicity of 0.28 *vu*; this matches the Lewis acidity of Ca, and hence anapaite has Ca as its interstitial cation. The structural unit of schertelite is somewhat more complicated than anapaite, and indicates how to treat OH. The bonds needed by the anions of the structural unit are 6 × 4 (for O atoms) + 3 × 6 (for OH and H_2O groups) = 42; the bonds provided by the cations of the structural unit are 4 × 2 (P) + 6 (Mg) + 2 × 10 (H) = 34. The additional bonds needed = 42 − 34 = 8 and the charge on the structural unit = 2^-; the resulting Lewis basicity = 2/8 = 0.25 *vu*, which corresponds to the Lewis acidity of $(NH_4)^-$, the interstitial cation in schertelite. Morinite is also an instructive example as it demonstrates the difference between F and OH, and shows how to deal with multiple interstitial cations. The bonds needed are 8 × 4 (O atoms) + 6 × 3 (F, OH and H_2O) = 50, the bonds present are 2 × 6 (Al) + 2 × 4 (P) + 5 × 2 (H) = 38, and the charge on the structural unit is 5^-; hence the Lewis basicity = 5/(50 − 38) = 0.25 *vu*. So morinite needs interstial cations with a total charge of 5^- and an aggregate Lewis acidity of 0.25 *vu*. The observed interstitial cations Ca_2Na have an aggregate Lewis acidity of (0.27 × 2 + 0.17)/3 = 0.24 *vu*, closely matching the Lewis basicity and the charge of the structural unit, and hence forming a stable mineral. The possibilities Na_5 and $CaNa_3$ have charges of 5^- but aggregate Lewis acidities of 0.17 and 0.20 *vu*, respectively, and hence cannot satisfy the valence-matching principle.

Infinite-chain minerals

Selected minerals from this class are given in Table 3, and the corresponding structural units are shown in Fig. 16. Childrenite and eosphorite are isostructural and have the $[M(TO_4)\phi_3]$ chain (Fig. 16*a*) as their structural unit. In this chain, $M\phi_6$ octahedra link through *trans* vertices to form an $[M\phi_5]$ unit that is further linked by tetrahedra in a staggered arrangement along the length of the chain. The $[M(TO_4)_2\phi_2]$ chain (Fig. 16*b*) is the basis of several families of phosphate, arsenate and sulphate minerals, specifically cassidyite and collinsite (members of the talmessite, $Ca_2[Mg(AsO_4)_2(H_2O)_2]$, group) and fairfieldite and messelite (members of the fairfieldite group). Octahedra of this chain are linked indirectly though pairs of tetrahedra. Each octahedron thus has one pair of *trans* vertices that do not link to tetrahedra; these vertices are (H_2O) groups. The $[M(TO_4)_2\phi]$ chain (Fig. 16*c*) is the structural unit in tancoite and the minerals of the jahnsite and segelerite groups (Table 3). Octahedra link

TABLE 3. $MT\phi_n$ and $MT_2\phi_n$ minerals based on infinite chains

Mineral	Formula	Space group	Ref.
Childrenite	$Mn^{2+}[Al(PO_4)(OH)_2(H_2O)]$	*Bbam*	(1)
Eosphorite	$Fe^{2+}[Al(PO_4)(OH)_2(H_2O)]$	*Bbam*	(2)
Cassidyite	$Ca_2[Ni(PO_4)_2(H_2O)_2]$	$P\bar{1}$	(3)
Collinsite	$Ca_2[Mg(PO_4)_2(H_2O)_2]$	$P\bar{1}$	(4)
Fairfieldite	$Ca_2[Mn(PO_4)_2(H_2O)_2]$	$P\bar{1}$	(5)
Messelite	$Ca_2[Fe^{2+}(PO_4)_2(H_2O)_2]$	$P\bar{1}$	(4)??
Jahnsite	$CaMnMg_2[Fe^{3+}(PO_4)_2(OH)]_2(H_2O)_8$	*P2/a*	(6)
Whiteite	$CaFe^{2+}Mg_2[Al(PO_4)_2(OH)]_2(H_2O)_8$	*P2/a*	(7)
Lun'okite	$Mn_2Mg_2[Al(PO_4)_2(OH)]_2(H_2O)_8$	*Pbca*	–
Overite	$Ca_2Mg_2[Al(PO_4)_2(OH)]_2(H_2O)_8$	*Pbca*	(8)
Segelerite	$Ca_2Mg_2[Fe^{3+}(PO_4)_2(OH)]_2(H_2O)_8$	*Pbca*	(8)
Wilhelmvierlingite	$Ca_2Mn_2[Fe^{3+}(PO_4)_2(OH)]_2(H_2O)_8$	*Pbca*	–
Goedkenite	$Sr_2[Al(PO_4)_2(OH)]$	$P2_1/m$	(9)
Tsumebite	$Pb_2[Cu(PO_4)(SO_4)(OH)]$	$P2_1/m$	(10)
Vauquelinite	$Pb_2[Cu(PO_4)(CrO_4)(OH)]$	$P2_1/n$	(11)

References: (1) Giuseppetti and Tadini (1984); (2) Hansen (1960); (3) White *et al.* (1967); (4) Brotherton *et al.* (1974); (5) Fanfani *et al.* (1970); (6) Moore and Araki (1974b); (7) Moore and Ito (1978); (8) Moore and Araki (1977a); Moore *et al.* (1975); (10) Nichols (1966); (11) Fanfani and Zanazzi (1968).

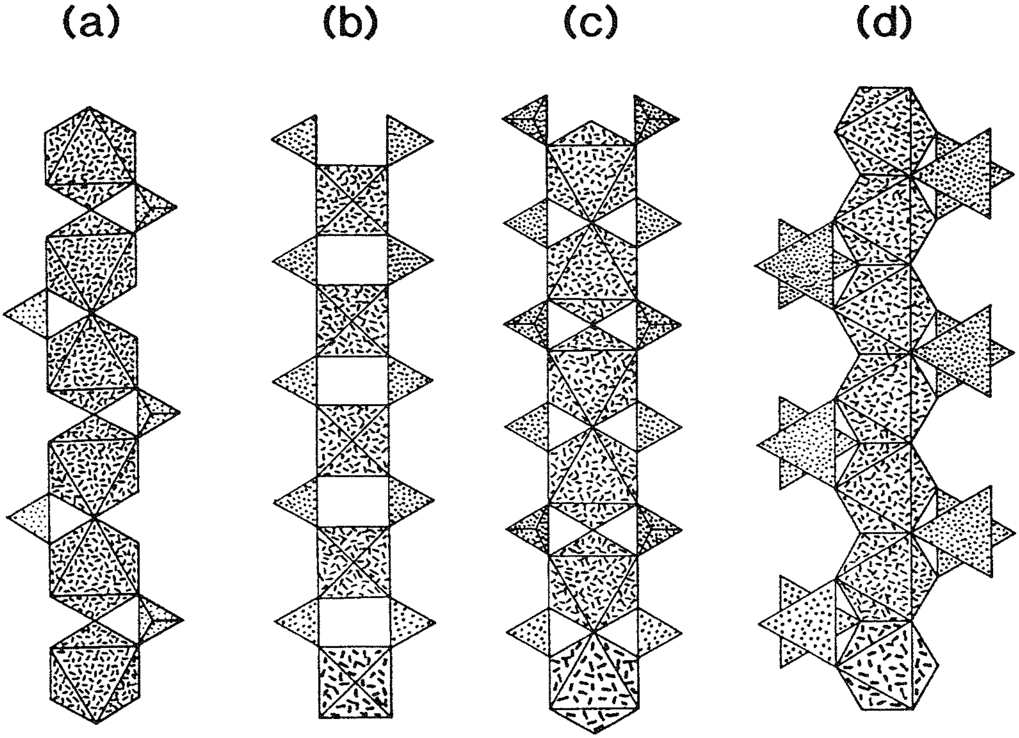


Fig. 16. Infinite-chain structural units of selected phosphate minerals; (*a*) [$M(TO_4)\phi_3$]; (*b*) [$M(TO_4)_2\phi_2$]; (*c*) [$M(TO_4)_2\phi$]; (*d*) [$M(TO_4)_2\phi$]; legend as in Fig. 15.

through *trans* vertices to form an [$M\phi_5$] chain which is then decorated by tetrahedra that link adjacent octahedra. This chain is somewhat similar to the [$M(TO_4)\phi_3$] chain (Fig. 16*a*), but is decorated by twice as many tetrahedra along its length. The [$M(TO_4)_2\phi$] chain of Fig. 16*d* is the structural unit in a wide variety of sulphate, chromate, phosphate, arsenate, vanadate and silicate minerals, including goedkinite, tsumebite and vauquelinite (Table 3). Although this chain has the same stoichiometry as the chain depicted in Fig. 16*c*, it is topologically very different. Octahedra share *trans* edges to form an [$M\phi_4$] chain that is decorated by pairs of tetrahedra arranged *en echelon* along its length.

Consider the chains of general stoichiometry [$M(TO_4)_2\phi_n$] (Fig. 16*b,c,d*). The first chain (Fig. 16*b*) has no linkage between octahedra, the second chain (Fig. 16*c*) has corner-linkage between octahedra, and the third chain (Fig. 16*d*) has edge-linkage between octahedra. These chains are found not only in phosphates but also in many other chemical groups of minerals (Hawthorne, 1985, 1990, 1992, 1994), and it is notable that they all have a fairly simple connectivity and there is just one type of chain for each type of connectivity between octahedra. Graphical enumeration shows that there are ~200 distinct chains based on repeat units of [$M(TO_4)_2\phi_n$] and [$M_2(TO_4)_4\phi_n$]. Few of these occur in minerals, and by far the most common chains of this stoichiometry are those shown in Fig. 16. Although there is only one type of [$M(TO_4)\phi_n$] chain in phosphates, the larger families of phosphate-arsenate-vanadate and sulphate-chromate minerals show [$M(TO_4)\phi_4$], [$M(TO_4)\phi_3$] and [$M(TO_4)\phi_2$] chains with connectivities analogous to those in the [$M(TO_4)_2\phi_n$] chains. Thus not only does Nature choose a small number of fundamental building blocks, she is also very economical in her ways of linking them together to form structural units.

The structural unit of childrenite and eosphorite has a Lewis basicity of 0.29 *vu*, suggesting that it would prefer Ca (Lewis acidity = 0.28 *vu*) rather than Mn^{2+} or Fe^{2+} (Lewis basicity ≈ 0.33 vu) as an interstitial cation. Cassidyite, collinsite, fairfieldite and messelite have structural units with a Lewis basicity of 0.25 *vu*; the closest match is with Ca, and Ca is the interstitial cation in all these minerals. Tancoite is extremely interesting when examined in this way. There is a 'symmetrical' H-bond in tancoite (Hawthorne, 1985) and this H atom is written as an interstitial cation in Table 3. In this case, the structural unit is $[Al(PO_4)_2(OH)]$ and has a Lewis basicity of 0.21 *vu*; taking the Lewis acidity of H as 0.50 *vu*, the aggregate Lewis acidity of the interstitial cations is $(0.17 \times 2 + 0.22 + 0.50)/4 = 0.26$ *vu*, not in particularly close agreement with the valence-matching principle. However, there is some question as to whether a symmetrical H-bond is stable; it is often thought that a double-well potential will give rise to H hopping rapidly between two asymmetric positions on either site of the central symmetric position. If this is the case at any instant, we should consider H as a constituent of the structural unit, which would be written as $[Al(PO_{3.5}\{OH\}_{0.5})_2(OH)]$ with a Lewis basicity of 0.19 *vu*. This matches exactly with the Lewis acidity of the interstitial cations Na_2Li (= $\{0.17 \times 2 + 0.22\}/3 = 0.19$ *vu*). This close correspondence to the valence-matching principle for the second case suggests that the apparently symmetrical H-bond in tancoite may actually be a time-averaged asymmetrical H-bond. The structural units of the jahnsite- and segelerite-group minerals have a Lewis basicity of 0.21 *vu*, whereas the aggregate H_2O-moderated Lewis acidity of the interstitial cations is 0.24 *vu*; note that additional interstitial (H_2O) would produce a better match between the structural unit and the interstitial cations, and the reason why there is not more interstitial (H_2O) is not clear. The structural unit of goedkenite, tsumebite and vauquelinite has a Lewis basicity of 0.21 *vu*, matching closely with Sr and Pb as interstitial cations.

Infinite-sheet minerals

Selected minerals from this class are given in Table 4, and the corresponding structural units are

TABLE 4. $MT\phi_n$ and $MT_2\phi_n$ minerals based on infinite sheets

Mineral	Formula	Space group	Ref.
Newberyite	$[Mg(PO_3OH)(H_2O)_3]$	*Pbca*	(1)
Minyulite	$K[Al_2(PO_4)_2F(H_2O)_4]$	*Pba*2	(2)
Gordonite	$Mg[Al_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_4{\cdot}2(H_2O)$	$P\bar{1}$	–
Laueite	$Mn^{2+}[Fe^{3+}_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_4{\cdot}2(H_2O)$	$P\bar{1}$	(3)
Paravauxite	$Fe^{2+}[Al_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_4{\cdot}2(H_2O)$	$P\bar{1}$	(4)
Sigloite	$(Fe^{3+},Fe^{2+})[Al_2(PO_4)_2(OH)_2(H_2O)_2](H_2O,OH)_4{\cdot}2(H_2O)$	$P\bar{1}$	(5)
Ushkovite	$Mg[Fe^{3+}_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_4{\cdot}2(H_2O)$	$P\bar{1}$	–
Stewartite	$Mn^{2+}[Fe^{3+}_2(PO_4)_2(OH)_2(H_2O)_2](H_2O)_4{\cdot}2(H_2O)$	$\bar{P}1$	(6)
Pseudolaueite	$Mn^{2+}[Fe^{3+}(PO_4)(OH)(H_2O)]_2(H_2O)_4{\cdot}2(H_2O)$	$P2_1/a$	(7)
Strunzite	$Mn^{2+}[Fe^{3+}(PO_4)(OH)(H_2O)]_2(H_2O)_4$	$P\bar{1}$	(8)
Ferrostrunzite	$Fe^{2+}[Fe^{3+}(PO_4)(OH)(H_2O)]_2(H_2O)_4$	$P\bar{1}$	–
Metavauxite	$Fe^{2+}[Al(PO_4)(OH)(H_2O)]_2(H_2O)_6$	$P2_1/c$	(9)
Olmsteadite	$KFe^{2+}_2[Nb(PO_4)_2O_2](H_2O)_2$	$Pb2_1m$	(10)
Brianite	$Na_2Ca[Mg(PO_4)_2]$	$P2_1/a$	(11)
Bermanite	$Mn^{2+}[Mn^{3+}(PO_4)(OH)]_2(H_2O)_4$	$P2_1$	(12)
Foggite	$Ca[Al(PO_4)(OH)_2](H_2O)$	$A2_122$	(13)
Earlshannonite	$Mn^{2+}[Fe^{3+}(PO_4)(OH)]_2(H_2O)_4$	$P2_1/c$	–
Whitmoreite	$Fe^{2+}[Fe^{3+}(PO_4)(OH)]_2(H_2O)_4$	$P2_1/c$	(14)
Mitridatite	$Ca_2[Fe^{3+}_3(PO_4)_3O_2](H_2O)_3$	*Aa*	(15)
Robertsite	$Ca_2[Mn^{3+}_3(PO_4)_3O_2](H_2O)_3$	*Aa*	(16)

References: (1) Sutor (1967); (2) Kampf (1977); (3) Moore (1965); (4) Baur (1969*a*); (5) Hawthorne (1988); (6) Moore and Araki (1974*a*); (7) Baur (1969*b*); (8) Fanfani *et* al. (1978); (9) Baur and Rama Rao (1967); (10) Moore *et al.* (1976); (11) Moore (1975*b*); (12) Kampf and Moore (1976); (13) Moore *et al.* (1975); (14) Moore *et al.* (1974); Moore and Araki (1977*b*); (16) Moore (1974).

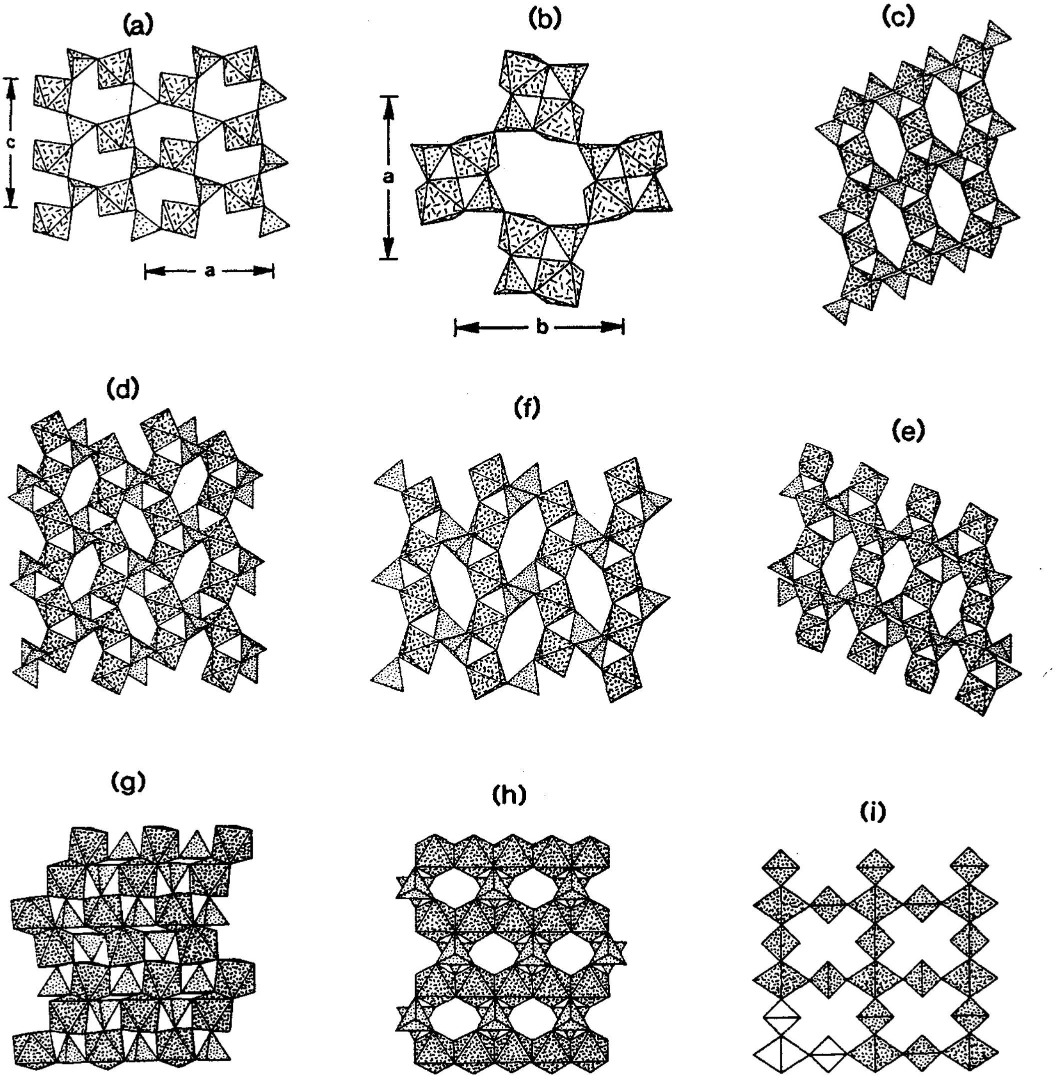


Fig. 17. Infinite-sheet structural units of selected phosphate minerals: (*a*) $[M(TO_4)\phi_3]$; $[M_2(TO_4)_2\phi_5]$; (*c*)–(*f*) $[M(TO_4)\phi_2]$; (*g*) $[M_2(TO_4)_2\phi_7]$; (*h*)$[M(TO_4)\phi]$; (*i*) $[M(TO_4)_2\phi_2]$; legend as in Fig. 15.

shown in Fig. 17. Newberyite is based on the $[M(T\phi_4)\phi_3]$ sheet (Fig. 17*a*) in which tetrahedra and octahedra occupy the vertices of a 6_3 net and link by sharing corners; each polyhedron shares three corners with adjacent polyhedra of different coordination number. Minyulite is based on the $[M_2(TO_4)_2\phi_5]$ sheet of Fig. 17*b*, in which the $[M_2(TO_4)_2\phi_7]$ clusters found in morinite (Fig. 15*c*) condense *via* corner-sharing between tetrahedra and octahedra of adjacent clusters to form a sheet. There are several sheets with the composition $[M(TO_4)\phi_2]$ (Fig. 17*c*–*f*), and these are structural units for the minerals of the laueite-group minerals, pseudolaueite, stewartite and metavauxite (Table 4). These sheets are formed by condensation of corner-sharing octahedral-tetrahedral chains of the type shown in Fig. 16*a* and *c*. The tetrahedra cross-link the chains to form sheets, and there is much isomeric variation in this type of linkage (Moore, 1975*a*). These sheets are linked to form crystals through insular divalent-metal octahedra, either by direct corner-linking to phosphate tetrahedra plus H-bonding, or by H-bonding alone. Again, there is considerable potential for stereoisomerism in the ligand arrangement of these linking octahedra, but only the *trans*-corner linkages occur. Whitmoreite is based on the $[M_2(TO_4)_2\phi_7]$ sheet (Fig. 17*g*) in which octahedral edge-sharing $[M_2\phi_{10}]$ dimers share vertices to form a very open sheet of octahedra; these sheets are decorated with tetrahedra that occlude the vacancies in the octahedral sheet. The sheet can also be considered as a condensation of the $[M_2(TO_4)_2\phi_7]$ morinite cluster (Fig. 15*c*) (Hawthorne, 1979). Tsumcorite and bermanite are based on the $[M(TO_4)\phi]$ sheet of Fig. 17*h*, in which chains of edge-sharing octahedra are cross-linked into a sheet by tetrahedra that also bridge along the length of the chain; note the similarity of the linkage in this sheet with that in the $[M(TO_4)_2\phi]$ chain of Fig. 16*d*. Olmsteadite is based on the $[M(TO_4)_2\phi_2]$ sheet (Fig. 17*i*) which consists of eight-membered rings of tetrahedra and octahedra that link to form a very open sheet. The prominent chains discernable in this sheet do not occur in any phosphate minerals, but are found as chain units in chalconthite, liroconite and brassite.

The structural unit in newberyite is neutral and hence newberyite has no interstitial cations; the structure is held together by direct H-bonding between the sheets. Minyulite has a structural unit with a Lewis basicity of 0.09 *vu*; of the common alkali and alkaline-earth cations, only K has a Lewis acidity close to this value (0.13 *vu*), and K is the interstitial cation. The minerals of the laueite group, together with stewartite, pseudolaueite and metavauxite, all have structural units with a Lewis basicity of 0.17 *vu*. The interstitial cations in these minerals are the small divalent cations Mg, Fe^{2+} and Mn^{2+}, moderated by their coordination by six (H_2O) groups: $2/(6 \times 2) = 0.17$ *vu*, an ideal match with the Lewis basicity of the structural unit. Strunzite and ferrostrunzite also have this stoichiometry of structural unit, but the complex interstitial cation is $Mn^{2+}(H_2O)_4$ with a Lewis acidity of $2/(6 + 4) = 0.20$ *vu*, still a reasonable match with the Lewis basicity of the structural unit. Bermanite has a structural unit with a Lewis basicity of 0.14 *vu*; the interstitial cation is Mn^{2+} as moderated by $(H_2O)_4$ to give a Lewis acidity of 0.20 *vu*. This is not a particularly good fit, but the significance of this is not clear as yet. The structural unit of foggite (Lewis basicity = 0.25 *vu*)matches well with its complex interstitial cation $Ca(H_2O)$ with a Lewis acidity of *0.26 vu*. Whitmoreite (Lewis basicity = 0.14 *vu*) does not match well with its interstitial cations (Lewis acidity = 0.20 *vu*) , and neither does mitridatite (Lewis basicity = 0.15 *vu*; Lewis acidity = 0.24 *vu*). However, olmsteadite (Lewis basicity = 0.28 *vu*; Lewis acidity = 0.27 *vu*) and brianite (Lewis basicity = 0.22 *vu*; Lewis acidity = 0.21 *vu*) match closely, despite the complexity of their interstitial cations (Table 5).

Infinite-framework minerals

Selected minerals from this class are given in Table 5, and the corresponding structural units are shown in Fig. 18. The $[M(TO_4)\phi]$ framework of Fig. 18*a* is the structural unit of the minerals of the amblygonite group, the phosphosiderite group, the strengite group and the lacroixite group; in addition, it occurs in a wide range of arsenates, vanadates, sulphates and silicates. Corner-sharing $[M\phi_5]$ chains extend along the *c*-axis and are cross-linked into a framework by sharing corners with (PO_4) tetrahedra. The resulting interstices may contain alkali and alkaline-earth cations (Table 5) and may also be vacant, depending on the charge on the framework. Jagowerite (Table 5) is based on the framework of Fig. 18*b*. Pairs of $(Al\phi_4)$ octahedra share an edge to form an $[M_2\phi_{10}]$ cluster, and these dimers share corners with (PO_4) tetrahedra in a way that resembles a fragment of the $[M(TO_4)_2\phi_2]$ chain in Fig. 16*b*. Melonjosephite is based on the framework of Fig. 18*c*. Octahedra share edges to form $[M\phi_4]$ chains extending along the *c*-direction, and the chains are decorated by (PO_4) tetrahedra linking vertices of adjacent octahedra of the chain; this is the $[M(TO_4)\phi]$ chain of Fig. 16*d*. Corner-linking chains of alternating octahedra and tetrahedra also extend along *c*, and the two types of chains link by sharing corners and edges to form a framework. Palermoite and bertossaite are based on the framework of Fig. 18*d*. Pairs of $(Al\phi_6)$ octahedra share edges to form $[Al_2\phi_{10}]$ dimers that then link by sharing vertices to form chains that extend along the *c*-direction; these chains are linked into a framework by sharing corners with (PO_4) tetrahedra. Alluaudite is based on the framework of Fig. 18*e*. Thick sheets of edge-sharing octahedra decorated with tetrahedra extend orthogonal to [010], and are linked by

TABLE 5. $MT\phi_n$ and $MT_2\phi_n$ minerals based on infinite frameworks

Mineral	Formula	Space group	Ref.
Kolbeckite	$[Sc(PO_4)(H_2O)_2]$	$P2_1/n$	–
Metavariscite	$[Al(PO_4)(H_2O)_2]$	$P2_1/n$	(1)
Phosphosiderite	$[Fe^{3+}(PO_4)(H_2O)_2]$	$P2_1/n$	(2)
Strengite	$[Fe^{3+}(PO_4)(H_2O)_2]$	$Pbca$	–
Variscite	$[Al(PO_4)(H_2O)_2]$	$Pbca$	(3)
Amblygonite*	$Li[Al(PO_4)F]$	$C\bar{1}$	(4,6)
Montebrasite*	$Li[Al(PO_4)(OH)]$	$C\bar{1}$	(5,6)
Natromontebrasite	$Na[Al(PO_4)(OH)]$	–	
Tavorite	$Li[Fe^{3+}(PO_4)(OH)]$	–	–
Isokite	$Ca[Mg(PO_4)F]$	$C2/c$	–
Lacroixite	$Na[Al(PO_4)F]$	$C2/c$	(7)
Panasqueraite	$Ca[Mg(PO_4)(OH)]$	$C2/c$	–
Jagowerite*	$Ba[Al(PO_4)(OH)]_2$	$P\bar{1}$	(8)
Melonjosephite	$Ca[(Fe^{2+},Fe^{3+})(PO_4)(OH)]$	$Pnam$	(9)
Bertossaite	$CaLi_2[Al(PO_4)(OH)]_4$	I^*aa	–
Palermoite	$SrLi_2[Al(PO_4)(OH)]_4$	$Imcb$	(10)
Leucophosphite	$K[Fe^{3+}_2(PO_4)_2(OH)(H_2O)](H_2O)_2$	$P2_1/n$	(11)
Alluaudite	$(Na,Ca)[Fe^{2+}(Mn,Fe^{2+},Fe^{3+},Mg)_2(PO_4)_3]$	$I2/a$	(12)
Hagendorfite	$(Na,Ca)[Mn^{2+}(Fe^{2+},Mg,Fe^{3+})_2(PO_4)_3]$	$I2/a$	–
Maghagendorfite	$Na[Mn^{2+}(Mg,Fe^{2+},Fe^{3+})_2(PO_4)_3]$	–	–
Varulite	$(Na,Ca)[Mn^{2+}(Mn,Fe^{2+},Fe^{3+})_2(PO_4)_3]$	–	–
Barbosalite	$Fe^{2+}[Fe^{3+}(PO_4)(OH)]_2$	$P2_1/c$	(13)
Lazulite	$Mg[Al(PO_4)(OH)]_2$	$P2_1/c$	(13)
Scorzalite	$Fe^{2+}[Al(PO_4)(OH)]_2$	$P2_1/c$	(13)

References: (1) Kniep and Mootz (1973); (2) Moore (1966); (3) Kniep *et al.* (1977); (4) Simonov and Belov (1958); (5) Baur (1959); (6) Groat *et al.* (1990); (7) Pajunen and Lahti (1985); (8) Meagher *et al.* (1974); (9) Kampf and Moore (1977); (10) Moore and Araki (1975); (11) Moore (1972); (12) Moore (1971); (13) Lindberg and Christ (1959)

corner-sharing between octahedra and between octahedra and tetrahedra. The minerals of the lazulite group are based on the framework of Fig. 18*f*. Triplets of octahedra share faces to form a strongly bonded trimer (shown shaded black in Fig. 18*f*). These trimers link *via* corner-sharing with (PO_4) tetrahedra and by corner-sharing between octahedra.

Several groups of structures (e.g. strengite and metavariscite) have neutral structural units, and hence no interstitial cations, although they all have H_2O groups as part of the structural unit. The structural units seem to be dominated by the stoichiometry $[M(TO_4)\phi]$. The Lewis basicity for this stoichiometry is 0.14 *vu* for M^{3+} and ϕ = OH, 0.13 *vu* for M^{3+} and ϕ = F, 0.28 *vu* for M^{2+} and ϕ = OH, and 0.25 *vu* for M^{2+} and ϕ = F. Amblygonite-montebrasite do not match very well: Li (= 0.22 *vu*) $\neq$ 0.14 *vu*. However, natromontebrasite, lacroixite, isokite and panasqueraite match quite well. Similarly, jagowerite, melonjosephite, bertossaite and palermoite do not match particularly well. The structural unit in leucophosphite has a Lewis basicity of 0.09 *vu*, and the interstitial K has the lowest Lewis acidity (0.13 *vu*) of the common monovalent cations. The alluaudite minerals have a Lewis basicity of 0.06 *vu*, a poor match for interstitial Na (0.17 *vu*) and Ca (0.28 *vu*).

This lack of agreement with the valence-matching rule is rather interesting, as it is much more prevalent for the framework phosphates than for the sheet, chain, etc. phosphates. The higher the dimensional linkage in the structural unit, the less compliance the arrangement has to adjust coordination number of the interstitial cation *via* structural movement or the incorporation of interstitial H_2O. At high temperature, such problems may be compensated by large thermal displacements. At low temperature, this mechanism will become less effective and the structure will tend to be destabilized. Collectively,

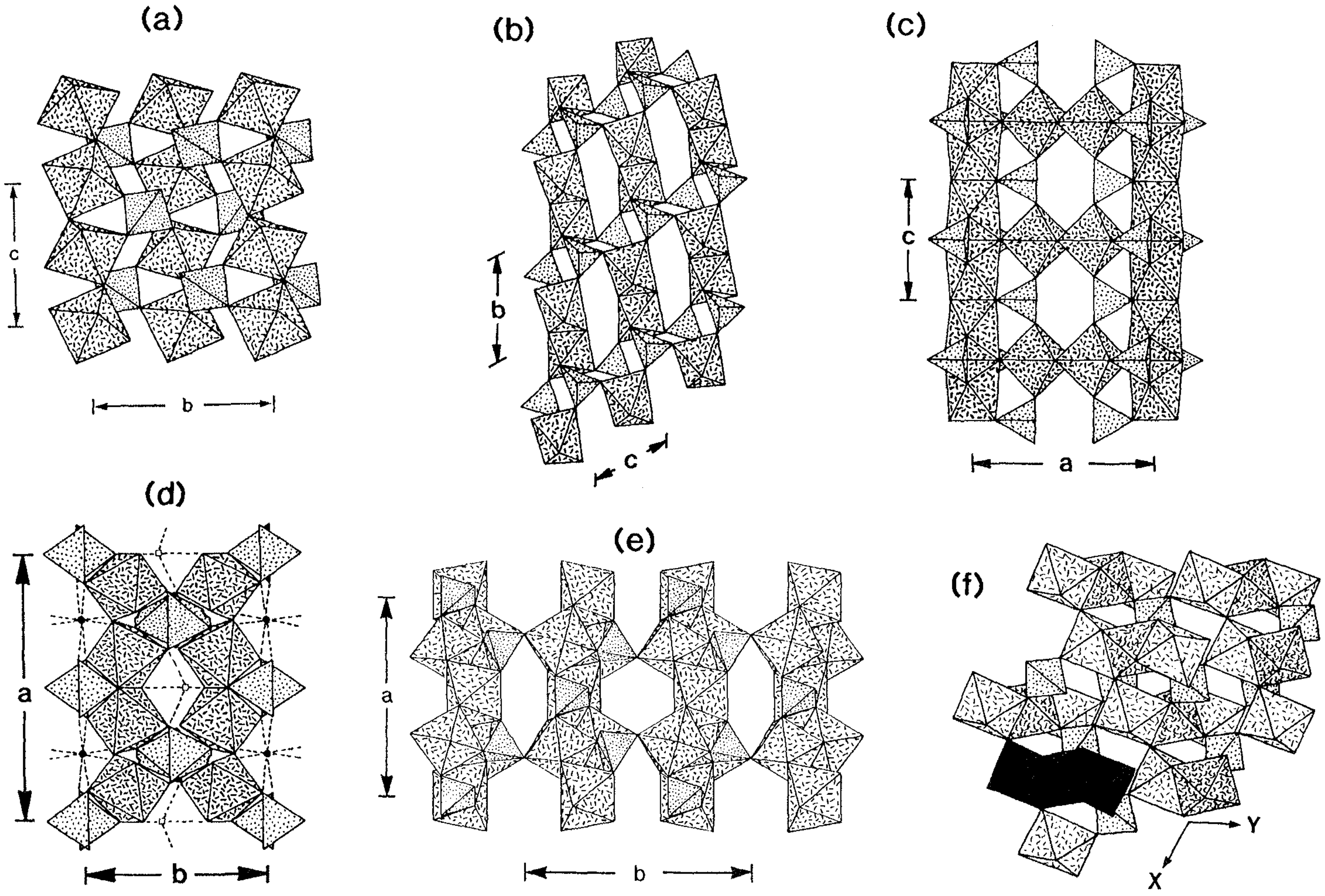


Fig. 18. Infinite-framework structural units of selected phosphate minerals: (*a*)–(*f*) all have $[M(TO_4)\phi]$ stoichiometry.

these issues suggest that framework structures should be replaced by sheet structures, chain structures, etc. with decreasing temperature, as actually is observed in complex pegmatites. A much more extensive examination of these aspects of valence matching in complex pegmatitic phosphates seems worthwhile.

Hydrogen as the agent of structural diversity

Let us examine the bond-valence structure of the (OH) and (H_2O) groups for the ideal donor and acceptor bond-valences of 0.8 and 0.2 *vu*, respectively (Fig. 19). For the (OH) group, the central oxygen receives 0.8 *vu* from the H, and hence must receive 1.2 *vu* from the cations to which it is bonded. The H receives 0.8 *vu* from the donor oxygen, and must form a H-bond of strength 0.2 *vu*. Note the very polar nature of the (OH) group. On the oxygen side of the group, it accepts ~ 1.2 *vu* from cations, and functions as an anion. On the H side of the group, it donates ~0.2 *vu* to an anion, and functions as a cation. Putting this into bond-valence phraseology, on one side, the (OH) group is a strong Lewis base; on the other side, it is a weak Lewis acid. We see the same type of behaviour for the (H_2O) group. On the oxygen side, it is a Lewis base, and on the H side it is a weaker Lewis acid.

The effect of this on a structural unit is easily apparent. On the Lewis-base side of each group, the strong cation-oxygen bond forms part of the structural unit. On the Lewis-acid side of each group, the H-bond is too weak to form part of the structural unit. So we see that both of these groups can attach themselves to a higher-valence cation and inhibit further polymerization in the structural unit. Thus a very important role of both (OH) and (H_2O) is to prevent polymerization of the structural unit in specific directions. Hence these groups essentially control the type of polymerization of the structural unit.

Figure 20 shows the structure of newberyite, $[Mg(PO_3OH)(H_2O)_3$. The structural unit is a sheet of corner-sharing ($Mg\phi_6$) octahedra and (PO_4) tetrahedra, with the polyhedra arranged at the vertices of a 6^3 net. In the (PO_4) tetrahedra, three of the ligands link to ($Mg\phi_6$) octahedra within the sheet. The other ligand is 'tied off' orthogonal to the sheet by the fact that the O atom is strongly bonded to a H-atom (i.e. it is an OH group) which then weakly H-bonds to the neighbouring sheet in the Y-direction. In the ($Mg\phi_6$) octahedra, three of the ligands link to (PO_4) tetrahedra within the sheets. The other ligands are 'tied off' by the fact that they are (H_2O) groups; the two H-atoms

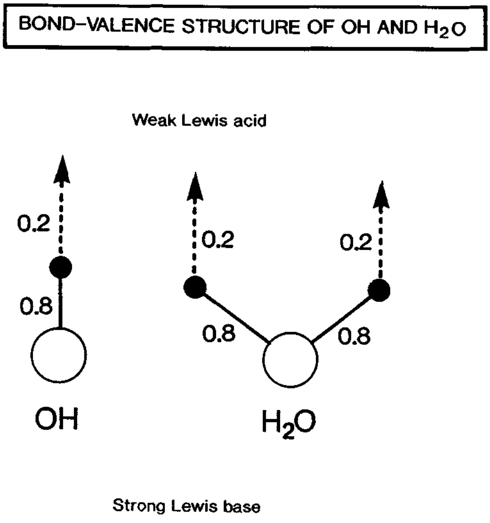


Fig. 19. The bond valence structure around (OH) and (H_2O), with bond valences shown in valence units; large unshaded circles: O; small shaded circles: H.

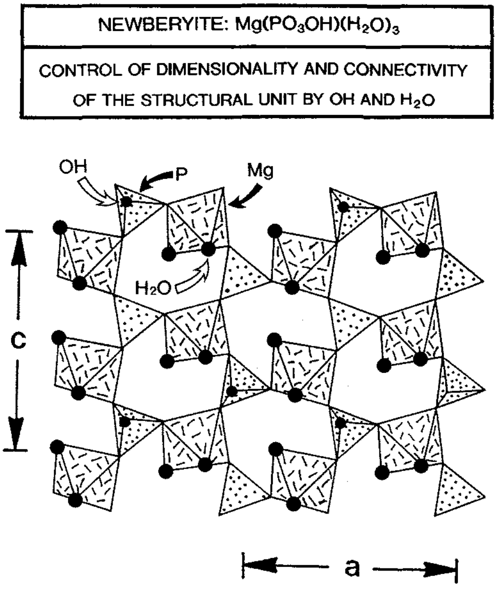


Fig. 20. The structure of newberyite, showing the (OH) and (H_2O) groups as shaded circles; legend as in Fig. 15.

weakly H-bond to the neighbouring sheets in the Y-direction. Thus the sheet-like nature of the structural unit in newberyite is controlled by the number and distribution of H-atoms in the structure.

Figure 21 shows the structure of collinsite, $Ca_2[Mg(PO_4)_2(H_2O)_2]$. The structural unit is a chain of corner-sharing $(Mg\phi_6)$ octahedra and (PO_4) tetrahedra. In the $(Mg\phi_6)$ octahedra, four of the ligands link to (PO_4) tetrahedra. The other two ligands of the $(Mg\phi_6)$ octahedra are 'tied off' by the fact that the O atoms are each strongly bonded to two H-atoms (i.e. they are H_2O groups) which weakly bond to the adjacent chains. The (H_2O) groups and their associated H-bonds force the chains to be separated, hence making room in the structure for interstitial Ca atoms. In the (PO_4) groups, two of the ligands link to $(Mg\phi_6)$ octahedra. The remaining two ligands are far from adjacent chains by virtue of the neighbouring (H_2O) groups, and hence cannot link to other $(Mg\phi_6)$ octahedra; instead, they link to interstitial Ca atoms and act as H-bond acceptors. Thus the chain-like nature of the structural unit in collinsite is controlled by the number and distribution of H-atoms in the structure.

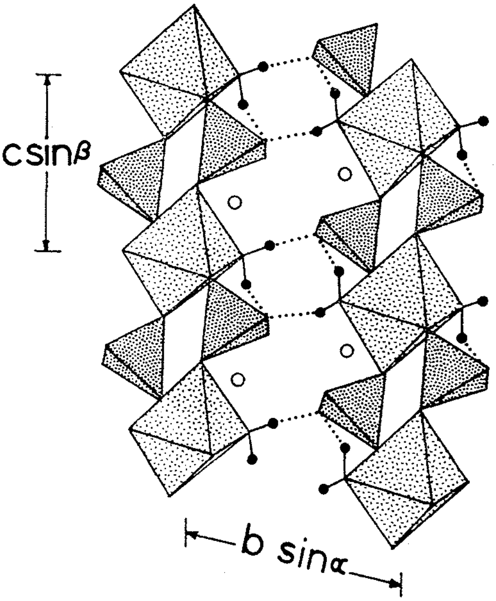


Fig. 21. The crystal structure of collinsite; (PO_4) tetrahedra shaded densely by dots, $(Mg\phi_6)$ octahedra shaded sparsely by dots, Ca atoms are shown as unshaded circles, H atoms are shown as shaded circles, H bonds are shown as dotted lines.

We may summarize the role of H in the structural unit as follows: *the dimensionality of the structural unit is controlled primarily by the amount and speciation of H in the structure.*

Conclusion

This approach to mineral structure, applied *via* the idea of a structural unit, can play a major role in developing structural hierarchies in order to bring about some sort of order to the plethora of hydroxy-hydrated-phosphate structures. Furthermore, by combining the idea of binary structural representation with bond-valence theory, I think we see the eventual possibility of rationalizing and even predicting stoichiometry and structural characteristics of these minerals, particularly those in complex low-temperature hydrothermal environments.

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