

## A CRYSTAL-CHEMICAL APPROACH TO THE COMPOSITION AND OCCURRENCE OF VANADIUM MINERALS†

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### ABSTRACT

We introduce a crystal-chemical approach to the composition and occurrence of vanadium minerals. Here, the structure of a mineral is divided into two parts: the *structural unit* with bonds of higher bond-valence, and the *interstitial complex*,  $[^{[m]}M^+_a \ ^{[n]}M^{2+_b} \ ^{[l]}M^{3+_c} (H_2O)_d (H_2O)_e (OH)_f]^{(a+2b+3c-f)+}$ , which connects the structural units to form a continuous structure. Average coordination numbers of oxygen in structural units of vanadium minerals are in the range [2.75] to [4]. There are characteristic ranges of average O-coordination numbers for specific structural units, and these values can be used to calculate the range of Lewis basicities of structural units in vanadium minerals. The characteristic Lewis basicities explain why some interstitial cations occur, and some do not occur, with a specific structural unit. Furthermore, the maximum and minimum number of interstitial transformer ( $H_2O$ ) groups can be predicted. The occurrence of different states of hydration in vanadium minerals is rationalized *via* bond-valence theory. Here, Lewis basicities and effective Lewis acidities of structural components in vanadium minerals can explain detailed structural changes during dehydration. The average basicity of a structural unit is independent of the average O-coordination number, and can be compared to structural units in minerals with different interstitial cations and hydration states. With increasing polymerization, there is a decrease in the average basicity of the structural unit. Examination of the conditions of crystallization of vanadate minerals and synthetic phases shows that the average basicity of the structural unit correlates with the pH of the environment of crystallization. The average basicity of aqueous species in a solution correlates linearly with the pH at the maximum concentration of the species in solution.

*Keywords:* vanadium minerals, bond-valence theory, hydration states, pH, crystallization, Eh–pH diagrams.

### SOMMAIRE

Nous adoptons une approche cristallochimique pour traiter de la composition et du mode de formation des minéraux de vanadium. Pour ce faire, nous considérons la structure d'un minéral en deux parties: l'*unité structurale* contient des liaisons ayant une valence de liaison plus élevée, et le *complexe interstitiel*,  $[^{[m]}M^+_a \ ^{[n]}M^{2+_b} \ ^{[l]}M^{3+_c} (H_2O)_d (H_2O)_e (OH)_f]^{(a+2b+3c-f)+}$ , assure la connectivité des unités structurales afin de former une structure continue. La coordinence moyenne des atomes d'oxygène dans les unités structurales des minéraux de vanadium va de [2.75] à [4]. Il y a des intervalles caractéristiques de la coordinence de l'oxygène pour des unités structurales spécifiques. Ces valeurs servent à calculer l'intervalle de basicité de Lewis des unités structurales. La basicité caractéristique de Lewis explique pourquoi certains cations interstitiels sont incorporés et non pas d'autres, avec une unité structurale spécifique. De plus, nous pouvons prédire le nombre maximum et minimum de groupes ( $H_2O$ ) transformateurs interstitiels. Nous nous servons de la théorie des valences de liaisons pour expliquer la présence de différents degrés d'hydratation parmi les minéraux de vanadium. Les valeurs de la basicité de Lewis et de l'acidité effective de Lewis des composants structuraux rendent compte des changements structuraux au cours d'une déshydratation. La basicité moyenne d'une unité structurale serait indépendante de la coordinence moyenne de l'oxygène, et se compare à celle des unités structurales de minéraux ayant des cations interstitiels et des degrés d'hydratation différents. A mesure qu'augmente le degré de polymérisation, il y a une diminution de la basicité moyenne de l'unité structurale. Un examen des conditions de cristallisation des minéraux vanadates et des phases synthétiques montre que la basicité moyenne d'une unité structurale est en corrélation avec l'acidité du milieu de cristallisation. La basicité moyenne des espèces présentes dans une solution aqueuse montre une corrélation linéaire avec le pH à concentration maximale de ces espèces en solution.

(Traduit par la Rédaction)

*Mots-clés:* minéraux de vanadium, théorie des valences de liaison, états d'hydratation, pH, cristallisation, diagrammes Eh–pH.

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† Dedicated to the memory of Howard T. Evans, Jr. (1919–2000). Dr. Evans served as Associate Editor of this journal over the period 1985–1987.

## INTRODUCTION

In a pioneering paper, Evans & Garrels (1958) examined the occurrence of vanadium minerals in the ore deposits of the Colorado Plateau. They used information from vanadium-mineral paragenesis, vanadate synthesis and polyvanadate anions in aqueous solution to assign stability fields to vanadium minerals on an Eh–pH diagram. In the sedimentary rocks of the Colorado Plateau, vanadium is transported primarily by groundwater, and has the oxidation states 4+ and 5+ (Wanty & Goldhaber 1992). There, the total concentration of V is in the range 9.8–240  $\mu\text{mol}$ , and polymerized vanadate species are not stable. Wanty & Goldhaber (1992) calculated an Eh–pH diagram for vanadate anions in a solution with  $V_{\text{total}} = 10 \mu\text{mol}$ ; the corresponding ions are as follows: for  $V^{5+}$ :  $\text{VO}_4^{3-}$ ,  $\text{HVO}_4^{2-}$ ,  $\text{H}_2\text{VO}_4^-$ ,  $\text{H}_3\text{VO}_4$  and  $\text{H}_4\text{VO}_4^+$ ; for  $V^{4+}$ :  $\text{VO}^{2+}$ ,  $\text{VO}(\text{OH})^+$ ; for  $V^{3+}$ :  $\text{V}^{3+}$ ,  $\text{VOH}^{2+}$  and  $\text{V}(\text{OH})_2^+$ . Here, we use bond-valence theory to establish a connection between the structural arrangements in vanadate minerals and their pH conditions of crystallization.

## THE CLASSIFICATION OF VANADIUM MINERALS

Evans & White (1987) developed a classification scheme for vanadium minerals according to their crystal-chemical character. They subdivided 119 vanadium minerals into twelve different groups: (1) sulfides, (2) species with isolated tetrahedra, (3) silicates, (4) species with isolated vanadate chains, (5) square-pyramidal  $(\text{VO})^{2+}$  species, (6) uranyl–divanadate  $(\text{V}_2\text{O}_8)^{6-}$  layer complexes, (7) isopoly- and heteropolymolecular complexes, (8) low-valence  $^{16}\text{V}$ -oxyhydroxides, (9) anhydrous oxides, (10) vanadium bronzes, (11) aluminous layer vanadates, and (12) vanadates of uncertain type. Our particular interest concerns vanadium minerals formed from aqueous solution, and these occur in groups (2), (4), (6), (7), (10) and (11). The classification scheme of Evans & White (1987) is similar to the proposal of Hawthorne (1983) that mineral structures be hierarchically ordered according to the polymerization of coordinations with higher bond-valences. In this way, Hawthorne (1983) divided a mineral structure into two parts: (1) polyhedra of higher bond-valence, which form the *structural unit*, and (2) *interstitial species*, cations, (OH) and  $(\text{H}_2\text{O})$  groups, which occupy the interstices between the structural units. In group (2) of the scheme of Evans & White (1987), isolated  $[\text{VO}_4]^{3-}$  and  $[\text{V}_2\text{O}_7]^{4-}$  groups can link to other polyhedra of higher bond-valence, e.g.,  $(\text{Cu}^{2+}\varphi_6)$ ,  $(\text{Zn}\varphi_6)$ ,  $(\text{Fe}^{2+/3+}\varphi_6)$  and  $(\text{Mn}^{2+}\varphi_6)$  ( $\varphi$ : undefined ligand). In this work, we consider only vanadate groups such as  $[\text{VO}_4]^{3-}$  and  $[\text{V}_2\text{O}_7]^{4-}$  as structural units and treat all other cations as interstitial components.

## SYNTHESIS OF VANADIUM COMPOUNDS FROM AQUEOUS SOLUTIONS

Synthesis of vanadates by Norbald (1873), Manasse (1887) and Ditte (1888) showed that polymerization of  $(\text{VO}_n)$  polyhedra increases with acidification of the parent aqueous solution. Synthetic vanadium compounds in the systems  $\text{Na}-\text{V}^{5+}-\text{H}_2\text{O}$  and  $\text{Ca}^{2+}-\text{V}^{5+}-\text{H}_2\text{O}$  have been characterized by Baker (1885), Kiehl & Manfredo (1937) and Marvin & Magin (1959), respectively. The earliest work on polyvanadate anions in aqueous solution was done by Jander & Jahr (1933), Ducret (1951) and Rossotti & Rossotti (1956); they gave detailed information on pH values and equilibrium constants for different polymerization reactions in aqueous solution. Pope (1983) reviewed the aqueous chemistry of isopolyvanadates, and concluded that the species  $[\text{VO}_4]^{3-}$ ,  $[\text{HVO}_4]^{2-}$ ,  $[\text{H}_2\text{VO}_4]^-$ ,  $[\text{H}_3\text{VO}_4]$ ,  $[\text{V}_2\text{O}_7]^{4-}$ ,  $[\text{H}_3\text{VO}_4]$ ,  $[\text{HV}_2\text{O}_7]^{3-}$ ,  $[\text{V}_3\text{O}_9]^{3-}$ ,  $[\text{V}_4\text{O}_{12}]^{4-}$ ,  $[\text{V}_{10}\text{O}_{28}]^{6-}$  in various states of protonation, and  $[\text{VO}_2]^+$ , occur in aqueous solution. Other reviews on aqueous polyvanadate chemistry have been presented by Heath & Howarth (1981), Pettersson *et al.* (1983, 1985) and Tytko & Mehmke (1983).

## COORDINATION AND CHARACTERISTIC BOND-LENGTHS IN VANADIUM MINERALS

Evans (1969) surveyed the crystal chemistry of vanadium minerals and examined the types of  $(\text{V}\varphi_n)$  coordination polyhedra that they contain. Shannon & Calvo (1973a) discussed the bond-length variation of tetrahedrally coordinated  $\text{V}^{5+}$  and calculated a grand mean  $\text{V}^{5+}-\text{O}$  bond length of 1.72(1) Å. Schindler *et al.* (2000) discussed bond-length variation in  $(\text{V}^{3+}\text{O}_n)$ ,  $(\text{V}^{4+}\text{O}_n)$  and  $(\text{V}^{5+}\text{O}_n)$  ( $n = 5, 6$ ) polyhedra. For  $(\text{V}^{4+}\text{O}_n)$  and  $(\text{V}^{5+}\text{O}_n)$  ( $n = 5, 6$ ) polyhedra, the bond-length distributions show distinct populations that were used to define *vanadyl*, *equatorial* and *trans* V–O bonds. Schindler *et al.* (2000) used these definitions to define different coordinations of V in the form of the notation  $[a + b + c]$ , where the sequence of numbers gives the number of vanadyl (*a*), equatorial (*b*) and *trans* (*c*) bonds, respectively. Thus, the coordination  $[2 + 2 + 2]$  indicates that there are 2 vanadyl, 2 equatorial and 2 *trans* bonds.

## POLYMERIZATION IN VANADATE MINERALS

Schindler *et al.* (2000) examined which linkages [vanadyl–vanadyl, vanadyl–equatorial, vanadyl–*trans*, equatorial–equatorial, equatorial–*trans* and *trans*–*trans*] of  $(\text{VO}_n)$  polyhedra are possible in terms of permissible bond-valence sums, and which linkages actually occur in minerals. These linkages were denoted as  $^{[n]}\text{V}^Z - {}_b\text{O}_b - {}^{[n]}\text{V}^Z$ , where  $[n]$  denotes the coordination, (e.g.,

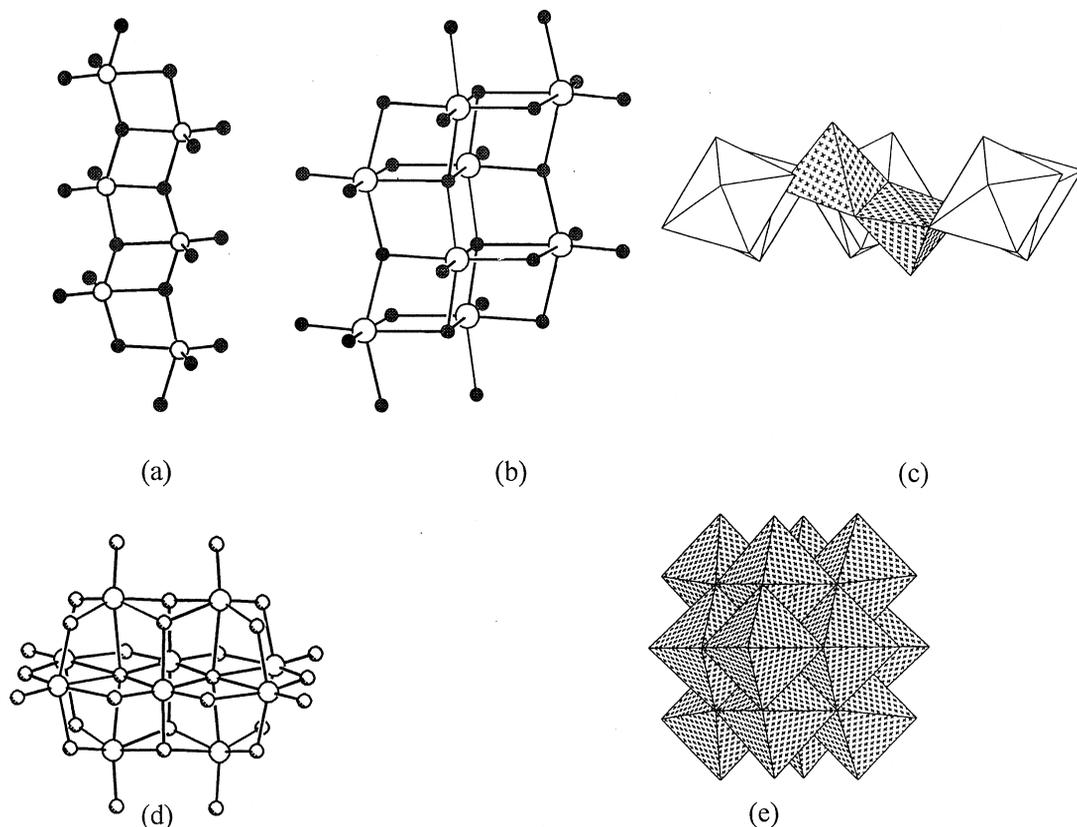


FIG. 1. Structural units in selected vanadate minerals. (a) Divanadate chains in rossite with edge-shared [5]-coordinated polyhedra. (b) The tetra vanadate chain in which V is in [6]-coordination. (c) Two  $[1+4]V^{5+}$  polyhedra share common edges in the carnotite structure (marked with crosses). (d) The  $[V_{10}O_{28}]^{6-}$  group in pascoite, with ten condensed  $(VO_6)$  polyhedra. (e) The  $[V_2^{4+}V^{5+}_{12}O_{40}]$  group in the structures of sherwoodite and  $K_7(AsV_{14}O_{40}(H_2O)_{12})$ . In (a), (b) and (d), the V atoms are indicated by large white circles.

$[1 + 4 + 1]$  or  $[2 + 3]$ ),  $b$  is the type of bond between vanadium and oxygen ( $v$ : vanadyl,  $eq$ : equatorial,  $t$ : *trans*), and  $Z$  is the valence state of vanadium ( $4+$  or  $5+$ ). For example, the notation of the linkages in the  $[VO_3]$  chain of rossite,  $Ca(VO_3)_2(H_2O)_4$  (Ahmed & Barnes 1963) would be  $[1+4]V^{5+} -_{eq}O_{eq} - [1+4]V^{5+}$  and  $[1+4]V^{5+} -_{eq}O_{eq} - [2+3]V^{5+}$  (Fig. 1a). These terms denote linkage through a common O-atom between equatorial bonds from  $V^{5+}$  in  $[1 + 4]$ -coordination, and linkage through a common O-atom between an equatorial bond from  $V^{5+}$  in  $[1 + 4]$ -coordination and from  $V^{5+}$  in  $[2 + 3]$ -coordination, respectively.

Furthermore, Schindler *et al.* (2000) showed that, from 132 possible combinations of binary  $[n]V^Z -_bO_b - [n]V^Z$  linkages, only 26 occur in minerals. They argued that one reason might be that many  $V^{4+}$  and  $V^{5+}$  minerals occur as secondary phases in the oxidation zone of rocks containing  $V^{3+}$  minerals. Under these conditions,

$5+$  is the most stable oxidation state for vanadium, accounting for its dominant role in the crystal chemistry of vanadium minerals.

Typical binary linkages involving  $V^{5+}$  occur in pascoite,  $Ca_3V_{10}O_{28}(H_2O)_{16}$ , which contains isolated heteropolyhedral  $[V_{10}O_{28}]^{6-}$  decavanadate polyanions (Swallow *et al.* 1966). Here,  $([1+4+1]V^{5+}O_6)$  and  $([2+2+2]V^{5+}O_6)$  polyhedra link by equatorial–equatorial, vanadyl–equatorial and *trans*–*trans* bonds (Fig. 1d). Another heteropolyhedral polyanion,  $[AlV^{5+}_{12}V^{4+}_2O_{40}]^{9-}$ , occurs in the structure of sherwoodite,  $Ca_{4.5}[AlV_{14}O_{40}](H_2O)_{28}$  (Evans & Konnert 1978; Fig. 1e). In the center of the polyanion, an  $(AlO_6)$  octahedron is surrounded by two  $([1+4+1]V^{4+}O_5)$  bipyramids and twelve  $([2+2+2]V^{5+}O_6)$  polyhedra. Here, the polyhedra are linked by the rare binary linkages  $[1+4+1]V^{4+} -_{O_t} - [2+2+2]V^{5+}$  and  $[1+4+1]V^{4+} -_{O_t} - [2+2+2]V^{5+}$ . The layer structure of carnotite,  $K_2(UO_2)_2(V_2O_8)(H_2O)_3$ , is built from edge-

sharing ( $[^{1+4}]V^{5+}O_n$ ) pyramids,  $[^{1+4}]V^{5+}_{-eq}O_{eq}-[^{1+4}]V^{5+}$ , connected by (UO<sub>7</sub>) polyhedra (Appleman & Evans 1965; Fig. 1c).

The natural vanadium bronzes may be classified according to whether the layers contain connected tetra-vanadate chains, divanadate chains or combinations of the two (Evans & Hughes 1990; Figs. 1a, 1b). Examples are hewettite, Ca(V<sub>6</sub>O<sub>16</sub>)(H<sub>2</sub>O)<sub>6</sub> (tetravanadate + divanadate chains; Evans 1989), corvusite, (Ca,Fe)(V<sub>8</sub>O<sub>20</sub>)(H<sub>2</sub>O)<sub>3</sub> (tetravanadate chains; Evans *et al.* 1994), and shcherbinaite, V<sub>2</sub>O<sub>5</sub> (divanadate chains; Hughes & Finger 1983). These are characterized by linkages between vanadyl-*trans*, equatorial-*trans*, equatorial-equatorial and *trans-trans* bonds of  $[^{2+3}]V^{5+}$ ,  $[^{2+2+2}]V^{5+}$ ,  $[^{1+1+1}]V^{5+}$ , and  $[^{1+1+1}]V^{4+}$  coordinations.

#### GENERAL CRYSTAL-CHEMICAL CONSIDERATIONS

Synthesis of vanadium compounds in aqueous solution, characterization of polyvanadate species in aqueous solution, and examination of vanadium-mineral parageneses give information on the conditions in which structural units in vanadium minerals are formed. The classification scheme for vanadium minerals, examination of V-O bond-length variations, and the types of coordination polyhedra and binary linkages give details about the structure and composition of structural units in minerals. From these considerations emerge the following questions:

(1) Can we predict the pH value at which a vanadium mineral was formed, when we know the chemical composition and bond topology of its structural unit?

(2) Why does the coordination number of vanadium change from [5] and [6] to [4] with increasing basicity of the parent solution?

(3) What controls the number of H<sub>2</sub>O groups and the type of interstitial cations in a structure?

(4) How does the structural unit respond to hydration and dehydration?

In order to answer these questions, we have to define specific bond-valence parameters for the structural units and the interstitial cations. These parameters are characteristic bond-valence, Lewis-acid and Lewis-base strengths, Lewis acidity and average basicity.

#### Bond-valence theory

Brown (1981) defined the characteristic bond-valence of a cation as the average bond-valence around that cation in a wide range of crystal structures. The characteristic bond-valence of a cation correlates with its electronegativity. Electronegativity is a measure of the electrophilic strength of the cation, and the correlation with characteristic bond-valence indicates that the latter is a measure of the Lewis-acid strength of the cation. Thus, Brown (1981) defined the Lewis-acid strength of a cation as its characteristic bond-valence, and the Lewis-base strength of an anion as its charac-

teristic bond-valence. From this emerges the valence-matching principle: stable structures will form when the Lewis-acid strength of a cation closely matches the Lewis-base strength of an anion.

#### Lewis basicities of structural units

Hawthorne (1985) introduced the idea of defining the structural unit as a complex (usually) oxyanion and the interstitial species as a complex (generally hydrated) cation. This *binary representation* of a crystal structure (Hawthorne 1990, 1992) allows examination of the interaction between a structural unit and the interstitial species with the valence-matching principle. Hawthorne (1997) described a scheme to calculate Lewis basicities of structural units in minerals.

*An example:* Hewettite, Ca(V<sub>6</sub>O<sub>16</sub>)(H<sub>2</sub>O)<sub>6</sub> (Evans 1989), contains the structural unit  $[^{6}V_4^{5}V_2O_{16}]^{2-}$ . Calculation of the Lewis basicity requires knowledge of the coordination numbers of the cations and anions in the structural unit. The coordination number of a cation is given by the type of (VO<sub>n</sub>) polyhedra, and the average O-coordination number can be calculated from the structural data, or predicted if no structural data are available. In the structural unit of hewettite, the average coordination number of O is [3]. Thus, there are  $16 \times 3 = 48$  bonds in the overall crystal structure that involve O-atoms of the structural unit. Within the structural unit, there are 34 bonds:  $6 \times 4$  bonds occur in the (V<sup>5+</sup>O<sub>6</sub>) polyhedra, and  $2 \times 5$  in the (V<sup>5+</sup>O<sub>5</sub>) polyhedra; there are no hydrogen bonds in the structural unit. To achieve a mean anion-coordination number of [3], the number of additional bonds required from outside the structural unit is  $48 - 34 = 14$ . The Lewis basicity of a structural unit (Hawthorne 1997) is defined as the charge of that unit divided by the number of bonds required by that unit to achieve its ideal coordination of O: for  $[^{6}V_4^{5}V_2O_{16}]^{2-}$ , the Lewis basicity is  $2/14 = 0.143$  *vu*. This Lewis basicity does not match the Lewis acidity of Ca (0.27 *vu*), and therefore the structure contains interstitial H<sub>2</sub>O groups that act as bond-valence transformers (Hawthorne 1992).

#### The transformer effect of (H<sub>2</sub>O) groups

Hawthorne (1992) described the different possible roles of (H<sub>2</sub>O) groups in crystal structures, and drew a strong distinction between (H<sub>2</sub>O) as part of the structural unit and (H<sub>2</sub>O) as part of the complex interstitial species. Evans (1939) designated the role of (H<sub>2</sub>O) as "to coordinate the cations and thereby effectively surround them with a neutral shell which increases their radius and enables their charge to be distributed over a greater number of anions". Hawthorne (1992) described the role of (H<sub>2</sub>O) as a bond-valence transformer in minerals, and showed that interstitial (H<sub>2</sub>O) can, in some cases, be quantitatively predicted on this basis. However, Hawthorne (1992) did not consider all possible

stereochemistries involving (H<sub>2</sub>O), and a brief reconsideration of this issue is necessary.

Let a cation, *M*, bond to an anion *X* (Fig. 2a); the anion *X* receives a bond-valence of *v* valence units (*vu*) from the cation, *M*. Consider another cation, *M*, that bonds to an (H<sub>2</sub>O) group, which, in turn, bonds to two anions, *X* (Fig. 2b). In the second case, the O-atom receives a bond-valence of *v vu* from the cation, *M*, and its bond-valence requirements are satisfied by two short O–H bonds of valence (1–*v*/2) *vu*. To satisfy the bond-valence requirements around each H atom, each H forms at least one H bond with its neighboring anions. In

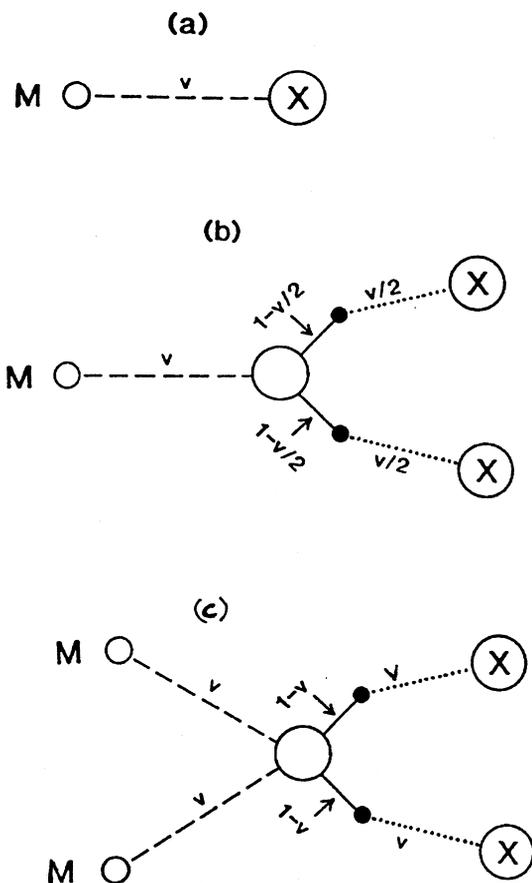


FIG. 2. (a) An interstitial cation, *M*, bonds to a ligand, *X*, with bond valence *v vu*. (b) Bond-valence transformer effect of an (H<sub>2</sub>O) group: a cation, *M*, bonds to an (H<sub>2</sub>O) group which, in turn, bonds to two anions, *X*; thus one bond (bond valence = *v vu*) is split into two weaker bonds (bond valence = *v/2 vu*). (c) The (H<sub>2</sub>O) group does not act as a bond-valence transformer: two cations, *M*, bond to an (H<sub>2</sub>O) group, which, in turn, bonds to two anions, *X*, which thus receive the same bond-valence as when each anion was bonded directly to one *M* cation.

Figure 2b, one of these hydrogen bonds involves the *X* anion, which thus receives a bond-valence of one half what it would receive were it bonded directly to the *M* cation. Thus the (H<sub>2</sub>O) group acts as a *bond-valence transformer*, causing one bond (bond valence = *v vu*) to be split into two weaker bonds (bond valence = *v/2 vu*).

Consider next the situation where two cations, *M*, bond to an (H<sub>2</sub>O) group, which, in turn, bonds to two anions *X* (Fig. 2c). Here the oxygen atom receives a bond valence of 2*v vu* from the two cations, and its bond-valence requirements are satisfied by two short O–H bonds, each of valence (1–*v*) *vu*. To satisfy the bond-valence requirements of each H atom, each H forms at least one H-bond with its neighboring anions. In Figure 2c, one of these H bonds involves the *X* anion, which thus receives the same bond-valence as when it was bonded directly to one *M* cation (Fig. 2a). In this case, therefore, the (H<sub>2</sub>O) group does not act as a bond-valence transformer.

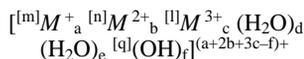
#### The valence-matching principle

As we have seen above, the valence-matching principle allows us to examine the quantitative interaction between the structural unit and the interstitial species in complex minerals.

*An example:* Let us again consider hewettite. The bond valence of the Ca–(H<sub>2</sub>O) bond is  $Z/cn = 2/7 = 0.286 vu$ , where *cn* is the *coordination number* of the cation. Each (H<sub>2</sub>O) is bonded to only one Ca atom, and hence each (H<sub>2</sub>O) group acts as a bond-valence transformer. Each O–H bond has a bond valence of  $(2 - 0.286) / 2 = 0.857 vu$ , and therefore, each H atom needs 0.143 *vu* from a hydrogen bond to satisfy its bond-valence requirement. From this calculation, it is apparent that each H<sub>2</sub>O group linked to only one Ca atom transforms the Ca–H<sub>2</sub>O bond (0.286 *vu*) into two weaker bonds (0.143 *vu*). In the hewettite structure, Ca is bonded to six H<sub>2</sub>O groups and one O atom of the structural unit. Thus, the number of bonds from Ca to the structural unit is  $6 \times 2 + 1 = 13$ , and the effective Lewis acidity of the [Ca(H<sub>2</sub>O)<sub>6</sub>O] group is  $2/13 = 0.15 vu$ . This number closely matches the Lewis basicity of the structural unit, as required by the valence-matching principle, and hewettite is a stable mineral.

#### COMPLEX INTERSTITIAL CATIONS

A general interstitial complex can be written as



where *M* is any type of interstitial mono-, di-, and trivalent cation, *d* denotes the number of (H<sub>2</sub>O) groups that act as bond-valence transformers (*i.e.*, split one *M*–O bond into two weaker *M*–H<sub>2</sub>O–O bonds), *e* denotes the number of (H<sub>2</sub>O) groups bonded to two interstitial cat-

ions or bonded to one interstitial cation and receiving one hydrogen bond from another interstitial (H<sub>2</sub>O) group. The (H<sub>2</sub>O) groups denoted by *d* do not act as bond-valence transformers, and there is no splitting of an *M*-O bond. To distinguish these two types of (H<sub>2</sub>O) groups, we name the first *transformer* (H<sub>2</sub>O) groups and the second *non-transformer* (H<sub>2</sub>O) groups. We do not differentiate between non-transformer (H<sub>2</sub>O) groups bonded to two *M* cations and those bonded to one *M*-cation and receiving one hydrogen bond from another (H<sub>2</sub>O) group. The (OH) groups in the last position are the interstitial (OH) groups; they must bond to more than one interstitial cation, and usually occur only with trivalent interstitial cations (*e.g.*, *REE*: rare-earth elements). Oxygen atoms of the structural unit that are directly bonded to interstitial *M* cations are not shown in this general formula; their number is the difference between the coordination number of the cation and the number of ligands listed in the general formula. For example, the interstitial complex  $[^{[n]}Ca(H_2O)_d(H_2O)_e]^{2+}$  has *d* transformer (H<sub>2</sub>O) groups, *e* non-transformer (H<sub>2</sub>O) groups and no (OH) groups. There are (*n* - *d* - *e*) O atoms of the structural unit that are bonded to the interstitial cation. The number of bonds from the interstitial  $[^{[m]}M^+_a [^{[n]}M^{2+}_b [^{[l]}M^{3+}_c (H_2O)_d (H_2O)_e [^q](OH)_f]^{(a+2b+3c-f)+}$  complex to the structural unit can be written as follows:

$$\sum \text{bonds} = (am + bn + cl) + d - f(q - 1)$$

Thus, the number of bonds from the interstitial complex  $[^{[8]}Ca^{2+}(H_2O)_2(H_2O)_4]$ , which has two transformer (H<sub>2</sub>O) groups, four non-transformer (H<sub>2</sub>O) groups and no (OH) groups, to the structural unit is 0 + 8 + 0 + 2 - 0 = 10.

The effective Lewis acidity of a complex can be defined as its charge divided by the number of bonds to the structural unit:  $(a + 2b + 3c - f) / [(am + bn + cl) + d - f(q - 1)]$ . For example, the effective Lewis acidity of the  $[^{[8]}Ca(H_2O)_2(H_2O)_4]^{2+}$  complex is  $(0 + 2 + 0 - 0) / (0 + 8 + 0 + 2 - 0) = 0.20$  *vu*. Examples of interstitial  $[^{[m]}M^+_a [^{[n]}M^{2+}_b [^{[l]}M^{3+}_c (H_2O)_d (H_2O)_e [^q](OH)_f]^{(a+2b+3c-f)+}$  complexes in Ca-vanadates are listed in Table 1, together with their effective Lewis acidities and the Lewis basicities of the corresponding structural units.

Comparison of the effective Lewis acidities and Lewis basicities of calcium vanadates in Table 1 shows them to be almost equal within specific structures. This is the case because we have calculated these parameters from the observed structural data. This approach is extremely useful in understanding the structural roles of all the different components of the structural unit and the interstitial species. If we wish to *predict* aspects of structure using this approach (*e.g.*, in the absence of structural data), we need to predict some of the component parameters in these calculations. Thus Hawthorne (1985, 1990, 1997) showed how interstitial cation chemistry and degree of hydration can be predicted with a fair degree of success by using predicted (rather than observed) mean coordination numbers for O. The first approach (*i.e.*, using observed coordination numbers for O-atoms) is used here in order to examine more closely the details of the structural units and interstitial complex cations in vanadate minerals.

#### STRUCTURAL UNITS IN VANADIUM MINERALS: COORDINATION NUMBERS OF OXYGEN

The key factor in the calculation of Lewis basicities is the average coordination number of O in the structural unit. This coordination number depends on the topology of the structural unit, and on the type and number of the interstitial components that are bonded to the structural unit. For example, we should expect that the average O-coordination numbers of a structural unit in sodium vanadates are higher than those in the corresponding calcium vanadates because (1) Na-O bonds have lower bond-valence, and therefore more Na cations can coordinate O-atoms of the structural unit, and (2) for a specific structural unit, the number of monovalent interstitial cations is twice the number of divalent interstitial cations in the corresponding Ca structures. For example, the average O-coordination number for  $[V_2O_7]^{4-}$  is [4.56] in Na<sub>4</sub>V<sub>2</sub>O<sub>7</sub>(H<sub>2</sub>O) and [3.6] in Ca<sub>2</sub>[V<sub>2</sub>O<sub>7</sub>](H<sub>2</sub>O)<sub>2</sub> (Konnert & Evans 1975); for  $[VO_3]^-$ , it is [4] in munirite, Na[VO<sub>3</sub>](H<sub>2</sub>O)<sub>1.89</sub> (Björnberg & Hedman 1977) and [3.2] in metarossite (Kelsey & Barnes 1960); for  $[V_{10}O_{28}]^{6-}$ , it is [3.67] in Na<sub>6</sub>[V<sub>10</sub>O<sub>28</sub>](H<sub>2</sub>O)<sub>18</sub> (Durif *et al.* 1980), and [3.5] in pascoite,

TABLE 1. Ca-VANADATE FORMED IN AQUEOUS SOLUTION: THE INTERSTITIAL  $[Ca_x(H_2O)_d(H_2O)_e(OH)_f]^{2b+}$  COMPLEX, ITS EFFECTIVE LEWIS ACIDITY ( $\langle la^e \rangle$ ), AVERAGE COORDINATION NUMBER OF OXYGEN ( $\langle cn^o \rangle$ ) AND LEWIS BASICITY (*lb*) OF THE STRUCTURAL UNIT

Compound	Formula	$[^{[n]}Ca_x(H_2O)_d(H_2O)_e(OH)_f]^{2b+}$ complex	$\langle la^e \rangle$ [ <i>vu</i> ]	$\langle cn^o \rangle$	<i>lb</i> [ <i>vu</i> ]
synthetic	Ca <sub>2</sub> [V <sub>2</sub> O <sub>7</sub> ](H <sub>2</sub> O) <sub>2</sub>	$[^{[7]}Ca^{8+}Ca(H_2O)_2(H_2O)_4(OH)_0]^{4+}$	0.23	3.6	0.23
Metarossite	Ca[(VO <sub>3</sub> ) <sub>2</sub> ](H <sub>2</sub> O) <sub>2</sub>	$[^{[8]}Ca(H_2O)(H_2O)_3(OH)_0]^{2+}$	0.22	3.2	0.22
Rossite	Ca[(VO <sub>3</sub> ) <sub>2</sub> ](H <sub>2</sub> O) <sub>4</sub>	$[^{[8]}Ca(H_2O)_3(H_2O)_2(OH)_0]^{2+}$	0.18	3.5	0.18
Pascoite	Ca <sub>3</sub> [V <sub>10</sub> O <sub>28</sub> ](H <sub>2</sub> O) <sub>17</sub>	$[^{[7]}Ca_3(H_2O)_{17}(H_2O)_0(OH)_0]^{6+}$	0.16	3.5	0.16
Hewettite	Ca[V <sub>6</sub> O <sub>16</sub> ](H <sub>2</sub> O) <sub>7</sub>	$[^{[7]}Ca(H_2O)_6(H_2O)_0(OH)_0]^{2+}$	0.15	3.0	0.14
Melanovanadite	Ca[V <sub>4</sub> O <sub>10</sub> ](H <sub>2</sub> O) <sub>5</sub>	$[^{[7]}Ca(H_2O)_5(H_2O)_0(OH)_0]^{2+}$	0.17	3.0	0.17

TABLE 2. CHARACTERISTIC RANGES OF AVERAGE COORDINATION NUMBERS OF OXYGEN (cn<sup>o</sup>) IN STRUCTURAL UNITS OF VANADIUM MINERALS

Structural unit	<cn <sup>o</sup> >	Examples	Formula	Reference
[VO <sub>4</sub> ] <sup>3-</sup>	[2.75]–[3.75]	schubnelite vanadinite	Fe[VO <sub>4</sub> ](H <sub>2</sub> O) Pb <sub>3</sub> [VO <sub>4</sub> ] <sub>3</sub> Cl	Schindler & Hawthorne (1999) Dai & Hughes (1989)
[V <sub>2</sub> O <sub>7</sub> ] <sup>4-</sup>	[2.5]–[3.7]	ziesite chervetite	Cu <sub>2</sub> [V <sub>2</sub> O <sub>7</sub> ] Pb <sub>2</sub> [V <sub>2</sub> O <sub>7</sub> ]	Hughes & Brown (1989) Shannon & Calvo (1973b)
[VO <sub>3</sub> ] <sup>-</sup>	[3.2]–[4.0]	metarossite munirite	Ca[VO <sub>3</sub> ](H <sub>2</sub> O) <sub>2</sub> Na[VO <sub>3</sub> ](H <sub>2</sub> O) <sub>2</sub>	Kelsey & Barnes (1960) Evans (1988)
Polyvanadate cluster	~[3.4]–[3.6]	pascoite sherwoodite	Ca <sub>3</sub> [V <sub>10</sub> O <sub>28</sub> ](H <sub>2</sub> O) <sub>17</sub> Ca <sub>4.5</sub> [AlV <sub>14</sub> O <sub>40</sub> ](H <sub>2</sub> O) <sub>40</sub>	Swallow <i>et al.</i> (1966) Evans & Konnert (1978)
V-bronze minerals	~[2.8]–[3.2]	metahewettite grantsite	Ca[V <sub>6</sub> O <sub>13</sub> ](H <sub>2</sub> O) <sub>3</sub> Na <sub>2</sub> Ca <sub>0.4</sub> V <sub>6</sub> O <sub>13</sub> (H <sub>2</sub> O) <sub>4</sub>	Qurashi (1961) Weeks <i>et al.</i> (1964)

Ca<sub>3</sub>[V<sub>10</sub>O<sub>28</sub>](H<sub>2</sub>O)<sub>17</sub> (Swallow *et al.* 1966). In addition to this major difference, the O-coordination number of the same structural unit also varies with the character of the complex interstitial cation.

Examination of structural units in vanadium minerals shows that (1) the average O-coordination number in the structural unit does not exceed [4], and (2) structural units in minerals have characteristic ranges of average O-coordination numbers (Table 2). Note that some synthetic materials exceed this range of coordination numbers [e.g., Na<sub>4</sub>V<sub>2</sub>O<sub>7</sub>(H<sub>2</sub>O) with a mean O-coordination number of [4.56]].

#### CHARACTERISTIC RANGE OF LEWIS BASICITY OF A STRUCTURAL UNIT

Hawthorne (1997) calculated the Lewis basicity of a structural unit by specifying an ideal coordination number for O; the result is a specific Lewis basicity for the structural unit. However, vanadates exhibit a range of O coordination numbers (as do other minerals), suggesting that a specific structural unit exhibits a range of Lewis basicity. This observation is in accord with the fact that a mineral is stable over a range of pH, rather than at a specific single value. If we use the range of O-coordination numbers in a structural unit (Table 2), we can calculate the range of Lewis basicity for this structural unit in minerals. According to the valence-matching principle, the effective Lewis acidity has to match

closely the Lewis basicity; thus a stable structure occurs if the average effective Lewis acidity of an interstitial cation complex is in the range of Lewis basicity of a given structural unit. The characteristic ranges of Lewis basicities for different structural units are listed in Table 3.

#### OCCURRENCE OF INTERSTITIAL CATIONS IN VANADIUM MINERALS

Applying the valence-matching principle to vanadium minerals allows us to systematize the effective Lewis acidities of [ <sup>[m]</sup>M<sup>+<sub>a</sub></sup> <sup>[n]</sup>M<sup>2+<sub>b</sub></sup> <sup>[l]</sup>M<sup>3+<sub>c</sub></sup> (H<sub>2</sub>O)<sub>d</sub> (H<sub>2</sub>O)<sub>e</sub> <sup>[q]</sup>(OH)<sub>f</sub> ] complexes that match the range of Lewis basicity of a specific structural unit.

#### Vanadium minerals with isolated [VO<sub>4</sub>]<sup>3-</sup> and [V<sub>2</sub>O<sub>7</sub>]<sup>4-</sup> groups

For these structural units, the valence-matching principle requires that the effective Lewis acidities of the cation complexes are in the range 0.22–0.43 *vu* (Table 3). Thus, the corresponding interstitial complexes cannot contain

- monovalent cations with coordination numbers greater than [4], or
- divalent cations with coordination numbers greater than [9].

For example, an interstitial complex that contains a monovalent cation in octahedral coordination has a maximum effective Lewis acidity of 0.17 *vu*. This value does not match the range of Lewis basicities of isolated [VO<sub>4</sub>]<sup>3-</sup> and [V<sub>2</sub>O<sub>7</sub>]<sup>4-</sup> groups; thus we should not expect a vanadium mineral to exist with [VO<sub>4</sub>]<sup>3-</sup> or [V<sub>2</sub>O<sub>7</sub>]<sup>4-</sup> as the structural unit and a [6]-coordinated interstitial monovalent cation. Possible interstitial species are divalent cations in [4]- to [9]-coordinations and trivalent cations with coordination numbers higher than [6]. On the basis of the valence-matching principle, these constraints predict that such compounds as Ca<sub>5</sub>(VO<sub>4</sub>)<sub>3</sub>OH (Kutoglu 1974) and Ca(V<sub>2</sub>O<sub>7</sub>)(H<sub>2</sub>O)<sub>2</sub> (Konnert & Evans 1975) are potential vanadium minerals, whereas such compounds as Na<sub>3</sub>(VO<sub>4</sub>) and K<sub>3</sub>(VO<sub>4</sub>)

TABLE 3. STRUCTURAL UNITS IN VANADATE MINERALS WITH RANGES OF AVERAGE COORDINATION NUMBER OF OXYGEN (<cn<sup>o</sup>>), AVERAGE BASICITY, RANGE OF THE LEWIS BASICITY, AND NUMBER OF TRANSFORMER (H<sub>2</sub>O)

unit	<cn <sup>o</sup> > (minerals)	GROUPS FOR <sup>17</sup> Ca, <sup>18</sup> Ca and <sup>16</sup> Na		
		average basicity [vu]	Lewis basicity [vu]	Number of transformer H <sub>2</sub> O groups per cation
(VO <sub>4</sub> ) <sup>3-</sup>	2.75–3.75	0.75	0.27–0.43	<sup>17</sup> Ca: 0
(V <sub>2</sub> O <sub>7</sub> ) <sup>4-</sup>	2.5–3.7	0.57	0.22–0.42	<sup>17</sup> Ca: 0, 1, 2, <sup>18</sup> Ca: 0, 1
(VO <sub>3</sub> ) <sup>-</sup>	3.2–4.0	0.33	0.14–0.22	<sup>17</sup> Ca: 2–7, <sup>18</sup> Ca: 1–6, <sup>16</sup> Na: 0, 1
(AlV <sub>4</sub> O <sub>40</sub> ) <sup>9-</sup>	3.4–3.6	0.23	0.17–0.20	<sup>17</sup> Ca: 3–5, <sup>18</sup> Ca: 2–4, <sup>16</sup> Na: 0
(V <sub>10</sub> O <sub>28</sub> ) <sup>8-</sup>	3.4–3.6	0.21	0.15–0.17	<sup>17</sup> Ca: 5–7, <sup>18</sup> Ca: 4–6, <sup>16</sup> Na: 0, 1
(V <sub>6</sub> O <sub>13</sub> ) <sup>3-</sup>	2.8–3.2	0.20	0.14–0.21	<sup>17</sup> Ca: 3–7, <sup>18</sup> Ca: 2–8, <sup>16</sup> Na: 0, 1
(V <sub>2</sub> O <sub>6</sub> ) <sup>2-</sup>	2.8–3.2	0.125	0.12–0.20	<sup>17</sup> Ca: 3–7, <sup>18</sup> Ca: 2–8, <sup>16</sup> Na: 0, 1, 2

(Olazcuaga *et al.* 1975) are not potential minerals. Vanadium minerals with  $[\text{VO}_4]^{3-}$  or  $[\text{V}_2\text{O}_7]^{4-}$  as structural units normally occur with such interstitial cations as  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Zn}$ ,  $\text{Fe}^{3+}$ ,  $\text{Bi}$  and  $\text{Y}$  (Table 4).

*Vanadium minerals with more highly polymerized ( $\text{V}_x\text{O}_y$ ) structural units*

The Lewis basicities of more highly polymerized structural units, such as  $[\text{VO}_3]^-$ ,  $[\text{AlV}_{14}\text{O}_{40}]^{9-}$ ,  $[\text{V}_{10}\text{O}_{28}]^{6-}$ ,  $[\text{V}_4\text{O}_{10}]^{2-}$  and  $[\text{V}_6\text{O}_{16}]^{2-}$ , are in the range 0.12–0.22 *vu* (Table 3). The valence-matching principle predicts that the following cations will occur in the corresponding  $[\text{M}^+ \text{M}^{2+} \text{M}^{3+} \text{c} (\text{H}_2\text{O})_d (\text{H}_2\text{O})_e]^{[q]} (\text{OH})_f]^{(a+2b+3c-f)+}$  interstitial complexes:

- monovalent cations with coordination numbers [5], [6] and [7] and maximum numbers of transformer ( $\text{H}_2\text{O}$ ) groups (d) of 3, 2 and 1, respectively;
- [8]-coordinated monovalent cations with no transformer ( $\text{H}_2\text{O}$ ) groups ( $d = 0$ );
- monovalent cations in [4]-coordination with a minimum of one transformer ( $\text{H}_2\text{O}$ ) group ( $d > 0$ );
- divalent cations in [6]-, [7]- and [8]-coordination with minimum numbers of transformer ( $\text{H}_2\text{O}$ ) groups of 3, 2 and 1, respectively.
- trivalent cations only with interstitial (OH) groups, with coordination numbers [8], [10] and [12], and with minimum numbers of transformer ( $\text{H}_2\text{O}$ ) groups of 6, 4 and 2, respectively.

*Examples:* (1) An interstitial complex with a trivalent REE-cation in [10]-coordination would have an effective Lewis acidity of 0.30 *vu* without transformer ( $\text{H}_2\text{O}$ ) groups. Thus, it requires a minimum of four transformer ( $\text{H}_2\text{O}$ ) groups to give an effective Lewis acidity of  $3 / (2 \times 4) + 6 = 0.21$  *vu* that falls within the range of Lewis basicity (0.12–0.22 *vu*) of the more highly polymerized structural units.

(2) An interstitial complex with Al in [6]-coordination would have a minimum Lewis acidity of 0.25 *vu* without interstitial (OH) groups. Thus, there must be one (OH) group for each Al in the interstitial complex. This interstitial (OH) group must be bonded to at least two Al atoms in order to satisfy its own bond-valence requirements. The incident bond-valence sum at the O atom could be  $0.6 + 0.6 + 0.8 = 2.0$  *vu* (0.8 *vu* is contributed by the H-atom). The charge on the  $[\text{Al}_2 (\text{H}_2\text{O})_d (\text{H}_2\text{O})_e (\text{OH})_2]$  complex is now:  $2 \times 3^+ - 2 \times 1^- = 4^+$ , and the valence-matching principle requires that six of the ten remaining ligands are transformer ( $\text{H}_2\text{O}$ ) groups. This would result in an effective Lewis acidity of  $4 / 12 + 6 = 0.22$  *vu*, matching the Lewis basicity of the highly polymerized structural units.

(3) An interstitial complex with a [7]-coordinated divalent cation would have a Lewis acidity of 0.29 *vu* without transformer ( $\text{H}_2\text{O}$ ) groups. This Lewis acidity does not match the range of Lewis basicities of highly polymerized structural units (0.12–0.22 *vu*). The valence-matching principle requires that the maximum

effective Lewis acidity of the interstitial  $[\text{Ca}^{2+} (\text{H}_2\text{O})_d (\text{H}_2\text{O})_e (\text{OH})_0]^{2+}$  complex is 0.22 *vu*, which (for a divalent cation) means that  $9 < (7 + d) < 17$ . Thus the [7]-coordinated divalent cation requires a minimum of two transformer ( $\text{H}_2\text{O}$ ) groups, resulting in  $7 + 2 = 9$  bonds to the structural unit. Vanadium minerals with higher polymerized structural units normally occur with large interstitial cations such as Na, Ca, K and Ba (Table 4).

For some structural units in vanadium minerals (Table 3), we calculated the required number of transformer ( $\text{H}_2\text{O}$ ) groups for interstitial complexes with  $\text{M} = {}^{77}\text{Ca}$ ,  ${}^{88}\text{Ca}$  and  ${}^{16}\text{Na}$ . For the higher polymerized structural units, these calculations show the following features:

- Na is coordinated by fewer transformer ( $\text{H}_2\text{O}$ ) groups than Ca;
- interstitial complexes with Ca always contain the minimum number of transformer ( $\text{H}_2\text{O}$ ) groups.

STRUCTURAL CHANGE DURING DEHYDRATION:  
A BOND-VALENCE APPROACH

Table 2 lists the ranges of O-coordination numbers typical of structural units in vanadium minerals; we have calculated the corresponding ranges of effective Lewis acidities for interstitial  $[\text{M}^+ \text{M}^{2+} \text{M}^{3+} \text{c} (\text{H}_2\text{O})_d (\text{H}_2\text{O})_e]^{[q]} (\text{OH})_f]^{(a+2b+3c-f)+}$  complexes in vanadium minerals with different types of structural units. Now, we show how the structures of vanadium minerals respond to dehydration where the effective Lewis acidity of the interstitial complex changes. Structural change in vanadium minerals can be rationalized using Lewis basicities and effective Lewis acidities.

*Rossite, metarossite and  $\text{Ca}[\text{VO}_3]_2$*

In rossite,  $\text{Ca}[\text{VO}_3](\text{H}_2\text{O})_4$  (Ahmed & Barnes 1963), the average coordination number of O is [3.5]. Calculation of the Lewis basicity of the structural unit gives 0.18 *vu*. Ca is coordinated by five  $\text{H}_2\text{O}$  groups and three O atoms of the structural unit. Two  $\text{H}_2\text{O}$  groups are coordinated by two Ca atoms, and the transformer effect of  $\text{H}_2\text{O}$  is not operative; hence the effective Lewis acidity of the  $[\text{Ca}(\text{H}_2\text{O})_3(\text{H}_2\text{O})_2]$  complex is  $2 / (3 \times 2 + 2 + 3) = 0.18$  *vu*, which matches the Lewis basicity of the structural unit (Table 3). In the transformation of rossite to metarossite,  $\text{Ca}[\text{VO}_3](\text{H}_2\text{O})_2$  (Kelsey & Barnes 1960), a (longer) equatorial V–O bond in rossite transforms to a (shorter) V=O vanadyl bond in metarossite (*i.e.*, a coordination change from  $[\text{V}^{5+}]^{(1+4)}$  to  $[\text{V}^{5+}]^{(2+3)}$ ). This change in vanadium coordination is induced by a change in the coordination number of the corresponding O-atom, and the average O-coordination number in the structural unit decreases from [3.5] to [3.2]. This results in an increase of Lewis basicity from 0.18 to 0.22 *vu*, and Ca is coordinated by three  $\text{H}_2\text{O}$  groups and five O-atoms of the structural unit. Once again, two  $\text{H}_2\text{O}$  groups are coordinated by two Ca at-

oms, resulting in an effective Lewis acidity of the  $[\text{Ca}(\text{H}_2\text{O})(\text{H}_2\text{O})_2\text{O}_5]$  complex of 0.22 *vu*. This matches with the Lewis basicity (0.22 *vu*) of the structural unit, and metarossite is a stable compound (Table 3).

Further dehydration of metarossite would form (synthetic)  $\text{Ca}[\text{VO}_3]_2$  (Bouloux *et al.* 1972), in which the interstitial  $[\text{Ca}(\text{H}_2\text{O})_0(\text{H}_2\text{O})_0(\text{OH})_0]$  complex has an effective Lewis acidity of 0.33 *vu*. In  $\text{Ca}[\text{VO}_3]_2$ , both  $\text{V}^{5+}$  atoms occur in [2 + 3]-coordination, and the mean O-coordination number is [2.7]. Thus the structure cannot respond by transformation of equatorial to vanadyl bonds because there cannot be more than two vanadyl bonds per  $\text{V}^{5+}$  atom (Schindler *et al.* 2000). Figure 1 shows the divanadate chain of the structural unit of rossite and metarossite. There are three different crystallographically independent O atoms: two O atoms that belong to vanadyl groups ( $\text{V}=\text{O}$ ), and one O that links three [2 + 3]-coordinated ( $\text{VO}_5$ ) polyhedra through equatorial bonds. Here, the structural unit responds to change of the individual O-coordination numbers and bond-valence requirements with variation of the equatorial bond-lengths (*i.e.*, a redistribution of bond valences inside the [2 + 3]-coordination polyhedra). Schindler *et al.* (2000) examined the individual bond-length distributions of [1 + 4], [2 + 3] and [1 + 4 + 1] coordinations of  $\text{V}^{5+}$ , and showed that there is more than one maximum in the equatorial bond-length distribution for each coordination. They suggested that this variability in equatorial bond-lengths is characteristic of ( $\text{V}^{5+}\text{O}_n$ ) coordinations representing different degrees of interaction between  $\text{O}(d\pi)$  and  $\text{V}(d\pi)$  orbitals. Thus, characteristic variations in individual bond-lengths of  $\text{V}^{5+}\text{O}_n$  polyhedra can balance local bond-valence requirements caused by different effective Lewis acidities and geometries of the interstitial cation complexes.

#### Hewettite and metaheawettite

In hewettite,  $\text{Ca}[\text{V}_6\text{O}_{16}](\text{H}_2\text{O})_7$ , the number of interstitial  $\text{H}_2\text{O}$  groups can vary between six and nine (Qurashi 1961); its space group is  $P2/m$ , and only the

lattice constants were observed to vary with the number of  $\text{H}_2\text{O}$  groups. If the number of  $\text{H}_2\text{O}$  groups drops below six ( $\sim 5.5$ ), there is a discontinuous transition to a new structure with space group  $A2/m$ . The new phase, metaheawettite, has the structural formula  $\text{Ca}[\text{V}_6\text{O}_{16}](\text{H}_2\text{O})_3$ . Use of the valence-matching principle explains the mechanism of this discontinuous phase transition in the following way. In hewettite, the Lewis basicity of the structural unit is 0.14 *vu*. The interstitial Ca atom is coordinated by six transformer  $\text{H}_2\text{O}$  groups and one O atom, and hence has a Lewis acidity of 0.15 *vu*. The Lewis-base strength of the structural unit approximately matches the Lewis-acid strength of the interstitial species, and thus the hewettite structure is stable. If the coordination of Ca changes from six transformer  $\text{H}_2\text{O}$  groups + one O atom to (for example) four transformer  $\text{H}_2\text{O}$  groups + three O atoms of the structural unit, then the effective Lewis acidity increases to  $2 / (2 \times 4 + 3) = 0.18$  *vu*; the Lewis acidity of this  $[\text{Ca}(\text{H}_2\text{O})_4(\text{H}_2\text{O})_0(\text{OH})_0]$  interstitial complex does not match the Lewis basicity of the structural unit, and thus the structural unit will respond to increased dehydration by forming a new arrangement with the appropriate Lewis basicity.

The structure of the  $[\text{V}_6\text{O}_{16}]^{2-}$  group in metaheawettite is unknown, but we can predict its structural change by analogy with the similar change in rossite–metarossite. Qurashi (1961) reported that the dehydration process in hewettite is easily reversible; thus we can exclude a change in the connectivity of the ( $\text{VO}_n$ ) polyhedra or a change in the gross coordination numbers of  $\text{V}^{5+}$ , because both changes would require breaking of bonds (*i.e.*, a reconstructive transformation). The maximum effective Lewis acidity of the  $[\text{Ca}(\text{H}_2\text{O})_3]$  complex cation is 0.20 *vu*, and decrease of the average O-coordination number from [3] to [2.75] would increase the corresponding Lewis basicity of the structural unit from 0.14 to 0.20 *vu*. Thus, we can predict what happens to the individual V coordinations in hewettite when the mean coordination number decreases from [3] to [2.75]. As in rossite and metarossite, decrease of O-coordination numbers results from transformation of longer equatorial bonds to shorter vanadyl bonds: thus, for dehydration of hewettite to metaheawettite, we expect a transformation from  $[\text{V}^{5+}]^{[1+4+1]}$  or  $[\text{V}^{5+}]^{[1+4]}$  to  $[\text{V}^{5+}]^{[2+2+2]}$  or  $[\text{V}^{5+}]^{[2+3]}$ , respectively.

TABLE 4. CHEMICAL COMPOSITIONS OF SEVERAL VANADIUM MINERALS WITH STRUCTURAL UNITS OF DIFFERENT DEGREES OF POLYMERIZATION\*

Minerals with $[\text{VO}_4]^{3-}$ and $[\text{V}_2\text{O}_7]^{2-}$ groups	Minerals with more highly polymerized structural units
vanadinite $\text{Pb}^{2+}_2[\text{VO}_4]_3\text{Cl}$	rossite $\text{Ca}[\text{VO}_3](\text{H}_2\text{O})_4$
descloizite $\text{ZnPb}^{2+}[\text{VO}_4](\text{OH})$	munirite $\text{Na}[\text{VO}_3](\text{H}_2\text{O})_2$
volborthite $\text{Cu}^{2+}_3[\text{VO}_4]_2(\text{H}_2\text{O})_3$	barnesite $\text{Na}_2[\text{V}_6\text{O}_{16}](\text{H}_2\text{O})_3$
pucherite $\text{Bi}[\text{VO}_4]$	grantsite $\text{Na}_5\text{Ca}_9[\text{V}_6\text{O}_{16}](\text{H}_2\text{O})_6$
stoiberite $\text{Cu}^{2+}_2\text{O}_2[\text{VO}_4]_2$	banermanite $\text{Na}[\text{V}_6\text{O}_{16}]$
wakefieldite-(Y) $\text{Y}[\text{VO}_4]$	fernandinite $\text{Ca}_9\text{Ba}[\text{V}_6\text{O}_{16}](\text{H}_2\text{O})_{10}$
ziesite $\text{Cu}^{2+}_2[\text{V}_2\text{O}_7]$	straczekite $\text{Ca}_2\text{K}[\text{Ba}][\text{V}_6\text{O}_{16}](\text{H}_2\text{O})_3$
blossite $\text{Cu}^{2+}_2[\text{V}_2\text{O}_7]$	hummerite $\text{K}_2\text{Mg}[\text{V}_{10}\text{O}_{28}](\text{H}_2\text{O})_{16}$
chervetite $\text{Pb}^{2+}_2[\text{V}_2\text{O}_7]$	huemulite $\text{Na}_4\text{Mg}[\text{V}_{10}\text{O}_{28}](\text{H}_2\text{O})_{24}$

\* after Evans & White (1987)

#### AVERAGE BASICITIES OF VANADATES AND THE pH RANGES OF THEIR STABILITY FIELDS

##### Average basicity of a structural unit

Table 3 shows that the Lewis basicities of the more highly polymerized structural units in vanadate minerals are similar; thus, the range of Lewis basicity of a structural unit cannot be used to compare the composition of the structural unit with conditions of crystallization. We require a parameter that is characteristic of only one specific structural unit and is independent of the

type of cation or the dehydration state of the mineral. Thus, we introduce here the notion of the average basicity of a structural unit: *The average basicity of a structural unit is defined as the average bond-valence sum per O atom contributed by the interstitial species and other structural units.*

For example, all structures with  $[\text{V}^{5+}\text{VO}_3]^-$  units have in common the charge of the unit, the number of O atoms and the coordination number of V. There are no hydrogen bonds from one structural unit to another structural unit, and thus the charge of the unit is the sum of bond valences from the structural unit to interstitial components. The average basicity is therefore the charge / number of O atoms =  $1/3 = 0.33 \text{ vu}$ . If H atoms occur in the structural unit, they will effectively decrease the charge of the structural unit in the following way. Each H atom requires, on average,  $0.20 \text{ vu}$  from a H bond. The sum of the bond valences required from the H bonds must be added to the charge of the structural unit. This is apparent when we consider that we count only bonds of higher bond-valence in a structural unit. Hydrogen bonds can connect different structural units or are linked to interstitial  $\text{H}_2\text{O}$  groups. The necessary  $0.20 \text{ vu}$  of the H bond can be provided by O atoms of  $\text{H}_2\text{O}$  groups; however, as shown above, each  $\text{H}_2\text{O}$  group itself requires the same bond-valence for their H bonds; thus, only O-atoms of the structural unit can provide the necessary  $0.20 \text{ vu}$ . As an example, the  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$  group has an average basicity of  $(4 + 2 \times 0.2) / 28 = 0.16 \text{ vu}$ . Different average basicities for  $(\text{VO}_n)$  structural units are listed in Table 3.

#### The system $\text{CaO}-\text{V}^{5+}_2\text{O}_5-\text{H}_2\text{O}$

Marvin & Magin (1959) examined the system  $\text{CaO}-\text{V}^{5+}_2\text{O}_5-\text{H}_2\text{O}$  between 20 and  $90^\circ\text{C}$  and assigned the phases to stability fields on a pH-T diagram (Fig. 3). With decreasing pH and increasing polymerization of the  $(\text{V}^{5+}\text{O}_n)$  polyhedra, the average basicity of the structural units decreases from  $0.75 \text{ vu}$  for an isolated  $[\text{V}^{5+}\text{O}_4]^{3-}$  unit to  $0.125 \text{ vu}$  for the  $[\text{V}_6\text{O}_{16}]^{2-}$  bronze layer units. The increase of average basicity from acid to neutral environments corresponds to depolymerization from the layer structures of the natural bronzes to isolated groups of heteropolyanions (pascoite) or isolated divanadate chains with [2 + 3]-coordination (rossite) (Fig. 3). Further increase in average basicity from the [2 + 3]-chain occurs by depolymerization of the chain to form isolated  $[\text{V}^{5+}_2\text{O}_7]^{4-}$  groups (Fig. 3), and also involves a change in coordination number of V from [5] to [4].

Depolymerization of the [2 + 3]-chain without change in V coordination number would produce isolated  $(\text{VO}_5)$  polyhedra with [2 + 3]-coordination in which the equatorial bonds have a bond-valence of  $0.65 \text{ vu}$  and require  $1.35 \text{ vu}$  additional incident bond-valence. Assuming a maximum of [4]-coordination for the equatorial O atoms, each bond to an interstitial cation must

have a bond-valence of  $0.45 \text{ vu}$ . The valence-matching principle requires a similarly large Lewis acidity from a cation, and thus the  $0.45 \text{ vu}$  requirement can be satisfied only by high-valence cations (e.g.,  $\text{U}^{6+}$  in carnotite, Fig. 1c), and not by univalent or divalent cations such as Na or Ca. Thus, depolymerization to isolated  $[\text{V}_2\text{O}_7]^{4-}$  and  $[\text{VO}_4]^{3-}$  structural units requires a change in coordination number of vanadium.

Evans & Garrels (1958) formulated a set of equations for polymerization processes in aqueous solution using the chemical data of Jander & Jahr (1933) and Ducret (1951):

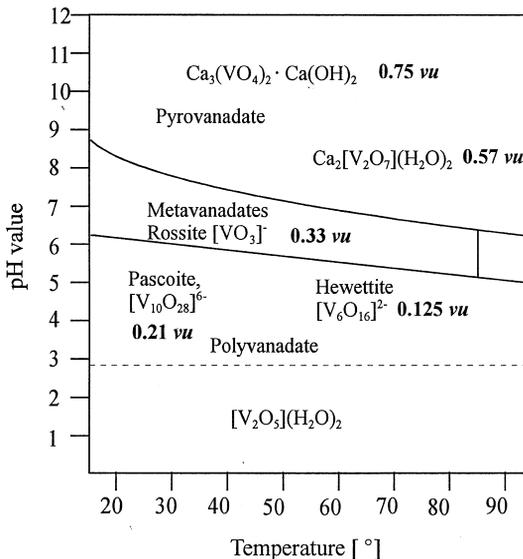
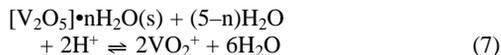
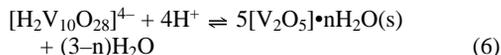
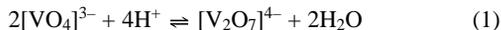


FIG. 3. The  $\text{CaO}-\text{V}_2\text{O}_5-\text{H}_2\text{O}$  system as a function of T and pH (Marvin & Magin 1959). The average basicities of the structural units (Table 3) are listed beside the corresponding minerals.

Other polyanion groups were described by Pettersson *et al.* (1983, 1985), who showed that with pH decreasing from 11 to 1, the following major and minor polyanion species occur in aqueous solution: (40 mmol [V], 0.6 mol NaCl):  $[\text{HVO}_4]^{2-}$ ,  $[\text{V}_2\text{O}_7]^{4-}$ ,  $[\text{HV}_2\text{O}_7]^{3-}$ ,  $[\text{V}_4\text{O}_{13}]^{6-}$ ,  $[\text{HV}_4\text{O}_{13}]^{5-}$ ,  $[\text{V}_4\text{O}_{12}]^{4-}$ ,  $[\text{V}_5\text{O}_{15}]^{5-}$ ,  $[\text{HV}_2\text{O}_7]^{3-}$ ,  $[\text{H}_2\text{VO}_4]^-$ ,  $[\text{V}_{10}\text{O}_{28}]^{6-}$ ,  $[\text{HV}_{10}\text{O}_{28}]^{5-}$ ,  $[\text{H}_2\text{V}_{10}\text{O}_{28}]^{4-}$ ,  $[\text{H}_3\text{V}_{10}\text{O}_{28}]^{3-}$ ,  $[\text{VO}_2]^+$ . Some polyanion structures in aqueous solution are not directly comparable to the structural units in minerals (*e.g.*,  $[\text{V}_4\text{O}_{12}]^{4-}$  versus  $[\text{VO}_3]^-$  in rossite). In general, with acidification of an aqueous solution, the average basicity of polyanions decreases with protonation of terminal O atoms or with increasing polymerization of the polyanion species.

### Vanadium minerals

Evans & Garrels (1958) examined the occurrence of vanadium minerals in the ore deposits of the Colorado Plateau, and assigned them and other  $(\text{V}_m\text{O}_n)$  anion groups to stability fields on an Eh–pH diagram (Fig. 4a). They assigned the mixed-valence natural-bronze structural units  $[\text{V}^{4.75+}_8\text{O}_{20}]^{2-}$  (corvusite, Evans *et al.* 1994) and  $[\text{V}^{4.5+}_4\text{O}_{10}]^{2-}$  (melanovanadite, Konnert & Evans 1987) to more reduced conditions and higher pH-values than the corresponding  $\text{V}^{5+}$  bronzes. The average basicities for  $[\text{V}^{4.75+}_8\text{O}_{20}]^{2-}$  and  $[\text{V}^{4.5+}_4\text{O}_{10}]^{2-}$  are 0.10 and 0.20 *vu*, respectively (Table 3, Fig. 4b). Müller *et al.* (1991) synthesized an  $[\text{As}^{5+}\text{V}^{5+}_{12}\text{V}^{4+}_2\text{O}_{40}]^{7-}$  group at pH 4.6; this group is structurally identical to the  $[\text{AlV}_{14}\text{O}_{40}]^{9-}$  group in sherwoodite. Thus, we assigned sherwoodite (with an average basicity of 0.23 *vu*) to the pH range of 4.0–6.0 and under more reduced conditions

than pascoite. In Figure 4b, the average basicities 0.57 and 0.75 *vu* are those from  $[\text{V}_2\text{O}_7]^{4-}$  and  $[\text{VO}_4]^{3-}$ , respectively (Table 3), and are arranged in the Eh–pH diagrams on the basis of the experimental work of Marvin & Magin (1959). These structural units do not occur in minerals formed in aqueous solutions at the Colorado Plateau. They occur in minerals like vanadinite,  $\text{Pb}^{2+}_5(\text{VO}_4)_3\text{Cl}$  (Dai & Hughes 1989), and descloizite,  $\text{ZnPb}^{2+}(\text{VO}_4)(\text{OH})$  (Hawthorne & Faggiani 1979), which are normally formed in an alkaline environment ( $\text{pH} = 8 \pm 1$ ) at higher temperature. Figure 4b shows a strong correlation at high and low Eh-values between the average basicities of the  $(\text{V}_m\text{O}_n)$  structural units and the pH ranges of the corresponding minerals.

Evans & Garrels (1958) found carnotite,  $\text{K}_2[(\text{UO}_2)_2(\text{V}_2\text{O}_8)](\text{H}_2\text{O})_3$  (average basicity = 0.17 *vu*), in the acid, as well in the alkaline, environment of the Colorado Plateau (Fig. 4a). Langmuir (1978) confirmed the observation of Evans & Garrels (1958), and showed that carnotite is stable over pH–Eh ranges of 4.5–8 and 1.0–0.0 V, respectively. He showed further that, depending on the partial pressure of  $\text{CO}_2$ , the minimal solubility of carnotite is between pH 6 and 8. This information shows that, independent of pH, minerals like carnotite can precipitate only where small concentrations of the corresponding ions [*i.e.*,  $(\text{UO}_2)^{2+}$  and  $(\text{VO}_4)^{3-}$ ] occur in solution.

### POLYVANADATE ANIONS IN AQUEOUS SOLUTION

Evans & Garrels (1958) assigned vanadium minerals to different stability fields on an Eh–pH diagram with the help of vanadium-mineral parageneses and thermo-

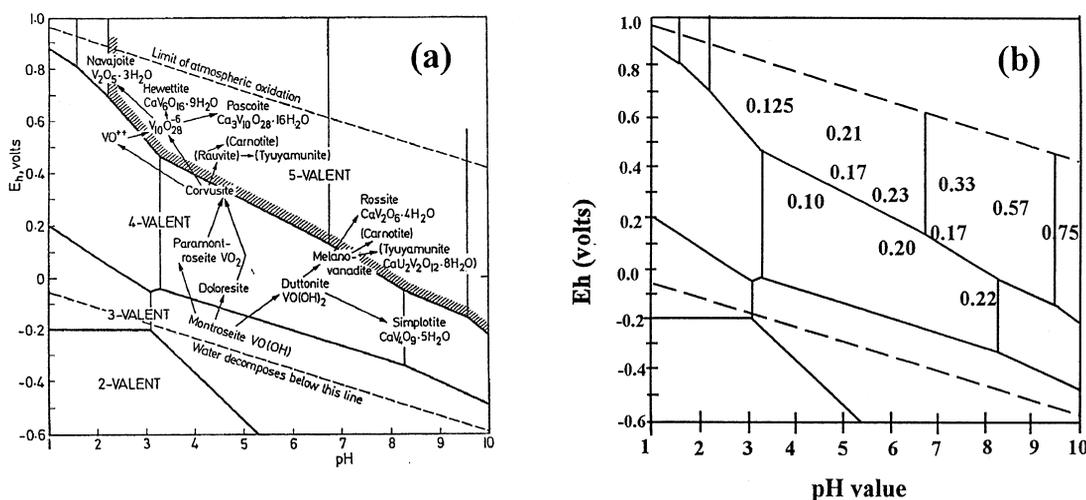


FIG. 4. (a) Aqueous equilibrium diagram for vanadium, showing the stability regions of various vanadium minerals (Evans & Garrels 1958). (b) The corresponding average basicities for the structural units of the minerals (see also text).

dynamic data of vanadate complexes in aqueous solution. Presuming that crystallization proceeds *via* condensation of the principal species in solution, correlation of the average basicities of aqueous species and their occurrence emphasizes the connection between the pH of the environment of crystallization and the structural units in the resulting minerals.

The aqueous chemistry of vanadate complexes has been examined extensively. Pope (1983) reviewed the aqueous chemistry of isopolyvanadates. The occurrence of an aqueous species at a specific value of pH depends on the total concentration of the element in solution and on the type of electrolytic medium. Here, we consider the results of polyvanadate analyses by Pettersson *et al.* (1983; pH range 1–10, 0.04 mol [V], 0.6 m NaCl solution) and Tytko & Mehmke (1983; pH range 6–16, 0.1 mol [V], 0.5 M NaCl). Table 5 lists the aqueous species and the pH at which they achieve maximum concentration in solution; the average basicities of the species also are listed. There is a strong linear correlation between the average basicity of the species and the pH value at maximum concentration of that species in solution (Fig. 5), in accord with our general contention.

AVERAGE BASICITIES OF STRUCTURAL UNITS  
AND Eh–pH VALUES OF THEIR ENVIRONMENT  
OF CRYSTALLIZATION

The example of carnotite shows that extremely stable minerals can occur over a large range of pH, and that the average basicity of their structural unit cannot be uniquely related to conditions of crystallization. This is obvious if we consider that the formation and stability of minerals depend not only on the pH value but also on the concentration of the elements in solution. However, comparison between the occurrence of polyvanadate anions in aqueous solution and the parageneses of va-

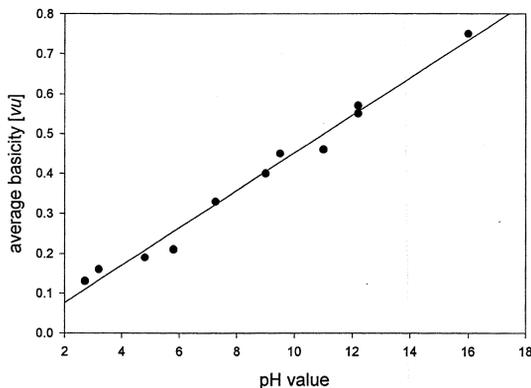


FIG. 5. Average basicities of synthetic  $[V_M O_N]$  species in aqueous solution as a function of pH at maximum concentration of the species in solution.

nadium minerals (Evans & Garrels 1958) shows that the type of aqueous species (its degree of polymerization and average basicity) is a primary control on the crystallization process of vanadium minerals.

At lower Eh-values, there is also a correlation between the average basicity of a structural unit and the pH of its environment. Here, further examination of mineral – aqueous systems is needed to better understand how Eh affects the characteristics of structural units.

CONCLUSIONS

Calculation of ranges of effective Lewis acidities in vanadium minerals with specific structural units shows that we can predict the type and coordination number of interstitial cations and the number of transformer ( $H_2O$ ) groups. In addition, using bond-valence theory, we can rationalize structural changes in vanadium minerals during isostructural dehydration: structural changes are characterized by lengthening and shortening of V–O bonds in the structural units. This approach takes us another step toward understanding how Nature combines different structural components in minerals. Average basicities of structural units and aqueous species correlate linearly with the pH-value of their formation or their maximum concentration in solution, respectively. We show that this is also true for minerals formed under more reducing conditions in aqueous systems from 20 to 100°C.

TABLE 5. AVERAGE BASICITY ( $\langle b^S \rangle$ )  
FOR SYNTHETIC VANADATE ( $[V_M O_N]$ )  
SPECIES WITH THE pH-VALUE OF  
THEIR MAXIMUM CONCENTRATION  
(pH<sup>max</sup>) IN AQUEOUS SOLUTION

Species	pH <sup>max</sup>	$\langle b^S \rangle$
$[VO_4]^{3-}$	16.0	0.75
$[HVO_4]^{2-}$	12.2	0.55
$[V_2O_7]^{4-}$	12.2	0.57
$[V_4O_{13}]^{5-}$	11	0.46
$[HV_2O_7]^{3-}$	9.5	0.45
$[HV_4O_{13}]^{5-}$	9	0.40
$[V_6O_{16}]^{5-}$	7.25	0.33
$[V_4O_{12}]^{4-}$	7.25	0.33
$[V_{10}O_{28}]^{6-}$	5.8	0.21
$[HV_{10}O_{28}]^{5-}$	4.8	0.19
$[H_2V_{10}O_{28}]^{4-}$	3.2	0.16
$[H_3V_{10}O_{28}]^{3-}$	2.7	0.13

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