A.S. Marfunin (Ed.)

Advanced Mineralogy

Volume 1
Composition, Structure, and Properties of Mineral Matter: Concepts, Results, and Problems

With 133 Figures and 40 Tables

Springer-Verlag
Berlin Heidelberg New York
London Paris Tokyo
Hong Kong Barcelona
Budapest

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5.6 Hydrogen Bonding in Minerals

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Hydrogen Bonds

Hydrogen is quite electropositive and can be represented as a cation, H^+, which usually has a coordination number of [2]. This arrangement generally undergoes a spontaneous distortion with the hydrogen moving off-centre towards one of the two coordinating anions. Hydrogen forms a strong covalent bond with the closer anion, and has a weak interaction with the more distant anion. Such an arrangement can be represented as D–H...A, where D is the strongly bonded donor anion and A is the weakly bonded acceptor anion; the H...A bond is referred to as a hydrogen bond. When the coordination number of hydrogen is greater than [2], there is one short D–H bond and two or more H...A hydrogen bonds; the latter are called bifurcated (or trifurcated) bonds. The geometry of this arrangement has been well-characterized by neutron diffraction, and is conveniently interpreted using bond-valence theory.

Hydrogen-Bearing Groups

There are five different hydrogen-bearing groups in minerals: $(OH)^-$, $(H_2O)^0$, $(H_3O)^+$, $(H_5O_2)^+$, and $(NH_4)^+$; sketches of local geometry and bond-valence distributions in these species are shown in Fig. 83. The positively charged groups act as complex cations and are extremely uncommon, although they have been identified in such minerals as hydronium jarosite $\{(H_3O)[Fe_3^{3+}(SO_4)_2(OH)_6]\}$, rhomboclase $\{(H_5O_2)Fe^{3+}(SO_4)_2(H_2O)_2]\}$ and tobelite $\{(NH_4)[Al_2(Si_3Al)O_{10}(OH)_2]\}$. On the other hand, $(OH)^-$ and $(H_2O)^0$ groups play very important roles in the structures of oxysalt minerals. The reason for this stems from the extremely directional nature of the bonding associated with these two groups; on the oxygen side of each group, they function as an anion, whereas on the hydrogen side of each group, they function as a cation, giving these two groups some very unique structural properties and allowing them to play four structurally different roles in minerals.

$(OH)^-$ and $(H_2O)^0$ in the Structural Unit. The structural unit of a mineral is that part of the structure that is strongly bonded together (e.g., a feldspar framework, a mica sheet). For both $(OH)^-$ and $(H_2O)^0$, the bonding on the anionic side of the group is fairly strong [~ 1.2 v.u. for $(OH)^-$ and ~ 0.4 v.u.

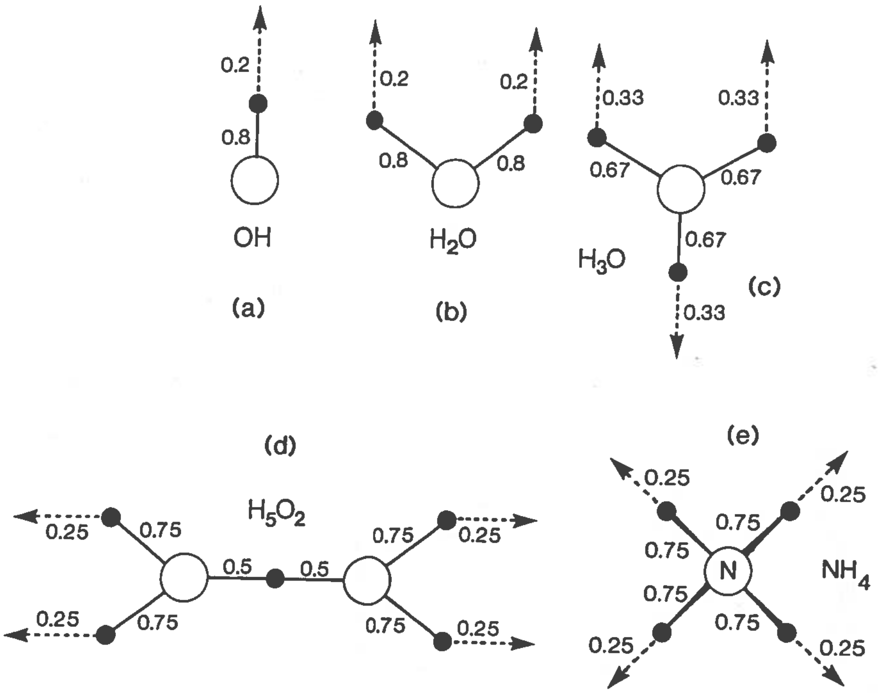

Fig. 83a–e. Hydrogen-bearing groups in minerals, showing geometry and bond-valence distributions. **a** $(OH)^-$. **b** $(H_2O)^0$. **c** $(H_3O)^+$. **d** $(H_5O_2)^+$. **e** $(NH_4)^+$

for $(H_2O)^0$] whereas the bonding on the cationic side of the group is much weaker (~ 0.2 v.u. for both groups). Thus on the anionic side of the group, the strong bonding constitutes part of the bond network of the structural unit; conversely, on the cationic side of the group, the hydrogen bond is too weak to form part of the bond network of the structural unit. The role of both $(OH)^-$ and $(H_2O)^0$ is thus to "tie off" the polymerization of the structural unit in specific directions. This is illustrated for artinite ($Mg_2(CO_3)(OH)_2(H_2O)_3$) in Fig. 84; the occurrence of both $(OH)^-$ and $(H_2O)^0$ as anions bonded to octahedrally coordinated Mg prevents further structural polymerization in any direction except along the length of the ribbon. *Thus the dimensionality of the structural unit of a mineral is primarily controlled by the amount and role of hydrogen in the structure.* As the character of the structural unit is the primary factor affecting the physical properties and stability of a mineral, it follows that hydrogen is perhaps the most significant element in controlling the properties and behaviour of minerals.

$(H_2O)^0$ Bonded Only to Interstitial Cations. Cations whose bonding is too weak to be considered as part of the bonding network of the structural unit are called interstitial cations; these are generally alkalis and alkaline earths. $(H_2O)^0$ can act

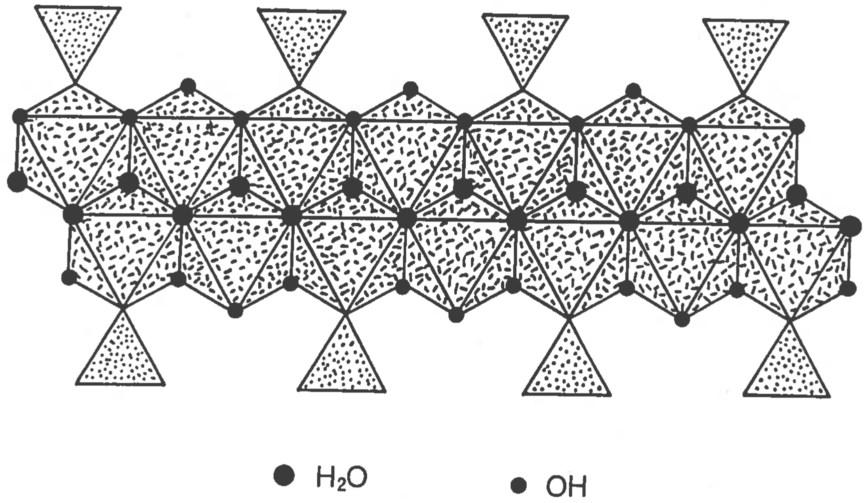

Fig. 84. The structural unit in artinite, a ribbon of (MgO_6) octahedra and (CO_3) triangles; all anions not bonded to carbon are either $(OH)^-$ or $(H_2O)^0$

as a ligand for these cations, and often does for one or more of the following reasons:

1. to satisfy bond-valence requirements around the interstitial cation in cases where there are insufficient anions available from adjacent structural units;
2. to transfer bond-valence from the interstitial cation to a distant unsatisfied anion of an adjacent structural unit;
3. to act as a bond-valence transformer between the interstitial cation and the anions of the structural unit.

The structure of stringhamite $\{Ca[Cu(SiO_4)](H_2O)\}$ is a good example (Fig. 85). The structural unit is a sheet of corner-sharing (SiO_4) tetrahedra and square-planar (CuO_4) groups arranged parallel to (010). These sheets are linked together by interstitial Ca atoms, each Ca linking to 4 anions of one sheet and 1 anion of the adjacent sheet. The coordination number of [5], rarely observed for Ca, is not adequate with regard to the satisfaction of local bond-valence requirements at the Ca, and 2 $(H_2O)^0$ complete the Ca coordination; in addition, these $(H_2O)^0$ groups carry the bond-valence (via hydrogen bonding) from Ca to anions too far away to bond directly to Ca. Thus the structural role of such $(H_2O)^0$ groups is very different from when $(H_2O)^0$ is part of the structural unit.

Hydrogen-Bonded Interstitial $(H_2O)^0$ *Groups.* In some structures, $(H_2O)^0$ groups occur as interstitial species without bonding to an interstitial cation, but still participate in a well-defined hydrogen-bonding network. $(H_2O)^0$ groups of this sort act both as hydrogen-bond donors and as hydrogen-bond acceptors. Minerals with such hydrogen-bonded networks can be envisaged as intermediate between anhydrous minerals and clathrate structures. An example is

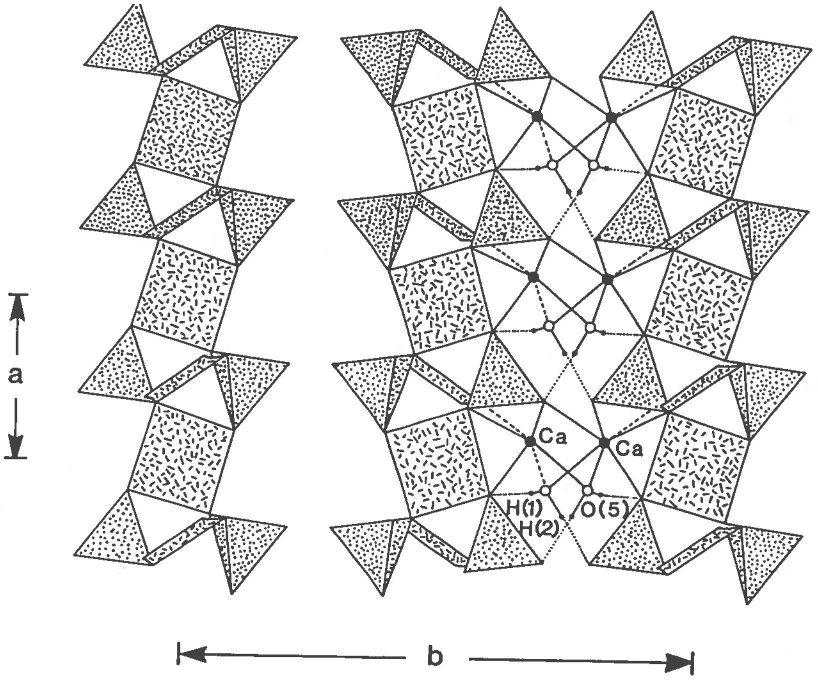

Fig. 85. The crystal structure of stringhamite, showing the structural units linked by Ca tha also bonds to two interstitital $(H_2O)^0$ groups

mandarinoite $\{[Fe_2^{3+}(SeO_3)_3(H_2O)_3](H_2O)_3\}$ (Fig. 86). The structural unit is a heteropolyhedral framework of corner-linking (SeO_3) triangular pyramids and (FeO_6) octahedra, with large cavities that are occupied by hydrogen-bonded $(H_2O)^0$ groups in well-defined positions. Thus of the 6 $(H_2O)^0$ groups in this mineral, three are part of the structural unit and 3 are hydrogen-bonded interstitial $(H_2O)^0$.

Occluded $(H_2O)^0$ *Groups.* In some structures, interstitial $(H_2O)^0$ is not involved in any static hydrogen bonding arrangement. Normally, such $(H_2O)^0$ groups are located in large holes or cavities within the structure, and their interaction with the rest of the structure is through a Van der Waals effect. Such groups are found in beryl, cordierite and the large-pore zeolites such as faujasite. Such $(H_2O)^0$ does not play a significant structural role, but can have important effects on such physical properties as specific gravity, refractive index and dielectric behavior.

Experimental Determination of H-Stereochemistry

There are three principal methods by which presence and stereochemical details of hydrogen-bearing groups can be detected: (1) neutron diffraction; (2) X-ray diffraction; (3) infrared spectroscopy.

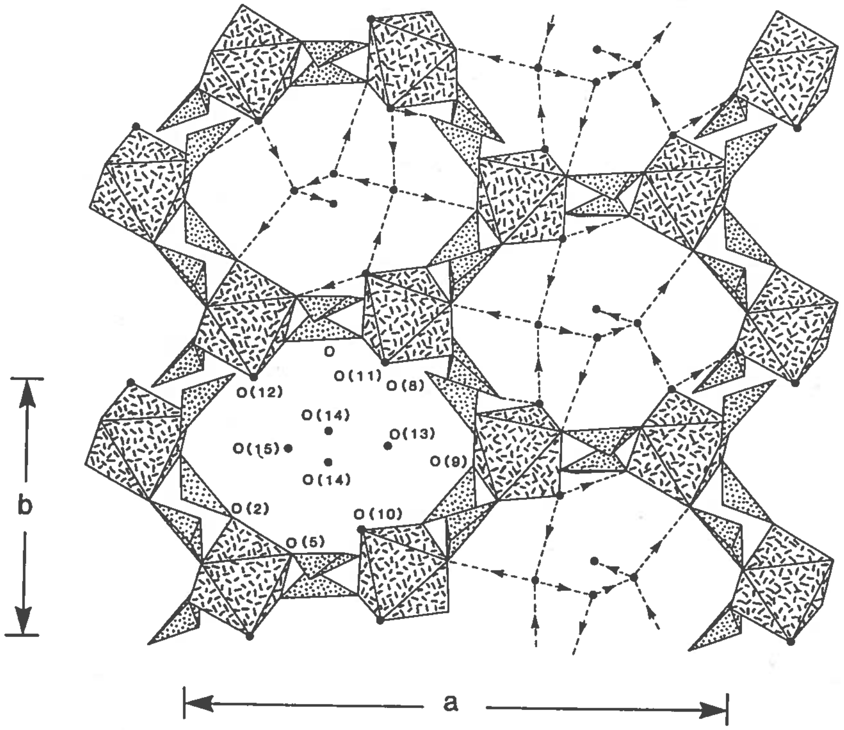

Fig. 86. The crystal structure of mandarinoite; note the two types of $(H_2O)^0$ groups, one bonded to cations of the structural unit, and the other held only by a network of hydrogen bonds

Neutron Diffraction. Hydrogen has a reasonably large negative neutron scattering length, and thus hydrogen can be accurately located in most minerals by crystal structure solution and refinement, the most direct and reliable way of deriving this information. Often, the available material is not suited to this experiment and other methods must be used.

X-Ray Diffraction. Hydrogen scatters X-rays very weakly, and the location of hydrogen atoms directly by crystal structure refinement of X-ray data can be difficult or unreliable. However, bond-valence and stereochemical arguments involving the rest of the structure are generally sufficient to derive accurate (although not very precise) hydrogen locations and/or details of hydrogen-bearing groups present.

Infrared Spectroscopy. Both $(OH)^-$ and $(H_2O)^0$ groups have fundamental vibrational motions that absorb radiation in the infrared region. The $(OH)^-$ group shows a single stretch usually around 3600 cm^{-1}, but varying between 3700 and 2000 cm^{-1} depending on the strength of the associated hydrogen

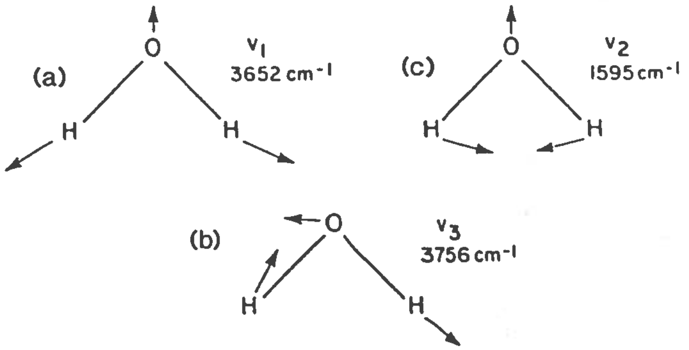

Fig. 87. The three normal modes of vibration for the H_2O group. **a** Symmetric stretch. **b** Asymmetric stretch. **c** Symmetric bend

Table 28. $(OH)^-$ and $(H_2O)^0$ principal absorption bands in minerals

Wavenumber	Group	Motion
1630 cm^{-1}	H_2O	H-O-H bend
3400	OH,H_2O	O-H stretch
3500	OH,H_2O	O-H stretch

bonding; weak hydrogen bonds have absorption frequencies around 3600 cm^{-1}, the frequency decreasing with increasing hydrogen-bond strength. The $(H_2O)^0$ group is a little more complicated. There are two fundamental stretching motions and one bending motion (Fig. 87), and these give rise to a set of characteristic absorptions in the infrared (Table 28), the exact energies of which are affected by details of local stereochemistry. Thus polarized infrared spectroscopy is a powerful method for detecting the presence of hydrogen in a mineral, and for determining its speciation. In turn, the method can also be used as a probe of local structure (particularly order/disorder) when details of the hydrogen speciation are known. This method has been particularly important in detecting the presence of minor to trace amounts of hydrogen in minerals previously thought to be anhydrous (e.g., olivine, feldspar, garnet).

Geometry of Hydrogen Bonds

Reliable local geometries for ordered hydrogen-bonded systems can be derived from neutron diffraction experiments. Statistical analysis of a large amount of such data gives the local geometries of Table 29. The value D-H...O for $(H_2O)^0$ shows a wide variation (range ~ 100-180°), but most values lie within 10° of the mean. The data of Table 29 are very useful for assigning hydrogen-bond arrangements in X-ray structural studies.

Table 29. Local geometries of hydrogen bonds involving $(OH)^-$ and $(H_2O)^0$

O–H	0.96 A	H...A	1.88 A
O–A	2.81	H–H	1.56
H–O–H	108°	O–H...A	170°

Solid Solution in Minerals

The $(OH)^-$ group is a common major constituent of many minerals, the amphiboles and the micas being of particular petrological significance. There are other (fairly) common monovalent anions (e.g., F^-,Cl^-) present in many geological environments, and there is the possibility of extensive monovalent anion solid solution. However, there are significant structural constraints on such substitutions. The most significant is the fact that the $(OH)^-$ is involved in hydrogen bonding, unlike the simple monovalent anions which are anionic in all directions. Thus F^- and Cl^- will generally substitute for $(OH)^-$ only when the $(OH)^-$ group is involved with weak hydrogen bonding and the local structure is able to adjust to the absence of hydrogen bonding around the substituent F^- or Cl^-. In common rock-forming minerals with such weak hydrogen bonding, both silicates (e.g., amphiboles, micas) and nonsilicates [e.g., amblygonite-montebrasite, $LiAl(PO_4)(OH,F)$] commonly show partial to complete solid solution of this sort, and it should be noted that the (OH) = F substitution is an important factor affecting the stability of such minerals.

Hydrogen Bonding and Complexity in Minerals

There are approximately 3500 known minerals, and the majority of these contain hydrogen as a major constituent. As noted above, both $(OH)^-$ and $(H_2O)^0$ exert a dominant control on the dimensionality of the structural unit. It is apparent that it is the availability of hydrogen, together with the weak and anharmonic nature of the hydrogen bond, that accounts for the gradual increase in number and complexity of minerals from the core through the mantle and crust to the surficial environment.

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