these cases more free serotonin can be formed or released than in the normal state (*6*). Therefore, a physiological situation can exist where greater amounts of the free form are available at synapses to produce its effect (*10*).

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Hydrogen Ion Incorporation in Crystals

Abstract. *The protons in crystal structures can be related to the oxygen lattice through several spatial arrangements. In orthosilicates (for example, hydrogarnets), so-called tetrahedral hydroxyls have been demonstrated by indirect methods. Similar methods, when applied to kehoeite and viséite, lead to the conclusion that* $(H_3O_2)^-$ *units can occur in the framework of analcime, a structure in which all apexes of oxygen tetrahedra are shared.*

"Water of crystallization" and the water liberated during the thermal decomposition of "acid salts" have been recognized for many years as ways in which hydrogen ions are incorporated in crystalline compounds. The possible incorporation in crystals of $(H_3O)^+$ has gained theoretical recognition. However, comparatively little is known about $(H_4O_4)^{4-}$ (so-called tetrahedral hydroxyls) or $(H_3O_2)^-$, a newly discovered structural component.

On chemical analysis, one of the oxides reported for many substances is water; it is conventionally reported as water liberated above 105°C (H_2O+) or below 105°C (H_2O-). This method of reporting analytical results is merely a convention, because more than a few hydrates lose part (or all) of their water of crystallization at temperatures below 100°C. No clue to the method of incorporation of the water within the crystal is ordinarily obtained in the absence of differential thermal analysis or thermogravimetric analysis.

Some increments of water, those involving hydroxyl ions, may be tenaciously retained; they may not be liberated below a temperature of 1000°C, or even higher.

Many of the tetrahedral oxygen configurations of several minerals, chiefly orthosilicates, but also orthophosphates, and a series of sulfate-silicate-carbonates (*1*) lack the small, highly charged, centrally located cation. The evidence, to be sure, is indirect, but the isostructural nature of $Ca_3Al_2(SiO_4)_3$ and $Ca_3Al_2(H_4O_4)_3$ can leave little doubt about the association, in this hydrogarnet series, of four hydrogen ions with four oxygens which would otherwise comprise a tetrahedral anion—for example $(SiO_4)^{4-}$. The evidence is not so much a question of an excess of water as it is the absence of silica, although the conformity between silica "deficiency" and "excess" water is astonishingly precise in several cases.

In addition to the series of hydrogarnets (*2*), excess water (accompanied by a deficiency in P or Si or S) has been proposed to explain the compositions of antigorite, coffinite, crandallite, montmorillonite, griphite, and apatite. Most of these examples are *ortho* compounds, but two phyllosilicates, antigorite and montmorillonite, are included. The structures of these two minerals contain sheets of SiO_4 tetrahedra which are joined at three apexes to produce $n(Si_2O_5)^{2-}$. Here again, the substitution of four protons for one silicon atom appears to be the rule (*3*).

Something different evidently occurs in tectosilicates, a well known example of which is analcime. The structure of analcime (*4*) is a three-dimensional framework of oxygen atoms in tetrahedral configuration; all four apexes are shared with other tetrahedra containing Si or Al ions to give the formula $Na(AlSi_2O_6)\cdot H_2O$. This framework, regardless of whether or not there is ordering among the Al and Si atoms, can be described as being constructed of $2n(SiO_2)^0$ and $n(AlO_2)^-$ units—remembering that their structural configuration is essentially tetrahedral in both cases.

Besides aluminum and silicon, an appreciable amount of phosphorus can occur as portions of this framework (*5*). However, the amounts of P, Al, and Si are quite inadequate to provide the framework of viséite. The deficiency of P, Al, and Si is compensated by protons; the proton to oxygen ratio is 3:2, that is, $n(H_3O_2)^-$ (*5*).

Recently, a more straightforward example of this $(H_3O_2)^-$ "anion" (*6*) has come to light as a result of crystallochemical investigation of kehoeite (*7*), a mineral described in 1893 but not previously classified. Briefly, the structural framework consists of essentially identical quantities of $(H_3O_2)^-$, $(AlO_2)^-$, and $(PO_2)^+$ units, rather than $(AlO_2)^-$ and $2(SiO_2)^0$, as in analcime. And while kehoeite and viséite both appear to be essentially isostructural with analcime, kehoeite contains no SiO_2, and its large cation is principally zinc, rather than calcium (viséite), sodium (analcime), or cesium (pollucite).

As is true for the so-called tetrahedral hydroxyls, the structural positions of the protons for $(H_3O_2)^-$ have not been determined by direct methods, such as neutron diffraction or nuclear magnetic resonance. Nevertheless, direct calculation of the number of oxygen atoms in the unit cell (*8*), in combination with chemical analysis and structural information obtained by x-ray diffraction, demonstrates analogies which cannot be explained except on the basis of protons substituting for P, Al, or Si ions (*9*).

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6. Although $(H_3O_2)^-$ is loosely referred to as an "anion" or "unit," it has no independent existence as such. It is merely a link in a continuous framework $n(XO_2)^{x-}$. In the case of kehoeite the minimal unit becomes $[(Al_{16}(H_3)_{16}P_{16})O_{96}]^{16-}$, which is the framework of one unit cell with an edge of 13.7 Å. The 16 negative charges of this framework are neutralized by eight zinc and calcium ions (5.5 Zn + 2.5 Ca).
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