# THE PROTON: A CATION LIKE THE OTHERS IN ROCK-FORMING MINERALS

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In hydrous rock-forming minerals, the hydroxyl hydrogen and the hydroxyl oxygen are usually considered as a whole and permanent entity, *i.e.* the hydroxyl group, which acts as a monovalent anion within the structure. The reality is more complicated and more interesting, since the hydroxyl proton leads its life independently. Depending on the local charge balances, the hydroxyl group can be considered as a point charge or as dipole in which oxygen and hydrogen play a different role, since hydrogen is able to share a part of its charge with surrounding oxygens, usually the underbonded oxygens of adjacent tetrahedra.

The properties of the OH group (O–H distance and resulting O–H stretching and bending wavenumbers) closely reflect the local variations of crystal-chemical properties in the mineral structure: charge distributions, and distances. An examination of these properties allow a careful description of the crystal-chemical landscape around the proton, up to the fifth cationic neighbour in favourable cases, and a prediction of many geochemical properties of H-bearing rock-forming phases.

The main factor controlling these properties is the nature (bulk charge, electronegativity) of the first cationic neighbours. The higher the bulk charge carried by the immediately adjacent cations, the weaker the O–H bond within the hydroxyl group. Contrary to a commonly accepted idea, the orientation of the OH dipole is not the main factor controlling these properties. An example is given by the comparison between talc $Mg_3Si_4O_{10}(OH)_2$, a trioctahedral 2:1 layer silicate, with the OH dipole bonded to $Mg_3$ and perpendicular to (001), and pyrophyllite, $(Al_2\square)Si_4O_{10}(OH)_2$ ($\square$ stands for an octahedral vacancy), with the OH group adjacent to $Al_2\square$ and strongly tilted towards (001). The resulting OH bond strength is the same in talc and pyrophyllite, as shown by the similarity between their OH-stretching wavenumbers ($3676 \pm 1$ cm$^{-1}$). As long as the local charge balance around the OH group remains constant, the bond strength within the OH group and the resulting OH-stretching wavenumber remain constant, whatever the mineral family. It is interesting to note that the trioctahedral OH group in the tetrasilicic magnesium mica $K(Mg_{2.5}\square_{0.5})Si_4O_{10}(OH)_2$, in richterite, a clinoamphibole, $(K,Na)(NaCa)Mg_5Si_8O_{22}(OH)_2$, and the inner OH-group in dravite, a tourmaline, $NaMg_3Al_6(BO_3)_3(Si_6O_{18})(OH)(OH)_3$, have the same OH-stretching wavenumber, 3735 cm$^{-1}$, within experimental uncertainties. In these there major silicate families, the OH group is bonded to $Mg_3$ and point towards an alkaline cation, in the middle of a ring of six $SiO_4$ tetrahedra, which can be summarised as follows: $Mg_3$-OH $\rightarrow$ $(6SiO_4)$-$A^+$ (with $A^+ = Na^+$ or $K^+$).

A decrease of the local charge carried by the first adjacent cations raises the O–H bond strength and consequently the OH-stretching wavenumber, up to 3755 cm$^{-1}$, the highest value known in any compound under room conditions, observed in tainiolite $K(Mg_2Li)Si_4O_{10}(OH)_2$. By contrast, as the bulk charge carried by the first cationic neighbours increases, for example $Mg_2Al$ or $Al_2Li$, the OH-stretching wavenumber drops to values around or below 3650 cm$^{-1}$, indicating that a part of the proton charge is shared with surrounding oxygens. This is observed in all mineral families.

Heterovalent cationic substitutions in octahedral sites adjacent to the OH-group are generally coupled with replacements in other polyhedra, *e.g.* the tetrahedral sites, the interlayer space in layer silicates, the pseudo-cubic antiprism *M*4 site in amphiboles, the second, third, ..., neighbours, must be considered.

Using selected synthetic minerals allows to determine the respective influence of all substitutions, up to the fifth cationic neighbouring sites in favourable cases, through a careful analysis of the perturbations induced on the OH group. In this way, it is possible to assign all observed OH vibrations to a peculiar environment, and then to deduce local order-disorder relations around the hydroxyl proton.

The influence of the $A^+$ cation can be analysed using $A^+$-bearing and $A^+$-free minerals. For example, the influence of $K^+$ on hydroxyl properties can be deduced from the comparison between talc [$Mg_3$–OH $\rightarrow$ $(6SiO_4)$] and the trioctahedral OH of the tetrasilicic Mg mica [$Mg_3$–OH $\rightarrow$ $(6SiO_4)$–K]. The shift induced by $K^+$ facing the OH group is +59 cm$^{-1}$. A similar value is observed in amphiboles, for example between tremolite $\square Ca_2Mg_5Si_8O_{22}(OH)_2$ and richterite $A^+(NaCa)Mg_5Si_8O_{22}(OH)_2$, and in tourmalines, Mg-foitite $\square(Mg_2Al)Al_6(BO_3)_3(Si_6O_{18})(OH)(OH)_3$, compared to dravite $NaMg_3Al_6(BO_3)_3(Si_6O_{18})(OH)(OH)_3$. Increasing the charge of the cation facing the hydroxyl group raises the OH-stretching wavenumber, as observed along the phlogopite $KMg_3(Si_3Al)O_{10}(OH)_2$–kinoshitalite $BaMg_3(Si_2Al_2)O_{10}(OH)_2$ join, where the $K^+/Ba^{2+}$ substitution provokes a shift of +20 cm$^{-1}$ in the OH-stretching wavenumber. The tilting of the OH group towards (001) in dioctahedral phases withdraws this interaction, as shown by the comparison between muscovite or paragonite $A^+(Al_2\square)(Si_3Al)O_{10}(OH)_2$, with $A^+ = K^+$ and $Na^+$, respectively, and phlogopite $KMg_3(Si_3Al)O_{10}(OH)_2$.

Contrary to a commonly accepted belief, the effect of the orientation of the OH group on the exchange properties of clay minerals is practically negligible, since the interlayer water molecules act as a screen between the hydroxyl proton and the compensating cation, and there is almost no interaction between them even in the case of trioctahedral smectites, like saponites. As a matter of fact, in one-layer high-charge saponites, the OH-stretching wavenumber is only 3682 cm$^{-1}$, *e.g.* very close to that of talc, a 2:1 layer silicate without interlayer compensating cation. Therefore, in smectites, only the charge location and the charge value have an influence on exchange properties, and the behaviours of the dioctahedral beidellites and trioctahedral saponites, both with tetrahedral charge, on one side, and of the dioctahedral montmorillonites and the trioctahedral hectorites, both with octahedral charge,

on the other side, are similar provided that the layer charge is the same.

The properties of the OH-group also allow to investigate the tetrahedral cationic distributions (mainly Si, Al), since the OH···O interactions depend on the charge balance on surrounding oxygens, *i.e.* the oxygens of tetrahedra. A careful quantitative investigation of OH-stretching band intensities for different first neighbours (octahedral), and second neighbours (tetrahedral) shows that the Si, Al distributions are generally not ordered, but follow a homogeneous charge distribution pattern, in agreement with high-resolution NMR data. Considering the influence of second cationic neighbours effects (*i.e.* tetrahedrally coordinated cations), on band positions and band intensities, leads to conclude that in many cases the extinction coefficients are constant, which allow quantitative determinations of cationic distributions around the hydroxyl proton.

The method is sensitive enough to enlight long distance effects, even for subtle substitutions like $Ca^{2+}/Mg^{2+}$ at $M4$ sites in clinoamphiboles along the tremolite $\Box Ca_2Mg_5Si_8O_{22}(OH)_2$–cummingtonite $\Box Mg_7Si_8O_{22}(OH)_2$ join, or $Na^+/Li^+$ along the ferri-clinoferroholmquistite $\Box Li_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$–riebeckite $\Box Na_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$ series. Owing to the distances, these long-range effects are not direct. They are induced through the structure by the propagation of tiny distortions required by local charge balance requirements.

In addition to this role of privileged observer, the proton $H^+$ frequently plays a key role in many situations. Deprotonation in the case of in situ oxidation of a variable charge cation, *i.e.* $Fe^{2+} \rightarrow Fe^{3+}$, in biotites, hornblendes, and so, no protonation when high cation ($Mn^{3+}$, $Ti^{4+}$) are incorporated to crystal structures, in micas like norrishite $K(Mn^{3+}_2Li)Si_4O_{10}O_2$ and many high-Ti phlogopites, or amphiboles like ungarettiite $NaNa_2(Mn^{2+}_2Mn^{3+}_3)Si_8O_{22}O_2$, obertiite $NaNa_2(Mg_3Fe^{3+}Ti)Si_8O_{22}O_2$ and dellaventuraite $NaNa_2(MgMn^{3+}_2LiTi)$ $Si_8O_{22}O_2$. Additional protonations are also known in hydrous minerals, for example in partially dioctahedral micas with a tetrahedrally coordinated cation, $Be^{2+}$, $Mg^{2+}$, $Ni^{2+}$ or $Co^{2+}$, or in clinoamphiboles (richterites), with $Li^+$ replacing $Ca^{2+}$ at the M4 site.

The approach is also very useful for identifying unusual coordinations for cations, for example $[4]M^{2+}$ in micas and in amphiboles like joesmithite, $PbCa_2Mg_5(Si_6Be_2)O_{22}(OH)_2$, or $[4]B^{3+}$ in high pressure olenite (a tourmaline) $NaAl_3Al_6(BO_3)_3(Si_3B_3O_{18})(OH)(OH)_3$.

The interactions of the hydroxyl proton with the neighbouring oxygens, influenced by the charge distributions and the distances, also control the possible $OH^-/F^-$ exchange properties, whatever the fluorine activity in the environment. When the hydroxyl proton has no or little interactions with its neighbours, it acts as a point charge in the structure and the $OH^-/F^-$ is easy. It is the case in most trioctahedral layer silicates, in all amphiboles and at the inner $OH^-$ site of tourmalines. By contrast, if the hydroxyl proton is involved in H-bonds with surrounding oxygens, its replacement by fluorine is more energetically difficult, and becomes impossible if OH···O bonds are strong. It is why dioctahedral layer silicates do not trap much fluorine, and why outer hydroxyl groups cannot be replaced by fluorine in tourmalines.