

## Hydrous components in the nominally anhydrous minerals

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Hydrous components in the nominally anhydrous minerals were first of significance for their impact on the mechanical strength of minerals and on the dielectric properties of synthetic materials. They are now known to influence a large number of chemical and physical properties of the host mineral and are thought to be an important contribution to the Earth's water cycle.

Detection, and concentration determination is now most conveniently achieved by infrared spectroscopy, but requires independent calibration for accurate analyses. IR spectra distinguish between OH and H<sub>2</sub>O and can also establish if the water is present in fluid inclusions or alteration products. NMR spectroscopy, likewise, can often determine the specific species in the mineral, but requires larger amounts of pure sample and cannot deal well with commonly encountered concentrations of paramagnetic ions. Nuclear profile analysis with N-15 ions has required a long development period, but has proven to be a highly useful absolute analytical method. Raman spectroscopy can detect OH, but, in our experience, has not proven reliable for absolute concentration determinations.

Minor amounts of OH are found in most common mantle phases and numerous crustal phases including many common silicates and oxides. Concentrations range from <10 ppm in pyrope garnets to percents in grossular garnets. Useful calibrations of the IR spectra now exist for olivine, certain garnets, pyroxenes, kyanite, zircon, and some oxides. Generic calibrations also have improved, but do not remove the need for mineral-specific calibrations for accurate work.

H<sub>2</sub>O is typically found at concentrations reaching 2% in ring silicates and minerals with large channels. In feldspars and feldspathoids concentrations range from near zero to nearly 0.2%

Studies of synthetic minerals have shown that significantly larger concentrations can be incorporated in silicates under high PT conditions and have led to the current discussion of the importance of OH in the deep mantle and the question of how many oceans of water exist at depth.

Recent work has also shown that water resides in some phases as nano-inclusions and may be an exsolution product in phases that formerly contained higher concentrations of OH in the deep earth.

## Hydrogen in the Al<sub>2</sub>SiO<sub>5</sub> polymorphs

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It has been shown that water can be incorporated within the structures of nominally anhydrous silicates and oxides [1]. This study examines incorporation of hydrogen within the aluminosilicate polymorphs, kyanite, andalusite and sillimanite. Potential hydrogen bonding sites within the aluminosilicate polymorphs were determined based on an analysis of the Laplacian of the electron density distribution, following the method of Ross et al. [2]. The CRYSTAL98 program [3] was used to generate analytical electron density distributions for kyanite, andalusite and sillimanite, and TOPOND [4] was used to locate the (3,-3) critical points. The location of the (3,-3) critical points indicate that the potential sites are large enough to accommodate hydrogen and also indicate that the O-H bonds in andalusite and sillimanite are highly directional. In andalusite, the O-H vectors lie within (001) and are approximately parallel to [-1 1 0] and [110]. In sillimanite, the O-H vectors also lie within (001) but are oriented closer to [010]. The location of potential sites for hydrogen in kyanite is less clear.

In addition, hydrogen was introduced in the structures using the Vienna Ab-initio Simulation Package (VASP) [5]. The results from these calculations not only determine the location of the hydrogen within the structure, but also provide binding energies for hydrogen in different sites of the structures. VASP calculations indicate H bonding near OA within the (001) plane of andalusite and in multiple locations in sillimanite and kyanite. Locations of hydrogen in the structures will be compared with polarized infrared spectroscopy.

### References

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