

Determination of hydrogen in feldspars by IR and NMR spectroscopy

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In the past decade, there have been several studies aimed at the quantification of the concentration of H in nominally anhydrous minerals. These studies were mostly directed at the common mantle minerals such as olivine, clinopyroxene, orthopyroxene and pyrope garnet that probably hold a major global reservoir of hydrogen in the earth's mantle. Unfortunately, there has been less effort directed at the quantification of the amount of H that occurs in the feldspar group and other crustal minerals. Infrared spectra of feldspars have shown that trace to minor amounts of structurally incorporated hydrogen occurs in feldspars that range from turbid to completely clear. A series of mid-IR and near-IR spectroscopic studies of feldspars showed that plagioclase contains structural OH groups and that alkali feldspars commonly incorporate OH groups, H₂O molecules, and NH₄⁺. The concentration of these hydrous species has previously been determined for only a few alkali feldspar samples using hydrogen manometry. Because many of the plagioclase feldspars typically have much lower H-contents than the alkali feldspars, previously there have been no published determinations of the absolute H contents for any of the plagioclase feldspars.

To address this lack of data, a universal absorption coefficient was determined for quantitative analysis of OH and H₂O in feldspars with the use of infrared spectroscopy. ¹H MAS (magic-angle spinning) NMR spectroscopy was used to determine the absolute H concentration in three alkali feldspars, and for the first time, eight plagioclase samples (Fig. 1). To accurately measure structural H concentration in samples with low H (<1000 ppm H₂O) it was necessary to eliminate the signal due to adsorbed water in the powdered NMR sample. The pegmatitic and metamorphic albite samples are transparent, but contain variable (40–280 ppm H₂O) concentrations of microscopic to sub-microscopic fluid inclusions. The pegmatitic albites also have sharp bands in the mid-IR similar to the OH bands found in quartz. The other plagioclase samples used in the IR calibration have broad anisotropic bands around 3200 cm⁻¹ in the mid-IR and weak combination stretch-bend bands near 4550 cm⁻¹ in the near-IR, indicative of structural OH. The OH vector in plagioclase is preferentially aligned parallel to the crystallographic *a*-axis. The concentration of structural OH in the plagioclase samples ranges from 210–510 ppm H₂O by weight.

The microcline samples contain structural H₂O molecules (1000–1400 ppm H₂O) and the sanidine sample contains structural OH (170 ppm H₂O). An approximately linear trend is produced when the total integrated mid-IR absorbance is plotted vs. the concentration of structural H determined from NMR (OH and H₂O) for plagioclase and alkali feldspars. The integral absorption coefficient for the total mid-IR peak area is $15.3 \pm 0.7 \text{ ppm}^{-1} \text{ cm}^{-2}$ [$107000 \pm 5000 \text{ L}/(\text{mol H}_2\text{O cm}^2)$] for natural feldspar samples that contain structural OH or H₂O. Measurements of band areas of unpolarized IR spectra on (001) cleavage fragments provide a reasonable estimate of H concentration for alkali feldspars, but this method does not work for most plagioclase samples.

This newly determined calibration of the infrared spectrum was used to establish the amount of hydrous components in eighty-five feldspars from a variety of igneous environments that spanned the range of naturally occurring compositions. We found that feldspars contain structural OH (0-512 ppm H₂O), H₂O (0-1350 ppm H₂O), and NH₄⁺ (0-1500 ppm NH₄⁺). Also commonly found were fluid inclusions and hydrous alteration products.

Although composition and structure will influence the type of hydrous species that are incorporated into a particular feldspar mineral, the concentration of these species does not appear to be controlled by the major-element composition. Perthitic microclines contained a heterogeneous distribution of hydrous species. They have H₂O or NH₄⁺ in the K-rich lamellae and dominantly fluid inclusions in Na-rich areas. In the plagioclase feldspars, structural OH is the dominant form of incorporation of hydrous components. In these feldspars, the hydrous component is not associated with either twin boundaries or exsolution lamellae.

Pegmatite feldspars contain all of the possible structural hydrous species, whereas volcanic feldspars contain only structural OH. Most plutonic feldspars have undergone partial or total isotopic and chemical equilibration with meteoric fluids during low-temperature (400-150°C) hydrothermal exchange, obliterating any structural hydrogen and creating substantial concentrations of fluid inclusions (up to 4000 ppm H₂O) in the exchanged regions. These commonly are evident as turbid regions in the sample.

We estimate that the amount of water stored as fluid inclusions within feldspars in the upper crust is about 10¹⁹ kg, a value that is small compared to the 10²¹ kg of water in the oceans, but roughly equivalent to the reservoir of water stored in hydrous minerals in the upper crust.

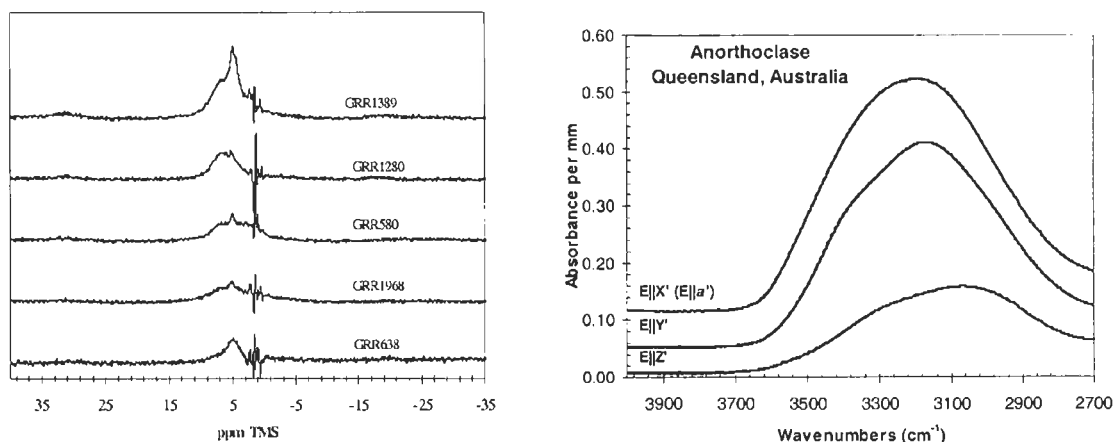


Figure 1. The ¹H NMR of a series of plagioclase feldspars and the OH spectrum of a plagioclase.