An infrared spectroscopic study of hydrogen feldspar (HAlSi$_3$O$_8$)

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Abstract

Hydrogen in H-feldspar obtained by ion-exchange was studied in the spectral range 1000–5500 cm^{-1} by single crystal IR microspectroscopy. Spectra were almost identical for H-feldspars prepared either from sanidine or from adularia. Two bands in the middle-infrared were identified by D/H exchange as OH vibration modes. One broad band with a maximum at 3000 cm^{-1} and shoulders at 2800, 3200 and 3500 cm^{-1} confirms previous work. An additional OH absorption band with a maximum at 2485 cm^{-1} was observed for the first time in feldspars. The pleochroism of the OH absorption bands suggests that the H-feldspar is composed of two phases, an amorphous phase and a feldspathic phase. The proportion of the amorphous phase is increased by heating, producing a shift of the maximum of the band at 3000 cm^{-1} towards higher wavenumber and a decrease of the intensity of the band at 2485 cm^{-1}. Near-infrared spectroscopy showed that hydrogen is present as hydroxyl groups bound to tetrahedral cations in both phases. Molecular water was not detected. The experimental results imply that hydrogen is incorporated in the H-feldspars as protons attached to bridging oxygen as well as to non-bridging oxygen. The complex structure of the IR spectra implies that the protons are distributed over a large number of sites in the cation cavity of the feldspars.

KEYWORDS: hydrogen feldspar, IR spectroscopy, hydrogen species, amorphization.

Introduction

NATURAL feldspars often contain traces of water from several to several hundreds of ppm (Wilkins and Sabine, 1973; Lehmann, 1984; Hofmeister and Rossman, 1985). At least a part of the water is present as structural defects (Hofmeister and Rossman, 1985; Beran, 1986, 1987). Structurally bound water (or hydrogen) can strongly influence the kinetic properties of feldspars. NaSi–CaAl inter-diffusion in plagioclase (Yund, 1986; Baschek and Johannes, 1992; Liu and Yund, 1992), oxygen diffusion in anorthite (Elphick *et al.*, 1988) and the kinetics of Al/Si disordering in albite (Goldsmith, 1986, 1987) are considerably enhanced by the presence of water or hydrogen.

Little work was done so far to study the structural and kinetic properties of hydrogen species in feldspars. Hofmeister and Rossman (1985) identi-fied hydroxyl groups bound to tetrahedral cations and molecular water by near-infrared spectroscopy. Orientations of OH dipoles in feldspars were determined for sanidine, microcline and labradorite by polarized infrared spectroscopy (Hofmeister and Rossman, 1985; Beran, 1986, 1987). Heating-induced transformation of one hydrogen species to another in a microcline was studied in-situ with IR spectroscopy by Aines and Rossman (1985).

The main problem for the characterization of hydrogen species in feldspars is their low concentra-tion in natural feldspars. A correlation to non-stoichiometric composition of the feldspar or to concentrations of other impurities is practically impossible. The purpose of the present study is to get some new insight into the properties of hydrogen structurally bound in feldspars by studying pure

hydrogen feldspar. Müller (1988) reported the preparation of a feldspar in which alkali cations are substituted almost completely by protons. The crystal structure of the resulting hydrogen feldspar was determined from single crystal an X-ray data (Paulus and Müller, 1988) as well as from X-ray powder pattern (Deubener et al., 1991).

The present study focusses on the role of the protons in the feldspar structure. Isotope exchange, partial cation exchange and various heating procedures were used to characterize the hydrogen species. A possible effect of Al/Si order was tested by using feldspars with different degrees of Al/Si order, sanidine and adularia, as starting materials.

Materials and experimental procedures

Starting materials were sanidine from Volkesfeld, Germany, and adularia from St. Gotthard, Switzerland. Compositions and lattice constants of the crystals are given by Deubener et al. (1991). Crystals were ground and sieved to grain sizes 100–250 μm. The sanidine fragments were almost platy. Polarized IR spectroscopy showed that the basic plane was (010). Sharp cleavages perpendicular to the basic plane were assigned to (001). The shape of the grains remained essentially unchanged by the exchange reactions. Additional cracks were formed mostly parallel to the main cleavage planes and were used for orientation in the IR measurements. Grains obtained from grinding adularia were often irregular in shape. Only a small fraction was platy and could be used for spectroscopic measurements, but the orientation of the plates could not be determined.

Na/K exchange was performed by heating the alkali feldspars twice for 3 days in molten NaCl at 810°C. The hydrogen feldspars were obtained by annealing the Na-exchanged feldspars twice for 3 days at 310°C in H_2SO_4. For Na/H re-exchange the hydrogen feldspars were annealed in molten $NaNO_3$ at 320°C for times of up to 8 days. An exchange of deuterons for protons was performed in a closed glass apparatus. The samples were loaded in a platinum container and inserted in a fused silica tube, which was connected to a D_2O reservoir held at room temperature.

Electron microprobe analysis of embedded and polished grains of the H-feldspar prepared from the Na-exchanged sanidine, further denoted as H-feldspar(san), were carried out using a CAMECA CAMEBAX microprobe. Water contents of feldspars were determined by Karl-Fischer titration.

IR spectra in the range 1000–5500 cm^{-1} were recorded by an IR microscope A590 attached to a FFT-IR spectrometer IFS88 (Fa. Bruker). 100 scans were accumulated for each spectrum. An aperture of 0.75 mm was used for measurement, resulting in a spot diameter of 50 μm. Spectra were always measured for several clear grains of each material. The spectra drawn in the figures are always from one single crystal typical for the material. Because of their platy shape the feldspar grains could be used without further preparation if they were mounted on KBr pressed pellets. Effects of water in the KBr were eliminated by measuring reference spectra directly beside the grains. A spectral resolution of 4 cm^{-1} was believed to be sufficient to characterize the broad absorption bands of the feldspars. Higher spectral resolution gave spectra of lower quality because of interference fringes. Most of the measurements were performed using a partially polarized beam as given by the spectrometer. In order to study the pleochroism of the OH-absorption bands a polarized beam was used (IR-polarizer KRS-5, Fa. Bruker). Spectra were recorded after rotation of the crystal in steps of 10 to 30°. Care was taken to get the same position of the beam on the sample in all measurements for determination of the pleochroism.

A direct comparison of band intensities in spectra of different grains is not possible because the hydrogen content of an individual grain used for IR measurement is not known (see below) and because the thickness of the grains is not sufficiently well defined. The thickness of an individual grain varied up to 5 μm due to steps on the surface. An additional problem was that the thickness must be determined directly by the IR-microscope. An estimate by focussing the optical stage of the IR-microscope indicates thicknesses of the grains between 20 and 60 μm, but the uncertainty was approximately 5 μm. Evaluation of interference fringes did not give better results.

Results

An average water content of 3.55 ± 0.15 wt.% was determined by Karl-Fischer titration for the hydrogen feldspar prepared from the Na-exchanged sanidine. This is slightly below the value expected for a complete exchange of alkalis by hydrogen (3.71 wt.%) and corresponds to an average exchange of the alkalis of 96 %. Electron microprobe analysis shows that the grains are homogeneous, but there exists a considerable variation in the degree of hydrogen/alkali exchange of individual grains (Table 1). This is probably due to different amounts of fractures produced by strain in the feldspar crystals during the exchange with molten NaCl (Petrovic, 1973). The average of all analyses and compositions of grains with maximum and minimum alkali contents are given in Table 1. Data for sanidine are included for comparison. Al_2O_3, SiO_2, Fe_2O_3 and BaO contents of the feldspars are almost identical to those of the starting material, if the data are considered on a

TABLE 1. Electron microprobe analyses (in wt.%) of H-feldspar(san) crystals with minimum and maximum alkali contents and average composition of 9 crystals. Data of sanidine (average of 6 analyses) are shown for comparison. Standard deviations are given in parentheses

	H-feldspar(san)					sanidine
	crystal 1 (rim)	crystal 1 (core)	crystal 2 (rim)	crystal 2 (core)	average for 9 crystals	
Na$_2$O	4.83	4.10	0.04	0.12	1.05 (1.58)	1.73 (0.06)
K$_2$O	1.72	2.67	0.30	0.12	1.11 (0.77)	14.48 (0.18)
CaO	0.00	0.00	0.06	0.01	0.02 (0.01)	0.00 (0.01)
BaO	0.81	0.92	0.78	0.77	0.89 (0.07)	0.61 (0.21)
Al$_2$O$_3$	20.01	20.01	21.56	21.12	20.86 (0.45)	18.71 (0.12)
Fe$_2$O$_3$	0.26	0.25	0.21	0.16	0.20 (0.05)	0.17 (0.03)
SiO$_2$	71.48	71.43	74.29	73.90	73.04 (0.92)	64.11 (0.48)
Total	99.20	99.41	97.24	96.18	97.11 (1.04)	99.81 (0.71

molar basis. Variations in alkali contents are correlated to variations in the sum of all oxides. Differences of the sums from 100 wt.% are caused mainly by H$_2$O. The average water content deduced from electron microprobe analysis agrees well with that determined by Karl-Fischer titration, if the large uncertainty of the electron microprobe analyses for water determination is taken into consideration.

Middle-infrared spectra (1000–4000 cm^{-1}). The high frequency part of the spectrum of H-feldspar(san) display two broad absorption bands with maxima at 3000 and 2485 cm^{-1} (Fig. 1). The spectra of the sanidine and the Na-feldspar show only very weak absorption bands in this spectral range. The hydrogen contents of these feldspars are more than two orders of magnitude below that of the H-feldspar(san), and spectral features due to OH vibration can only be resolved in thicker samples. In order to identify the absorption bands due to OH vibrations, the H-feldspar(san) was exchanged with D$_2$O vapour. As shown below the spectral features depend on the heat treatment of the feldspars.
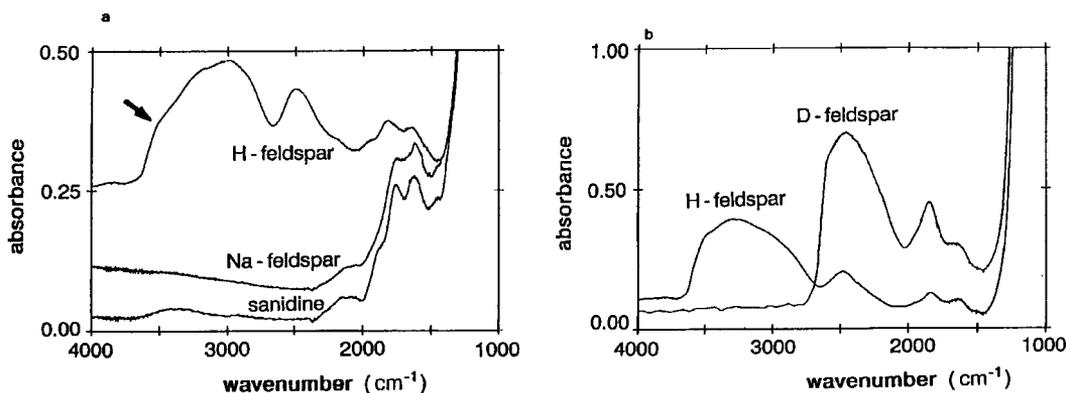

FIG. 1. Identification of OH absorption bands of hydrogen feldspar. Spectra were taken from (010) fragments (thickness: ca. 50 μm) using a partially polarized beam with an E-vector predominantly oriented parallel to the *a*-axis. Spectra in this and in the following figures are plotted with an offset in absorbance for clarity. (*a*) Comparison of H-feldspar(san) with Na-feldspar and with sanidine. Bands above 2300 cm^{-1} are due to OH vibration, those below 2300 cm^{-1} to overtones of lattice modes. The shoulder at 3500 cm^{-1} (arrow) of the spectrum of the H-feldspar is attributed to an amorphous phase. (*b*) Comparison of H-feldspar(san) steam-treated at 500°C with D-feldspar(san) obtained by D/H exchange for 24 hours at 500°C. The absorption bands of the H-feldspar(san) with maxima at 3275 and 2485 cm^{-1} are shifted to lower wavenumber for the D-feldspar(san), 2440 and 1840 cm^{-1}, respectively. The OD vibration band at 1840 cm^{-1} is superposed onto the band due to lattice modes at the same wavenumber.
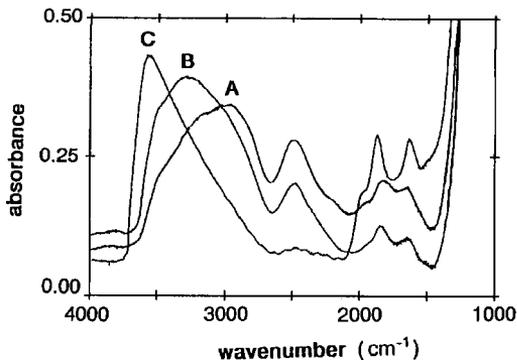
FIG. 2. Effect of heat-treatment on IR spectra of H-feldspar(san). Spectra were taken from (010) fragments (thickness: ca. 50 μm) using a partially polarized beam with the E-vector predominantly oriented parallel to the a-axis. A: sample after H/Na exchange. B: sample heated in steam for 5 hours at 500°C. C: sample heated for 0.5 minutes in dry argon at 550°C.

Therefore, the H-feldspar(san) was steam-treated for 5 hours at the same temperature (500°C) as used for the isotope exchange. The frequency shifts by D/H exchange are for both high frequency bands of the H-feldspar, in good agreement with the theoretical value of $v_{OH}/v_{OD} = 1.37$ (Langer and Lattard, 1980; Freund, 1982), proving that these bands are due to OH vibration modes.

Two main bands are visible in the spectral range 1500–2200 cm^{-1} for all three feldspars. Both bands are shifted towards higher wavenumbers for the H-feldspar as compared to the Na-feldspar and the sanidine (positions of the maxima — H-feldspar: 1840 and 1630 cm^{-1}; Na-feldspar: 1760 and 1610 cm^{-1}; sanidine: 1750 and 1615 cm^{-1}). In the case of the hydrogen feldspar these bands did not change as a consequence of the D/H exchange. These bands are assigned to overtones of fundamental lattice vibrations.

Effect of heating on the IR spectra of H-feldspar. Heating of the H-feldspar(san) in steam at 500°C for 5 hours slightly reduced the average water content to 3.38 wt.%. As shown in Fig. 2 this heat treatment gave a shift of the maximum at 3000 cm^{-1} towards higher frequency (3275 cm^{-1}) and the high frequency side of the peak became steeper. The position of the peak at 2485 cm^{-1} is unchanged, but its intensity was decreased relatively to that of the maximum of the main band. Heating-up the H-feldspar(san) in a dry argon stream in the Karl Fischer titration apparatus using a ramp of 50°C/min up to 500°C and holding this temperature for 4 minutes gave a decrease of the average water content

to 2.61 ± 0.15 wt.%. The IR spectra were identical to those of the steam-treated material. Heating-up to 550°C in the Karl-Fischer titration apparatus using a heating rate of 100°C/minute and holding this temperature for 0.5 minutes gave a strong decrease of the average water content to 0.84 wt.%. After this procedure the peak at 2485 cm^{-1} became very weak. The maximum of the main band was shifted to 3560 cm^{-1} and the dependence of the absorbance of polarized radiation on orientation was lost. The shape of the peak resembles that found for hydrous glasses (see e.g. Stolper, 1982, for comparison). Further heating to higher temperature (800°C) decreases the intensity of the absorption band but its shape and its position remain unchanged.

Pleochroism of the OH absorption bands of H-feldspar(san). The OH vibration spectra of the H-feldspar(san) is composed of two principally different contributions (Fig. 3). At 3000 and at 2485 cm^{-1} the largest absorbance of polarized radiation in (010) was observed, if the E-vector vibrates approximately parallel to the a-axis. The ratio of the absorbance using E ∥ a to that using E ⊥ a varied between 1.3 and 3.3 for 8 crystals analysed. These spectral features are assigned to protons in a feldspathic environment. In contrast to the peaks at 3000 and 2485 cm^{-1}, the shoulder at 3500 cm^{-1} showed no significant dependence on the orientation of the crystal to the radiation. It is highly probable that this shoulder is due to OH groups in random orientations, as present in an amorphous phase. This is supported by the heating experiments showing a successive transformation of the feldspar to an amorphous phase. Probably, even in the H-feldspar as obtained after the ion-exchange, an amorphous phase is present in addition to a feldspathic phase. A confirmation of this can only be given by IR measurements in a different crystal section. But the preparation of the crystals for such measurements was not possible because of their small sizes.

The H-feldspar(san) was etched for 15 minutes with 5% HF in order to test if the destruction of the feldspar structure occurred only at the surface or also in the interior of the crystals. After etching, the crystals showed dissolution textures at the surface, but the IR spectra were identical to those of unetched H-feldspar(san). This indicates that the formation of the amorphous phase is not restricted to the surfaces.

Near-infrared spectra (3700–5500 cm^{-1}). Spectra of H-feldspar(san) show two weak peaks at about 4500 and about 4000 cm^{-1} (Fig. 4). In accordance to previous studies, the peak at about 4500 cm^{-1} can be attributed to the combination of stretching and bending modes of SiOH or AlOH groups (Scholze, 1960; Hunt and Salisbury, 1970; Hunt et al., 1971; Bartholomew et al., 1980; Wu, 1980; Stolper, 1982), and that at about 4000 cm^{-1} to the combination of
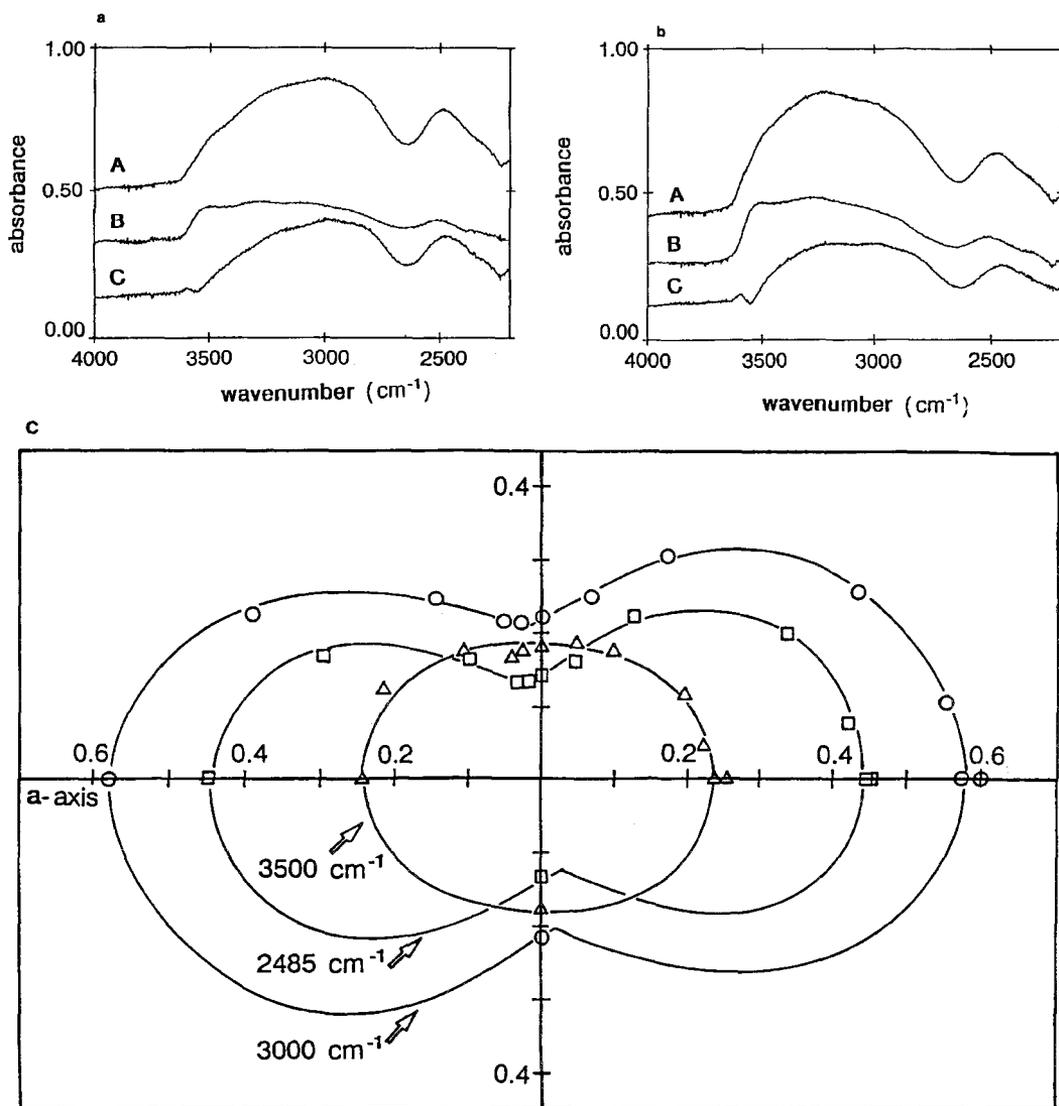
Fig. 3. Polarized IR absorption spectra of crystal plates parallel to (010) of H-feldspar(san), as obtained after H/Na exchange (a) and after steam-treatment at 500°C (b). Thickness of samples: c. 50 μm. A: E ∥ a. B: E ⊥ a. C: spectrum A - spectrum B. (c) OH absorption figure on a (010) plate of H-feldspar(san) as obtained after H/Na exchange. Plotted are radiants in absorbance for 2485 cm^{-1} (squares), 3000 cm^{-1} (circles) and 3500 cm^{-1} (triangles). The absorbance values were corrected by subtraction of the absorbance obtained in a range not influenced by the fundamental OH vibration (3800 cm^{-1}). The two possible orientations of the c-axis could not be distinguished under the IR microscope.

fundamental OH stretching modes and low energy lattice modes of the silicate network (Kats, 1962; Stolper, 1982; Stone and Walrafen, 1982). A peak at about 5200 cm^{-1} indicative of molecular water (Stolper, 1982) was not observed in any of the spectra. From this it is estimated that molecular water, if present in the hydrogen feldspars, was always below 10% of the total water content.

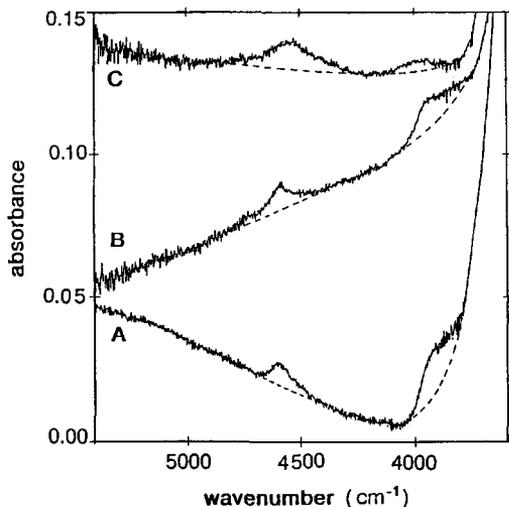*Effect of Al/Si order on OH absorption spectra.* In order to study the effect of the degree of Al/Si order a

FIG. 4. Near-infrared spectra of H-feldspars(san) measured after various heat treatments. Spectra were taken from (010) fragments (thickness: c. 50μm) using a partially polarized beam with the E-vector predominantly oriented parallel to the a-axis. Dashed lines give the baselines of the absorption peaks drawn by hand. A: sample after H/Na exchange. B: sample heated in steam for 5 hours at 500°C. C: sample heated for 0.5 minutes in dry argon at 550°C. The maximum absorbances of the fundamental OH band above 3000 cm^{-1} were similar for all three samples (A: 0.51 at 3000 cm^{-1}; B: 0.58 at 3275 cm^{-1}; C: 0.51 at 3550°C). Baseline-corrected intensities of the peaks close to 4500 cm^{-1} are almost identical for all three samples indicating similar amounts of hydroxyl groups. The exact position of the peaks in the near-infrared depend on the heat treatment of the samples: The high-frequency peak shifted from 4590 cm^{-1} (A) to 4580 cm^{-1} (B) and 4540 cm^{-1} (C). The peak at lower frequency had an approximate identical position for (B) and (C), but is shifted to 3990 cm^{-1} for (C).

second hydrogen feldspar was prepared from an adularia (H-feldspar(ad)). The degree of Al/Si order is slightly higher in the adularia than in the sanidine and is not changed by the ion exchange reactions. A hydrogen feldspar with a higher degree of Al/Si order than that obtained from the adularia would be likely, but attempts to synthesize such a hydrogen feldspar from microcline failed (Deubener et al., 1991). After the same treatment as used for the sanidine, the degree of H/Na exchange was smaller in the H-feldspar(ad) (average water content: 2.85 ± 0.11 wt.%).

A direct comparison of the IR spectra of the H-feldspar(ad) and the H-feldspar(san) was not possible
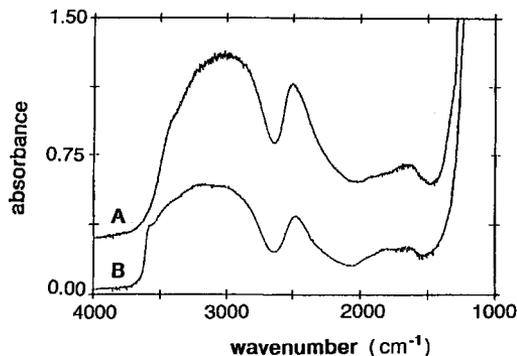

FIG. 5. IR absorption spectra of crystal plates of a H-feldspar prepared from adularia. Spectra were recorded with a partially polarized beam in an orientation giving maximum absorbance of the OH-peaks. Thickness of samples: c. 50 μm. A: sample after H/Na exchange. B: sample heated in steam for 5 hours at 500°C.

because the orientation of the H-feldspar(ad) crystals could not be determined under the microscope. However, the spectra obtained using a partially polarized beam oriented to give maximum absorbance are very similar for both H-feldspars (see Figs. 1 and 5). Also the same shift of the maximum towards higher wavenumbers by heating was observed. Furthermore, the absorbance of the maxima at 3000 and 2485 cm^{-1} in spectra obtained by polarized radiation showed a dependence on orientation comparable to that of the H-feldspar(san). These results suggests that the effect of Al/Si order on the proton positions in the feldspar structure can not be large.

Na/H re-exchange. Partial re-exchange of Na for hydrogen was performed with steam-treated material of H-feldspar(san) and of H-feldspar(ad). After heating samples for 2 days at 320°C in molten $NaNO_3$ the average water content of the H-feldspar(san) decreases to 1.84 ± 0.10 wt.% and that of the H-feldspar(ad) to 1.07 ± 0.08 wt.%. The hydrogen could not be completely exchanged by sodium even after two additional 3 days treatment under the same conditions. OH absorption bands were still present in the IR spectra (Fig. 6). A distinct peak at 3565 cm^{-1} is visible in the spectra of the partially re-exchanged H-feldspars. In the case of the H-feldspar(san) this peak is independent of the orientation of polarized radiation, but for the H-feldspar(ad) this peak shows a noticeable pleochroism. It can not be concluded from the spectra whether the peak at 3565 cm^{-1} is produced by protons in an amorphous environment, as identified by the heating experiments, or a new type of environment for protons is formed by the incorporation of Na. Also,
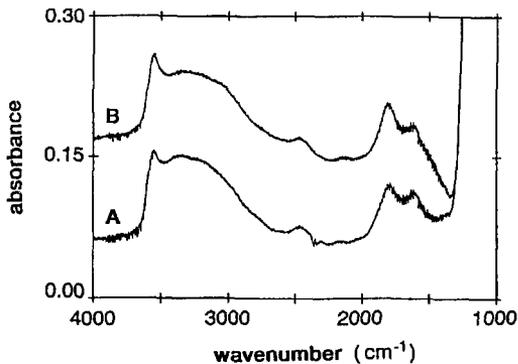
FIG. 6. Polarized IR absorption spectra of H-feld-spar(san) obtained after partial re-exchange with molten NaNO$_3$ at 320°C for a total time of 8 days. Thickness of sample: c. 50 μm. A: E ∥ a. B: E ⊥ a.

the possiblity that this peak is due to small amounts of a hydrous contaminating phase produced by the exchange reaction cannot be excludet. The partially Na/H re-exchanged feldspars are located intermediate between the H-feldspars and the alkali feldspars in plots b vs. c parameter (Deubener, 1989). This implies that the majority of the protons are in the feldspathic structure.

It is obvious, by considering the spectra of the partially Na/H re-exchanged H-feldspar(san) (Fig. 6) and those of steam-treated H-feldspar(san) (Fig. 2), that the protons in a feldspathic environment are preferentially exchanged relative to those in an amorphous environment.

Discussion

Characterization of hydrogen in the feldspar structure. The pleochroic scheme had shown two types of hydrogen in the H-feldspar(san). From the heating experiments it is concluded that these types belong to different phases, an amorphous phase and a feldspathic phase. The IR-spectra of the feldspathic phase can be obtained qualitatively by calculating difference spectra (spectra using E ∥ a minus spectra using E ⊥ a). Another possibility for the elimination of contributions of the amorphous phase is to subtract from the measured spectrum a spectrum like that of hydrous glasses. The spectra obtained by both calculation methods are similar. Because isotropic contributions of the feldspathic phase are eliminated in difference spectra, and because the shape of the spectrum due to the amorphous phase is not known exactly, both methods do not reproduce exactly the spectral features of the feldspathic phase exactly.

In the difference spectrum the high frequency OH band shows a maximum at 3000 cm^{-1} and shoulders

at 2800 and 3200 cm^{-1} for the H-feldspar(san), as obtained after H/Na exchange (Fig. 3a). The absorbance at 3200 cm^{-1} is increased relative to that at 3000 cm^{-1} after steam-treatment at 500°C (Fig. 3b). Consequently, the shift of the maximum of the main OH absorption band displayed in Fig. 2 is not produced only by the increase of the portion of the amorphous phase, but also by changes in the distribution of the hydrogen on the various sites in the feldspathic structure.

The measured spectra and the difference spectra could not be decomposed in a finite number (5 to 6) of mixed gaussians and lorentzians. Probably, a large number of different sites exists for hydrogen in the cation cavity of the feldspar structure.

The energy of the low-frequency band is smaller than the energies commonly observed for OH stretching bands in silicate minerals. One explanation for the low frequency of this band is a strong hydrogen bonding to adjacent oxygen atoms. This can result from the collapsing of the feldspar framework due to the lack of large cations. The correlation between the wavenumber of OH stretching vibration and the O-H···O distance (Nakamoto et al., 1955; Schwarzmann, 1962) gives, for a wavenumber of 2485 cm^{-1}, an oxygen-oxygen distance of 2.55 Å. But the geometry of the hydrogen bonding is not necessarily linear, as suggested by the notation O−H···O. Cecarelli et al. (1981) have shown that hydrogen bonding to two adjacent oxygens (bifurcated hydrogen) is very common in organic materials. For such a geometry the oxygen–oxygen distance must not be as short as in the linear O-H···O to give the same wavenumber. Therefore, experimentally determined oxygen−oxygen distances give no direct information as to the possible sites of the protons in the feldspar structure.

Another possible explanation for the low-frequency band is that the hydrogen is bound to a bridging oxygen. In this case, the force constant of the O−H bond is considerably smaller than that for a hydrogen connected to a bridging oxygen. Consequently the OH absorption will be at a lower frequency. In the intact feldspar structure all oxygens form bridges between tetrahedra. The formal charge of oxygen connected to Al^{3+} is −1/4 and hydrogen can only be weakly bound if the framework remains intact. A position of the hydrogen close to the Al^{3+} is indicated by small contact times in NMR cross polarization from ^{1}H to ^{27}Al (Mortuza et al., 1993).

A likely candidate for binding a proton is the oxygen O$_A$(2). This oxygen has the shortest distance to the alkali cation in NaAlSi$_3$O$_8$ and KAlSi$_3$O$_8$ and, therefore, the largest electron excess after removal of the alkali cation. In the monoclinic structure of the H-feldspar the O$_A$(2)-H dipole would be oriented approximately in the direction of the a-axis. This is

in agreement with the observation of maximum absorbances in the (010) plane of the H-feldspar(san), if the E-vector vibrates approximately parallel to the a-axis.

Considering the irregularity of the cation cavity in the feldspar structure, it is surprising that all anisotropic components of the spectra show the most effective absorption of polarized radiation for the same orientation of the E-vector to the crystal. The orientation of the OH dipoles should be different for the various sites of hydrogen (with various OH bond strength) and a dependence of the pleochroism on the wavenumber would be expected. One might argue that hydrogen associated with cleavage fractures can be responsible for the pleochroism. However, the stoichiometric composition of the H-feldspar and the X-ray measurements clearly show that most of the hydrogen must be within the crystals and not at fractures. At the moment we can not explain why the complex high-frequency OH band shows no dependence of the pleochroism on wavenumber, but the phenomenon is not uncommon for feldspars. Beran (1987) found the same for the complex OH absorption band of a plagioclase.

The same pleochroic scheme at 3000 cm^{-1} and at 2485 cm^{-1} and the low frequency of the second OH band can be explained by considering the results of the near-infrared spectroscopy in the following way. Two principally different types of hydrogen are present in the feldspar structure. One type is bound loosely to a bridging oxygen and a three-coordinated oxygen is formed. This type is responsible for the absorption band at 2500 cm^{-1} and gives no contribution to the NIR band at 4500 cm^{-1}. The second type of hydrogen which is predominant, consists of free TOH groups. These are formed by breaking $T-O-T$ bridges, three-coordinated T atoms (probably Al) must be created by this reaction if the framework is not rearranged. These TOH groups produce the high-frequency band in the middle infrared and, together with the hydrogen in the amorphous structure, the NIR band at 4500 cm^{-1}. Probably, there is a strong interaction of the three-coordinated T atom and the hydroxyl group and both types of hydrogen may easily transform into each other. Therefore, hydrogen connected to the same type of oxygen (e.g. $O_a(2)$) can be either at a bridging oxygen or at a nonbridging oxygen. The direction of the OH vector only will be slightly changed if the distance between the O atom and one of the T atoms is increased.

Amorphization of the hydrogen feldspar. Even in the H-feldspar without heat-treatment there was a noticeable amount of an amorphous phase. Heating-up of the H-feldspar increases the proportion of the amorphous phase. The framework of the crystal becomes locally more and more destroyed before

dehydration starts significantly (see Fig. 2). This is in accordance with observations in powder X ray diffraction. The steam-treated material show a broadening and a loss of intensity of the diffraction pattern.

Due to the difficulties in separating quantitatively the effects of the amorphous and the feldspathic phases in the spectra, and to the unknown pleochroism of the OH absorption bands in planes perpendicular to (010), it is not possible to quantify the proportions of protons in an amorphous and in a feldspathic phase. However, the amorphization can be monitored qualitatively by the absorbance ratio A(3500 cm^{-1})/A(2485 cm^{-1}) of spectra with the E-vector predominantly oriented parallel to the a-axis. The feldspathic contribution alone is small at 3500 cm^{-1}, and the peak at 2485 cm^{-1} is not influenced by the amorphous contribution. The ratio A(3500 cm^{-1})/A(2485 cm^{-1}) of the spectra plotted in Fig. 2 increases from 0.54 (after H/Na exchange) to 1.67 (steam-treated at 500°C) and 13.7 (heated at 550°C).

Considering these intensity ratios, the stoichiometric composition of the H-feldspar and the sharpness of the X-ray diffraction patterns, it is concluded that feldspathic structure formed the major part of the crystals in the H-feldspars before heat-treatment.

Comparison to OH defects in sanidine. Sanidine from Volkesfeld contains traces of structurally bound hydrogen. The concentration is approximately 1 % of that of the H-feldspar. As shown by Hofmeister and Rossmann (1985) and Beran (1987) the OH absorption spectra in the middle-infrared are composed mainly of two bands with different pleochroic schemes. Maximum absorbance of polarized radiation was observed at 3400 cm^{-1} for E ∥ a and at 3050 cm^{-1} for E ∥ b. Weak bands at 2500 cm^{-1} were assigned to lattice modes by Hofmeister and Rossmann (1985). Unfortunately IR spectra of sanidine shown in literature were cut at 2500 cm^{-1}. Our own findings show that a band at c. 2470 cm^{-1} exists with maximum absorbance of polarized radiation for the same orientation as for the band at 3050 cm^{-1}. Study of partially dehydrated sanidine indicates that the absorbances at 2470 cm^{-1} and at 3050 cm^{-1} are correlated. This implies that the band at 2470 cm^{-1} of sanidine is also due to hydrogen, as found for H-feldspar.

Near-infrared spectra of sanidine are contradictory. Hofmeister and Rossman (1985) observed a peak at about 4500 cm^{-1} and concluded that hydrogen is present mainly as OH groups. In contrast, Beran (1987) reported a weak peak at 5200 cm^{-1} but no peak at 4500 cm^{-1}. He proposed a model of water allocation in sanidine as H_2O molecules. Our own findings show that the peak at 4500 cm^{-1} is not well resolved in all sanidine crystals of Volkesfeld and

this may explain the results of Beran (1987). We found no evidence for the presence of molecular water.

In conclusion the spectral features of the sanidine show similarities with those of the hydrogen feldspars. Protons attached to bridging oxygen seemed to be present in the sanidine in addition to protons attached to non-bridging oxygen. Considering the peak areas at 3000 and at 2500 cm^{-1} and the wavenumber-dependence of the absorption coefficient (Paterson, 1982), protons attached to non-bridging oxygen predominate in both hydrogen feldspar and sanidine.

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