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A Model of Water Allocation in Alkali Feldspar, Derived from Infrared-Spectroscopic Investigations

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Abstract. Polarized *infrared* (IR) spectra of sanidine crystals from Volkesfeld, Eifel show the existence of two broad pleochroic absorption bands at 3,400 and 3,050 cm^{-1}. Because overtones near 5,150 cm^{-1} were observed, the former bands are assigned to OH stretching frequencies of H_2O molecules. On the basis of the pleochroic scheme of the bands it is proposed that H_2O molecules occur as structural constituents entering the *M* site of the sanidine structure; the plane of the H_2O molecules lies parallel to the symmetry plane.

Introduction

The presence of small amounts of water in nominally anhydrous silicate minerals has considerable effects on their mechanical properties, and on the rate of diffusion controlled processes. Griggs (1967) first mentioned that feldspars are weaker after exposure to water (Tullis 1983; Gandais and Willaime 1984). It is further known that even trace amounts of water greatly affect the Al/Si ordering and disordering rate of alkali feldspar and greatly enhance oxygen diffusion (Yund 1983, 1984). Also color is induced by incorporation of water into the structure of feldspar (Hofmeister and Rossman 1983, 1985a, b). Reported feldspar analyses often include H_2O^+ contents from a few hundredths up to several tenths weight percent (Deer et al. 1963; Martin and Donnay 1972). At one extreme, as noted by Smith (1974b), many of these H_2O^+ values can be dismissed as a result of impurities; at the other extreme H_2O^+ values can be explained either by H_2O molecules or by $(H_3O)^+$ ions entering the *M* site of the feldspar structure or by OH groups replacing O atoms.

Single crystal *infrared* (IR) absorption spectra provide an experimental approach for ascertaining the presence of structural H_2O and OH (Beran 1974, 1976; Beran and Putnis 1983; Aines and Rossman 1984). Quantitative water determinations made by sensitive electrolytic techniques, together with IR absorption spectra, have established the presence of small and variable amounts of water in the structure of various feldspars. Wilkins and Sabine (1973) determined the H_2O^+ content of an adularia with an absorption maximum at c. 3,250 cm^{-1} as 0.08 weight percent. Hydroxyl appears to be a characteristic trace constituent of this feldspar. Lehmann (1984) reported OH contents of alkali feldspars varying from 500–16,000 $OH/10^6$ Al and described a broad absorption band of adularia near 3,300 cm^{-1}. The author stated that either water molecules are present in the structure or randomly oriented OH groups with strong hydrogen bonding between them. Hofmeister and Rossman (1985a, b) reported water contents in alkali feldspars varying from a few ppm up to 0.1 weight percent. Mostly broad absorption bands between 3,630 and 3,050 cm^{-1} show a variable amount of anisotropy and are due to fluid inclusion water and to structural water. NIR spectra of microclines show absorption bands at c. 5,250 cm^{-1}, attributed to the combination vibration of H_2O molecules (Hofmeister and Rossman 1985a). Sanidines which become smoky upon irradiation possess broad absorptions near 3,400 cm^{-1} and weak OH overtones at 4,550 cm^{-1} (Hofmeister and Rossman 1985b).

The aim of this paper is to present a polarized IR study of a gem-quality alkali feldspar in the region of the OH stretching frequency and to give a structural interpretation of the experimental results.

Sample Description and Experimental

The alkali feldspar material used for this work was found at Volkesfeld, Laacher Vulkangebiet, Eifel. It consists of large, transparent, smoky colored crystals of sanidine. The locality of the sample was described by Bank (1967) and Frechen (1976). Only microscopically inclusion-free, optically clear, and homogeneous parts of the crystals were used for the preparation of oriented polished plane-parallel plates. Polarized IR spectroscopic measurements were performed on these crystal plates with a computer controlled IR spectrophotometer Perkin-Elmer 580 B, Interdata 6/16, and a gold-plated silver bromide polarizer. NIR measurements were performed with an UV/VIS/NIR spectrophotometer Perkin-Elmer 330. Analytical water determination was performed by means of an elemental analyzer Perkin-Elmer 240. Data on the chemical composition of the Volkesfeld sanidines (Or content 86 mol.%) were obtained from microprobe analysis by Hofmeister and Rossman (1984) and by Weitz (1972) from XRF analysis (Table 1). EPR spectroscopic data on Fe^{3+} in these sanidines are reported by Hofmeister and Rossman (1984) as well as Petrov and Hafner (1985). Speit and Lehmann (1976), Hofmeister and Rossman (1985b) investigated smoky color in gem-quality sanidine from Volkesfeld. Laves and Hafner (1962) reported polarized IR absorptions between 2,800 and 1,300 cm^{-1} of sanidine from the Volkesfeld area.

The quantitative water determination of the sanidine sample of this study yielded a value of 0.036 (9) weight

Table 1. Data on the sanidine from Volkesfeld

Locality of sample: Volkesfeld, Riedener Kessel,
Laacher Vulkangebiet, Eifel, West-Germany (Bank 1967)

Chemical composition in wt.%:
SiO_2 – 63.14, Al_2O_3 – 18.48, FeO – 0.15,
BaO – 0.79, Na_2O – 1.59, K_2O – 14.60;
Or content 86 mol.% (Hofmeister and Rossman 1984).
Total Fe as Fe^{3+} (Hofmeister and Rossman 1984; Petrov and Hafner 1985).
Ca – 0.02, Sr – 0.15, Rb – 0.02 (Weitz 1972).

Water content:
0.004 (1) wt.% H, corresponding H_2O^+ – 0.036 (9) wt.% (analysts: S. Frenczko and J. Zak).
4,000 OH/10^6 Al, corresponding H_2O^+ – 0.013 wt.% (Lehmann 1984)
H_2O^+ – 0.017 wt.% (Hofmeister and Rossman 1985b)

Lattice constants:
$a = 8.549$ (5), b 13.028 (5), $c = 7.188$ (5) Å,
$\beta = 116.02$ (5)° (Weitz 1972)
(Space group $C\ 2/m$)

percent H_2O. Lehmann (1984) determined the water content of a Volkesfeld sanidine as 0.013 weight percent. The water content determined by Hofmeister and Rossman (1985b) amounts to 0.017 weight percent H_2O (Table 1). Speit and Lehmann (1976) measured the IR absorption spectrum between 4,000 and 2,000 cm^{-1} and reported a rather broad band near 3,300 cm^{-1}. Polarized absorption spectra of Volkesfeld sanidine between 4,000 and 2,500 cm^{-1} are reported by Hofmeister and Rossman (1985b). Based on weak OH overtones detected at 4,550 cm^{-1} and the absence of H_2O combination bands at 5,260 cm^{-1} in a crystal 1 cm thick the authors concluded that molecular H_2O comprises less than 15 percent of total "water", the remainder being Si–OH or Al–OH.

Results

The IR spectrum of a (010) cleavage plate of the Volkesfeld sanidine shows a broad absorption band centered at 3,400 cm^{-1} with a diffuse "shoulder" on the lower wavelength side. The IR spectra of a (001) cleavage plate and of a plate cut perpendicular to the **a**-axis show that the maximum of the "shoulder" is centered at 3,050 cm^{-1}. Using polarized IR radiation strong pleochroism of these two broad bands was observed (Fig. 1). The results of the orientation dependent absorption of the bands at 3,400 and 3,050 cm^{-1} are summarized in Figure 2 in crystal plates perpendicular to the **a**-axis and parallel to (001) and (010) respectively. The spectra were recorded after rotation of the polarizer by steps of 10°. Plotted are radiants of linear extinction coefficients in cm^{-1} measured over background at band maximum. Assuming an H_2O^+ content of 0.036 weight percent (Table 1) the linear molar extinction coefficient ε for the 3,400 cm^{-1} band recorded on a (010) plate with non-polarized convergent IR radiation amounts to $32\ l \cdot Mol^{-1} \cdot cm^{-1}$. Validity of Beer's law was proved by plotting log (I_0/I) versus the thickness of (010) cleavage plates from 0.01 to 0.1 cm. The extinction coefficient is comparable to that of glass.

NIR absorption spectra taken on a microscopically inclusion-free (010) cleavage plate show the combination band of molecular H_2O centered at c. 5,150 cm^{-1} and a very weak combination band of (Si, Al)-OH groups at 4,550 cm^{-1} (Fig. 3). This proves that in the sanidine crystals of this study the main part of water is present as molecular H_2O, although the weak band at 4,550 cm^{-1} indicates the presence of OH groups. Hofmeister and Rossman (1985b) concluded from overtone measurements and from spectra taken at liquid nitrogen temperatures that OH groups are the main constituents of total water in sanidine from Volkesfeld.

Figure 2 shows that the absorption band at 3,400 cm^{-1} has maximum absorption when the dielectric vector **E** of the polarized radiation vibrates parallel to [100] in the section (001) and parallel to **c*** in the section perpendicular to [100]. In the (010) plate, this band shows a relatively weak pleochroism. The angle between the direction of maximum absorption and the direction of vibration of n_α is +10°. The value for the extinction angle on (010) is +5°. In (010) the absorption band at 3,050 cm^{-1} shows a very weak pleochroism with maximum absorption when **E** vibrates perpendicular to the direction of maximum absorption of the band at 3,400 cm^{-1}, whereas in (001) and in

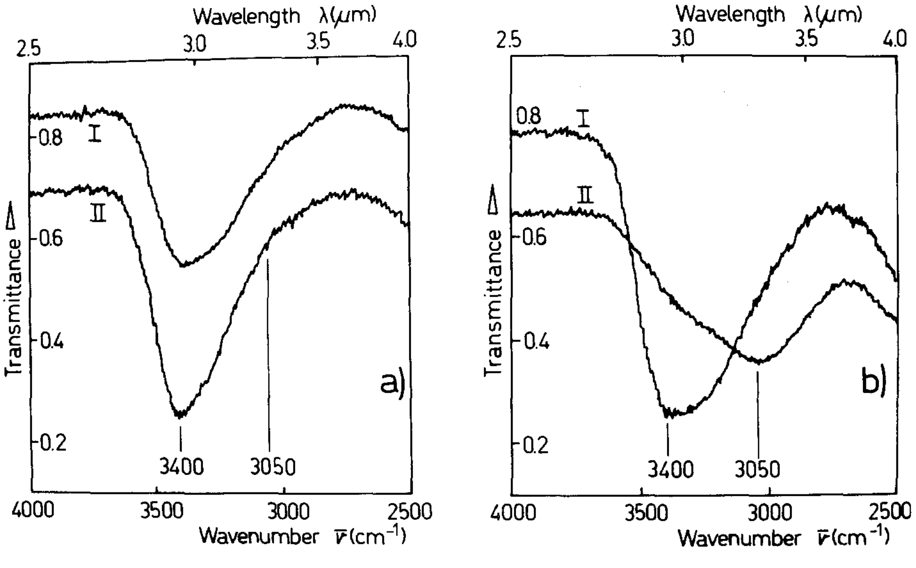

Fig. 1a, b. Polarized absorption spectra of sanidine in the range of 4,000–2,500 cm^{-1}; ordinate expanded computer replot from accumulated scans. Sample thickness 0.05 cm. (**a**) Plate parallel to (010); absorption curve I – dielectric vector **E** of the polarized radiation vibrates perpendicular to the direction of vibration of n_α; II – **E** vibrates parallel to n_α. (**b**) Plate perpendicular to the **a**-axis; I – **E** vibrates perpendicular to the **b**-axis; II – **E** vibrates parallel to the **b**-axis

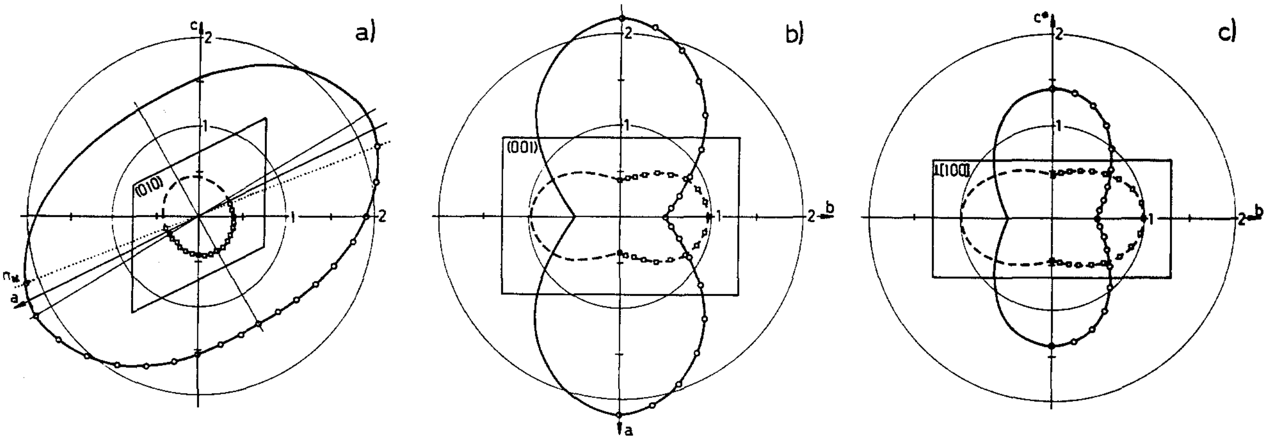

Fig. 2a–c. Absorption figures of the absorption bands at 3,400 cm^{-1} (continuous line, symbol: circle) and 3,050 cm^{-1} (dashed line, symbol: square); plotted are radiants of linear extinction coefficients in cm^{-1}: log $(I_0/I)/t$ (t – thickness of the crystal plate in cm). (a) In (010). (b) In (001). (c) In a plate perpendicular to the **a**-axis

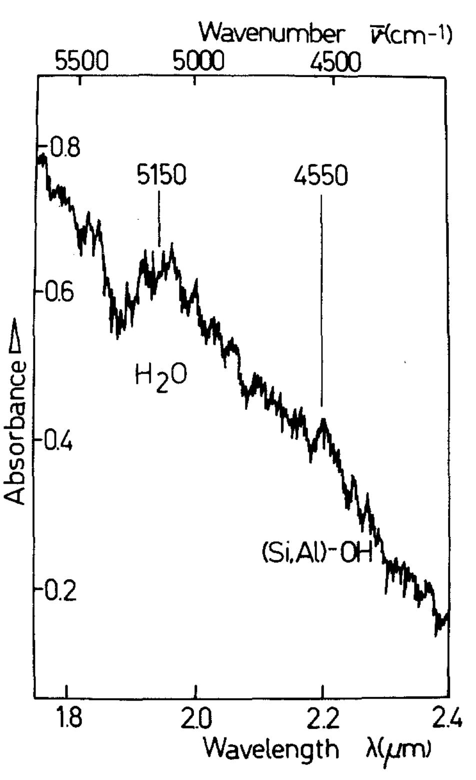

Fig. 3. Near-infrared absorption spectrum of an inclusion-free sanidine (010) cleavage plate in the range of 5,700–4,200 cm^{-1}. Sample thickness 0.45 cm. Shown are absorption features due to molecular H_2O at c. 5,150 cm^{-1} and a very weak band centered at 4,550 cm^{-1} due to (Si, Al)-OH groups

the section perpendicular to [100] a strong pleochroism occurs with maximum absorption when **E** vibrates parallel to [010].

Attempts were made to substitute H by D in order to further confirm the presence of OH stretching vibrations. However, deuteration experiments at 350° C for times up to several days led to loss of clarity due to incipient alteration. Upon heating in air to 700° C for 3 days, in (010) crystal plates of a few mm in size the "shoulder" at 3,050 cm^{-1} became a little more intense. Further heating to 900° C for 4 days reduced the intensities of both bands, at 3,400 and 3,050 cm^{-1}, to approximately one half of their original value. Heating temperatures of 1,050° C for 3 days caused the two bands to disappear.

Discussion

The pleochroic scheme of the absorption bands cannot be explained by different density of submicroscopic fluid inclusion water. The conclusion regarding the origin of the pleochroic bands, which were measured on three oriented crystal plates, must be that H_2O is structural. According to geometrical considerations, a plausible site for the H_2O is the M site. Hence, a minor substitution of the M site by H_2O molecules seems to be the most likely interpretation. Charge balance could occur by substitution of Ca^{2+}, Sr^{2+}, Ba^{2+} for K^+ and Na^+ or by replacing Al^{3+} by Si^{4+}. It is relevant, therefore, by considering the sanidine sturcture and the pleochroic scheme found here, to propose a model for the orientation of the H_2O molecules.

The feldspar minerals are alumosilicates with general formula MT_4O_8 and a three-dimensional framework of corner-sharing AlO_4 and SiO_4 tetrahedra, as first recognized by Machatschki (1928). M cations occupy large, irregular cavities in the tetrahedral framework. The simplest feldspar structure – that of $C\,2/m$ sanidine, $KAlSi_3O_8$ – was determined by Taylor (1933). The structural parameters used in the present work refer to the structure refinement of a sanidine from the Volkesfeld locality by Weitz (1972) (Table 1; cf. also Kroll 1984). For a detailed description of the sanidine structure the reader is referred to Smith (1974a) and Ribbe (1983, 1984).

Attributing the strong absorption band at 3,400 cm^{-1} to the asymmetric stretching frequency (ν_3) and the weak band at 3,050 cm^{-1} to the symmetric stretching frequency (ν_1) of an H_2O molecule, the extremely strong pleochroism of the band at 3,400 cm^{-1} in (001) and in the section perpendicular to [100] indicates a strong orientation of the plane of the H_2O molecules parallel to (010). To facilitate the discussion, Figure 4a presents the possible orientations of H_2O in the (010) plane (H_2O-type A). The angle between the H – H-axis of the "intermediate" H_2O molecule which is drawn with full lines and circles and the **a**-axis amounts to + 5°. The "extreme" orientation of the dashed line and dotted line H_2O molecules (Fig. 4a) is also consistent with

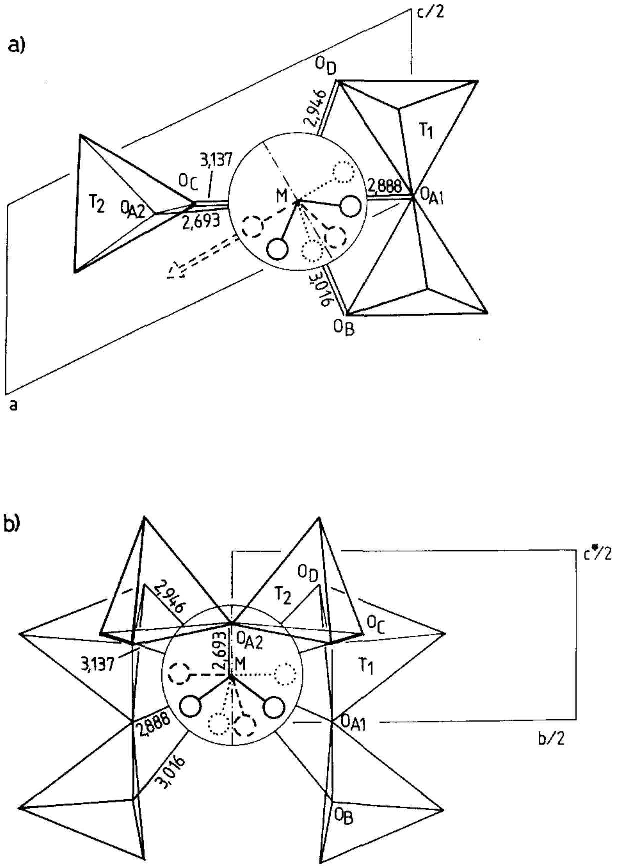

Fig. 4a, b. Schematic diagram of possible orientations of H_2O molecules entering the *M* site of the sanidine structure. The bond lengths are in Å. Possible H-positions are drawn as small circles. Large thin lined circles represent the size of the K^+ ions in *M* site. (**a**) Projection parallel to the **b**-axis. The orientation of the H_2O-type A molecules lying in the symmetry plane results from the pleochroism of the band at 3,400 cm^{-1}; full line H_2O-type A – "intermediate" orientation, dashed line and dotted line H_2O – "extreme" orientation; dashed arrow – direction of maximum absorption as evident from Figure 2a; dash-dotted line – plane of the H_2O-type B molecules. (**b**) Projection parallel to the **a**-axis. The orientation of the H_2O-type B molecules lying perpendicular to the symmetry plane results from the pleochroism of the band at 3,050 cm^{-1}; full line H_2O-type B – "intermediate" orientation, dashed line and dotted line H_2O – "extreme" orientation neglecting the symmetry plane; dash dotted line – plane of the H_2O-type A molecules (symmetry plane)

the weak pleochroism of the absorption band at 3,400 cm^{-1} in (010). The relatively high wavenumber of the asymmetric stretching frequency is indicative of weak hydrogen bonds (Hamilton and Ibers 1968). Because of the short distance $M-O_{A2}$ (2.693 Å) there is no indication for hydrogen bonding of H_2O molecules with O_{A2} atoms (Fig. 4a).

In response to the great difference in the wavenumbers of the two bands in the fundamental region and in response to the pleochroic scheme of the band at 3,050 cm^{-1}, a model with two types of H_2O molecules has to be discussed. Attributing the broad absorption band centered at 3,400 cm^{-1} as well as the broad band centered at 3,050 cm^{-1} to $\nu_3+\nu_1$ frequencies, the pleochroism of the band at 3,050 cm^{-1} in (001) and in the section perpendicular to [100] (Fig. 2b and c) is indicative of a second type of H_2O molecules (H_2O-type B) lying perpendicular to the plane of the H_2O-type A molecules (Fig. 4b). The weak pleochroism of this band in (010) is consistent with a preferred orientation of the H_2O-type B plane perpendicular to the H – H-axis of the "intermediate" H_2O-type A. The low wavenumber (3,050 cm^{-1}) suggests a shifting of the H_2O-type B molecules within this plane to form strong hydrogen bonds with the O_B atoms (Fig. 4b).

Hofmeister and Rossman (1985b) stated that most of the water present in their sanidine sample from the Volkesfeld area is bound as hydroxyl. Assuming a model of OH incorporation the two bands at 3,400 and 3,050 cm^{-1} must be due to two different types of OH groups. However, the orientation of the OH groups must be consistent with the pleochroic scheme of the absorption bands presented in this study.

The changes of the optic axial angles of alkali feldspars may be explained by Al/Si order – disorder transformations (Stewart and Ribbe 1983). As stated by Bertelmann et al. (1985) the diffusion of Al/Si in sanidines of the Eifel is extraordinarily fast. The unusual annealing behaviour of Volkesfeld sanidine with regard to the time rate of the changes of the optic angles (Zeipert and Wondratschek 1981; Su et al. 1984; Bertelmann et al. 1985) might be due to the content of structural water.

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