

Water Content of Some Nominally Anhydrous Silicates

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Abstract

Quantitative water determinations made by a sensitive electrolytic technique, together with infrared absorption spectra taken through thick single-crystal plates, have established the presence of small and variable amounts of OH ions in the structures of various nominally anhydrous silicate minerals. The OH spectra, consisting chiefly of sharp bands in the region from 3000 to 3700 cm^{-1} , were verified by deuterium exchange. The OH contents found (as wt percent H_2O) are: kyanite, 0.009 to 0.062 range in 19 specimens; andalusite, 0.048; sillimanite, present; grossular, 0.056 to 2.29 in 4 specimens; andradite, 0.148 to 0.67 in 4 specimens; pyrope, 0.009; diopside, 0.020; rhodonite, 0.008; andesine, 0.55; adularia, 0.080; olivine, 0.008. The structural role of the OH is not entirely certain, but an examination of various possibilities indicates that isolated OH ions occupy oxygen sites associated with vacancies or charge imbalance in cation sites.

Introduction

The quantitative analytical determination of water varies from a relatively easy to a very difficult task, depending on the precision desired and a variety of other circumstances. M. H. Hey (1954) has commented that doubts concerning the true amount and the function of water in a mineral analysis are probably the commonest cause of uncertainty in calculating the unit cell contents. The term water is here used in the sense that the end result of the analysis is reported as H_2O , without reference to the manner in which the hydrogen is contained in the crystal structure. Among the most difficult water analyses are those where the water is retained to high temperatures and both the water content and the amount of sample available for analysis are very small. The practical limits conventionally obtaining in the past for mineral analyses can perhaps be stated as a few tenths of a per cent H_2O in samples ranging down to a few hundred milligrams in weight. Water contents of less than 1.0 wt percent generally have been reported as ignition loss. This matter becomes involved with weight changes attending redox processes and the volatilization of elements such as alkalis, boron and halogens. There is the further possibility that the water may derive from liquid inclusions or from traces of hydrous al-

teration products that go unnoticed in the relatively large samples generally employed.

In the present study we have investigated the water contents of a variety of nominally anhydrous silicates. Infrared spectroscopy on single-crystal plates was used to establish the presence of water in these minerals and to elucidate the manner in which it is incorporated in their crystal structures. The amount of water present was then quantitatively determined on very small samples, handpicked under a microscope, by a newly developed electrolytic technique. By using these methods most of the uncertainties inherent in conventional methods of analysis were eliminated.

Methods of Analysis

Infrared Spectroscopy. This method provides an extremely sensitive and convenient means for detecting trace amounts of water, and has the added advantage of being a non-destructive technique. Admixed materials also may be detected and identified from their spectra. The presence of a few parts per million water in a mineral can produce detectable OH stretching bands in the absorption spectrum, provided that this spectrum is obtained from a plate several millimeters thick. Thick single-crystal plates of silicates are opaque to infrared radiation below 2500–2000 wavenumbers, the sharp absorption edge observed in this region being due to absorption at frequencies corresponding to the first overtones of the silicate stretching vibrations. However, the region of hydroxyl stretching vibrations is usually between 3750 and 3000 wavenumbers where silicates

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are otherwise rather transparent. Even so, infrared spectroscopy is in general not suited for the quantitative determination of water because for single-crystal plates, which are necessary for the study of water contents below about 0.1 percent, the amount of the absorption is dependent not only on plate thickness but also on bond orientation and other structural factors. Plates of different orientation and minerals of different structure would have to be separately calibrated. Further, compositional variation within a single mineral species may complicate both the absorption intensities and frequencies. On the other hand, the very sensitivity to structural environment that limits the use of infrared spectroscopy for quantitative analytical work makes it a powerful tool for crystallographic studies.

We have used this technique to analyze cleaved or sawn single-crystal plates from 1 to 10 millimeters thick. Spectra were taken using Perkin-Elmer Model 337 and Cary Model 90 spectrometers. No attempt was made to calibrate the spectra accurately but the quoted frequencies should be correct to $\pm 4 \text{ cm}^{-1}$. Absorption bands in the $3000\text{--}3750 \text{ cm}^{-1}$ region were observed in the spectra of all of the minerals examined. Although these bands fall within the region of OH stretching fundamentals, the possibility existed with the thick specimens used that they were due in part to weak overtone and combination bands of lower frequency lattice fundamentals. It was therefore necessary to confirm the presence of OH bands by deuterium substitution. This was attempted for all specimens under uniform conditions of 750°C and about 100 bars D_2O pressure in a 25 cc cold seal stainless steel bomb. The heating periods ranged up to five days. When this treatment shifted the previously observed bands to lower frequencies by a factor of about 1.36, the theoretical value of OH-OD exchange, the presence of OH stretching vibrations was confirmed.

Electrolytic Water Determination. This method is based on the electrolysis of the water afforded by heating of a weighed sample, the water content being quantitatively measured by the current involved. In practice, the sample is heated at a uniform rate in a stream of dry nitrogen, which sweeps the water into an electrolytic cell. This is a glass tube containing a pair of helically-wound platinum electrodes embedded in a thin film of P_2O_5 . Water vapor entering the cell is quantitatively absorbed by the P_2O_5 , rendering the cell conductive, and is immediately electrolyzed by a DC voltage constantly applied

across the electrodes. The cell is regenerative, and the current provides a continuous and linear measurement of the rate at which water enters the cell. The instrument provides a continuous dehydration curve as a function of temperature and allows the amount of water associated with each of separate dehydration events to be accurately measured. This feature is especially important when trace amounts of essential (OH) in the sample are present together with water from other sources and with different temperature dependency. The total amount of water liberated by the sample during each of the several dehydration events that may be involved is determined by integrating the current either by measurement of the area under the chart peaks, or independently of the chart, by a voltage to frequency converter and an electromechanical counter calibrated directly in micrograms of water.

We have modified a commercial instrument of this kind, a Type 26-321A Solids Moisture Analyzer available from the Instrument Products Division, DuPont Company, Wilmington, Delaware. The principal changes involved: (1) substituting a Pt-wound furnace capable of reaching 1500° for the original sample oven; (2) the addition of temperature controllers to limit the maximum furnace temperature and to provide control over the rate of heating; and (3) the addition of a Moseley Model 7100B strip chart recorder for continuous display of the water yield and sample temperature. The electronic circuitry was modified by the insertion of precision resistors in series with the cell, to monitor the current accurately. The data readout systems are provided with range selector switches so that the sensitivity can be adjusted to the requirements of the sample being analyzed. A schematic diagram of the equipment is shown in Figure 1.

The water content of commercial dry nitrogen

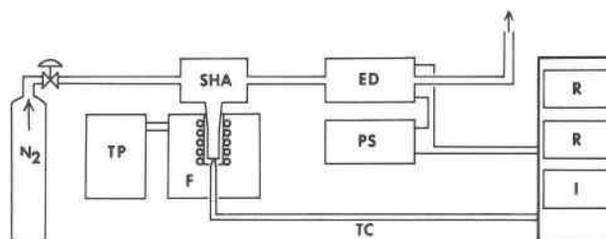


FIG. 1. Block diagram of water determination apparatus. Key: TP temperature programmer; SHA sample holder assembly; F furnace; ED electrolytic cell; PS power supply; TC thermocouple; R recorder; I integrator.

varies from tank to tank but ranges below about 7 ppm. The water could be trapped out, but we have measured it as background to subtract from the sample measurement. The rate of gas flow is kept constant during a run, and generally is in the range of 40 to 80 cc/min. A Matheson Model 662-BBS gas flow meter was employed on the exit port from the electrolysis cell to monitor the flow. The heating rate employed in the furnace usually has been 15°C/min. The rates of gas flow and of heating, and the total water content of the sample, all interact with the counting limits of the electrolysis cell. Control can be effected through the sample weight to the extent that precision is not reduced below some desired limit. In addition to H₂O, the cell is responsive to HF and certain organic compounds.

The accuracy of the cell as employed here is 1 to 2 micrograms of water or 1 to 2 percent of the total water content, whichever is larger. The accuracy achieved in an analysis is a function of the sample weight and water content and of the shape of the dehydration curve. Optimum results are obtained when the water is lost sharply over a small range of temperature. The most important source of error is in the precise determination of background, especially with samples below the optimum weight for a given water content. Since it is desirable to employ the smallest possible sample, to facilitate selection of pure material, the minimum sample weight needed to attain a desired precision of measurement can be estimated from the sensitivity of the cell and a preliminary knowledge of the water content.

We have employed a Mettler Model M5 microbalance having an accuracy of ± 2 microgram. The sample, usually consisting of grains from 100 to 200 mesh in size, was weighed on metal foil, transferred to the sample holder, and the foil reweighed. The dehydration of larger grains may be sluggish.

In our work, the analyses were made on the same plates for which the infrared spectra were obtained. The runs were started at or near room temperature and all of the water discriminated as a function of temperature, including adsorbed moisture, liquid inclusions and essential (OH) in the minerals studied, was evaluated. The reported analyses refer specifically to the high temperature H₂O found associated with the infrared hydroxyl absorption spectra. Leadhillite, Pb₄(SO₄)(CO₃)(OH)₂, was used as a calibration standard. Quantitative measurements of the water content of this substance at sample

weights ranging from 26 mg to below 0.1 mg are given together with data on CuSO₄·5H₂O and descloizite in Table 1. Dehydration curves obtained on leadhillite are shown in Figure 2, and are representative of the data obtained on the silicates studied.

Mineral Descriptions

Earlier Work. Hydroxyl ion already has been found by infrared study in a number of nominally anhydrous minerals and synthetic compounds, but quantitative measurements of the water content are lacking. In quartz, studied by Brunner *et al* (1961), Kats (1962), Kats *et al* (1962), and others, some but not all of the infrared absorption bands observed in the 3400 cm⁻¹ regions have been proved to be due to OH by deuteration at 1000°C. Beran and Zemann (1969a,b) have reported OH in natural rutile, anatase, brookite and andalusite. The presence of OH also has been proven in various materials grown from fusion in an oxyhydrogen flame, including rutile (Sofer, 1961; von Hippel *et al*, 1962), spinel (Farrell *et al*, 1965) and barium titanate (Coufova, 1966). In all cases where sharp bands have been observed in the infrared spectrum, detailed studies

TABLE 1. Water Determinations on Leadhillite, CuSO₄·5H₂O, and Descloizite

Total sample	Weight in milligrams		% H ₂ O*
	Total sample	Measured water	
Leadhillite, Pb ₄ (SO ₄)(CO ₃) ₂ (OH) ₂ ; H ₂ O=1.670 % (calc.)			
26.16	0.439	1.68	
21.92	0.363	1.66	
14.33	0.241	1.68	
12.015	0.2025	1.685	
6.162	0.103	1.67	
3.82	0.063	1.65	
3.44	0.060	1.74	
2.292	0.0369	1.61	
0.626	0.0113	1.8	
0.338	0.0054	1.6	
0.089	0.00169	1.9	
CuSO ₄ ·5H ₂ O; H ₂ O=36.08 % (calc.)			
8.95	3.23	36.1	
6.88	2.46	35.8	
2.28	0.82	36.0	
Descloizite, Pb ₂ ZnCu(VO ₄) ₂ (OH) ₂ ; H ₂ O=2.23 % (calc.)			
12.15	2.82	2.32	
19.00	4.30	2.26	

* The errors of the determination arising from weighing, background determination and various other sources in the system are difficult to assess. They are estimated at $\pm 0.02-0.05$ for samples over a few milligrams in weight, at ± 0.2 for the 0.X mg samples and ± 0.4 for the 0.089 mg sample.

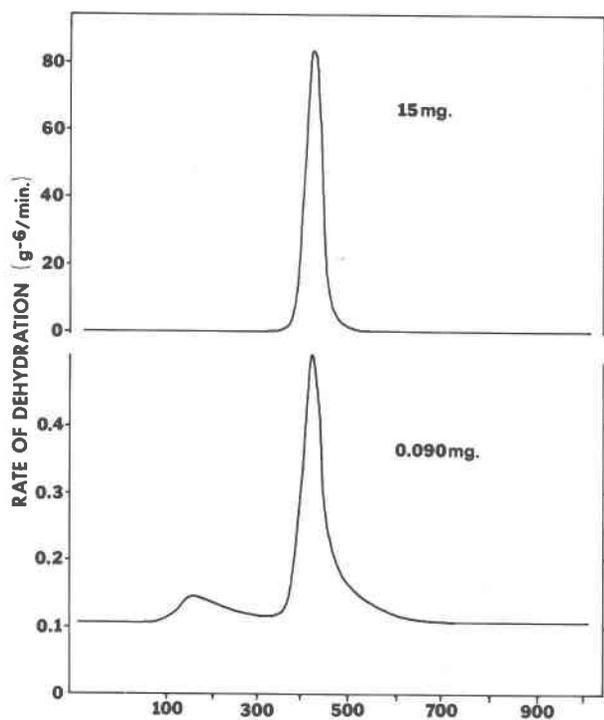


FIG. 2. Chart recordings of dehydration of leadhillite samples weighing 0.090 and 15 mg. The small peak in the lower graph represents adsorbed water.

strongly suggest that the protons are associated with substitutional defects in the crystal structure.

Kyanite, Al_2SiO_5 . The infrared spectra of kyanite were obtained on (100) single-crystal cleavage plates from the following 19 localities: Ambodianina, Madagascar; Bakersville, North Carolina; Campo Longo, Switzerland; Cassia County, Idaho; Chesterfield, Massachusetts; Elovyi Navoloki, Karelia, USSR; Ennis, Montana; Itabira, Minas Geraes, Brazil; Katherinenberg, Urals, USSR; Langtaufers, Vintschgau, Switzerland; Litchfield, Connecticut; Mt. Campione, Ticino, Switzerland; Petschau, Bohemia; Pregratten, Tyrol, Switzerland; Rothenbachl, Tyrol, Switzerland; Saualpe, Carinthia, Austria; Sultan Hamid, Kenya; Windham, Maine; and Yancey County, North Carolina. Representative spectra are shown in Figure 3. The spectra fall into three or four loosely defined groups. Some or all of the complex band systems centering at about 3650, 3440 and 3260 cm^{-1} form conspicuous features in the spectra of many kyanites. Although usually of low intensity three sharp bands at 3387, 3411, and 3440 cm^{-1} are found in most specimens. The several bands between 3200 and 3700 cm^{-1} are due to OH;

this was established by deuteration of kyanite from St. Gotthard, Switzerland, which shifted the absorptions from the OH to the OD region by the required factor 1.36.

The most intense OH spectrum was afforded by a specimen from Yancey County, North Carolina; this contained 0.06 percent H_2O (Table 2). The weakest spectrum was found in kyanite from an unknown locality from North Carolina, with 0.009 percent H_2O . In view of the range of specimens examined, it must be considered unusual to find material with a larger water content. Nevertheless, analyses of kyanite in the literature report larger amounts of water, extending to over 0.5 percent. The water of these analyses, determined by less precise methods on large samples, may in very large part represent foreign material. A tendency toward opacity in kyanite is often associated with an intense infrared absorption centered at 3628 cm^{-1} and attributed to muscovite inclusions (Vedder and McDonald, 1963). There is no correlation between

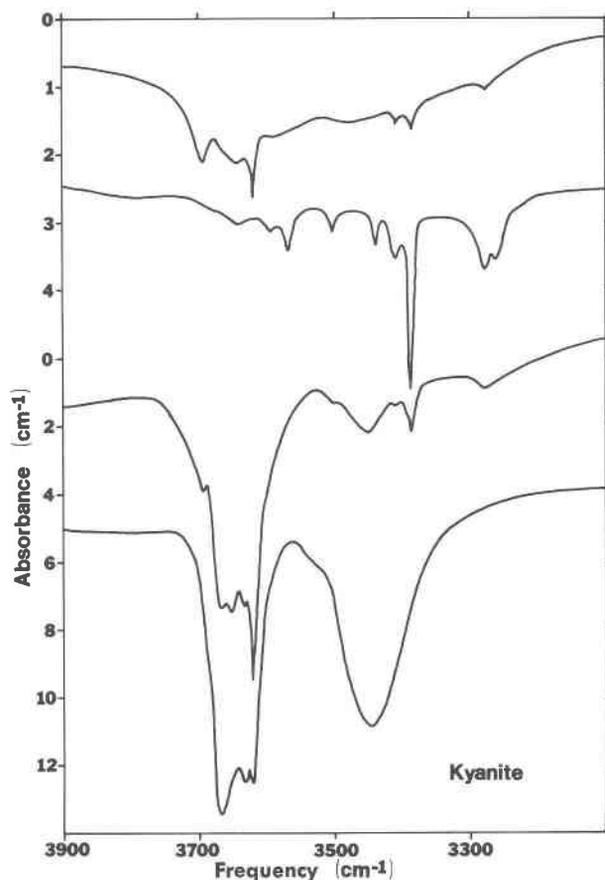


FIG. 3. Representative IR spectra obtained from single-crystal plates of kyanite.

TABLE 2. Water Determinations on Silicates

Mineral	Locality	Milligram Weight		
		Total Sample	Determined Water	Percent H ₂ O
Kyanite	North Carolina	104.58	0.065	0.062
do.	do.	355.18	0.034	0.009
Andalusite	Minas Geraes	101.30	0.048	0.048
Adularia	Val Naips, Switz.	138.46	0.110	0.080
Andesine	Sannidal, Norway	212.07	1.17	0.55
Rhodonite	Broken Hill, N.S.W.	252.0	0.020	0.008
Diopside	Rotenkopf, Tyrol	203.64	0.041	0.020
Olivine	Salerno, Italy	399.73	0.032	0.0080
Grossular	Asbestos, Quebec	100.05	0.148	0.148
do.	Val Malenco, Italy	95.15	0.053	0.056
do.	Transvaal*	3.277	0.075	2.28
do.	(duplicate)	7.538	0.173	2.29
Andradite	Graham Co., Ariz.	192.97	0.286	0.148
do.	Franklin, N.J.	369.47	1.20	0.33
do.	do.	46.73	0.312	0.67
do.	Africa	41.74	0.045	0.108
Spessartine	Sterling Hill, N.J.	73.69	1.89	2.57
do.	do.	8.171	0.204	2.50
do.	Amelia, Virginia	363.99	0.228	0.063
Pyrope	Norway	72.18	0.0065	0.009
Plazolite	Crestmore, Calif.	2.223	0.242	10.9

* We are not certain that the extremely fine grained samples employed were entirely free from admixture.

the infrared absorption spectrum of kyanite and its color, and no obvious relation between the spectrum and the paragenesis.

The sharp band spectra suggest that a wide variety of distinct structural sites are possible for protons in kyanite. The deuteration experiments indicate that some of the sites are unstable over the conditions of temperature and water vapor pressure employed. For example, the band at 3502 cm⁻¹ in the spectrum of the untreated St. Gotthard material all but disappears after the first period of heating and exchange. An unsuccessful attempt was made to rehydroxylate the thermally dehydrated St. Gotthard material at 750°C and 1000 bars H₂O pressure.

Andalusite, Al₂SiO₅. Only two specimens of andalusite were available of sufficient size and transparency for infrared study. Both showed a rich spectrum in the hydroxyl stretching region, suggesting the presence of a varied assemblage of structural sites associated with protons. The specimen which gave the simpler spectrum (Fig. 4) was green in color. All of the hydroxyl bands are strongly polarized. This specimen was submitted to the deuteration treatment for about five days. Although complete exchange was not achieved, we may infer from the similarity of the OH and OD spectra obtained that all bands in the 3700 to 3200 cm⁻¹ region are due to OH. A direct determination of OH, as H₂O, gave 0.048 percent (Table 2). Water contents over 0.5 percent have been reported in

andalusite, but the readiness with which this mineral alters to sericite and the common presence of finely divided foreign material in the crystals makes these determinations very dubious.

Sillimanite, Al₂SiO₅. The only sillimanite sample of sufficient size and purity for infrared examination was a cleaved, transparent pebble of gem quality from Ceylon, kindly supplied by the U.S. National Museum. The spectrum is again quite different from those of the other Al₂SiO₅ polymorphs, but the nature of the material did not allow us to attempt an OH—OD exchange or a water determination. With little doubt, however, the bands between 3000 and 3700 cm⁻¹ (Fig. 4) are due to OH stretching vibrations. Sillimanite, like kyanite and andalusite, alters readily and the high water contents that have been reported doubtless are due to foreign material.

Garnet, A₃B₂(SiO₄)₃. Garnet is of particular interest because it has been established experimentally that large amounts of water can be incorporated structurally. This was initially reported by Flint, McMurdie and Wells (1941), in Ca₃Al₂(SiO₄)₃ and Ca₃Fe₂(SiO₄)₃, and later by Ito and Frondel (1967) and Ito (1968a,b) in a variety of synthetic garnets. Partial or complete series have been obtained to the hydroxide end-compositions, and the mechanism has been formulated as A₃B₂(SiO₄)_{3-x}(OH)_{4+x}. The actual mechanisms involved, however, may be more complicated.

Determinations of the water content of 11 natural garnets has given values for the OH content, as H₂O, in the range from 0.009 to 2.57 percent (Table 2). Infrared spectra were obtained on these specimens and on a number of additional specimens representing a variety of environments. The data indicates

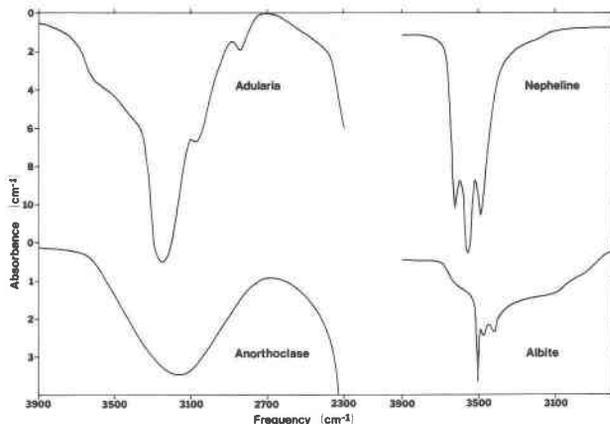


FIG. 4. IR spectra obtained from single-crystal plates of andalusite, sillimanite, diopside and olivine.

that pyrope and almandine have very weak absorptions in the OH stretching region, a small band at about 3500 and perhaps another at 3670 cm^{-1} being typical. The lowest measured water content was found in pyrope. Grossular, andradite and spessartine have much larger water contents and all specimens show rather complex spectra. It is not known if the factors controlling the OH content are compositional or environmental.

The rate of hydrogen-deuterium exchange in garnet was found to vary with the specimen employed and may well be composition-dependent. Of three specimens of approximately the same thickness, and treated identically, only a green andradite had a complete exchange. The other two specimens, a grossular and an andradite, were about 30 percent exchanged. A slight modification of the OH spectrum after an initial heating in either H_2O or D_2O vapor, already noticed in quartz and many other minerals, was observed here with spessartine. The original spectrum of a spessartine low in OH became modified during the period of exchange to resemble the complex OH spectrum of a spessartine high in OH. This modified OH spectrum was duplicated in the OD region following exchange.

Natural hydrogrossular is relatively fine-grained. The small particle size, however, evidently is not associated with the OH content because we have found relatively high water contents in coarsely crystallized garnets. The highest water content, 2.57 percent, was found in a dodecahedral crystal of calcian spessartine about 2 inches in size from Sterling Hill, New Jersey, (composition 21 an, 62 sp, 17 gr). A sample of relatively highly hydrated hydrogrossular (plazolite), found to contain 10.9 percent water, lost the water at about 780°C, several hundred degrees below that of the other garnets.

Diopside, $\text{CaMgSi}_2\text{O}_6$. Several (110) sections of a transparent green diopside from Rotenkopf, Tyrol, were examined in the infrared. All showed a spectrum of several bands in the OH stretching region (Fig. 4). Deuteration was easily effected, with approximately 50 percent conversion after 16 hour heating period. Direct determination of the OH as H_2O , gave 0.020 percent (Table 2). Evidence of OH absorption also was found in diopside from Madagascar and from Jefferson County, New York, but no further study was made.

Rhodonite, $\text{CaMn}_4\text{Si}_5\text{O}_{15}$. A random section, near (100), of a transparent reddish brown rhodonite crystal associated with galena, from Broken Hill,

New South Wales, showed an OH spectrum. The spectrum was verified by deuteration. The OH content, as H_2O , was determined as 0.008 percent (Table 2).

Olivine, $(\text{Mg,Fe})_2\text{SiO}_4$. A random section near (100) of a transparent green olivine pebble from Fort Defiance, Arizona, gave a sharp band spectrum between 3300 and 3700 cm^{-1} (Fig. 4) that almost certainly represents OH. Repeated efforts to deuterate this olivine at 750°C failed. The water content was determined as 0.0080 percent (Table 2).

Feldspars. Feldspars from a variety of environments of formation were examined in the infrared. Sections on (010) were employed. We observed, as did Brunner *et al.* (1961), that adsorptions are characteristically present in the OH stretching region. However, only the albite from Amelia, Virginia, had a sharp line spectrum such as those found in all of the other minerals examined (Fig. 5). It was proved by deuteration that the bands between 3400 and 3600 cm^{-1} are due to OH. All other specimens of andesine, adularia, orthoclase, labradorite and anorthoclase examined gave spectra of very broad diffuse bands in the region between 3750 and 3000 cm^{-1} . One of these specimens, an anorthoclase from Mt. Franklin, Australia (Fig. 5) with a single broad absorption centered at 3150 cm^{-1} , was partly deuterated over a period of several days. The OH content of specimens of adularia and andesine was determined as 0.080 and 0.55 percent H_2O , respectively (Table 2).

Hydroxyl appears to be a characteristic trace constituent of the feldspars. The oxonium ion, H_3O^+ , also may be present although in a different structural site as discussed below.

Other Minerals. In addition to the foregoing, we have found by infrared examination of single-crystal

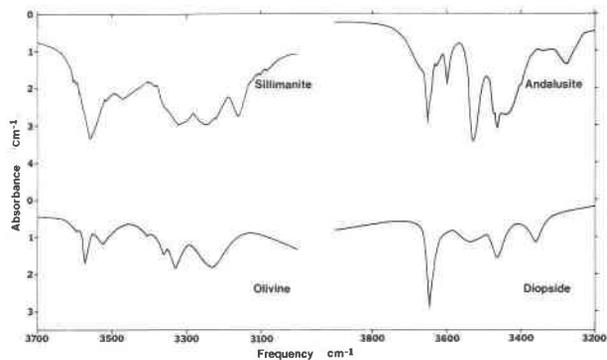


FIG. 5. IR spectra obtained from single-crystal plates of albite, anorthoclase, adularia and nepheline.

plates evidence of OH in phenakite from the Pikes Peak region, Colorado; nepheline from Mt. Albani, Italy (Fig. 5); titanite from Switzerland; and rutile from Harford County, Maryland. Neither deuteration experiments nor direct water determinations were undertaken.

Discussion

The structural role of water present in the silicates examined is open to several different interpretations. These include the so-called hydrogarnet substitution, with $(\text{SiO}_4) = (\text{OH})_4$; the oxonium ion, H_3O^+ ; molecular H_2O , either interstitially or as liquid inclusions; OH ions associated with dislocations and surfaces; and isolated, substitutional OH ions. These possible interpretations may now be discussed.

The substitution of a tetrahedral $(\text{OH})_4$ group for an (SiO_4) tetrahedron usually has been appealed to when abnormally high amounts of water have been observed in silicates. It has not been conclusively proved, however, that this substitution occurs outside of the garnet group. As the result of examining a large number of variously substituted synthetic hydrogarnets, we have observed consistencies in the hydroxyl spectra. The detailed results will be published later, but the major feature of any hydrogarnet spectrum is a single intense and rather broad band of characteristic shape centered at about 3620 cm^{-1} . We have not found this spectrum in the silicates described here. Instead a number of sharper bands are present and most, if not all, must represent water accommodated in other ways.

The evidence for H_3O^+ in silicates remains, as Vedder (1965) has commented, more suggestive than conclusive. In the uranyl arsenate troegerite and several other minerals (Wilkins *et al.*, 1973), absorptions at about 2900, 1700 and 1150 cm^{-1} are attributed to oxonium ions. The two lower frequencies are to be regarded as especially characteristic, but are not accessible in thick plates of silicates. In contrast to the hydrogarnet substitution which may, on present understanding, be expected in any silicate, the oxonium ion, H_3O^+ , is most likely to occur in silicates by replacement of another large univalent cation such as K^+ or NH_4^+ . This substitution hence is unlikely in the silicates we have examined except for the feldspars, which do indeed often show a typical spectra.

There is clear spectroscopic evidence of isolated H_2O molecules in cordierite (Farrell and Newnham, 1967) and beryl (Wood and Nassau, 1968), but in

both cases channels exist in the structure of the right size to accommodate H_2O molecules. Isolated H_2O molecules could conceivably occur in the structure of any silicate, either in an interstitial position or replacing anions or cations. Although an interstitial position would appear to be ruled out on the basis of molecular size, and charge considerations make the other two positions energetically improbable, they cannot be dismissed without more detailed scrutiny. Liquid water has a distinctive spectrum, overlapping absorptions from the two stretching modes forming a very broad band centered at about 3450 cm^{-1} . This band was not observed in any sample we analyzed, although it can be detected in quartz containing liquid inclusions.

It has been pointed out that observed OH bands may result from hydroxyl ions associated with dislocations. Mitchell and Rigden (1957) considered this type of control in a study of quartz. Kats (1962) has shown, however, that the hydroxyl ions in quartz cannot be accommodated in this way because one has to expect preferential effects in the growth direction of the crystal, whereas the dichroic ratio $\alpha E_{\perp} / \alpha E_{\parallel}$ is always the same for the same absorption bands. Although we do not, as yet, have sufficient information on dichroism in the minerals we examined to appeal to the same argument, there is rather clear evidence from the observed ratios of H-D exchange that the water content is not specifically associated with dislocations. Evaluating this problem is difficult, because relatively little is known about the dislocation types and density in the silicates we have examined; however, it is certain that they form an important structural element. Because dislocation lines and surfaces are regions of rapid diffusion in crystals, and are accessible from grain surfaces, hydrogen-deuterium exchange involving such imperfections should take place at relatively rapid rates, more comparable to those on surfaces than to the diffusion mechanisms in the bulk of the solid. The hydrogen-deuterium exchange rates on surfaces are fast; both rutile and anatase, for example, were found by Yates (1961) and Lewis and Parfit (1966) to completely exchange within 25 min at 350°C using D_2 gas under 5 cm pressure. Hydrogen-deuterium exchange can be effected on silica surfaces at room temperature (McDonald, 1957). In contrast, some of the fastest rates observed by us were on kyanite, where almost complete exchange was effected only after 200 hours at 750°C and about 100 bars D_2O pressure. Our

data are more consistent with a diffusional mechanism in the solid, the process perhaps being carried on by diffusion of atomic deuterium.

After consideration of various possible locations of water, none of which are satisfactory, we are left with the possibility that the water may be present in the crystal structure as isolated OH ions that take the place of oxygen ions or that occupy vacant sites. This would cause local charge imbalance that may be compensated by the substitution into an associated site of ions of other than normal charge. In general, the proton will seek a position of potential minimum and the frequencies of the stretching and librational motions, together with the orientation of the OH dipole, will be characteristic of a particular mechanism of substitution.

This housing mechanism of the OH ions is consistent with the range of frequencies observed because there are so many distinct types of accommodation possible. Our preliminary examination of kyanite and the detailed study with polarized radiation of andalusite by Beran and Zemmann (1969a) indicate that the different types of OH ions have unique orientations in the crystal structure. Furthermore, many of the hydroxyl bands are remarkable for their narrow band widths, being only a few wavenumbers, even at 25°C. Other broader bands have fine structure showing that they consist, in fact, of overlapping sets of bands. Bands as sharp as we have observed can only be obtained from hydroxyl ions situated in a very regular environment. This is to be expected from hydroxyl ions associated with substitutional defects which are isolated from each other by regions of regular structure.

Conclusions

Chemical analyses have long suggested the presence of small amounts of water in the common anhydrous silicate minerals. Our infrared absorption and isotopic substitution experiments, accompanied by precise quantitative measurement of the water detected, leave no doubt that small amounts of water are characteristically present in the structure of natural silicates. The absolute amounts we have found, however, seem to be one or more orders of magnitude smaller than those reported by older analytical techniques. This may be attributed in part to our use of samples that were demonstrated to be free from foreign material.

We have examined possible ways in which water may be included within a mineral which has no

apparent site for it in the crystal structure. For the limited range of specimens studied, there is no clear evidence in favor of the water being present in the hydrogarnet substitution, as the oxonium ion, as liquid water in inclusions, as isolated H₂O molecules, or as hydroxyl ions specifically associated with dislocations. All available evidence is in favor of the observed water being present as hydroxyl ions associated with cation sites where there is charge imbalance in the structure due to substitution of ions of non-equivalent charge or due to cation omission. This is in agreement with the conclusions of previous workers on quartz, andalusite, TiO₂ polymorphs, and barium titanate. It may be commented that substitutional OH of this type may be present in nominally anhydrous silicates and in silicates that contain water, in other structural roles, as an essential or vicarious constituent.

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