

Joaquinite: The Nature of its Water Content and the Question of Four-Coordinated Ferrous Iron¹

GEORGE R. ROSSMAN

*Department of Geological and Planetary Sciences,
California Institute of Technology, Pasadena, California 91125*

Abstract

The polarized optical and infrared spectra of oriented crystals of joaquinite from San Benito County, California, have been obtained. The infrared spectra have polarized absorption bands at 3561, 3500, and 1607 cm^{-1} , which are assigned to the vibrations of crystallographically ordered molecular water in joaquinite. The optical spectra show features due to neodymium and divalent iron. The near infrared absorptions near 1000 and 2100 nm are discussed in terms of six-coordinated iron(II) rather than the four-coordinated iron(II) proposed from X-ray structural studies.

Introduction

Joaquinite is a rare silicate mineral best known from its association with benitoite and neptunite at the Dalles Gem Mine, San Benito County, California. Its structural properties have recently been determined (Cannillo, Mazzi, and Rossi, 1972; Laird and Albee, 1972). Cannillo and coworkers proposed a unit cell formula of $\text{Ba}_4\text{Fe}_2\text{Re}_4\text{Ti}_4\text{O}_4[\text{Si}_4\text{O}_{12}]_4$; Laird and Albee, and Semenov and coworkers (1967) have proposed similar formulae but have included hydroxide ions. Cannillo's structure determination suggests that joaquinite contains four-coordinated iron(II) in an unusual coordination geometry. Four-coordinated iron(II) is rare in silicate minerals. The electronic spectroscopy of four-coordinated iron(II) is accordingly poorly examined. Square planar Fe(II) has been studied by Burns, Clark, and Stone (1966) in gillespite and by Rossman (in preparation) in eudialyte, whereas mineralogical tetrahedral Fe(II) has been studied in spinels (Slack, Ham, and Chrenko, 1966; Mao and Bell, in preparation) and staurolite (Burns, 1970). The spectroscopy of other four-coordination geometries has not been characterized in silicate mineral systems.

The role of OH in the structure of joaquinite remains unsettled. Semenov *et al* (1967) reported 1.5 wt percent H_2O in their analysis of Greenland joaquinite and concluded that there was one hydroxide

per formula unit (based on two Ba). Laird and Albee (1972) found that electron microprobe analyses totaled to less than 100 percent and attributed the deficiency in the total from 100 percent to water. They concluded that hydroxide is present to the extent of about 3.3 OH per two Ba. They presented infrared spectral evidence to substantiate the conclusion that there is crystallographically oriented OH in joaquinite. Cannillo *et al* (1972) elected not to assign hydroxide to the structure; instead, they suggested that hydroxide (or water) could be occurring in cavities in the structure but has no structural role.

A study of the optical and infrared spectra of single euhedral grains of joaquinite has been conducted to characterize both the four-coordinated iron and the role of the OH content. The results of that study are reported herein. A comparison of the spectra of four-coordinated iron(II) in a variety of minerals will appear at a later date.

Experimental Details

The joaquinite specimens used in this study came from the vicinity of the Dalles Gem Mine near New Idria, San Benito County, California. Their identity was verified through morphology, mineral association, and the infrared spectra. They consisted of roughly equidimensional, yellow-brown crystals 0.6 to 1.2 mm in size which, although clear and transparent, had several fractures within the crystals.

Crystals were first oriented by external morphology, ground to the appropriate thickness and polished with 0.3 μm Al_2O_3 powder. In all cases,

¹ Contribution No. 2465, Division of Geological and Planetary Sciences, California Institute of Technology.

sections from the center of the crystal were used. The optical spectra of self-supporting thin slabs were obtained at 23°C with a Cary 171 spectrophotometer equipped with dual calcite polarizers. The crystals were then further ground and polished to a thickness appropriate for the infrared spectra which were obtained at ~28°C with a Perkin Elmer 180 spectrophotometer equipped with a common-beam wire-grid polarizer. Absorbances are defined as $\log I_0/I$; ϵ values are in liters mole⁻¹cm⁻¹.

Optical and X-ray Orientation

The optical orientation of joaquinite was originally presented by Palache and Foshag (1932), who reported $a = X$, $b = Y$, $c = Z$ and an orthorhombic cell $a = 9.61 \text{ \AA}$, $b = 10.45 \text{ \AA}$, $c = 22.4 \text{ \AA}$. This convention was followed by Semenov *et al* (1967). Both Laird and Albee (1972) and Cannillo *et al* (1972) have demonstrated that joaquinite has a monoclinic unit cell which can twin on the (001) plane to form an orthorhombic cell expanded along the monoclinic c^* axis. Cannillo and coworkers designated the axes in the orthorhombic cell, following the precedent of Palache and Foshag, setting $a_{or} = 9.58 \text{ \AA}$, $b_{or} = 10.50 \text{ \AA}$, and $c_{or} = 88.84 \text{ \AA}$, which is four times the c dimension specified by the earlier workers. They designated the axes of the monoclinic unit cell following the conventions for the monoclinic crystal system, interchanging the orthorhombic a and b axes, so that $a_m = 10.50 \text{ \AA}$, $b_m = 9.58 \text{ \AA}$ and $c_m = 11.78 \text{ \AA}$. Laird and Albee followed the same convention for the monoclinic cell with $a_m = 10.51 \text{ \AA}$, $b_m = 9.66 \text{ \AA}$, and $c_m = 11.82 \text{ \AA}$, but chose an orthorhombic cell— $a_{or} = 10.48 \text{ \AA}$, $b_{or} = 9.66 \text{ \AA}$, and $c_{or} = 22.26 \text{ \AA}$ —whose a and b axes coincide with the monoclinic a and b axes.

The orientation convention used in this report was dictated by the crystals used in the experiments. Crystals were cut according to external morphology and the optical orientations of Palache and Foshag (1932) to yield cuts with centered Bxa and Bxo figures. Extinction was sharp and uniform throughout the crystal along the apparent orthorhombic directions, indicating that the crystal used for the Bxo slice is submicroscopically twinned to produce an orthorhombic crystal on the scale of the optical experiment. Orientations were, therefore, chosen to follow the convention of Palache and Foshag but modified by the axial lengths reported by Laird and Albee; thus $\alpha = a_{or} = 9.66 \text{ \AA}$, $\beta = b_{or} = 10.48 \text{ \AA}$, and $\gamma = c_{or} = 22.26 \text{ \AA}$ where c_{or} is in the direction of the monoclinic c_m^* .

Analytical

Electron microprobe analyses were obtained by Arthur Chodos with an automated MAC v microprobe for the specimens whose spectra are illustrated. Reporting total iron as FeO, the Bxa sample had 3.29 wt percent FeO (average of 4 points) and the Bxo sample had 3.49 percent FeO (average of 3 points). More detailed electron microprobe analyses of several specimens from this locality are reported by Laird and Albee (1972), who report FeO values (ΣFe as FeO) from 3.76 to 4.55 wt percent. No evidence of trivalent iron was found in the optical studies reported below.

The Water Content

The near-infrared optical spectrum (Fig. 1) shows for γ -polarization a sharp band at 1935 nm and a weak band at ~1440 nm. These absorption bands respectively occur at wavelength regions in which the combination mode, stretch-plus-bend, of molecular H₂O, and the first overtone of the symmetric stretch of water occur. Their existence implies the presence of molecular water in joaquinite, and the pronounced polarization of these bands means that the water is structurally ordered. These observations motivated a study of the single-crystal infrared spectra in the water and hydroxide absorption regions using the methods of Labotka and Rossman (1974).

The infrared spectrum of powdered joaquinite (Laird and Albee, 1972) showed O-H stretching modes at ~3560 and 3500 cm⁻¹. These frequencies are in the range in which the O-H stretching motions of hydroxide ions in minerals are commonly found. Because these frequencies are higher than the O-H stretching frequencies of both liquid and coordinated water, and because these two absorption bands are narrow compared to those of liquid water, it would be straightforward to assign them to weakly hydrogen-bonded hydroxide ions which, presumably, are crystallographically ordered.

The polarized crystal infrared spectral data (Fig. 2) provide additional important information regarding the nature of the hydroxyl content: (1) The 3561 cm⁻¹ band is γ -polarized and the 3500 cm⁻¹ band is β -polarized. This confirms that the O-H units are crystallographically ordered. (2) The 1607 cm⁻¹ absorption band is β -polarized. This feature can only be assigned to the ν_2 deformation of molecular water. Molecular water in the gas phase has been shown to have three infrared-active fundamental absorption

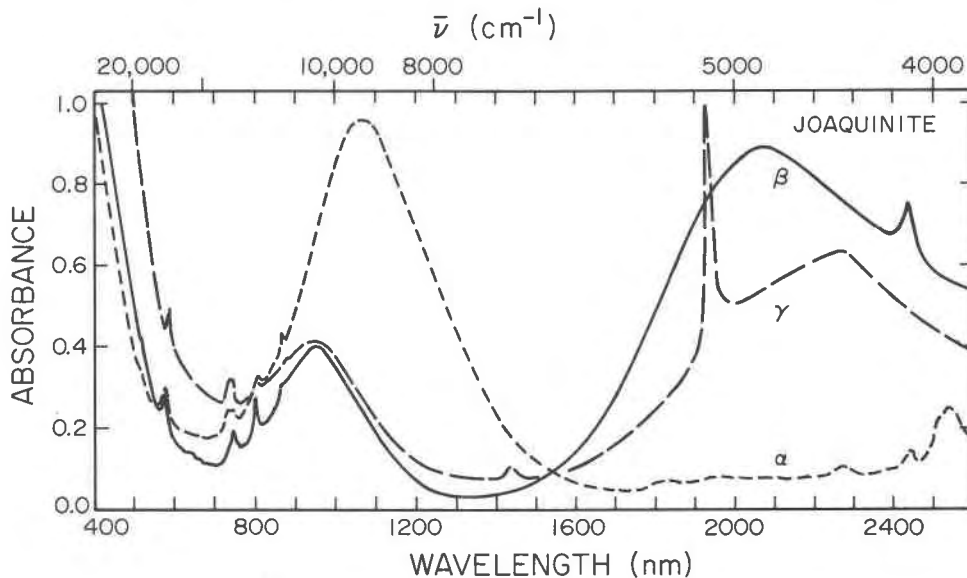


FIG. 1. Polarized optical absorption spectrum of San Benito County, California, joaquinite crystals at 295K. 0.20 mm thick *Bxa* crystal for α , β , 0.19 mm thick *Bxo* crystal for γ .

bands. They correspond to the ν_2 deformation at 1595 cm^{-1} , the ν_1 symmetric stretch at 3657 cm^{-1} , and the ν_3 antisymmetric stretch at 3756 cm^{-1} (Benedict and Plyler, 1951; Benedict, Claasen, and Shaw, 1952). The polarization of the molecular water absorptions is readily predicted from group theory (Nakamoto, 1963). The ν_2 and the ν_1 modes are both expected to be polarized in the direction of the two-fold axis of the molecule whereas ν_3 is polarized in the plane of the molecule. The assignment of the 3561 cm^{-1} band to ν_3 and the 3500 cm^{-1} band to ν_1 is consistent with these constraints. (3) The 1935 nm band (5168 cm^{-1}), polarized along c_{or} , is assigned to the combination $\nu_2 + \nu_3$ of molecular H_2O . The ν_2 energy is known, so by algebraic difference, the stretching frequency, ν_3 , must be at 3561 cm^{-1} . It should be γ -polarized as is the combination $\nu_2 + \nu_3$, which in fact it is. This confirms the assignment of the ν_3 band. Other features can be assigned as overtones, such as the 3190 cm^{-1} β -polarized band, which is $2\nu_2$. All of the spectroscopic features which arise from O-H units can be explained in terms of molecular water.

The structural model of the water in joaquinite consists of molecules well-isolated from each other oriented parallel to (100) with their symmetry axis parallel to [010]. They are essentially unbonded, lacking significant hydrogen bonding and coordination to a cation through oxygen, instead being held in cages by physical entrapment and long-range electrostatic

forces. Discrete hydroxide ions are absent. This model is consistent with the proposal of Cannillo *et al* (1972) that the hydroxyl or water resides within cavities within the structure in a fashion similar to beryl.

The spectroscopic and thermal properties of the water in joaquinite are similar to those of water in beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$). Wood and Nassau (1968) have used infrared spectroscopy to study isolated water molecules trapped in the channels of beryl. The general features of the spectra of water in beryl, which they reported, are similar to those of joaquinite, but richer in structure due to the presence of two structurally distinct types of water and to the presence of low-energy hindered rotational motions that are coupled with the stretching and bending of the water molecules. In beryl, the water is tightly trapped in the channels by alkali ions and was not released from some crystals in heating experiments until a temperature of 1350°C was reached.

The DTA curve of joaquinite (Semenov *et al*, 1967) shows an endotherm at 770°C , which has been suggested to be due to the release of water. Release of H_2O at such a high temperature is generally attributed to the dehydroxylation of hydroxide groups in the mineral rather than due to release of pre-existing molecular H_2O . The fact that the water is unable to escape until this temperature is reached indicates that it is tightly trapped in joaquinite.

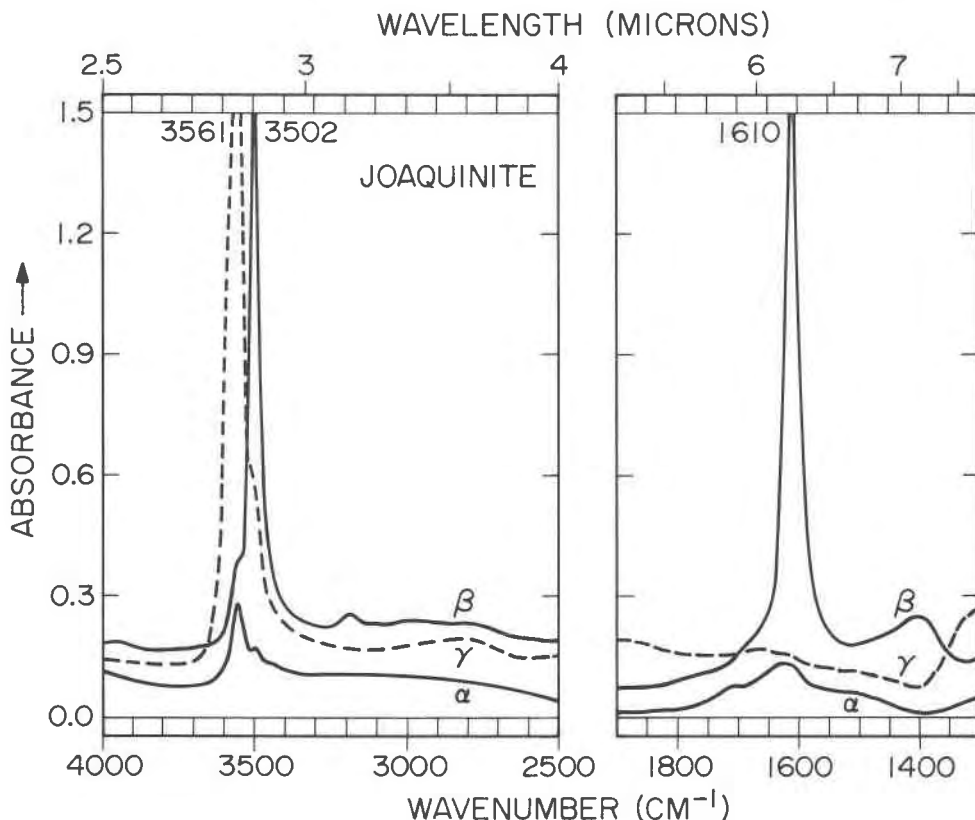


FIG. 2. Polarized infrared absorption spectra of San Benito County, California, joaquinite; crystals 18 μm thick, at 305K. For clarity, the α and β spectra in the 4000-2500 cm^{-1} region have been displaced vertically 0.05 and 0.10 units respectively, and in the 1800-1400 cm^{-1} region γ and β have been displaced 0.10 and 0.05 units respectively.

The inclusion of hydroxide ion in the formula of joaquinite no longer appears necessary. When the detailed chemical analyses of Laird and Albee (1972) are compared to the idealized formula for joaquinite proposed by Cannillo *et al* (1972) from the X-ray structural data, $\text{Ba}_4\text{Ti}_4\text{Fe}_2\text{RE}_4\text{Si}_{16}\text{O}_{52}$, it is found that the total cation charge 105.3 (based on 16 Si) from the microprobe analyses compares favorably with the anion charge of 104 demanded by 52 oxygen ions. This agreement must be considered to be close, particularly because Laird and Albee's data refer to averaged analyses over numerous points of an inhomogeneous sample and include 0.4 Li^+ based on site-occupancy considerations rather than direct analyses. Even closer agreement was obtained (total charge 104.7) by examining unpublished data of Laird and Albee taken on a single point on their joaquinite sample. The role of the sodium in joaquinite still requires clarification. Iron is present to an extent well below the two atoms per formula unit in the idealized formula. The deficiency of atoms, however,

can be made up by inclusion of Na^+ , K^+ , and Li^+ plus minor amounts of other divalent cations found in the analyses. The joaquinite formula proposed by Laird and Albee suggested that a substitution occurs between Fe^{2+} and Na^+ on a six-fold site as well as a substitution of Sr into the rare earth site. An idealized formula of San Benito joaquinite is accordingly stated as $\text{Ba}_4(\text{RE},\text{Sr})_4(\text{Fe},\text{Na})_2\text{Ti}_4\text{Si}_{16}\text{O}_{52} \cdot x\text{H}_2\text{O}$, where x is a variable quantity roughly equal to 2.

Optical Spectrum and Discussion

The polarized optical spectrum of joaquinite (Fig. 1) shows two prominent regions of absorption near 1000 nm and 2100 nm. Numerous sharp and relatively weak features occur through the range 400-900 nm which are rare earth absorption bands, predominantly those of Nd^{3+} , which is the most abundant spectroscopically important rare earth element found in the San Benito joaquinite. These bands will not be considered further. The sharp, narrow absorption

feature at 1935 nm in γ -polarization has been discussed in connection with the water content. The charge-transfer tail which begins to rise at about 700 nm rises to at least 350 nm without additional features. It has its greatest absorbance in the visible region in the γ -polarization and, as such, is responsible for the pleochroism of joaquinite.

The two broad near-infrared bands are both polarized and shift slightly in band maxima with polarization. The intensities decrease in the order α at 1070 nm $>$ $\beta \approx \gamma$ both at 955 nm. The components of the lower energy band are polarized β at 2080 nm $>$ γ at 2270 nm $\gg \alpha$ which is effectively absent. These two bands are interpreted as absorption bands of the Fe^{2+} . The intensities of the bands are within the range commonly encountered with Fe(II) . In the polarization of maximum band intensity, ϵ_{1070} and ϵ_{2080} both equal 24.

The X-ray structural data indicate that the optical spectrum should be interpreted in terms of four coordinated Fe(II) . In their structure determination, Cannillo *et al* found two Fe-O(4) bond distances of 2.16 Å and two Fe-O(8) distances of 2.21 Å (oxygen position designations from Cannillo *et al*, 1972). The O-Fe-O bond angles depart greatly from both the ideal tetrahedral angle of 109° and from the square planar angle of 90° . The iron is located in a site of C_{2v} symmetry which can be approximated as an octahedral site from which two oxide ions have been completely removed. The remaining oxygens have O-Fe-O bond angles not greatly changed from the octahedral values. They are O(8)-Fe-O(8) 173° , O(4)-Fe-O(4) 94° , two O(4)-Fe-O(8) at 81° , and two O(4)-Fe-O(8) at 95° . These details of the iron coordination polyhedron must be considered with caution in view of high R value (16%), which was due to the poor quality of the crystal used in the structure determination.

In C_{2v} symmetry the degenerate E and T electronic states of tetrahedral and square-planar four-coordinated iron will be split so that five states—two 5A_1 , 5A_2 , 5B_1 , and 5B_2 —exist. A detailed analysis of the splitting of energy states of Fe(II) in C_{2v} geometry in enstatite has been presented by Runciman, Sengupta, and Marshall (1973). The qualitative symmetry aspects of that analysis are applicable to the joaquinite problem, because the iron site reported for joaquinite corresponds to the $M(2)$ site in enstatite with the $M(2)\text{-O(3)}$ and $M(2)\text{-O(6)}$ bands (oxygen position designations from Runciman *et al*) elongated to the point that the O(3) and O(6) ions are no longer within the coordination sphere of $M(2)$,

and the $M(2)\text{-O(5)}$ and $M(2)\text{-O(2)}$ bonds elongated to 2.21 Å.

The spectrum of joaquinite bears a surprisingly close resemblance to the enstatite spectrum. The spectra of both minerals have prominent absorption bands near 1000 and 2000 nm, which are polarized in different directions. The energies of the joaquinite absorption bands are roughly 10 percent lower than those of enstatite. The prominent 506 nm spin-forbidden band of enstatite has a corresponding band in joaquinite at 523 nm. The resemblance is surprising because it would be expected that four-coordinated C_{2v} iron(II) would have absorption bands at a much lower energy than six-coordinated C_{2v} Fe(II) in a fashion similar to 4/9 energy reduction between O_h and T_d Fe(II) . One structural aspect of the iron site is disturbing. If the site is viewed as an octahedron from which two equatorial ligands have been removed, the two axial oxygens are bent toward the remaining two equatorial oxygens, placing the iron outside the volume of the distorted tetrahedron delineated by connecting the positions of the four oxygen ligands.

These observations suggest that the iron is six-coordinated in a highly distorted octahedral site resembling the $M(2)$ site of enstatite. In view of the structural complexity, which results from twinning and the questions remaining regarding the details of the iron site, detailed analysis of the joaquinite optical spectrum is not warranted, but must await X-ray structural data from untwinned crystals.

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