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OH^- in pyroxene: An experimental study of incorporation mechanisms and stability

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ABSTRACT

Most pyroxenes contain trace amounts of OH^- that are lost when heated at 700 °C (1 atm) under either air or H_2. When Si-deficient Fe^{3+}-rich pyroxenes (ferrian diopside and esseneite) are heated in H_2, an up to 70-fold increase of the intensity of the infrared OH^- absorption bands occurs, which is well correlated with Si deficiency in the tetrahedral site. Mössbauer and optical spectroscopy indicate that these samples have substantial amounts of Fe^{3+} in the tetrahedral position. After the uptake of H_2, optical spectra show that the amount of Fe^{2+} in the M(2) site has increased, corresponding to charge compensation according to the reaction $Fe^{3+} + O^{2-} + \frac{1}{2}H_2 = Fe^{2+} + OH^-$. Heating in air at 600–700 °C decreases or removes the OH^- bands. The OH^- bands from air-heated samples are restored by subsequent heating in H_2. Hydrothermal experiments (600 to 800 °C and 1- to 2-kbar H_2O pressure) do not increase the amount of OH^- but do redistribute some of the absorption intensity among the OH^- bands. Experiments performed in D_2O show that OD^- readily replaces OH^-. Therefore the diffusion of H^+ through the pyroxene crystal cannot be a rate-limiting process, and hence a more fundamental change than just a mechanical introduction is required to incorporate OH^- in the pyroxene structure. The thermal stability of the OH^- in pyroxene is comparable to OH^- in Fe-rich amphiboles and suggests that pyroxenes can provide information about the activity of hydrous components prevalent during their crystallization.

INTRODUCTION

Pyroxene is regarded as a nonhydrous member of the biopyribole mineral group, but may contain small amounts of crystallographically incorporated OH^- (Beran and Zemann, 1986; Skogby et al., in preparation). Little is known about the mechanisms of OH^- incorporation in pyroxenes. It is also not known if OH^- is stably bound in pyroxenes and thus reflects fundamental geologic processes or if it is a highly labile species that can diffuse into the crystals through hydrothermal or redox processes after crystallization.

Comparisons can be made between OH^- in pyroxenes and the normal hydrous biopyriboles. OH^- absorption bands in infrared spectra of pyroxenes often occur at somewhat lower wavenumbers as compared to sheet silicates and amphiboles (Skogby et al., in preparation). Two classes of spectroscopic features occur, one at higher wavenumbers consisting of sharp absorptions resembling those of amphiboles ("amphibole" bands) and the other at lower wavenumbers consisting of comparatively broad absorptions that have not been associated with any other phase ("pyroxene" bands). The position of OH^- absorption bands depends on a number of factors, including the strength of the hydrogen bond, and is affected by cation substitutions in the coordination polyhedra. Substitutions in biotite involving Fe^{3+} and vacancies shift absorption bands to lower wavenumbers (Vedder and Wilkins, 1969). In amphiboles, Ti on the M(1,2,3) sites and substitution of Al for Si also strongly shift the bands to lower wavenumbers (Hawthorne, 1981). Since one class of OH^- bands in pyroxenes occurs at comparatively low wavenumbers, the OH^- ion might be present in coordination polyhedra involving these types of substitutions.

In the normal hydrous biopyriboles, oxidation and hydroxylation reactions have been extensively studied, e.g., micas (Vedder and Wilkins, 1969) and amphiboles (Addison et al., 1962; Clowe et al., 1988). Biotite loses OH^- in three different stages during heating in air. From 400 to 500 °C, hydrogen is lost with concomitant oxidation of Fe^{2+}. At 500–800 °C, H_2O is lost from sites near octahedral vacancies by condensation of two OH^-, leaving O^{2-} and an anion vacancy. Hydroxide bound to a fully occupied octahedral layer is retained up to temperatures above 1000 °C. In amphiboles, the oxidation-dehydrogenation equilibrium $Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + \frac{1}{2}H_2$ has been studied at different oxygen fugacities by Clowe et al. (1988). They concluded that significant variation in Fe^{3+} can be achieved in amphiboles by variation of f_{O_2}. Similar oxidation and dehydroxylation reactions can also be expected to occur in OH^--containing pyroxenes.

Pyroxenes frequently alter to hydrous silicates such as talc and amphibole. Using HRTEM techniques, Veblen and Bish (1981, 1988) distinguished a number of different

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TABLE 1. Sample types, localities, and occurrence

No.	Sample	Locality	Occurrence	Ref. no.
2	Diopside	Rajasthan, India	metamorphic	CIT 11221
8	Aegirine-augite	Magnet Cove, Arkansas	nepheline syenite pegmatite	CIT 349
12	Diopside	Sinnidal, Norway	metamorphic	GRR 1621
13	Diopside, Fe-rich	Sydenham, Ontario	metamorphic pyroxenite	GRR 1620
18	Enstatite	Alpine, Texas	lower crustal	ALP-1*
21	Ferrian diopside	Kauai, Hawii	oxidized alkali picrite	GRR 603
25	Aegirine	Magnet Cove, Arkansas	nepheline syenite pegmatite	CIT 11832
28	Ferrian diopside	Vesuvius, Italy	rhyolitic pumice	NMNH C2429
29	Aegirine	Mt. St. Hilaire, Quebec	nepheline syenite	CIT 8449
35	Esseneite	Buffalo, Wyoming	buchite	I-90**
50	Diopside		synthetic	$Di_{80}Hd_{20}$†
105	Pargasite	Pargas, Finland	marble	CIT 2573

Note: NMNH = National Museum of Natural History, Smithsonian Institution. CIT = California Institute of Technology Mineral Reference Collection.
* Duba et al. (1979).
** Foit et al. (1987).
† Dollase and Gustafsson (1982).

mechanisms of hydration reactions in pyroxenes, leading to intergrowths of biopyriboles. These sometimes very fine intergrowths can also occur in samples that appear to be unaltered in thin section. Such intergrown hydrous biopyriboles seem to give rise to sharp "amphibole" bands around 3670 cm^{-1} (Ingrin et al., 1989). The aims of this study are to explore the relationship between amphibole and pyroxene OH^- and to examine the stability of the various OH^- environments in pyroxenes.

EXPERIMENTAL PROCEDURES

Pyroxenes of different composition from various crustal origins have been studied (Table 1). Hydrothermal experiments were conducted at 1- to 2-kbar H_2O pressure to incorporate more OH^- in the pyroxene structure. They were performed at 600–800 °C using cold-sealed pressure vessels without addition of f_{O_2} buffers. Single-crystal samples were loaded into Au tubes together with at least double the sample weight of water and then crimped shut. In some cases, a small amount of silica was added to allow for alteration of the pyroxene to amphibole. In some experiments, the water was exchanged for a 1*M* NaOH solution, to increase the OH^- activity. A dilute HCl solution (1.8 vol%) was also tried.

Heating experiments both under H_2 and air at 1-atm pressure were conducted in a Lindberg tube furnace. The

TABLE 2. Structural formulae of pyroxenes obtained from electron-microprobe analyses

No.	2	12	13	21	28	35	29	25	8	18*
	Di	Di	Di	Di	Di	Es	Ae	Ae	Ae-Aug	En
	India	Norway	Ontario	Hawaii	Italy	Wyoming	Quebec	Arkansas	Arkansas	Texas
T site										
Si	2.006	1.997	1.981	1.710	1.801	1.360	2.007	2.002	1.986	1.815
Al	—	0.003	0.019	0.228	0.199	0.636	—	—	0.014	0.185
Fe^{3+}	—	—	—	0.062	—	0.004	—	—	—	—
	2.006	2.000	2.000	2.000	2.000	2.000	2.007	2.002	2.000	2.000
M(1) site										
Al	0.016	0.052	0.027	0.049	0.069	—	0.041	0.025	0.017	0.089
Fe^{3+}	—	0.036	0.068	0.183	0.081	0.601	0.804	0.760	0.622	0.071
Ti	—	0.002	0.001	0.062	0.032	0.029	0.010	0.030	0.014	0.014
Cr	—	0.001	0.001	—	0.002	—	—	0.001	0.001	0.001
Mg	0.916	0.824	0.485	0.706	0.739	0.339	0.016	0.053	0.182	0.825
Fe^{2+}	0.068	0.085	0.413	—	0.077	0.026	0.073	0.111	0.120	—
Mn	—	—	0.005	—	—	0.004	0.028	0.015	0.012	—
	1.000	1.000	1.000	1.000	1.000	1.000	0.972	0.995	0.968	1.000
M(2) site										
Mg	—	—	—	0.042	—	—	—	—	—	0.542
Fe^{2+}	0.001	0.041	—	0.013	0.045	—	—	—	—	0.386
Mn	0.002	0.001	0.020	0.004	0.004	—	—	—	—	0.006
Na	0.020	0.091	0.080	0.059	0.018	0.017	0.878	0.851	0.655	0.010
Ca	0.971	0.867	0.900	0.882	0.933	0.982	0.142	0.152	0.377	0.058
	0.994	1.000	1.000	1.000	1.000	1.000	1.020	1.003	1.032	1.000

Note: Site occupancies are dictated by the tetrahedral-site preference Si > Al > Fe^{3+}, except for sample 21 for which the Fe^{3+}/Fe^{2+} ratio and distribution are from Mössbauer spectroscopy. Element proportions were normalized to four cations. The values represent mean of 3 analyzed points on each sample. Optical spectra suggest that there is tetrahedral Fe^{3+} (see text) in samples 21, 28, and 35.
* Analysis from Duba et al. (1979).

TABLE 3. Results of hydrothermal experiments

T (°C)	*P* (kbar)	Time (d)	Additional components	Result*
			Diopside no. 2 (India)	
600	1.00	1	—	46% decrease of 3350 cm^{-1} 29% increase of 3450 cm^{-1}
750	2.00	7	—	shift (−11 cm^{-1}) of 3450 cm^{-1} and 10% increase 35% decrease of 3530 cm^{-1} 40% decrease of 3350 cm^{-1}
800	1.00	7	SiO_2	shift (−17 cm^{-1}) of 3450 cm^{-1} and 35% increase 75% decrease of 3530 cm^{-1} 50% decrease of 3350 cm^{-1}
700	2.00	3	HCl**	700% increase of 3675 cm^{-1} ("amphibole" band); after polishing, 30% stronger than the original intensity
600	1.00	1	D_2O	50% OH^-, 50% OD^-
700	2.00	1	D_2O	30% OH^-, 70% OD^-
			Diopside no. 12 (Norway)	
700	2.00	7	SiO_2	150% increase of 3640 cm^{-1} 58% decrease of 3530 cm^{-1} 100% increase of 3450 cm^{-1}
			Diopside no. 13 (Ontario)	
750	2.00	7	—	80% decrease of 3515 cm^{-1}; color change: green to brownish green
700	2.00	7	NaOH†	original OH^- bands absent; broad H_2O band

* Refers to the most prominant spectroscopic features in the OH^- region. Changes in the weaker features also occurred but are not tabulated.

** 24 μL of 1.8 vol% HCl was added to the 12-mg sample.

† 20 μL of 1*M* NaOH solution was added to the 19-mg sample.

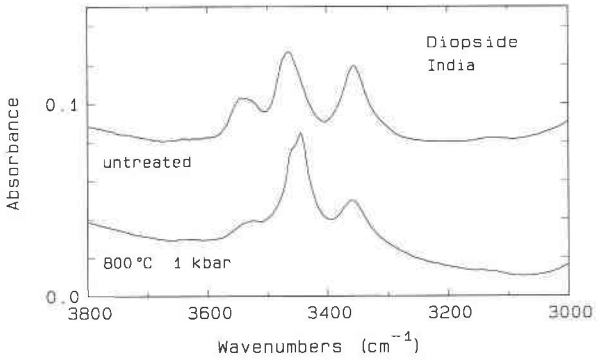

Fig. 1. Infrared absorption spectra of diopside no. 2 (India) in γ polarization, plotted for 1-mm thickness. Spectra were measured on a (010) section before and after hydrothermal treatment at 800 °C and 1-kbar H_2O pressure for 7 d.

samples were held in a porcelain boat. For the H_2 experiments, the tube was flushed with H_2 for 30 min before heating started.

Polarized infrared spectra were obtained in the three principal vibration directions using a Nicolet 60SX Fourier transform IR spectrophotometer and $LiIO_3$ polarizer. Prior to spectroscopic measurements, most samples were oriented by morphology and interference figures and then ground and doubly polished to an appropriate thickness. The esseneite sample (no. 35) was available only in very small grains and could not be oriented. The principal OH^- stretching motion around 3600 cm^{-1} was studied for all pyroxene samples. For an amphibole sample studied as a reference mineral, the first overtone at 7100 cm^{-1} was used, since the principal band usually will be off-scale for single-crystal measurements on amphiboles because of very strong absorption. Visible spectra were obtained with a Cary 171 spectrophotometer and $CaCO_3$ Glan-Thompson polarizer.

Chemical analyses were conducted with an automated, five-crystal-spectrometer JEOL 733 electron microprobe at 15 nA. Data were corrected using the program CITZAF (Armstrong, 1988) employing the absorption correction of Armstrong (1982), the atomic-number correction of Love et al. (1978), and the fluorescence correction of Reed (1965) as modified by Armstrong (1988). The structural formulae of the samples normalized to four cations are listed in Table 2.

RESULTS

Hydrothermal experiments

Three diopsides with different Fe amounts were used in hydrothermal experiments (nos. 2, 12, 13). IR spectra of diopside usually have four "pyroxene" absorption bands. After hydrothermal treatment at 600 °C and 1–2 kbar, the absorption intensities of two of the bands increased slightly, coupled with a decrease in intensity of the two other bands. The sum of the intensity of these four bands did not change when the hydrothermal experiments were performed in H_2O. The results of the hydrothermal experiments are summarized in Table 3. Polarized spectra of the India diopside before and after treatment at 800 °C and 2 kbar are shown in Figure 1.

The band at 3450 cm^{-1} became sharper and more intense at the expense of the two flanking bands. It also moved to lower wavenumbers and a shoulder appeared, suggesting that the original band was a composite. The observed changes occurred at temperatures and experimental durations where intracrystalline cation exchange is expected.

The India diopside was also hydrothermally treated in D_2O. Because of the larger mass of the D atom, the stretching frequency of the O–D dipole is lower (by a factor of about $1/\sqrt{2}$) than for an O–H dipole in the same environment. After treatment, new absorption bands occurred in the infrared spectra around 2600 cm^{-1} (Fig. 2). The intensity of the original bands around 3600 cm^{-1} decreased to the same extent, showing that exchange of D for H took place without change of the total amount of OH^- and OD^-. Heating at 600 °C and 1 kbar for 1 day exchanged about 50% of the OH^- for OD^-, whereas heating at 700 °C and 2 kbar for 1 day increased the exchange to about 70%.

To test the effect of pH on the OH^- stability, hydrothermal experiments were performed with HCl or NaOH

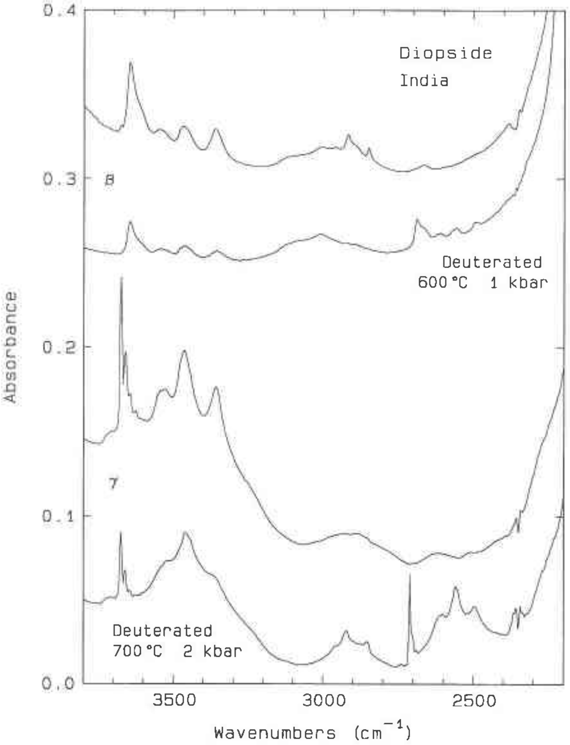

Fig. 2. Polarized IR spectra of diopside no. 2 before and after hydrothermal treatment in D_2O for 1 d. Spectra normalized to 1-mm thickness. Note the appearance of O–D stretching bands around 2600 cm^{-1} in the treated samples. The sharp peaks at 3675 cm^{-1} in the bottom two (γ) spectra correspond to the "amphibole-OH^-." β-spectra obtained on a (100) section, γ on a (010) section. Weak bands near 2850–2960 cm^{-1} are from organic contaminants.

Table 4. Heating experiments at 1 atm

Atm.	T (°C)	Time (h)	Result
			Diopside no. 2 (India)
1% H_2	600	6	60% decrease of 3350 cm^{-1}
H_2	600	6	10% increase of 3470 cm^{-1}
H_2	750	6	15% decrease of 3470 cm^{-1}, shift (−20 cm^{-1}) 50% decrease of 3350 cm^{-1}
H_2	825	6	20% decrease of 3350 cm^{-1}
Air	600	6	45% decrease of 3450 cm^{-1} 50% decrease of 3350 cm^{-1}
Air	700	14	3450 cm^{-1} and 3350 cm^{-1} absent
H_2	600	6	results from experiment in air at 600 °C (6 h) restored
H_2	700	6	results from experiment in H_2 at 825 °C (6 h) restored
			Different sample of diopside no. 2 (India)
Air, H_2*	1000, 700*	6, 6*	90% decrease of 3675 cm^{-1}, 3540 cm^{-1} absent 40% increase of 3470 cm^{-1}, shift (−20 cm^{-1}) 40% decrease of 3350 cm^{-1}
			Diopside no. 12 (Norway)
1% H_2	600	6	no major change
H_2	600	6	40% increase of 3640 cm^{-1}
H_2	750	6	40% decrease of 3540 cm^{-1}
H_2	825	6	30% increase of 3640 cm^{-1} 60% decrease of 3540 cm^{-1}
Air	600	6	80% decrease of 3450 cm^{-1}, 3350 cm^{-1} absent
Air	700	14	3540 cm^{-1}, 3450 cm^{-1}, 3350 cm^{-1} absent
H_2	600	6	results from experiment in H_2 at 825 °C (6 h) restored
H_2	700	6	no change
			Diopside no. 13 (Ontario)
1% H_2	600	6	no change
H_2	600	6	no change
H_2	750	6	75% decrease of 3520 cm^{-1} 100% increase of 3440 cm^{-1}
H_2	825	6	3675 cm^{-1} (amphibole band) absent
Air	600	6	all bands absent
H_2	600	6	results from experiment in H_2 at 825 °C (6 h) restored
			Aegirine-augite no. 8 (Arkansas)
H_2	600	6	15% decrease of 3620 cm^{-1} (only band)
H_2	750	6	20% decrease of 3620 cm^{-1}
H_2	825	6	5% decrease of 3620 cm^{-1}
Air	600	6	band absent
H_2	600	6	3620 cm^{-1} 45% of original intensity
H_2	700	6	results from experiment in H_2 at 825 °C (6 h) restored 60% of original intensity

Note: For each mineral, the entries represent a sequence of successive experiments conducted on the same sample. 1% H_2 atmosphere included Ar as the carrier gas. Changes in intensities are given as a percentage of the intensity of the different bands in the previous experiment.

* Different sample. First heated in air at 1000 °C, then heated in H_2 at 700 °C.

added to the capsules. A diopside crystal treated in HCl at 700 °C and 2 kbar became covered by a thin white layer of fine-grained material. Needle-shaped crystals also grew along the *c* axis on the (001) surfaces. IR spectra showed that the amphibole band at 3675 cm^{-1} strongly increased. After removing the white layer and repolishing the sample, this absorption band was much less intense, suggesting formation of amphibole on the grain's surface by a dissolution and precipitation process. However, the amphbile band was about 30% stronger after repolishing than it was for the untreated sample, indicating that some transformation of pyroxene to amphibole also occurred in the interior of the crystal. Treatment in NaOH solution resulted in etch pits on the grain's surface and broadening of the OH^- absorption bands. A very broad band around 3400 cm^{-1} due to molecular water also appeared.

A subset of the hydrothermal experiments was conducted on the Fe-rich diopside no. 13 to test the effect of Fe substitution: treatment in H_2O decreased the absorption of all bands. A change in color from green to brownish green indicated that the sample was somewhat oxidized. Treatment in NaOH solution resulted in the disappearance of all the OH^- absorption bands, leaving only a broad liquid-H_2O band. The appearance of the sample indicated that it started to dissolve.

Heating experiments

Diopside and aegirine-augite. Three diopsides (nos. 2, 12, 13) and an aegirine-augite (no. 8) sample were subjected to heating experiments in H_2 at 1-atm pressure at successively higher temperatures (Table 4). The behavior of the India diopside (no. 2) was similar to that in the

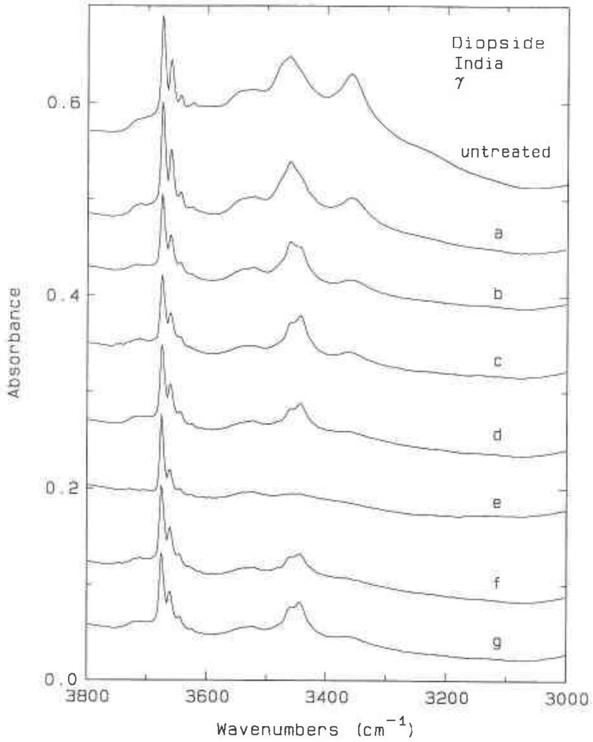

Fig. 3. Polarized γ spectra from 1-atm heating experiments conducted on the India diopside. All spectra normalized to 1-mm thickness. (a) H_2, 600 °C, 6 h; (b) H_2, 750 °C, 6 h; (c) H_2, 825 °C, 6 h; (d) air, 600 °C, 6 h; (e) air, 700 °C, 14 h; (f) H_2, 600 °C, 6 h; (g) H_2, 700 °C, 6 h. The spectra represent successive experiments performed on the same sample, showing changes in the "pyroxene" OH^- bands between 3300 and 3600 cm^{-1}. Crystal thickness 1.05 mm.

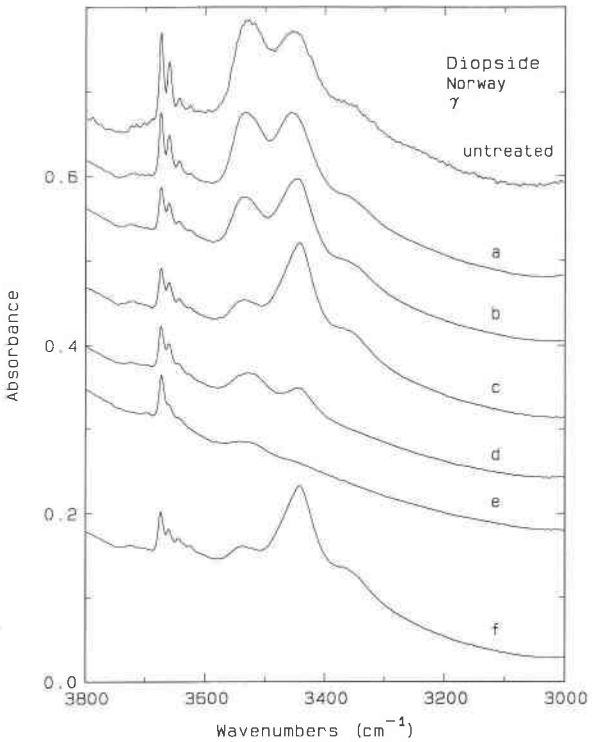

Fig. 4. Polarized γ spectra from 1-atm heating experiments conducted on the Norwegian diopside. All spectra normalized to 1-mm thickness. (a) H_2, 600 °C, 6 h; (b) H_2, 750 °C, 6 h; (c) H_2, 825 °C, 6 h; (d) air, 600 °C, 6 h; (e) air, 700 °C, 14 h; (f) H_2, 600 °C, 6 h. The spectra represent successive experiments performed on the same sample. Crystal thickness 0.61 mm.

hydrothermal experiments. The 3450 cm^{-1} peak became sharper and moved to somewhat lower wavenumbers. All bands decreased in intensity, with the flanking peaks decreasing faster (Fig. 3). One difference compared to the hydrothermal experiments is that the intensity of all peaks decreased after exposure to higher temperatures (750–825 °C). The Fe-rich diopside (no. 13) and the aegirine-augite samples also lost OH^--band intensity during heating in H_2. The Norwegian diopside (no. 12) had a similar behavior (Fig. 4), except that the band at 3645 cm^{-1} in the α direction became stronger, which also occurred in the hydrothermal experiments on this sample.

Samples heated in air showed a strong decrease in the pyroxene OH^- absorption bands. After heating at 600 °C for 6 h, all bands in the spectra of the Fe-rich diopside and aegirine-augite were absent, whereas the OH^- bands for the Fe-poor diopsides from India and Norway decreased. Further heating at 700 °C for 14 h removed most of the remaining bands in the diopsides, leaving only the "amphibole band" at 3675 cm^{-1}.

It was possible to restore the removed bands by heating the samples in a H_2 atmosphere. After 6 h at 600 °C, all the original OH^- bands returned, but with a lower intensity than before treatment. The "amphibole" band (3675 cm^{-1}) in the Fe-rich diopside sample (no. 13) did not reappear. Further heating in H_2 at 700 °C increased the absorbance for the Fe-poor diopsides but not for the Fe-rich diopside and the aegirine-augite. The bands did not return to the intensity they had in the untreated sample; they were restored, however, to approximately the intensity they had after the highest-temperature heating in H_2.

The reversibility of the OH^- bands in the India diopside was demonstrated by first heating a portion of the crystal in air for 6 h at 1000 °C to remove all the OH^- bands. After the fragment was heated in H_2 at 700 °C for 6 h, most of the bands were restored with intensities close to the natural sample, except for the "amphibole" band, which reappeared only weakly.

Ferrian diopside, esseneite, and aegirine. Ferrian diopside, esseneite, and aegirine show a different behavior from aegirine-augite and diopside when heated in the H_2 atmosphere. The two ferrian diopside samples (nos. 21, 28) that before treatment had a maximum absorbance of less than 0.10/mm were heated in H_2 at 700 °C. After heating, the absorbance of the strongest bands increased to 2.95/mm and 1.57/mm (Table 5, Figs. 5, 6). The esseneite sample also showed a strong increase in absorption (Fig. 7). Similar results were obtained for two aegir-

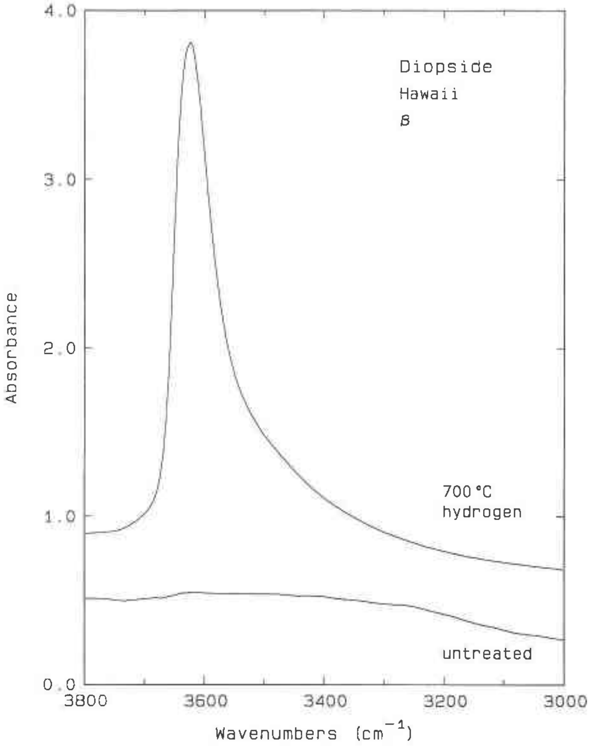

Fig. 5. Ferrian diopside (Hawaii) in β polarization, before (bottom) and after (top) heating in H_2 at 700 °C for 16 h, normalized to 1-mm thickness. Absorption intensities also increase in the other optical directions but to a lesser extent. Sample thickness 0.458 mm, (100) section.

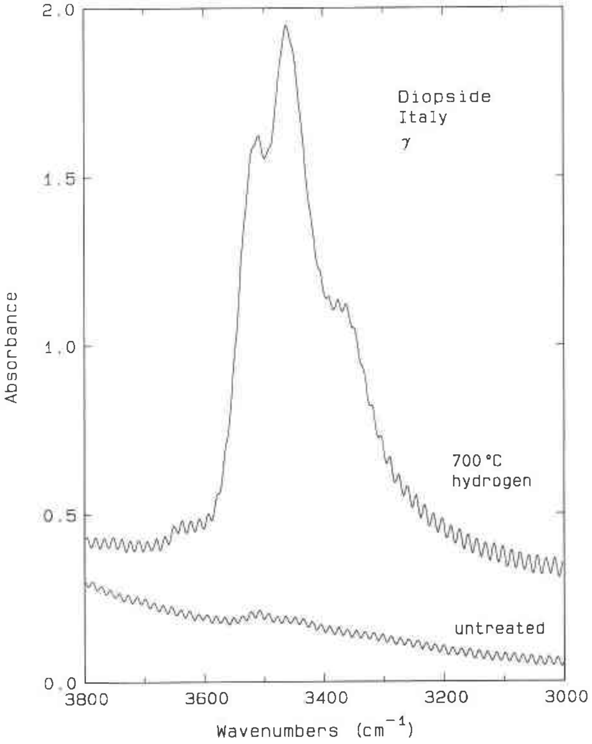

Fig. 6. Ferrian diopside (Italy) in γ polarization, before (bottom) and after (top) heating in H_2 at 700 °C for 6 h, normalized to 1-mm thickness. The absorption intensities increase weakly in the other optical directions. Sample thickness 0.20 mm, (010) section. The high-frequency sinusoidal modulation is due to interference fringes, not sample absorption.

ine samples (nos. 25, 29), but with a smaller increase in absorbance (Table 5). The absorbance for the H_2-heated samples is correlated with the Si deficiency of the samples (Fig. 8). Spectra obtained in the visible region for the ferrian diopside samples show that a weak Fe^{2+}_{M2} peak at 1020 nm increases after heating in H_2 (Fig. 9). For the Hawaii sample (no. 21), the increase of Fe^{2+}_{M2} was estimated to be 0.014 per formula unit using a molar absorptivity of $\epsilon = 40$ obtained from orthopyroxene data (Goldman and Rossman, 1979). The increase of OH^- was estimated to be 0.019 per formula unit using $\epsilon = 100$, which represents a mean value of OH^- absorptivity in minerals (Rossman et al., 1988; Skogby et al., in preparation). When the H_2-reduced samples were heated in air at 700 °C, the OH^- and Fe^{2+}_{M2} decreased (Fig. 10).

Orthopyroxene. An enstatite sample (no. 18) with a maximum absorbance of 0.25/mm at 3575 cm^{-1} was also heated in H_2. The heating procedure resulted in small variations in intensity between absorption bands but no total increase.

Synthetic clinopyroxene. In order to see whether OH^- also occurs in synthetic pyroxenes, a synthetic sample of $Di_{80}Hd_{20}$ composition (Dollase and Gustafson, 1982) was also studied. The spectrum of this sample as received showed a sharp "amphibole" (or talc) band at 3675 cm^{-1}. After the powder was heated in H_2, this band remained,

Table 5. Heating experiments at 1 atm

No.	Sample	Atm.	T (°C)	Time (h)	Result
21	Ferrian diopside (Kauai)	H_2	700	6	3620 cm^{-1} increases from 0.04 to 2.95 per mm
28	Ferrian diopside (Italy)	H_2	700	6	3460 cm^{-1} increases from 0.08 to 1.57 per mm
25	Aegirine (Arkansas)	H_2	700	6	3650 cm^{-1} increases from 0.03 to 0.05 per mm
29	Aegirine (Quebec)	H_2	700	6	3650 cm^{-1} increases from 0.03 to 0.07 per mm
18	Enstatite (Texas)	H_2	700	6	small variations, no total increase
50	Synthetic $Di_{80}Hd_{20}$	H_2	700	3	new peak at 3640 cm^{-1} (amphibole)
35	Esseneite (Wyoming)	H_2	700	20	3610 cm^{-1} increases from 0.05 to 2.40 per mm

Note: Only the strongest absorption bands are tabulated. Other bands also increase in intensity. H_2 atmosphere means 100% H_2 gas.

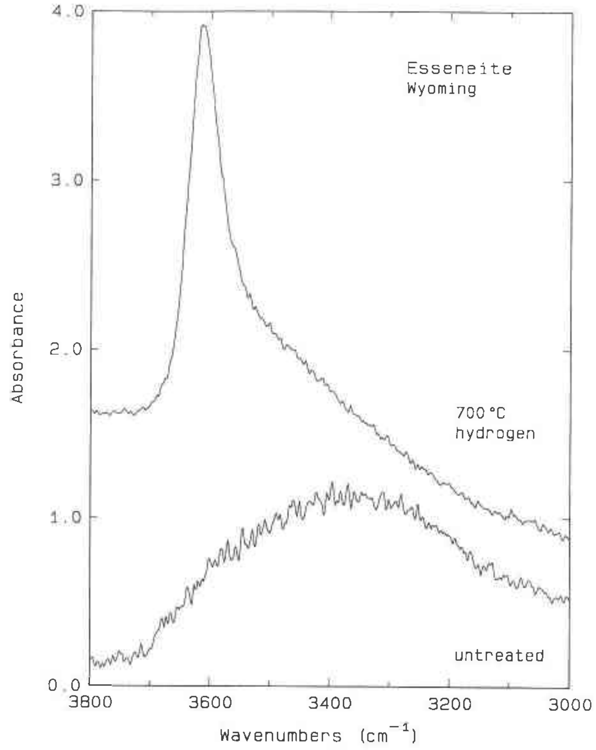

Fig. 7. Unpolarized IR spectra of esseneite (Wyoming) before (bottom) and after (top) heating in H_2 at 700 °C for 20 h. The very broad absorption centered around 3400 cm^{-1} is due to liquid water. Fluid inclusions could be seen in this sample under the microscope. Sample thickness 0.11 mm; orientation not determined. Spectra normalized to 1-mm thickness.

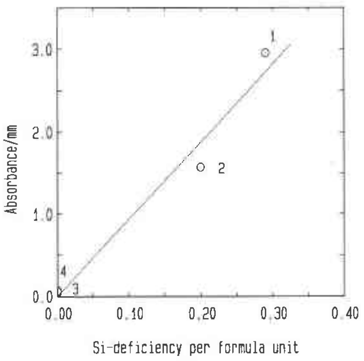

Fig. 8. Maximum absorbance of the principal optical directions for Fe^{3+} clinopyroxenes heated in H_2 at 700 °C, plotted versus Si deficiency in the tetrahedral site. Esseneite was not included because its maximum absorbance was not determined.

and a new sharp band at 3645 cm^{-1} appeared with slightly lower intensity, probably also due to amphibole. No lower-wavenumber "pyroxene" OH^- was detected.

Amphibole. A pargasite sample (Pargas, Finland, composition given in Goldman and Rossman, 1977) was heated in air at 700 °C. After 16 h, the OH^- vibrational overtone at 7200 cm^{-1} decreased to 70% of the original intensity (Table 6, Fig. 11). Heating for an additional 70 h further reduced the intensity to about 25%. After the final heating step, the color had changed from gray-green to reddish brown. Heating the oxidized amphibole in H_2 (at 700 °C for 20 h) increased the absorbance slightly and changed the color back to gray-green.

DISCUSSION AND CONCLUSIONS

Two mechanisms to increase the OH^- content of pyroxene crystals appear possible. The first involves alteration of pyroxene to amphibole or other hydrous phases and is detected by the appearance of "amphibole"-like OH^- bands in the 3700–3600 cm^{-1} region in the IR spectrum. The second mechanism involves diffusion of H^+ into the crystal to combine with O^{2-} at crystallographic positions in the pyroxene structure itself and gives rise to lower energy OH^- bands ("pyroxene"-bands) in the 3650–3300 cm^{-1} region of the IR spectrum. The first process requires the presence of SiO_2 for chemical balance according to the reaction pyroxene + SiO_2 + H_2O = amphibole. The second process has to be electrochemically balanced by cation substitutions, vacancies, or reduction and also requires a suitable environment for the OH^- ion in the pyroxene structure.

The hydrothermal experiments with pyroxene crystals in H_2O failed to increase the amount of "amphibole" OH^-. It is possible that the alteration of pyroxene to amphibole was prevented by kinetic effects and that experiments at higher temperatures and pressures where the amphibole is "more" stable would give other results. Only in the experiment using an HCl solution did the amphibole OH^- increase. This experiment showed that most of the amphibole formed on the grain's surface, but that some also formed in the interior of the crystal.

In no case was it possible to increase the amount of lower-wavenumber "pyroxene" OH^- in the pyroxene crystals by hydrothermal treatment. The minor relative variations in absorbance among bands detected for all samples can be due either to redistribution of the OH^- ions or intracrystalline cation exchange, which would change the local OH^- environments. The D_2O experi-

TABLE 6. Heating experiments at 1 atm on amphibole

Atm.	*T* (°C)	Time (h)	Result	Final color
—	—	—	7200 cm^{-1} band intensity 100%*	gray-green*
Air	700	16	7200 cm^{-1} decrease to 70%	brown
Air	700	70	7200 cm^{-1} decrease to 25%	reddish brown
H_2	700	20	7200 cm^{-1} increase to 30%	gray-green

Note: The entries represent a sequence of successive experiments conducted on the same sample [sample no. 105—pargasite from Finland (CIT 2573)].

* Natural, untreated sample.

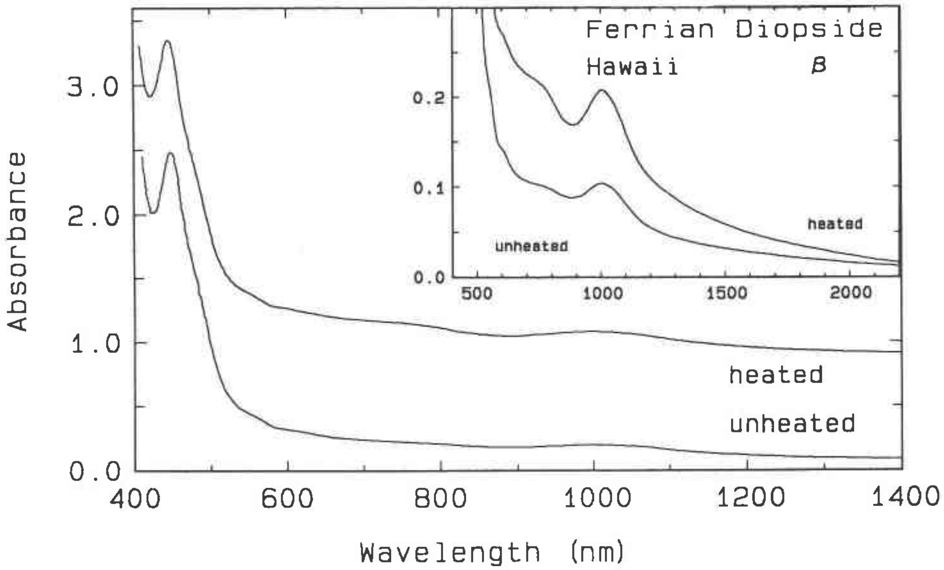

Fig. 9. Spectra of ferrian diopside (no. 21, Hawaii) in β polarization before and after heating in hydrogen at 700 °C for 6 h. The Fe$^{2+}_{M2}$ band at 1020 nm increases during treatment. The band at 450 nm has been assigned to tetrahedral Fe^{3+} (Bell and Mao, 1972). The y scale has been expanded in the inset figure. Plotted thickness: 100 μm.

ments show that the diffusion of D$^+$ through the crystal, which should be very similar to H$^+$, is not a rate-limiting process for the incorporation of OH$^-$ in pyroxene. Thus, it is clear that a more fundamental change than just a mechanical introduction is required to incorporate OH$^-$ in the pyroxene structure.

The heating experiments on diopsides and aegirine-augite in H$_2$ at 1-atm pressure resulted in a decrease in OH$^-$-band intensities. Similar results from reducing experiments on micas have been interpreted as dehydration by condensation of two OH$^-$ ions, leaving O^{2-} and a vacancy while H$_2$O diffuses out of the crystal. Such a reaction does not involve reduction. It is not known if this process in pyroxenes is also coupled with cation vacancies as is the case in biotites (Vedder and Wilkins, 1969). In hydrothermal experiments, this process may be prevented by the high H$_2$O activity.

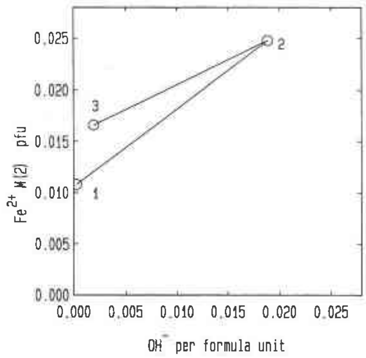

Fig. 10. Amount of Fe$^{2+}_{M(2)}$ plotted versus amount of OH$^-$ for the Hawaii ferrian diopside. (1) Untreated sample. (2) Heated in H$_2$ at 700 °C for 16 h. (3) Heated in air at 700 °C for 16 h.

The Fe^{3+}-rich, Si-deficient pyroxenes (ferrian diopside nos. 21 and 28 and esseneite no. 35) showed a strong increase in OH$^-$-band intensity after heating in H$_2$. Moreover, the increase is correlated with the silica deficiency at the tetrahedral sites (Fig. 8). Some of this deficiency seems to be compensated by Fe^{3+}. Optical spectra of these samples all have a band at 450 nm, which has been assigned to tetrahedral Fe^{3+} (Bell and Mao, 1972). The microprobe analysis suggests that the esseneite contains some tetrahedral Fe^{3+}. The assignment of Fe^{3+} to the tetrahedral site in these three samples is further supported by Mössbauer spectroscopy obtained by M. D. Dyar on the Hawaii sample, which show that 24% of total Fe is tetrahedrally coordinated Fe^{3+} (Fig. 12, Table 7). The amount of Fe^{3+} that replaces Si might be somewhat higher than the calculated distribution of cations shows (Table 2), since some disordering of Fe^{3+} and Al among the M(1) and the tetrahedral site can be expected at high temperatures (Ghose et al., 1986). The Mössbauer analysis suggests that this is the case for the Hawaii diopside (no. 21).

The strong OH$^-$ absorptions in the infrared spectra of the H$_2$-treated ferrian diopsides and esseneite are more intense than those we found in any natural, untreated sample. This suggests that ferrian diopside and esseneite have a comparatively high concentration of environments suitable for the OH$^-$ ion. These environments seem to be connected with tetrahedral Fe^{3+}. Heating in H$_2$ of samples without Fe^{3+} in these sites does not increase the OH$^-$ absorption. For example, optical spectra obtained from orthopyroxene (no. 18) and aegirine-augite (no. 8, cf. Amthauer and Rossman, 1984) show no evidence for

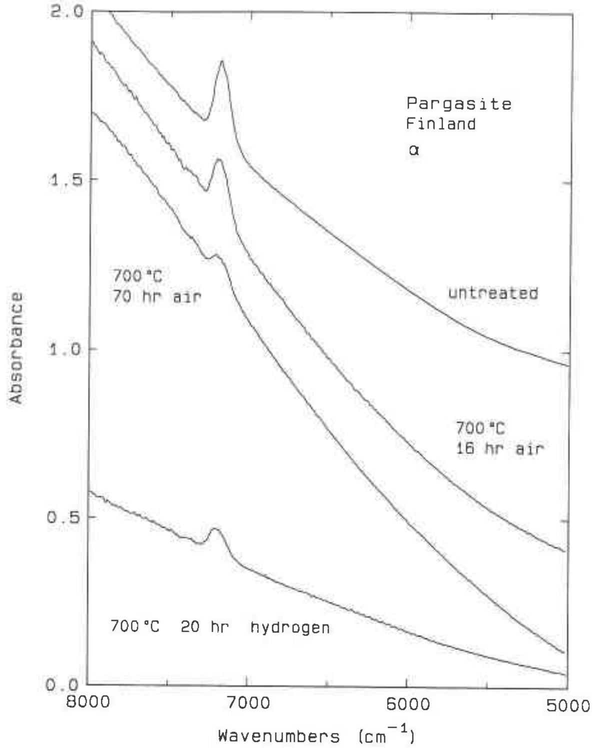

Fig. 11. Spectra of pargasite, α polarization after various heating experiments. The peak at 7360 cm^{-1} is an overtone of the principal OH$^-$ stretching band. Sample thickness 0.22 mm, (010) section. Spectra normalized to 1-mm thickness.

TABLE 7. Mössbauer parameters for ferrian diopside (no. 21)

Assignment	Isomer shift	Quadrupole splitting	Half-width	Area (%)
Fe^{3+} (T_d)	0.29	1.38	0.47	24.1
Fe^{3+} (O_h)	0.38	0.81	0.47	70.7
Fe^{2+} (O_h)	1.23	2.19	0.47	5.2

Note: Peak assignments from Bancroft et al. (1971), Akasaka (1983), and Dollase and Gustafson (1982).

tetrahedral Fe^{3+}, and heating experiments in H_2 on these samples did not increase their OH$^-$ band intensity.

The removal of OH$^-$ bands by heating in air and their restoration by heating in H_2 suggest that OH$^-$ is lost through an oxidation-dehydrogenation reaction of the type

$$Fe^{2+} + OH^- = Fe^{3+} + O^{2-} + \tfrac{1}{2}H_2,$$

which has been extensively studied in micas and amphiboles (Vedder and Wilkins, 1969; Addison et al., 1962). Support for both the forward (Fe^{2+} oxidation) reaction and the reverse reaction (Fe^{3+} reduction) is provided by the optical spectra, which show the decrease of and growth of Fe^{2+} bands with heating in air and H_2, respectively (sample no. 21, Fig. 10). The results indicate that there is a 1:1.4 Fe^{2+} to OH$^-$ stoichiometry for the oxidation-dehydrogenation reaction. With the uncertainty of molar absorptivities taken into account, the ratio could well be 1:1. The increase of Fe^{2+} in the M(2) position by reduction of Fe^{3+} is likely coupled with intracrystalline cation

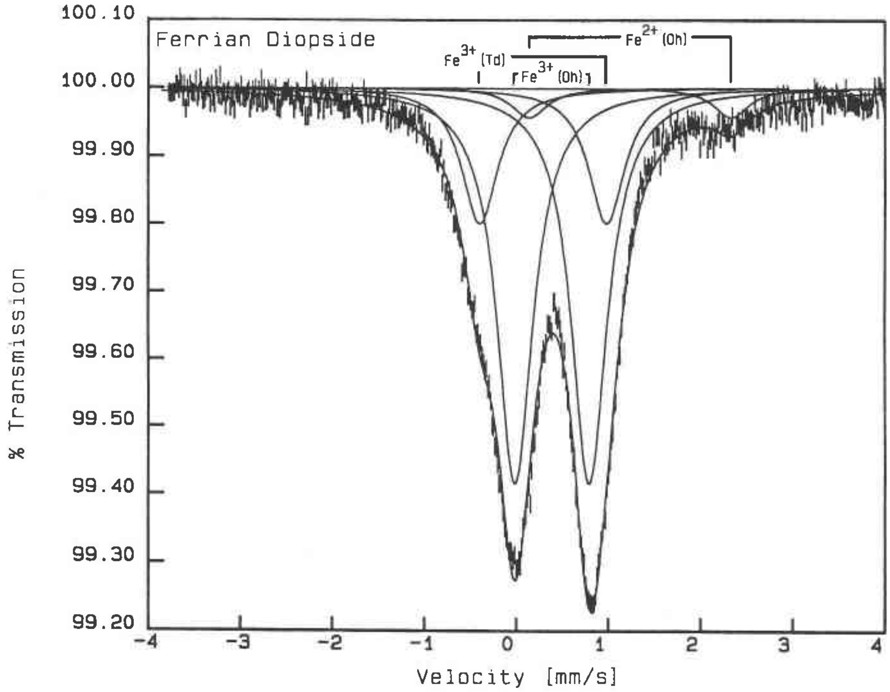

Fig. 12. Mössbauer spectrum of ferrian diopside no. 21 resolved into doublets from both tetrahedral and octahedral Fe^{3+} and octahedral Fe^{2+} (Table 7). Data provided by M. D. Dyar.

exchange, since Fe^{3+} cannot be expected to occupy the M(2) position. The simplest exchange reaction might include Fe^{3+} on the M(1) position:

$$Fe^{3+}_{M(1)} + Mg_{M(2)} + O^{2-} + \tfrac{1}{2}H_2 = Mg_{M(1)} + Fe^{2+}_{M(2)} + OH^-.$$

Exchange of Fe^{2+} and Mg among the M(1) and M(2) positions is known to occur in clinopyroxenes at the heating temperatures used in this study (McCallister et al., 1976).

The thermal stabilities of "amphibole" OH^- and "pyroxene" OH^- during heating in air are different. The "pyroxene" OH^- was lost in all diopsides during heating in air at 700 °C, whereas the "amphibole" OH^- was retained in Fe-poor samples. Pargasite heated under the same conditions also retained most of the OH^-. When samples heated in air were subsequently heated in H_2, the "pyroxene" OH^- was restored, whereas "amphibole" OH^- was not restored. These results suggest that the "amphibole" OH^- mainly is lost by the OH^- condensation process, which is not reversible under H_2 atmosphere. A complete loss of "amphibole" OH^- by the oxidation-dehydrogenation reaction cannot be expected for Fe-poor samples since the amount of OH^- is much higher than the amount of Fe^{2+}. For "pyroxene" OH^-, this reaction will proceed readily because the amount of OH^- is very much lower than the Fe content.

Because it is not possible to increase the amount of OH^- in most pyroxenes by heating them in a H_2 atmosphere, even for samples with a high Fe^{3+} content, there must be special local environments that facilitate the incorporation of OH^- in the Si-deficient Fe^{3+}-rich pyroxenes. These environments might include Si-Fe^{3+} substitutions and vacancies. It is possible that these samples had higher concentrations of OH^- during their crystallization, which was later lost by oxidation, since these samples all come from near-surface, highly oxidized environments (cf. no. 21, Johnston and Stout, 1984; no. 35, Foit et al., 1987).

Incorporation of OH^- in pyroxene during crystallization may be regarded as an equilibrium reaction where the nominally anhydrous pyroxenes respond to the H_2O activity of the environment. The stability of pyroxene OH^- is of great importance since stably bound OH^- might provide information regarding the activity of hydrous components when the pyroxene crystallized. During heating experiments, OH^- in pyroxene and Fe-rich amphibole show a similar stability. Since OH^- in Fe-rich amphibole is stable in nature, the small amounts of OH^- in pyroxene can also be expected to be stable. Our data suggest that OH^- does not easily enter the pyroxene structure after crystallization, unless OH^- has been removed by the oxidation-dehydrogenation reaction. Experiments addressing the kinetic properties of this reaction will provide useful information about the OH^- stability during cooling processes of magmatic and metamorphic rocks.

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REFERENCES CITED

Addison, C.C., Addison, W.E., Neal, G.H., and Sharp, J.H. (1962) Amphiboles: Part I. The oxidation of crocidolite. Journal of the Chemical Society, 1962, 1468–1471.

Akasaka, M. (1983) ^{57}Fe Mössbauer study of clinopyroxenes in the join $CaFe^{3+}AlSiO_6$ - $CaTiAl_2O_6$. Physics and Chemistry of Minerals, 9, 205–211.

Amthauer, G. and Rossman, G.R. (1984) Mixed valence of iron in minerals with cation clusters. Physics and Chemistry of Minerals, 11, 37–51.

Armstrong, J.T. (1982) New ZAF and a-factor correction procedures for the quantitative analysis of individual microparticles. In K.F.J. Heinrich, Ed., Microbeam analysis—1982, p. 175–180. San Francisco Press, San Francisco.

——— (1988) Quantitative analysis of silicate and oxide materials: Comparison of Monte Carlo, ZAF, and ϕ (ρz) procedures. In D.E. Newbury, Ed., Microbeam analysis—1988, p. 239–246. San Francisco Press, San Francisco.

Bancroft, G.M., Williams, P.G.L., and Burns, R.G. (1971) Mössbauer spectra of minerals along the diopside-hedenbergite tie line. American Mineralogist, 56, 1617–1625.

Bell, P.M., and Mao, H.K. (1972) Crystal-field determination of Fe^{3+}. Carnegie Institution of Washington Year Book 71, 531–534.

Beran, A., and Zemann, J. (1986) The pleochroism of a gem-quality enstatite in the region of the OH stretching frequency, with a stereochemical interpretation. Tschermaks Mineralogische und Petrologische Mitteilungen, 35, 19–25.

Clowe, C.A., Popp, R.K., and Fritz, S.J. (1988) Experimental investigation of the effect of oxygen fugacity on ferric-ferrous ratios and unit cell parameters of four natural clinoamphiboles. American Mineralogist, 73, 487–499.

Dollase, W.A., and Gustafson, W.I. (1982) ^{57}Fe Mössbauer spectral analysis of the sodic clinopyroxenes. American Mineralogist, 67, 311–327.

Duba, A., Dennison, M., Irving, A.J., Thornber, C.R., and Huebner, J.S. (1979) Electrical conductivity of aluminous orthopyroxene. Abstract. Tenth Lunar and Planetary Science Conference, p. 318–319. Lunar and Planetary Institute, Houston, Texas.

Foit, F.F., Hooper, R.L., and Rosenberg, P.E. (1987) An unusual pyroxene, melilite, and iron oxide mineral assemblage in a coal-fire buchite from Buffalo, Wyoming. American Mineralogist, 72, 137–147.

Ghose, S., Okamura, F.P., and Ohashi, H. (1986) The crystal structure of $CaFe^{3+}SiAlO_6$ and the crystal chemistry of Fe^{3+}-Al^{3+} substitution in calcium Tschermak's pyroxene. Contributions to Mineralogy and Petrology, 92, 530–535.

Goldman, D.S., and Rossman, G.R. (1977) The identification of Fe^{2+} in the M(4) site of calcic amphiboles. American Mineralogist, 62, 205–216.

——— (1979) Determination of quantitative cation distribution in orthopyroxenes from electronic absorption spectra. Physics and Chemistry of Minerals, 4, 43–53.

Hawthorne, F.C. (1981) Crystal chemistry of the amphiboles. In P.H. Ribbe, Ed., Amphiboles and other hydrous pyriboles—Mineralogy. Mineralogical Society of America Reviews in Mineralogy, 9A, p. 1–102.

Ingrin, I., Latrous, K., Doukhan, J.C., and Doukhan, N. (1989) Water in diopside: An electron microscopy and infrared spectroscopy study. European Journal of Mineralogy, in press.

Johnston, A.D., and Stout, J.H. (1984) A highly oxidized ferrian salite-, kennedyite-, forsterite-, and rhönite-bearing alkali gabbro from Kauai, Hawaii, and its mantle xenoliths. American Mineralogist, 69, 57–68.

Love, G., Cox, M.G., and Scott, V.D. (1978) A versatile atomic number correction for electron-probe microanalysis. Journal of Physics D, 11, 7–27.

McCallister, R.H., Finger, L.W., and Ohashi, Y. (1976) Intracrystalline Fe^{2+}-Mg equilibria in three natural Ca-rich clinopyroxenes. American Mineralogist, 61, 671–676.

Reed, S.J.B. (1965) Characteristic fluorescence correction in electron-probe microanalysis. British Journal of Applied Physics, 16, 913–926.

Rossman, G.R., Rauch, F., Livi, R., Tombrello, T.A., Shi, C.R., and Zhou, Z.Y. (1988) Nuclear reaction analysis of hydrogen in almandine, pyrope and spessartite garnets. Neues Jahrbuch für Mineralogie Monatshefte, 172–178.

Veblen, D.R., and Bish, D.L. (1988) TEM and X-ray study of orthopyroxene megacrysts: Microstructures and crystal chemistry. American Mineralogist, 73, 677–691.

Veblen, D.R., and Buseck, P.R. (1981) Hydrous pyriboles and sheet silicates in pyroxenes and uralites: Intergrown microstructures and reaction mechanisms. American Mineralogist, 66, 1107–1134.

Vedder, W., and Wilkins, R.W.T. (1969) Dehydroxylation and rehydroxylation, oxidation and reduction of micas. American Mineralogist, 54, 482–509.

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