

SHORT COMMUNICATIONS

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Hydroxyl-stretching frequencies of serpentine minerals

IN this study factors affecting the hydroxyl-stretching modes of some serpentines are investigated. Previously (Yariv and Heller-Kallai, 1975) the relationship between some features of the 400 to 1400 cm^{-1} region of the spectra of these minerals and their structures was discussed.

Fig. 1 shows the 3200 to 4000 cm^{-1} region of spectra of representative samples that had been heated above 300 °C. Table I lists the observed frequencies and the ionic composition of the samples studied. This was calculated from chemical analyses on the basis of $\text{O}_{10}(\text{OH})_8$ per formula unit. When analyses were carried out on the microprobe only total iron could be determined.

Samples were examined in the form of KBr, KCl, NaCl, and CsCl discs of various concentrations, using a Perkin-Elmer 237 grating instrument. The samples were heated overnight at a range of temperatures up to 620 °C and cooled in a desiccator. Some of the samples were also heated at 200 °C under vacuum. The spectra obtained were independent of the alkali halide used. Discs heated in air to temperatures below 300 °C contained adsorbed moisture, but above this temperature the spectra were identical with those of corresponding samples heated in vacuum. Moreover, on heating above 300 °C no further changes occurred in the spectra up to the dehydroxylation temperature. All the hydroxyl-stretching bands persisted with the same relative intensity and disappeared

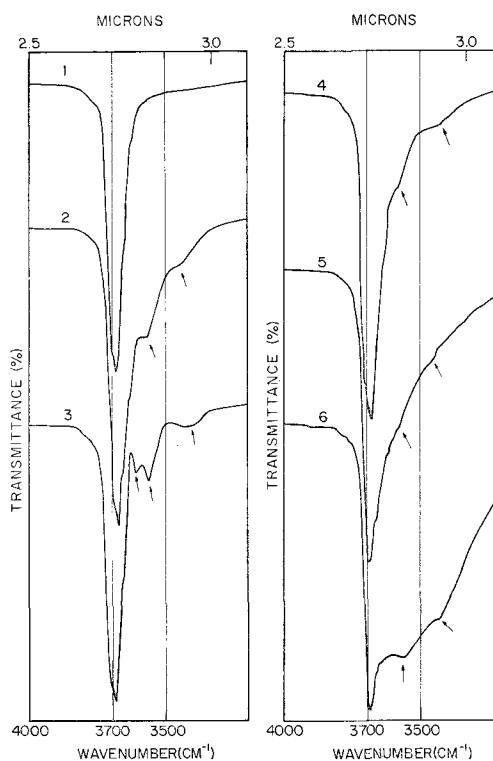


FIG. 1. The 3200 to 4000 cm^{-1} region of some serpentine minerals. KBr disks heated above 300 °C. 1, F14; 2, F15; 3, F47; 4, F19; 5, SG645; 6, SG361.

TABLE I. *Ionic composition and hydroxyl-stretching frequencies of some serpentine minerals*

		Ions in tetrahedral co-ordination			Ions in octahedral co-ordination				Hydroxyl vibration frequencies (cm ⁻¹)
		Si	Al	Fe	Mg	Al	Fe ²⁺	Fe ³⁺	
F8	(A) (1)	4.00	—	—	5.99	0.01	—	0.01	3702 w. sh., 3676, 3620 sh.
	(2)	4.09	—	—	5.73	—	0.01	0.01	
F14	(A) (1)	4.05	—	—	5.82	0.04	—	0.03	3702 w. sh., 3685, 3650 w. sh., 3620 w. sh.
	(2)	4.08	—	—	5.72	0.05	0.02	0.01	
F1	(A) (1)	4.01	—	—	5.76	0.15	—	0.08	3702 w. sh., 3676, 3655 w. sh., 3620 sh., 3570 sh.
	(2)	4.05	—	—	5.63	0.15	0.03	—	
F13	(A) (1)	4.04	—	—	5.63	0.04	—	0.24	3700 w. sh., 3688, 3650 w. sh.
	(2)	4.04	—	—	5.53	0.11	0.19	0.02	
HU176	(A) (1)	4.03	—	—	5.31	0.03	—	0.41	3700 w. sh., 3673, 3620 w. sh., 3585 sh., 3555 sh.
HU4050	(L) (3)	4.12	—	—	5.32	0.05	0.05	0.14	3695, 3650 sh.
F19	(A) (1)	3.94	0.06	—	5.67	0.13	—	0.30	3702 w. sh., 3685 sh., 3670, 3625 sh., 3565 sh., 3420 sh.
	(2)	4.05	—	—	5.20	0.21	0.38	0.03	
6 (2)	(1)	3.93	0.02	0.05	5.88	—	—	0.18	3690, 3650 sh., 3600 w., 3550 w., 3400 v. br.
F47	(L) (2)	3.87	0.13	—	5.68	—	—	0.27	3700 v. w. sh., 3688, 3655 w. sh., 3605 w., 3555 m., 3400 br.
HU904	(L) (3)	3.87	0.13	—	5.61	0.12	0.06	0.14	3700 w. sh., 3688, 3650 sh., 3570 sh., 3400 sh.
F15	(A) (1)	3.85	0.15	—	5.23	0.65	—	0.45	3700 v. w. sh., 3675, 3655 v. w. sh., 3640 v. w. sh., 3625 v. w. sh., 3565 m., 3435 br. sh.
	(2)	3.94	0.06	—	5.01	0.30	0.33	0.13	
HU11759	(L) (3)	3.76	0.24	—	5.32	—	0.20	0.40	3690, 3655 sh., 3570 br. sh., 3425 v. br. sh.
SG645	(L) (4)	3.51	0.49	—	5.80	0.26	0.05	—	3690, 3655 w. sh., 3625 v. w. sh., 3570, 3440 v. br.
SG361	(L) (4)	2.84	1.16	—	4.84	0.10	—	1.03	3685, 3655 w. sh., 3644 w. sh., 3570 s., 3440 v. br.

The strongest absorption band is italicized. v—very; w—weak; br—broad; sh—shoulder.

A—antigorite; L—lizardite.

(1) Microprobe analysis; (2) Analyst—Faust and Fahey (1962); (3) Analyst—Rahel Bilu; (4) Analyst—Geochemistry Division, Geological Survey of Israel.

Samples prefixed F are described in Faust and Fahey (1962).

Samples prefixed HU are from the mineral collection of the Hebrew University (HU176 Zermatt, Switzerland; HU4050 Cyprus; HU904 Nova Lima, Brazil; HU11759 Lizard, Cornwall).

6(2) Layered orthoserpentine, Unst, Shetland (O. Rushton).

SG645 Metamorphic rock, Samaria, Israel.

SG361 is representative of Al-rich serpentines from the 'Mottled Zone' Israel.

simultaneously at about 600 °C. It may therefore be concluded that samples heated in air above 300 °C or in vacuum at 200 °C are free from adsorbed moisture.

Luce (1971) contends that chrysotiles and lizardites differ from antigorites in the hydroxyl-stretching region. According to Luce chrysotile and lizardite show a strong band at 3690 cm⁻¹ and a medium one at 3640 to 3645 cm⁻¹, while the strong band in antigorites appears at 3680 cm⁻¹ and a band at about 3650 cm⁻¹ is either weak or absent. While this generalization appears to apply to the spectra of chrysotile and antigorite reported in the literature and in the present study, it is not necessarily correct for lizardite: e.g. samples F47, SG 645, and SG 361 show shoulders at 3650 cm⁻¹ that are no more pronounced than those in antigorite spectra.

An attempt to establish a correlation between the frequency of the bands and the

composition of the octahedral layer, similar to that in biotites (Wilkins, 1967), proved only partially successful. Veniale and van der Marel (1963) attributed a band at 3550 cm^{-1} in antigorite as opposed to one at 3650 cm^{-1} in chrysotile to the higher Fe content of the former. The data in Table I suggest that a shoulder appears at about 3560 cm^{-1} when substitution of trivalent ions is appreciable.

A striking correlation obtains between substitution in the tetrahedral sheet and the presence of a band at about 3400 cm^{-1} . This may be relatively sharp (fig. 1 (3)) or very broad, corresponding to a range of frequencies (fig. 1 (5)). It is absent whenever there is no isomorphous substitution in the tetrahedral sheet. In the samples available for the present study tetrahedral substitution was always associated with octahedral substitution. Luce (1971) reports the spectrum of a sample of chrysotile (Globe type F24) that has some Fe^{3+} for Si but no octahedral substitution; no appreciable absorption is observed near 3400 cm^{-1} . This suggests that both tetrahedral and octahedral substitution are required for such absorption.

A band in the 3400 to 3435 cm^{-1} region appears in the spectra of trioctahedral chlorites and septechlorites (e.g. Tuddenham and Lyon, 1959; Hayashi and Oinuma, 1967) and has been attributed to H bonding. Absorption in this region also occurs in the spectrum of an Al-rich serpentine reported by Jahanbagloo and Zoltai (1968); despite the presence of adsorbed water the difference between Al serpentine on the one hand and Mg serpentine and kaolinite on the other is evident.

It seems reasonable to attribute the absorption band at about 3400 cm^{-1} in serpentines to the formation of some hydrogen bonds. Other possible factors that must be considered are the presence of impurities such as 7 \AA chlorites and coupling and crystal field effects. Contamination of the antigorite samples examined can be excluded on the basis of the electron-probe analyses, which showed them to be homogeneous. Moreover, the IR spectra of the samples listed in Table I are entirely compatible with those of serpentine minerals reported in the literature. It is improbable that moisture should persist under the experimental conditions used, i.e. under vacuum at $200\text{ }^\circ\text{C}$ or on heating up to $600\text{ }^\circ\text{C}$ and, in addition, that it should be retained only by samples containing tetrahedral substituents. It also seems improbable that coupling should reduce the hydroxyl vibration frequency to a value as low as 3400 cm^{-1} . Crystal field effects due to octahedral substitution may be discounted as a decisive factor, since there is no correlation between the appearance of the band and the composition of the octahedral sheet.

It is plausible that substitution of trivalent ions in the tetrahedral and octahedral sheets, by increasing the polarity of the sheets, increases the delocalization of some hydrogen atoms. It was previously shown that tetrahedral Al for Si substitution in montmorillonite enhances the electron-donating ability of the basal oxygen sheets (Yariv and Heller, 1970). In view of recent studies, which have demonstrated that the interlayer bonding in diphormic minerals is largely electrostatic (Cruz *et al.*, 1972; Giese, 1973), further investigation of the effect of substitution in serpentine minerals seems to be of interest.

Whatever the assignment of the absorption band at 3400 cm^{-1} in serpentine spectra, its occurrence seems to be diagnostic for substitution in the tetrahedral sheet.

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REFERENCES

- CRUZ (M.), JACOBS (H.), and FRIPIAT (J. J.), 1972. *International Clay Conference Madrid*, **1**, 59.
 FAUST (G. T.) and FAHEY (J. J.), 1962. *U.S. Geological Survey Prof. Paper* **384A**.
 GIESE (R. F., Jr.), 1973. *Clays and Clay Minerals*, **21**, 145.
 HISOTA (H. I.) and OINUMA (K.), 1967. *Amer. Min.* **52**, 1206.
 JAHANBAGLOO (I. C.) and ZOLTAI (T.), 1968. *Ibid.* **53**, 14.
 LUCE (R. W.), 1971. *U.S. Geol. Survey Prof. Paper*, **750B**, 199.
 TUDDENHAM (W. M.) and LYON (R. J. P.), 1959. *Anal. Chem.* **31**, 377.
 VENIALE (F.) and VAN DER MAREL (H. W.), 1963. *Beitr. Min. Petr.* **9**, 198.
 WILKINS (R. W. T.), 1967. *Min. Mag.* **36**, 325.
 YARIV (S.) and HELLER (L.), 1970. *Israel Journ. Chemistry*, **8**, 935.
 — and HELLER-KALLAI (L.), 1975. *Clays and Clay Minerals*, in press.

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A nickel-bearing aluminium serpentine (septechlorite) from Western Australia

PERCUSSION drill samples from Woodline Well, Western Australia, reported up to 3.9 wt % Ni, but with no visible sulphide. Woodline Well is situated approximately 8 km west of the Poseidon-Western Mining Corporation nickel mine at South Windarra. The sulphide nickel at South Windarra lies within an Archaean ultramafic complex at the south-west contact within a banded iron formation. It has an east-west strike, dips 45° south and forms the westernmost part of the limb of a regional anticline, terminated by a granite intrusion. The intersection at Woodline Well probably represents the xenolithic remnants of an ultramafic, that once extended west from South Windarra. The drill chip samples came from the oxidized zone above the water table.

X-ray diffractographic examination of the samples indicated major quartz, 'serpentine', hornblende, and talc with minor feldspar, chlorite, and magnetite. A mineralogical examination detected no sulphide or discrete nickel component.

After screening, the plus 200 mesh fraction was subjected to methylene iodide heavy medium and magnetic separations. Nickel enrichment occurred in the light,