
ATTI ACCADEMIA NAZIONALE DEI LINCEI
CLASSE SCIENZE FISICHE MATEMATICHE NATURALI
RENDICONTI

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**Further studies on "deweylite" (samples from
Predazzo, Italy)**

*Atti della Accademia Nazionale dei Lincei. Classe di Scienze Fisiche,
Matematiche e Naturali. Rendiconti, Serie 8, Vol. **58** (1975), n.4, p. 618–627.*

Accademia Nazionale dei Lincei

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Mineralogia. — *Further studies on "deweylite" (samples from Predazzo, Italy)* (*). Nota di NORIS MORANDI e LUCIANO POPPI, presentata (**) del Socio P. GALLITELLI.

RIASSUNTO. — Viene presa in esame la tematica legata alla cosiddetta "deweylite", da molti Autori ritenuta una specie mineralogica a sé stante. I risultati di osservazioni eseguite al microscopio elettronico e stereoscan, alla diffrazione elettronica e all'infrarosso in aggiunta ai dati relativi a ricerche roentgenografiche, termiche e chimiche, permettono di escludere tale possibilità.

La cosiddetta "deweylite" risulta essere un termine del gruppo del serpentino, morfologicamente e strutturalmente correlabile con il clinocrisotilo. In particolare la diffrazione elettronica mette in evidenza un completo disordine traslazionale lungo l'asse *b* e che gli individui cilindrici sono in realtà degli aggregati di cristalli minori accartocciati parallelamente all'asse di allungamento del cilindro con un reticolo tendenzialmente elicoidale. La elevata percentuale di H_2O^- , presente nel minerale, risulta subordinata a uno squilibrio di cariche determinato da un difetto di posizioni occupate al centro degli ottaedri.

INTRODUCTION

Research carried out by Morandi and Poppi (1974) on samples of deweylite from Mezzavalle (Predazzo, Italy) revealed certain similarities between this mineral and the chrysotile member of the serpentine group. The similarity between the behaviour of deweylite and that of a sample of serpentine dry-ground for 12 hours suggested a possible interpretation of the abnormally high H_2O^- content of the former. However, the structural data were insufficient to support such a hypothesis, and so further research was undertaken on one of the samples of deweylite in the hope of obtaining more precise information about its structure.

The sample selected for examination was n. 4 of the series described by Morandi and Poppi (1974) since it was most representative (of its class) as regards chemical composition and thermal and X-ray patterns. The sample was examined by electron microscopy, infrared absorption spectroscopy and chemical tests.

RESULTS

Transmission and scanning electron microscopy.

Traditional methods for the observation of clay minerals under the electron microscope, using an AEI-EM6 instrument, showed that deweylite occurs in elongated crystals the edges of which are often irregular, particularly

(*) Research carried out in the Institute of Mineralogy and Petrography of the University of Bologna under the joint auspices of the CNR (Rome) and the Royal Society (London) and financed by a study grant made available to one of the Authors (N.M.) under the European science Exchange Programme.

(**) Nella seduta del 12 aprile 1975.

on the ends (Pl. I *a*). In the smaller crystals a central, more transparent zone, may be observed along the longitudinal axis, indicating a tubular morphology.

A few freshly broken fragments were examined in a scanning electron microscope, the Cambridge Stereoscan A 4. The scanning electron micrographs in Pl. II (*a* and *b*), show detail on the surface of deweylite at two different magnifications. It can be seen that the sample is made up radiated globular aggregates of very fine particles (Morandi and Poppi, 1974, p. 51). Individual crystals sticking out from the surface are cylindrical (in shape) and usually curved (Pl. II *b*, *c*).

In order to examine the surface at higher resolution, a carbon replica, preshadowed with platinum-carbon (Comer and Turley, 1955) of a freshly fractured surface was prepared and examined in the transmission microscope. Stereo-pairs were recorded by tilting the specimen 5° between successive exposures of the same field of view and these give a three-dimensional and detailed picture of the features previously described. Furthermore, some cylindrical crystals lying perpendicular to the plane of the photograph exhibit an internal cavity sufficiently large to be clearly visible (arrowed) (Pl. I *b*).

Electron Diffraction.

A large number of electron diffraction patterns were recorded from 6 different specimens. Al, evaporated on the specimen support, was used as a calibration in measuring *d*-spacings. The conclusions from a detailed analysis of 12 diffraction patterns are as follows:

- 1) all the electron diffraction patterns recorded from longitudinally well-developed crystals and other more rounded crystals exhibit reflections distributed on layer lines. The indexing of reflections and the orientation of the lattice (fig. 1) are same as are commonly reported for chrysotile;
- 2) $o\ 0\ l$ and $o\ k\ o$ reflections are present along the zero-layer line the former being very well defined and occurring at regular intervals, while the latter are split into pairs and more blurred;

3) $h\ k\ o$ reflections of the odd-order layer lines are distinctly split into pairs and blur in a long comet-like tail. The separation of reflections increases with *k*. The 110, 130, 330 reflections are often blurred in a circular manner so as sometimes to form almost complete rings which coincide with the 020, 040, and 060 positions although reflections in the 040 position of the zero-order layer line were never observed. The splitting of $h\ k\ o$ and $o\ k\ o$ reflections is not of the same proportions in all patterns, but is constantly present, that visible in Pl. II *d* being a typical example:

4) on the even-order layer lines $h\ o\ l$ and $h\ o\ \bar{l}$ spots are grouped in pairs about the intersections of an orthogonal network (fig. 1). In the even-order layer lines different reflections of lower intensity are also present and some diffractions show $h\ o\ l$ reflections which are so blurred as to form actual lineations;

5) in one diffraction $oo\ell$ and $o\bar{k}o$ reflections form triplets that are very close together and are orientated in the direction of the layer lines.

These observations agree with the findings reported in more recent literature on the electron diffraction of minerals of the serpentine group and they show that deweylite has a cylindrical monoclinic lattice with its longitudinal axis orientated towards α . Furthermore: the splitting of the diffuse $h\bar{k}o$ reflections into pairs indicates a helical configuration of the layers in a single fibril; the presence of supplementary reflections in the even-order layer lines would indicate a super lattice parameter in the c direction deriving either from slightly different translations in the α direction of corresponding

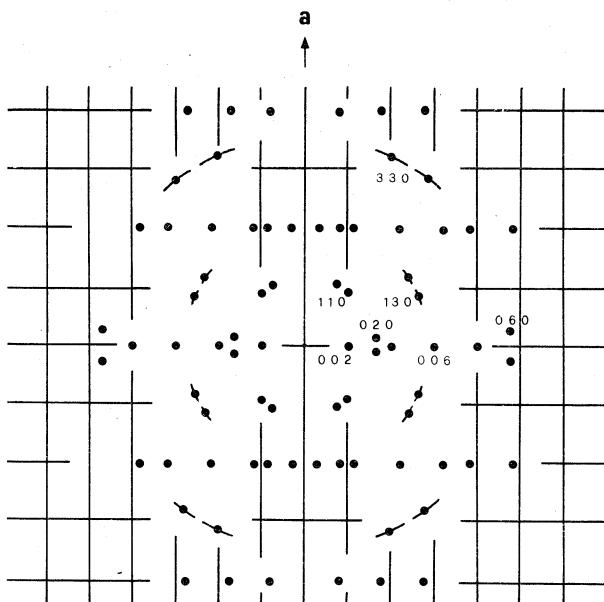


Fig. 1. - Electron diffraction scheme for deweylite from Mezzavalle (Predazzo).

atoms in adjoining layers (Zvyagin, 1967), or from the disordered sequences of A and B type layers, inverted with respect to the direction of the fibre axis (Gard, 1971); finally, the tail-like structures of the $h\bar{k}o$ and $o\bar{k}o$ reflections indicate a complete translational disorder in the b direction. In the case of deweylite, the patterns are characterized by fine structure which shows both the translational disorder in the b direction (supplementary reflections in the $h\bar{o}\ell$ layers) and the dispersion of axes α and b with respect to the fixed direction c (arcs in 110 , 130 , 330 reflections). This shows that the individual fibre of deweylite consists of a number of separate structural units helically disposed around the fiber axis and ordered mainly with the α direction parallel to the axis itself.

Measurements of the unit-cell dimensions were made from those patterns in which the relevant reflections were sharp and equally well defined on either side of the central beam spot; diffraction rings from evaporated Al were used for calibration. The measurements performed with the diffraction

pattern reader were compared with those obtained by direct projection the slide on to graph paper. The latter technique was particularly useful in assessing the quality of diffraction for it showed if the reflections were in the position predicted theoretically or if there were distortions. The results are follows: $a = 5.356 \pm 0.005 \text{ \AA}$; $b = 9.25 \text{ \AA}$; $c = 14.82 \pm 0.02 \text{ \AA}$. The b value is the least precise since the $o \cdot k \cdot o$ reflections are often blurred; c is shown with the value typical of a double cell (and not with possible other values that are multiples of 7 \AA) by analogy with what generally reported for monoclinic chrysotile. Fig. 1 shows a distribution scheme for the more intense reflections with the faithful reproduction of some of the fine structure in the electron diffraction patterns from deweylite sample n. 4.

Infra-red spectra.

The infra-red absorption spectra of the deweylite were recorded on a "Grubb-parson Spectromaster". Randomly oriented specimens were obtained by the potassium-bromide pressed-disk technique (Russell, 1974). Fig. 2 *a*, *b*, *c*, *d*, *e*, *f*, *g* show portions of spectra determined in the interval $4000\text{-}2000 \text{ cm}^{-1}$

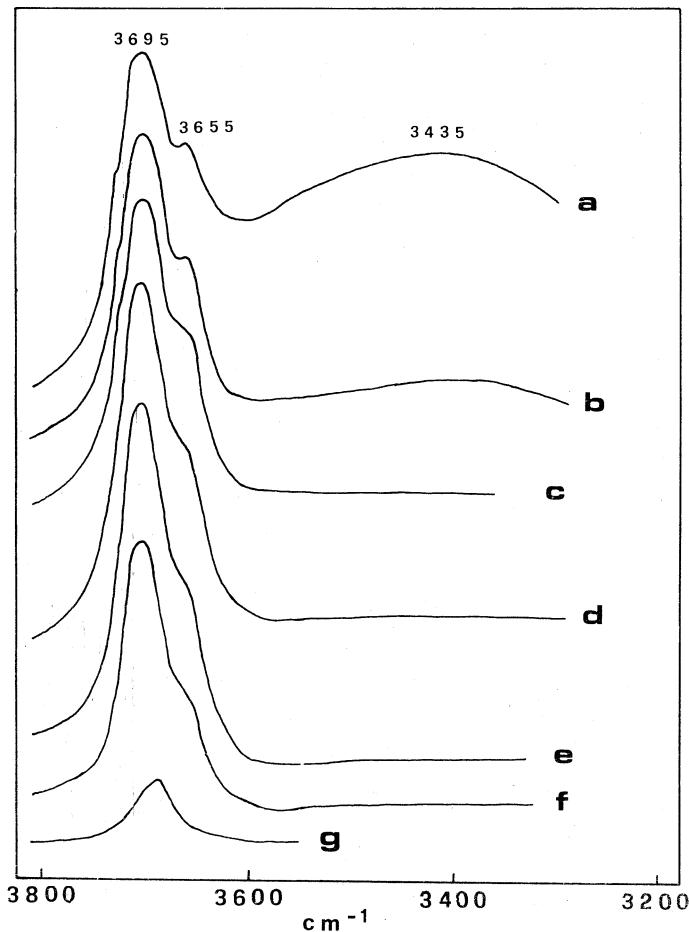


Fig. 2. — IR spectra of deweylite from Mezzavalle (Predazzo): *a*) natural; *b*), *c*), *d*), *e*), *f*), *g*) heated at 100°C , 200°C , 300°C , 450°C , 550°C , 600°C , respectively, for 20 hours.

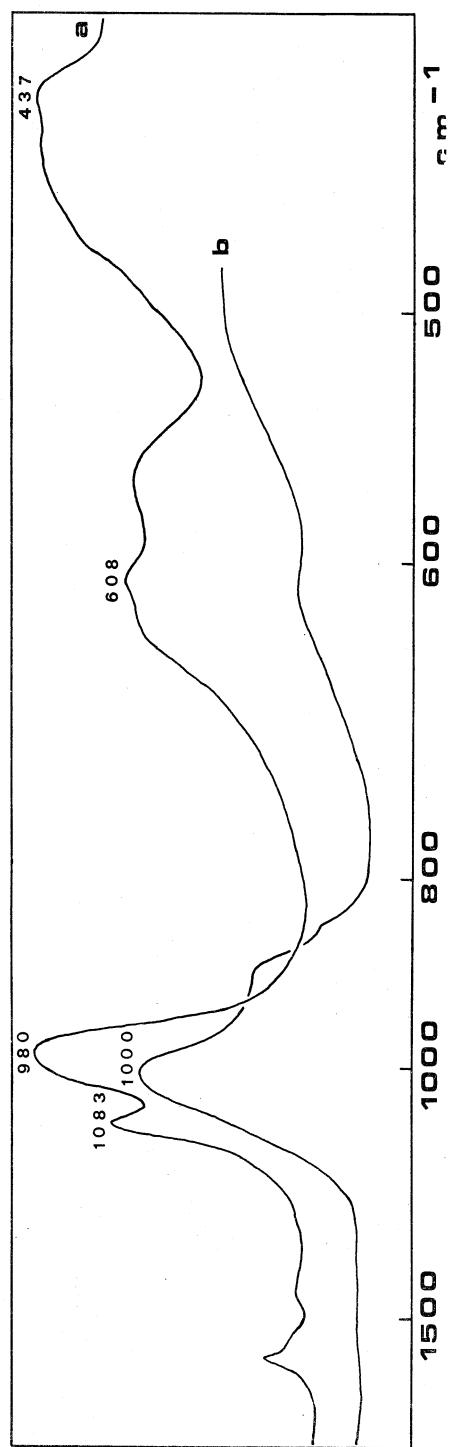


Fig. 3. – IR spectra of deweylite from Mezzavalle (Predazzo): a) natural; b) heated at 600°C for 15 hours.

on natural deweylite and then heated at 100 °C, 200 °C, 300 °C, 450 °C, 550 °C and 600 °C for a fixed time (20 hr). The natural sample shows two bands at 3695 cm⁻¹ and 3655 cm⁻¹, the latter being less intense than the former, and a third, extremely wide band at 3435 cm⁻¹. The first two can be ascribed to OH absorption and the third to water absorption; the latter disappears completely on heating to 200 °C, while the first two bands progressively diminish in intensity and they disappear completely at 600 °C to be replaced by a little band at about 3680 cm⁻¹. Fig. 3 shows the spectra determined in the interval 2000–400 cm⁻¹ on natural deweylite (*a*) and then heated at 600 °C for 15 hours (*b*). The spectra determined at intermediate temperatures do not differ significantly from that of the natural sample. The (*b*) spectrum, obtained with almost completely dehydroxylated material, exhibits peaks at quite different frequencies from those of the starting material owing to the complete re-arrangement of the bonds in the silicate layers. No band of the IR spectrum can be attributed to talc, by contrast with the findings of Speckman and Majundar (1971). The characteristics in the IR absorption spectra of natural deweylite are certainly covered by the wide range of variations distinguishing the different terms of the serpentine group (Brindley and Zussman, 1959; Luce, 1971; Pampuch and Ptak, 1970).

The results obtained from the deweylite in question can be utilised for the following remarks:

1) heating to temperature above 100 °C and subsequent dehydratation has particular effect upon the bande at 3655 cm⁻¹, which tends to shift to higher values and diminish in intensity. Furthermore, the band at 3695 cm⁻¹ diminishes in intensity at 550 °C and after heating at 600 °C disappears completely and is replaced by a residual band at 3680 cm⁻¹. These results are in good agreement with the thermal behaviour of deweylite reported by Morandi and Poppi (1974) and confirmed by a test conducted with a Du Pont thermobalance (fig. 4). This test was carried out on 11.41 mg of unpowdered deweylite, with the heating speed of 50 °C/min. Weight loss is in agreement with the data reported by Morandi and Poppi (1974). The DTG curve is important insomuch as it clearly distinguishes the various weight losses from one another: at 250 °C the loss of H₂O⁻ is complete; at 480 °C there is a loss of OH; at 690 °C the main loss of OH occurs; at about 840 °C there is a final, much reduced, loss of OH. From the foregoing it may be deduced that the lattice hydroxyls are retained by different bonding forces, corresponding to the three peaks appearing in the DTG curve above 250 °C.

If the variations found in the interval 3700–3650 cm⁻¹ of the IR spectra are compared with the thermal behaviour of deweylite, it may be deduced that:

a) the absorption band at 3655 cm⁻¹ can be associated with the OH of the octahedral layer which are in direct contact with the water molecules present in the mineral;

b) the band at 3695 cm⁻¹ can be associated with the remaining OH of the octahedral layer.

2) The dehydration process affects the absorption band at 3655 cm^{-1} corresponding to the vibration of one hydroxyl group, yet does not modify the frequency or the intensity of the band at 1083 and 980 cm^{-1} , which are associated with Si—O vibrations in the silicate layer. From this it may be deduced that the H_2O dipoles mainly face the hydroxyl group of the octahedral layer, which, as a result, is not completely neutral. This conclusion agrees with the chemical analysis reported by Morandi and Poppi (1974), which exhibits vacancies at the centre of the octahedra.

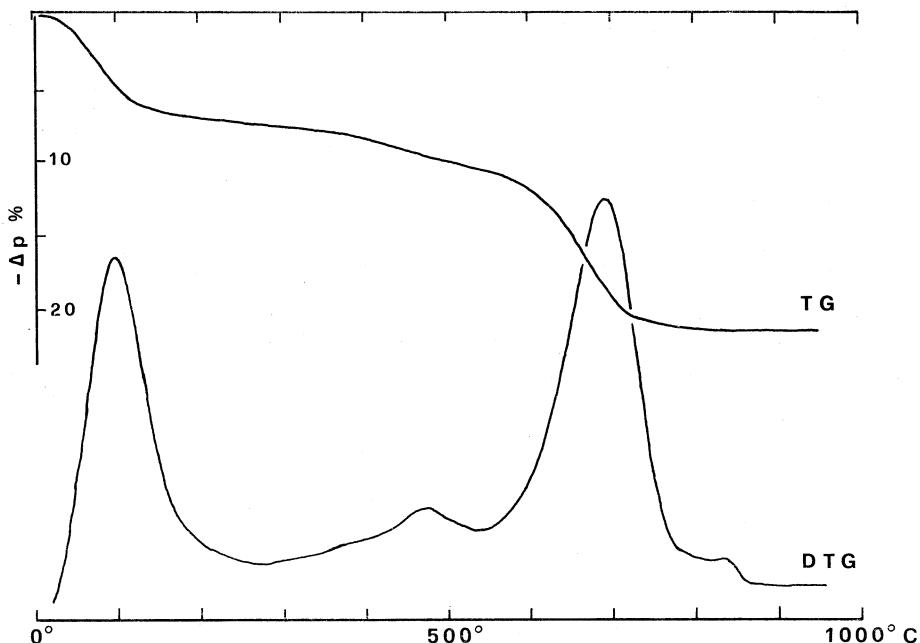


Fig. 4. -- TG and DTG curves of deweylite from Mezzavalle (Predazzo). Test carried out on 11.41 mg of unpowdered deweylite with the heating speed of $50\text{ }^{\circ}\text{C}/\text{min}$.

3) The natural deweylite spectrum resembles not only that of chrysotile and lizardite in the high-frequency area ($3800\text{-}3600\text{ cm}^{-1}$) but also that of antigorite in the $1100\text{-}400\text{ cm}^{-1}$ area. Comparison is made on the basis of the spectra and data supplied by Brindley and Zussman (1959), Veniale and Van der Marel (1963), Luce (1971) and Farmer (1947). Furthermore, the bands at 980 and 450 cm^{-1} , all of which can be attributed to Si—O bond vibrations in the silicate layer, are markedly broadened, this indicating that the tetrahedral layer is more disordered than that of others minerals of the serpentine group.

Chemical Investigation.

Table I shows the chemical analysis data of deweylite (sample n. 4) reported by Morandi and Poppi (1974). These data could give rise to the doubt that the excess of SiO_2 is due to the presence of non-crystalline silica,

TABLE I
Deweyleite n. 4 (Morandi and Poppi, 1974)

	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	FeO	MgO	MnO	CaO	Na ₂ O	K ₂ O	H ₂ O	Total
Chemical data	40.16	0.70	—	—	0.14	37.06	0.09	0.18	—	—	22.08	100.41

Structural formula [Mg_{5.64} Fe''_{0.01} Mn_{0.01} Al_{0.08}] [Si_{4.10}] O₁₀(OH)₈

that CaO content may take its place in the chemical formula as an effective component and, finally, that the sample may be nickeliferous by analogy with many other minerals of the serpentine group. The chemical investigation carried out afford a negative answer to all these doubts:

- 1) determination of free silica, following the method proposed by Follett, McHardy, Mitchell and Smith (1965), affords values which are so close to zero as to fall within the margin of error of the method;
- 2) microprobe determinations of Ca and Ni carried out on a flat section of the sample shows that the two elements are absent. Very probably the CaO of analysis is to be ascribed to calcite in veins which has polluted the sample in question.

CONCLUSIONS

The deweyleite from Mezzavalle has the chemical, X-ray and thermal characteristics that many Authors claim place it as a separate mineralogical species within the serpentine group (Selfridge, 1936; Sudo and Minato, 1949; Konta, 1952; Minato and Muraoka, 1958; Lapham, 1961; Masatomo and coworkers, 1971). However, the findings of the present study together with those already cited (Morandi and Poppi, 1974) clearly show that a close similarity exists between this mineral and the clino-chrysotile member of the same group, thus discounting the notion of a separate mineralogical species. This similarity is confirmed by the tubular morphology observed by transmission and scanning electron microscopy and by the electron diffraction data. It is thus possible to state that the lattice of the mineral in question is characterized by a complete translational disorder in the β direction; furthermore, it is seen that the individual fibres are in reality "bundles" of lesser crystals paked parallel to the longitudinal axis of the fibre each crystal having a helical lattice with α tending to be parallel to the longitudinal direction.

Comparison of the IR with the chemical and thermal data suggest an explanation for the hight percentage of H₂O⁻ present in the mineral and which is unusual for a 1 : 1 trioctahedral layer silicate: the H₂O dipoles mainly

opposite the hydroxyl group of the octahedral layer and their number is dependent on a charge imbalance caused by a defect of occupied positions at the centre of the octahedra; furthermore, the translational disorder of each crystalline component, the disorder in which these combine to form the various cylindrical units, the small size of the single crystals and, finally, the tubular morphology with ample internal cavity all contribute to increasing the surface activity of the material and to justify the high percentage of H_2O^- .

Data derived from a large number of electron diffraction patterns show the tubes vary markedly in their structural characteristics suggesting that each is an individual within the range of disordered chrysotile.

The "deweylite" from Mezzavalle, which is undoubtedly of hydrothermal genesis (Morandi and Poppi, 1974; Lapham, 1961), may therefore be considered of use in defining the vast range of conditions for genesis of chrysotile. If lattice order, like chemical composition, can be thought to depend directly on the temperature at which chrysotile is formed, further research into layer silicates in serpentine rocks may help to formulate a corrent genetic picture.

Acknowledgments. This study was carried out in the laboratories of the Macaulay Institute for Soil Research of Aberdeen in collaboration with the staff of the departments of Pedology and Spectrochemistry, to whom the Authors extend their warm thanks.

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