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ZINCIAN ACTINOLITE ASBESTOS

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A b s t r a c t. A naturally occurring Zn-rich amphibole has been investigated by optical, X-ray, electron probe and electron microscopic methods. It contains approximately 6 wt. % ZnO and is asbestiform in character. The asbestos fibrils show abundant Wadsley defects on (*010*) and multiple twinning on (*100*). Fibrils with an ordered triple chain structure have been observed.

INTRODUCTION

Fibrous amphiboles of unusual compositions have been synthesized (e.g. Fedoseev et al. 1970; Grigorieva et al. 1975) including some with major substitutions of Co, Cu, Zn and Pb. In naturally occurring amphiboles, although a wide variety of substitutions are found (mainly Mg, Fe, Al, Mn, Ti; Ca, Na and Si, Al) appreciable substitution by Zn is rather uncommon. One locality well known for unusual zinc minerals is that of Franklin, New Jersey, U.S.A. Amphiboles with high concentrations of Mn and Zn have been described from the skarn ore body from this locality, e.g. Palache (1928), Klein & Ito (1968), but apart from Zn-containing crocidolite (riebeckite asbestos; Palache, 1928), other Zn-amphiboles described are not asbestiform. The specimen of interest originates from the same locality and was obtained from the mineral collection of the Geology Department, University of Manchester. This zincian actinolite asbestos has been studied by optical microscopy, scanning and transmission electron microscopy, electron microprobe and X-ray powder and single crystal methods.

EXPERIMENTAL

O p t i c a l o b s e r v a t i o n s. In hand specimen the fibres are pale green and due to surrounding calcite appear stiff. Lightly crushed specimens when viewed under the optical microscope yield fibres the majority of which exhibit straight extinction; only a few fibres were found to show extinction angles ranging from 9° to 19°. Fibres exhibiting straight extinction can be interpreted as either composed of smaller fibrils in random orientation and/or multiply twinned on (*100*) or as single crystals lying on

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(*100*). The fibres tend to mat during grinding and do not separate easily, a behaviour characteristic of asbestos. The refractive index parallel to the fibres' length was measured as $n_{\gamma} = 1.634$.

S.E.M. Scanning electron microscopic observations revealed the character and morphology of this specimen. Fibres are closely packed in the bundle and do not appear to be easily separable (Phot. 1) as has been noticed also during optical observations. The micrographs give the impression that the fibrils have a somewhat rounded morphology. The widths of fibrils range from 0.1 to 0.5 μm. Fibres are not perfectly parallel in the bundle and frequently fibres lying across the main bundle were observed. A few bent fibres are visible on the micrograph shown (arrowed), an indication of flexibility.

X-ray diffraction. A small fibre (20 μm) was mounted on oscillation arcs in a "single crystal" X-ray goniometer. The X-ray photographs from a stationary (Phot. 2) and oscillating specimen are typical "fibre" photographs, and are equivalent to a rotation photograph from a single crystal. The reflections are in the form of arcs rather than spots, due to slight mis-orientation of the component fibrils in the bundle. This indicates that the small "fibre" examined is not a single crystal but consists of a number of smaller units, i.e. fibrils randomly oriented around the c-axis (fibres' length). This confirms the asbestiform nature of the specimen.

A diffractometer powder pattern was obtained using CuK_{α} radiation with scan speed of 1/2° (2Θ) /min. A least-squares computer program was used to obtain the cell parameters from the observed 2Θ (CuK_{α}) and *hkl* values using the 14 strongest reflections. Peak positions were measured with respect to those of quartz used as internal standard.

The cell parameters of the zincian-tremolite asbestos are:

a (Å) = 9.871 ±0.007
b (Å) = 18.153 ±0.01
c (Å) = 5.287 ±0.004
β (°) = 104.79 ±0.09
V (Å^3) = 915.99 ±0.7

and they are similar to those reported for Zn-rich tremolites and actinolites from the Franklin deposit by Klein & Ito (1968).

Chemistry. Table 1 gives the composition of the Zn-rich specimen examined by means of the electron microprobe; also it shows the ranges of cation content found for a number of fibres. The Zn content of 6 wt. % ZnO (0.7 atoms/formula unit) is unusually high in a natural amphibole. Al content is low and appears to be mainly $[Al]^6$. In some fibres increasing Mg content is accompanied by decreasing Fe. According to the I.M.A. classification (Leake, 1978) the specimen should be regarded as zincian actinolite asbestos.

Klein & Ito (1968) have suggested that in tremolite Zn occurs in M1, M2, M3 sites. Grigorieva et al. (1975) concluded that Zn preferably occupies M2 in fluor-richterites containing Ni^{2+}, Co^{2+}, Zn^{2+} and Mn^{2+}. The Zn site preference shown by Hawthorne and Grundy (1977) for zincian tirodite is $M1 > M3 \geq M2 > M4$. In the present case therefore, it is thought that Zn is most likely to occupy M1, M2, M3 along with Mg, Fe, Al.

There is a deficiency of Ca+Na in M4 and it is suggested that the Mn in excess of that needed to fill the octahedral sites will occupy M4. Finally, any excess of X cations above those needed to fill M4 can be accomodated in the amphibole A sites.

Transmission electron microscopy. The specimens prepared in the form of a suspension in de-ionized water were deposited on carbon coated copper grids and were studied using a Philips 400T transmission electron microscope operated at 120 KV.

Table 1

Zincian actinolite asbestos chemical analysis by electron microprobe (average of 6)

Oxides	Wt. % oxide	No. of cations (On basis of 23 oxygen equivalents)			Range	
SiO_2	55.144	Si	7.97	Z 8.00	Si	7.92 – 8.00
TiO_2	n.d.	Al^{IV}	0.03		Ti	0.00
Al_2O_3	0.732	Al^{VI}	0.09	Y 5.00	Al	0.09 – 0.19
*FeO	4.331	Fe	0.52		Fe	0.48 – 0.57
MgO	16.415	Mg	3.54		Mg	3.44 – 3.72
ZnO	5.982	Zn	0.64		Zn	0.60 – 0.70
MnO	3.302	Mn	0.40	X 2.00	Mn	0.35 – 0.43
CaO	10.577	Ca	1.64		Ca	1.54 – 1.69
Na_2O	0.954	Na	0.27	A 0.11	Na	0.20 – 0.35
K_2O	0.059	K	0.01		K	0.00 – 0.04
Total	97.496					

* Total iron as FeO; H_2O content not determined.

Many fibres exhibited multiple lamellar twinning on (*100*), made visible by diffraction contrast (Phot. 3) and also demonstrated by electron diffraction. The twin lamellae have thicknesses of approximately 220 Å.

High resolution lattice images of fibres in orientations with [*100*] or [*101*] parallel to the electron beam, revealed the presence (Phot. 4) of multiple chain – Wadsley defects on (*010*) frequently described for amphibole asbestos, e. g. Chisholm (1973), Hutchison et al. (1975), Veblen et al. (1977) and also in non-asbestos amphiboles e.g. Mallinson et al. (1980), Dorling and Zussman (1980). Electron diffraction patterns from areas with the defects showed streaking along b^* (Phot. 4, inset).

In some fibres "ordered" regions of triple and wider chains were observed e.g. (Phot. 5) and the corresponding electron diffraction patterns showed additional reflections appropriate to the larger b parameter (Phot. 5 inset).

It was observed that the defect areas rapidly suffered damage in the electron beam. The observed widths of fibrils are in the range 0.05 μm to 0.5 μm which appears to be consistent with S.E.M. observations, which indicate separation of fibres along their interfibrillar boundaries.

CONCLUSIONS

The results of all the methods of investigation employed here lead to the conclusion that this fibrous specimen of unusual chemistry is truly asbestiform in habit. Macroscopic fibres are built of fine fibrils (0.05 to 0.5 μm in width), with random azimuthal orientation around the z axis, some of which are multiply twinned.

The present investigation shows that in natural as well as in synthesized amphiboles, asbestiform habit is not restricted to the simple pure MgFe compositions; appreciable Zn can be present.

The fibrils show abundant planar (Wadsley) defects on (*010*) and some regions with ordered triple-chain structure have been observed. They also show the multiple twinning which is very characteristic of asbestiform amphiboles.

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AZBESTOWY AKTYNOLIT CYNKOWY

Streszczenie

Aktynolit cynkowy z Franklin, New Jersey (USA) poddano badaniom metodami optycznymi i rentgenowskimi, za pomocą mikrosondy elektronowej oraz transmisyjnego i scanningowego mikroskopu elektronowego. Stwierdzono, że aktynolit ten zawiera około 6% wag. ZnO i ma charakter azbestowy. Włókna wykazują liczne defekty Wadsleya według (*010*) oraz wielokrotne zbliźniaczenia według (*100*). W niektórych włóknach zaobserwowano obecność potrójnych łańcuchów krzemotlenowych.

OBJAŚNIENIA FOTOGRAFII

Fot. 1. Zdjęcie scanningowe ukazujące morfologię włókien aktynolitu cynkowego. Strzałkami zaznaczono wygięte włókna
Fot. 2. Rentgenowskie zdjęcie nieruchomego preparatu azbestowego aktynolitu cynkowego, uzyskane metodą pojedynczego kryształu
Fot. 3. Mikrofotografia elektronowa włókna azbestowego wykazującego zbliźniaczenia według (*100*), widoczne dzięki kontrastowi dyfrakcyjnemu
Fot. 4. Jednowymiarowy obraz sieci włókna aktynolitu cynkowego, uzyskany za pomocą wiązki równoległej do [*101*]. Widoczne 9 Å (*020*) wstęgi odpowiadają szerokości podwójnego łańcucha amfibolowego. Defekty Wadsleya (*010*) zaznaczono strzałkami
Wstawka: dyfraktogram elektronowy w kierunku [*101*] z refleksami rozmytymi równolegle do b^*
Fot. 5. a) Mikrofotografia elektronowa (dużej rozdzielczości) włókna azbestowego zawierającego wstawkę uporządkowanej struktury składającej się z potrójnych łańcuchów. Elektronogram odpowiada orientacji włókna. b) Powiększenie obszaru zaznaczonego na fot. 5a. c) Szkic dyfraktogramu elektronowego ukazanego na wstawce do fot. 5a, na którym uwydatniono słabsze refleksy. Wskaźniki dla normalnej komórki amfibolowej

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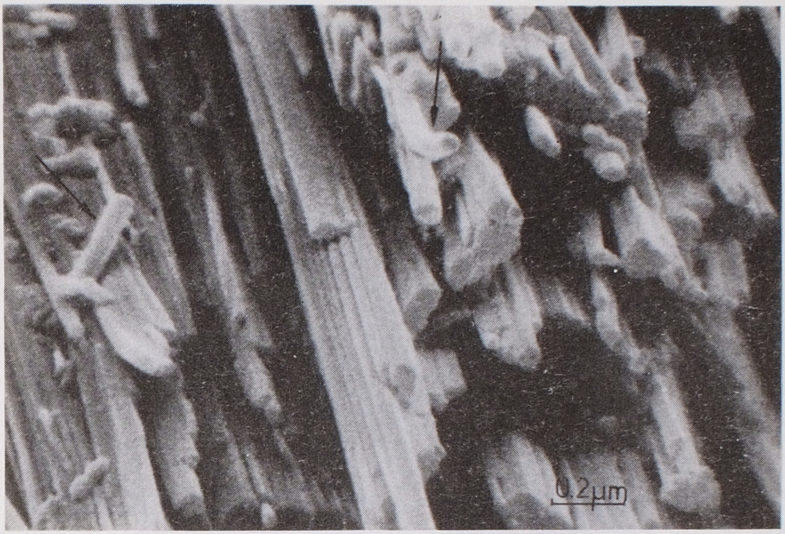
АСБЕСТОВЫЙ ЦИНКОВЫЙ АКТИНОЛИТ

Резюме

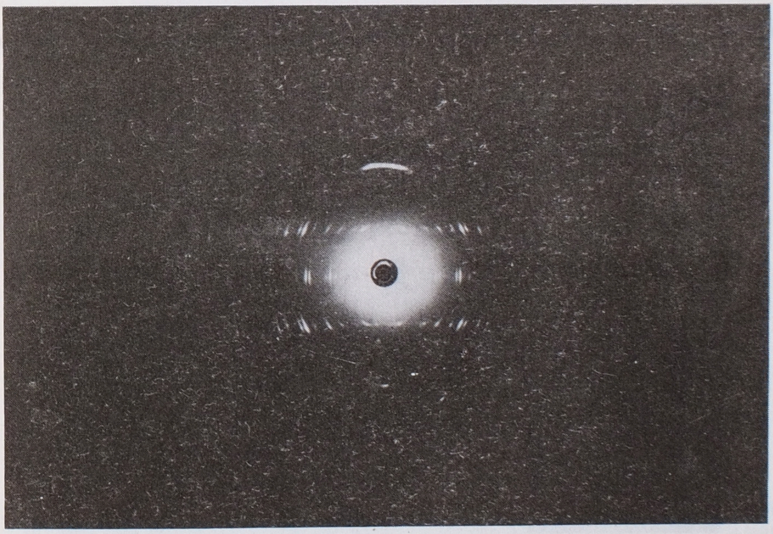
Цинковый актинолит из Франклина в штате Нью Джерси (США) исследовался оптическими и рентгеновскими методами, а также с помощью электронной микросонды и трансмиссионным и сканинговым электронными микроскопами. Установлено, что актинолит содержит около 6 вес. % ZnO и носит характер асбеста. В волокнах наблюдаются многочисленные дефекты Уодслея и полисинтетические двойники по (*100*). В некоторых волокнах наблюдалось присутствие тройных цепей кремнеокислов.

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Фото 1. Сканинговая микрофотография показывающая морфологию волокон цинкового актинолита. Стрелками обозначены выгнутые волокна
Фото 2. Рентгенограмма неподвижного препарата асбестового цинкового актинолита, полученная методом единичного кристалла
Фото 3. Электронная микрофотография асбестового волокна показывающая двойники по (*100*) видимые благодаря дифракционному контрасту
Фото 4. Одноразмерный образ решетки волокна цинкового актинолита, полученный с помощью пучка параллельного к [*101*]. Видимые "ленты" 9Å (*020*) соответствуют ширине двойной амфиболовой цепи. Дефекты Уодслея (*010*) обозначены стрелками.
Вставка: электронная дифрактограмма по направлению [*101*] с рефлексами размытыми параллельно b^*.
Фото 5. а) Электронная микрофотография (большой раздельной способности) асбестового волокна, содержащего "вставку" упорядоченной структуры, состоящей из тройных цепей. Электронограмма соответствует ориентировке волокна.
б) Увеличение участка, обозначенного на фотографии 5а. с) Эскиз электронной дифрактограммы, показанной на вставке к фотографии 5а, на которой подчеркнуты более слабые рефлексы.
Индексы для нормальной амфиболовой ячейки



Phot. 1. Scanning electron micrograph showing morphology of zincian actinolite fibres. Bent fibres are marked



Phot. 2. X-ray "single crystal" photograph of stationary specimen of zincian actinolite asbestos

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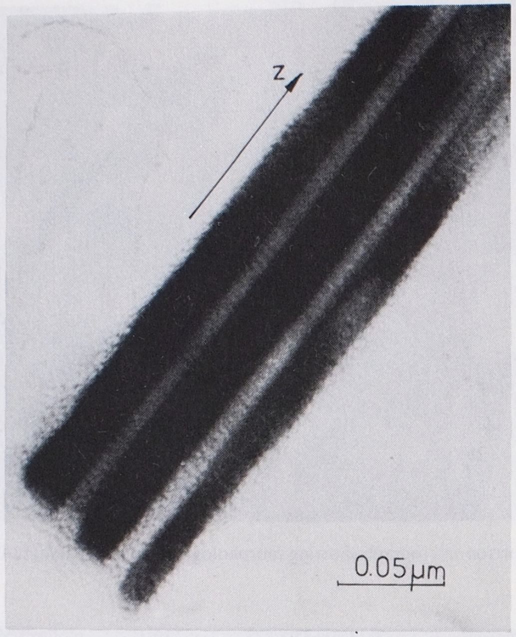
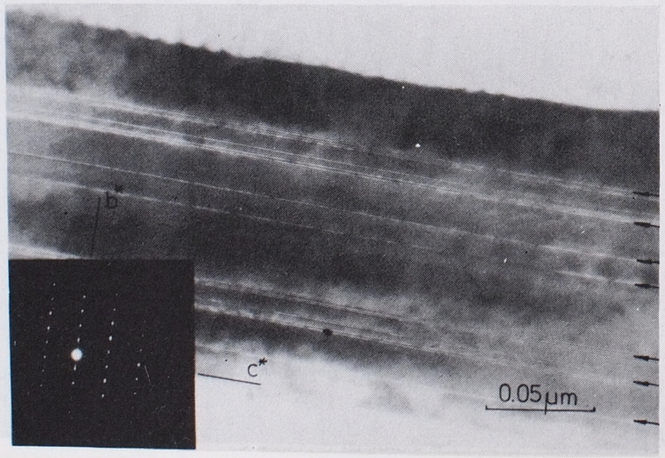
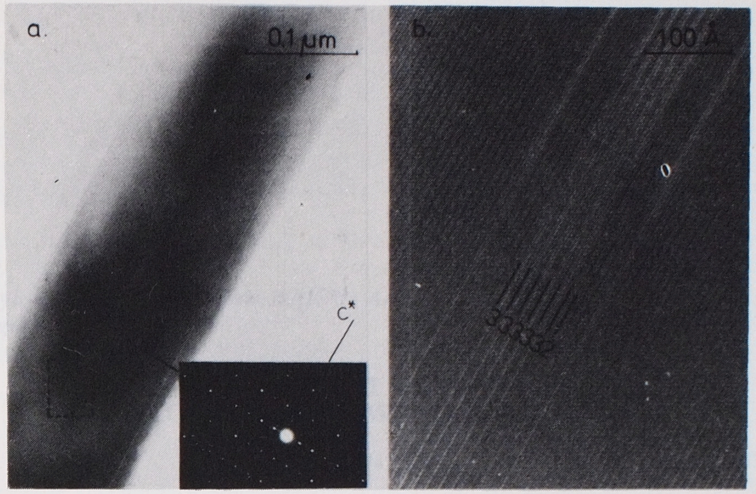
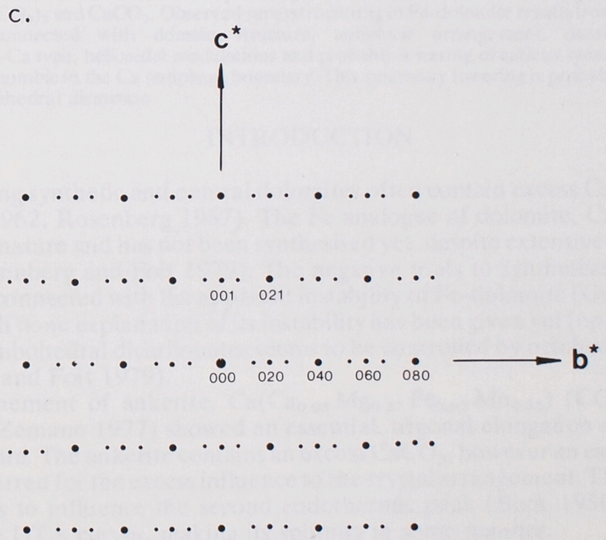


Phot. 3. Electron micrograph of asbestos fibre exhibiting (*100*) lamellar twinning by diffraction contrast



Phot. 4. One dimensional lattice image of Zn-actinolite fibre with the electron beam parallel to [*101*] 9 Å (*020*) lattice fringes correspond to an amphibole double chain width. Multiple chain Wadsley defects on (*010*) are marked
Inset: [*101*] electron diffraction pattern with streaking parallel to *b**.





Phot. 5. a) High resolution electron micrograph of asbestos fibre containing a slab of ordered triple chain structure with corresponding electron diffraction pattern. b) Enlargement of the area marked in 5a. c) Sketch of electron diffraction pattern as on inset enhancing the weaker reflections. Indices are for the normal amphibole cell.