MÖSSBAUER CHARACTERISTICS OF UICC* STANDARD REFERENCE ASBESTOS SAMPLES

G. STROINK, C. BLAAUW, C. G. WHITE AND W. LEIPER

Department of Physics, Dalhousie University, Halifax, Nova Scotia B3H 3J5

ABSTRACT

The UICC standard reference samples of chrysotile and amphibole asbestos were investigated at room temperature using ^{57}Fe Mössbauer spectroscopy. The Fe^{3+}/Fe^{2+} ratios determined agree with the results of previous chemical analyses. The Mössbauer spectra of the chrysotile samples show a complex central part due to the presence, in the structure, of Fe^{3+} at the Mg and Si sites and Fe^{2+} at the Mg sites. The spectra also show the Mössbauer lines characteristic of magnetite. No clear indication of magnetite could be found in the spectra of the amphibole samples; these spectra show several overlapping doublets with quadrupole splittings and isomer shifts typical of Fe^{2+} at the M_1, M_2, M_3 and M_4 positions in the structure and Fe^{3+} at the M_1, M_2 and M_3 positions. This assignment of the doublets is in agreement with previous Mössbauer investigations of minerals with analogous structures.

Keywords: Mössbauer, chrysotile, anthophyllite, amosite, crocidolite, asbestos, magnetite, Fe^{3+}/Fe^{2+} ratio.

SOMMAIRE

Les étalons UICC de chrysotile et d'amphibole asbestiforme ont été étudiés par spectroscopie Mössbauer ^{57}Fe à température ambiante. Les valeurs du rapport Fe^{3+}/Fe^{2+} ainsi déterminées concordent avec les résultats des analyses chimiques. Les spectres des échantillons de chrysotile montrent une portion centrale complexe due à la présence, dans la structure cristalline, de Fe^{3+} dans les positions du Mg et du Si et de Fe^{2+} dans celle du Mg; de plus, le spectre de la magnétite s'y superpose à celui du chrysotile. Par contre, la magnétite n'a pu être identifiée avec certitude dans les échantillons d'amphibole, dont les spectres montrent plusieurs doublets superposés, avec dédoublements du quadrupole et déplacements isomères caractéristiques de Fe^{2+} en M_1, M_2, M_3 et M_4 et Fe^{3+} en M_1, M_2 et M_3. Cette interprétation des doublets est conforme aux conclusions d'études Mössbauer antérieures portant sur des minéraux de structure analogue.

(Traduit par la Rédaction)

Mots-clés. Mössbauer, chrysotile, anthophyllite amosite, crocidolite, asbeste, magnétite, rapport Fe^{3+}/Fe^{2+}.

INTRODUCTION

The UICC has sponsored the preparation and distribution of the most common types of asbestos (Timbrell *et al.* 1968, Timbrell & Rendall 1972). The samples are known as the UICC standard reference asbestos samples. They include: (a) Canadian chrysotile, (b) Rhodesian chrysotile, (c) Finnish anthophyllite, (d) South African amosite and (e) South African crocidolite. These samples were created to provide researchers with samples of essentially the same composition upon which to investigate the properties of asbestos, using a wide range of techniques. Characteristics of the UICC samples, including chemical composition, size distribution and X-ray-diffraction spectra, have been well documented (Timbrell 1970, Rendall 1970), but there has been no systematic Mössbauer investigation. This paper presents the results of ^{57}Fe Mössbauer measurements made at room temperature.

EXPERIMENTAL

Two Mössbauer absorbers were prepared for each of the UICC samples. For the chrysotiles and anthophyllite, approximately 1 g was used for each absorber; for amosite and crocidolite, which contain more iron, approximately 0.20 g was used. This quantity of sample material was sufficient to characterize each UICC sample (Timbrell & Rendall 1972).

One of the two absorbers was prepared by pressing the asbestos fibres, with a length of the order of 10 μm (Timbrell 1970), firmly between two plastic discs 4 cm² in area. Such an absorber is typically a few millimetres thick. It is possible that under such circumstances some of the fibres orient themselves parallel to the discs. Such preferential orientation of

*Union internationale contre le cancer.

the crystals could influence the measurements. To ensure a random orientation of the fibres, we made a second absorber by pouring the asbestos fibres into a plastic container having a fixed area and a thickness of approximately 3 cm² and 4 mm, respectively. No force was used to compress the fibres. To detect any magnetite, commonly present in asbestos samples (Blaauw et al. 1979), we used the first absorber to measure the spectrum between −10 mm/s and + 10 mm/s. To increase the resolution of the central lines we used the second absorber to measure the spectrum between −3.5 and +3.5 mm/s. No difference could be observed in the central portion of the Mössbauer spectra of each asbestos sample prepared by using the two different methods, indicating that the fibres in the first absorber were also randomly oriented.

The spectra were obtained using a conventional constant acceleration drive-system and a 25 mCi Rh ^{57}Co Mössbauer source. Metallic iron was used to calibrate the spectrometer and to act as a reference standard for the isomer shift. The spectra were fitted by computer using a least-squares fitting procedure to obtain the best fit of the data to Lorentzian lineshapes. Where a doublet is present, the program assumes equal linewidths and intensities for both peaks. Other constraints used in fitting the spectra are discussed with each sample.

CHRYSOTILE ASBESTOS

The ideal chemical formula of chrysotile is $Mg_3Si_2O_5(OH)_4$. Some substitution of Fe and Ni for Mg and of Al for Si may take place. The structure consists of 2 two-dimensional sheets bonded together. The tetrahedral sheet consists of silicon–oxygen tetrahedra, SiO_4. The octahedral sheet consists of magnesium-bearing octahedra, similar to those in brucite $Mg(OH)_2$. The two sheets are bonded through the replacement of the apical oxygen of the tetrahedral sheet for two-thirds of the hydroxyl in the base of the octahedral sheet (Wicks 1979).

Recently the present authors carried out an investigation of chrysotile asbestos samples from four Canadian mining locations (Blaauw et al. 1979). The UICC material includes two chrysotile samples, Rhodesian chrysotile and Canadian chrysotile. The latter sample contains material from 8 mines, in quantities roughly proportional to their annual production. Half the material originates from the mining area around the town of Asbestos; the remainder comes from 7 other locations (Timbrell et al. 1968, Timbrell & Rendall 1972).

In Figure 1 the spectra of both chrysotile samples are shown. The general appearance of these spectra, which are fairly complex, is in agreement with results that were expected on the basis of our previous work. Part of the spectrum is due to magnetite particles contained in the samples. It is well known that the rock in which asbestos fibres are found often contains magnetite. During processing in the mills, small particles of magnetite become mixed in with the fibres, and the final asbestos product contains quantities of magnetite that can be considerable.

The Mössbauer spectrum of magnetite, Fe_3O_4, at room temperature contains two subspectra, corresponding to Fe in tetrahedral and octahedral sites. Because the magnetic moments associated with the Fe ions are ordered (ferro-
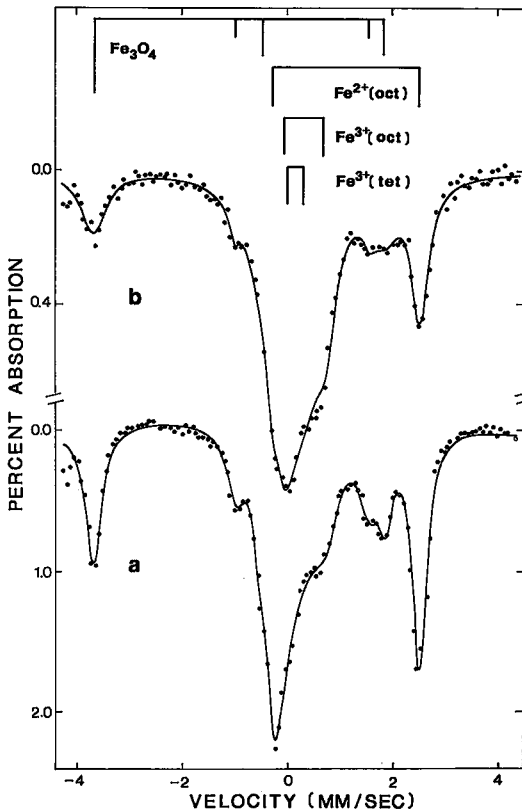

FIG. 1. ^{57}Fe Mössbauer spectra of UICC standard reference asbestos samples: (a) Canadian chrysotile, (b) Rhodesian chrysotile.

magnetically), each of the subspectra is Zee-mann-split into 6 peaks, so that a total of 12 lines are observed. The location of the lines is well known (Evans & Hafner 1969).

The central part of this spectrum appears in the spectra of the asbestos samples in Figure 1. Only a few lines appear because the measurements of the spectra in Figure 1 were plotted only at a smaller velocity range to show the complex spectra of chrysotile itself more clearly. In the computer analysis of the spectra, discussed in more detail below, the positions of the lines resulting from magnetite were held fixed at their known velocity values.

To analyze the lines corresponding to the chrysotile component of the spectra, we used the following procedure. In earlier work (Blaauw et al. 1979) we established that the spectrum of chrysotile consists of three doublets, two of them due to Fe^{3+} at the Mg and Si sites of the chrysotile structure, and one doublet due to Fe^{2+} at the Mg sites. It was found that, although the Fe^{3+}/Fe^{2+} intensity ratio varied considerably according to mining locations, the positions of the lines were not measurably affected by the changes in the Fe site-occupancy. Therefore, in the computer analysis of the chrysotile components of the spectra in Figure 1, we also kept the values of the velocities of the lines fixed at the previously determined values. Because of the complexity of the central part of the spectra, it is doubtful whether a meaningful improvement of the fits can be obtained by relaxing the restrictions imposed on the line positions.

In Figure 1 the coordination sites in chrysotile to which the doublets correspond are indicated, and in Table 1 we give the numerical isomer values of the parameters of interest in the spectra. The values of the isomer shift (IS) and the quadrupole splitting (QS) and the assignment of the two Fe^{3+} doublets to the Mg and Si sites were discussed by Blaauw et al. (1979). Here we comment on the Fe^{3+}/Fe^{2+} ratio in chrysotile and the amount of magnetite present in the two samples. From the last column in Table 1 we conclude that of the total amount of iron present in the UICC chrysotile, about half is in the form of magnetite and the other half is bound in the chrysotile. In our previous work we found the amount of iron in chrysotile to be in the range 1–1.5%. If this amount is the same for the chrysotile in the UICC samples, then it follows from our results that the total amount of iron in those

TABLE 1. MÖSSBAUER CHARACTERISTICS OF UICC STANDARD REFERENCE ASBESTOS SAMPLES

UICC Sample	Fe^{2+}(oct) IS	QS	Fe^{3+}(oct) IS	QS	Fe^{3+} IS	QS	$\dfrac{I_{Fe^{3+}}\text{(chrysotile)}}{I_{Fe}\text{(chrysotile)}}$ 0.05	$\dfrac{I_{Fe}\text{(magnetite)}}{I_{Fe}\text{(total)}}$ 0.05
Canadian chryso-tile	1.12	2.65	0.34	0.75	0.20	0.34	0.75	0.60
Rhodesian chryso-tile	1.12	2.65	0.34	0.75	0.20	0.34	0.85	0.50

Values of Mössbauer parameters are expressed in mm/s.

samples must be between 2 and 3%. This is in good agreement with the results of a neutron-activation analysis of the UICC samples, which gave values of 2.5 and 3% for Rhodesian and Canadian chrysotile, respectively (Rendall 1970).

Table 1 also shows the ratio of Fe^{3+} to the total Fe content of chrysotile, from which the corresponding Fe^{3+}/Fe^{2+} ratio is easily calculated. From the data in Table 1 we can find the overall Fe^{3+}/Fe^{2+} ratio in each sample, assuming this ratio to be 2 for magnetite. We calculate values of 2.3 and 3.0 for Canadian and Rhodesian chrysotiles, respectively. These values are well within the range of values 1.6–2.8 and 1.0–3.8 found in the results of chemical analyses of several samples of the Canadian and Rhodesian chrysotiles, respectively (Rendall 1970).

AMPHIBOLE ASBESTOS

The non-chrysotile types of UICC asbestos (amosite, anthophyllite and crocidolite) all belong to the amphibole group. The most general chemical formula for amphiboles is $A_{0-1}X_2Y_5Z_8O_{22}(OH,F)_2$, where A represents Na or K, X can be a variety of mono- and divalent atoms in the M_4 sites, Y can be a variety of di- and trivalent atoms in the M_1, M_2 and M_3 sites, and Z represents Si or Al in the tetrahedral sites. The M_1, M_2, M_3 and M_4 sites may all contain Fe as Fe^{2+} and for first three sites also as Fe^{3+} (Cameron & Papike 1979, Whittaker 1979). Therefore, Mössbauer spectra of ^{57}Fe in these materials are potentially complex. In Figure 2 the spectra obtained for these three samples are shown, together with the positions of the Mössbauer doublets corresponding to the best analysis of the spectra. Numerical results are given in Table 2.
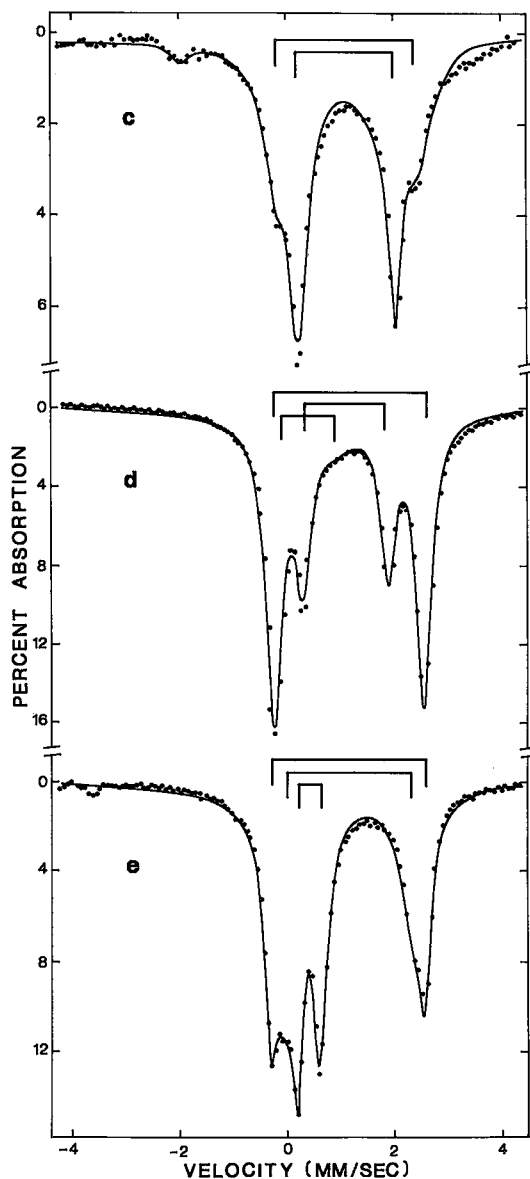
FIG. 2. ^{57}Fe Mössbauer spectra of UICC standard reference asbestos samples: (c) anthophyllite, (d) amosite, (e) crocidolite.

TABLE 2. MÖSSBAUER CHARACTERISTICS OF UICC STANDARD REFERENCE ASBESTOS SAMPLES

UICC Sample	Fe_I^{2+}				Fe_I^{2+}				Fe^{3+}			
	IS	QS	Γ	$\frac{I}{I_{tot}}$	IS	QS	Γ	$\frac{I}{I_{tot}}$	IS	QS	Γ	$\frac{I}{I_{tot}}$
crocid-olite	1.12	2.90	0.34	0.39	1.13	2.42	0.34	0.20	0.38	0.42	0.31	0.42
amosite	1.14	2.80	0.38	0.53	1.07	1.58	0.52	0.38	0.37	1.06	0.68	0.09
antho-phyll-ite	1.11	2.64	0.48	0.38	1.10	1.82	0.32	0.62				

Values of Mössbauer parameters are expressed in mm/s. Γ: linewidth.

straints on the magnitude of the linewidths, the computer analysis yields an unreasonably small linewidth for the first doublet. The reason for this might be the presence of a small amount of magnetite, ignored in this analysis, but whose presence is suggested by the small peak near −4 mm/s in Figure 2e. Because of this difficulty the linewidths of the two Fe^{2+} doublets were constrained to be the same. The Mössbauer parameters of the UICC sample, given in Table 2, are essentially the same as those of Whitfield & Freeman (1967). The ratio of their doublets, 37:24:39, differs slightly from our ratio of 39:20:42; our ratio does not change significantly if we constrain all three linewidths to be the same, as was done in the analysis of Whitfield & Freeman.

Values for the Fe^{2+}/Fe^{3+} ratio of iron in UICC crocidolite, as given by Rendall (1970), vary between 1.0 and 2.6. This ratio can also be calculated from the content of the major constituents of the material, which are also given in the data sheets with a possible error of $\pm 5\%$. We have ignored the influence of trace elements and assumed that in the structural formula the stoichiometry $Si_8O_{22}(OH)_2$ would remain invariant. The requirements are then that (1) the sum of the remaining major constituents Al, Fe, Mg and Na must be seven and their ratio must reflect their weight percentages as given in the data sheets, and (2) the sum of their valences as given in the formula must be 14. From these conditions we calculate a Fe^{2+}/Fe^{3+} ratio of 1.9, somewhat larger than the value of 1.4 corresponding to the Mössbauer data in Table 2. Using the Fe^{2+}/Fe^{3+} ratio observed from the Mössbauer analysis, we find that the chemical formula of UICC crocidolite is probably close to $Na_{1.56}Mg_{2.42}$ $Fe^{2+}_{2.97}Fe^{3+}_{2.12}Al_{0.43}Si_8O_{22}(OH)_2$.

Amosite

Amosite, of chemical composition $(Mg,Fe)_7$ $Si_8O_{22}(OH)_2$, is the asbestiform variety of cum-

Crocidolite

Crocidolite is the asbestiform variety of riebeckite, whose chemical composition is generally close to $Na_2Fe^{2+}_3Fe^{3+}_2Si_8O_{22}(OH)_2$. The Mössbauer spectrum shown in Figure 2 was analyzed in terms of three doublets, the one with the smallest quadrupole splitting corresponding to Fe^{3+} and the others to Fe^{2+}. With no con-

mingtonite. The series cummingtonite–grunerite has been studied extensively (Bancroft et al. 1967, Hafner & Ghose 1971, Ghose & Weidner 1972, Barabanov & Tomilaov 1973, Kamineni 1973). Generally, two Fe^{2+} doublets are found. The outer doublet with the larger quadrupole splitting has been assigned to Fe^{2+} in the M_1, M_2 and M_3 positions, the inner doublet to Fe^{2+} in M_4. The intensity ratio of the two doublets, which varies considerably for different samples, is generally assumed to depend both upon the iron content of the samples and upon the conditions under which they were formed. In our sample the best computer fit to the spectrum was obtained by assuming the presence of some trivalent iron. The spectrum in Figure 2 shows that the presence of a Fe^{3+} doublet is visible mainly as an asymmetry near the middle of the Fe^{2+} doublets. Of all the previous investigators of amosite, only Hafner & Ghose (1971) mentioned the existence of this asymmetry. Although the resolution of our data obtained at the low-velocity range is better than that of Hafner & Ghose, the intensity of this doublet is too small to make any conclusion about its origin. The Fe^{3+}/Fe^{2+} ratio of 10%, as obtained from the Mössbauer spectrum (Table 2), is within the range in values of $\simeq 6$ to 20% determined from chemical analyses of UICC material (Rendall 1970).

Anthophyllite

Anthophyllite has the same chemical formula as cummingtonite, but has a different crystal structure and generally contains less iron. Previous investigations of this material have shown that the spectrum consists of two Fe^{2+} doublets, in agreement with our results (Bancroft et al. 1966, Seifert 1977). Here, as in cummingtonite, the outer doublet has been assigned to Fe^{2+} at the M_1, M_2 and M_3 sites, and the inner doublet to Fe^{2+} at the M_4 sites. Analyzing the Mössbauer spectrum of anthophyllite with our computer program and using no additional constraints did not give reasonable values for the linewidths. Instead, the linewidths of the two doublets were fixed until a good fit was obtained for the shoulders in the Fe^{2+} doublets. The misfit near the centre is probably due to Fe^{3+}. If present, this amount is even smaller than that in amosite; no attempt was made to include this possibility in the computer analysis. The data sheets do not give values for the amount of Fe^{2+} and Fe^{3+} in anthophyllite.

The value we obtained for the quadrupole splitting of Fe^{2+} at the M_4 site in UICC material, which contains ≈ 0.5 Fe and 0.2 Al per formula unit as calculated from results of chemical analyses given by Rendall (1970), agrees quite well with values obtained by Bancroft et al. (1966) and by Seifert (1977) for samples of similar composition. The literature values for the splitting of the doublet corresponding to the M_1, M_2 and M_3 sites show considerable scatter. The value we obtained falls within the range of values previously observed.

REFERENCES

BANCROFT, G.M., BURNS, R.G. & MADDOCK, A.G. (1967): Determination of cation distribution in the cummingtonite–grunerite series by Mössbauer spectra. Amer. Mineral, 52, 1009-1026.

———, MADDOCK, A.G., BURNS, R.G. & STRENS, R.G.J. (1966): Cation distribution in anthophyllite from Mössbauer and infra-red spectroscopy. Nature 212, 913-915.

BARABANOV, A.V. & TOMILAOV, S.B. (1973): Mössbauer study of the isomorphous series anthophyllite–gedrite and cummingtonite–grunerite. Geochem. Int., 1240-1247.

BLAAUW, C., STROINK, G., LEIPER, W. & ZENTILLI, M. (1979): Mössbauer analysis of some Canadian chrysotiles. Can. Mineral. 17, 713-717.

CAMERON, M. & PAPIKE, J.J. (1979): Amphibole crystal chemistry: a review. Fortschr. Mineral. 57, 28-67.

EVANS, B.J. & HAFNER, S.S. (1969): ^{57}Fe hyperfine fields in magnetite (Fe_3O_4). J. Appl. Phys. 40, 1411-1413.

GHOSE, S. & WEIDNER, J.R. (1972): Mg^{2+}–Fe^{2+} order–disorder in cummingtonite, $(Mg,Fe)_7Si_8O_{22}(OH)_2$: a new geothermometer. Earth Planet. Sci. Lett. 16, 346-354.

HAFNER, S.S. & GHOSE, S. (1971): Iron and magnesium distribution in cummingtonites $(Fe,Mg)_7 Si_8O_{22}(OH)_2$. Z. Krist. 133, 301-326.

KAMINENI, D.C. (1973): X-ray and Mössbauer characteristics of cummingtonite from Yellowknife, District of MacKenzie. Can. Mineral. 12, 230-232.

RENDALL, R.E.G. (1970): Data sheets on the chemical and physical properties of the UICC standard reference samples. In Pneumoconiosis, Proc. Third Int. Conf. (1969), Johannesburg (H. A. Shapiro, ed.), Oxford Univ. Press, Cape Town, South Africa.

SEIFERT, F. (1977): Compositional dependence of the hyperfine interaction of ^{57}Fe in anthophyllite. *Phys. Chem. Minerals* **1**, 43-52.

TIMBRELL, V. (1970): Characteristics of the International Union Against Cancer standard reference samples of asbestos. *In* Pneumonoconiosis, Proc. Third Int. Conf. (1969), Johannesburg (H.A. Shapiro, ed.), Oxford Univ. Press, Cape Town, South Africa.

————, GILSON, J.C. & WEBSTER, I. (1968): UICC standard reference samples of asbestos. *Int. J. Cancer* **3**, 406-408.

———— & RENDALL, R.E.G. (1972): Preparation of the UICC standard reference samples of asbestos. *Powder Technol.* **5**, 279-287.

WHITFIELD, H.J. & FREEMAN, A.G. (1967): Mössbauer study of amphiboles. *J. Inorg. Nucl. Chem.* **29**, 903-914.

WHITTAKER, E.J.W. (1979): Mineralogy, chemistry and crystallography of amphibole asbestos. *In* Mineralogical Techniques of Asbestos Determination (R.L. Ledoux, ed.), *Mineral. Assoc. Can. Short Course* **4**, 1-34.

WICKS, F.J. (1979): Mineralogy, chemistry and crystallography of chrysotile asbestos. *In* Mineralogical Techniques of Asbestos Determination (R.L. Ledoux, ed.), *Mineral. Assoc. Can. Short Course* **4**, 35-78.