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MÖSSBAUER ANALYSIS OF SOME CANADIAN CHRYSOTILES

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ABSTRACT

Representative chrysotile-asbestos fibres from several mining areas in Canada have been investigated by ^{57}Fe Mössbauer spectroscopy. The total Fe content of the fibres was determined by electron microprobe analysis to be of the order of 1% by weight. The Fe^{3+}/Fe^{2+} atomic ratio R of iron in the fibres depends strongly on the mining area. In analyzed fibres from Clinton Creek, Yukon Territory, Fe^{3+} predominates ($R \sim 11$). For fibres from Cassiar, B.C., R is approximately 2, whereas for fibres from Thetford, Qué. and from Advocate, Nfld., this ratio is in the order of 0.5. These results contradict those of previously reported analyses for fibres from these areas. We found that Fe^{2+} occupies only the octahedral (Mg) site in chrysotile, whereas Fe^{3+} is distributed between the octahedral and the tetrahedral (Si) sites. No significant contribution to the Mössbauer spectra from iron in impurities could be detected in fibre samples separated by hand from the ore, but samples of finished product grades contain considerable amounts of magnetite. For the isomer shift (relative to metallic iron) and the quadrupole splitting of Fe^{2+}, we measured 1.12 and 2.65 mm/s, respectively. For Fe^{3+} the corresponding numbers are 0.34 and 0.75 for the octahedral site and 0.20 and 0.34 for the tetrahedral site. These results can be interpreted in terms of systematics of Mössbauer parameters in trioctahedral sheet silicates.

SOMMAIRE

Des échantillons de fibres d'asbeste-chrysotile, de différents districts miniers du Canada, ont été étudiés par spectroscopie Mössbauer ^{57}Fe. Leur teneur totale en Fe, déterminée par analyse à la microsonde électronique, est de l'ordre de 1% en poids. Le rapport atomique $R = Fe^{3+}/Fe^{2+}$ des fibres varie fortement d'un district à un autre. Les fibres de Clinton Creek (T.Y.) contiennent surtout Fe^{3+} ($R \sim 11$). Celles de Cassiar (C.B.) donnent $R \sim 2$; celles de Thetford (Québec) et d'Advocate (Terre-Neuve), $R \sim 0.5$. Ces résultats et ceux d'analyses antérieures de fibres des mêmes régions sont contradictoires. Nous trouvons Fe^{2+} uniquement dans les sites octaédriques (Mg) du chrysotile, tandis que les ions Fe^{3+} se partagent entre sites octaédriques et sites tétraédriques (Si). Les spectres Mössbauer obtenus sur échantillons de fibres séparés du minerai par triage à main ne permettent pas de déceler, en quantité appréciable, de fer provenant d'impuretés; dans le produit fini, par contre, la magnétite est abondante. Nous avons mesuré le déplacement isomère, par rapport au fer métallique, et le couplage du quadrupole; nous trouvons respectivement: pour Fe^{2+}: 1.12 et 2.65 mm/s; pour Fe^{3+} (site octaédrique) 0.34 et 0.75 mm/s et pour Fe^{3+} (site tétraédrique) 0.20 et 0.34 mm/s. Nos résultats peuvent s'interpréter au moyen des paramètres Mössbauer des phyllosilicates trioctaédriques.

(Traduit par la Rédaction)

INTRODUCTION

Chrysotile $Mg_6Si_4O_{10}(OH)_8$ is a sheet silicate (Hurlbut & Klein 1977) in which iron can replace both Mg and Si in the crystal structure. Mössbauer spectroscopy, now well established as an investigative technique in mineral research, yields information about the valence state, chemical bonding, coordination and magnetic state of iron atoms present in a compound. Though a number of sheet silicates have been investigated by ^{57}Fe Mössbauer spectroscopy in recent years, no data have been presented for either chrysotile or the structurally related minerals antigorite and lizardite. This paper deals with the results of a ^{57}Fe Mössbauer investigation of chrysotile asbestos from four geographically distinct Canadian mining locations.

SAMPLE MATERIAL AND EXPERIMENTAL DETAILS

Material for investigation was obtained from four mining regions in Canada. Throughout this paper, these locations will be referred to using capital letters A, B, C and D, corresponding to the following locations: A. Cassiar Asbestos Corp. Ltd., Clinton Creek mine, Clinton Creek, Y.T.; B. Cassiar Asbestos Corp. Ltd., Cassiar mine, Cassiar, B.C.; C. Asbestos Corp. Ltd., British-Canadian and King Beaver mines, Thetford, Qué.; D. Canadian Johns-Manville Co. Ltd., Advocate mine, Baie Verte, Nfld. We collected hand-specimen ore samples from each mine as well as samples of the graded products of the mills. From each mining area we investigated four samples, two of pure chrysotile asbestos and two of different product grades. Each sample consisted of approximately 1.5 g of material, the optimum amount for our experimental geometry. The two samples of pure chrysotile consisted of fibres that had been separated by hand from different pieces of rock, taking care that no observable impurity material was present. Each of these samples was analyzed by powder X-ray diffraction for phase determination. Only minor quantities of mineral phases other than chrysotile could be detected. The two samples of different product grades were in all cases contaminated by varying amounts of magnetite, and their Mössbauer spectra contained a substantial component which had to be ascribed to magnetite.

Mössbauer spectra were obtained using a conventional constant-acceleration spectrometer and a 25 mCi $Rh^{57}Co$ source. Metallic iron was used to calibrate the spectrometer and as a reference material for the isomer shift.

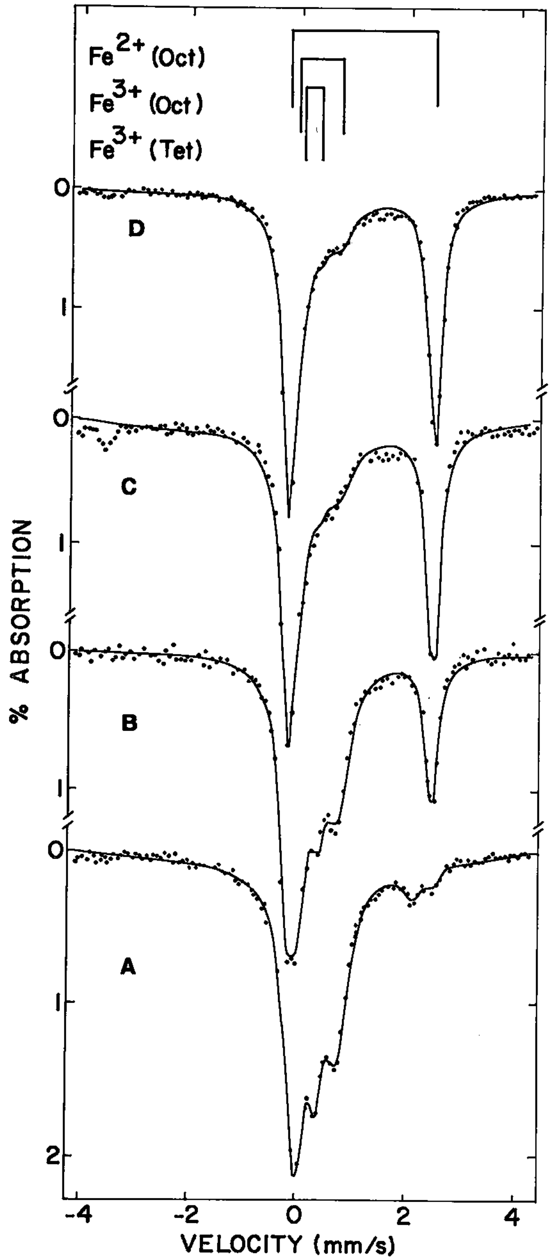

FIG. 1. Room-temperature ^{57}Fe Mössbauer spectra of clean fibres of chrysotile from distinct mining locations. The smooth lines are a computer fit to the experimental points in terms of Lorentzian lines, as described in the text. The positions of the three doublets, corresponding to Fe in three different structural states in chrysotile, are indicated. The additional line at +2.2 mm/s in spectrum A is probably part of an Fe^{2+} doublet due to an impurity in that sample.

EXPERIMENTAL RESULTS

The appearance of the chrysotile Mössbauer spectra, some of which are shown in Figure 1, suggests that they should be analyzed in terms of three doublets. From the Mössbauer parameters it could be deduced that two of those doublets correspond to Fe^{3+} and the third corresponds to Fe^{2+}. The relative intensities of the subspectra of the two valence states of iron vary strongly for the distinct localities, but are similar for all four samples from any specific mining location. Because a number of the Mössbauer peaks in the spectra overlap to some extent, it was not possible to fit the spectra unambiguously to a number of unconstrained Mössbauer peaks; instead, some restraints had to be imposed. The results presented here were obtained in the following manner, based on the assumption that the line positions corresponding to Fe in a specific ionic state and structural position would be the same for different samples. We note that at no time was evidence found to doubt the validity of this assumption. The positions and line widths of the three doublets were determined from those spectra in which they dominated, *i.e.*, the two Fe^{3+}

doublets from location A and the Fe^{2+} doublet from D. These line positions and line widths were then held fixed at those values for all the other spectra. In this way satisfactory analyses were obtained for all spectra. In Figure 1 the positions of the lines determined for the spectra in this manner are indicated and the calculated curves corresponding to these fits shown as smooth lines.

In the analysis of spectra from A, a rather large line-width was obtained for the doublet with the largest quadrupole splitting. This may indicate that line broadening occurs for this doublet (*e.g.*, owing to a distribution of values of this splitting for Fe atoms at the corresponding structural site) but this conclusion is uncertain. The considerable overlap of the lines of the two doublets makes it impossible to determine the correct fitting-procedure. We fitted the spectra constraining all line widths to be equal. The result was only slightly less satisfactory than the former fit, but the relative intensities of the two doublets were about equal in this case, whereas a ratio of ~2:1 was found in the unconstrained fit. Thus, not too much significance should be attached to the precise values of the ratio of the Fe^{3+} doublets.

The results of the computer analysis are presented in Tables 1 and 2. The assignment of the distinct components of the spectra to Fe in specific sites and valence states is discussed later in this paper.

DISCUSSION

Mössbauer parameters and Fe site designations

The Mössbauer parameters of the spectra are indicative of high-spin Fe^{2+} for the doublet with the largest *IS* and *QS*, and to high-spin Fe^{3+} for the two other doublets. Fe can replace both Mg and Si in the chrysotile structure. For Mg this can be either as Fe^{2+} or as Fe^{3+}. The tetrahedral site is, however, too small to accommodate the Fe^{2+} ion. Thus, it is not surprising that two Fe^{3+} and one Fe^{2+} spectra are found.

It remains to determine in which way the Fe^{3+} should be assigned to the appropriate sites. Systematics of Mössbauer parameters observed in other silicates suggest that the spectrum with *IS* = 0.20, *QS* = 0.34 mm/s should be assigned to the tetrahedral (Si) site and the other one to the octahedral (Mg) site. Isomer-shift data for Fe^{3+} in tetrahedral sites in silicates were recently discussed by Annersten & Olesch (1978), and a linear relationship was established between the *IS* and the average Fe–O distance for Fe in the tetrahedral site, in qualitative agreement with the results expected for corresponding changes in electron density at the $^{57}Fe^{3+}$ nucleus. If we use this linear relationship between the *IS* and the average Fe–O distance, then from the *IS* of 0.20 mm/s as measured by us, we would predict an Fe–O distance in the tetrahedral site of chrysotile of 1.65 Å, in good agreement with the values of 1.62 Å and 1.64 Å given by Wicks & Whittaker (1975). Isomer shifts (relative to metallic iron) of Fe^{3+} in octahedral sites in sheet silicates are generally found to be in the range of 0.35–0.55 mm/s (Taylor *et al.* 1968, Häggström *et al.* 1969, Yassoglou *et al.* 1972, Annersten 1974, Bancroft & Brown 1975), suggesting that the site with *IS* = 0.34 mm/s is octahedral, rather than the one with *IS* = 0.20 mm/s.

TABLE 1. MÖSSBAUER PARAMETERS OF IRON IN CHRYSOTILE AT ROOM TEMPERATURE

Structural site	Valence state	IS ±0.02 mm/s	QS ±0.04 mm/s
Octahedral	2+	1.12	2.65
Octahedral	3+	0.34	0.75
Tetrahedral	3+	0.20	0.34

We consider the Fe^{3+} *QS* to be a less meaningful parameter to distinguish between the sites. The structural environment of the Fe site plays a dominant role in determining the value of this parameter, and a large range of values is found for different sheet silicates. A quantitative analysis of *QS* values requires accurate structural and Mössbauer data for different sheet silicates and is beyond the scope of this paper.

The Fe^{2+} Mössbauer parameters are in good agreement with values observed in other sheet silicates. The *IS* value of 1.12 mm/s does not differ from that found for Fe^{2+} in corresponding sites in biotites; for the *QS* of Fe^{2+} we expect variations depending on the structural environment of the site. For example, values in the range 2.1–3.9 mm/s have been observed in biotite (Häggström *et al.* 1969, Annersten 1974, Pol'shin *et al.* 1972, Bancroft & Brown 1975). Our measured value of *QS* (2.65 mm/s) falls within this range.

Intensity ratios

The experimentally determined Fe^{2+}/Fe^{3+} intensity ratios clearly vary with source of the sample material and reflect differences in conditions during the formation of the chrysotile. It is interesting to compare our results with those of previous work, in which chemical analyses were used to determine these ratios. In

TABLE 2. QUANTITIES OF IRON IN 2+ AND 3+ VALENCE STATES SUBSTITUTING IN CHRYSOTILE

Location/description	Fe total[1] (weight %)	Ratio (in %) Fe^{3+}(oct)/ Fe^{3+}(total)	Ratio Fe^{2+}/Fe(total) in %			
			This work	HWH[2]	M[3]	RBD[4]
A clean fibres	1.83	72	4		9	
clean fibres	1.12	76	11			
grade CP		69	11			
grade CT		69	8			
B clean fibres	1.04	73	30		11	
clean fibres	1.02	69	29			
grade AAA		68	28			
grade AZ		72	27			
C clean fibres	0.91	72	65	14,16	32,19	44,2
clean fibres	1.05	72	66	37,35	13,30	44
grade BC-4-110-4D		73	62		35,17	
grade BC-362-3T		76	59			
D clean fibres	1.28	72	72	37,30		
clean fibres	1.08	72	78	45,27		
grade group 4		79	58			
grade group 6		73	64			

[1] Determined by electron microprobe; [2] Hahn-Weinheimer & Hirner (1975); [3] Monkman (1975); [4] Roy et al. (1975).

Table 2 we have presented the results of three previous investigations with our own results. For results from Québec, previous work includes that from other mines in the same area. From these data we come to the following conclusions: (i) Though some variations are found in our own samples for each location, the results for a particular area are fairly consistent; the differences between different areas represent a real effect. (ii) Large discrepancies exist between our results and those of previous investigations. We believe that our results are more representative for the actual Fe^{2+}/Fe^{3+} ratio of iron in the chrysotile fibres because: (a) chemical analysis is known to be generally less reliable for determinations of this kind, and (b) with Mössbauer analysis, iron contained in impurity contamination (*e.g.*, magnetite, brucite, *etc.*) shows up as different peaks in the Mössbauer spectrum and can be properly taken into account, whereas with chemical analysis no such distinction can be made. The intensity ratios determined by Mössbauer spectroscopy may contain a systematic error, because in determining these ratios, the recoil-free fractions have been taken to be equal. Actually, one may expect differences for Fe^{2+} and Fe^{3+}, and for Fe^{3+} in the two structural sites. However, these differences are not expected to be more than of the order of 10% and thus cannot explain the discrepancies observed. More measurements with well-defined material should be made to resolve these occasionally rather large differences.

The intensity ratio of Fe^{3+}(oct) to Fe^{3+} (total) for the two different sites is fairly consistent in all our samples. As discussed previously, these results must be regarded with some reservation. They do suggest that there is some preference for Fe^{3+} to occupy octahedral sites. We note that for Fe^{3+} substitution in pure chrysotile with stoichiometric composition the condition of charge neutrality would require equal amounts of Fe^{3+} in the two sites.

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