The ^{119}Sn Mössbauer spectra, cell dimensions, and minor element contents of some cassiterites

THE Mössbauer effect, utilizing ^{119}Sn resonance, can be used to study tin bonding in major Sn-bearing minerals, but as far as we know the only application to cassiterites has been the work of Shumilovskii *et al.* (1964) and Kalmakov *et al.* (1965) on tin assaying in cassiterite mixtures. In the work reported here, the spectral widths of the Mössbauer ^{119}Sn line in a group of cassiterite specimens and their unit-cell volumes have been related to the concentration of minor elements present in each sample. The cassiterites studied varied from colourless crystals (BM 1969, 106) to black and virtually opaque specimens. It has been recognized for some time that there is a relation between the colour of cassiterite and its Fe content (Stumpfl, 1963) although a reason for this has not previously been given.
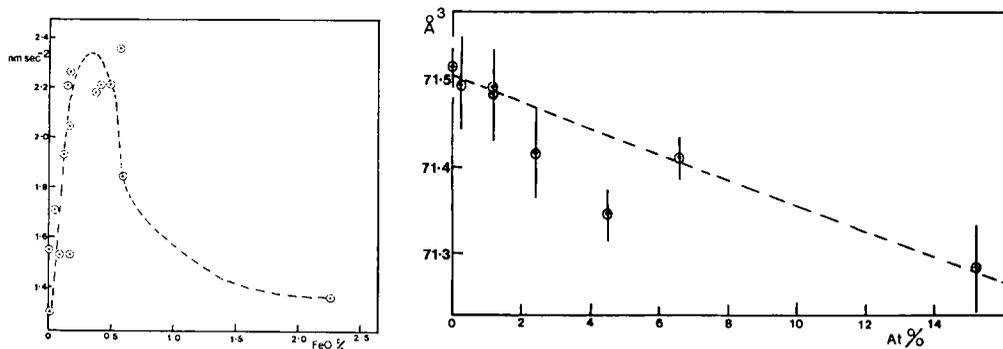
FIGS. 1 and 2: FIG. 1 (left). Mössbauer line-width plotted against iron content of cassiterites. FIG. 2 (right). Cell volumes and estimated errors plotted against total impurity content of cassiterites in atomic per cent.

A small portion of each cassiterite specimen was crushed for exposure to ^{119}Sn γ-radiation from a BaSnO$_3$ Mössbauer source. In addition a few fragments were prepared for electron probe microanalysis and the concentrations of Fe, Mn, Ti, Ta, and Nb determined relative to pure metal standards. The cell dimensions were obtained from 114·6 mm diameter X-ray powder patterns (Co-$K\alpha$ radiation) by a high-angle extrapolation method using small amounts of material removed from the polished sections as near as possible to the spots analysed. The electron-probe analyses are given in Table I after correction for matrix effects. They are listed in order of increasing iron content, which is presented as FeO. Several authors (Banerjee *et al.*, 1970; Grubb and Hannaford, 1966) have reported variable Fe^{2+}/Fe^{3+} ratios from a number of cassiterites, but in the present work the iron oxidation state could not be

determined with any certainty except for BM 1973, 215. Table I also shows the Mössbauer line widths at half maximum peak height for samples of the same thickness, and the cell dimensions determined on eight of the specimens.

The Mössbauer chemical shift for all the samples is zero but the spectral line width is found to be sensitive to the maximum impurity concentration in the samples. Consequently we have tried, as far as possible, to work on homogeneous material, but where this has not proved possible the maximum localized impurity level has been

TABLE I. *Chemical, Mössbauer, and X-ray data for cassiterites*

No.	FeO	MnO	TiO_2	Ta_2O_5	Nb_2O_5	Imp.*	M.l.w.†	a	c	V
1	–	–	0.02	–	0,02	0.06	1.55	–	–	–
2	0.01	–	–	–	–	0.03	1.30	4.7375Å	3.1864Å	71.515Å³
3	0.05	–	0.06	0.02	0.02	0.25	1.71	4.7371	3.186	71.494
4	0.09	–	0.06	0.05	–	0.34	1.48	–	–	–
5	0.12	–	0.73	1.03	0.03	2.36	1.93	4.7360	3.184	71.416
6	0.15	–	0.10	–	–	0.49	2.21	–	–	–
7	0.16	0.01	0.20	0.75	0.07	1.32	2.04	–	–	–
8	0.17	–	–	–	–	0.36	1.53	–	–	–
9	0.17	–	–	0.08	–	0.39	2.26	–	–	–
10	0.38	0.34	–	3.69	2.29	6.64	2.18	4.7381	3.1809	71.410
11	0.41	0.01	0.16	–	0.02	1.20	2.21	4.7370	3.186	71.491
12	0.49	0.01	–	0.05	0.14	1.29	2.21	–	–	–
13	0.57	0.01	–	–	–	1.22	2.36	4.7375	3.185	71.484
14	0.59	0.04	0.49	0.06	1.99	4.50	1.84	4.7361	3.1807	71.345
15	2.27	0.17	0.04	13.67	0.51	15.21	1.36	4.7388	3.1744	71.285

* Impurities. atoms %.
† Mössbauer line width, $mm.sec^{-2}$.

1. BM 80996, artificial.
2. BM 1969,106, Uganda.
3. BM 91123, Schlaggenwald, Bohemia.
4. BM 1975,428, St.Agnes, Cornwall.
5. BM 1917,627, Mamkwadi, Winneba, Ghana.
6. BM 37371, Pitkäranta, Impilahti, Viipuri, Finland.
7. BM 1928,79, Muika, Kiambi, Katanga, Zaïre.
8. BM 1975,429, Morbihan, Brittany.
9. BM 1938,264, Araca, Cordillera Tres Cruces, dep. La Paz, Bolivia.
10. BM 1925,950, Sakangyi, Mogok, Upper Burma.

11. BM 1921,738, New England district, New South Wales.   12. BM 1912,559, Lerui N'Kano, Nigeria.
13. BM 54898, Johore, Malay Leninsula.
14. BM 62822,Montebras , Dept. Creuse, France.
15. BM 1973,215, Taquaral, Minas Gerais, Brazil (also determined SnO_2 84.18%, total 100.84%).

determined. The line width is most sensitive to the iron content of the cassiterite specimen, showing a sharp increase from 1·30 mm/sec² for the pure colourless cassiterite from Uganda (BM 1969, 106) to 2·36 mm/sec² for a Malayan specimen (BM 54898) containing 0·57 % FeO (fig. 1). Further increases in the FeO concentration cause the spectral width to contract again, until in BM 1973, 215, containing 2·27 % FeO, it has returned to the value associated with impurity-free cassiterite. This specimen, containing also major Ta_2O_5, gave a sufficiently strong signal for the determination by the Mössbauer technique of the iron oxidation state, confirming it as exclusively Fe^{2+}.

The changes in the line widths of the Mössbauer resonance lines are caused by changes in the electronic environment of the Sn atoms in the cassiterites. There are two ways in which these environments could be altered in the minerals studied:

The electronic environments could be altered indirectly because of the presence of the impurity ions and the effects these have on the unit-cell dimensions.

The electronic environments could be altered as a direct result of the presence of impurity ions with different electronic configurations from that of Sn in SnO_2.

Variations in the cell dimensions of cassiterites are known to occur. Walia (1971) has reported a gradual increase in the lattice parameters with increasing iron content,

but our results show that the reverse is the case. The cell volume, when plotted against the total impurity content in atomic per cent (fig. 2) shows a marked decrease at higher impurity levels The measurements indicate that (Fe, Ti) impurities give rise to a relatively larger reduction in cell volume than equivalent concentrations of (Ta, Nb), the c parameter showing the larger variation in both cases. There is, however, no relationship between the cell-dimension variation with impurity concentration and the Mössbauer line-width variation. The changes in line width cannot therefore be due to the indirect influence of impurity ions on the cell dimensions.

It has been shown in previous work (Donaldson *et al.*, 1975) that colour in compounds of p-block elements of higher symmetry and lower oxidation state is due to direct population of non-valence-shell bands by the non-bonding electron pair in the p-block element. In particular the black colour in tetragonal SnO is explained by the population of a solid-state band formed by overlap of empty non-valence shell orbitals on the tin (the Sn–Sn distance in SnO is about 3·8 Å) by the non-bonding pair of electrons on Sn(II). In SnO_2 the Sn–Sn distances are similar (3·70 Å) and band formation must occur in a similar way to that in SnO but pure cassiterite is colourless because there are no non-bonding or unpaired electrons available in SnO_2 to populate that band. When Fe^{2+} or Fe^{3+} is present, however, two effects can occur that can lead to the population of the bands and give rise to the dark colour of normal cassiterite crystals:

The band can be populated by the d-orbital electrons from the iron atoms.

The electrostatic imbalance caused by substitution of an Fe ion for Sn(IV) can be corrected either by oxygen deficiency, or by the formation of Sn(II) in the lattice, or both. If any Sn(II) were formed, its non-bonding electrons would populate the band as they do in SnO. The amount of Sn(II) formed would be very small for the impurity levels considered in this paper and could not be detected as a separate Mössbauer resonance. The Sn–Sn bands are most likely to consist of tin non-valence shell d orbitals with the t_{2g} band lower in energy because of crystal field effects.

We suggest that the changes in Mössbauer line widths observed in this study can be explained in terms of the direct electronic effects of the presence of impurities, the initial increase being due to the lower symmetries of the electronic environments caused by the presence of low levels of impurity. The line width reaches a maximum at about 0·5 % FeO and then decreases as the population of a solid state band involving Sn orbitals by Fe d orbitals or Sn(II) non-bonding orbitals produces a more symmetrical environment for the tin.

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Metamict columbite re-examined

METAMICT columbite from Yinnietharra, Western Australia, was first described by Bowley (1923) as 'manganomossite' or possibly as 'mangano-columbite'. In a later study, Hutton (1957) tentatively identified the mineral as metamict tantalite. In a more detailed chemical and X-ray diffraction study, Hutton (1959) identified the specimen as metamict columbite. A history of the nomenclature of the specimen as well as an excellent description of its physical, chemical and structural properties is found in Hutton's (1959) study.

The cause for re-examination of the specimen is that it represents the only described occurrence of metamict columbite. Closely related orthorhombic, rare-earth, AB_2O_6-type Nb–Ta–Ti oxides (e.g. euxenite, priorite, polycrase, and aeschynite) are often found in the metamict state, but columbite is not. The existence of a metamict columbite is of interest in that it may provide a key to the understanding of the process of metamictization. Of critical importance is the determination of whether the specimen in its pre-metamict form was indeed columbite and whether it consists of a homogeneous single phase.

Hutton (1959) in an effort to insure that only a single phase was analysed examined autoradiographs of a polished section and carefully prepared the sample for chemical analysis by electromagnetic fractionation. Still, some doubt as to the homogeneity of the specimen remained as the 'Autoradiographs show that zonary distribution of radioactivity may or may not be present . . . .'

Chemical analysis of the same specimen analysed by Hutton (1959) was repeated using an electron microprobe (ARL, Stanford University). The microprobe standards were metal oxides and museum specimens analysed by the Atomic Energy Commission for the late Dr. C. O. Hutton. H_2O was not determined. Results of the analyses are