TIN AND INDIUM IN MICA, AS DETERMINED SPECTROCHEMICALLY

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ABSTRACT

Spectrochemical analysis has shown that small quantities of tin are invariably detected in mica; the concentration of SnO_2 varies from $<0.0005\%$ to nearly 0.5%. Experimental evidence indicates that in specimens enriched in tin, some is present as included cassiterite and some is evidently located in the mineral structure, probably in octahedral co-ordination; in specimens which contain lower concentrations of tin, it is all held as a structure constituent.

Very small quantities of indium (maximum 0.0006% In_2O_3) could be detected in some mica specimens, in which it is probably present as a structure constituent in octahedral co-ordination. Specimens relatively rich in indium are also enriched in tin. The suggestion of a possible radiogenic origin of indium—by the electron capture decay, $Sn^{115} \rightarrow In^{115}$—is discounted.

A rapid survey of the tin content of pegmatitic micas is suggested as a possible aid for prospecting for tin.

An outline is given of spectrochemical procedure, but one item, namely, that of a correction for interference of Mn 3256.137 with In 3256.090 is covered in detail.

INTRODUCTION

In many specimens of mica which had been investigated spectrochemically, sensitive tin lines could be detected: in a few specimens, indium could also be detected. Because data on the abundance and distribution of these two elements in mica are lacking, an attempt was made to make quantitative determinations of tin and indium, using their emission spectra as a means of analysis.

It may be worth noting here that spectrochemical analysis has one advantage over all other methods of analysis, namely, that once the spectra of a given mineral have been recorded, the photographic plate provides not only a permanent record of the presence of the element(s) sought, but also of other elements. In this example, the quantitative analyses given in this paper are a direct consequence of an investigation of the geochemistry of rubidium, thallium, and lithium in micas. On the plates that had recorded the spectra of these three elements, tin and indium lines were also found, and with very little extra effort the same plates could be used for the analysis of these latter two elements. Had other methods of analysis been employed for rubidium, thallium, and lithium, the presence in mica of tin and indium would not have been observed. There are many examples of such observations.

Analytical Procedure

(1) *General*

The operating technique is basically the same as has been described by one of us before (Ahrens, 1) for the spectrochemical determination of thallium, rubidium, lithium, and lead in minerals. The reader is referred to the above paper for operating details not given here.

Lines selected for the analysis of tin and indium were, Sn 3262.328 and In 3256.09. (Wavelengths used in this paper are from the M.I.T. Wavelength Tables of G. R. Harrison: published by John Wiley and Sons.)

Fortunately, some specimens of muscovite (Uranoop River area, Namaqualand, Union of South Africa) gave no spectroscopic evidence of the presence of tin and indium, and were consequently used as base material to which were added small quantities of SnO_2 (as cassiterite) and In_2O_3. This gave a series of standards covering the concentration range, 0.000032 to 1.0% SnO_2 and In_2O_3. The use of a base material, the composition of which is both chemically and physically identical with the material to be analyzed is advantageous in spectrochemical analysis.

The use of a relatively low amperage (3 amps) was found satisfactory: a very satisfactory sensitivity (limits of detection, 0.0005% for tin and ~0.00003% for indium) was obtainable. The reproducibility, expressed as standard deviation, was approximately ±12–15% for both elements, when analyses were made in duplicate, and sufficed for the investigation in hand.

(2) *Correction for interference of Mn 3256.14 with In 3256.09*

Two sensitive indium lines, In 3256 and In 3258, are located close to the tin line (Sn 3262) employed, and their use was attempted. In 3258 was found considerably less sensitive than In 3256, and could be detected very faintly in only a very few specimens; In 3256 was therefore used, but with caution, because interference from Mn 3256.14 was encountered in some specimens of lepidolite. Correction from such interference was made as follows.

It was assumed that if Mn 3256.14 were emitted, the measured intensity of In 3256.09 and Mn 3256.14 on the plate could be regarded as a simple summation of the relative intensities of these two lines. Ideally this would hold only if the wavelengths of the two lines are identical: whether one may use a summation will, therefore, depend on the wavelength difference of the two lines and the dispersion of the spectrograph. For the above two lines, the displacement on the plate is very nearly 0.01 mm. for the spectrograph used (large Hilger quartz) and this displacement was regarded as sufficiently small to permit a summation of intensities. If then, the intensity of Mn 3256 can be determined, a subtraction of its intensity from the total (In, Mn 3256) intensity would give the intensity of In 3256 alone.

The relative intensity of Mn 3256 in any specimen was determined as follows.

First, the intensity ratio of Mn 3256 to that of a slightly more intense manganese line in this general spectral region had to be determined in the absence of indium: for this purpose a synthetic standard can be used. Manganese emits several lines of similar wavelength to Mn 3256, one of which, Mn 3248.516, is slightly more intense than Mn 3256 and belongs to the same multiplet. Because Mn 3256 and Mn 3248 have the same multiplet assignment, their intensity ratio is constant and is independent of source fluctuations: once determined, therefore, the intensity ratio value can be safely used for all matrixes and conditions of arcing. Seward (2) has examined the line intensities of the spectrum of manganese, and from his relative intensity values, the ratio I 3248/I 3256 is calculated as 0.61. We also made intensity ratio measurements on this multiplet line pair and obtained a value of 0.57 which accords reasonably well with that calculated from Seward's measurements: for correction purposes the mean of 0.57 and 0.61 was used.

If Mn 3248 is absent in an analysis, no interference of Mn 3256 with In 3256 will occur; if Mn 3248 is present, correction is made by a subtraction of 0.59 of the intensity of Mn 3248 from Mn, In 3256. Before these corrections are made, background is corrected in the usual way. The amount of interference from Mn 3256 was found to vary considerably. No specimen of muscovite showed interference, whereas in some specimens of lepidolite, the line at λ 3256 was evidently due to manganese alone. In three specimens where correction could be applied, the amount of interference varied from 10–50%.

Fortunately for the purpose of correction for interference, manganese and indium volatilize into the arc column very differently. In mica indium is very volatile and its lines are emitted with peak intensity during the early period of arcing, during which period the spectra of the alkali metals are most intense, whereas the manganese lines only reach their peak intensities after a large proportion of the alkali metals have volatilized. Because the peak intensities of manganese and indium lines do not coincide with respect to time, correction is facilitated as interference can be minimized by recording only the relatively early period of each exposure. Further, a low amperage and no admixture of carbon powder help; selective volatilization is accentuated and thereby the intensity of the interfering line is further reduced in the early arcing period.

RESULTS

The results of the analyses of indium and tin in the mica specimens are given in Table 1. Most specimens are from pegmatites.

TABLE 1

	Locality	% SnO_2	% In_2O_3
(A) MUSCOVITE			
(1)	Mica Siding, N.E. Transvaal	0.007	<0.00003%
(2)	S.A. Mica Mines, Selati Riv., N.E. Transvaal	0.0085	<0.00003
(3)	near Mica Siding, N.E. Transvaal	0.014	<0.00003
(4)	Godwa Mine, Leydsdorp, N.E. Transvaal	0.030	<0.00003
(5)	Maori Mine, Olifants Riv., Transvaal	0.0019	<0.00003
(6)	Maori Mine, Olifants Riv., Transvaal	0.0088	<0.00003
(7)	Port Yelland, Zululand	0.0015	<0.00003
(8)	Otjimboyo, South West Africa	0.073	0.00007
(9)	near Usakos, South West Africa	0.16	0.00008
(10)	Usakos, South West Africa	0.075	0.0002
(11)	Erongo Tin Fields, S.W. Africa	0.40	0.0003
(12)	Uranoop Riv. area, Namaqualand	0.001	<0.00003
(13)	Uranoop Riv. area, Namaqualand	0.0005	<0.00003
(14)	Uranoop Riv. area, Namaqualand	0.0005	<0.00003
(15)	Uranoop Riv. area, Namaqualand	0.0005	<0.00003
(16)	Uranoop Riv. area, Namaqualand	0.001	<0.00003
(17)	Uranoop Riv. area, Namaqualand	0.0015	<0.00003
(18)	Uranoop Riv. area, Namaqualand	0.009	<0.00003
(19)	Uranoop Riv. area, Namaqualand	0.011	<0.00003
(20)	Uranoop Riv. area, Namaqualand	0.010	<0.00003
(21)	Uranoop Riv. area, Namaqualand	0.0005	<0.00003
(22)	Uranoop Riv. area, Namaqualand	0.0017	<0.00003
(23)	Uranoop Riv. area, Namaqualand	0.002	<0.00003
(24)	Illovo Riv., Mid-Illovo, Natal	0.13	<0.00003
(25)	near Johannesburg, Transvaal	0.026	<0.00003
(26)	Steinkopf Reserve, Namaqualand	0.20	0.00034
(27)	Noemaas, near Steinkopf, Namaqualand	0.0072	<0.00003
(28)	Kenhardt, Namaqualand	0.070	<0.00003
(29)	George, Cape Province	0.011	0.00003?
(30)	Sea Point, Cape Province	0.09	<0.00003
(31)	Salisbury, Southern Rhodesia	0.004	<0.00003
(32)	Southern Rhodesia	0.013	<0.00003
(33)	Bucko, Kenya	0.068	<0.00003
(34)	Stoneham, Maine, U.S.A.	0.45	<0.00003
(35)	North Carolina, U.S.A.	0.0048	<0.00003
(36)	Gabel, Silesia	0.0035	<0.00003
(37)	Skutterud, Norway	0.0032	<0.00003
(38)	Zillerthaler Alps, Tyrol	0.02	<0.00003

TABLE 1—*Continued*

Locality	% SnO_2	% In_2O_3
(B) BIOTITE		
(39) St. Stephen, Cornwall	0.004	<0.00003
(40) Miask, Urals	0.0062	<0.00003
(41) Erzgebirge, Germany	0.0083	<0.00003
(42) Illovo Riv., Mid-Illovo, Natal	0.013	<0.00003
(C) LEPIDOLITE		
(43) Black Hills, South Dakota	0.08	0.0005
(44) Maine, U.S.A.	0.039	<0.00003
(45) San Diego County, California	0.0085	<0.00003
(46) Pala, California	0.011	<0.00003
(47) Portuguese East Africa	0.0027	<0.00003
(48) Warmbaths, South West Africa	0.0005	<0.00003
(49) Arandis, Omaruru, S. West Africa	0.018	<0.00003
(50) Okongava Ost 72, Karibib, S.W. Africa	0.002	0.00003?
(51) Okongava Ost 72, Karibib, S.W. Africa	0.0015	0.00003?
(52) Albrecht's Höhe, S.W. Africa	0.02	0.00004
(53) Omaruru, S.W. Africa	0.09	0.0006
(54) Jackalswater, Namaqualand	0.0005	<0.00003
(55) Jackalswater, Namaqualand	0.0005	<0.00003
(D) PHLOGOPITE		
(56) Antwerp, New York State	0.0005	<0.00003
(57) Burgess, Ontario, Canada	0.0005	<0.00003
(58) Loole Kop., E. Transvaal	0.002	<0.00003
(E) SUNDRY		
(59) Zinnwaldite: Zinnwald, Saxony, Germany	0.44	<0.00003
(60) Manganophyllite: Långban, Sweden	0.0023	<0.00003
(61) Margarite: Chester, Massachusetts	0.039	<0.00003

DISCUSSION

(*a*) *Tin*

The presence of tin in mica has been reported by Borovik (3): he gave no indication of the amount present.

From Table 1 it is readily seen that tin in a small amount is a ubiquitous constituent of mica. The quantities found vary considerably, namely, from less than 0.0005% to 0.4–0.5% SnO_2: the latter concentration appears to be a maximum likely to be present in mica. A large proportion of specimens contain a concentration of tin within the range 0.005–0.05% SnO_2.

The manner in which tin is located in the mica structure is somewhat problematical. Borovik (3) concluded that in a specimen of muscovite he examined, it was located as a structure constituent. He treated his specimen with HF, and after filtration analyzed the evaporated filtrate and also the residue. Most tin was found in the filtrate and on the assumption that cassiterite is resistant to attack by HF, he could conclude that tin was a constituent of the structure of the muscovite specimen he examined.

Some of the specimens richest in tin described in this paper were examined microscopically, and some included cassiterite could be observed. The quantity of included cassiterite appeared, however, to be quite insufficient to account for as high a tin content as about 0.4%. HF treatment, as described above, was made and spectrochemical analysis showed a considerable concentration of tin in both filtrate and residue. It seems, therefore, that in the specimens richest in tin, this element is present partly as included cassiterite and partly as a structure constituent. The specimens relatively poor in tin showed an absence of cassiterite under the microscope and in these tin is probably all present as a structure constituent.

The radius of Sn^{++++}, a relatively stable ion of tin, is 0.68 Å, and Sn^{++++} should be able to enter the mica structure octahedrally (6-fold co-ordination).

(*b*) *Indium*

The geochemistry of indium in Finnish minerals has been investigated by Erämetsä (4) and in one of seven specimens of muscovite he examined, indium could be detected and was determined as 0.0001% In. Of the mica specimens we examined, indium could definitely be detected in five of thirty-eight muscovite specimens and in three of thirteen lepidolite specimens. Doubtful traces ($\sim$0.00003% In_2O_3) were observed in a few mica specimens.

The radius of the stable indium ion, In^{+++} is 0.92 Å. Although a little large for large-scale substitution, an ion of this size should be capable of entering mica structures octahedrally and it seems that the traces of indium in mica are present as structure constituents. Erämetsä (4) has observed indium in silicates and has reported what appears to be almost a freak amphibole from Finland, in which as much as 0.1–1.0% indium was found.

The association of tin and indium in mica

Each of the seven specimens of mica which contain a relatively high concentration of indium, namely, $>$0.00005% In_2O_3, contain an unusually high amount of tin. Relevant data, taken from Table 1, are given in Table 2.

A paper by Eastman (5) has drawn attention to the general geochemical association of tin and indium in minerals, and in this paper

TABLE 2

Specimen No. in Table 1	% SnO_2	% In_2O_3
8	0.073	0.00007
9	0.16	0.00008
10	0.075	0.0002
11	0.40	0.0003
26	0.20	0.00034
43	0.08	0.0005
53	0.09	0.0006

Eastman utilizes the Sn-In association as evidence in support of a prediction he made earlier (Eastman, 6) that Sn^{115} probably decays to In^{115}. It will be recalled that Sn^{115} and In^{115} are neighboring isobars, and, the present existence of such an isobaric pair violates a rule of nuclear stability. Mattauch and Fluegge (7) and Kohman (8) have also indicated that in the pair $Sn^{115}-In^{115}$, the former should be unstable and should decay by orbital electron capture to In^{115}, which would of course be a reasonable explanation for In-Sn association in the micas, each of which is pre-Cambrian and is 750×10^6 years old or more. Direct evidence, however, does not support significant decay of Sn^{115}. Thus activity observations by Rusinov and Igelnitzky (9) have failed to reveal possible electron capture decay in tin specimens and Ahrens (10) has found pegmatitic cassiterite (S. E. Manitoba, Canada) of extreme age, namely, 2100×10^6 years, to contain only a doubtful trace of 0.0001% In or less: consequently the fairly common association of indium with tin can not be due to electron capture decay in Sn^{115}.

As is well known, tin concentrates in later pegmatitic emanations, and likewise it is feasible that indium could be enriched in residual liquors because of the relatively large size (for octahedral co-ordination) of In^{+++}, which would tend to be rejected in favor of the smaller-sized ions—for example, those of iron, magnesium and aluminum—in minerals of earlier crystallization.

The presence of tin in mica as a possible aid for tin prospecting

From two general areas, namely, the Usakos-Karibib-Omaruru area in South West Africa, and the Uranoop River area in Namaqualand, several specimens of mica have been analyzed from various pegmatites. In the former area, many of the muscovite specimens (Nos. 8, 9, 10 and 11 of Table 1) are unusually rich in tin, in particular the specimen from Erongo (No. 11) which contains about 0.4% SnO_2, and which is from a pegmatite near a tin mine. In general, the whole of the Usakos-Karibib-

Omaruru area contains cassiterite deposits associated with granite-pegmatites. The Uranoop River area, Namaqualand, however is barren of cassiterite deposits according to de Villiers (11) and each of the twelve muscovite specimens from this region (Nos. 12–25 in Table 1) carry unusually low concentrations of tin.

Although these data are scant, they indicate that if micas from a pegmatite area show a characteristic enrichment in tin, deposits of cassiterite are likely to have been formed, whereas if the muscovites are low in tin, the area is probably barren of such deposits. In a given pegmatite area, mica specimens can usually be quickly collected from suitably spaced pegmatites: spectrochemical analyses of the samples can be made very rapidly, and the results of the analyses may be a clue to whether the area should be closely prospected as a possible tin-rich area, or disregarded. It may be added that the other common pegmatite minerals, albite, microcline, and quartz, invariably do not contain detectable amounts of tin, and would therefore be useless as possible tin prospecting indicators.

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