ON THE OCCURRENCE OF TIN IN NORWEGIAN MINERALS

ΒY

IVAR OFTEDAL

Abstract. A large number of Norwegian minerals were examined by means of optical spectrograms. In the present paper are listed those which were found to contain tin. They are almost exclusively minerals from sulphidic ore deposits and minerals from pegmatites. (In some pegmatite minerals tin has been found earlier by chemical methods. These are quoted, with references, as completely as possible.) Tin contents as high as 1% are quite exceptional and have so far been found (not counting the nordenskiöldine) only in samples of yttrotantalite, samarskite, thortveitite, and perhaps ilmenorutile. Tin contents lower than 0.001% in sulphide minerals and lower than 0,01% in the other minerals can generally not be detected by the method here applied, therefore these figures will mark the upper limit of the contents for those minerals in which no tin was found. Although this investigation reveals the occurrence of tin in a considerable number of Norwegian minerals it confirms the general impression that Norway is particularly poor in tin: the highest percentages are found only in very rare minerals.

It is well known that tin has been found in Norway only in rare cases and in quite small quantities. The following is a complete list of the data I have been able to trace in existing literature.

In Gmelin-Kraut's Handbuch (l. c.) is quoted that tin has been found in tritomite from Brevik, in fergusonite from Hampemyr, Tromøy, and in "all Scandinavian epidotes".

I. and W. Noddack ² have given Sn-concentrations for more than 40 Norwegian minerals. The figures are, however, mostly far below the sensitivity limit of the method applied in the present investigation, so that it is no use quoting them for comparison. It also

A collection of older data and references concerning tin in minerals in general is found in Gmelin-Kraut's Handb. d. anorg. Chemie, Bd. IV, 1, 233 ff., 1911

² Die Geochemie des Rheniums, Zeitschr. phys. Chem., Abt. A, 154, 214 ff. 1931.

| (| The | percentages | are | given | in | round f | guires | calculated | as | Sn) | |
|---|------|-------------|-----|-------|------------------------|----------|--------|------------|----|-------|--|
| | 1116 | percentuges | uic | given | $\iota\iota\iota\iota$ | i ouna i | izuics | cuicuiuicu | us | OIL.I | |

| Mineral | º/₀ Sn | Reference |
|---|---|--|
| Nordenskiöldine, Langesundsfjord Xenotime, -,- Polymignite, Stavern Pyrochlore -,- | 0. 1 0.1 | W. C. Brøgger, Zeitschr. Krist. 16, 1890. |
| Fergusonite, Berg, Råde -,- Arendal (3 anal.) Mossite, Råde Columbite, Ånnerød, Våler -,- Fuglevik, Råde Euxenite, Alve, Tromøy Blomstrandine, Arendal -,- Hidra (Hitterøy) Samarskite, Ødegårdsletten, Våler | 0.8 0.5 0.2 0.6 0.4 0.2 0.2 0.1 0.5 | W. C. Brøgger, Vid. Akad. Skr. I, 1906, No. 6, |
| -,- Aslaktaket -,- Yttrotantalite, Berg, Råde -,- Hattevik, Dillingøy "Ånnerødite", Ånnerød, Våler Xenotime, Hvaløy -, Narestø b. Arendal Monazite, Hvaløy -,- Dillingøy -,- Moss (2 anal.) Euxenite, Setesdal (2 anal.) -,- Eitland, Farsund Priorite, Frikstad, Iveland Risørite, Gryting, Gjerrestad | 1.0 2.4 0.1 0.2 0.1 0.1 0.1 0.2 0.1 0.1 tr. | W. C. Br., G.F.F. Sthlm., 5, 1881. C. Blomstrand, G. F. F. Sthlm., 9, 1887. Anal. 1909-10, quoted in Doelter's Handb.d.MinCh., Bd. III, 1, 1918. J. Schetelig, Vid. Akad. Skr. I, 1922, No. 1. |

makes some difficulty that many of the localities are given only approximately and one or two obviously incorrectly (e. g. cleveite, Brevik). However, one or two cases of definite disagreement will be mentioned in their turn.

The following older data are considered doubtful by the authors.

| Eucrasite, Langesundsfjord | W. C. Brøgger, Z. Krist. 16, 1890. |
|--------------------------------|---|
| Vesuvianite, Talvik, Seiland | Tom. Barth, Vid. Akad. Skr. I, 1927, No. 8. |
| Cassiterite, Glitrevatn, Modum | W. C. Brøgger, 1. c., p. 76, and V. M. |
| | Goldschmidt, Kontaktmetam, p. 280. |

All the minerals listed, not counting the doubtful cassiterite and the certainly also doubtful epidote, are pegmatite minerals, mostly rare. The only real tin-mineral, the nordenskiöldine, is extremely rare in Norway¹.

Larger quantities of nordenskiöldine have lately been found in Arandis, SW-Africa. P. Ramdohr, N. Jahrb. f. Min. &c., BB. 68, 288, 1934.

In the course of some spectrographic work, primarily not done for the special purpose of tracing tin, I found that tin enters into a considerable number of Norwegian minerals, also of other kinds than those listed above. The concentrations are, however, very low, only seldom as high as 1%. The first accidental observations I have now supplemented systematically to some extent. But of course the following does not pretend to approach a complete account of the distribution of tin in Norway.

The spectrograms were all made with a quarz spectrograph, constructed by dr. R. Mannkopff in Göttingen, in the ultraviolet. For the identification of tin were used the two lines 3175.04 and 2839.99, sometimes chequed by several others. In the region of these lines the spectrograph gives a dispersion corresponding to 5 to 7 Å per mm on the plates, and the lines are very sharp and narrow. Under these circumstances the two tin lines are both disturbed by other elements only in very special cases, so that by careful work and not too low intensities there is no danger of making mistakes. As to the concentration of the tin the order of magnitude was determined by comparison with spectra of standard mixtures containing known percentages of tin ranging from 1% to 0.001%. As the intensities of the spectral lines of a minor constituent at a given concentration may depend considerably on the nature of the main substance the mixtures were made to correspond roughly to the types of minerals examined. The minerals found to contain tin and listed below are almost exclusively sulphides (mostly zinc blendes and galenas) and rare earth minerals, therefore sets of standard mixtures were made with ZnS, PbS, thalenite, and blomstrandine (poor in tin) as main substances, further albite was used for one mixture. The intensities of the tin lines in equivalent ZnS and PbS mixtures agree very well, and it is possible to trace tin in them down to a concentration somewhat below 0.001%. found that these mixtures give good results not only for zinc blendes and galenas but also for chalcopyrite, and it may be assumed that they will apply fairly well also to other sulphide minerals. The thalenite mixture was made for comparison with rare earth silicate minerals. The tin lines here turn out to be somewhat weaker than in equivalent sulphide mixtures and can hardly be traced much below In the blomstrandine mixtures, made in view of the rare earth niobates and tantalates, the tin lines are still weaker at corresponding concentrations and disappear entirely at about 0.01%. This strong weakening is — in any case partly — due to the fact that spectra of rare earth niobates and tantalates generally show a very heavy continuous background blackening. The albite mixture shows rather high intensities of the tin lines, not very much lower than the equivalent sulphide mixtures. It was used for the examination of ordinary silicate minerals and tentatively also in a few other cases (e. g. chrysoberyl).

As an artificial mixture is physically different from the powder of the corresponding natural mineral and therefore may behave differently in the carbon arc the comparability of their two spectra is not beforehand secured. Special precautions may be necessary to produce reliable comparison spectra. In the above cases it seems well ascertained that fairly good comparison spectra have been obtained, so that the following figures will give roughly the correct values of the Sn-concentrations. The percentages are generally expressed only in whole powers of 10. The signs > and < sometimes prefixed are meant to alter the values not more than half way to the next power of 10.

1. Sulphidic ore deposits.

The minor constituents of Norwegian sulphide minerals, especially zinc blendes and galenas, will be dealt with more fully in a future publication. Here will be listed only those in which tin has been found.

a. Contact deposits of the Oslo Region.

Minerals from some twenty different localities have been examined, including the majority of the larger zinc and lead deposits. They are on the whole extremely poor in tin, the only positive data being the following:

¹ The importance of this background effect has been emphasized very much by L. W. Strock. See Tidsskr. f. Kjemi og Bergy. Nr. 6, 1938.

| | | ⁰ / ₀ Sn |
|-------------|----------------------|--------------------------------|
| Zinc blende | Kirkeby, Hakadal | 0.001 trace |

The tin supposed to be present in quarz porphyry greisen in the Glitrevann district could not be detected in a sample labelled Ilenseter—Maurtjern, collected by V. M. Goldschmidt. I may also mention that epidote from Glomsrudkollen was examined with negative result.

b. Deposits in the southern Pre-Cambrian area.

Minerals from nearly 30 single localities were examined, including deposits of various kinds and certainly very different ages. Tin was found in the following:

| | | 0/o Sn |
|---|--|---|
| Chalcopyrite. Zinc blende. Galena Niccolite. Zinc ore. | Hen, Ädalen Kongsberg district Skara, Eiker Sandåen, Gjerpen Espeland Mine, Vegardshei Stølsvik, Hisøy | trace < 0.001 0.01 trace < 0.001 0.001 |

I may mention in particular that among the localities examined with negative results were 5 copper deposits in Telemark and Nore, the Bleka Mine, Bandak and Knaben (molybdenite), Skutterud, Tråk in Bamble, Skytmyr in Froland (zinc blende), Flåt Nickel Mine.

c. Deposits in other parts of Norway, mainly of Caledonian age.

Minerals from about 25 localities were examined. Tin was found in the following:

¹ Traces of tin have been found also in other Oslo Region garnets (Gjellebekk and Kalkovnen, Grua). V. M. Goldschmidt, unpublished data from Göttingen. Verbal information.

| · | | % Sn |
|--|---|---|
| Galena¹. Zinc blende Galena Lead-zinc ore Plumosite² Zinc blende Chalcopyrite Galena³. "Bismuthinite"³ Zinc blende | Skjoldevik near Haugesund Krækjaheia, Hardangervidda Hestekletten, Røros Storvarts, Røros Eiterjorden, Beiarn Svenningdalen Forvik, Helgeland Bjørkåsen Mine, Ofoten Murstrand 4, Ofoten Hamrefjell 4 | <0.001 trace 0.001 <0.001 <0.001 0.001 0.001 >0.01 >0.01 <0.01 >0.01 trace |

Among the deposits examined with negative results were Vigsnes, Røstvangen, (in these only zinc blende examined) Løkken and Mofjellet.

2. Other ore deposits.

I have examined iron ores from Lyngrot, Klodeberg, Alve, Solberg, zinc blende from the iron deposits Langsæ, Mørefjær, Bråstad and epidote from Torbjørnsbu, all these in the Arendal district, further iron ores from Dobbe mine near Kragerø, from Søftestad, Rødsand, Sør-Varanger and from a number of smaller deposits, without finding tin in any of them. The same applies to chromite ore from Feragen, to tungsten ore from Ørsdalen and — it may be added here — to minerals from apatite deposits in Bamble and in the districts of Kragerø, Risør and Arendal. In sphene from Kragerø (in chlorite) was found trace (<0.01%) of tin.

¹ Rich in Bi, octahedral parting. J. Schetelig, N. g. t. 4, 147, 1916-17.

² Specimen lately given to the Museum by Dr. C. W. Carstens, along with a specimen of berthierite from Ringvassøy. The latter did not show any trace of tin.

³ The samples were kindly sent me by Mr. J. Ellingsen, Superintendent of the Bjørkåsen Mines. The galena is rich in Bi and shows excellent octahedral parting. The "bismuthinite" is very rich in lead and might belong to the doubtful species galenobismuthite. More information about these minerals will be given elsewhere.

⁴ Samples sent me for examination by Mr. Steinar Foslie of the Geological Survey. I am indebted to him for the permission to publish the results.

3. Pegmatite minerals.

a. Oslo Region.

The following minerals from the Langesund and Larvik districts have been found to contain tin:

| | º/₀ Sn |
|---|---|
| Galena Eucolite Mosandrite Polymignite Pyrochlore | < 0.001 0.001 0.01 < 0.01 0.01 0.1 |

No tin was found in zinc blende, molybdenite, zircon, orangite, lepidomelane, cryptoperthite.

b. Granite pegmatites of the southern Pre-Cambrian area.

Moss district.

| | º/₀ Sn |
|------------|------------|
| Brøggerite | 0.1 > 1 |

Tin was not found in columbite (Ånnerød) and fergusonite (Berg).

Kragerø district.

| | | % Sn |
|-----------|--------|------------|
| Columbite | Tangen | 0.1 0.1 |

Tin was not found in phenacite, hellandite, alvite, thorite.

| Ţ | >; | ca | r— | Λ | re | nd | la' | 1 |
|---|----|----|-----|---|-----|----|-----|---|
| г | τı | SO | r — | А | 1.6 | ш | IH. | |

| | ⁰ /₀ Sn |
|--------------|--------------------|
| | 0.1 |
| MørefjærAlve | 0.1 |

Tin was not found in risørite (Gryting), allanite (Noddeland), orangite (Fogne), thorite, microcline and oligoclase (Arendal).

Iveland—Evje.

| | | ⁰/₀ Sn |
|--------------------------|----------------------|--------|
| Galena | Landsverk | 0.001 |
| Chrysoberyl | Nateland (2 samples) | 0.1 |
| Ilmenite ("platejern") | Iveland | < 0.01 |
| Magnetite | Torvelona | 0.01 |
| Spessartite | — , | > 0.01 |
| Thortveitite 1 | — | > 1 |
| | Ljosland | 1 |
| | Tjomstøl | 1 |
| — | Eftevatn | 1 |
| | Iveland | 0.1 |
| | Unneland | < 0.1 |
| | Håverstad | 1 |
| Ilmenorutile | | > 0.1 |
| Yttrotitanite | Iveland | 0.1 |
| Samarskite | Tveit | 0.1 |
| Blomstrandine | Kåbuland | 0.01 |
| Microlite | Landås ² | 0.1 |
| Tantalite | <u> </u> | 0.01 |
| Spessartite ³ | — | 0 01 |
| Mica (greenish) | | 0.01 |
| Topaz ³ | — | 0.001 |

¹ For comparison was also examined the thortveitite from Befanamo, Madagascar. The spectrum indicates about 1 % Sn, in very good agreement with the Iveland thortveitites. Trace of tin has earlier been found in the Madagascar thortveitite, Ch. Boulanger et G. Urbain, C. R. Paris, No. 23, 1922, quoted by Schetelig, Vid. Akad. Skr. I, 1922, No. 1. p. 83.

For situations and descriptions of localities in Iveland and Evje see H. Bjørlykke, N. g. t. 14, 1935, 211 ff. Many of the specimens examined are taken from his research material.

³ Topaz and spessartite from Landås are exceptionally rich in *germanium*. The topaz probably contains about 0.1 % Ge, and the spessartite somewhat less.

Tin was not found in bismuthinite (Iveland), molybdenite (Tveit), biotite (Ljosland), cleavelandite-quarz-beryl-alvite (Landås), beryl (Torvelona: trace of tin is present but also scandium, so that the tin is probably due to intermixture with thortveitite), thalenite (Ivedal and Høgetveit), gadolinite (Frikstad), xenotime (Ertveit), monazite (Mølland and Nateland), fergusonite (Høgetveit).

Hidra (Hitterø).

| | º/₀ Sn |
|-----------|------------|
| Polycrase | 0.1 0.1 |

Tin was not found in molybdenite, gadolinite, malacon.

c. Pegmatites of Northern Norway. Hundholmen, Tysfjord.

Thalenite, gadolinite, yttrofluorite did not show any trace of tin.

Seiland.

Biotite and the vesuvianite mentioned above were examined, with negative results.

4. Spectra of a few **ordinary rock-forming minerals**, e. g. rhomb porphyry felspar, biotite from micaschist, olivine from dunite, did not show any trace of tin.

Conclusion.

It will be seen that small quantities of tin are found in a considerable variety of Norwegian minerals which, however, largely belong to only two main types of deposits, namely sulphidic ores and pegmatites. The average concentration of tin in the upper lithosphere is according to V. M. Goldschmidt¹ about 40 g per ton (0.004%), so that most of the figures given in this paper represent

¹ Geochem. Verteilungsges. IX, Vid.-Akad. Skr. I. 1937, No. 4, p. 92.

relative enrichments. Compared with the concentrations in the surrounding rocks the enrichments are doubtless in general, and probably without exception, very strong. This means a confirmation of the experience of the mining geologists that Norway is particularly poor in tin.

The tin contents in sulphide minerals will be dealt with elsewhere. It may only be mentioned here that tin, when present in sulpidic ore deposits of types common in Norway, is found to enter almost exclusively into galena, zinc blende, and chalcopyrite and not into pyrite and pyrrhotite. The distribution of tin between galena and zinc blende in one and the same deposit is highly variable with the type of deposit and is obviously a function of the conditions of formation. The contents are all very low but have been found both in Pre-Cambrian, Caledonian and Oslo Region deposits. The highest concentrations have been found in the Bjørkåsen Mine, Ofoten. Tin has so far not been detected in any deposit belonging to the Telemark System, nor in pentlandite-pyrrhotite ore.

As to the pegmatite minerals a comparison shows that the earlier data only partly agree with the spectrographic results. In some cases the contents of tin given in the old analyses could not be detected in the spectra (e. g. fergusonite, Berg and columbite, Ånnerød), and in numerous cases the spectra show tin which had not earlier been detected. This discrepancy is certainly due to the fact that the detection and determination of small quantities of tin in minerals of types here dealt with is very difficult by ordinary chemical methods. Also, if X-ray spectral analysis is being used, tin belongs to the elements whose wavelengths are particularly unfavorable. Tin is present in pegmatites all over the region between Flekkefjord and Moss, both in the Pre-Cambrian granite pegmatites

The presence of tin in galena, zinc blende and chalcopyrite has been observed earlier. For galena see K. Hoehne, Chemie d. Erde 9, 219, 1935—36. For zinc blende a number of references could be given. For chalcopyrite no data seem to have been published, but Professor Goldschmidt has told me that some chalcopyrites examined in his institute in Göttingen were found to contain tin. He also calls attention to the obvious explanation of the presence of tin in chalcopyrite and zinc blende, namely the structural relationship of these two minerals and stannite. In accordance herewith inclusions of stannite obviously formed by exsolution are sometimes found in zinc blendes and similarly inclusions of zinc blende and chalcopyrite in stannite. Schneiderhöhn-Ramdohr, Lehrb. d. Erzmikroskopie, Bd. 2, pp. 107, 475. 1931.

and in the syenitic and nepheline-syenitic pegmatites of the Oslo Region. It appears (not counting the nordenskiöldine) to enter preferably into the following minerals, arranged according to decreasing content of tin (down to about $0.1\,$ 0 $_{0}$): 1

| Samarskite |
|--|
| Ilmenorutile — Yttrotitanite — Microlite — |
| Yttrotitanite — Microlite — |
| Microlite |
| |
| Samarskita |
| Samarskite |
| Chrysoberyl — |
| Ilmenorutile Arendal district |
| Euxenite |
| ColumbiteKragerø |
| Betafite |
| BlomstrandineHidra |
| Polycrase — |
| PyrochloreOslo Region |

From these data the Østfold and Iveland pegmatites seem to be richer in tin than other Norwegian pegmatites. On the other hand the highest concentrations in different localities are not always found in corresponding minerals, and a given mineral species may show widely varying tin contents in different localities within the same district, so that it is perhaps not justified to stress this conclusion on the ground of the above material. Tin seems to be generally absent from the following minerals, even if some of them occur in company with tin-bearing minerals:

Molybdenite zircon-malacon-alvite-thorite-orangite thalenite-hellandite-(allanite)

In connection with this list I 'quote some of the data given by I. and W. Noddack (I. c.). Samarskite, Moss: 0.005%; Thortveitite, Iveland: 0.0002%. Blomstrandine, Hidra: 0.004%. These figures are all very much lower than my results. We have to allow for the possibility that the content of tin may vary widely in different samples even from the same locality, but it is in any case extremely improbable that a sample of thortveitite from Iveland should be practically without tin. It will be seen (p. 321) that I have examined thortveitites from 5 different localities in Iveland, and my result was in all cases 0.1% or more. The one with a somewhat lower content is from Evje, but even here the concentration was found to be higher than 0.01%.

gadolinite-beryl-phenacite (xenotime)-(monazite) fergusonite quarz-felspars-biotite.

For those in brackets the observational data are rather scanty in view of the wide distribution of these minerals.

Reasonable crystallochemical explanations of the presence of tin in many pegmatite minerals can be offered. If we assume that the ionic radius of tin (Sn4+: 0.74 Å) is sufficiently similar to those of titanium and scandium (Ti4+: 0.64 Å, Sc^{3+} : 0.83 Å) for a partial replacement, remembering also that the charge of the tin ion is not lower than those of the others1, this will account for the tin found in titanium minerals², many niobate-tantalates and in thortveitite. However, the matter is complicated and it is for instance difficult to see why yttrotantalite and samarskite, as it seems, contain much more tin than the euxenite minerals which are really rich in titanium. Here we obviously have to assume a replacement also of Nb⁵⁺ (0.69 Å) and Ta⁵⁺ (\sim 0.7 Å) by Sn⁴⁺; such a replacement is known from the isomorphous mixtures tapiolite-cassiterite. Among the things which are still more difficult to explain is the considerable content of tin found in chrysoberyl. It may be worth noting that the minerals with the highest Sn-contents include some of the very rarest species in our pegmatites.

The apparent absence of tin in the Norwegian iron ore deposits is remarkable.

Acknowledgement. I wish to thank Professor dr. V. M. Gold-schmidt for placing at my disposal the facilities of the Raw Material Laboratory and the mineral collections of the Mineralogisk-geologisk museum, and not least for many suggestions of great value.

Oslo, Mineralogisk-geologisk museum, April 1939.

¹ The rule here applied has first been published by V. M. Goldschmidt and Cl. Peters, Nachr. Ges. Wiss. Göttingen, Math.-Phys. Kl. 1931, p. 271.

² A titanite from Arandis, SW-Africa has been found to contain at least 10% Sn. P. Ramdohr, N. Jahrb. f. Min. &c, BB. 70, 15, 1936.