THE SIGNIFICANCE OF THE VARIABLE IRON CONTENT OF THE "WOLFRAMITES"* OF THE WEST OF ENGLAND

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Abstract

It is stressed that very little work has been done on the variations in the percentages of iron and/or manganese in wolframites despite the fact that important geochemical conceptions might accrue from it.

The limited published information on the subject is reviewed, and the method used by the writers for determining the iron content of a representative selection of wolframites from the West of England is noted.

Perhaps the most important result of the work is the indication that the wolframites of the pegmatites are the poorest in iron (and, therefore, the richest in manganese) whilst, in general, those of the "normal" hypothermal lodes are the richest. Wolframites from greisen-bordered veins tend to occupy an intermediate position.

As it is well known that manganese tends to concentrate in late pegmatitic and pneumatolytic—or early hypothermal—fractions (see, for example, Rankama, K. and Sahama, T. G., 1950, p.644) it appeared likely to the writers that there might be some correlation between the manganese content of wolframites from a particular metallogenetic province and the stage in the post-granitic phase of ore-development at which they were formed provided that at any given stage the requisite amounts of iron and manganese were available. (Obviously, for example, manganese might proxy for iron if the ore-forming agents were deficient in the later element, and this would lead to the crystallisation of a wolframite whose composition would not be truly characteristic of the particular conditions of temperature and pressure pertaining at that time.) That is to say, it seemed reasonable to suppose that generally the early pegmatite wolframite might be comparatively rich in manganese whilst the "normal" hypothermal wolframites might be comparatively poor in this element. It was also thought that if this first premise proved to be correct, partial-analyses of wolframites from different horizons of the same ore-body might — provided a sufficient number of samples

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* In this paper the term "wolframite" is used to denote any member of the ferberite-wolframite-hübnerite series irrespective of its iron content.

could be obtained — shed some light on the exact manner of its formation. With these ideas in mind a representative collection of wolframites from the West of England has been made and analysed, and at the outset it can be stated that the first of the above premises has been demonstrated to be essentially correct, whilst sufficient samples have not yet been obtained from a single ore-body to test the second adequately.

For the purposes of this research it has been assumed that the manganese content of any given wolframite varies inversely as the iron content, and consequently meaningful information could be obtained it the iron alone were determined. (This decision to determine only the iron was based solely on analytical considerations.) It is, of course, realised that certain elements can substitute to some extent for the iron and manganese (see, for example, Redinha, J. S., 1952) and that there might be preferential substitution. However, there is no evidence that the degree of substitution is ever likely to be of such magnitude that it would cause a seriously distorted picture of the iron-manganese distribution in the wolframites of the various types of ore-body to be obtained by adopting the course followed in the present investigation.

A review of related work

It must be stressed that there is a paucity of information — as far as the writers are aware — concerning variations in the compositions of "wolframites".

Redinha (1952) determined the trace elements present in 34 Portuguese wolframites by spectrographic methods and noted that all but one of the specimens examined by him were manganese-rich varieties. He concluded that the single iron-rich specimen (from Covas — Vila Nova de Cerveira) crystallised later, and at a somewhat lower temperature, than the others, and was of the opinion that this was supported by the trace elements present.

Li, K. C. and Wang, C. Y. (1947) — in their monograph on tungsten — limit their observations on variations in the iron and manganese contents of wolframites to the fact that whilst the wolframites from two Chinese deposits — which, judging by their mineralogic characteristics (much felspar, intense tourmalinisation of the wall-rock, etc.) were developed early in the sequence of ore-formation — possessed FeO : MnO ratios of 1 : 5 and 1 : 1 respectively, those from two later (lower temperature) deposits were characterised by ratios of 3 : 2 and 2 : 1, respectively (p.37).

Recently Berman, J. B. and Campbell, W. J. (1955) published the iron content of wolframites from a number of countries but they omitted all details of the deposits from which their samples were obtained. These workers also noted that as much as 20 per cent., or more, of the iron in naturally occurring wolframite might be in the ferric state, and that on oxidation in air at elevated temperatures most of the iron becomes trivalent but a certain amount resists this change and the percentage of non-oxidisable iron increases with the manganese content.

Analytical technique

Fresh fragments of wolframite were selected from coarsely-crushed hand-specimens and then further reduced, and the final selection of material for analysis was made under a binocular microscope. These grains were ground to an impalpable powder and 0.5 g. was weighed and decomposed by treatment, first with hot conc. HCl, and then with hot conc. HNO_3. After dilution the yellow WO_3 was removed by filtration and the iron was precipitated as $Fe(OH)_3$ by addition of 0.880 ammonia to the filtrate. The residue was treated with 0.880 ammonia which, by dissolving the WO_3 as $(NH_4)_2WO_4$, showed that none of the sample had resisted the acid attack. The $Fe(OH)_3$ was dissolved in dilute HCl and the ferric iron reduced by the well-known $SnCl_2/HgCl_2$ method. Finally the iron content was determined by titrating with standard $K_2Cr_2O_7$ using barium diphenylamine sulphonate as an internal indicator.

Discussion of the results (see Fig. 1)

Unquestionably the heavy-mineral pegmatites were the first of the post-granite ore-bodies to be formed in the West of England, and there are good mineralogic — and other — reasons for thinking that the greisen-bordered veins were amongst the earliest of the remaining types to be developed. These views are supported by the results of the investigations recorded in this paper in that in general there is an enrichment in iron (and, therefore, impoverishment in manganese) as one passes from pegmatite wolframite, via that of the greisen-bordered vein type, to what might be termed the normal

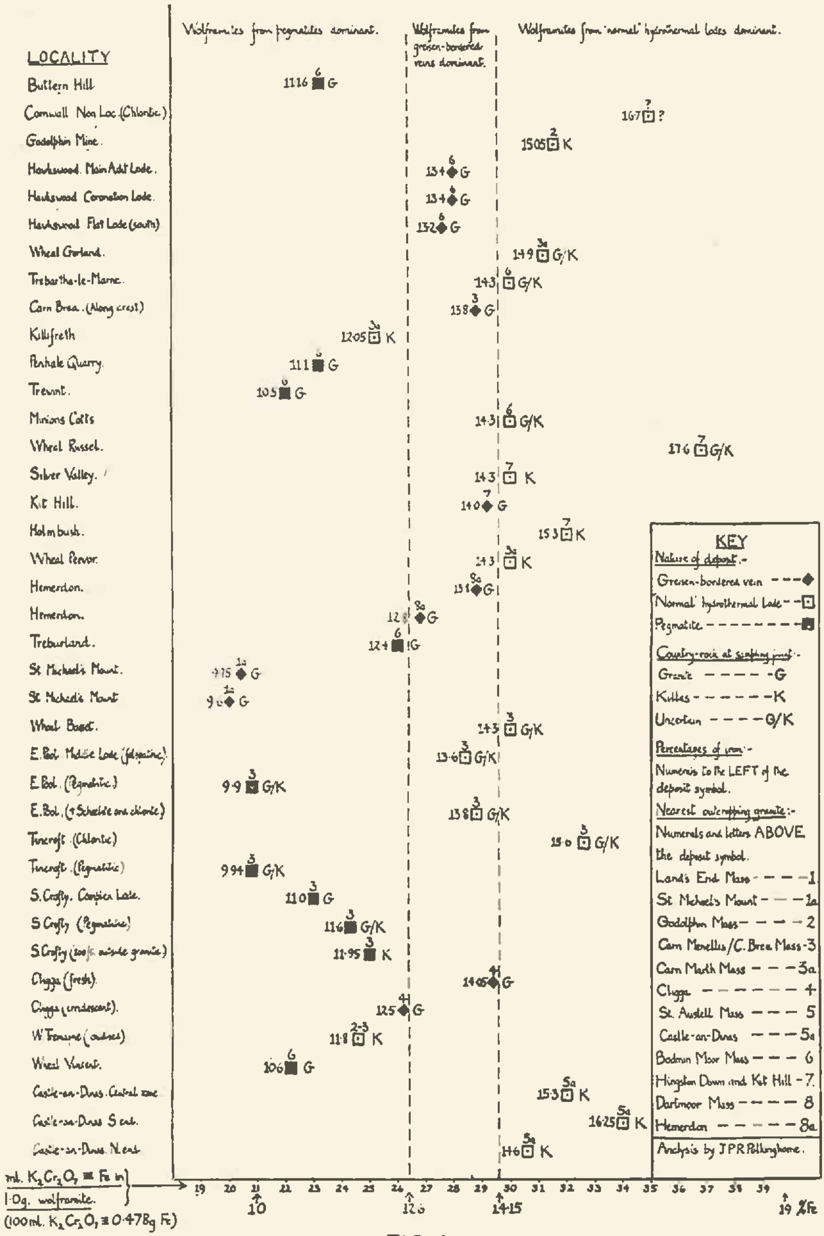
Wolframites from pegmatites dominant.
Wolframites from greisen-bordered veins dominant.
Wolframites from 'normal' hydrothermal lodes dominant.
LOCALITY
Buttern Hill
Cornwall Non Loc. (Chloritic)
Godolphin Mine.
Hawkswood. Main Adit Lode.
Hawkswood Coronation Lode.
Hawkswood Flat Lode (south)
Wheal Garland.
Trebartha-le-Marne.
Carn Brea. (Along crest)
Killifreth
Penhale Quarry.
Trewint.
Minions Cotts
Wheal Russel.
Silver Valley.
Kit Hill.
Holmbush.
Wheal Fevor.
Hemerdon.
Hemerdon.
Treburland.
St Michael's Mount.
St Michael's Mount
Wheal Basset.
E. Pool. (Pegmatitic)
E. Pool. (+ Scheelite and chlorite)
Tincroft (Chloritic)
Tincroft (Pegmatitic)
S. Crofty. Complex Lode.
S Crofty (Pegmatitic)
Cligga (fresh).
Cligga (iridescent).
W. Trenance (outcrop)
Wheal Vincent.
Castle-an-Dinas. Central zone
Castle-an-Dinas S end.
Castle-an-Dinas. N end
KEY
Nature of deposit:-
Greisen-bordered vein
'Normal' hydrothermal lode
Pegmatite
Granite - G
Killas - K
Uncertain - G/K
Percentages of iron:-
Numerals to the LEFT of the deposit symbol.
Nearest outcropping granite:-
Numerals and letters ABOVE the deposit symbol.
Land's End Mass - 1
St Michael's Mount - 1a
Godolphin Mass - 2
Carn Menellis/C. Brea Mass - 3
Carn Marth Mass - 3a
Cligga - 4
St Austell Mass - 5
Castle-an-Dinas - 5a
Bodmin Moor Mass - 6
Hingston Down and Kit Hill - 7
Dartmoor Mass - 8
Hemerdon - 8a
Analysis by J.P.R. Pilkinghorne.
ml. $K_2Cr_2O_7 \equiv$ Fe in 1.0g. wolframite.
(100ml. $K_2Cr_2O_7 \equiv 0.478$g Fe)
19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39
10
12.6
14.15
19 % Fe

FIG. 1.

hypothermal lode type. The picture is, however, marred by certain anomalies — some of which are more apparent than real — and these, together with certain other interesting features of the results, are now discussed.

The wolframites from the lodes in killas at West Tremayne and Killifreth contain percentages of iron which are intermediate between those from the pegmatites and the greisen-bordered veins. As only a limited amount of dull wolframite from West Tremayne was available it was expected that its iron content would be somewhat lower than that of fresh material as the writers had demonstrated—by analysing fresh and slightly oxidised wolframites from Cligga and elsewhere — that during oxidation there is a tendency for iron to be leached rather more readily than manganese: they are, therefore, convinced that the slight oxidation of the Tremayne sample is the sole reason for its anomalous composition. This view is strengthened by the fact that the wolframite is intimately associated with iron-bearing sulphides — so probably sufficient iron was present in the ore-forming solution for wolframite of "normal" composition to be developed. Furthermore, there is no reason for believing that an abnormal iron/manganese ratio was established as a result of the mineralising agents abstracting manganese from the country rock.

Killifreth Mine is in killas which is intruded by greenstone and intersected by granitic veins (suggesting the granite contact is near), porphyry dykes and lodes. According to Dines (1956, p.404) the Middle Lode — when in killas — " shows a comb structure and here and there consists of stanniferous schorl-rock and clear quartz with wolfram and molybdenite in layers . . . The lode has yielded also chalcopyrite, mispickel, blende and pyrite ". The presence of schorl ("black" tourmaline) indicates that the development of this lode commenced at a very early stage — possibly during the waning stages of pegmatite formation — and, therefore, the comparatively low iron content of the wolframite is probably in no way anomalous. It is, nevertheless, unfortunate that wolframite from a similar lode has not been available for comparison.

The lodes of Hawkswood Mine are in granite, and although some of them contain a little felspar and are not everywhere greisen-edged, the iron-content of their wolframites establishes — beyond all reasonable doubt — that they are somewhat unusual members of the greisen-bordered group. Furthermore, although the Coronation Lode and Main Adit Lode of this mine appear to peter out against the hanging- and foot-wall, respectively, of a porphyry dyke, so that their true relationship is in doubt, the fact that their wolframites contain precisely the same amount of iron strongly suggests that they are parts of the same ore-body.

One of the most interesting facts which has emerged from this work is that — with two notable exceptions — all the wolframites yet examined from greisen-bordered veins contain practically the same amount of iron. This observation suggests that such deposits were developed under unique conditions which persisted for only a comparatively short space of time and lends support, therefore, to the view that these bodies should be allotted a special place in any genetical classification of ore-deposits. The two wolframites with anomalous compositions are both from St. Michael's Mount, and the unusually low iron-content in these is doubtless due to a marked paucity of this element in the ore-forming agents. This is indicated by the almost complete absence of iron-containing heavy minerals — wolframite apart — in all but a few of the lodes of St. Michael's Mount. In fact, there is good mineralogic and structural evidence for believing that the few exceptional veins — which contain chalcopyrite, etc. — are distinctly later than the typical cassiterite/wolframite lodes of the Mount. (Hosking, K. F. G., unpublished studies.)

The wolframite from the vicinity of Russel United Mines (near Gunnislake and the eastern contact of the Hingston Down granite mass) is notable because of its unusually high iron content. The hand-specimen, from which the material for analysis was obtained, consisted of a portion of a quartz/wolframite vein in kaolinised granite, and largely as a result of the analysis it must be concluded that there is a distinct possibility that the lode was formed late and presumably at a comparatively low temperature. It may not be entirely coincidental that in the New Consols Mine, about 2½ miles to the N.W. of the Russel area, Vokes and Jeffery (1954-55, p.157) found a little wolframite associated with quartz, siderite and pyrite which they believe was formed much later — and at a considerably lower temperature — than the comparatively commonly occurring, arsenopyrite-associated wolframite of the mine. It is also stated that

" the fact that the deposition of wolframite may not be confined to high-temperature conditions was recognised by Lindgren (1933). He describes the tungsten deposits of Boulder County, Colorado, which he places in the mesothermal group. Here the principal mineral is ferberite, which occurs in a fine-grained mixture with quartz, or as beautiful crystals coating druses, associated with quartz crystals. It seems that the small patch of wolframite crystals at New Consols is a minute representative of such medium-temperature tungsten deposits ".

The occurrence of wolframite in pegmatites and also in normal hypothermal lodes within the same mine is not uncommon in the Camborne-Redruth area, but there is a marked compositional difference between the wolframites of these two classes of deposit which is demonstrated, for example, by the partial-analyses of the East Pool Mine samples. The outstanding difference between the iron content of the pegmatite wolframites and those of the other types of deposit constitutes a strong reason for believing that the heavy minerals in pegmatites are — at least sometimes — truly pegmatite minerals and not the products of subsequent pneumatoylic and/or hydrothermal phases of mineralisation. It also suggests that the development of a heavy-mineral pegmatite was an event which was controlled by completely different factors from those which determined, for example, the zonal distribution of minerals within the lodes proper. However, the presence of felspar in a deposit does not ipso facto, indicate that the latter is a pegmatite, although it suggests that its development started at a comparatively early stage in the period of ore-deposition. This is demonstrated by the comparatively high iron-content of the wolframite of the Middle Lode of East Pool Mine — a lode which is characterised by the presence of appreciable quantities of pyrite, arsenopyrite, quartz and microcline felspar, in addition to the mineral under discussion.

It is somewhat surprising that the three wolframites from Castle-an-Dinas Lode contain iron in amounts which suggest that the deposit was formed rather late with respect to the granite with which it is genetically related, but which — as far as the writers are aware — cannot be seen in the mine. If this suggestion is correct there must have been a very considerable time lapse between the emplacement of the pre-lode granite and the tongue of granite which passes through the ore-body. It is of further interest to note that the sample with the highest iron-content differs physically from the others and is termed " steely wolfram " by the mine-manager. It seems likely that the results obtained by determining the iron-content of a comprehensive suite of wolframites from the various horizons of this mine would clarify the manner of development of the ore-body. (For details of the geology of Castle-an-Dinas Mine see Kear, D., 1951-52, pp.129-140.

Finally, the results suggest that provided the compositional characteristics of wolframites from the various types of deposit of a metallogentic province are known, the determination of the iron-content of eluvial wolframites found there should generally indicate the nature of the primary deposits from which they were derived, and this would facilitate prospecting. There is, of course, always the possibility that the wolframite—like that of St. Michael's Mount — might have an anomalous composition which would lead to an erroneous conception of the type of primary ore-body from which it was derived. However, the available data gives reason for believing that wolframites with abnormal iron-contents are rare.

Conclusion

In conclusion it must be stated that it is a matter of regret that suitable samples from a much larger number of localities were not available for analysis, but the difficulty of obtaining material from mines which have — for the most part — long ceased to operate needs no elaboration. It is, however, hoped to obtain further samples, and, in particular, to collect sufficient material from Cligga, St. Michael's Mount and Castle-an-Dinas to determine to what extent this method of investigation can contribute to the understanding of the mode of formation of specific wolframite deposits. Perhaps, therefore, this paper should be termed an interim report.

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