MINERALOGICAL STUDY ON THE WOLFRAMITE SERIES
FROM THE CHUGOKU DISTRICT, SOUTHWEST JAPAN (I)
RELATIONSHIPS BETWEEN LATTICE PARAMETERS
AND CHEMICAL COMPOSITIONS

AKIRA SOEDA, SETSUO TAKENO and MAKOTO WATANABE
Institute of Geology and Mineralogy, Faculty of Science, Hiroshima
University, Hiroshima, 730, Japan

In the Chugoku district, Southwest Japan, wolframites occur mainly in veins in and
around the Late Cretaceous to Early Tertiary granitic rocks. In the present paper, the
mineralogical characteristics and regional variation in Fe/Mn ratios of the wolframite series
from 27 localities in the district, together with those from some other regions are discussed
in terms of the lattice parameters and mineralogical association.

The relationship obtained between chemical composition and the values of $a_0$, $b_0$, $c_0$
and $\beta$ agree mostly with the previous results. Among them, it is worthwhile to note that
with the exception of Mn-rich member, the $\beta$ value almost remains constant, conflicting
with the previous studies. In calculation, however, $\beta$ can also change linearly with variation
of the composition accompanying with the linear change of the values, $d_{011}$-$d_{110}$ and/or
quartz (102)-wolframite (200).

The unit cell volume of the series expands with the increasing substitution of iron with
manganese with or without other cations. The lengthening of $a_0$, $b_0$, and $c_0$, especially of
the former two is responsible for the expansion. The compositional distribution of the
natural wolframite series, characterized by the relatively rare occurrence of Mn-rich member,
may be indicative of the degree of difficulty in the Fe/Mn substitution and the possibility
of the presence of immiscibility gap in the series.

As was pointed out by Sasaki (1959), the natural wolframites deviate slightly from
the relationships between composition and unit cell parameters obtained with synthetic
compounds. This is best explained by the influence of some cations such as Nb and Y other
than Fe and Mn in the crystal structure of the mineral, supporting the conclusions reached
by the previous workers. In this connection, the presence of 1 per cent order of Nb in Mn-
rich wolframites from the Sekigane mine may give an evidence in support of this.

Regional variation of Fe/Mn ratios in the wolframite series from the Chugoku district
is examined in relation to the granite province with which the wolframite deposits are
intimately associated. There seems to exist a tendency, though not so remarkable, that
wolframites in the granitic rocks of the Sanin-Shirakawa Zone, characterized by relatively
higher oxidation state, are rich in manganese, while wolframites in those of the Sanyo-
Naegi Zone, characterized by relatively lower oxidation state, are rich in iron. All the
samples with composition close to huebnerite end member came from the manganese
deposits or Paleozoic formation nearby or rich in manganese deposits. Sasaki (1960) also
reached the same conclusion.

Thus, it is concluded that composition of the wolframite series may vary according to
the bulk chemical composition of surrounding rocks through which the ore fluids migrated
and to the oxidation state of the ore fluids and perhaps of related granitic magma. Other
possible factors to affect on the Fe/Mn ratios are physicochemical ones such as temperature
and acidity of the ore fluids.

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INTRODUCTION

In the Chugoku district, Southwest Japan, the tungsten and molybdenum ore deposits are distributed in and around the Late Cretaceous to Early Tertiary granitic rocks (Fig. 1). Kinosaki (1952) divided the granitic rocks of the district into two rock provinces based on their metallogenetic characters: one is the San-in granite province (later re-defined as the Sanin-Shirakawa Zone by Ishihara (1973) and Tsusue and Ishihara (1974)), and the other is the Hiroshima granite province (the Sanyo-Naegi Zone, ditto). The definition of the granitic provinces by Tsusue and Ishihara (1974) will be used in this paper. The granitic rocks of the former are characterized by hydrothermal Mo (molybdenite) and clay (sericite) mineralization, while those in the latter by pneumatolytic and hydrothermal tungsten ( wolframite) mineralization (Kinosaki, 1952). This study is essentially an extension of the pioneer work by Kinosaki (1952).

Subsequent studies by Ishihara (1971, 1973), Kanaya and Ishihara (1973), Shibata and Ishihara (1974), Tsusue and Ishihara (1974), and Ishihara and Matsuhisa (1977) confirmed the difference of the above two granitic rocks in their petrological and geochemical properties. One of their conspicuous matters is the K-Ar age determinations on silicates with or without Mo or W mineralization, with the resultant disclosure of the geochronological difference between the two types of the granitic rocks: one is related to the molybdenum mineralization, ranging from 46.6 to 65.2 m.y., and the other is related to tungsten mineralization, varying from 64.2 to 95.8 m.y. (Ishihara, 1971; Shibata and Ishihara, 1974). For recently determined isotopic ages of minerals and rocks in Southwest Japan, see the compilation by Nozawa (1970). Moreover, Ishihara (1971) pointed out that tungsten deposits tend to be associated with less acid intrusives than molybdenum deposits. In addition, the difference in the oxidation state between the two types of granitic rocks was suggested by Ishihara (1971) and Tsusue and Ishihara (1974).

On the other hand, concerning these tungsten ore deposits themselves and the mineralogical properties of the wolframite series, only a little researches have been done to date. For instance, Sasaki (1959) investigated the lattice parameters of synthetic and natural wolframite series. On the basis of the X-ray analyses of the series from 42 localities in Japan, Sasaki (1961) and Sasaki and Ishihara (1976) concluded that the wolframite series from the “plutonic-type ore deposits” show a wide compositional variation from pure FeWO$_4$ to pure MnWO$_4$ end members of the series. While, those from “subvolcanic-type ore deposits” are tend to have composition of the end members. Also Sasaki (1961) placed stress on the effect of chemical composition of surrounding rocks on the composition of the series. Recently, Hsu (1976) examined the stability relations of the wolframite series and concluded that the variation of Fe/Mn ratios in the series is of little value as a clue to estimate physico-chemical environments during ore deposition.

However, detailed investigations have not been done yet on the series from the ore deposits genetically related to the granitic rocks of the Chugoku district.

In this paper, the natural wolframite series from 27 localities were investigated. Most of the specimens were collected from the ore deposits in the granitic rocks of
different petrological and geochemical properties which might, in part, be responsible for the diversity of the mineralogical characteristics of the wolframite series in the district. For the comparative study, wolframites from some other localities, such as those from the Hagidaira mine were also examined. By means of the lattice parameter measurements, ore microscopy, and X-ray fluorescence analyses, the mineralogical characteristics of the wolframite series and their regional variation of Fe/Mn ratios in the series from the Chugoku district will be discussed. The detailed examinations of chemical compositions of the series using electron microprobe are now in progress and will be published in near future.

We are grateful to Dr. A. Sasaki, Geological Survey of Japan, to Dr. L.C. Hsu, University of Nevada, and to Dr. H. Schröcke, der Universität München, for their helpful suggestions on the wolframite works. Thanks are extended to Dr. K. Kinosaki, a pioneer in research of W-Mo ore deposits and granitic province of the Chugoku district, for his constant encouragements during the course of this study. Miss N. Fukuhara of this Institute assisted us in preparation of the manuscript. The present study was in part financially supported by the Grant-in-Aid for Science Research from the Ministry of Education of Japan.

**OUTLINE OF WOLFRAMITE-BEARING ORE DEPOSITS IN THE CHUGOKU DISTRICT**

With the exception of scheelite, the tungsten ore deposits in the Chugoku district occur mainly as wolframite-quartz veins in the granitic rocks of the two rock provinces, to which they are assumed to be genetically linked. Following their rock provinces, general descriptions of the ore deposits are given below.

**A. Ore deposits in granitic rocks of the Sanyo-Naegi Zone**

The tungsten ore deposits, occurring as quartz-wolframite veins, are most widely distributed in this rock province. The host granitic rocks are commonly “greisenized” near the veins. This type of veins occur usually at the marginal part of the granitic rocks and their distribution is restricted to a rather narrow zone in the eastern part of the district, while the zone expands towards the central part. In the western part of the Sanyo-Naegi Zone, as is seen in Fig. 1, the ore deposits are most frequently distributed even near the Sanin-Shirakawa Zone. K-Ar ages on minerals of granitic rocks of the Sanyo-Naegi Zone are in the range 50 to 100 m.y., including those of the Ryoke Zone (Ishihara, 1973), while alteration products associated with tungsten mineralization give an age ranging from 64.2 to 95.8 m.y. (Ishihara, 1973; Shibata and Ishihara, 1974).

As is seen in the figure, some of the ore deposits occur in the sedimentary rocks of Paleozoic Age which is intruded by granitic rocks. These ore deposits are also quartz-wolframite veins accompanied with greisenization. In pyrometasomatic deposits, wolframite is sometimes present as pseudomorph after scheelite (Sato, 1977). The mineral assemblage of these types of veins is very similar to that of the adjacent ore deposits of contact metasomatic or hydrothermal origins. Representative ore minerals are chalcopyrite, pyrite, pyrrhotite, sphalerite, galena, molybdenite, and scheelite, with small amounts of As, Bi, and Sn minerals. Common gangue minerals are quartz, muscovite (sericite), topaz,
fluorite, and potash feldspars. It should be noted that in all of the veins, wolframite decreases with increasing depth, resulting in the presence of abundant quartz and small amounts of molybdenite in the lower part of the ore deposits.

The following ore deposits are included in this category and the descriptions of these ore deposits are summarized in the Appendix.


B. Ore deposits in granitic rocks of the Sanin-Shirakawa Zone

The tungsten ore deposits of the Sanin-Shirakawa Zone, though poor in number and production, occur as wolframite-molybdenite-quartz veins or networks in granitic rocks. There is a tendency that the ore deposits concerned are distributed along the southern margin of the granitic rocks of the Sanin-Shirakawa Zone, of which K-Ar ages on minerals of the granitic rocks vary from 25 to 75 m.y. (Ishihara, 1973), while alteration products such as muscovite associated with molybdenum mineralization give an age ranging from 46.6 to 65.2 m.y. (Ishihara, 1973; Shibata and Ishihara, 1974). In this type of ore deposits, molybdenite is much more abundant than wolframite and the mineral assemblage observed is more simple than those described before. Associated ore minerals are pyrite, chalcopyrite, magnetite, and/or pyrrhotite. The veins are characteristically greisenized, containing sericite (muscovite), potash feldspars, garnet, so-called “green biotite”, and rarely andalusite. In contrast to the ore deposits of the Sanyo-Naegi Zone, as was suggested by Kinosaki (1952), it is
noted that "pneumatolytic" minerals such as topaz are lacking in those of the Sanin-Shirakawa Zone.

The following ore deposits are belonging to this granitic province and the descriptions of the ore deposits and specimens are given in the Appendix.

C. Ore deposits outside of the Chugoku District

For the comparative studies, wolfr-

Table 1. Unit cell parameters of the wolframite series from Chugoku district. Data for samples from other regions are also included.

<table>
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<tr>
<th>Sp. No.</th>
<th>a₀ (Å)</th>
<th>b₀ (Å)</th>
<th>c₀ (Å)</th>
<th>β (°)</th>
<th>V (Å³)</th>
<th>a₁₁-c₁₁ (Å)</th>
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<td>STW76-12</td>
<td>4.790</td>
<td>5.737</td>
<td>4.974</td>
<td>90.01</td>
<td>136.69</td>
<td>0.0888</td>
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<td>770824-07</td>
<td>4.770</td>
<td>5.727</td>
<td>4.970</td>
<td>90.00</td>
<td>135.78</td>
<td>0.0938</td>
</tr>
<tr>
<td>770824-08</td>
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<td>5.726</td>
<td>4.969</td>
<td>90.01</td>
<td>135.67</td>
<td>0.0933</td>
</tr>
<tr>
<td>STW76-01</td>
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<td>5.721</td>
<td>4.963</td>
<td>90.02</td>
<td>135.60</td>
<td>0.0957</td>
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<td>5.723</td>
<td>4.962</td>
<td>90.01</td>
<td>135.20</td>
<td>0.0949</td>
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<td>ASS771103-08 (Kichinan)</td>
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<td>4.966</td>
<td>90.06</td>
<td>135.96</td>
<td>0.0867</td>
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<td>STW76-11 (Ono)</td>
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<td>135.08</td>
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<td>136.17</td>
<td>0.0901</td>
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<td>STW76-25 (Komaki)</td>
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<td>4.970</td>
<td>90.08</td>
<td>136.45</td>
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<td>7701115-03 (Shikatatagahara)</td>
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<td>4.970</td>
<td>90.03</td>
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<td>4.961</td>
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<td>134.41</td>
<td>0.1038</td>
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<td>H5707001 (Hagidaira)</td>
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<td>5.763</td>
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<td>138.71</td>
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<td>4.958</td>
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<td>5.731</td>
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<td>0.0922</td>
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<td>STW6-15 (Nakikawa)</td>
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<td>STW6-23 (Handai)</td>
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<td>4.978</td>
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<td>5.876</td>
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<td>Ebina Bi-W-Qtz veins*</td>
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<td>5.711</td>
<td>4.971</td>
<td>90.02</td>
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<td>Punkai Sn-W-Qtz veins*</td>
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<td>Hagidaira W-Qtz veins*</td>
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<td>5.755</td>
<td>4.998</td>
<td>91.03</td>
<td>n.d.</td>
<td>0.0758</td>
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<td>Ashio polymetallic veins**</td>
<td>4.733</td>
<td>5.707</td>
<td>4.967</td>
<td>90.00</td>
<td>n.d.</td>
<td>0.097</td>
</tr>
</tbody>
</table>

Synthetic wolframite series*

FeWO₄  | 4.734  | 5.708  | 4.965  | 90.00 | n.d.   | n.d.        |
Fe₀.₄Mn₀.₆WO₄  | 4.738 | 5.733  | 4.983  | 90.35 | n.d.   | n.d.        |

* : taken from Sasaki (1959)  ** : taken from Nakamura (1964)  n.d.: no data
amites from following ore deposits were also examined. The descriptions of these specimens are given in the Appendix.

Kaneuchi mine, Kyoto Pref., Ikuno mine, Hyogo Pref., Hagidaire mine, Gunma Pref., Takatori mine, Ibaragi Pref., Wakkawa mine, Niigata Pref., Mandai mine, Korea, Nampoto, China and Coldspring, U.S.A.

**MEASUREMENTS OF LATTICE PARAMETERS**

A. Experimental procedures

The X-ray measurements were carried out with Rigaku Geigerflex and the experimental conditions were as follows: Ni-filtered Cu(Kα) radiation at 30KV and 15mA; scanning speed, 1°(2θ)/min. (excepting some cases); chart speed, 20 or 30mm/min.; time constant, 4 sec.; angular aperture, 1°; receiving slit, 0.2 mm.

Smear mounts on glass slides were prepared with quartz as an internal standard. The unit cell parameters were calculated from the following sharp reflections: (010), (100), (011), (110), (111), (111), (020), and (002). An outline of the calculations using the computer is described in the later section. In the case of iron-rich members, such as those from the Fujigatani, Ikuno and Ichinohata mines, (111) reflection was not used for the calculations because of difficulty of separation of the reflections, (111) and (111). For the determination of the difference \(d_{111} - d_{110}\), (011) and (110) peaks were measured relative to quartz (111) and (101) reflections. The results are shown in Table 1. After repeating at least 8 times scanning, the mean d-values were obtained for each spacing.

B. Calculations of Lattice parameters

For the calculations of the unit cell parameters, the diffraction peaks which show strong enough intensity were restricted to below 40° in 2θ for Cu(Kα) radiations. In this range, the wolframite series has the following ten reflections; (010), (100), (011), (110), (111), (111), (020), (002), (120) and (200). Using the d-spacings of wolframite reported by Sasaki (XPDF 12-727), preliminary calculations were made with HITAC 8700 computer programmed on the basis of the least square method modified from Sakurai (1986). The calculated results with the ten reflections are as follows: \(a_0=4.785\) Å, \(b_0=5.732\) Å, \(c_0=4.978\) Å, \(β=90.58°\), and calculated unit cell volume is 136.51 Å³. These values are almost equal to those of Sasaki’s with the resultant differences of \(a_0=0.001\) Å, \(b_0=0.001\) Å, \(c_0=0.005\) Å, \(β=0.23°\). With 9 reflections, excluding (200) reflection from the ten reflections, the results are almost the same. Moreover, the best values of the calculated lattice parameters, the closest ones to those of Sasaki’s, are obtained with the 8 reflections of (010), (100), (011), (110), (111), (111), (020) and (002). In the case of iron-rich members as mentioned before, we can not use the (111) reflection, but even with 7 reflections, the results are almost the same as those of 10 reflections. Thus, the unit cell parameters described in this paper were calculated using 8 or 7 reflections, which are listed in Table 1.

**RESULTS AND DISCUSSION**

A. Interrelations of lattice parameters

Using the measured d(110) and d(001) spacings, \(Δd_{111} - d_{110}\) values are plotted on the line proposed by Sasaki (1959) (Fig. 2). According to Sasaki, the \(Δ\) value represents...
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Fig. 2. Relationship between $\Delta (d_{011}-d_{110})$ and composition (in mol. % MnWO$_4$). The composition was determined by the curve proposed by Sasaki (1959).

Fig. 3. Relationships between $a_0$, $b_0$, $c_0$, and $\beta$. 
the approximate composition of the wolframite series, with an accuracy of ±10 mol per cent. As is seen in the figure, the values vary from 0.1038 (those from the Ikuno mine) to 0.0727 (those from the Hagidaria mine). Therefore, the specimens investigated here cover all the compositional range of naturally occurring wolframite series. However, it is worth while to mention that almost all the specimens are distributed in the range exceeding about 0.08 Å in d values which approximately corresponds to the composition ranging from pure FeWO₄ to about 30 mol per cent FeWO₄.

Fig. 3 shows the relations between unit cell volume and a₀, b₀ and c₀. From the figure, it is evident that a gradual expansion of the volume depends mainly on the gradual increase in a₀ and b₀. The value of c₀ increases also linearly with increasing volume. In view of the interrelations among the unit cell parameters and their compositional dependency, it may be concluded that with increasing replacement of Fe with Mn, the unit cell volume expands gradually. On the other hand, the β values show none of the conspicuous variation with the expansion of the unit cell volume. This relation is depicted in Fig. 4. In this figure, the values of β remain constant, with the exception of Mn-rich member. This result is conflicting with the previous results. For instance, according to Sasaki (1959), β increases gradually with increasing MnWO₄ component from the pseudo-orthorhombic lattice (β=90.00) to pure MnWO₄ (β=90.53). From the present results, however, it is concluded that the expansion of the lattice volume depends mostly on the lengthening of a₀, b₀ and c₀, especially of the former two, which is caused by increasing substitution of the smaller Fe²⁺ ions with the larger Mn²⁺ ions and/or any other cations such as rare earth elements.

![Fig. 4. Relationships between V and a₀, b₀ and c₀.](image-url)
B. Possible relations between lattice parameters and chemical composition

It had been already established that some of the unit cell parameters of the wolframite series have intimate relations to their chemical composition. Among them, as mentioned previously, our $\beta$ value does not show any linear relation to the composition. According to the previous investigations, the deviation of $\beta$ from 90° is very small. Therefore, one can assume the value of $\sin \beta$ to be almost equal to 1.00. For example, the largest value of $\beta$ observed on the series is that of synthetic pure MnWO$_4$ reported by Sasaki (1959) ($\beta=90.53$) and the resultant $\sin \beta$ is 0.9999. In general, $\sin \beta$, excluding the largest one above, lies in the range of 1.0±0.00001. To be noted is that d-spacings of (0kl) and (hk0) of a mineral with monoclinic structure are affected only by the value of $\cos \beta$. Consequently, both values of the difference $(d_{011}-d_{110})$ (Sasaki, 1959) and of the difference (quartz (102)–wolframite (200) (Hsu, 1976) are not dependent on the $\beta$. This means that the linear relationships between chemical composition and the differences afore-mentioned are independent of the variation of $\beta$. In other words, $\beta$ can remain unchanged or also change linearly with the variation of the composition accompanying linear change of the above mentioned differences.

To determine $\beta$ of the series with monoclinic symmetry, the following process will be necessary as was pointed out by Takano (1957): using the d-spacings of (h00), (0k0), (0kl) and (hk0), preliminary calculation is made assuming orthorhombic structure. This is because the effects of these spacings on $\beta$ are negligible. Then, on the basis of the preliminarily determined lattice parameters, $\beta$ can be calculated using the values of $d(hkl)$ or $d(h0l)$. It is pointed out that recalculations are required for the refinement of the unit cell parameters including $\beta$.

In the present experiments, however, $a_0$, $b_0$, $c_0$ and $\beta$ are computed simultaneously having the equal importance for the all reflections used by the least square method. In consequence, there is a possibility that our $\beta$ values may differ from those calculated by the above process. However, we do not recognize which is better at the present state.

It is reasonably accepted that the crystal structure of pure FeWO$_4$ ($\beta=90.00$) is not distorted, while the distortion along c-axis becomes significant with increasing substitution of Fe with Mn. With increasing Mn content, the distortion may increase to some extent. However, there is no certain reason for the continuous distortion towards the end member MnWO$_4$.

It is also possible that the expansion of the unit cell volume may permit the substitution of the larger Mn$^{2+}$ ions instead of the smaller Fe$^{2+}$ ions without further distortion along c-axis. Relatively rare occurrences of Mn-rich wolframites in nature, except for end member MnWO$_4$, suggest strongly that certain difficulty is encountered with large amounts of substitution of Fe with Mn. This will be treated from another point of view. The compositional distribution of natural wolframite series may indicate the degree of difficulty or easiness of the substitution. Of course, an environmental condition such as an effect of $fO_2$ on the crystal structure, including relative concentration of Fe and Mn, should be considered, which will be discussed in near future.

Then, some discussion on the deviation of composition between natural samples
and synthetic compounds are made. As was pointed out by Sasaki (1959), natural wolframites deviate slightly from the line obtained with synthetic materials, the line

Table 2. Qualitative X-ray fluorescence analyses of wolframite samples. In most cases, the analyses were made on bulk samples.

<table>
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<th>Element</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>As</th>
<th>Y</th>
<th>Nb</th>
<th>Mo</th>
<th>Sn</th>
<th>Ta</th>
<th>Bi</th>
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<td>+++</td>
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<td>STW76-24 (Nampoto)</td>
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<td>-</td>
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</tr>
</tbody>
</table>

- : not detected  + : present  ++ : medium  +++ : abundant
showing a relation between chemical composition and lattice parameters. This deviation is clearly displayed in Fig. 5, in which the dotted line is determined on the basis of synthetic compounds. Taking into consideration of the previous discussions such as those by Sasaki (1959) and Sleight (1972), the deviation is best explained by the influence of some cations other than Fe and Mn present in the crystal structure of the series. In this respect, our preliminary results of X-ray fluorescence analyses (Table 2) indicate that the presence of one per cent order of Nb in the series from the Sekigane mine may give an evidence in support of this. Also listed in the table are qualitative analytical results for samples from some other localities.

Finally, it is pointed out that Sasaki's results on which the present discussions are based have a weak point because they are not grounded on the chemical analyses. Therefore, quantitative analyses such as microprobe analyses will be a great help in attacking the problems of the composition-lattice parameter relationships and above stated deviation, which are now in progress in our laboratory.

C. Regional variations of iron/manganese ratios in wolframite series from Chugoku District

Spatial distribution of the regional variations are schematically depicted in Fig. 1. Of the wolframite series here investigated, sample from the Hagidaira mine, Gunma Pref., is most enriched in manganese, almost pure huebnerite, which is also evidenced by the analytical data described in Appendix. The specimen occurs in quartz-manganese veins which cut the bedded manganese deposits. To be noted is that all the samples having composition close to MnWO₄ end member came from manganese deposits or Paleozoic formation nearby or rich in manganese deposits, supporting the conclusion reached by Sasaki (1960; personal comm., 1977). Relatively Mn-rich specimens such as those from the Takatori, Kaneuchi and Masuda mines are also found in similar geologic setting to the above. While, relatively high oxidation state may be characteristic of the ore fluids and perhaps of granitic magma of the granitic rocks of the Sanin-Shirakawa Zone, possibly, in part, responsible for relatively Mn-rich series from the Sekigane** and Komaki mines. This is because a part of iron dissolved in the ore fluids goes into solid phase to form magnetite due to its less resistivity to oxidation relative to manganese, resulting in relative enrichment of Mn in the fluids to precipitate relatively Mn-rich members. Such an explanation is supported by the observations that magnetite deposits are occur in the granitic rocks to which the Sekigane Mo-W deposits are related and that the iron oxide minerals are intimately associated with Mo-W ores at the Komaki mine. On the other hand, evidence is lacking that the remaining ore deposits under consideration from Southwest Japan occur in Mn-rich horizon or adjacent to manganese ore deposits. These deposits are characterized by the ore fluids and perhaps of granitic magma of the Sanyo-Naegi Zone of low oxidation state. For instance, this is evidenced by the fact that in the skarn-type tungsten-copper deposits within the Kiwada scheelite province (Soeda, 1963), Yamaguchi Pref., ferrous iron is fixed into skarn silicates

** On the basis of Hsu's method (1976), four samples from this mine, of which unit cell parameters are not measured, are relatively rich in manganese such as 17, 47, 52 and 79 mol per cent MnWO₄, respectively.
to considerable degree and iron oxide is poor. The wolframite series from the Fujigatani mine of the province is close to the ferberlite end member. The low oxidation condition may, in part, be responsible for the deposition of Fe-rich members.

The samples from the Asahara mine area are exceptionally high in Mn compared with those from the adjacent Mizuwakare and Yamate (Shitekurayama) mines, which are all apparently related to the granitic rocks of almost same property. Aside from this, it has been the subject of much controversy that the temperature of formation is an important factor to control Fe/Mn ratios in the wolframite series, resulting in conflicting discussions (ex. Baumann and Starke, 1964, 1965; Ganeev and Sechina, 1960; Lawrence, 1961). This subject has been critically discussed in the recent works of Clark (1970), Taylor and Hosking (1970), Grooves and Baker (1972) and Hsu (1976). Special attention should be paid to the fact that the concept of temperature dependency of Fe/Mn ratios of the series has been discussed on the basis of empirical observation rather than experimental or theoretical considerations. This problem is now being attacked using the fluids inclusions in quartz and some transparent minerals closely coexisting with the wolframite series. For the preceding discussion, it is concluded that composition of the wolframite series may vary according to the bulk chemical composition of the surrounding rocks through which the ore fluids travelled and to oxidation state of the ore fluids and perhaps of related granitic magma. As was suggested by Hsu (1976), variations in Fe/Mn ratios of source materials may also be of significant importance. Possible effects of physicochemical parameters such as temperature and acidity of the ore fluids will be discussed in a subsequent paper.

Furthermore, seeing from the compositional distribution based on our X-ray analyses and some other works, it is suggested that, although an existence of a complete solid solution series between the binary FeWO₄ and MnWO₄ system has been demonstrated experimentally (Schröke, 1969; Hsu, 1976), there may be an immiscibility gap in the system, particularly in a region close to the huebnerite end member, in the case of natural ore-forming environment of intermediate temperature.

SUMMARY AND CONCLUSIONS

From the foregoing descriptions and discussions, the main conclusions reached are summarized as follow:

(1) The relationships between chemical composition and unit cell parameters of a₀, b₀, c₀ and β agree mostly with the previous results. However, it is worth while to emphasize that β value remains almost constant, conflicting with the previous conclusion.

(2) The lattice volume of the wolframite series expands with increasing replacement of iron by manganese and/or some other cations. The lengthening of a₀, b₀, and c₀, especially of the former two is responsible for the expansion.

(3) As was mentioned by Sasaki (1959), the naturally occurring wolframites deviate slightly from the relation between composition and lattice parameter obtained with synthetic compounds. This may be due to the influence of some cations such as niobium and yttrium in the lattice, supporting the conclusion reached by the previous workers. In this connection, the considerable amounts of niobium in the wolframite series from the Sekigane mine...
may give an evidence in support of this.

(4) As to regional variation of Fe/Mn ratios in the series from the Chugoku district, there seems to exist a tendency, though not so remarkable, that wolframites in the granitic rocks of the Sanin-Shirakawa Zone, characterized by relatively high oxidation state, are rich in Mn, while wolframites in those of the Sanyo-Naegi Zone, characterized by relatively low oxidation state, are rich in Fe.

(5) All the specimens having composition close to MnWO₄ end member came from manganese or Paleozoic formation nearby or rich in Mn deposits, supporting the conclusion reached by Sasaki (1960).

(6) Thus, it follows that composition of the wolframite series may vary according to the bulk chemical composition of surrounding rocks through which the ore fluids travelled and to the oxidation state of ore fluids and perhaps of related granitic magma. Other possible factors to affect the Fe/Mn ratios are temperature and acidity of the ore fluids, details of which will be discussed in a subsequent paper.

(7) The compositional distribution of natural wolframite series, characterized by the relatively rare occurrences of Mn-rich member, may indicate the degree of difficulty of the Fe/Mn substitution in the crystal structure and the probable existence of immiscibility gap in the system.

APPENDIX

Descriptions of ore deposits and samples used in this experiments

The ore deposits from which wolframites obtained will be briefly described in the following. All of the mines of the Chugoku district are now closed except Fujigatani mine, Yamaguchi Prefecture.

A. Ore deposits in granitic rocks of the Sanyo-Naegi Zone

(A-1) Masuda mine, Shimane Pref. (STW76-12) The ore deposits of the mine are wolframite-quartz veins, lying in the Masago granodiorite complex with which ore deposits of various types are spatially associated. This specimen consists of columnar or platy crystals up to 1 cm long in intimate association with small amount of chalcopyrite, molybdenite, arsenopyrite, pyrite, cassiterite and other gangues including topaz.

(A-2) Kiyomizu mine, Shimane Pref. (MW770824-07). The ore deposits of the mine are wolframite-molybdenite-quartz veins in the Masago granodiorite complex described above. Wolframite investigated occurs as tabular crystals intimately associating with small amounts of molybdenite, scheelite and mica minerals.

(A-3) Kiyomizu mine (MW770824-08). This sample consists of platy crystals up to 6 cm long in close association with some flaky molybdenite and mica minerals in quartz vein.

(A-4) Jutoku mine, Yamaguchi Pref. (STW76-01). The ore deposits of the mine are wolframite-quartz veins in extensively altered fine to medium grained granitic rocks. This specimen occurs as platy crystals up to 5 mm long closely associating with abundant scheelite and chalcopyrite with small amounts of arsenopyrite, pyrite, bismuthinite and covellite.

(A-5) Ninkoji mine, Yamaguchi Pref. (ASST771103-01). The ore deposits of the mine are wolframite-quartz veins in granitic rocks. Wolframite studied is small-sized platy crystals up to 3 mm long with small amounts of chlorite and so-called “green biotite”.

(A-6) Kichinan mine, Yamaguchi Pref. (ASST771103). The ore deposits of the
mine are wolframite-muscovite-quartz veins in granitic rocks. The specimen occurs as tabular crystals in close association with muscovite.

(A-7) Mukaigatao mine (STW76–03). According to Kinosaki (1952), the ore deposits of the mine are wolframite-quartz veins, occurring at the contact of biotite granite with thermally metamorphosed rocks of Paleozoic time. This sample consists of platy crystals with small amounts of chalcopyrite, pyrite, native bismuth, molybdenite and feldspars altered.

(A-8) Fujigatani mine, Yamaguchi Pref. (STW76–27). The ore deposits of the mine are of contact metasomatic type, producing mainly tungsten and copper. Powdered samples presented by Dr. S. Higashimoto, Geological Survey of Japan, came from tailings and the details of the occurrence are not known.

(A-9) Soo mine, Yamaguchi Pref. (STW76–28). The ore deposits of the mine are polymetallic (Cu-Fe-Mo-Sn-W-U) veins in granitic rocks. In places, chalcopyrite-stannite and bornite-mausonite-stannoidite associations are characteristically observed (Soeda and Hirowatari, 1971). Topaz, fluorite and muscovite are present in small amounts. Sample examined came from tailings.

(A-10) Ono mine, Hiroshima Pref. (STW76–11). The ore deposits of the mine are polymetallic (W-Mo-Cu-Fe-As-Bi-Pb) quartz veins in granitic rocks. Small amounts of platy wolframite up to 1 cm long occur with chalcopyrite, molybdenite, native bismuth, arsenopyrite, pyrite, marcasite, galena, fluorite and potash feldspars.

(A-11) Mihara-Sogo mine, Hiroshima Pref. (STW76–29). The ore deposits of the mine are tungsten-quartz veins filling joints within silicified and greisenized biotite granite (Underground Resources in Hiroshima Prefecture, 1953). This specimen consists of small sized platy crystals, closely associating with chalcopyrite, bornite, arsenopyrite, covellite and chlorite.

(A-12) Aji mine, Hiroshima Pref. (STW76–30). The ore deposits of the mine are wolframite-quartz veins with partially pegmatitic portion, occurring in biotite granite (Kinosaki, 1952). Platy wolframite up to 5 mm long, subjected to secondary alteration occurs intimately associated with scheelite and molybdenite in quartz vein.

(A-13) Setoda mine, Hiroshima Pref. (STW76–10). The ore deposits of the mine are tungsten-copper-quartz veins with some pyrite, topaz, potash feldspars and spinel, occurring mainly in fine-grained granitic rocks altered. This specimen consists of tabular crystals up to 1.5 cm long closely associated with chalcopyrite, pyrrhotite, bornite, wittichenite, molybdenite, stannoidite, mawsonite, native bismuth and sericite (Soeda and Hirowatari, 1972).

(A-14) Ichinohata mine, Hiroshima Pref. (STW76–08). The ore deposits of the mine are wolframite-quartz veins in quartz porphyry (Kinosaki, 1952). Wolframite studied occurs as platy crystals in association with sphalerite and native bismuth with small amounts of topaz.

(A-15) Asahara mine, Okayama Pref. (STW76–31). The ore deposits of the mine are wolframite-quartz veins in biotite granite (Kinosaki, 1952). Wolframite of platy form up to 2 cm long came from the mineral collections of Hiroshima University, occurring in close association with chalcopyrite, sphalerite, galena, pyrite and covellite.

(A-16) Ibara mine, Okayama Pref. (STW76–09). The ore deposits of the mine are wolframite-quartz veins, occurring both
in granitic rock and in Paleozoic sedimentary rocks (Kinosaki, 1952). Wolframite, came from the mineral collections of Hiroshima University, occurs as tabular crystals up to 1 cm long in intimate association with pyrite, marcasite, chalcopyrite, molybdenite, scheelite, native bismuth and fluorite.

(A-17) Yamate (Shitekurayama) mine, Okayama Pref. (STW76-32). The ore deposits of the mine are wolframite-muscovite-quartz veins in fine-grained granitic rock. Wolframite examined occurs as platy crystals up to 1.5 cm long in quartz vein with small amounts of scheelite, molybdenite, native bismuth, chalcopyrite, bornite, pyrite, cassiterite, topaz and chlorite. The 3R polytype mixed with 2H1 of molybdenite was reported from the deposit (Watanabe and Soeda, 1978).

(A-18) Mizuwakare mine, Okayama Pref. (STW76-06). The ore deposits of the mine are wolframite-muscovite-quartz veins in fine-grained granitic rock. Wolframite examined occurs as large platy crystals up to 2 cm long in quartz vein with some chalcopyrite, pyrrhotite, molybdenite, scheelite, muscovite and chlorite.

(A-19) Mabi mine, Okayama Pref. (ASST771110-03). The ore deposits are wolframite-muscovite-quartz veins in greisenized granitic rock. Wolframite investigated occurs as large platy crystals intimately associated with scheelite, quartz and muscovite, forming a pod in extensively altered granitic rocks of medium-grained.

(B-1) Sekigane mine, Tottori Pref. (STW76-05). The ore deposits of the mine are wolframite-muscovite-quartz veins with abundant molybdenite in strongly altered (greisenized) biotite granite. Wolframite examined occurs as fine-grained and massive aggregates in close association with scheelite, molybdenite, chalcopyrite, pyrite and calcite.

(B-2) Sekigane mine (SG770801-06). Samples (SG770801-06, -08, -09 and -10) were kindly presented by the manager's survivors of the mine. These specimens occur as massive aggregates intimately associating with scheelite, quartz and muscovite, forming a pod in extensively altered granitic rocks of medium-grained.

(B-3) Sekigane mine (SG770801-08). Wolframite investigated consists of large platy crystals up to 8 cm long in close association with scheelite, muscovite and small amounts of chalcopyrite and pyrite in quartz vein.

(B-4) Sekigane mine (SG770801-09). The specimen occurs as granular aggregates with some muscovite and scheelite replacing wolframite in strongly altered granitic rock.

(B-5) Sekigane mine (SG770801-10). Wolframite studied are present as tabular crystals up to 3 cm long in intimate association with quartz.

(B-6) Komaki mine, Shimane Pref. (STW76-25). The ore deposits of the mine are molybdenite-garnet-'green biotite'-sericite-andalusite-quartz networks, which form a kind of ore pipe in fine- to medium-grained granitic rocks. Wolframite, scheelite, pyrrhotite, magnetite, pyrite and chalcopyrite are present as accessory minerals.
(Tsuboya and Ishihara, 1961). Samples (STW76–25 and –26) were presented by Dr. S. Ishihara, Geological Survey of Japan. Wolframite examined occurs as columnar crystals up to 3 mm in intimate association with quartz, muscovite, "green biotite" and small amounts of pyrite and magnetite, which came from a branch of the Ichiman ore deposit.

(B–7) Komaki mine (STW76–26). This specimen came from concentrates after table floatation. Details of the occurrence are not known.

(B–8) Shikatagahara mine, Shimane Pref. (MW77115–03). The ore deposits of the mine are wolframite-quartz veins with some molybdenite, occurring in medium-grained biotite granite which is characterized by the presence of abundant hydrothermal biotite and chlorite. Wolframite studied is rarely associated with other ore minerals such as magnetite partly replaced by hematite. The specimen consists of platy crystals, partly replaced by scheelite. According to Kinosaki (1952), wolframite occurs also in the pegmatitic portion of the granite.

C. Ore deposits outside of the Chugoku District

(C–1) Kaneuchi mine, Kyoto Pref. (STW76–14). The ore deposits of the mine are wolframite-quartz veins, occurring in Paleozoic sedimentary rocks. They are assumed to be genetically linked to granitic cupola possibly lying in depth (Imai et al., 1972). This specimen consists of platy materials up to 5 cm long in close association with bornite, pyrrhotite, sphalerite, scheelite, arsenopyrite, chalcopyrite, native bismuth, muscovite, potash feldspars and some others, which came from the Gessei No. 4 deposit.

(C–2) Ikuno mine, Hyogo Pref. (STW76–13). The ore deposits of the mine are well-known polymetallic (Cu-Pb-Zn-Sn-W) veins of subvolcanic type, which occur in sedimentary rocks, pyroclastics and intrusives of Upper Cretaceous Age. This sample, came from the mineral collections of Hiroshima University, occurs as platy crystals up to 3 cm long, closely associating with arsenopyrite, chalcopyrite, bismuthinite, stannite and some other minerals, which was taken from the Kanagase deposit.

(C–3) Hagidaira mine, Gunma Pref. (H5707001). The ore deposits of the mine are bedded manganese deposits in the Paleozoic sedimentary rocks metamorphosed to biotite hornfels caused by granodiorite intrusion (Hirowatari and Takeda, 1982). This specimen presented by Prof. F. Hirowatari, Kyushu University is in quartz vein with pyrite, pyrrhotite, chalcopyrite and rhodochrosite, cutting the ore body composed mainly of rhodonite, spessartine and quartz. Chemical composition of this specimen (in wt. per cent) is: MnO, 21.87; FeO, 1.22; WO3, 75.54; SiO2, 1.25; CaO and MgO, trace (Prof. F. Hirowatari, private comm.).

(C–4) Takatori mine, Ibaragi Pref. (STW76–16). The ore deposits of the mine are hypothermal tungsten-quartz veins in slightly metamorphosed sediments of Paleozoic Age (Takenouchi and Imai, 1971). The specimens (STW76–16 to –18) came from the mineral collections of Hiroshima University. Wolframite examined occurs as platy crystals up to 10 cm long in association with chalcopyrite, bornite, wittichenite, magnetite, scheelite and pyrite in quartz vein.

(C–5) Takatori mine (STW76–17). This sample consists of columnar or platy materials up to 8 cm long closely associating with
small amounts of chalcopyrite and pyrite.

(C-6) Takatori mine (STW76-18). Wolframite investigated occurs as platy crystals intimately intergrown with minor pyrite, chalcopyrite, sphalerite, stannite and chlorite in quartz vein.

(C-7) Wakikawa mine, Niigata Pref. (STW76-15). The ore deposits of the mine, now closed, are molybdenite-wolframite-quartz veins in argillized zone of granitic rock (Tatsumi, 1954). This specimen occurs as small-sized tabular crystals in close association with flaky molybdenite in quartz vein.

(C-8) Mandai mine, Korea (STW76-23). Samples from the Mandai and Nampoto, China, came from the mineral collections of Hiroshima University. Unfortunately, no information is available for these deposits. Wolframite examined occurs as large platy crystals up to 5 cm long with quartz and scheelite. The latter consists of both individual single crystals and materials replacing wolframite.

(C-9) Nampoto, China (STW76-24). This specimen consists of large tabular crystals more than 10 cm long characterized by strong fissility, with some thin layer of muscovite.

(C-10) Coldspring, U.S.A. (STW76-02). This sample from the Coldspring tungsten mine, Colorado, of which information was not obtained, came from the mineral collections of Hiroshima University. Wolframite studied is fine-grained and granular aggregates.

(C-11) Unknown Locality–1 (STW76-20). Wolframite samples of unknown locality–1 and –2 came from the mineral collections of Hiroshima University. They were probably from the Chugoku district. This specimen occurs as large and massive aggregates.

(C-12) Unknown Locality–2 (STW76-21). Wolframite examined consists of large platy crystals up to 10 cm long closely associating with quartz and some mica minerals.

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中国地方産鉱マンガン重石に関する研究 (1)
格子定数と化学組成の相関関係

添田 晶・竹野 節夫・渡辺 淳

中国地方27鉱山および他地域8鉱山産鉱マンガン重石39試料について、その産状を明らかにし、主にX線粉末回折法を用いてその格子定数と鉱マンガン重石の化学組成 (Fe/Mn 比) の相関性を検討し、かつ花崗岩岩区との関連においてその広域的組成変化の要因を考察し、得られた結果は次の知く要約される。

(1) 鉱マンガン重石の格子定数 a₀, b₀, c₀, V と化学組成の関係は、従来の研究結果 (例、Sasaki (1959)) とよく一致する。β については組成と相関性を示さず、従来の結果とは相反する。
(2) 従来得られている成因物についての組成と格子定数との関係は、天然物についてのそれからわずかにずれるが、これは後者中に、Fe, Mn以外にNb, Ta等の微量元素の存在することによるものと考えられる。
(3) Mn 純成分に近い鉱マンガン重石の産出が比較的稀なことは、Fe/Mn の置換の困難さおよびこの系に不混和領域が存在する可能性を示唆している。
(4) 中国地方において鉱マンガン重石は、山陰・白川帯の花崗岩類に由来するとと思われるものに Mn が多く、山陽一苗木帯のものに Fe が多い傾向がある。
(5) 鉱マンガン重石の産状および選挙成鉱物鉱物酸化鉱物などを考慮すると、その Fe/Mn 比は酸化物成は関係花崗岩マグマの酸性度、更には鉱床の母岩の化学組成に関連するものと考えられる。