

## Manganbabingtonite from Mitani, Kochi City, Japan

By

Satoshi MATSUBARA and Akira KATO

Department of Geology, National Science Museum, Tokyo

**Abstract** Manganbabingtonite from Mitani, Kochi City, occurs as veinlets cutting massive magnetite ore involved in high pressure and low temperature crystalline schists within Kurosegawa Tectonic Zone. This is the first occurrence of this mineral in Japan.

Two chemical analyses gave  $\text{SiO}_2$  52.61, 52.20;  $\text{Al}_2\text{O}_3$  0.35, 0.00;  $\text{Fe}_2\text{O}_3$  13.53, 13.90;  $\text{FeO}$  1.76, 5.13;  $\text{MnO}$  13.21, 6.99;  $\text{MgO}$  0.00, 0.33;  $\text{CaO}$  17.71, 19.20; totals 99.17, 97.75%, after the assignment of total Fe to FeO and  $\text{Fe}_2\text{O}_3$ . These yield empirical formulae:  $(\text{Ca}_{1.80}\text{Mn}_{0.20})\Sigma_{2.00}(\text{Mn}_{0.86}\text{Fe}^{2+}_{0.14})\Sigma_{1.00}(\text{Fe}^{3+}_{0.97}\text{Al}_{0.04})\Sigma_{1.01}\text{Si}_{5.00}\text{O}_{14.51}$  and  $(\text{Ca}_{1.87}\text{Mn}_{0.03})\Sigma_{2.00}(\text{Mn}_{0.53}\text{Fe}^{2+}_{0.47}\text{Mg}_{0.05})\Sigma_{0.98}\text{Fe}^{3+}_{1.00}\text{Si}_{5.00}\text{O}_{14.49}$ , respectively, on the basis of total cation=9. The former has the highest MnO content known so far and the deficiency of Ca, which is accounted for by the excess of  $\text{Mn}^{2+}$ .

The X-ray powder diffraction pattern is indexed on a triclinic cell with  $a=7.492$ ,  $b=12.32$ ,  $c=6.701$  Å,  $\alpha=85.2^\circ$ ,  $\beta=93.9^\circ$ ,  $\gamma=112.2^\circ$ .

The associated minerals include ilvaite, howieite, riebeckite, aegirine, greenalite, albite and potash feldspar besides magnetite. All the iron silicates in them are more or less manganiferous, but none of them is with  $\text{Mn}^{2+} > \text{Fe}^{2+}$ . This relation is uniquely seen in manganbabingtonite, which corresponds approximately to  $\text{Fe}^{3+}$ -rich derivative of manganian hedenbergite.

The present material owes the formation to the metamorphism of a manganiferous ironstone accompanying a minor limestone as the source of calcium, according to the comparison with the nearby ironstone localities in the same tectonic zone, where manganian howieite or taneyamalite is found.

### Introduction

Manganbabingtonite was firstly found from Eastern Sayan, U.S.S.R. (VINOGRADOVA *et al.*, 1966), as a product of contact metasomatism accompanying lead and zinc mineralization, and the  $\text{Mn}^{2+} : \text{Fe}^{2+}$  ratio is 62:38. In 1978 the subsequent occurrence was reported by BURT and LONDON from Aravaipa, Arizona, U.S.A., where it occurs as vuggy replacement of hedenbergite-johannsenite skarn, accompanying lead and zinc mineralization as well. The material is closer to  $\text{Mn}^{2+}$  end member with the ratio  $\text{Mn}^{2+} : \text{Fe}^{2+}=77:23$ . While, the present material is found in regionally metamorphosed ironstone and far richer in  $\text{Mn}^{2+}$  which substitutes a part of Ca, and with the  $\text{Mn}^{2+} : \text{Fe}^{2+}$  ratio up to 86:14. It occurs as veinlets cutting massive magnetite ores in high pressure and low temperature crystalline schists developed in Kurosegawa Tectonic Zone. The present work is for the description of this mineral together with the chemical analyses of the associated iron silicates and

the consideration of original rocks from which the observed assemblages were derived.

### Occurrence

In the southern part of Shikoku is Kurosegawa Tectonic Zone, where crystalline schists and ultrabasic bodies are exposed with the general trend of E-W direction (MARUYAMA, 1981). The former comprises some metamorphic equivalents of minor manganiferous ironstone beds, and the occurrence of manganoan howieite was reported in some of them (KATO *et al.*, 1984). The beds were mined during the World War II, and the most dominant ore was massive hematite.

At Mitani, Kochi City, located about 3 km NNW of Kochi Station, JR Shikoku Co. Ltd., there is a small stream with N-S direction (Fig. 1). The stream cuts the constituents of Kurosegawa Tectonic Zone and there are many blocks of crystalline schists and ultrabasic rocks on the river bed. The studied materials were blocks of metamorphosed ironstone therefrom. Seeing from the distribution and the estimated location of the horizon of ironstone, the blocks were all derived from one of the metamorphosed ironstone beds. The blocks are generally round and black in colour. They are with submetallic to dull luster and conchoidal fracture, and composed of massive aggregate of very fine grains of magnetite and ilvaite with various ratio. In the block are dark grey green thin veinlets sharply cutting the aggregates rich in ilvaite. They consist generally of very fine grains of aegirine and manganbabingtonite of various ratio, and some of them have visible black stringers of howieite in the center.

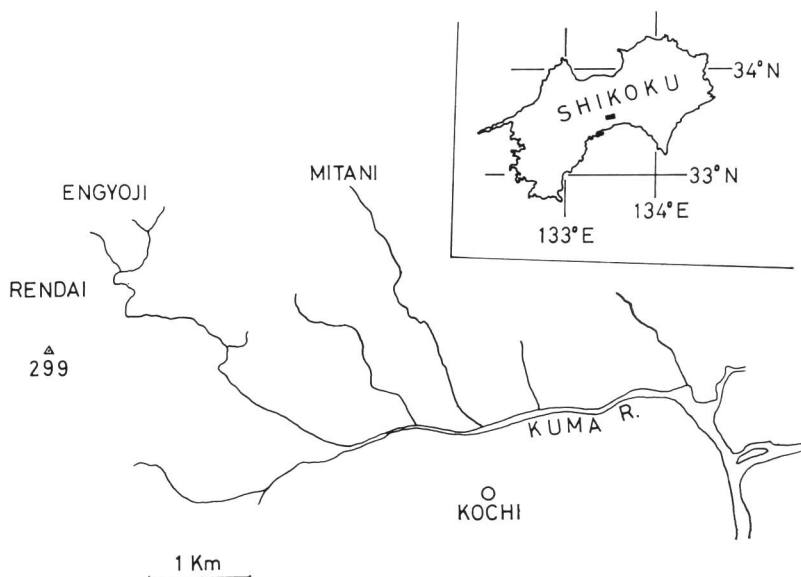
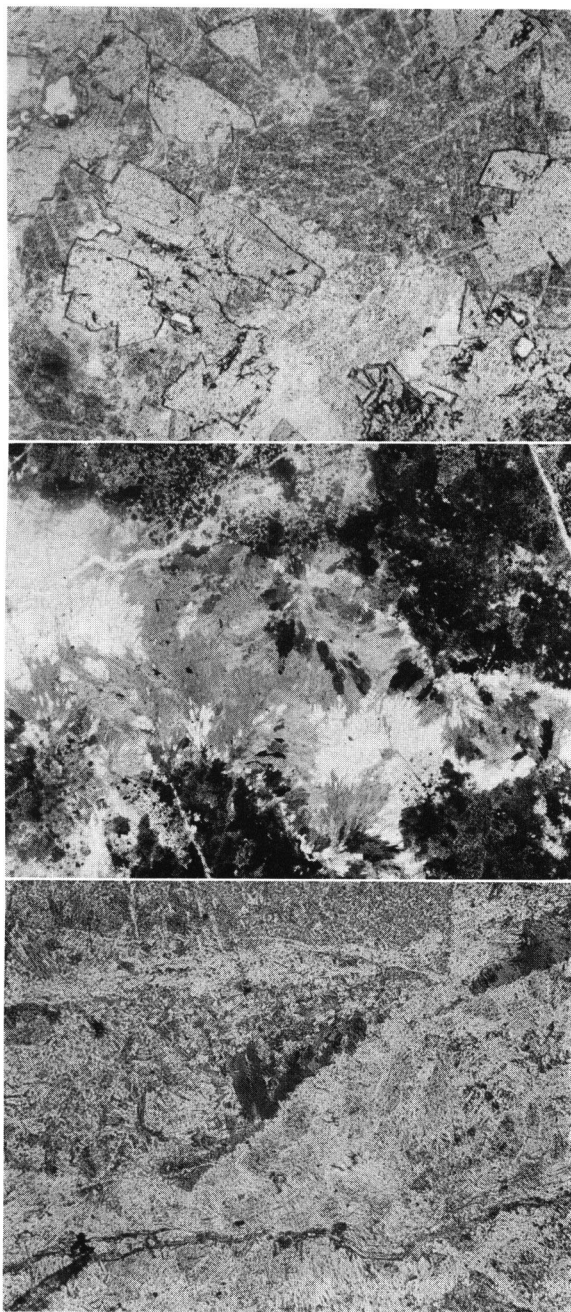


Fig. 1. The index map of manganbabingtonite locality (Mitani).



Figs. 2-4.

2 (top).

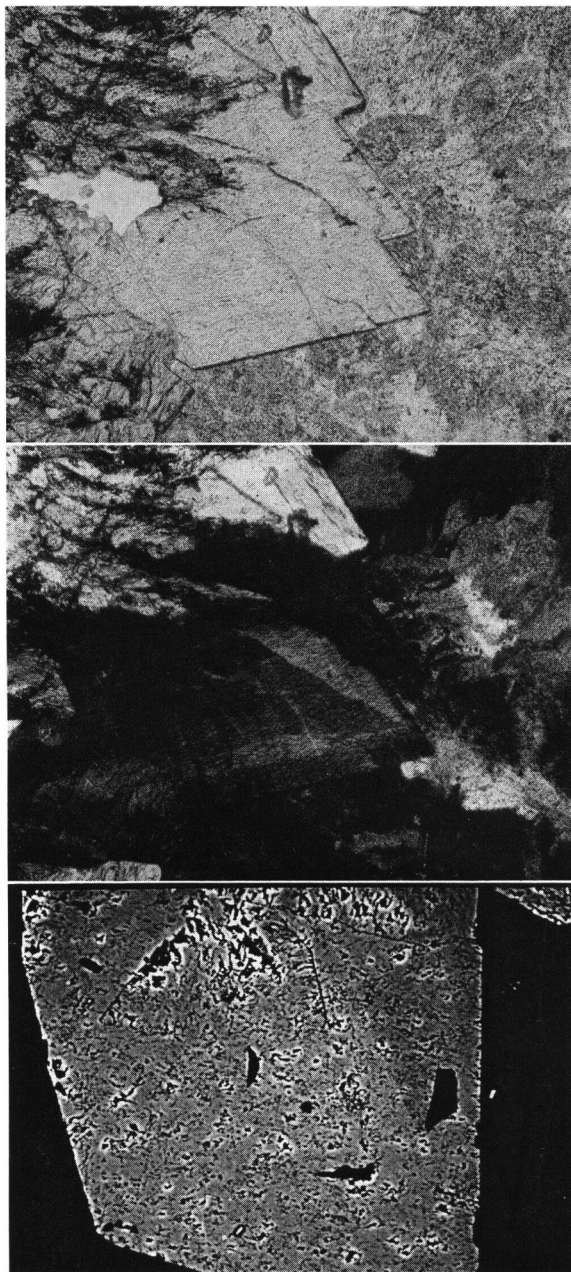
Photomicrograph of manganbabingtonite crystals (high relief) with albite and potash feldspar in veinlet. One polar. Field view: approx.  $1.9 \times 1.4$  mm.

3 (middle).

Photomicrograph of howieite (fibrous) in manganbabingtonite-howieite vein cutting massive ilvaite. Field view: approx.  $1.9 \times 1.4$  mm.

4 (bottom).

Photomicrograph of riebeckite (dark grey prism in the center) between the bands of aegirine (left above) and manganbabingtonite (right down). Field view: approx.  $0.8 \times 0.6$  mm.



Figs. 5-7.

5 (top).

Photomicrograph of manganbabingtonite crystal with a sector zoning. Very feebly visible in one polar. Field view: approx.  $0.8 \times 0.6$  mm.

6 (middle).

Ditto. Crossed polars.

7 (bottom).

Back scattered electron image of manganbabingtonite. Dark (Mn-rich) and light (Mn-poor) areas constitute a sector zoning. Field view: approx.  $173 \times 118$   $\mu$ m.

Also, the others include white interstitial albite in the center of veinlets instead, where dark submillimeter order greenish black manganbabingtonite idiomorphs are found. Besides the veinlets including manganbabingtonite, slightly yellowish ones of similar dimension are found in the massive aggregates of ilvaite with magnetite. The constituents are identified as andradite, riebeckite and aegirine after the X-ray powder study. Its relation to those including manganbabingtonite was unknown.

Under the microscope, all the veinlets are composed of some bands, which have rather simpler mineral assemblages, that is, one or two minerals. The most common one involving manganbabingtonite has aegirine bands composed of unoriented grains of 0.0n millimeter order along the walls composed of mosaic aggregate of ilvaite grains of less than 0.1 millimeter across. Then along this band, mosaic aggregates of manganbabingtonite grains of similar dimension are present without any other minerals. The center of veinlets is occupied by coarser idiomorphs of manganbabingtonite with interstitial albite and potash feldspar (Fig. 2). The total width of examined veinlets reaches a centimeter. The mineral association of veinlets involving howieite (Fig. 3) has riebeckite-aegirine bands along the walls (Fig. 4), then, bands of aegirine grains with interstitial howieite, and manganbabingtonite aggregates in the center. Also, some veinlets consist of manganbabingtonite walls and howieite aggregates in the center, and both units are nearly monomineralic like the bands found in the veinlets cutting the magnetite-ilvaite aggregates.

Most of magnetite-ilvaite aggregates suffer slight weathering, which formed limonitic material and gypsum along fractures.

There are magnetite aggregates devoid of manganbabingtonite. They are intersected by veinlets of howieite, which is cut by aegirine veinlets, and them by hematite veinlets. All of them have simpler mineral assemblages, for example, howieite veinlets consist of howieite with minor potash feldspar only. They are also intersected by veinlets of ilvaite and of greenalite, and both of them are nearly monomineralic.

Finer manganbabingtonite grains have lighter colour in general and very light yellowish to yellowish green pleochroic colours, whereas coarser grains have more greenish margins, which are generally richer in FeO. Also, some of them demonstrate a sector zoning due to the difference in MnO contents (Figs. 5~7). Optically manganbabingtonite is similar to the associated aegirine, which is, as seen in some of metamorphosed bedded manganese ore deposits in Japan, very light in colour and has light yellowish to yellowish brown pleochroic colours, but has higher refractive indices.

### Chemical Analyses of Manganbabingtonite and the Associated Minerals

The chemical analyses of manganbabingtonite, ilvaite, howieite, riebeckite, aegirine and greenalite were made after the employment of Link Systems energy-dispersive X-ray spectrometer (Table 1).

Table 1. Chemical analyses of manganbabingtonite and the associated minerals from Mitani.

|                                | 1     | 2     | 3     | 4      | 5     | 6      | 7     |
|--------------------------------|-------|-------|-------|--------|-------|--------|-------|
| SiO <sub>2</sub>               | 52.61 | 52.20 | 29.08 | 42.16  | 51.78 | 50.61  | 31.49 |
| TiO <sub>2</sub>               | 0     | 0     | 0     | 0      | 0.40  | 0      | 0     |
| Al <sub>2</sub> O <sub>3</sub> | 0.35  | 0     | 0     | 1.31   | 0.65  | 2.07   | 4.99  |
| Fe <sub>2</sub> O <sub>3</sub> | 13.53 | 13.90 | 20.15 | —      | 11.95 | 30.34* | 20.34 |
| FeO                            | 1.76  | 5.13  | 29.43 | 36.14* | 25.52 | —      | 26.15 |
| MnO                            | 13.21 | 6.99  | 5.90  | 11.93  | 1.08  | 1.18   | 5.51  |
| MgO                            | 0     | 0.33  | 0.23  | 0.81   | 0     | 0      | 0.47  |
| CaO                            | 17.71 | 19.20 | 13.39 | 0      | 0.78  | 4.79   | 0.47  |
| Na <sub>2</sub> O              | 0     | 0     | 0     | 2.04   | 6.77  | 11.96  | 0     |
| K <sub>2</sub> O               | 0     | 0     | 0     | 0      | 0.32  | 0      | 0     |
| total                          | 99.17 | 97.75 | 98.18 | 94.39  | 99.25 | 100.95 | 89.42 |

1. Manganbabingtonite. The most MnO-rich analysis. FeO and Fe<sub>2</sub>O<sub>3</sub> were calculated on the basis of total cation=9 and the total positive charge=29.
2. Manganbabingtonite. The most MnO-poor analysis. FeO and Fe<sub>2</sub>O<sub>3</sub> were calculated in the same way as above.
3. Ilvaite. FeO and Fe<sub>2</sub>O<sub>3</sub> were calculated on the basis of total cation=6 and the total positive charge=17.
4. Howieite. \*total Fe.
5. Riebeckite. FeO and Fe<sub>2</sub>O<sub>3</sub> were calculated after the method of Rock and LEAKE (1984).
6. Aegirine. \*total Fe.
7. Greenalite. FeO and Fe<sub>2</sub>O<sub>3</sub> were calculated on the basis of total positive charge=28 and the difference from 100% to be due to H<sub>2</sub>O.

Two manganbabingtonite analyses are given to indicate the range of MnO contents. The empirical formulae were calculated on the basis of Si=5 and after the allotment of total Fe to FeO and Fe<sub>2</sub>O<sub>3</sub> as follows: (Ca<sub>1.80</sub>Mn<sub>0.20</sub>)<sub>Σ2.00</sub>(Mn<sub>0.86</sub>Fe<sup>2+</sup><sub>0.14</sub>)<sub>Σ2.00</sub>(Fe<sup>3+</sup><sub>0.97</sub>Al<sub>0.04</sub>)<sub>Σ1.01</sub>Si<sub>5.00</sub>O<sub>14.02</sub> and (Ca<sub>1.97</sub>Mn<sub>0.03</sub>)<sub>Σ2.00</sub>(Mn<sub>0.53</sub>Fe<sup>2+</sup><sub>0.41</sub>Mg<sub>0.05</sub>)<sub>Σ0.99</sub>Fe<sup>3+</sup><sub>1.00</sub>Si<sub>5.00</sub>O<sub>13.98</sub>, respectively. The calculated H<sub>2</sub>O contents for them are 1.58 and 1.56 wt.%, respectively. As already stated, the MnO-richer analysis indicates the highest MnO content in manganbabingtonite known to date. It is quite certain that a part of Ca is substituted by the excess of Mn<sup>2+</sup> up to Ca: Mn<sup>2+</sup>=9:1, and the degree of this substitution is more promoted in Fe<sup>2+</sup>-poorer analyses. A back scattered electron image demonstrates a sector zoning coming from the compositional difference represented by variable Fe<sup>2+</sup>: Mn<sup>2+</sup> ratio (Fig. 7).

The chemical analysis of ilvaite is presented after the allotment of total Fe to FeO and Fe<sub>2</sub>O<sub>3</sub>. It is moderately manganoan with the Fe<sup>2+</sup>: Mn<sup>2+</sup> mole ratio close to 5:1. The empirical formula calculated on the basis of total cation=6 is: (C<sub>0.97</sub>Mn<sub>0.03</sub>)<sub>Σ1.00</sub>(Fe<sup>2+</sup><sub>1.67</sub>Mn<sub>0.31</sub>Mg<sub>0.02</sub>)<sub>Σ2.00</sub>Fe<sup>3+</sup><sub>1.03</sub>Si<sub>1.97</sub>O<sub>8.49</sub>. The calculated H<sub>2</sub>O content is 2.15 wt. %.

The chemical composition of howieite is also characterized by its higher MnO content. On account of uncertainty of total cationic valency, the empirical formula

specifying the valency states of iron could not be derived, but the higher MnO content makes it possible to call the material as manganoan howieite, though it is lower than those in howieite from the neighbouring localities within Kochi City (KATO *et al.*, 1984). The composition of cationic part calculated on the basis of total cation=25 is:  $\text{Na}_{1.11}\text{Fe}_{8.47}\text{Mn}_{2.83}\text{Mg}_{0.34}\text{Al}_{0.43}\text{Si}_{11.92}$ .

The chemical composition of riebeckite was derived after the reference to the calculation method of ROCK and LEAKE (1984). One of the characteristics of this material is the higher MnO content, although it does not reach the limit allowing the usage of adjective "manganoan" (LEAKE, 1978). The empirical formula for the anhydrous part is:  $(\text{Na}_{0.16}\text{K}_{0.08})_{\Sigma 0.22}(\text{Na}_{1.87}\text{Ca}_{0.13})_{\Sigma 2.00}(\text{Fe}^{2+}_{3.30}\text{Fe}^{3+}_{1.39}\text{Mn}_{0.14}\text{Al}_{0.12}\text{Ti}_{0.05})_{\Sigma 5.00}\text{Si}_{8.01}\text{O}_{23}$ .

The chemical analysis of aegirine proves that it is compositionally closer to theoretical  $\text{NaFeSi}_2\text{O}_6$ , or contains about 87 mole % thereof. It is worth mentioning that aegirine of similar composition is reported from the regionally metamorphosed bedded manganese ore deposit of the Kamisugai mine, Ehime Prefecture (KATO *et al.*, 1982). The chemical compositions of aegirine from contact metamorphosed bedded manganese ore deposits in Japan are lower in  $\text{NaFeSi}_2\text{O}_6$  mole percent than them (NAMBU *et al.*, 1980). The empirical formula calculated on the basis of total cation=4 is:  $(\text{Na}_{0.88}\text{Ca}_{0.12})_{\Sigma 1.00}(\text{Fe}^{3+}_{0.87}\text{Ca}_{0.08}\text{Mn}_{0.04}\text{Al}_{0.01})_{\Sigma 1.00}(\text{Si}_{1.92}\text{Al}_{0.08})_{\Sigma 2.00}\text{O}_{5.96}$ .

The chemical analysis of greenalite is also characterized by higher MnO content, although the empirical formula is not definitely derived on account of uncertainty of valency state of Fe coming from the indefinite number of total cations in the formula. The empirical formula was obtained from the microprobe analysis in Table 1 after the partial conversion of Fe into ferric state to make the total cationic valency=28, where the addition of desired  $\text{H}_2\text{O}$  content was calculated to make 100% total. The empirical formula thus derived is:  $(\text{Fe}^{2+}_{2.50}\text{Fe}^{3+}_{1.75}\text{Mn}_{0.53}\text{Al}_{0.27}\text{Mg}_{0.08}\text{Ca}_{0.06})_{\Sigma 5.19}(\text{Si}_{3.60}\text{Al}_{0.40})_{\Sigma 4.00}\text{O}_{10}(\text{OH})_8$ . The derived  $\text{H}_2\text{O}$  content is 10.49 wt. %.

### X-Ray Powder Study

A part of veinlet composed of grains with higher MnO content was used to obtain the X-ray powder pattern by the diffractometer method using Cu/Ni radiation (Table 2). It is comparable with that of the original material (VINOGRADOVA *et al.*, 1966). The recyclic calculation of d-values using cell parameters tentatively derived from the pattern after the reference to those of babingtonite (ARAKI and ZOLTAI, 1972) is concluded after the delivery of the following parameters:  $a=7.492$ ,  $b=12.32$ ,  $c=6.701$  Å,  $\alpha=85.2^\circ$ ,  $\beta=93.9^\circ$ ,  $\gamma=112.2^\circ$ . The calculated d-values are well coincident with the observed ones. The  $b$ -axis is taken to indicate the length of  $\text{Si}_5\text{O}_{15}$  chain unit.

### Consideration on the Genesis

The mineral assemblage of babingtonite is genetically discussed by BURT (1970),

Table 2. The X-ray powder data for manganbabingtonite from Mitani.

| I   | d <sub>obs</sub> | d <sub>cal</sub> | hkl         | I  | d <sub>obs</sub> | d <sub>cal</sub> | hkl          |
|-----|------------------|------------------|-------------|----|------------------|------------------|--------------|
| 10  | 11.38            | 11.38            | 010         | 8  | 1.884            | 1.885            | 332          |
| 55  | 6.932            | 6.931            | 100         |    |                  | 1.884            | 142          |
| 70  | 6.671            | 6.672            | 001         |    |                  | 1.881            | 240          |
| 5   | 5.121            | 5.129            | 110         | 6  | 1.859            | 1.861            | 430          |
|     |                  | 5.120            | $\bar{1}11$ |    |                  | 1.859            | 213          |
| 15  | 4.721            | 4.721            | $1\bar{1}1$ |    |                  | 1.856            | 15 $\bar{1}$ |
|     |                  | 4.715            | 101         | 25 | 1.816            | 1.818            | 232          |
| 18  | 4.084            | 4.076            | $1\bar{2}1$ |    |                  | 1.817            | 410          |
| 18  | 3.770            | 3.762            | 120         |    |                  | 1.817            | 243          |
| 18  | 3.729            | 3.727            | $2\bar{1}0$ |    |                  | 1.812            | 440          |
| 90  | 3.466            | 3.466            | 200         | 12 | 1.800            | 1.801            | $\bar{1}62$  |
| 40  | 3.341            | 3.345            | $2\bar{1}1$ |    |                  | 1.801            | 241          |
|     |                  | 3.336            | 002         |    |                  | 1.796            | 061          |
| 10  | 3.292            | 3.298            | 221         | 8  | 1.783            | 1.785            | 441          |
| 15  | 3.250            | 3.249            | $12\bar{1}$ | 8  | 1.779            | 1.777            | 411          |
| 25  | 3.164            | 3.170            | $2\bar{1}1$ | 5  | 1.762            | 1.760            | 431          |
| 75  | 3.127            | 3.128            | $\bar{1}12$ |    |                  | 1.759            | 233          |
|     |                  | 3.126            | $20\bar{1}$ | 8  | 1.726            | 1.731            | 411          |
| 18  | 3.062            | 3.067            | 140         |    |                  | 1.725            | 450          |
|     |                  | 3.054            | $10\bar{2}$ | 10 | 1.712            | 1.713            | 441          |
| 75  | 3.019            | 3.027            | 201         |    |                  | 1.710            | 330          |
|     |                  | 3.017            | 231         | 8  | 1.691            | 1.694            | 253          |
|     |                  | 3.016            | 210         |    |                  | 1.694            | 313          |
| 100 | 2.955            | 2.961            | 102         | 35 | 1.663            | 1.664            | 322          |
|     |                  | 2.960            | 022         |    |                  | 1.661            | 401          |
| 35  | 2.884            | 2.881            | $\bar{1}41$ |    |                  | 1.660            | 243          |
| 30  | 2.748            | 2.746            | 122         | 18 | 1.645            | 1.647            | 322          |
| 18  | 2.635            | 2.642            | 241         |    |                  | 1.645            | 143          |
|     |                  | 2.631            | $13\bar{1}$ |    |                  | 1.643            | 053          |
| 25  | 2.573            | 2.587            | 032         | 20 | 1.641            | 1.642            | 250          |
|     |                  | 2.567            | 212         | 15 | 1.625            | 1.625            | 410          |
| 15  | 2.556            | 2.560            | 041         |    |                  | 1.625            | 242          |
|     |                  | 2.560            | $\bar{2}22$ | 5  | 1.607            | 1.607            | 062          |
| 20  | 2.489            | 2.490            | $3\bar{2}0$ |    |                  | 1.604            | 251          |
| 30  | 2.465            | 2.472            | $12\bar{2}$ | 18 | 1.580            | 1.583            | 143          |
|     |                  | 2.462            | 132         |    |                  | 1.581            | 353          |
| 40  | 2.452            | 2.452            | 150         |    |                  | 1.577            | 432          |
|     |                  | 2.452            | $20\bar{2}$ | 20 | 1.564            | 1.564            | $\bar{1}63$  |
|     |                  | 2.450            | $3\bar{1}0$ |    |                  | 1.563            | $40\bar{2}$  |
| 10  | 2.277            | 2.282            | $251$       | 8  | 1.541            | 1.543            | 053          |
|     |                  | 2.281            | 321         |    |                  | 1.540            | 442          |
|     |                  | 2.277            | 050         | 15 | 1.478            | 1.480            | 520          |
| 15  | 2.245            | 2.243            | $151$       |    |                  | 1.480            | 531          |
| 35  | 2.203            | 2.209            | 013         |    |                  | 1.477            | 412          |
|     |                  | 2.197            | 051         | 12 | 1.462            | 1.463            | 521          |
| 40  | 2.179            | 2.184            | 230         | 25 | 1.431            | 1.430            | $2\bar{6}3$  |
|     |                  | 2.176            | $\bar{1}13$ | 22 | 1.426            | 1.426            | 541          |

Table 2. (continued)

| I  | d <sub>obs</sub> | d <sub>cal</sub> | hkl | I  | d <sub>obs</sub> | d <sub>cal</sub> | hkl |
|----|------------------|------------------|-----|----|------------------|------------------|-----|
| 15 | 2.118            | 2.117            | 023 | 8  | 1.403            | 1.405            | 462 |
|    |                  | 2.115            | 310 |    |                  | 1.401            | 063 |
|    |                  | 2.115            | 051 | 30 | 1.393            | 1.394            | 403 |
| 15 | 2.074            | 2.079            | 113 |    |                  | 1.393            | 551 |
|    |                  | 2.069            | 231 |    |                  | 1.392            | 430 |
|    |                  | 2.066            | 322 | 5  | 1.370            | 1.371            | 552 |
| 20 | 2.036            | 2.038            | 242 |    |                  | 1.368            | 501 |
|    |                  | 2.037            | 332 | 5  | 1.347            | 1.348            | 512 |
|    |                  | 2.034            | 222 |    |                  | 1.347            | 501 |
|    |                  | 2.034            | 160 | 15 | 1.323            | 1.325            | 522 |
| 5  | 1.969            | 1.974            | 033 |    |                  | 1.320            | 542 |
|    |                  | 1.968            | 223 |    |                  |                  |     |
|    |                  | 1.965            | 213 |    |                  |                  |     |

$$a=7.492, b=12.32, c=6.701 \text{ \AA}, \alpha=85.2, \beta=93.9, \gamma=112.2^\circ, V=570.21 \text{ \AA}^3.$$

who concluded the rather narrow chemical and physical conditions favouring the formation of babingtonite and accounted for the rather rare occurrence. His conclusion is not strictly applicable to the present case on account of compositional difference. And, furthermore, the present occurrence suggests the metamorphic origin due to the closer association with such a metamorphic mineral as howieite, which is also found in nearby ironstone localities as a constituent of crystalline schists forming a part of wallrocks of ironstone ore beds (KATO *et al.*, 1984). However, it is admittedly a fissure mineral. Seeing from the earlier formation of manganbabingtonite than howieite, which also cuts the massive magnetite ore probably suffering the same metamorphism as that produced howieite in nearby localities, that manganbabingtonite is a metamorphic mineral as well as the associated howieite is very likely.

According to MUIR WOOD (1979), the formation of manganoan howieite is favoured under a metamorphic condition corresponding to lower pressure part of glaucophane schist facies. This proves that manganbabingtonite can be produced under the same metamorphic condition as this. Since the materials with lower MnO contents have the same order of  $\text{Mn}^{2+} : \text{Fe}^{2+}$  ratio as those from contact metasomatic skarns, the condition of formation of manganbabingtonite is considered to be rather extensive. And, if the rarer occurrence is taken into consideration, it is very likely that the formation is largely favoured by chemical condition allowing the co-existence of  $\text{Mn}^{2+}$  with  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$ . Although greenalite is found to be slightly aluminian, all the associated minerals with manganbabingtonite are not aluminous except for feldspars.

From these evidences, it is concluded that the original rocks before metamorphism were ironstone composed of iron oxides or hydroxides comprising minor manganese accompanying calcium carbonate rock as the source of such calcium minerals as ilvaite, manganbabingtonite, and andradite. At Maki, one of the other localities

of manganoan howieite located about 5 km WNW of Mitani, the associated minerals includes such a calcium mineral as ilvaite and an aluminum mineral as spessartine, but manganbabingtonite has not been observed in the association. In order to account for the differences between the mineral associations seen in these localities, the presence of any rock containing calcium is necessary. If such a calcium mineral as plagioclase was present in the mineral association accompanied by the ironstone before metamorphism, the metamorphic products must contain aluminum minerals. But, the total aluminum contents in the associated minerals with manganbabingtonite are generally low. Therefore, such a calcium-bearing rock as limestone seems to be most probable as the source of calcium accompanied by the ironstone, although no remnant calcium carbonate is left. Therefore, the present manganbabingtonite can be dealt with as a constituent of metamorphic skarn, although it suffered metamorphism of lower temperature and higher pressure condition corresponding to the lower pressure side of glaucophane schist facies metamorphism, provided that the condition is similar to that of the nearby manganoan howieite localities.

This conclusion leads to the consideration about a phase with the compositional similarity to manganbabingtonite. It corresponds to a  $\text{Fe}^{3+}$ -rich derivative of manganoan hedenbergite, if minor difference in water content is neglected. More precisely, ideal manganbabingtonite is comparable with the intermediate member between hedenbergite and johannsenite plus quartz. That is, the formula  $\text{Ca}_2\text{Mn}^{2+}\text{Fe}^{3+}[\text{Si}_5\text{O}_{14}\text{OH}]$  corresponds to  $\text{Ca}_2\text{Fe}^{2+}\text{Mn}^{2+}[\text{Si}_2\text{O}_6]_2 + \text{SiO}_2 + \text{OH}^-$ , indicating that it is an alternate formed under a higher vapour pressure and oxidizing condition than that favoured the formation of manganoan hedenbergite or ferroan johannsenite, which is seen in such metamorphic skarns as those from Broken Hill mine, New South Wales (HUTTON, 1956).

As reported by BURT and LONDON (1978), manganbabingtonite was formed later than hedenbergite-johannsenite skarns at Arapaiva, Arizona, reflecting the change of condition of formation to oxidizing one. Although the textural break is observed between skarns composed of manganbabingtonite and of hedenbergite-johannsenite at this locality, that they were formed in the same site suggests the ranges of formation of two to be closely situated or neighbouring to each on a diagram including Eh and probably discrete.

### Acknowledgements

We thank Mr. Yoshinobu Tamura, who firstly brought the materials into our attention.

### References

- ARAKI, T. & T. ZOLTAI, 1972. Crystal structure of babingtonite. *Zeit. Krist.*, **135**: 355–373.  
BURT, D. M., 1971. On the paragenesis of babingtonite. *Soc. Mining Geol. Japan*, Special Issue,

3: 375–380.

- BURT, D. M. & D. LONDON, 1978. Manganbabingtonite and ilvaite from hedenbergite-johannsenite skarns, Aravaipa, Arizona. *Abstr. Annual Meet. Geol. Soc. Amer.*, **98**:
- HUTTON, C. O., 1956. Manganpyrosmalite, bustamite and ferroan johannsenite from Broken Hill, New South Wales, Australia. *Amer. Miner.*, **41**: 581–591.
- KATO, A., S. MATSUBARA, & T. TIBA, 1982. A pale coloured aegirine from the Kamisugai mine, Ehime Prefecture, Japan. *Bull. Natn. Sci. Museum*, Tokyo. Ser. C, **8**: 37–42.
- KATO, A., S. MATSUBARA, & Y. SAITO, 1984. Howieite in the Kurosegawa Tectonic Zone in Shikoku, Southwestern Japan. *Proc. Japan. Acad.*, Ser. B, **60**: 65–68.
- LEAKE, B. F., 1978. Nomenclature of amphiboles. *Amer. Miner.*, **63**: 1023–1052.
- MARUYAMA, S., 1981. The Kurosegawa melange zone in the Ino district to the north of Kochi City, Central Shikoku. *Jour. Geol. Soc. Japan*, **87**: 569–583.
- MUIR WOOD, R., 1979. The iron-rich blueschist facies minerals: 2. Howieite. *Miner. Mag.*, **43**: 363–370.
- NAMBU, M., K. TANIDA, & T. KITAMURA, 1980. Chemical composition of manganese bearing pyroxene from Japan and its classification. *Jour. Miner. Soc. Japan*, **14**: Special Issue, 3, 117–128. (In Japanese.)
- ROCK, N. S. M. & B. E. LEAKE, 1984. The International Mineralogical Association amphibole nomenclature scheme: Computerization and its consequence. *Miner. Mag.*, **48**: 211–227.
- VINOGRADOVA, R. A., V. A. SYCHKOVA, & Yu. K. KABALOV, 1966. Manganbabingtonite from the Rudnyy Kaskad deposit (Eastern Sayan). *Doklady Akad. Nauk SSSR*, **169**: 434–437 (In Russian.)

