INTRODUCTION

On the basis of chemical and Mössbauer spectroscopic data, some natural melanites and schorlomites have been shown to contain Fe²⁺, Fe³⁺, Ti³⁺ and Ti⁴⁺ (Huggins et al., 1977; Schwartz et al., 1980). The coexisting of Fe²⁺ and Ti³⁺ in the octahedral sites suggests that the garnets were formed at low oxygen fugacities (Huggins et al., 1977).

Onuki et al. (1981) have described Ti-rich hydroandradites from metamorphosed ultramafics and associated gabbroic rocks whose metamorphic grade ranges from the glaucophane schist facies to the pumpellyite-actinolite facies in the Sanbagawa terrain. They have suggested, based on the electron micro-probe data, that these Ti-rich hydroandradites contain Fe²⁺ and Ti³⁺. In this brief paper accessory minerals stably coexisting with Ti-rich hydroandradites will be described in order to estimate the oxygen fugacity prevailed at the stage of their formation.

Accessory mineral assemblages were determined microscopically, but electron microprobe analyses were performed on the accessory minerals of two metamorphosed serpentinites.

ACCESSORY MINERALS AND THEIR ASSEMBLAGES

In a metamorphosed wehrlitic serpentinite, specimen 80801, awaruite occurs as very fine grains (less than 10 microns in diameter). Although a few pentlandites are also found, awaruite is never in contact with pentlandite, implying that the native metal was not directly originated from pentlandite. Relic chromite is not surrounded by magnetite, but is rimmed by sphene. Magnetite is rarely present.

Specimen 80808, also a metamorphosed
serpentinite derived from wehrlite, contains the assemblage ilmenite+magnetite, besides sphene, pentlandite and haycockite (Cu-Fe sulfide). Both sulfide minerals occur as isolated grains. The genetic relationship between the two minerals is uncertain. Furthermore, there is a perovskite grain, possibly a relic phase like chromite. Other Ti-rich hydroandradite-bearing rocks also contain the assemblage ilmenite+magnetite.

Table 1 gives electron micro-probe analyses of accessory minerals. The awaruite is homogeneous from grain to grain. The awaruite analysis is the average of three point analyses. Because of very fine grain-size, only one spot analysis was possible for each grain. Pentlandite is rather heterogeneous. The composition of pentlandite is the average of analyses of two grains for specimen 80801 and represents each point analysis for specimen 80808. The sum of metal atoms in these pentlandite analyses on the basis of 8 sulphurs is 8.7–8.9. The calculated formula of the Cu-Fe-S mineral in specimen 80808 is very close to Cu₄Fe₅S₈, haycockite, firstly described by Cabri and Hall (1972). Analysed ilmenites are highly manganoan and virtually free from Fe₂O₃. Magnetite is almost pure Fe₃O₄ without exception.

Table 1. EPMA analyses of accessory minerals

<table>
<thead>
<tr>
<th></th>
<th>80801</th>
<th>80808</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Ni</td>
<td>74.54</td>
<td>34.08</td>
</tr>
<tr>
<td>Fe</td>
<td>25.82</td>
<td>27.70</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
<td>4.95</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>33.63</td>
</tr>
<tr>
<td>Total</td>
<td>100.36</td>
<td>100.36</td>
</tr>
<tr>
<td>Ni/Fe</td>
<td>2.27</td>
<td>1.17</td>
</tr>
</tbody>
</table>

1: Awaruite (Ni²⁺Fe³⁺Fe⁴⁺Fe⁵⁺Fe⁶⁺).  
2: Pentlandite (Ni₄₋₅Fe₃₋₄₈Co₀₋₁₈S₀₋₈.₀₀).  
3: Pentlandite (Ni₅₋₆Fe₄₋₅Co₀₋₁₂S₀₋₈.₀₀).  
4: Pentlandite (Ni₅₋₆Fe₃₋₄₈Co₀₋₁₈S₀₋₈.₀₀).  
5: Haycockite (Cu₄₋₅Fe₂₋₃₈Co₀₋₁₈S₀₋₈.₀₀).  
6: Chromite (relic). 7 and 8: Ilmenites.  
9: Perovskite (relic ?). 10: Magnetite.

Discussion

Within the limits of available data, Ti-rich hydroandradite is associated with ilmenite+magnetite or awaruite+magnetite. Therefore, Ti-rich hydroandradite should be formed under a restricted range of oxygen fugacity whose upper limit is defined by the stability of the ilmenite+magnetite assemblage.
In the following discussion, the thermodynamic calculation was done using the data summarized by Robie et al. (1978) and neglecting the effect of pressure on solid phases. The upper limit of oxygen fugacity for the stability of ilmenite+magnetite may approximately be restricted by the following equilibrium.

\[ 2\text{Fe}_3\text{O}_4 + 6\text{TiO}_2 = 6\text{FeTiO}_3 + \text{O}_2 \]

We have the following two relations.

\[ \Delta G^o = -4.575T \log f_{O_2} \text{ and } \]

\[ \Delta G^o = 114776 - 58.85T. \]

Here,

\( \Delta G^o \): The change of free energy by the reaction (in cal).

\( f_{O_2} \): Fugacity of oxygen (in atm).

\( T \): Equilibrium temperature on absolute scale.

Thus, \( \log f_{O_2} = \frac{-25088}{T} + 12.86 \) (1)

If the prevailing temperature is around 300°C, the oxygen fugacity for the formation of Ti-rich hydroandradite may be less than about 10^{-31} atm from equation (1).

However, ilmenite coexisting with Ti-rich hydroandradite is highly manganan. Mariko et al. (1975) stated that the upper limit of oxygen fugacity for the ilmenite+magnetite assemblage may be shifted to a slightly higher value by the moderate substitution of Fe by Mn in ilmenite.

The oxygen fugacity for the hematite+magnetite equilibrium is obtained as follows.

\[ \log f_{O_2} = \frac{-25334}{T} + 13.86 \] (2)

The equilibrium oxygen fugacity of equation (2) is higher than that of equation (1) above 246°K, but the difference is of no significance. Thus, the upper limit of oxygen fugacity for the formation of Ti-rich hydroandradite may be not so largely different from the equilibrium oxygen fugacity of the hematite+magnetite assemblage.

In the low-grade metabasites of the Sanbagawa terrain the assemblage ilmenite+magnetite or hematite+magnetite is very rare (Kanehira et al., 1964; Itaya and Otsuki, 1978). Ti-rich hydroandradite may be formed at lower oxygen fugacities than those prevailed in most of low-grade metabasites in the Sanbagawa terrain.

**ACKNOWLEDGEMENTS**

The authors wish to express their gratitude to Professor Emeritus Kenzo Yagi of Hokkaido University for his critical reading on the early draft of the manuscript. Grateful acknowledgement is due to Professor Shohei Banno of Kyoto University for reviewing the manuscript. Their thanks are also due to Professor Ken-ichiro Aoki and Dr. Hirokazu Fujimaki of Tohoku University, who kindly allowed us to use the EPMA (EDX) and to Dr. Tetsumaru Itaya, at that time, of Tohoku University for his kind advice in microscopic observations on the polished sections.

This study was supported by the Grant in Aid for Scientific Research from Ministry of Education, Japan.

**REFERENCES**


Kanehira, K., Banno, S. and Nishida, K. (1964), Sulfide and oxide minerals in some meta-


岩石化・造岩鉱物学ノート（10）
三波川帯の変成超苦鉱質岩中のチタンに富んだハイドロアンドラライトと
共存するアワル鉱および他の副成分鉱物

大貫 仁・吉田 武義・根建 心具

三波川変成帯の蛇紋岩中でチタンに富んだハイドロアンドラライトと安定に共存する副成分鉱物はマンガンに富んだイルメナイト＋磁鉄鉱あるいはアワル鉱＋磁鉄鉱の組合せで特徴づけられる。したがって、チタンに富んだハイドロアンドラライトは比較的低い酸素分圧下で形成されたことが示唆される。