

Howieite and Mn-rich stilpnomelane from metasiliceous rock in the lawsonite-blueschist facies Otao unit of Kurosegawa belt, Kyushu

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Howieite (Hw) and Mn-rich stilpnomelane (Mn-stilp) were newly found from meta-manganese siliceous rocks intercalated with a lawsonite-bearing blueschist, showing a peak P-T conditions around less than 300 C and 6-8 kbar, in the western part of Otao unit of the Kurosegawa belt, Yatsushiro. Hw- and Mn-stilp are closely associated with fine-grained matrix forming phases of riebeckite($\text{Na}_{2.22}\text{Ca}_{0.04}$)($\text{Fe}_{2+2.08}\text{Mg}_{0.48}\text{Mn}_{0.21}\text{Fe}_{3+1.68}\text{Al}_{0.54}$) $\text{Si}_{8.30}\text{O}_{23}$, lawsonite, aegirine($\text{Na}_{0.99}\text{Ca}_{0.06}$)($\text{Fe}_{3+0.77}\text{Al}_{0.20}$) Si_2 , calcite and quartz. However, chlorite, white mica and albite, which are dominant phases under lower grade metasiliceous rocks, were not detected. Both Hw and Mn-stilp occur as acicular to fine-grained aggregates and show yellow to pale yellowish pleochroism and hence it is hard to distinguish them under the optical microscope. The identification of them was done by the backscatter electron image observation and EPMA. Hw is relatively homogeneous in each grain with following average composition, ($\text{Na}_{1.21}\text{K}_{0.01}\text{Ba}_{0.01}$)($\text{Fe}_{2+6.00}\text{Mn}_{4.15}\text{Al}_{0.91}\text{Mg}_{0.73}\text{Ti}_{0.07}$) $\text{Si}_{12.25}\text{O}_{37.5}$ assuming all iron as FeO. Mn-stilp is heterogeneous in composition even in one grain, especially showing wide variation of K from 0.78 wt% to 3.18 wt%, and shows following composition range assuming all iron as FeO, ($\text{K}_{0.18-0.74}\text{Na}_{0.07-0.30}\text{Ba}_{0.06-1.12}\text{Ca}_{0.04-0.09}$)($\text{Fe}_{2+2.61-3.18}\text{Mn}_{1.67-2.27}\text{Al}_{1.16-1.37}\text{Mg}_{0.47-0.62}\text{Ti}_{0.01-0.16}$) $\text{Si}_{7.92-8.08}\text{O}_{23-24.5}$. Transmission electron microscope observation reveals that the space group and the lattice parameter are coincide with those of Hw (space group: $P1^-$ or $P1$; $a \sim 21.9 \times 10^{-10}\text{m}$, $b \sim 21.9 \times 10^{-10}\text{m}$, $c \sim 17.7 \times 10^{-10}\text{m}$, $\alpha \sim 125^\circ$, $\beta \sim 95.9^\circ$, and $\gamma \sim 120^\circ$), and Mn-stilp (space group: $P1^-$; $a \sim 10.2 \times 10^{-10}\text{m}$, $b \sim 9.8 \times 10^{-10}\text{m}$, $c \sim 9.6 \times 10^{-10}\text{m}$, $\alpha \sim 91.2^\circ$, $\beta \sim 70.8^\circ$, and $\gamma \sim 108.1^\circ$). Moreover, Hw and Mn-stilp are intercalated with each other with from a few hundred to $500 \times 10^{-10}\text{m}$ thick layers. The latter may cause a slight chemical difference from the ideal Hw composition, $\text{Na}(\text{Fe}_{2+}, \text{Fe}_{3+}, \text{Mn}_{2+}, \text{Mg}, \text{Al})_{12}\text{Si}_{12}(\text{O}, \text{OH})_{44}$ and a wide compositional variation of Mn-stilp against the ideal formula, $(\text{K}, \text{Na}, \text{Ca})_{0.6}(\text{Mg}, \text{Fe}_{2+}, \text{Fe}_{3+})_6\text{Si}_8\text{Al}(\text{O}, \text{OH})_{27-28}\text{H}_2\text{O}$.

The first description of Hw has been done by Agrell et al. (1965) from metamorphosed banded Mn ore bed in the LT/HP Franciscan metamorphic belt along with deerite, $(\text{Fe}_{2+}, \text{Mn}_{2+})_6(\text{Fe}_{3+}, \text{Al})_3\text{Si}_6\text{O}_{20}(\text{OH})_5$, and zussmanite, $\text{K}(\text{Fe}_{2+}, \text{Mg}, \text{Mn}_{2+})_{13}(\text{Si}, \text{Al})_{18}\text{O}_{42}(\text{OH})_{12}$. After that, Schreyer and Abraham (1977) and Wood (1979) reported the occurrence of Hw from blueschist facies meta-ironstones. Taneyamalite (Tan), Mn-endmember of Hw, has been firstly reported from Mn ore beds of Taneyama mine in the same area as this study by Aoki et al. (1981) and from Iwaizawa Mine, belonging to the Chichibu belt, Kanto Mountains, by Matsubara (1981). Other findings of Hw and taneyamalite were reported from lower-grade metasiliceous rock in the iron-manganese ore beds of Mikabu belt, Chichibu belt and Kurosegawa belt in Shikoku, but they were not reported from the Sanbagawa belt in strict sense (Minagawa and Matsuda, 2002). These facts suggest that Hw-Tan series minerals are stable under lower temperature conditions less than 300 C, such as blueschist and pumpellyite-actinolite facies and they may decompose to other phases with the increase of metamorphic grade, although detail reaction systems are not been clear.

The geo-tectonic significance of Hw-taneyamalite series minerals and stilp has not been unraveled yet. However, the meta-manganese siliceous rocks studied in this study do not contain representative hydrous phases such as chlorite and white mica, but contain high modal amount of Hw and Mn-stilp (more than 20 vol.%) and scarce amount of lawsonite (ca. 4 vol.%) and riebeckite (ca. 4 vol.%). As Hw and Mn-stilp contain a significant amount of H₂O (ca. 4.5 - 10 wt% judging from EPMA data), we emphasize that Hw and Mn-stilp act as a major water container in the lower grade iron/manganese meta-siliceous rocks.