Japan Geoscience Union Meeting 2010
(May 23-28 2010 at Makuhari, Chiba, Japan)
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SMP055-05 Room: Function Room B Time: May 23 14:45-15:00

H2O storages in meta-manganese siliceous rocks of the lawsonite blueschist facies

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This study aims to reveal the water conservation mechanism in meta-manganese siliceous rocks metamorphosed under the lawsonite-blueschist (Lws-BS) facies, formed around < 350 C and 0.8-1. 0 GPa and to estimate water contents in them by modal analysis, collected from the Kurosegawa belt in the Yatsushiro area, Kyushu, Japan, in order to understand the fluid circulation system in the subduction zone.
The meta-siliceous rocks in the study area are mainly composed of quartz, albite, K-feldspar, Na-pyroxene, lawsonite, pumpellyite, Sr-epidote, Na-amphibole, chlorite, stilpnomelane, howieite, muscovite, braunite, hematite, manganese oxides, iron sulfide, carbonate and titanite. There is a following relationship between colors of meta-siliceous rock and the main constitunent minerals; White part composed of quartz, red to pink part composed of hematite or lawsonite, pale green part composed of howieite, pale yellow part composed of pumpellyite, brown part composed of stilpnomelane and black part of composed of braunite. The mineral assemblages of hydrous minerals are closely correlated with the Oxygen fugacity (fO2) state in the host rocks. The meta-siliceous rocks in lower fO2 state (log fO2 < ca. -30 at 300 C and 1.0 GPa), which is defined by the existence of iron sulfide, contain variety of hydrous minerals such as stilpnomelane (including ca. 7 -13 wt% of H2O per mole), howieite (ca. 4-7 wt%), Na-amphibole (ca. 2 wt%) and lawsonite (ca. 1 2 wt%). The meta-siliceous rocks in higher fO2 state (ca. -20 > log fO2 > -5), which is defined by the existence of braunite (Mn2+Mn3+6SiO12), contain mainly pumpellyite (ca. 6-8 wt%) as hydrous minerals, but do not stilpnomelane nor howieite, as such higher oxidation states do not allow iron to be divalent but to be trivalent. A sample of the meta-siliceous rock in the higher fO2 state contains a peculiar lawsonite, which contains a significant amount of (Mn3+ + Fe3+), substituting ca. 5-10 mol% of Al of the ideal lawsonite formula. This substitution type in the lawsonite has not been reported yet.
H2O content of Lws-BS and meta-siliceous rock were estimated based on the modal amount of constituent minerals. OD7A, a homogeneous brownish meta-siliceous rock with a lower fO2 state, contains ca. 1.5 wt% H2O mainly in lawsonite, stilpnomelane, muscovite and Na-amphibole. Backscattered image observation of sample OT9B, a reddish banded meta-siliceous rock with an intermediate fO2 state, reveals that OT9B contains ca. 5.0 wt% of H2O mainly in lawsonite, chlorite and Na-amphibole. Fujimoto (2007) estimated the similar H2O content (5.0 wt%) from another Lws-BS in the same study area but he reported less amount of H2O (1.8 wt%) for an epidote-blueschist in the Sambagawa belt. These results suggest that H2O content in the metabasite drastically decreases with the increase of metamorphic grade, i.e., from the Lws-BS to the epidote-blueschist, mainly due to the decomposition of lawsonite, as suggested by model calculation of Hacker et al. (2003).
Lawsonite and pumpellyite in the meta-manganese siliceous rock would decompose to epidote + some other phases and supply dehydrated fluids into the subduction system with the increase of metamorphic temperature from the Lws-BS facies to the epidote-amphibolite facies, as well as the case in the metabasite mentioned above. However, the stability condition of stilpnomelane and howieite are not well known. To elucidate the stability field of howieite, model Schreinemakers'

bundle was constructed in a model MnO-Al2O3 system with howieite, carpholite, caryopilite, sudoite and chloritoid with excess quartz, albite and H2O. A plausible net identified from literature data predicts that Mn-end member of carpholite and howieite can coexist under the Lws-BS facies conditions in Mn-rich rocks, and Mn-end member of carpholite would decompose to Mn-chloritoid with the increase of temperature. However, higher-temperature limit of howieite can not be determined in this study.

Keywords: Mn3+-bearing lawsonite, hydrous phase, oxide state, meta-siliceous rocks, subduction zones