

Mineralogy of Highly-Oxidized Lawsonite-Blueschist Facies Metachert from the Hakoishi sub-unit, the Kurosegawa Belt, Kyushu and Proposal for the Piedmontite Forming Reaction

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Deep-fluids are thought to play an essential role in various physical-chemical phenomena taking place in the plate convergent areas, e.g., earthquakes, arc volcanisms and pollution of the mantle (e.g., Tatsumi, 1989; Hacker et al., 2003). While aqueous fluid is expected to compensate for this kind of fluid and attracts major attentions, oxygen has not been considered well concerning its influences on composition, generation depth and behaviour of deep-fluids. Redox conditions are expected to reflect the behaviour of oxygen and strongly control mineral assemblages. Therefore, redox conditions can be discussed on the basis of the observed mineral assemblages, and vice versa.

This study deals with mineral assemblages in metachert samples from the Hakoishi sub-unit of the Kurosegawa Belt in the Yatsushiro area, Kyushu, Japan. In the area, rocks with various origins are identified as blocks in the serpentinite melange. The Hakoishi sub-unit suffered the lawsonite-blueschist (LBS) facies metamorphism under 0.45 –0.8 GPa and 200 –300 C (Sato et al., 2016). The protolith of the LBS is estimated as mafic rocks with 500 Ma U-Pb zircon age and associated chert and K-Ar white mica age of 280-299 Ma are reported (Osanai et al., 2014; Sato et al., 2016). Therefore, the studied metacherts are expected to record the redox conditions at the shallower part (ca. 15 –25 km) of the cold subduction zone.

In metacherts of the sub-unit, various Mn-bearing minerals are reported. Taneyamalite was first reported by Aoki et al. (1980), and howieite by Ibuki (2010). In addition, Ibuki (2010) sub-divided the metachert samples into three groups in terms of redox conditions based on the colour of metachert in appearance. This study mainly introduces the mineral assemblage of braunite-bearing samples which are classified as highly oxidized group (OT10I/J). These samples contain Mn³⁺-bearing hydro-silicates, such as piedmontite and okhotskite, along with Na-pyroxene and Na-amphibole at the peak metamorphic stage minerals and Mn⁴⁺-bearing hydro-oxides in later stage veins. In this report, we will discuss the impact of the redox conditions on the mineral assemblages.

All Fe and most of Mn are oxidized to trivalent in these samples. All the analysed sodic pyroxenes are poor in Ca-Fe-Mg pyroxene component ($Di < 15$) and mainly composed of Aeg and Jd components, which vary depending on the local chemical compositions. In addition, most of analysed amphiboles are close to the ideal magnesio-riebeckite ($Mg\# > 0.9$, $Al\# < 0.25$), though glaucophane is reported from LBS in the Hakoishi sub-unit.

Lawsonite and pumpellyite are widely identified in the LBS, but no epidote is reported (Sato et al., 2016). However in the metachert samples, piedmontite, Mn³⁺-bearing epidote, is identified but no lawsonite is recognized. In addition, piedmontite grains commonly contain a few wt. % of REE as oxides. These facts suggest that highly oxidized condition allow the occurrence of the epidote group mineral in metachert of LBS facies, together with some certain elements.

Mn hydro-oxides, such as todorokite and pyrolusite, are identified from post-metamorphic veins, which are developed throughout the samples. These veins contain Mn⁴⁺, suggesting the intrusion of extra-oxidized fluids. In LBS of the Hakoishi sub-unit, albite and carbonate veins are dominant, although they are less developed. The fluid might be as oxidized as the modern seawater, and the presence of these veins may support the ideas of Tumiati et al. (2015), concerning the transportation of oxygen along veins.

Comparison with Mn-bearing mineral assemblage reported in the Kokuriki mine, Hokkaido (Kimura et al., 1995), suffered Pmp-Act facies (Sakakibara, 1991), a following metamorphic reactions might be suggested, $2 \text{ Mn-Pmp} + \text{O}_2 = 2 \text{ Pmt} + 3 \text{ H}_2\text{O}$, which is one of intimate relationship between the Oxygen and deep fluid.

Keywords: okhotskite, piedmontite, lawsonite-blueschist, deep-fluids, redox condition, the Kurosegawa Belt