The estimation of redox state based on the fluid-deposited graphite and sulfide minerals in fault rocks

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The redox state in fault rocks provide valuable information on the physicochemical properties related to the fluids during seismic activity (O'hara and Huggins, 2005). However, there are very few studies on direct clues for fluid activities obtained from fluid inclusion (Boullier et al. 2001) and estimation of fluid contents using micro-FTIR (Famin et al. 2008). It is usually difficult to distinguish between syngenetic and postgenetic fluid activities from altered and hydrated fault rocks and pseudotachylytes that indicate paleo-seismic activity (Kirkpatrick and Rowe 2013).

Here we focus on carbon- and sulfur-bearing minerals in fault zones in order to understand the dynamic changes of oxygen fugacity (fO_2) and sulfur fugacity (fS_2). The study area, located in the Hidaka metamorphic belt, Hokkaido, Japan, is a metasedimentary unit where cataclasites, ultracataclasites and two different types of pseudotachylytes; Pst I and Pst II are distributed. Pyrrhotite (N[FeS] = 0.92–0.94) + Kfs assemblage is found in Pst I matrix, whereas biotite microlite + Kfs assemblages with fluid deposited graphite is only found in Pst II matrix. The fluid deposited graphite is only observed in the Pst II matrix, which was generated at around 1200 degree C, and characterized by the breakdown of plagioclase and apatite. The carbon isotope composition of the fluid deposited graphite were between –18.2 and –25.4 permil, shifting the carbon isotope values of +2 ~ +3 permil from the metamorphic graphite in protolith, cataclasite and Pst I.

Our observations suggest that the graphite and sulfide minerals converted to COHS fluids by frictional melting, and then reprecipitate as secondary minerals under favorable fO_2-fS_2 environments. In order to assess the redox state, we attempt to estimate the P-T-fO_2-fS_2 phase diagram during frictional melting. The thermal decomposition of biotite coexisting with graphite and sulfide minerals are deduced as:

Annite in biotite + 3Pyrite + 1.5Graphite = Sanidine + 6Pyrrhotite + H_2O + 1.5 CO_2
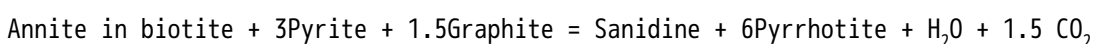
The breakdown of biotite changes the redox state to the more oxidation state at ranges between delta FMQ +0.5 ~ + 3.0. Under a high-temperature condition (> 1200 degree C), biotite microlite + Kfs with fluid deposited graphite are usually observed instead of pyrrhotite in pseudotachylytes. This suggests the negative shift to biotite stability field by lowering fS_2 and fO_2. In addition, using the positive 2~3 permil shift by carbon isotope fractionation, the calculated xCO_2 (= CO_2 / CH_4 + CO_2) ranges between 0.12 and 0.03. The calculated fO_2 is evaluated between –21.6 and –22.0 log $_{10}$ units, suggesting the CH_4 dominant fluid based on the estimated ideal fluid mixing model. When the fluid composition encounters the graphite saturation surface in COH diagram by supersaturation, the fluid deposited graphite begins to precipitate with hydrous silicates such as hydroxyapatite and titanite, and shift the large carbon isotope fractionation by small fluctuation in xH_2O. Such precipitation model is in good agreement with the microtextural observations in pseudotachylyte matrix. The most important implication of our finding is that the redox state in both types of pseudotachylytes are controlled by graphite breakdown. Our finding of fluid deposited graphite in pseudotachylytes suggest that sediments can produce the COHS fluids by frictional melting and the graphite play as a reducing agent in fault rocks.

References: Boullier et al. (2001), JGR, 106, 21965-21977. Famin et al. (2008), EPSL, 265, 487–497. Kirkpatrick and Rowe, (2013), JSG, 52, 183-198. O'hara and Huggins (2005), CMP, 148, 602-614.

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