

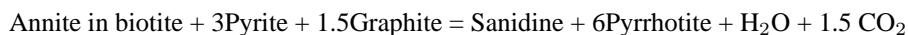
Dynamic fluctuation of redox state during frictional melting and crystallization of graphite-bearing pseudotachylites

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We carried out a stable carbon isotopic study of graphite-bearing pseudotachylites to characterize the origin, role and behavior of different forms of carbon during frictional melting. The study area, located in the Hidaka Metamorphic belt, exposes metasedimentary rocks and various magmatic intrusions and are extensively deformed as evidenced by the presence of various types of fault rocks such as graphite-bearing cataclasite, ultracataclasite and pseudotachylites. In particular, graphite-bearing pseudotachylites are observed in the brittle shear zones, which are a few mm to maximum 5 cm in width. They are mainly divided into two types (Pst-I and Pst-II) based on the occurrences, microstructures and mineral assemblages of lithic fragments and secondary minerals. The graphite in each domain of Pst-I and Pst-II were separately analyzed for carbon isotopic composition. Disseminated graphite in protolith has a narrow range of $\delta^{13}\text{C}$ values between -23.6 and -25.8 ‰ (n = 13), and cataclasite, ultracataclasite and Pst I also have similar values between -24.1 and -27.0 ‰ (n = 25). On the other hand, the graphite separated from Pst II matrix on slab sections show values between -18.2 and -23.6 ‰ (n = 16), shifting the carbon isotope values to 2-3 ‰ higher from host metamorphic graphite. In particular, there is a clear correlation between stable carbon isotope composition and volume fraction of lithic fragments in each domain.

Our data indicate that metamorphic graphite in fault rocks were converted into $\text{H}_2\text{O}-\text{CO}_2$ or $\text{H}_2\text{O}-\text{CH}_4$ fluids under very-high temperature condition of frictional melting. Subsequently, a part of the COHS fluid re-precipitated as fluid-deposited graphite and the remaining was expelled as COHS fluids into fault zones during quenching stage. On the basis of chemical compositions and mineral assemblages in the pseudotachylites, we attempt to estimate the P-T- $f\text{O}_2$ - $f\text{S}_2$ phase diagram during frictional melting and crystallization of pseudotachylites. The thermal decomposition of biotite coexisting with graphite and sulfide minerals are deduced by following reaction;



The dehydration and decarbonation processes in this reaction are mainly driven by temperature, $f\text{S}_2$, and $f\text{O}_2$, and the breakdown of biotite that is ferromagnesian mineral change the redox state to the more oxidation state at ranges between $\Delta\text{FMQ} +0.5$ to $+3.0$. Such high $f\text{O}_2$ and $f\text{S}_2$ environments are only observed in the domains which show relatively low-temperature condition (Pst I matrix) during frictional melting. On the other hand, in the domains which show high temperature conditions (>1200 degree C) biotite microlite are observed in pseudotachylites instead of pyrrhotite. This suggests the negative jump to biotite stable field of ASM buffer by lowering $f\text{S}_2$ under high-temperature condition. In addition, we tried to estimate the redox state at precipitation stage using graphite-fluid fractionation model. The difference between disseminated graphite and fluid deposited graphite show the positive 2-3 ‰ shifting by carbon isotope fractionation, suggesting the presence of CH_4 -rich COHS fluid during precipitation stage. Under CH_4 - H_2O dominant fluid in COH diagram, we can explain the carbon isotope variation of fluid deposited graphite at around $\Delta\text{FMQ} -3.0$ by hydration reactions during the crystallization of titanite and hydroxyapatite. Such reducing conditions are only observed in the high temperature frictionally melted domains (Pst II matrix).

Thus, oxidation and precipitation processes of graphite are mainly controlled by the breakdown of ferromagnesian minerals and we revealed that the redox state and TOC values dynamically changed within each pseudotachylite matrix. In addition, our data imply that redox state in pseudotachylite sensitively change in melting domains at ranges of $\Delta\text{FMQ} -3.0$ to $+3.0$ as a function of melting temperature and bulk chemistry.

Keywords: Graphite, stable carbon isotope, pseudotachylite, redox state