Abstract

Tungsten (W) is a strategic metal with many applications, including energy storage, electrode material, abrasives, industrial catalyst, and penetrating projectiles. W deposits are also enriched in other critical metals such as Li, Rb, Cs, Sc, Nb, and Ta, critical elements for sustainable energy production. Understanding the nature and the source of the ore fluid and the controls on their transport, mobilization, and mineralization is desirable to aid exploration work. In the Aravalli-Delhi Belt of western India, Proterozoic granite magmatism and associated large-scale hydrothermal activity have given rise to three W deposits/mineralization at Balda, Motiya, and Degana and a wollastonite deposit at Belka Pahar. In this study, the major, trace element and B, Li isotopic composition of tourmaline, zinnwaldite, and wolframite are used to constrain the nature of the W-bearing hydrothermal fluid and the processes involved in the precipitation of wolframite. Tourmaline from the Balda and Motiya W-prospect are of schorl composition, have high alkali and low Ca contents and moderate X-site vacancies. The high V/Sc ratios of tourmalines in the mineralized veins and wall-rock tourmalinites indicate an essential role of biotite dissolution and fluid-rock interaction that contributed Fe-Mn for the precipitation of tourmaline and wolframite. The B isotope variation in the granite-pegmatite-vein system can be explained by fluid exsolution with the mineralized vein forming from exsolved fluid and topaz-bearing granites and pegmatites crystallizing from residual melts. The $\delta^{11}B$ of the mineralizing fluid is estimated to be ca. – 7.4 ‰ at Balda and ca. – 7.6 ‰ at Motiya, and were possibly derived from S type-granites, consistent with extensive tourmalinization and muscovitization of wall rocks, and high concentration of elements such as F, Li, B, Sn, Mn in the tourmaline and the reconstructed fluid. The W bearing fluid was primarily derived from a fractionated granitic source, and precipitation of wolframite and tourmaline involved interaction of the hydrothermal fluid with the surrounding pelitic schists. At Degana, a high concentration of Li, Rb, Cs, Nb, Ta in zinnwaldite, a Li, Rb rich mica, and the reconstructed fluid, suggest that the ore fluid was sourced from a late fractionated magma. The Li isotopic composition of the ore fluid is estimated to be +14 to +19 ‰, significantly heavier compared to average granite composition (−5 to + 7‰) and the upper and middle continental crust and can be best explained by fluid exsolution from highly enriched, late fractionated granite melt, consistent with the high concentration of incompatible elements in zinnwaldite. Alteration of the host granite, formation of greisen, large-scale albitization, and muscovitization are indicative of fluid-rock interaction. The change in chemical and Li isotope composition from early mica to late altered mica in the greisen indicates prolonged interaction of the hydrothermal fluid with the host rocks. In the Belka Pahar wollastonite skarn deposit, garnet and scheelite chemistry is used to characterize the changes in the composition of the fluid with the progress of the fluid-rock interaction. Two types of garnet are recognized in the Belka Pahar skarn rocks: prograde garnet (Grt_1) and retrograde oscillatory-zoned Grt_2, which is further sub-divided into three generations Grt_{2a}, Grt_{2b} and Grt_{2c}. The Grt_1 ($And_{27–47}$) and Grt_{2a} ($And_{50–60}$) yield high Y-concentration and high HREE/LREE ratio which is in stark contrast to the late-retrograde Grt_{2b} (And_{40-50}) and Grt_{2c} ($And_{27–40}$), which are characterized by high F, low Y concentration, and HREE depleted REE pattern. The chemistry of different generations of garnet suggests a shift in pH conditions of the fluid from neutral to acidic to less acidic conditions. The crystallization of F-rich garnet, vesuvianite, and fluorite indicate an increase in F-concentration in the later-stage fluid. Increase of W concentration in Grt_{2b} and co-precipitation of scheelite and fluorite also suggests its possible link with scheelite precipitation. The high grossular component in the Grt_{2b} and Grt_{2c} suggest transport of Al in the hydrothermal fluid as F-complexes. Composition of the fluid extrapolated from the scheelite composition agrees with the LREE enriched pattern exhibited by all skarn minerals. Principal Component Analysis done on a compiled garnet dataset shows that the trace element composition of garnet can be a useful indicator of fluid composition and can be used as an indicator of associated ore type.

Keywords: granite, hydrothermal fluid, tungsten, fluid exsolution, fluid-rock interaction, tourmaline, zinnwaldite, garnet, wolframite, scheelite