Stability of Sn(IV)-F complex at magmatic-hydrothermal conditions

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It is widely thought that tin mineralization happens at acidic and reduced conditions and Sn(II)-Cl complex is the main species controlling tin mobility. However, it is found that some tin deposits in South China were formed at relatively-oxidized conditions, with a genetic association with fluorine-rich highly-evolved and/or A-type granites. Hosted in these rocks are $\sim\!20\%$ of the world's tin and $>\!20\%$ of the fluorite reserves. Which role on earth fluorine plays on tin mineralization is still obscure.

Property of ore-forming aqueous metal complex play a crucial role in controlling metal dissolution, migration, and precipitation [1]. Here we investigated the stability of potassium tin fluoride (K_2SnF_6) in aqueous solution at temperatures from 250 to 550 °C and pressure of 100 MPa, to probe into the capability of Sn(IV) mobility mediated by the fluorine at magmatic-hydrothermal conditions. We determined the cumulative hydrolysis constants (K) of this kind of Sn(IV)-F complex at varied temperatures (T), and a nice linear fitting of lnK=-10615/T+12.058.

Given that ore-forming fluids usually contain various components, further thermodynamic calculation used the cumulative hydrolysis constants to give a quantitative evaluation on the mobility of Sn(IV) in F-rich fluids with given temperature, pH and fluorine content. The result show that when the fluids contain less than 0.6 wt.% F, stability of Sn(IV)-F complex is dominated by the pH and temperature, only resulting in minor Sn(IV) migration (no more than several hundred ppm); when the fluorine in fluids is more than 2 wt.%, stability of Sn(IV)-F complex is less influenced by the pH and temperature, which could lead to the migration of up to ten thousand ppm Sn(IV). Compared with Sn(II)-Cl and Sn(IV)-Cl complexes, Sn(IV)-F complex has systematically lower capability of transporting Sn at the reduced and low-F fluids, but has the same or even higher capability at the oxidized and F-rich fluids. These suggest the fluorine may contribute more to tin mineralization than has been previously recognized.

Reference:

[1]Ding, X., et al. 2018. Geofluids, doi:10.1155/2018/14 52409.