

Nb-Ta oxide minerals in granites and pegmatites: Tracers of magmatic to post-magmatic evolution

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Accessory Nb-Ta oxide minerals occur in some highly fractionated granites and granitic pegmatites. Their internal zoning, compositional variations and breakdown products are sensitive indicators of magmatic to post-magmatic evolution of the parental rocks.

Regular fine to coarse oscillatory zoning of columbite-tantalite and Nb,Ta-rich rutile with repeated Nb- and Ta-rich zones indicates their primary magmatic crystallization. Increasing Ta/Nb, (Nb+Ta)/Ti and Mn/Fe ratios in the Nb-Ta phases traces the degree of magmatic fractionation, whereas W, Sn, Sc, Zr, Y, U and Mg contents reflect mainly their local compositional environment. Moreover, presence of Ti,Fe³⁺-rich Nb-Ta minerals (titanian ixiolite, rutile) could serve as an indicator of higher oxygen-fugacity (fO_2) conditions in comparison to the Ti-poor, Fe²⁺-rich ordered columbite-tantalite + ferrotapiolite assemblage. Minerals of the foordite-thoreaulite series (Sn²⁺Nb₂O₆ – Sn²⁺Ta₂O₆) represent an example of primary magmatic phases in specific Sn-rich and low fO_2 pegmatitic environment in contrast to common occurrence of cassiterite + W,Ti-rich Nb,Ta minerals (columbite-tantalite, ixiolite, rutile) in rare-element tin-bearing leucogranites.

Late-magmatic to subsolidus alteration, recrystallization and breakdown of the primary Nb-Ta oxide minerals is widespread. Complex irregular convoluted zones reveal partial leaching and replacement of the primary phases; erratic Nb-Ta distribution is typical for the secondary columbite-tantalite. Mosaic patchy zoning of Nb-Ta-Ti phases manifest their recrystallization probably due to younger thermal/pressure metamorphic overprint. Subsolidus exsolution textures are typical for Fe³⁺,Ti,Sc,W,Sn-rich, primary Nb-Ta phases (e.g. Nb-Ta rutile, ixiolite); they indicate a breakdown of the primary phases and element redistribution during granite/pegmatite cooling and uplift.

Increasing of fluid activity and fO_2 during late- to post-magmatic stage caused a breakdown of Sn²⁺-bearing foordite-thoreaulite and precipitation of secondary cassiterite + columbite-tantalite. Moreover, an influx of late-magmatic to hydrothermal Na,Ca-rich fluids facilitates replacement of columbite-tantalite, ixiolite and Nb-Ta rutile by fersmite, pyrochlore-group and other alkali-rich Nb-Ta minerals. Rarely, an activity of Sb,Pb-bearing hydrothermal fluids caused a precipitation of specific secondary Nb-Ta minerals (plumbomicrolite, stibiobetafite, stibiotantalite, Nb,Ta-rich roméite etc.).

Thermodynamic price tags for a wet mantle

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The exciting discovery of Wadsleyite as mineral host for hydrogen or as a 'hydrous material' in the mantle has redox-equilibria-implications relative to other published redox models for the Earth's mantle. Such redox models for the Earth's mantle suggest that along the geotherm, shallow mantle conditions range from the log fO_2 given by the buffer (FMQ) to levels of redox of $\Delta(FMQ) = -2$. These models have been based on studies that include: (1) xenolith studies by several methods (as reviewed by Ulmer *et al.*, 1987) (2) stability of diamonds relative to other redox buffers (for example, Eggler and Baker, 1982 or Ulmer *et al.*, 1978). Most redox models for the Earth's mantle do incorporate more reduced conditions for greater depth in the mantle: the log fO_2 given by the buffer (IW) at the core mantle boundary is one logical reason for this model. Deeper xenolith studies also suggest this. (Haggerty and Tompkins, 1983 or Ulmer *et al.*, 1987). Even more reduced conditions for the mantle are implied by the abundant existence of the mantle mineral, Moissanite, (SiC) whose redox stability in log fO_2 can be represented by $\Delta(IW) \approx -8$ at pressures up to 9.0 GPa and temperatures up to 1730 K. Furthermore, the kinetics of oxidation of SiC exposed to carbonates or iron oxides from 2.0 to 15.0 GPa and temperatures as low as 1173 K has been measured in hours, not days or months! (Ulmer *et al.*, 1998)

To have mantle phases, either with hydroxyl, or as true hydrates, that can be compatible in the redox state of the mantle seems a problem? A companion manuscript at this meeting explores redox EOS calculations of water stability in the mantle. (*cf.*, Woermann *et al.*). To our thinking, one possibility may be the influence of defects in the Wadsleyite. No direct data yet seem available for this suggestion; it is by analogue to the large range of redox values demonstrated by defect olivines that this idea should be pursued.

References

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