Nanoscale mineralogy of zirconium in iron-oxides

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Zirconium is an element of major petrogenetic interest, necessitating a thorough understanding of the mineral hosts for the element and how it is distributed in a given rock sample. Empirical studies have indicated that the crystal structure of hematite can accept Zr, even if Zr concentrations reported in iron-oxide minerals are often attributed to detrital input of zircon ($ZrSiO_4$) during crystal growth. Ores from the Peculiar Knob (PK) iron deposit, Mount Woods Inlier, South Australia, occur within a metamorphosed BIF sequence that has been correlated with Archean BIFs of the Middleback Ranges ~500 km SSE. Mechanisms leading to ore formation are however debated and include metamorphism or interaction with hydrothermal fluids associated with emplacement of ~1590 Ma Hiltaba Suite granites. Coarse-grained (mm-scale), massive martite ore from PK features dusty inclusions of a Zr-bearing mineral associated with interstitial zircon tens-of-µm in size. Although optically homogenous, LA-ICP-MS element maps show that martite cores are enriched in Zr (up to several hundred ppm), Ti, Hf, Cr, and W, with grain margins depleted in these elements, but enriched in Sb and Nb. Using HAADF-STEM imaging and EDS STEM mapping of FIB-prepared foils, we identify the dust-like mineral inclusions within martite as needle-like baddeleyite (ZrO_2). These inclusions display epitaxial growth, with martite suggesting formation from released Zr originally hosted in the iron-oxide lattice. The occurrence of two Zr-minerals with contrasting relationships to host martite (included and interstitial), suggests that the ores underwent a protracted geological history. We attribute formation of baddeleyite needles during martitization of initial BIF magnetite. Later fluid percolation (granite-related?) led to development of martite grain rims, intergranular fracturing and crystallization of zircon+quartz assemblages. Results show: (i) the ore formed via multiple overprinting of an initial BIF protolith and likely involved metamorphic and hydrothermal processes; (ii) major implications for U-Pb dating of hydrothermal minerals.