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Exceptional alteration of cassiterite, rutile, zircon, xenotime and monazite during weathering of VHMS mineralisation

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Heavy minerals such as cassiterite, rutile, zircon, xenotime and monazite strongly resist physical and chemical weathering conditions. These minerals are residually concentrated, together with Ag-rich Au grains, in a near-surface silcrete (silicified collapsed breccias) body during supergene weathering of the Scuddles Cu-Zn VHMS deposits in the Golden Grove district, Western Australia. The VHMS deposits are hosted in a volcanoclastic sequence dominated by dacite, rhyodacite and siltstone that weathered from the base to: (1) a supergene sulphide enrichment zone; (2) supergene carbonate -/sulphate-/phosphate-rich zone; (3) Fe oxide-rich zone; (4) leached kaolinitic saprolite that grades laterally into silcrete; and (5) mottled clays/ferruginous duricrust zone.

The silcrete body was formed in two stages: 1) intensive weathering by strongly acidic and highly saline (halogen-rich) fluids generated by oxidation of sulphides. These fluids caused dissolution of clays and labile minerals, followed by collapse/surface reduction, residual concentration of resistate minerals and leaching of alkali and alkaline earth elements. However, sulphides such as pyrite, chalcopyrite, sphalerite, galena and argentite are preserved as inclusions in cassiterite, rutile and quartz. 2) Strong reactions between the acidic fluids and the residual components led to intensive alteration of cassiterite, rutile, zircon, xenotime, monazite and Au-Ag alloy and cements of complex mineral paragenesis and variable chemical compositions were formed. Initially, a Ag halide cement hosting microcrystalline, spongy Au aggregates in cavities and fractures was formed. Gold (up to 35 ppm) and Ag (up to 1100 ppm) are probably derived from leaching of the primary Au-Ag alloys and remobilization by a halogen-rich solution sourced directly from the VHMS mineralization. The precipitation of Ag halides and Au in the silcrete may have taken place in response to a rise in pH and/or dilution of the halide concentration. This is evidenced by a weak reaction between Ag halides and the residual components. Textural relationships showed that the Ag halide cement and cassiterite, rutile, zircon, xenotime, monazite and quartz have been severely corroded and dissolved probably by another phase of more vigorous reaction with a strongly acidic, Ti-rich solution. This solution is suggested to be formed by dissolution of primary rutile and resulted in an initial precipitation of anatase in cavities. By further reaction of the Ti-rich solution with cassiterite, monazite, xenotime, muscovite, quartz and the preexisting Ag halides, chemically heterogeneous, very fine-grained cements of nanocrystalline minerals were formed. EDX showed that these cements consist of Si, Ti and Zr, corresponding to a mixture of quartz, anatase and zircon and/or Bi-, Pb-, P-, Ag-, Sb-, Ti-rich aluminosilicates that were probably formed by release of trace elements from the sulphide inclusions in rutile, cassiterite and Ag halides. Alteration of cassiterite, rutile, zircon, xenotime and monazite during weathering of VHMS mineralisation is considered exceptional and requires strongly acidic and highly saline fluids. The

anomalous concentration of Au and Ag in the silcrete body makes it a preferred sampling medium in regolith for targeting VHMS mineralisation.



Figure 1. A) A cassiterite (cst) grain replaced by anatase (ant). **B&C)** Cassiterite and quartz (qtz) grains (photo B) and Ag halide cement hosting Au (photo C) are corroded by Pb-, Bi-, Ag-, P-, Sb- and Ti-rich aluminosilicates.