CASSITERITE AND RUTILE AS INDICATOR MINERALS FOR EXPLORING THE VMS SYSTEM

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SUMMARY

Cassiterite and rutile strongly resist physical and chemical weathering and can be used as indicator minerals for mineralisation. These minerals are residually concentrated in a near-surface silcrete duricrust capping a deeply weathered profile developed over the Scuddles Cu-Zn-Pb VMS deposit, Golden Grove, Western Australia. These minerals were extracted by panning of rock chips from Reverse Circulation drill holes and studied by optical, scanning electron microscopy and mapped and analysed by electron probe.

The formation of silcrete involved destruction of all labile minerals, removal of clays and leaching of alkali, alkaline earth and transition (e.g. Fe, Mn, V, Ni, Co, Cu, Zn) elements. This is followed by residual concentration of high field strength elements in resistate minerals and silica cementation. The main driving force in the formation of silcrete is the oxidation of massive sulphides generating strongly acidic and highly saline fluids. Under these conditions, silica was probably transported as either silicic acid from destabilising aluminosilicates or as an aqueous sol under neutral to low pH conditions. In addition, Au and Ag were remobilised from the massive sulphide mineralisation as a halide complex.

Cassiterite, rutile and quartz in silcrete contain inclusions of pyrite, chalcopyrite, sphalerite, galena and argentite identical to those in the underlying VMS. Thus, they are considered as indicator minerals for VMS exploration. Bioturbation and organic acids produced by decay of plants from the upper lateritic profile remobilised clays downward as colloid, recycled Au from Ag halides and attacked resistant heavy minerals. Oxidation of sulphide inclusions in cassiterite, rutile and quartz intensely corroded these minerals and liberated trace elements (i.e., Sn, Ti, Pb, Sb, Bi, Hg, Se, Ge, W, Mo and Te) to form cements of complex chemical compositions. These cements and Au-Ag halides form a multi-element anomaly in silcrete delineating the underlying VMS deposits at Scuddles.

Key words: Weathering profile, resistate minerals, Golden Grove, Scuddles, Western Australia.

INTRODUCTION

Resistate indicator minerals have become an important tool for exploration, geological mapping and bedrock identification over the past two decades. They are now classified into suites for detecting a broad spectrum of ore deposits covered by recently deposited unconsolidated glacial sediments (e.g., McClenaghan, 2005). Indicator minerals can also be a useful tool of exploration in deeply weathered lateritic terrains when combined with geochemical and geomorphological methods (e.g., Friedrich et al., 1992).

The extraction of indicator minerals form exploration sample media makes them sufficiently abundant for mineralogical and geochemical analyses. Indicator minerals are visually distinctive, able to survive physical and chemical weathering, erosion and/or clastic transport. They are characterised by their high density (>2.8 S.G.) and silt or sand size (e.g., McClenaghan, 2005). Indicator minerals in sediments and soils can be used to detect larger halos than the mineralized target itself and the associated alteration.

The resistate indicator minerals are ultrastable and become residually enriched during weathering as a result of the chemical transformation of the rock-forming minerals. These minerals generally increases by a factor up to 10, depending on rock type and intensity of weathering, from the least weathered saprolite horizons at the bottom of the profile to the intensely weathered horizons at the top as a result of progressive residual enrichment (e.g., Friedrich et al., 1992).

The present contribution reports the presence of residually concentrated cassiterite and rutile, together with minor zircon, xenotime, monazite, gahnite, magnetite and chromite, in a near-surface silcrete duricrust capping a deeply weathered profile over the Scuddles Cu-Zn-Pb VMS deposit, Golden Grove, Western Australia. These minerals were identified by optical and scanning electron microscopy and mapped for their elemental composition by electron probe. Cassiterite and rutile are the most common heavy minerals in silcrete and they can be used effectively as indicators for the VMS mineralisation at Scuddles. Although these minerals are ultrastable and strongly resist physical and chemical weathering, they show evidence of exceptional alteration and intensive corrosion in the Scuddles silcrete. Thus, trace and pathfinder elements from these minerals are released during weathering forming secondary cement and multi-element anomaly in silcrete over the VMS deposits.

GOLDEN GROVE BACKGROUND GEOLOGY

Golden Grove is approximately 225 km due east of the coastal port town of Geraldton and 375 km north-northeast of Perth, Western Australia (Fig. 1). The Gossan Hill and Scuddles VHMS deposits occur on the north-east flank of the Warriedar fold belt within the Golden Grove domain of the Murchison province (e.g., Ashley et al., 1988). Golden Grove is made up of two underground and three open pit VHMS deposits situated within the Archaean Yalgoo-Singleton Greenstone Belt, Murchison Province in the western Yilgarn Craton of Western Australia (Fig. 1). Host rocks to the Cu, Zn (Pb) +/- Au-Ag ores are dominated by weakly metamorphosed

rhyodacitic tuffaceous volcaniclastic sequences that were intruded by a series of mafic to felsic volcanic sills and dykes (Ashley et al., 1988).

The underground mines at Golden Grove are approximately 4 km apart (Gossan Hill to the south and Scuddles to the north) and have been the focus of mine production since operations commenced in 1991. Gossan Hill total resources were 10.7 Mt at 7.1% Zn, 2.4% Cu, 0.7% Pb, 1.4 g/t Au and 61 g/t Ag, and at Scuddles were 3.73 Mt at 4% Zn, 2.7% Cu, 0.28% Pb, 0.58g/t Au and 36 g/t Ag (MMG Golden Grove 2016). Since 2013, additional production has included shallow open pit operations, comprising one copper oxide/transitional pit and two smaller gossan-hosted gold pits. These open pits are situated directly above the Gossan Hill underground deposit. Oxide Au resources at Gossan Hill is 0.46 Mt at 3.3 g/t Au and 70 g/t Ag (MMG Golden Grove 2016). The gold bearing silcrete body from this study is alternatively located within the near surface region above the Scuddles underground VHMS deposit. The Scuddles gold open pit was constructed in 2016 with total resources of 0.24 Mt at 2.7 g/t Au and 58 g/t Ag (MMG Golden Grove 2016).

Figure 1: A map showing the Yilgarn Craton tectonic domains and the Warriedar fold belt within the Golden Grove domain of the Murchison province

SAMPLING AND METHODS

Sample selection and description

Field observations were undertaken by logging and description of 108 reverse circulation (RC) and 12 diamond drill holes cut through and surround the silcrete body in Scuddles mine area. Out of the 108 RC drill holes, regolith profiles of twenty-two drill holes were subdivided into five units and correlated laterally. Textures and fabrics of each regolith unit are described from polished slabs. Thirty-one core samples were selected from the diamond drill holes SC125, SC126 and SC128 and prepared for polished thin sections and petrographic examinations. Seventy-one samples of rock chips are collected from SCRC012 drill hole and the supergene Cu oxide enrichment zone from SCRC015 drill hole for X-ray diffraction and chemical analyses. Rock chips of RC drill holes were sieved and panning was used to recover indicator minerals and gold in the field.

Mineralogical and geochemical analyses

Polished thin sections from each regolith unit were examined using a Zeiss Axio lmager polarising microscope to determine petrography. Polished, carbon-coated thin sections of bulk samples and mineral concentrates were studied using a Zeiss Ultra-Plus field emission gun scanning electron microscope with an attached Bruker X-Flash energy-dispersive x-ray detector for elemental analyses at the Australian Resources Research Centre (ARRC), CSIRO, Perth, Australia. An accelerating voltage of 20 kV with a beam current of 3 nA was used. SEM observations were made in back-scattered electron (BSE) mode for element maps and secondary electron mode for morphological characteristics of Au, Ag halides and cassiterite.

Seventy-one rock chip samples were collected from SCRC012 and SCRC015 drill holes and analysed using X-ray fluorescence (XRF) for ten major elements and inductively coupled plasma-mass spectroscopy and atomic emission spectroscopy (ICP-MS/AES) for fifty-eight trace elements at ALS Laboratories, Perth, Western Australia. Thirty-one trace elements including rare earth elements (REEs: La-Lu and Y), high field strength elements (HFSEs: Zr, Hf, Nb, Ta, Th, U, W and Sn), large ion lithophile elements (LILEs: Ba, Cs, Sr and Rb), Ga, Ge, V, Cr and Ga were analysed by ICP-MS after fusion with Li metaborate/lithium tetraborate flux at 1025°C. This method was particularly used to address potential problems stemming from incomplete dissolution of refractory minerals. Silver, Cd, Co, Cu, Li, Mo, Ni, Pb, Sc and Zn) were analysed by digestion in a mixture of four-acids ($HClO_4$, HNO_3, HF and HCl) and analysed by ICP-AES. Arsenic, Bi, Hg, In, Re, Sb, Se, Te, Tl and Sc were analysed by digestion with aqua regia and analysed by ICP-MS.

The total carbon (C%) content was obtained by combustion of samples in a LECO induction furnace. The total sulphur (S%) was analysed using a Leco sulphur analyzer and measured by an IR detection system. Gold was analysed by fire assay fusion, whereas halogens (Cl, I and Br) are analysed by instrumental neutron activation analysis at Becquerel laboratories Inc., Ontario, Canada. Fluorine is analysed by KOH fusion and ion chromatography at ALS, Vancouver, Canada. Chemical compositions of galena, sphalerite, pyrite, pyrrhotite and chalcopyrite were analysed in carbon-coated polished thin sections with a JEOL 8530F Electron microprobe at the Centre for Microscopy, Characterisation and Analysis (University of Western Australia). Operating conditions were 20 kV accelerating voltage, spot size 5 μm and 50 nA emission current.

RESULTS

Stratigraphy of the weathering profile

At Scuddles, a supergene/lateritic weathering profile varies from 50 to 100 m in thickness and is developed on an Archaean siliceous/cherty volcano-sedimentary sequence. From the base, the ideal supergene/lateritic weathering profile (Fig. 2) is subdivided into 5 main zones: 1) a supergene sulphide enrichment zone; 2) an oxidate zone of supergene Cu-Zn-Pb oxides, sulphates, carbonates, phosphates, silicates, halides, and native Ag and Cu; 3) ferruginous saprolite (Fe oxide-rich zone; 20-50 m thick), 4) a bleached zone, 20-50 m thick, dominated by a kaolinitic saprolite that changes laterally into a silcrete body close to the west of the VHMS deposits at Scuddles; and 5) a ferruginous zone, up to 10 m thick, consisting of mottled saprolite and pisolitic duricrust. The weathering profile is overlain by 10-50 cm colluvium/alluvium of reworked lateritic gravel (Fig. 2).
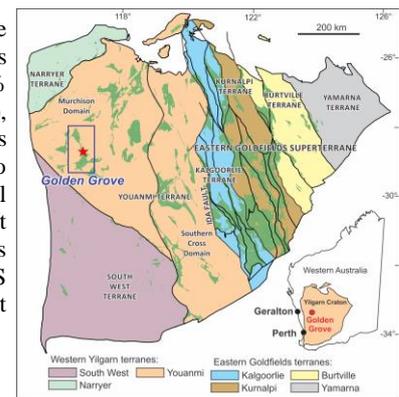
The bleached zone, 25-70 m in thickness, consists of massive, off-white, highly porous kaolinitic saprolite that becomes progressively silicified and changes laterally, with a sharp contact, into a silcrete body, approximately 60 m wide and 265 m long (Fig. 2A).

Field observations from open pit mining showed that the formation of silcrete is lithologically-controlled, being developed on the thinly bedded sandstones of the GG6 member of the Golden Grove Formation (Fig 2A). Conversely, kaolinitic saprolite is developed on dacite and rhyodacite of the SC2 member of the Scuddles Formation. The silcrete body is located to the south of the Scuddles VHMS deposits which is dissected by a set of parallel to subparallel, NNE-SSW trending faults. It is internally massive and consists of microcrystalline quartz, however; silcrete layers in few drill holes consist of silicified breccias of very poorly sorted, matrix-supported angular rock fragments with a vitreous appearance and inherited laminated sedimentary textures that are cemented by white, microcrystalline siliceous cement.

Mineralogically, silcrete consists of >90% quartz with <10% resistate heavy minerals (i.e., cassiterite, rutile, zircon, xenotime, monazite, gahnite ($ZnAl_2O_4$), magnetite and chromite) and secondary supergene Au-Ag halides (Fig. 3). Element maps and EDX analyses of mineral concentrates showed that Ag halide grains show compositional zoning and consist of a mixture of chlorargyrite (AgCl) and bromargyrite (AgBr) collectively known as "embolite" after Boyle (1997) and iodargyrite (AgI) which is the main host for Au (Fig. 4A). Residual native Ag and Au-Ag electrum grains are also identified in the silcrete. When present, native Ag grains are altered to Ag halides and the primary Au-Ag electrum is altered along rims to Ag-depleted Au leaving an inner Ag-rich core. However, BSE images and EDX analyses showed that more than 99 % of Au grains in the silcrete are Ag-poor and form nano- to microcrystalline colloform, spongy and dendritic-shaped aggregates and nuggets. Conversely, in the supergene sulphide and oxide-enriched zones, Au occurs as primary, Au-Ag grains in its crystallisation position associated with malachite and chalcocite after complete weathering of chalcopyrite. Cassiterite and rutile are the most abundant minerals in the panned concentrates and they contain inclusions of base metal sulphides (Fig. 3B, C), quartz and xenotime inclusions similar to those in host rocks and the supergene sulphide and oxide enrichment zones. In silcrete, cassiterite and rutile are intensely corroded with their mineral inclusions being partially to completely oxidised. As a result, new cement of poorly to nanocrystalline anatase, Ti-bearing aluminosilicates and Ti-, Pb-, Bi-, Sb-bearing phase were formed (Fig. 4B, C). Gold is also recycled during corrosion of Ag halides and is intimately associated with variably crystalline kaolinite in dissolution cracks and voids within Ag halides (Fig. 4D).

Geochemistry of silcrete

Silcrete consists of >90% SiO_2 with depletion in Al_2O_3 (<5wt.%), Fe_2O_3 (<5wt.%) and the alkali and alkaline earth elements including K_2O, Rb, Cs, Ba, Sr and Tl. The high field strength elements (HFSE) such as Ti (up to 2wt.%), Zr, Hf, Nb, Ta, Y, U, Sn and rare earth elements (REEs) are residually concentrated in the silcrete.

Silcrete is characterised by a multi-element anomaly of Au (up to 35 ppm), Ag (up to 1030 ppm), halogens (Cl, Br, I), Sn, W, Pb, Bi, Hg, Sb, Se, Ge and Mo compared to the surrounding barren kaolinitic saprolite (Fig. 5). Electron probe microanalyses of sulphide inclusions in cassiterite and rutile have similar chemical composition to those in the VMS deposits. Sulphides include galena, sphalerite, pyrite and chalcopyrite. Bismuth, Sb and Ag
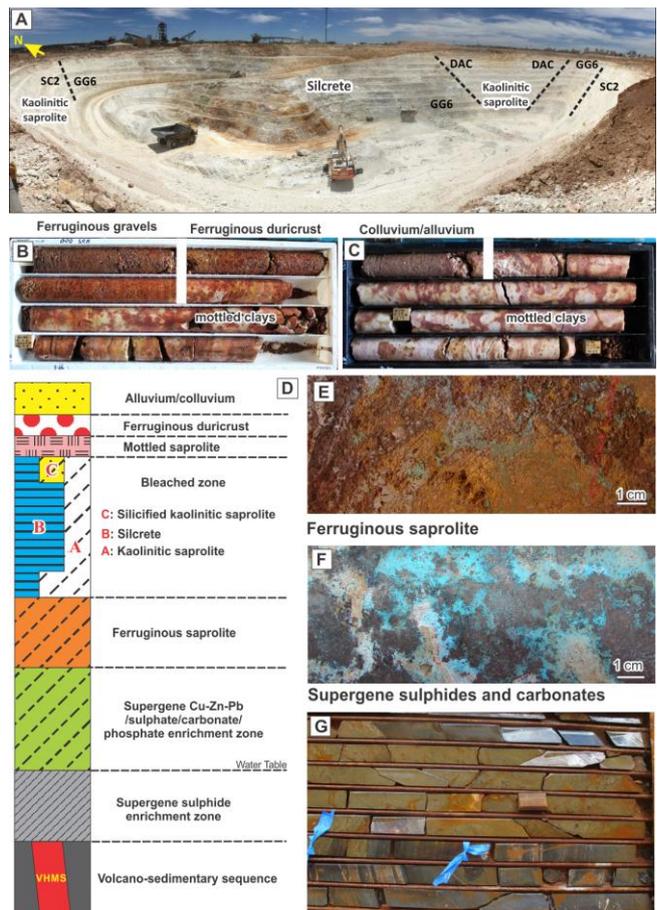

Figure 2: A) The Scuddles open mine pit shows silcrete with a sharp contact with the surrounding kaolinitic saprolite. **B&C)** A mottled saprolite overlain by ferruginous duricrust or colluvium/alluvium (C). Ideal stratigraphic column of the weathering profile at Scuddles. **E)** Ferruginous saprolite. **F)** Supergene sulphides (chalcocite) and carbonates (malachite). **G)** Massive primary Cu-Zn sulphides.
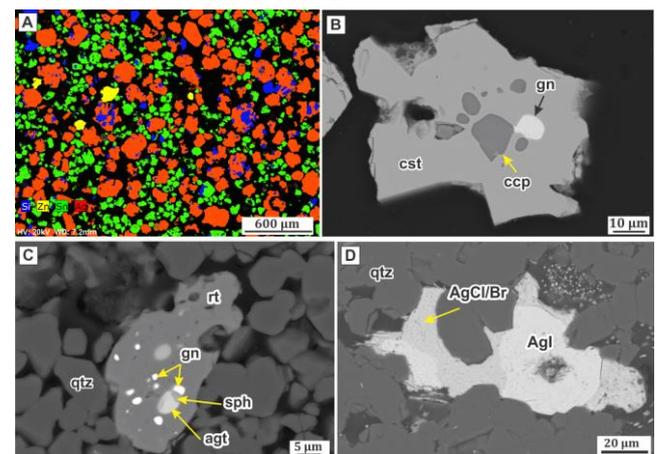

Figure 3: A) An element map of heavy mineral concentrates extracted by panning of rock chips showing cassiterite (green) and Ag halides (red) are the main minerals. Gahnite (yellow) and quartz (blue) are minor components. **B&C)** cassiterite (cst) and rutile (rt) with galena (gn), chalcopyrite (ccp), sphalerite (sph) and argentite (agt) inclusions. **D)** Silver halide cement in silcrete (embolite (AgCl/Br) and iodargyrite (AGI)).

are the main trace elements of galena, whereas Cd, Se, As and Mo are the main trace elements in chalcopyrite and sphalerite. Oxidation of sulphide inclusions, particularly galena creates Bi, Pb, Sb-rich cement that corrodes cassiterite and Ag halides.

CONCLUSIONS

The silcrete body capping the weathering profile over the Scuddles Cu-Zn-Pb deposit is a potential sampling medium for exploring blind VHMS systems in a felsic volcanic-sedimentary succession. It can be used as equivalent or alternative to gossan. Silcrete at Scuddles is similar to the silica-barite rocks capping weathering profiles over VMS deposits in the Arabo-Nubian Shield (Barrie et al., 2016).

The formation of silcrete at Scuddles involved three stages:

1. Oxidation of VMS and generation of strongly acidic condition that released silica from aluminosilicates and Au and Ag from VMS that precipitated as a halide complex by groundwater. Water table was possibly near-surface during mid to late Tertiary and the recitation of Au and Ag was facilitated by the fracture and fault systems.

2. Leaching of alkali and alkaline element and removal of labile minerals led to residual concentration of indicator minerals such as cassiterite and rutile which contain inclusions of Cu, Pb and Zn sulphides identical to those identified in the underlying VMS deposits.
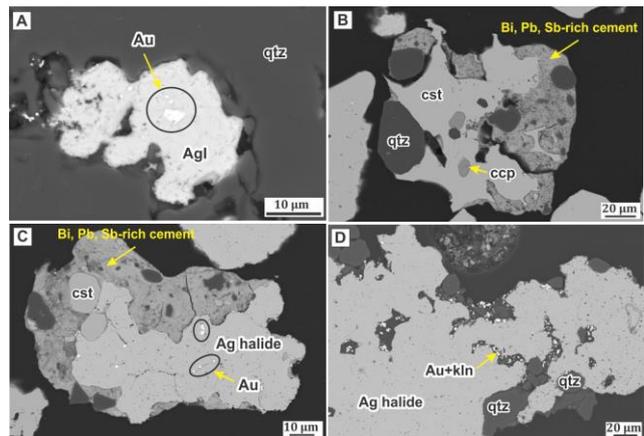

Figure 4: A) Silver iodide (AGI) containing Au. B) Cassiterite (cst) containing chalcopyrite (ccp) and corroded by Bi, Pb, Sb-rich cement. C) Silver halides and cassiterite (cst) and Au are corroded by Bi, Pb, Sb-rich cement. D) Gold and kaolinite (kln) fill dissolution cavities in Ag halide cement.
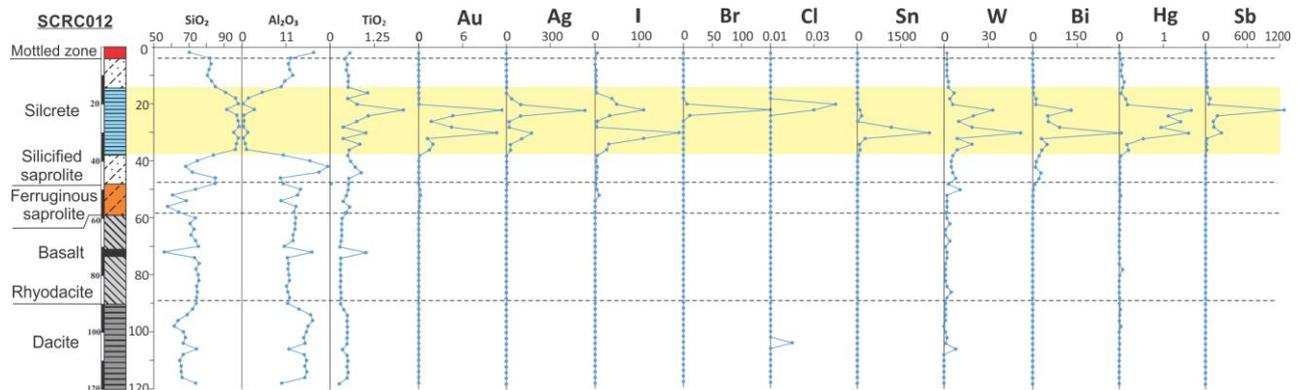
3. The association of Au with clays in dissolution cavities within Ag halides highlights the role of surface lateritic weathering in mobilising Au as organic/colloid complexes.

Figure 5: Vertical stratigraphy of weathering profile of drill hole SCRC012 with a bleached zone dominated by silcrete which rich in SiO_2, TiO_2, a multi-element association of Au, Ag, I, Br, Cl, Sn, W, Bi, Hg and Sb and depleted in Al_2O_3. The concentrations of Au, Ag, I, Br, Sn, W, Bi, Hg and Sb are in ppm.

ACKNOWLEDGMENTS

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