

Trace element signatures in U-W-Sn-Mo zoned hematite from the IOCG deposit at Olympic Dam, South Australia

Max R. Verdugo-Ihl, Cristiana L. Ciobanu, Nigel J. Cook, Liam Courtney-Davies
University of Adelaide, Australia

Kathy J. Ehrig
BHP Billiton Olympic Dam, Australia

Sarah Gilbert
University of Adelaide, Australia

Abstract. Hematite is the dominant gangue component of the Olympic Dam Cu-U-Au-Ag orebody, South Australia. A distinct oscillatory-zoned hematite, conspicuously rich in ‘granitophile’ elements (U, W, Sn, Mo) is recognized throughout the ~2 km vertical extent of deposit zonation, from deep pyrite-chalcocite to shallow bornite-chalcocite orezones, as well as throughout the entire NW-SE strike of the orebody. Concentrations of granitophile elements are retained, albeit at lower concentrations, in later replacement hematites. Comparison of trace element datasets for U-W-Sn-Mo-zoned hematite relative to replacement hematite provides evidence for localized fluid-mineral reaction and for the importance of reactions coupling dissolution with reprecipitation rates in driving element exchange. The oscillatory-zoned hematite is analogous to that previously dated by LA-ICP-MS, confirming that this generation of hematite was formed at ~1.6 Ga during the onset of the IOCG mineralising system. Such ‘granitophile’-rich hematite may be common in other IOCG deposits, and typifies precipitation from fluids rich in these elements during the main hydrothermal stages. Lack of evidence for this type elsewhere is most likely attributable to advanced overprinting in which such signatures are largely obliterated.

1 Introduction

Inherent to all iron-oxide copper gold (IOCG) deposits is the abundance of Fe-oxides as hematite (α -Fe₂O₃) and/or magnetite (Fe₃O₄). The increasing volume of published trace/minor element data for minerals from hydrothermal ores (Cook et al. 2016 and references therein) include studies of Fe-oxides for fingerprinting mineral deposits of different types (e.g. Dupuis and Beaudoin 2011). Trace element signatures of magnetite from end-member IOCG deposits *sensu lato* such as Kiruna (Sweden) and El Laco (Chile) have been obtained to support debates around their magmatic versus hydrothermal origins (Dare et al. 2015; Knipping et al. 2015). In contrast, trace elements in Fe-oxides from *sensu stricto* IOCG-systems, and specifically hematite, have not been studied in detail despite being the main products of alteration closely associated with mineralising processes. Among the exceptions is hematite from the IOCG deposit at Olympic Dam (OD), South Australia (S.A.), which was found to incorporate a wide range of trace elements, including HFSE, REE+Y (REY) and is particularly rich in U, W, Sn, and Mo (hereafter

‘granitophile’ elements) (Ciobanu et al. 2013; 2015; Cook et al. 2016). Incorporation of U and its decay products within grains showing oscillatory zonation patterns facilitates its use as a mineral geochronometer for directly dating hydrothermal ore-forming processes in IOCG deposits from S.A. and elsewhere (Ciobanu et al. 2013; Courtney-Davies et al. 2016). Hematite from OD shows incredible textural diversity including pseudomorphic replacement of pre-existing minerals and/or rock fragments, overgrowths of hematite with distinct trace/minor element signatures, as well as cycles of (inter)conversion with magnetite, all of which is mirrored by a complexity of preserved trace element signatures (Ciobanu et al. 2013; 2015; Cook et al. 2016). Hence, studies of hematite signatures and their variation can offer insights into the processes responsible for the genesis and overprinting of IOCG-deposits, as well as providing a temporal context for regional metallogenic events.

2 Geological background

Olympic Dam is a giant, Cu-U-Au-Ag deposit (10,400 Mt @ 0.77 % Cu, 250 ppm U₃O₈, 1 ppm Ag and 0.32 ppm Au; BHP Billiton 2016) located on the eastern margin of the Gawler Craton. It belongs to the Olympic Cu-Au Province (e.g. Skirrow et al. 2007) in which IOCG mineralisation is associated with ~1.6 Ga magmatism (Hiltaba Intrusive Suite; HIS and Gawler Range Volcanics, GRV), although ongoing work at OD shows the importance of subsequent overprinting events to account for the spectacular metal endowment of the deposit. The deposit is hosted within the Olympic Dam Breccia Complex (ODBC), which is confined to the Roxby Downs Granite (RDG; Fig. 1), a HIS granitoid. Latest, high-precision U-Pb dating of magmatic and hydrothermal zircon in RDG and ODBC shows that brecciation and hydrothermal alteration (at least the early stage) is coeval with RDG crystallisation at ~1595 Ma (e.g. Jagodzinski 2005 and unpublished data). U-Pb geochronology of oscillatory-zoned hematite from two locations in the deposit shows overlaps with the zircon ages (Ciobanu et al. 2013; Courtney-Davies et al. 2016).

The RDG displays a gradational continuum from altered, through fractured to brecciated lithologies, associated with an increase in Fe-metasomatism and

multiple episodes of brecciation and displacement. OD is mineralogically zoned at the deposit scale, characterized by an inwards-, roughly concentric and quasi-continuous Cu(-Fe)-sulphide zonation that spans vertically and horizontally from pyrite-chalcocopyrite (Py-Cp) through chalcocopyrite-bornite (Cp-Bn) to bornite-chalcocite (Bn-Cc) dominated assemblages (Ehrig et al. 2012), a pattern considered to represent a primary feature of hypogene ore precipitation (Ciobanu et al. 2017). Hematite is the main Fe-oxide within the orebody, even though at depth and along the deposit margins magnetite is also present and shows various, complex replacement textures with hematite (Ehrig et al. 2012; Ciobanu et al. 2015).

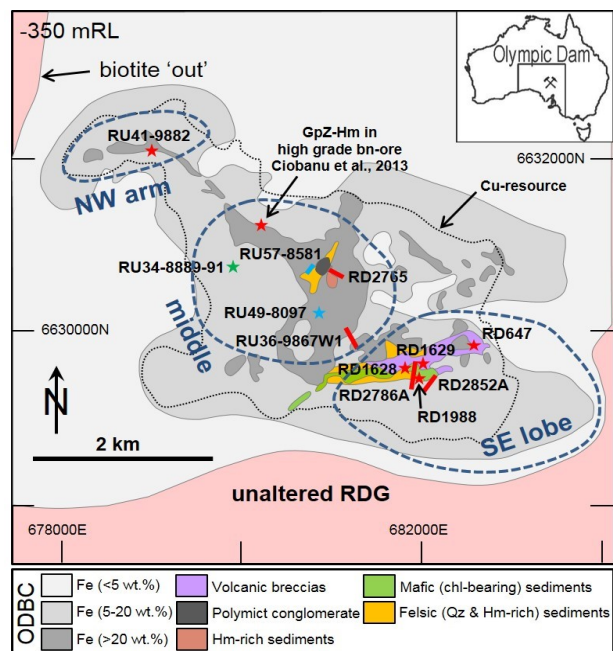


Figure 1. Sketch map of OD showing sampled drillholes. Different categories of hematite (Hm) as follows: red: oscillatory-zoned (GpZ-Hm); green: carbonate replacement (RC-Hm); blue: replacement, undifferentiated. After Ehrig et al. (2012).

3 Sampling approach and methodology

The present study is undertaken on ~50 samples collected from drillholes intersecting different parts of the OD orebody along its ~6 km strike and throughout the entire ~2 km vertical zonation in the SE lobe. These were selected to represent the lithological complexity, e.g. (i) presence of blocks of sediments and brecciated felsic volcanics in the SE lobe; (ii) sediments in the ‘barren core’ from the middle part of the deposit (>20 wt.% Fe); (iii) high-grade chalcocite and bornite ores from the middle (RU34-8889-8891) and NW arm (RU41-9882) of the deposit, respectively. Polished blocks were analysed using reflected light microscopy, scanning electron microscopy in back-scatter electron mode (BSE), electron probe microanalysis (EPMA) and laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) for trace elements using BHVO-2G and NIST610 as reference

standards. All instrumentation is housed at Adelaide Microscopy, The University of Adelaide.

4 Results

Oscillatory zonation in hematite with respect to concentrations of U+W+Sn+Mo is recognised throughout most samples from across the deposit area, including from the shallow Bn-Cc orezone in the SE lobe, in hematite-richest breccias from the ‘barren core’, and in high-grade bornite ores from the NW arm of the deposit (Fig. 1). This type of hematite (GpZ-Hm; Fig. 2) occurs as single grains of variable size (tens to hundreds of μm), and more rarely as lamellar aggregates. Remarkable concentrations of granitophile elements, routinely measured by LA-ICP-MS (see below), are confirmed by EPMA analysis (e.g. up to wt.% levels of UO_3 and WO_3 ; Fig. 2a). Overprinting of such hematite is recognised, including marginal corrosion and replacement, brecciation, porosity, fields of discrete inclusions (U-, W-, or REE-minerals), as well as cross-cutting veinlets. In most cases, GpZ-Hm grains display varying degrees of pseudomorphic replacement, leading to overgrowths of hematite poor in granitophile elements (Fig. 2a). There are, however, also grains with a clast-like morphology, little apparent replacement, and excellent preservation of compositional zoning (Fig. 2b). These are specific to samples from the ‘barren core’, or from entrapped sediments from the SE lobe.

SE lobe; Bn-Cc zone
(RD2852A; sample RX6583)

Middle; Bn-Cp zone
(RD2765; sample MV101)

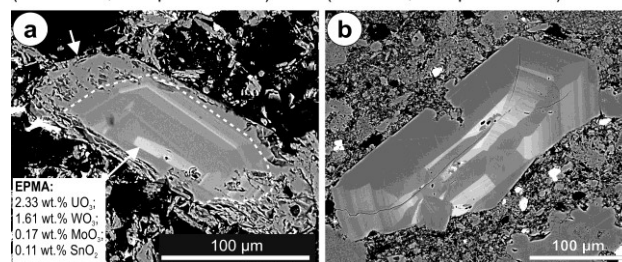


Figure 2. BSE images showing oscillatory-zoned hematite and styles of overprinting.

Although the abundance of GpZ-Hm is higher in samples analysed here from the SE lobe, this type of hematite is relatively minor on the deposit-scale (~10 vol.% within a given sample) relative to other hematite types. These include porous aggregates, and fine-grained hematite filling single grains of other minerals (feldspars in RDG or volcanic rocks), other rock fragments, or the dominant fine-grained hematite that makes up the matrix for breccias, notably in samples from the ‘barren core’ of the deposit. One type of replacement hematite is defined by fine aggregates of hematite filling coarser lamellae (mm-size) arranged within an overall rhombic outline (RC-Hm). The pre-existing mineral may have been a carbonate. Importantly, such aggregates host abundant chalcocite and define high-grade chalcocite-only ores in the middle part of the deposit.

Trace element data for zoned hematite show variation with respect to REY, HFSE (particularly Nb and V), as well as in the relative proportions of the granitophile elements, e.g. U vs. W+Sn+Mo (Fig. 3). Concentrations of U and W can both reach up to several wt.%; in some cases, hematite grains rich in U and W co-exist in the same sample (e.g. in the Cp-Py zone at depth in the SE lobe). Sn and Mo concentrations are generally subordinate: up to hundreds of ppm (exceptionally thousands of ppm Sn in samples from the SE lobe). Such variation is, however, neither systematic with respect to location within the deposit nor throughout its vertical extent. Replacement hematite, particularly in samples from the middle part of the deposit (included here for comparison) can also be relatively rich in granitophile elements, albeit 1-2 orders of magnitude lower than in GpZ-Hm (Fig. 3). There is an apparent decrease in the U content of hematite from SE to NW. GpZ-Hm in samples from the SE lobe and ‘barren core’ appear the poorest in HFSE relative to other types.

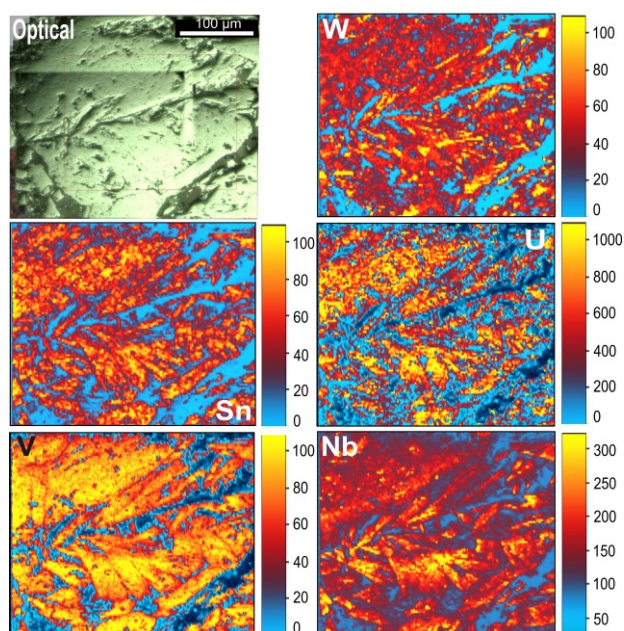


Figure 3. LA-ICP-MS maps of carbonate replacement hematite (see text for further detail). Scales in counts-per-second $\times 10^3$.

The relatively homogenous distribution of granitophile elements and HFSE in the RC-Hm type (Fig. 3) seems to map out the coarse lamellae rather than fine-grained nature of the hematite filling. RC-Hm also stands out by having the highest, consistent Nb+V concentrations (Fig. 4c). In contrast, Σ REY concentrations display a relatively constant spread, with a wide range across several orders of magnitude, irrespective of hematite type (Fig. 4a).

Chondrite-normalised REY fractionation trends (Fig. 5) show that GpZ-Hm is, for the most part, poor in REY, but nevertheless displays a consistent pattern defined by relative LREE enrichment. Other REY trends, including flat to slightly concave profiles, are obtained from grains with higher- Σ REY throughout all categories of hematite. RC-Hm is an exception, however, and shows conspicuous,

concave, HREE-enriched trends throughout all analyses.

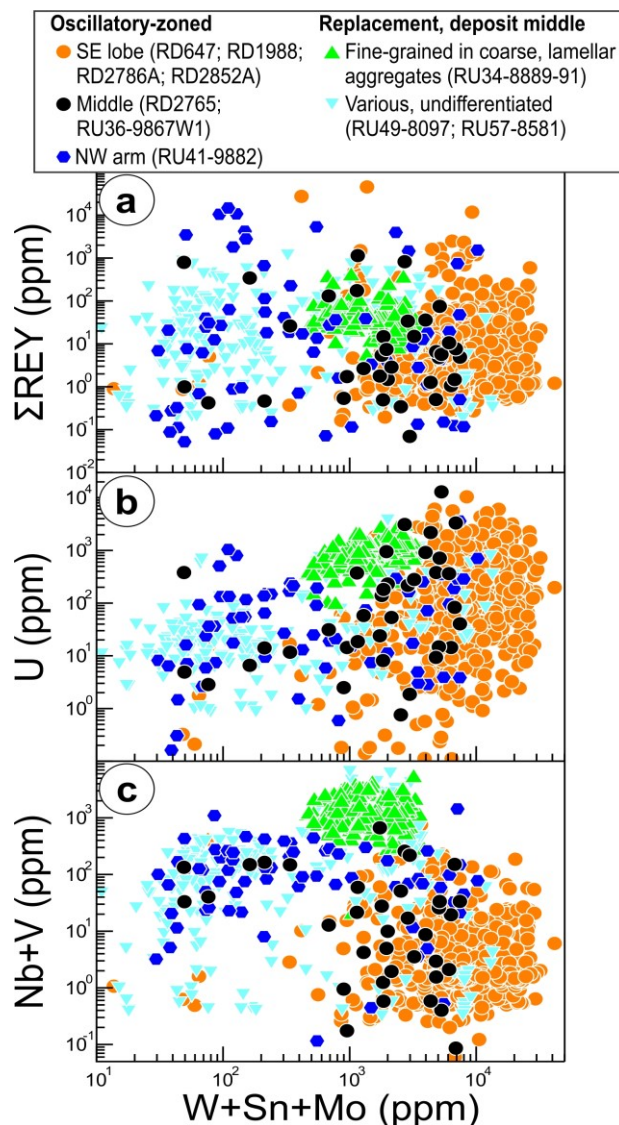


Figure 4. Scatter plots showing variation in trace element signatures of different types of hematite.

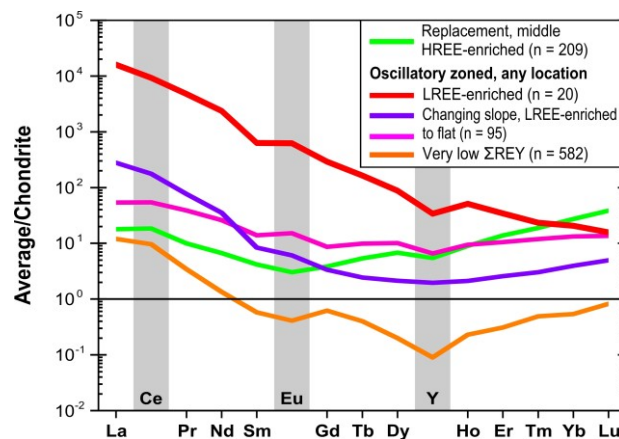


Figure 5. Chondrite normalized REY fractionation trends of different types of hematite.

5 Discussion and implications

‘Granitophile’-rich, oscillatory-zoned hematite previously reported from a couple of locations in the OD deposit (Ciobanu et al. 2013; 2015) is now recognised as present throughout the ~2 km vertical extent of deposit zonation (from deep Py-Cp to shallow Bn-Cc orezones), as well as throughout the entire NW-SE strike of the orebody. Such hematite has been also dated by LA-ICP-MS, using GJ-1 zircon as primary standard, and shows the same ~1.6 Ga age (Courtney-Davies et al. unpublished data), firmly indicating that this generation of hematite was formed during the onset of the IOCG mineralising system.

GpZ-Hm is a poor host for REY; higher ΣREY are mostly attributable to discrete inclusions of REE-minerals. The change in REY fractionation trend from LREE, dominant throughout most hematite types, to HREE-enriched, as documented here for RC-Hm, can be related to pH variation, as this parameter can strongly impact on REE solubility (Midgisov et al. 2016 and references therein). This is concordant with the interpretation of replacement of a pre-existing carbonate, strongly reactive to the acidic fluids leading to hydrolytic (sericite-hematite) alteration, and could also account for the formation of high-grade chalcocite ore. One of the interesting findings is the potential that HFSE may have for understanding primary deposit zonation, or the importance of different protoliths relative to granitophile-rich hydrothermal fluids.

The fact that concentrations of U and other granitophile elements are retained throughout all replacement hematites, some of which are clearly formed on behalf of the oscillatory-zoned type, suggests the importance of reactions coupling dissolution with reprecipitation rates (CDRR) throughout the ODBC, retaining such elements close to the sites of fluid-mineral interaction. The data for U-W-Sn-Mo-zoned hematite can be considered as evidence for localised fluid-mineral reaction throughout the ODBC and the importance of CDRR in driving element exchange as was shown for OD uraninite (Macmillan et al. 2016a, b) and for feldspar alteration in the RDG outside the orebody (Kontonikas-Charos et al. 2017).

Comparable compositional zonation with respect to W+U was shown for hematite from other deposits in the Olympic Cu-Au Province and from Carajas, Brazil (Courtney-Davies et al. 2016), irrelevant of host lithologies (granitoid hosted or not). It is likely that ‘granitophile’-rich hematite is one of the main types in IOCG deposits, and typifies precipitation from fluids rich in these elements during the main hydrothermal stages, assuming no other minerals that are normally good ‘granitophile’ carriers are formed at the same time (e.g. skarn calc-silicates). A lack of evidence for this type elsewhere is most likely attributable to advanced overprinting (obliteration of such signature), and/or poor mineralogical/petrological studies.

Acknowledgments

This is a contribution to the ‘FOX’ project, supported by

BHP Billiton Olympic Dam and South Australian Mining and Petroleum Services Centre of Excellence.

References

- BHP Billiton (2016) <http://www.bhpbilliton.com/~media/bhp/documents/investors/annual-reports/2016/bhpbillitonannualreport2016.pdf>.
- Ciobanu CL, Cook NJ, Ehrig K (2017) Ore minerals down to the nano-scale: Cu-(Fe)-sulphides from the Iron Oxide Copper Gold deposit at Olympic Dam, South Australia. *Ore Geol Rev* 81:1218-1235
- Ciobanu CL, Cook NJ, Ehrig K, Wade BP, Kamenetsky VS (2015) Trace element signatures in iron oxides from the Olympic IOCG deposit, South Australia. *Mineral Resources in a Sustainable World, 13th SGA Biennial Meeting 2015, Nancy*:1071-1074
- Ciobanu CL, Wade B, Cook NJ, Schmidt Mumm A, Giles D (2013) Uranium-bearing hematite from the Olympic Dam Cu-U-Au deposit, South Australia; a geochemical tracer and reconnaissance Pb-Pb geochronometer. *Precamb Res* 238:129-147
- Cook NJ, Ciobanu CL, George L, Zhu Z-Y, Wade BP, Ehrig K (2016) Trace element analysis of minerals in magmatic-hydrothermal ores by laser ablation inductively-coupled plasma mass spectrometry: approaches and opportunities. *Minerals* 6(4), 111; doi:10.3390/min6040111
- Courtney-Davies L, Zhu Z, Ciobanu CL, Wade BP, Cook NJ, Ehrig K, Cabral AR, Kennedy A (2016) Matrix-matched iron-oxide laser ablation ICP-MS U-Pb geochronology using mixed solution standards. *Minerals* 6(3), 85; doi:10.3390/min6030085
- Dare SAS, Barnes S-J, Beaudoin G (2015) Did the massive magnetite “lava flows” of El Laco (Chile) form by magmatic or hydrothermal processes? New constraints from magnetite composition by LA-ICP-MS. *Mineral Deposita* 50:607-617
- Dupuis C, Beaudoin G (2011) Discriminant diagrams for iron oxide trace element fingerprinting of mineral deposit types. *Mineral Deposita* 46:319-335
- Ehrig K, McPhie J, Kamenetsky V (2012) Geology and mineralogical zonation of the Olympic Dam Iron Oxide Cu-U-Au-Ag deposit, South Australia. *SEG Spec Publ* 16:237-267
- Jagodzinski EA (2005) Compilation of SHRIMP U-Pb Geochronological Data. Olympic Domain, Gawler Craton, South Australia, 2001–2003. *Geoscience Australia, Record* 2005/20
- Knipping JL, Bilenker LD, Simon AC, Reich M, Barra F, Deditius AP, Lundstrom C, Bindeman I, Munizaga R (2015) Giant Kiruna-type deposits form by efficient flotation of magmatic magnetite suspensions. *Geology* 43:591-594
- Kontonikas-Charos A, Ciobanu CL, Cook NJ, Ehrig K, Krneta S, Kamenetsky VS (2017) Feldspar evolution in the Roxby Downs Granite, host to Fe-oxide Cu-Au-(U) mineralisation at Olympic Dam, South Australia. *Ore Geol Rev* 80:838-859
- Macmillan E, Ciobanu CL, Ehrig K, Cook NJ, Pring A (2016a) Chemical zoning and lattice distortion: Uraninite from Olympic Dam, South Australia. *Amer Mineral* 101:2351-2354
- Macmillan E, Cook NJ, Ehrig E, Ciobanu CL, Pring A (2016b) Uraninite from the Olympic Dam IOCG-U-Ag deposit: linking textural and compositional variation to temporal evolution. *Amer Mineral* 101:1295-1320
- Migdisov A, Williams-Jones A, Brugger J, Caporuscio F (2016) Hydrothermal transport, deposition, and fractionation of the REE: Experimental data and thermodynamic calculations. *Chem Geol* 439:13-42
- Skirrow RG, Bastrakov E, Evgeniy N, Barovich K, Fraser GL, Creaser RA, Fanning CM, Raymond OL, Davidson GJ (2007) Timing of iron oxide Cu-Au-(U) hydrothermal activity and Nd isotope constraints on metal sources in the Gawler craton, South Australia. *Econ Geol* 102:1441-1470