The effect of titanite crystallisation on Eu and Ce anomalies in zircon and its implications for the assessment of porphyry Cu deposit fertility

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ABSTRACT

The redox sensitivity of Ce and Eu anomalies in zircon has been clearly demonstrated by experimental studies, and these may represent an important tool in the exploration for porphyry Cu deposits which are thought to be derived from oxidised magmas. These deposits are significant because they are the source of much of the world's copper and almost all of the molybdenum and rhenium, key elements in many modern technologies. However, Ce and Eu anomalies in zircon are also affected by the co-crystallisation of REE bearing phases, such as titanite. Here, we report the trace element chemistry of zircons from titanite-bearing intrusions associated with mineralisation at the world class Oyu Tolgoi porphyry Cu-Au deposit (Mongolia). Based on these data, we suggest that neither zircon Eu/Eu^* , nor $\text{Ce}^{4+}/\text{Ce}^{3+}$ are robust proxies for melt redox conditions, because they are both too strongly dependent on melt REE concentrations, which are usually poorly constrained and controlled by the crystallisation of titanite and other REE-bearing phases. In spite of this, Eu/Eu^* can

broadly distinguish between fertile and barren systems, so may still be an indicator of porphyry magma fertility, and a useful tool for exploration.

Keywords: zircon; titanite; porphyry Cu; redox; rare earth elements; economic geology

1 INTRODUCTION

1.1 Zircon as a tracer of magmatic redox state

Zircon (ZrSiO_4) has proved to be one of the most useful minerals in the study of igneous and metamorphic petrogenesis because of its robustness as a geochronometer, the sensitivity of certain trace element substitutions to intensive parameters (e.g. temperature; Ferry and Watson, 2007), and its resistance to high-temperature diffusive re-equilibration. One aspect of zircon chemistry which has received significant recent interest is the effect of magmatic redox conditions on the partitioning of the rare earth elements (REE) Ce and Eu. Uniquely among the REE, which are usually trivalent, Ce and Eu may also exist as Ce^{4+} and Eu^{2+} . Ce^{4+} is more compatible in zircon than other REE^{3+} cations (including Ce^{3+}) as it is able to directly substitute for Zr^{4+} , which has a similar ionic radius. For the same reasons, Eu^{3+} is more compatible in zircon than Eu^{2+} . Many accessory phases (including titanite) prefer to incorporate Ce^{3+} , but zircon may take Ce^{4+} in spite of the extremely low melt $\text{Ce}^{4+}/\Sigma\text{Ce}$ ratio (≈ 0.0001 Burnham and Berry, 2014) at typical melt $f\text{O}_2$ and zircon saturation temperatures (750°C ; at the fayalite-magnetite-quartz (FMQ) buffer). This results in a positive Ce anomaly in zircon (Fig. 1 a). In felsic melts under the same T - $f\text{O}_2$ conditions, the low $\text{Eu}^{3+}/\Sigma\text{Eu}$ ratio (≈ 0.5 ; Burnham et al., 2015) causes Eu to be less compatible in zircon and more compatible in plagioclase (which preferentially incorporates Eu^{2+}). For this reason, zircons commonly display negative Eu anomalies (Fig. 1 a). For practical purposes, these anomalies are quantified as the ratio between the measured Eu or Ce concentration and the concentration

that would be expected if these elements behaved in a similar manner to neighbouring REE which have similar ionic radii and the same charge (or, Ce^{*} and Eu^{*}), i.e. $Ce/Ce^{*} = Ce_N / (La_N \times Pr_N)^{0.5}$, and $Eu/Eu^{*} = Eu_N / (Sm_N \times Gd_N)^{0.5}$, where the subscript 'N' denotes chondrite-normalised values (Sun and McDonough, 1989). If no anomaly exists, both ratios will be unity. Although direct quantification of Ce^{4+}/Ce^{3+} or Eu^{3+}/Eu^{2+} ratios in zircon is analytically challenging (Dilles et al., 2015; Trail et al., 2015), Ballard et al. (2002) presented a method whereby these ratios can be calculated from the partitioning behaviour of other REE into zircon, estimated using the lattice strain model of Blundy and Wood (1994).

Experimental studies have shown that the magnitude of Ce and Eu anomalies varies as a function of melt fO_2 (e.g. Burnham and Berry, 2012; Trail et al., 2012), such that zircons from more oxidised systems have larger positive Ce anomalies, and smaller negative Eu anomalies (Fig. 1 a). This redox sensitivity is of particular relevance in the exploration for porphyry-type copper ore deposits, which form due to the sequestration of metals into S-, Cl-rich fluids, themselves exsolved from especially oxidised arc magmas (Sillitoe, 2010; Wilkinson, 2013). Zircons from magmatic rocks closely associated with mineralisation have been shown to have high values of Ce^{4+}/Ce^{3+} and Eu/Eu^{*} , with moderately elevated Ce/Ce^{*} (Fig. 2), ascribed by most authors to oxidising conditions at the time of crystallisation (e.g. Ballard et al., 2002; Liang et al., 2006; Zhang et al., 2013; Wang et al., 2013; Chelle-Michou et al., 2014; Cocker et al., 2015; Dilles et al., 2015; Shen et al., 2015; Lu et al., 2016). It was suggested by these authors that this characteristic may be used to distinguish magmatic systems with high and low ore-forming potential.

1.2 Impact on zircon chemistry of co-crystallising phases

Although clearly influenced by melt oxidation state, Ce and Eu anomalies in zircon may also be inherited from the melts from which it crystallises. These, in turn, are strongly

influenced by the prior or concurrent crystallisation of other REE-bearing phases, which may act to enrich or deplete the melt in Eu and Ce if these elements are more or less compatible than neighbouring REE. Ce anomalies in magmas, which are difficult to quantify (O'Neill, 2016), are extremely rare because Ce^{4+} occurs in vanishingly small quantities compared to Ce^{3+} under typical terrestrial redox conditions (Burnham and Berry, 2014), so very few phases preferentially partition Ce over La or Pr, and those that do (e.g. zircon) do not generally crystallise in significant enough quantities to generate Ce anomalies. As a result, Ce anomalies in zircon may be a more robust proxy for melt redox conditions. On the other hand, negative Eu anomalies are very common in igneous rocks because Eu^{2+} , which accounts for a significant fraction of total Eu under typical arc conditions (Burnham et al., 2015), is an order of magnitude more compatible in plagioclase feldspar than the other REE (e.g. Dunn and Sen, 1994), and plagioclase fractionation is an important process in the evolution of most magmas. Thus, the crystallisation of plagioclase prior to, or during, zircon saturation would deplete the melt in Eu, generating a negative Eu anomaly which would be inherited by zircons crystallising subsequently (Smythe and Brennan, 2015).

Although plagioclase is the most commonly cited example, many other major and accessory mineral phases also have Eu anomalies (Fig. 1 b). Titanite (CaTiSiO_5) is an accessory phase commonly associated with oxidised magmas (e.g. Wones, 1989) and contains high concentrations of REE. Calculated partition coefficient (K_D) values for REE in titanite are all >100 (Bachmann et al., 2005; Colombini et al., 2011), meaning that during fractional crystallisation titanite has the potential to strongly influence the REE concentration of the residual melt and consequently zircons in equilibrium with the melt (Marks et al., 2008; Claiborne et al., 2010; Chelle-Michou et al., 2014; Lee et al., 2017). In addition, titanite has the potential to affect the Eu anomaly of residual melts. The K_D of Eu in titanite is the mean of the K_D s for Eu^{2+} (similar to Sr^{2+} , which has $K_D = 0.37$) and Eu^{3+} ($K_D \sim 1000$;

Bachmann et al., 2005), weighted according to the abundance of these species, which varies as a function of fO_2 . As Eu^{2+} is common in terrestrial magmas, Eu is significantly less compatible in titanite than either Sm or Gd ($K_{DS} = 930$ and 855 respectively; Bachmann et al., 2005). This means that the crystallisation of titanite has the potential to impart a significant positive Eu anomaly on residual melts, which may be inherited by phases which crystallise subsequently (e.g. Buret et al., 2016; Lee et al., 2017). Critical to this is the timing of titanite crystallisation. If titanite crystallises near-solidus, and *in-situ* in the shallow crust (i.e. is not fractionated from the melt), then the REE concentrations and Eu anomalies in late-stage residual melts and co-crystallising phases (e.g. zircon) may be dramatically affected, but the composition of bulk magmas may be unaffected. Because titanite is a common accessory mineral in intrusive rocks associated with porphyry Cu deposits (Table 1), the effect of titanite crystallisation on zircon Eu anomalies has a great bearing on the usefulness of zircon as a mineral indicator of magma redox and thus porphyry Cu deposit ‘fertility’ (i.e. ore forming potential).

1.3 The Oyu Tolgoi porphyry Cu-Au deposits

Oyu Tolgoi is a cluster of Palaeozoic porphyry Cu deposits located in the southern Gobi Desert in Mongolia. The deposits are of Late Devonian age, and form a discontinuous belt of mineralisation approximately 22 km in length and ~5 km wide (Fig. 3 a). The total indicated and inferred resource of 3,093 Mt at 0.84 % wt. Cu and 0.33 g/t Au (0.6 wt. % Cu equivalent cut-off; Rio Tinto 2011, Annual Report), makes the district one of the largest centres of porphyry mineralisation in the world (Crane and Kavalieris, 2012). The highest-grade mineralisation is found at Hugo Dummett, the deepest ore body, with >2.5 wt. % Cu and 0.5 to 2 g/t Au, whereas the most southerly deposit, Heruga, has lower Cu (0.48 wt. %) and Au (0.48 g/t) grades (0.6 wt. % Cu equivalent cut-off; Rio Tinto 2011, Annual Report).

Both Heruga and Hugo Dummett share some common characteristics. In both cases, mineralisation is hosted primarily in a thick sequence of tholeiitic augite basalt, and is related to the emplacement of large-volume quartz monzodiorite intrusions (QMD; Fig. 3 b). These intrusions have been dated to between 368 to 372 Ma (Wainwright et al., 2011). Both deposits are overlain by a <500 m thick sequence of Late Devonian volcanic rocks of intermediate composition (Dvs; the 'Unmineralized Dacite Sequence' of Wainwright et al., 2011; Crane and Kavalieris, 2012) which, based on whole rock geochemistry, is considered to be co-magmatic with the QMD (Crane and Kavalieris, 2012). The Dvs has been dated to 369 ± 1 Ma. The upper portions of the Dvs in both deposits are cut by a district-scale thrust fault (the Contact Fault) which emplaces an allochthonous sequence of basaltic breccias interbedded with red and green siltstones, known as the Oyu Tolgoi Hanging Wall sequence (OTHS). This is poorly constrained but likely of late Devonian age. Both the autochthonous (mineralised) and allochthonous (unmineralised) rocks, as well as the Contact Fault, are cross-cut by narrow, anastomosing biotite granodiorite dykes (BiGd), which postdate mineralisation. U-Pb dating of the BiGd yields ages of 365.3 ± 1.5 Ma (Wainwright et al., 2011), constraining movement along the Contact Fault to the late Devonian. Whole rock data for the QMD, Dvs, and BiGd do not show significant Eu anomalies (Crane and Kavalieris, 2012).

Here, we present LA-ICP-MS trace element data of zircons from titanite-bearing intrusions and volcanic rocks from Oyu Tolgoi and assess the extent to which REE compositions of zircon, including the magnitude of the Eu and Ce anomalies, may be controlled by a titanite crystallisation. We conclude that without fully evaluating this effect in petrogenetic models, zircon may be compromised as a mineral indicator of porphyry Cu deposit fertility.

2. MATERIALS AND METHODS

2.1 Sample selection

Zircon grains were separated from 15 drill core rock samples: 13 from the QMD mineralised intrusion, and one each from the BiGd and the Dvs. Of the QMD samples, 7 were from Hugo Dummett and 6 were from Heruga. These rocks were selected to represent the variety of textural variants observed, as well as the range of whole rock geochemistry (see supplementary online material). All samples were collected in one field season, from August to September 2012.

2.2 Zircon separation

Although some zircons were observed in polished thin sections, there were too few grains of sufficient size to analyse by LA-ICP-MS ($>30\text{ }\mu\text{m}$ spot size) so zircon separation had to be conducted. Rock crushing and mineral separation were undertaken by Apatite to Zircon inc., Idaho, USA. Samples were crushed by Bico jaw crusher and then sieved through $300\text{ }\mu\text{m}$ mesh. Fine sands were then run through an IEC centrifuge with lithium metatungstate to remove grains with density $<2.8\text{ g cm}^{-3}$. Residual heavy components were dried and run through a Franz magnetic separator at varying current (0.5 A, 1.0 A, and 1.6 A). Zircons were separated from other minerals in the non-magnetic fraction by diiodomethane liquid. Once separated, zircons were picked and mounted in 25 mm diameter epoxy resin blocks that were then ground and polished to their midsections.

3. EXPERIMENTAL

All analytical work was carried out in the Imaging and Analysis Centre at the Natural History Museum, London, UK.

3.1 Scanning electron microscopy (SEM) and electron probe microanalysis (EPMA)

Zoning in zircon grains was characterised using SEM-cathodoluminescence (SEM-CL) imaging (Zeiss EVO SEM, beam current 3.0 ± 0.3 nA, accelerating voltage 20 kV). Silicon was determined by EPMA (Cameca SX100, beam current 40 nA, accelerating voltage 20 kV, beam size 10 μm) to check for homogeneity and potentially to use for internal standardisation of LA-ICP-MS data. However, given the narrow range of Si values obtained ($2\sigma = 0.2$ wt.% Si, $n = 111$), the mean value of 15.3 wt.% Si was used to calibrate laser ablation data. Zircon standard ST100 was also analysed by EPMA to test the calibration. Measured values of Si (mean = 15.2 ± 0.2 wt.%, 1σ , $n = 5$) were between -0.19 and +1.5 % of the certified value for this standard.

3.2 Laser ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS)

All zircon trace element analyses were conducted using an Agilent 7500cs quadrupole ICP-MS coupled to an ESI New Wave UP193FX laser ablation system. Zircons were analysed for the following isotope masses: ^{49}Ti , ^{89}Y , ^{93}Nb , ^{139}La , ^{140}Ce , ^{141}Pr , ^{145}Nd , ^{147}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{167}Er , ^{169}Tm , ^{173}Yb , ^{175}Lu , ^{177}Hf , ^{181}Ta , ^{208}Pb , ^{232}Th , and ^{238}U . Other isotopes were also analysed to assess potential interference and contamination (Fig. A.1). NIST-612 and BCR were used as the primary and secondary standards respectively. A fluence of 2.5 to 3.0 J cm^{-2} and a spot size of 30 μm were used. Measured values of the BCR calibrated with NIST-612 show a bias of $\pm 10\%$ for most elements (Fig. A.1). Full results can be found in the supplementary online material.

4. THEORY

4.1 Calculating zircon $\text{Ce}^{4+}/\text{Ce}^{3+}$ and Ce/Ce^*

Direct determination of the Ce oxidation state in zircon requires the use of synchrotron techniques, such as X-ray Absorption Near Edge Structure (XANES)

spectroscopy (Trail et al., 2015). However, it is theoretically possible to estimate zircon Ce^{4+}/Ce^{3+} from zircon chemistry (which can be determined by more widely available techniques) if the zircon/melt partitioning of other trivalent and tetravalent cations is well constrained. Ballard et al. (2002) presented a method for calculating Ce^{4+}/Ce^{3+} which relies on the premise that the total Ce is equal to the sum of Ce in its two oxidation states:

$$Ce_{\text{zircon}} = Ce_{\text{zircon}}^{3+} + Ce_{\text{zircon}}^{4+} \dots\dots\dots \text{Eq. 1}$$

$$Ce_{\text{melt}} = Ce_{\text{melt}}^{3+} + Ce_{\text{melt}}^{4+} \dots\dots\dots \text{Eq. 2}$$

Given that Ce^{3+} and Ce^{4+} have separate partition coefficients into zircon, these may be introduced into these equations which, when combined and rearranged, produce the following formula:

$$Ce^{4+}/Ce^{3+}_{\text{zircon}} = \frac{Ce_{\text{melt}} - \frac{Ce_{\text{zircon}}}{D_{\text{Ce}(3+)}^{\text{zircon/melt}}}}{\frac{Ce_{\text{zircon}}}{D_{\text{Ce}(4+)}^{\text{zircon/melt}}} - Ce_{\text{melt}}} \dots\dots\dots \text{Eq. 3}$$

where $D_{\text{Ce}(3+)}^{\text{zircon/melt}}$ and $D_{\text{Ce}(4+)}^{\text{zircon/melt}}$ are the partition coefficients for Ce^{3+} and Ce^{4+} respectively (Ballard et al., 2002). These coefficients can be estimated by assuming that the partitioning behaviours of Ce^{3+} and Ce^{4+} are intermediate between those of other 3+ and 4+ cations with larger and smaller ionic radii, i.e. REE for Ce^{3+} , and Hf⁴⁺, Zr⁴⁺, Th⁴⁺, and U⁴⁺ for Ce^{4+} . Using the lattice strain model (Blundy and Wood, 1994), plots of $\ln D_{\text{REE}}^{\text{zircon/melt}}$ vs. ionic radius for trivalent REE produce straight line arrays, from which the calculated value of D_{Ce} will deviate. By applying a trend line to these plots, and by interpolating between D_{La} and D_{Pr} , an estimate for $D_{\text{Ce}(3+)}$ may be determined. The same process may be used to interpolate a value for $D_{\text{Ce}(4+)}$ using D_{Hf} and D_{Th} (Ballard et al., 2002).

Some limitations have been identified with the zircon Ce^{4+}/Ce^{3+} method. Ballard et al. (2002) used REE whole rock data (REE_{WR}) as a proxy for melt chemistry when calculating

$D_{\text{REE}}^{\text{zircon/melt}}$. However, Dilles et al. (2015) concluded that C_{WR} may not be a good proxy for C_{melt} because the crystallisation (but not fractionation) of REE-bearing phases would cause a decrease in C_{melt} with no change in C_{WR} . They also noted that attempts to determine melt redox conditions from zircon $\text{Ce}^{4+}/\text{Ce}^{3+}$ using the redox-controlled experimental calibration of Trail et al. (2012) led to unrealistically high $f\text{O}_2$ for a range of magmatic rocks.

Calculating Ce/Ce^* is also problematic because La and Pr are typically present in very low concentrations in zircon (10s – 100s of ppb; Hoskin and Schaltegger, 2003) which are frequently below the limit of detection of LA-ICP-MS techniques. Furthermore, the presence of extremely small ($<1\ \mu\text{m}$) inclusions of LREE-enriched phases, such as apatite, monazite, and titanite, can yield unrealistically high La and Pr concentrations, which lead to falsely low estimates of Ce/Ce^* . This has led some authors to use a ratio between Ce and a more abundant element as a proxy for Ce enrichment or depletion (such as Ce/Nd ; e.g. Chelle-Michou et al., 2014). Here, we suggest an alternative formulation for Ce^* , using the same geometric relationship previously used, using the following relationship:

$$\text{Nd}_N = \sqrt{(\text{Ce}^* \times \text{Sm}_N)} \dots\dots\dots \text{Eq. 4}$$

Which, when rearranged, yields an expression for Ce^* :

$$\text{Ce}^* = \frac{(\text{Nd}_N)^2}{\text{Sm}_N} \dots\dots\dots \text{Eq. 5}$$

This will provide a slightly higher value of Ce^* than the conventional method (i.e. slightly lower Ce/Ce^*) because of the concave-downwards shape of zircon REE plots. However, this formulation is much more robust than the conventional method as it does not require the accurate determination of either La or Pr. Herein, this method is used to calculate Ce/Ce^* in zircon, including in literature data where possible.

4.2 Eu and Ce anomalies in zircons from barren and fertile systems

A literature summary of Eu/Eu^* , Ce/Ce^* , and $\text{Ce}^{4+}/\text{Ce}^{3+}$ values of zircons from a variety of porphyry ore deposits compared to barren or weakly mineralised systems is presented in Table 1 and Figure 2 (literature data sources available in supplementary online material). There is a large degree of overlap between barren and fertile systems in terms of both Eu/Eu^* (Fig. 2) and $\text{Ce}^{4+}/\text{Ce}^{3+}$ (Table 1) although mean values for these parameters are generally higher in fertile systems. Ce/Ce^* values show a much greater overlap between fertile and barren systems than Eu/Eu^* (Fig. 2 a)

Specific $\text{Ce}^{4+}/\text{Ce}^{3+}$ thresholds have been suggested as distinguishing criteria between fertile porphyry deposits and barren/weakly mineralised systems (e.g. 300, Ballard et al., 2002; 120, Liang et al., 2006; Shen et al., 2015). In these studies, and in others (e.g. Muñoz et al., 2012; Wang et al., 2013; Cocker et al., 2015), high $f\text{O}_2$ was suggested as the cause of high Eu/Eu^* and $\text{Ce}^{4+}/\text{Ce}^{3+}$.

In barren systems, primitive zircons (i.e. low Hf and Yb/Gd, high Th/U) have low Ce/Ce^* which increase with increasing Hf (a tracer of fractional crystallisation; Claiborne et al., 2010). By contrast, primitive zircons have high Eu/Eu^* (~0.7) which typically decreases with fractionation. The rate of Eu/Eu^* decrease is much lower in intrusions more closely related to mineralisation such that Eu/Eu^* is maintained to higher Hf. In some cases, there is even a slight increase in Eu/Eu^* (e.g. Dilles et al., 2015), although Eu/Eu^* values in excess of unity are rare. If both parameters were sensitive to redox conditions alone then they would both be expected to increase with increasing fractionation. The fact that this is not seen highlights the problem of interpreting melt redox from zircon chemistry alone.

5. RESULTS

5.1 Petrography

Zircon grains analysed in this study ranged in size from >30 μm to <500 μm . Although smaller grains were observed, these grains were not sufficiently large to analyse by LA-ICP-MS. Zoning is common to all zircons. Many show distinct cores and rims, separated by a dissolution boundary that truncates the zoning of the core (Fig. 4). Most rims have a brighter CL response than the cores. Oscillatory zoning with no truncated cores was also observed in some grains.

Titanite inclusions, ranging in size from <1 μm to 30 μm , are common in zircons from QMD samples from both Heruga and Hugo Dummett. Where they are present in zircons with distinct cores and rims, they are ubiquitously observed in the overgrowth rims (Fig. 4). Titanite may be found in the cores of zircons which display oscillatory zoning, although these examples are rarer. Inclusions of K-feldspar, albite, quartz, hornblende, apatite and magnetite are also present. These phases were all identified by EDS analysis (e.g. Fig. 4 c)

Despite its frequent occurrence as inclusions in zircon, titanite is a rare accessory phase in the groundmass of QMD samples and is absent in strongly altered rocks. These observations suggest that titanite was originally a common accessory phase in the QMD but was frequently destroyed by subsequent alteration, leaving behind only those grains included within robust zircon crystals.

5.2 Trace element geochemistry

In this section, the chemistry of zircons from Oyu Tolgoi are compared to zircons from typical granitic rocks derived from the literature (see supplementary online material). Zircons from QMD samples can be broadly divided into two chemically distinct groups, which are most easily distinguishable in terms of their Ta content. Frequency peaks occur at ~0.1 and ~0.4 ppm Ta; only 13 of 399 analyses show Ta concentrations between 0.2 and 0.25 ppm (Fig. 5 a,b). Zircons with Ta <0.2 have lower median Nb, Ta/Nb, and Ti-in-zircon

temperatures, as well as higher median Yb/Gd, Eu/Eu*, Ce/Ce*, and Ce^{4+}/Ce^{3+} than zircons with Ta values >0.2 ppm (Table 2). In zircons where overgrowth rims occur, the rims have lower Ta concentrations and higher Yb/Gd, Eu/Eu* than the cores (Fig. 4). Due to their geochemical and textural differences, QMD zircon analyses are discussed separately here as ‘low-Ta’ (<0.2 ppm Ta) and ‘high-Ta’ (>0.2 ppm Ta) groups. This bimodality is not observed in every studied rock, but is observed in approximately equal proportions in rocks from Heruga and Hugo Dummett. By contrast, the vast majority of BiGd and Dvs zircons fall in the high-Ta group so the distinction is primarily a feature of the ore-associated QMD.

Zircons of the high-Ta group from the QMD, BiGd and Dvs have Ta/Nb ratios which are typical of zircons from granitoids. However, the low-Ta group zircons have a significantly lower Ta/Nb ratio, with values never more than 0.34 (Fig. 5 b). Hf concentrations are predominantly lower in high-Ta zircons from the Dvs than either the QMD or BiGd, although all these groups are enriched in Hf with respect to the low-Ta group (Fig. 5 c).

Chondrite-normalised REE patterns of high-Ta QMD, BiGd, and Dvs zircons are similar to zircons from typical felsic arc rocks, with comparable $\sum REE$ and Yb/Gd values (Table 2). The moderately low Eu/Eu*, Ce/Ce*, and Ce^{4+}/Ce^{3+} ratios of the high-Ta zircons are also broadly typical of crustal zircons (Table 1). On the other hand, REE patterns of the low-Ta QMD group are systematically different to typical felsic arc zircons, in that they show strong MREE depletion, and concomitantly lower $\sum REE$ (Fig. 6.00 b). Eu/Eu* ratios are much higher than either the high-Ta group, or typical zircons from felsic arc rocks, with several values in excess of unity, and a maximum value of 1.52. Similarly, Ce^{4+}/Ce^{3+} ratios, calculated after Ballard et al. (2002) are exceptionally high, although Ce/Ce* values are only mildly elevated with respect to the high-Ta group. There is no clear difference between zircons from the QMD at Heruga or Hugo Dummett in terms of any of these parameters.

Estimates of crystallisation temperature were calculated using the Ti-in-zircon thermometer of Ferry and Watson (2007), using a TiO_2 activity of 0.7 and SiO_2 activity of 1, in line with previous studies (e.g. Claiborne et al., 2010; Dilles et al., 2015). In general, the low-Ta zircons yield lower crystallisation temperatures than the high-Ta group (Fig. 5 c; Table 2). We were unable to calculate zircon saturation temperatures from whole rock geochemistry because of pervasive hydrothermal alteration of the samples.

The geochemical bimodality described here was not observed by Wainwright et al. (2011) in their study of Oyu Tolgoi zircons, and most of the zircons they analysed fall into our high-Ta group. This may be because these authors preferentially analysed the larger cores which are predominantly high-Ta.

6. DISCUSSION

6.1 The origin of low-Ta zircons

The low-Ta zircons have geochemical features that are not commonly observed in crustal zircons. Values of <0.2 ppm Ta and <1 ppm Nb are rare in zircons from arc rocks and occur primarily in dolerite and lamproite (Belousova et al., 2002). The frequent occurrence of low-Ta rims on high-Ta cores separated by a dissolution boundary indicates that these grains record a change in magma chemistry and/or temperature which is important to understand in the context of their unusual occurrence in the system at Oyu Tolgoi. The exceptionally high Eu/Eu^* and $\text{Ce}^{4+}/\text{Ce}^{3+}$ values of the low-Ta group could be interpreted in terms of unusually oxidising conditions with attendant implications for porphyry deposit genesis.

A possible explanation for the observed textural and geochemical characteristics is an influx of a hot, mafic magma as this would decrease the bulk Hf, Ta and Nb and increase Eu/Eu^* . The concomitant increase in temperature would cause the melt to become undersaturated in Zr, causing any pre-existing zircons to resorb. However, temperature

estimates for the low-Ta group zircons are ~50°C lower than the cores (Table 2). Also, the low Ta/Nb ratio of the low-Ta group cannot be easily explained by an influx of mafic melt as this would have a higher Ta/Nb ratio (Stepanov and Hermann, 2013). For these reasons, this process, at least on its own, is considered unlikely to be the origin of the low-Ta zones and grains.

Alternatively, the depleted MREE, low Ta and Nb, and lower Ta/Nb of the low-Ta group may be explained by the co-crystallisation of titanite. Although Wu et al. (2003) demonstrated that MREE depletion may occur in highly fractionated granitoids due to the fractionation of apatite, allanite, and monazite, the latter two phases were not observed in the Oyu Tolgoi intrusions, which are intermediate in composition. MREE depletion may be more simply explained by titanite fractionation, as K_{Ds} for MREE in titanite are higher than LREE or HREE (Fig. 1 a). Ta and Nb are both strongly compatible in titanite and Ta is more compatible than Nb ($D_{Nb} = 109$, $D_{Ta} = 145$; Colombini et al., 2011). As a result, the crystallisation of titanite during late-stage petrogenesis would deplete the residual melt in Nb and Ta, and decrease the Ta/Nb ratio (Stepanov and Hermann, 2013; Stepanov et al., 2014). Ta and Nb values are unlikely to be influenced directly by melt redox conditions because both elements occur exclusively as Nb^{5+} and Ta^{5+} in terrestrial melts (Burnham et al., 2012) and Nb and Ta partitioning into zircon has been shown experimentally to be independent of fO_2 (Burnham and Berry, 2012). If partitioning of both elements into zircon is controlled by Henry's Law, zircons would be expected to inherit low Nb, Ta, and Ta/Nb from melts from which titanite has crystallised.

The common occurrence of titanite inclusions within low-Ta zircon grains and/or associated with low-Ta zones provides strong support for this hypothesis. However, the presence of dissolution boundaries and the inclusion of titanite in subsequently forming rims requires explanation. It is possible that a combination of the two aforementioned mechanisms

is required, i.e. that influx of mafic magma caused zircon resorption and sufficiently modified melt composition (including oxidation) such that titanite was stabilised. The lower apparent crystallisation temperatures could reflect a delayed saturation of zircon in the new magma due to its modified composition. If this interpretation is correct, this would lend support to models that invoke mafic magma as a key trigger for porphyry ore genesis (e.g. Halter et al., 2005; Wilkinson, 2013), a process previously suggested to occur at Oyu Tolgoi (Wainwright et al., 2011), and provides a possible tool for fingerprinting the process.

6.2 The effect of titanite crystallisation on zircon Eu/Eu*

Eu/Eu* values in excess of 1, as observed in the low-Ta group (Table 2), cannot be accounted for by changes in redox alone because even under highly oxidised conditions, D_{Eu} would be intermediate between D_{Sm} and D_{Gd} (Burnham and Berry, 2012; Trail et al., 2012). Thus, $Eu/Eu^* > 1$ must be due, at least in part, to melts that are enriched in Eu with respect to Sm and Gd. Positive whole rock Eu anomalies can occur in intrusions associated with porphyry systems (e.g. Lang and Titley, 1999), where they are ascribed to the suppression of plagioclase crystallisation due to high H_2O_{melt} , coupled with oxidised conditions.

However, elevated Eu/Eu* in residual liquids may also be expected from the crystallisation of titanite (Glazner et al., 2008). It is therefore possible that high Eu/Eu* values in low-Ta zircons at Oyu Tolgoi may reflect melts that have crystallised or are crystallising titanite. To investigate this, we modelled the crystallisation of small volumes of titanite from melts of average QMD composition using Rayleigh fractionation. For full details of the modelling method, see the supplementary online material. The results of this analysis show that melts which are crystallising small amounts of titanite would be in equilibrium with zircons that are progressively depleted in MREE with respect to HREE (i.e.

higher Yb/Gd), and have increasing Eu/Eu* values (Fig. 7 b). Positive zircon Eu anomalies were generated by our model after just 0.34 % titanite crystallisation. Chondrite-normalised REE patterns produced by our models also show a striking similarity to Oyu Tolgoi zircons, reproducing the median REE patterns of the low-Ta group after ~0.2% crystallisation of a 100% titanite fractionation assemblage (i.e. $F = 0.998$; Fig. 7 a). The model is largely insensitive to starting composition due to the large K_D values (Fig. A.2).

The competing effects of titanite vs. plagioclase crystallisation on Eu anomalies were also modelled, using a hypothetical starting composition with a Eu/Eu* value of 1. According to this model, the ratio of plagioclase to titanite that would need to crystallise in order to maintain a neutral Eu anomaly is 99.69:0.31 plagioclase:titanite (Fig. 7 c). The partitioning of Eu into both titanite and plagioclase is likely to be redox controlled, meaning the magnitude of this ratio may also be affected by changes in melt fO_2 . However, this result demonstrates that even if plagioclase overwhelmingly dominates the crystallising assemblage, positive Eu anomalies may be generated in residual melts if titanite also fractionates, even in vanishingly small amounts, and such anomalies may be inherited by zircon. The effects of plagioclase fractionation on Eu anomalies may also be negated by the fractionation of hornblende, which also preferentially partitions Sm and Gd over Eu (Fig. 1 b).

These results demonstrate that high Eu/Eu* in zircons can be generated easily by processes which are redox independent. Although titanite crystallisation only occurs in relatively oxidised melts, the redox conditions required are not atypically high compared to typical arc magmas (FMQ+2 at ~750°C; Wones, 1989). In addition, titanite crystallisation can be induced by changes in melt chemistry, such as increases in the Ca/Al ratio, which would cause it to crystallise at the expense of quartz, K-feldspar, and ilmenite (e.g. Frost et al., 2000). These changes in melt chemistry could occur due to an influx of mafic melt, meaning that the onset of titanite crystallisation may not necessarily indicate an increase in

melt fO_2 . Titanite is extremely common in porphyry-related igneous rocks (Table 1), with reported plagioclase:titanite ratios ranging between 98.9:1.1 and 97.3:2.7 (e.g. Yerington batholith; Dilles, 1987). However, its effects on residual melts are unlikely to be recorded in the whole rock geochemistry because it is typically present in the porphyry intrusions (i.e. not fractionated). As a result, the effect of titanite crystallisation, at least on late-stage zircon Eu chemistry, may be difficult or impossible to quantify from whole rock data. The decreases in whole rock Nb, and increases in Eu/Eu* and Yb/Gd ratios that are predicted by our model are not seen at Oyu Tolgoi (see Fig. A.5), so we are confident that titanite fractionation was not a significant process in the petrogenesis of these rocks. Consequently, all attempts to use Eu in zircon to determine the redox condition of magmas at the time of zircon crystallisation must be treated with caution unless evidence for a lack of titanite co-crystallisation (e.g. high-Ta zircons) is presented.

6.3 Ce^{4+}/Ce^{3+} and Ce/Ce^* as redox proxies: practical problems

The method of Ballard et al. (2002) for calculating Ce^{4+}/Ce^{3+} faces several practical challenges to its application. The main problem lies in selecting appropriate melt compositions to use for Ce_{melt} , and for calculating $D_{Ce(3+)}^{zircon/melt}$, and $D_{Ce(4+)}^{zircon/melt}$. This is less problematic for zircons in glassy volcanic rocks (e.g. Marshall et al., 2009), or where melt inclusions in zircon are abundant and may be easily analysed (e.g. Thomas et al., 2002). However, in plutonic rocks, where zircons may record a protracted and complex history of fractional crystallisation and crustal assimilation, it may not be possible to estimate melt compositions. Using whole rock compositions as a proxy for melt compositions is inherently problematic for plutonic rocks because whole rock geochemistry does not generally reflect melt composition at any point of magmatic evolution. Furthermore, in the case of xenocrystic or detrital zircons, or zircons from rocks which have been affected by hydrothermal alteration

(ubiquitous in porphyry deposits), not even the (unmodified) whole rock geochemistry is available.

The $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio is much more sensitive to variations in $D_{\text{Ce}^{3+}}$ than to either of the other melt-dependent variables from Eq. 3 (i.e. $D_{\text{Ce}^{4+}}$ or Ce_{melt} ; Fig. 8 a-c), so carefully constraining this parameter in particular is essential for a reliable calculation of $\text{Ce}^{4+}/\text{Ce}^{3+}$. However, because zircons from a given rock have a wide range of REE concentrations, and these values are all divided by the same whole rock value to estimate $D_{\text{Ce}^{3+}}$, the range of calculated $D_{\text{Ce}^{3+}}$ (and consequently, calculated $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratios) can vary by up to 3 orders of magnitude for a single rock (Fig. 8 b). This variability is unlikely to represent a real change in oxidation state. Calculated values for $D_{\text{REE}}^{\text{zircon/whole rock}}$ for other REE that are not redox-sensitive (e.g. D_{Gd}) are up to 5 orders of magnitude lower than experimentally-determined partition coefficients at similar temperatures, and are especially low in the low-Ta zircons from Oyu Tolgoi that co-crystallised with titanite (Fig. 8 d). If titanite crystallisation precedes or accompanies zircon crystallisation, REE_{melt} will be lower than REE_{WR} , causing estimates of $\text{Ce}^{4+}/\text{Ce}^{3+}$ to be erroneously high. Thus, calculated $\text{Ce}^{4+}/\text{Ce}^{3+}$ may vary considerably without any change in $f\text{O}_2$.

It has been suggested that the crystallisation of LREE-rich phases such as titanite could remove trivalent cations (including Ce^{3+}) from the melt, thereby increasing the melt $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio, and driving Ce/Ce^* zircon ratios to high values without any change in melt redox conditions (Claiborne et al., 2010). However, the oxidation state of the melt is likely to be buffered by Fe such that the $\text{Ce}^{4+}/\text{Ce}^{3+}$ ratio would be unaffected by minor Ce^{3+} removal. The fact that we do not observe any clear variation of Ce/Ce^* with any proxy for titanite fractionation supports this notion (Fig. A.3). Consequently, we consider that the Ce/Ce^* ratio is likely to be the most robust measure of ambient magma redox conditions in zircon. Despite

this, the difficulties in determining Ce/Ce^* precisely preclude it from being an accurate oxybarometer. For example, experimentally calibrated estimates of fO_2 which use the Ce anomaly (e.g. Trail et al., 2012) produce values of fO_2 derived from zircons from this study that have an unrealistically wide interquartile range and high median (c.f. Dilles et al., 2015). In addition, calibrations of the magnitude of Ce anomalies with fO_2 which require knowledge of melt H_2O and major element chemistry (e.g. Smythe and Brenan, 2015) are not possible for zircons from hydrothermally altered rocks, or xenocrystic or detrital zircons. We therefore suggest that zircon Ce/Ce^* , calculated using Eq. 5, may be used but only as a semi-quantitative measure of magma redox conditions.

6.4 Implications for zircon as an indicator of porphyry fertility

Notwithstanding the problems associated with using Eu/Eu^* , Ce/Ce^* , and Ce^{4+}/Ce^{3+} as accurate measures of magma redox state, there still exists an empirical relationship between fertile porphyry systems and the occurrence of zircons with higher average values for these parameters (Fig. 2; Table 1). Consequently, zircon may still be useful in exploration, although must be used with caution, and in concert with more conventional exploration techniques. With respect to the application of elevated Eu/Eu^* , we conclude that only high-Ta zircons ($Ta > 0.2$ ppm) should be used to minimise the chances of misleading signals due to titanite crystallisation.

The magnitude of the Eu and Ce anomalies appears to be independent of deposit size or grade. For example, at Oyu Tolgoi, there is no significant distinction between zircons from Hugo Dummett (high Cu grade and tonnage), and Heruga (lower Cu grade and tonnage; Fig. 5). It is worth noting that both systems are hosted in the same rocks and formed during the same magmatic epoch, i.e. broadly under the same geodynamic conditions and probably derived from the same or similar magma source. Thus, the divergent grade and size of these

deposits is due to other factors, such as fluid chemistry, and/or fluid focussing (Richards, 2013).

Significantly, at Oyu Tolgoi, we suggest that zircons with low Ta and linear chondrite-normalised REE patterns are tracers of titanite crystallisation, and that both low-Ta zircon and titanite presence are near-unique identifiers of the fertile porphyry phase (QMD). This is potentially very powerful for porphyry exploration: the occurrence of demonstrably porphyry-related titanite in stream sediments would be a fertility indicator in itself, and the identification of zircons with high Ce/Ce* and Eu/Eu* would also be a positive sign.

7. CONCLUSIONS

The redox sensitivity of Eu and Ce in zircon are both systematic and well documented. However, attempts to use this to estimate the prevalent redox conditions of magmas at the time of zircon crystallisation face some significant challenges:

- 1) Eu/Eu* in zircon is sensitive to melt Eu/Eu*, which may be significantly increased by the co-crystallisation of vanishingly small amounts of titanite. Such effects would be undetectable in whole rock analysis if titanite crystallises at a late stage, and is not fractionated.
- 2) Titanite crystallisation may also cause overestimates in calculated zircon $\text{Ce}^{4+}/\text{Ce}^{3+}$ values, as the calculation of this parameter assumes the melt and whole rock REE concentrations are similar, which would not be the case where titanite has crystallised, but not fractionated.
- 3) $\text{Ce}^{4+}/\text{Ce}^{3+}$ estimates derived from zircon compositions that rely on whole rock REE data are likely to be in error because whole rock compositions are unlikely to reflect melt composition at the time of zircon crystallisation.

4) Ce/Ce* in zircon is unlikely to be affected by titanite crystallisation although it remains problematic in its determination because the LREE in zircon are close to or below the detection limit for common microanalytical methods. The use of Eq. 5 is proposed as an alternative means to estimate Ce/Ce* that is less impacted by analytical limitations.

We suggest that the elevated mean values of Eu/Eu* and Ce⁴⁺/Ce³⁺ in zircons from fertile porphyry systems is attributable to some combination of elevated *f*O₂, and Eu-enrichment/REE-depletion by titanite crystallisation. Low Ta and Nb content and high Yb/Gd ratios of zircons may provide a screening method for identification of those that have had their compositions modified by this process.

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526 **Figure Captions**

527 *Figure 1. Experimentally-determined partition coefficients for: (a) REE in zircon, showing the redox sensitivity of Eu and Ce*
528 *(Burnham and Berry, 2012); and (b) REE in titanite (solid line: Bachmann et al., 2005; dotted line: Luhr and Carmichael*
529 *1980), hornblende (Klein, 1997) and plagioclase (Dunn and Sen, 1994). Both titanite and hornblende partition Sm and Gd*
530 *more strongly than Eu, whereas plagioclase has a preference for Eu. The crystallisation of these phases would impart*
531 *positive and negative Eu anomalies respectively on residual melts. The conditions under which the experiments of Burnham*
532 *and Berry (2012) were conducted are not representative of natural systems (ZrO-doped synthetic andesites at ~1300°C) and*
533 *are presented here solely to show the redox-dependent partitioning of Ce and Eu.*

534 **Figure 1 = 1/2 page width**

535

536 *Figure 2. A comparison between zircon data from barren and fertile rocks drawn from the literature and from this study. (a)*
537 *Ce/Ce* vs Eu/Eu*, showing greater overlap in Ce/Ce* than in Eu/Eu*. (b) Histogram for Eu/Eu* values in zircons from*
538 *barren and fertile intrusions. Data sources are described in the online supplementary information. Ce⁴⁺/Ce³⁺ is not plotted*
539 *here due to the paucity of published data for both barren and fertile systems.*

540 **Figure 2 = full page width**

541

542 *Figure 3. (a) Distribution and grade of the Oyu Tolgoi porphyry Cu deposits (from Crane and Kavalieris, 2012); (b)*
543 *representative cross section through the Heruga deposit, showing the typical relationships between the units studied herein.*

544 **Figure 3 = full page width**

545

546 *Figure 4. SEM-cathodoluminescence images of zircon grains from quartz monzodiorite intrusions of Oyu Tolgoi. Zircons are*
547 *from both studied deposits: Heruga (A-D, I, J, and L) and Hugo Dummett (E, F, G, H, and K). Several grains contain distinct*
548 *rims and cores, which are separated by a dissolution boundary (e.g. A, E-H, and L), and rims contain inclusions of titanite*
549 *(Ttn), which was identified by EDS analysis (inset). Zones which contain titanite have higher Eu/Eu*, Yb/Gd, and lower Ta*
550 *than zones without titanite. Other mineral inclusions are albite (Ab), K-feldspar (K-spar), hornblende (Hbld), and apatite*
551 *(Ap). Scale bar in all figures is 100 µm.*

552 **Figure 4 = full page width**

553

554 *Figure 5. (a) Histogram showing the bimodal distribution of Ta in zircons from the quartz monzodiorite at Oyu Tolgoi. White*
555 *bars are Heruga, black bars are Hugo Dummett. (b) Nb vs. Ta plot showing the lower Ta/Nb ratio that characterises zircons*
556 *with <0.2 ppm Ta (vertical dashed line). (c) Temperature vs. Hf plot and (d) Eu/Eu* vs. Hf plot for zircons from Oyu Tolgoi.*
557 *These do not show the clear negative correlation seen in other deposits for the total population, but such a trend is resolved*
558 *if only the high-Ta group is considered. Low-Ta group zircons have higher Eu/Eu* and lower temperature at a given Hf with*
559 *respect to the high-Ta group. Temperatures calculated using the method of Ferry and Watson (2007).*

560 **Figure 5 = full page width**

561

562 *Figure 6. Chondrite-normalised REE patterns for (a) high-Ta zircons and (b) low-Ta zircons from the quartz monzodiorite at*
563 *Oyu Tolgoi. Central white lines are mean values. Note the MREE enrichment and more pronounced negative Eu anomalies in*
564 *the high-Ta zircons.*

565 **Figure 6 = full page width**

566

567 *Figure 7. (a,b) Modelling the fractionation of 100% titanite bulk composition from a melt with average QMD composition.*
568 *(a) Chondrite-normalised REE patterns for zircons modelled to be in equilibrium with average QMD composition (dotted*

line) and a model composition of QMD with 0.2% ($F = 0.998$) fractionation of a 100% titanite bulk composition (grey dashed line). Full model results (inset) are in increments of 0.05% crystallisation. The average low-Ta and high-Ta zircons are also plotted, and are a close match for the modelled REE patterns. (b) The positive correlation of Eu/Eu^* and Yb/Gd in Oyu Tolgoi zircons (including data from Wainwright et al., 2011) is matched by the model results presented in (a). (c) If a bulk composition of 0.31 wt.% titanite and 99.69 wt.% plagioclase is considered, a melt $\text{Eu}/\text{Eu}^* = 1.0$ can be maintained regardless of the degree of fractionation.

Figure 7 = 1/2 page width

Figure 8. (a-c) Calculated $\text{Ce}^{4+}/\text{Ce}^{3+}$ for quartz monzodiorite zircons plotted against the parameters which are used in its calculation; (a) $D_{\text{Ce}(4+)}$, (b) $D_{\text{Ce}(3+)}$, (c) Ce (ppm; whole rock). Of these parameters, the value of $\text{Ce}^{4+}/\text{Ce}^{3+}$ is most strongly influenced by $D_{\text{Ce}(3+)}$ values. (d) $\ln D_{\text{Gd}}$ (zircon/whole rock) calculated for Oyu Tolgoi zircons are not comparable to experimentally-determined $\ln D_{\text{Gd}}$ values from the literature. This suggests that using whole rock REE as a proxy for melt leads to unrealistic D_{REE} partition coefficients, which in turn leads to incorrect values for $\text{Ce}^{4+}/\text{Ce}^{3+}$. Gd is chosen for comparative purposes because it is not redox sensitive. Low-Ta zircons (black circles) and high-Ta zircons (white diamonds) are shown.

Figure 8 = full page width

Table 1. Mean values of Eu/Eu^* , Ce/Ce^* and $\text{Ce}^{4+}/\text{Ce}^{3+}$ for zircons from barren and fertile rocks from the literature.

Deposit	Country	Deposit type	n=	Eu/Eu*			Ce/Ce*			Ce ⁴⁺ /Ce ³⁺			Titanite present?	Source	
				Mean	±σ	min - max	Mean	±σ	min - max	Mean	±σ	min - max			
South America															
El Salvador	Chile	Porphyry Cu (+ Mo)	172	0.57	0.13	0.24 - 0.85	169	126	6 - 680				Yes	Lee et al., 2017	
El Teniente	Chile	Porphyry Cu-Mo	37	0.52	0.09	0.17 - 0.64	54	52	5 - 177	432	516	28 - 2718	Yes	Muñoz et al. (2012) Rabbia et al. (2009)	
Chuquicamata	Chile	Porphyry Cu-Mo	79	0.47	0.12	0.17 - 0.95	235	172	<1 - 1006	757	526	40 - 2341	Yes, inferred	Ballard et al. (2002)	
Bajo de la Alumbreira	Argentina	Porphyry Cu-Au	529	0.56	0.05	0.11 - 0.73	241	128	19 - 1138				Yes	Buret et al. (2016)	
Coroccohuayco	Peru	Porphyry-skarn	54	0.6	0.14	0.24 - 0.90	129	97	12 - 373				Yes	Chelle-Michou et al. (2014)	
Asia															
Various	China		58	0.65	0.22	0.05 - 1.87				411	462	36 - 2736	Yes	Wang et al. (2013)	
Dexing	China	Porphyry Cu	22	0.43	0.07	0.29 - 0.56	34	26	6 - 122	127	84	33 - 398	Not rep.	Zhang et al. (2013)	
Yulong	China	Porphyry Cu (+ Mo)	77							204	19	5 - 756	Not rep.	Liang et al. (2006)	
Zhanaga	China	Porphyry Cu (+ Mo)	47							334	36	26 - 729	“	Liang et al. (2006)	
Mangzong	China	Porphyry Cu (+ Mo)	24							201	52	18 - 1230	“	Liang et al. (2006)	
Duoxiasongduo	China	Porphyry Cu (+ Mo)	47							250	37	10 - 1314	“	Liang et al. (2006)	
Malasongduo	China	Porphyry Cu (+ Mo)	38							258	47	17 - 1304	“	Liang et al. (2006)	
CAOB porphyry	Various	Porphyry Cu (Au Mo)	76	0.48	0.12	0.24 - 0.79	70	42	12 - 139	184	119	28 - 592	N/A	Shen et al. (2015)	
Oyu Tolgoi	Mongolia	Porphyry Cu-Au	Low-Ta	117	0.81	0.22	0.46 – 1.52	122	102	16 – 539	1322	988	62 – 5402	Yes	This study
	Mongolia	Porphyry Cu-Au	High-Ta	343	0.43	0.07	0.18 - 0.71	144	127	5 - 870	331	301	16 - 1656	No	This study
	Mongolia	Post-mineralisation (BiGd)	High-Ta	29	0.48	0.21	0.02 - 0.77	123	153	7 - 705	443	501	13 - 2201	No	This study
	Mongolia	Coeval unmineralised volcanics (Dvs)	High-Ta	32	0.46	0.16	0.3 - 0.95	86	63	15 - 1294	194	148	26 - 583	No	This study
Barren															
Detrital zircons	Global	Barren (detrital)	1015	0.37	0.3	0.01 - 3.14	22	40	<1 - 475				Unknown	lizaku et al. (2010)	
GEOROC	Global	Barren (literature)	492	0.30	0.24		157						Unknown	http://georoc.mpch-mainz.gwdg.de/	
Yulong	China	Non-ore producing	68							101	30	28 - 112	Not rep.	Liang et al. (2006)	
Various	China	Barren (adakites)	39	0.44	0.09	0.31 - 0.61				84	76	16 - 371	Not rep.	Wang et al. (2013)	
Chuquicamata	Chile	Not ore associated	131	0.29	0.13	0.05 - 0.72	50	84	2 - 728	122	224	5 - 2205	Yes, inferred	Ballard et al. (2002)	

Sample name	Low Ta n = 110			High Ta n = 289			BiGd n = 29			Dvs n = 32			Typical granite			
Lithology	min	mean	max	min	mean	max	min	mean	max	min	mean	max	min	mean	max	n=
Ti	1.81	4.53	9.66	3.17	8.33	16.6	2.16	7.76	25.1	1.75	8.17	13.5	0.93	20.3	838	550
Y	128	370	1151	261	822	5868	217	920	3259	295	1245	3013	7.7	1856	22190	1730
Nb	0.27	0.65	2.04	0.59	1.56	14.1	0.52	3.52	37.1	0.61	2.73	13.8	0.48	16.0	564	317
La	0.02	0.05	0.12	0.02	0.06	0.21	0.02	0.08	0.34	0.04	0.07	0.14	0.002	13.9	5253	703
Ce	3.28	7.82	28.0	3.41	12.5	100	1.42	13.1	39.3	5.53	17.0	116	0.28	58.2	7011	757
Pr	0.02	0.04	0.13	0.02	0.07	0.52	0.02	0.13	0.85	0.02	0.10	0.33	0.01	2.35	79	415
Nd	0.19	0.42	1.96	0.19	0.99	8.58	0.23	1.70	12.3	0.26	1.64	4.46	0.04	13.9	461	798
Sm	0.13	0.58	3.26	0.40	2.35	25.2	0.33	3.09	16.7	0.16	3.52	10.4	0.3	10.9	337	758
Eu	0.08	0.35	1.22	0.12	0.77	6.77	0.19	0.80	3.06	0.07	1.16	4.21	0.01	1.55	39	754
Gd	0.96	3.49	17.1	2.59	13.5	137	2.06	17.2	77.1	1.28	20.4	60.6	1.9	44.4	474	578
Tb	0.42	1.34	5.43	1.16	4.93	46.8	0.87	5.87	25.7	0.67	7.44	21.2	0.73	15.3	100	570
Dy	6.55	20.1	73.8	17.0	65.1	557	13.2	75.6	334	14.4	98.6	270	1.6	193	2156	1214
Ho	3.50	9.95	30.4	8.27	26.6	209	6.11	29.6	119	7.48	40.1	101	5	64.1	339	570
Er	23.9	62.5	191	43.6	137	948	36.7	150	523	51.7	206	486	19.3	733	8241	1022
Tm	7.78	19.3	58.4	12.2	34.2	220	10.6	36.0	98.0	14.3	51.1	113	2.58	58.3	272	570
Yb	118	277	860	137	387	2179	124	397	930	171	590	1290	4.7	579	7109	1097
Lu	24.5	59.8	199	24.1	65.5	342	23.2	74.5	189	28.7	96.4	180	2.2	136	6513	944
Hf	6126	7778	9492	6134	8500	11529	6855	8919	11792	6324	8155	11926	870	10817	99500	1531
Ta	0.02	0.11	0.19	0.20	0.51	3.72	0.10	0.86	8.69	0.10	0.63	2.23	0.10	2.31	15	153
Pb	0.38	1.44	9.12	0.33	1.81	32.2	0.28	3.51	19.9	0.38	3.30	40.5	0.01	136	62000	2948
Th	9.32	39.7	275	8.95	47.7	921	7.36	95.0	505	11.0	87.4	1047	0.01	544	46210	7879
U	31.8	82.0	278	31.7	88.2	780	36.2	210	772	30.9	137	732	0.01	1270	1798000	10494
Eu/Eu*	0.46	0.81	1.52	0.18	0.43	0.71	0.02	0.48	0.77	0.30	0.46	0.95	0.01	0.23	2	575
Ce/Ce*	15.7	122	539	5.31	144	870	6.59	123	705	15	85.8	1294	0.6	73.3	1501	736
Ce ⁴⁺ /Ce ³⁺	61.6	1322	5402	16.4	331	1656	12.7	443	2201	26.3	194	583	-	-	-	-
Yb _N /Gd _N	26.1	108	191	19.2	40.3	135	9.55	47.4	199	22.6	63.8	594	0.9	17.6	85.9	578
ΣREE	201	463	1393	259	750	4779	228	804	2170	313	1133	2486	1	1422	15645	1355
Th/U	0.24	0.42	1.09	0.26	0.49	1.29	0.05	0.46	0.95	0.20	0.51	1.43	<0.001	0.84	148	7525
Ta/Nb	0.08	0.17	0.34	0.10	0.35	0.54	0.09	0.27	0.44	0.12	0.27	0.48	0.04	0.35	0.99	86
T (°C)	633	702	777	676	757	834	646	738	882	630	753	811	-	-	-	-

607 *Table 2. Summary statistics of low- and high-Ta (QMD), BiGd, and Dvs zircon geochemistry.*

608 FOOTNOTE TO TABLE 2:

609 *'Typical granite' data from GEOROC ([http://georoc.mpch-](http://georoc.mpch-mainz.gwdg.de/georoc/Csv_Downloads/Minerals_comp/ZIRCONS.csv)*
610 *mainz.gwdg.de/georoc/Csv_Downloads/Minerals_comp/ZIRCONS.csv)*

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