

# REE-Y, Ti, and P Remobilization in Magmatic Rocks by Hydrothermal Alteration during Cu-Au Deposit Formation

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## Abstract

Chondrite-normalized rare earth element (REE) plots of whole-rock geochemical analyses are commonly used to describe the history of magmatic systems. In the particular case of porphyry copper deposits, which are produced by ore-forming magmatic-hydrothermal systems, whole-rock REE concentrations commonly show an unusual depletion in the final phase of magmatism associated with the main ore-forming stage. Interpretation of REE signatures requires establishing whether they result from magmatic or hydrothermal fractionation processes, or a combination of both. We investigated whole-rock trace-element and REE patterns of samples from the giant Ok Tedi porphyry copper-gold deposit, Papua New Guinea, and found that REEs were most depleted in zones of greatest hydrothermal alteration. REE-rich accessory phases zircon, apatite, and titanite have lower modal abundances and become smaller and more anhedral in these intensely altered zones as compared to less altered rocks. This mineralogical change is accompanied by depletions in P, Ti, Y, and Zr, and deviations of Zr/Hf and Y/Ho from chondritic trace-element ratios—chemical signatures indicative of hydrothermal fractionation. We conclude that destruction of REE-rich accessory minerals, particularly apatite, has led to hydrothermal remobilization and depletion of REEs. This implies that intrusive rocks that experienced high-salinity, oxidized fluid-rock interaction at temperatures  $>400^{\circ}\text{C}$  may have had their original magmatic REE signature modified.

## Introduction

THE FINAL PULSE of magmatism in porphyry copper deposits and similar magmatic-hydrothermal complexes often predates or is contemporaneous with the main period of metal deposition, e.g., at Bajo de la Alumbra (Harris et al., 2004), Grasberg (Pollard and Taylor, 2002) and Northparkes (Lickfold et al., 2003). The metal-enriched intrusive rocks are commonly characterized by a notable modification of the REE pattern and depletion of REE concentration when compared to unaltered magmatic rocks, with examples being the porphyry copper deposits of northwest Arizona (Lang and Titley, 1998), the El Indio-Pascua Au-Ag-Cu belt of Chile-Argentina (Bissig et al., 2003), the Lachlan fold belt Cu-Au district (Blevin, 2002; Lickfold et al., 2007), the central Andean ore belt (Kay and Mpodozis, 2001) and the Kerman arc in Iran (Shafiei et al., 2009). These chemical signatures can be used to constrain the melt source of these ore deposit magmas (e.g., Lang and Titley, 1998; Shafiei et al., 2009), under the assumption that REEs are immobile in hydrothermal fluids.

In this paper we investigate the often-implicit assumption that REEs are immobile during fluid-rock interaction associated with porphyry copper deposits. We first review the published evidence from experimental and natural systems that argues for REE mobility. We proceed to introduce the geology of the giant Ok Tedi porphyry Cu-Au deposit, Papua New Guinea, and establish the likely nature of the hydrothermal fluids related to the mineralization. We then investigate the REE distribution and mineral textures in samples of the intrusive complex. The REE contents are strongly affected by hydrothermal alteration and there are also distinct textural and mineralogical changes, the most important being the

modal decrease of REE-bearing accessory phases in the altered magmatic rocks.

## Background and Rationale

In this section, we establish a basic understanding of REE transportation in upper crustal geological fluids, show how evidence from geochemical analyses of rock samples supports the mobility of REE, Y, and Zr, and establish a basic understanding of the theoretical considerations that underpin the mobility of REE, Y, and Zr in geothermal fluids, including porphyry copper-type fluids.

The long-standing paradigm is that in nonpegmatite silicate melts, REE partitioning is controlled by their charge and radius (Goldschmidt, 1937). This implies that element pairs with near-identical charges and radii (e.g., Y-Ho and Zr-Hf) should not fractionate from each other during magmatic differentiation processes such as melting and crystallization. Typical magmatic rocks should therefore have a narrow range of Y/Ho and Zr/Hf close to the chondritic ratio of  $27.7 \pm 2.7$  and  $36.6 \pm 2.9$ , respectively (Bau, 1996). In contrast, seawater, hydrothermal vein fluorite, and hydrogenetic Fe-Mn crusts fall outside the “chondrite box” on a Zr/Hf vs. Y/Ho plot, thereby discriminating rocks that have experienced interaction with or are formed from aqueous phases (Bau, 1996). Such a plot is therefore useful to show the effects of hydrothermal element fractionation in magmatic hydrothermal complexes (e.g., Dostal and Chatterjee, 2000).

## REE measured in upper crustal fluids and hydrothermally altered rocks

Analyses of geothermal fluids from a variety of geologic settings generally contain 100 to 10,000 times lower concentration of REEs than chondrites (Douville et al., 1999; Wood, 2003, 2006). Thus, fluid-rock ratios of more than  $10^2$  to  $10^3$  could change REE rock patterns (Bau, 1991). At higher

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temperatures and/or higher acidity than typical surface water, REE solubility may increase dramatically (Wood, 2003). For example, Banks et al. (1994) found 200 to 1,300 ppm total REE in fluid inclusions from hydrothermal quartz, which is 50 to 325 times higher than chondrite. Furthermore, detailed microanalytical work has shown that Zr, REE, and HFSE-bearing accessory minerals are present within fluid inclusions in magmatic hydrothermal complexes (e.g., Salvi et al., 2000). However, directly measured REE concentrations in fluids at elevated temperatures and pressures are scarce (Wood, 2003). We therefore turn to the rock record.

Hydrothermally altered rocks show abundant evidence for the mobilization of REE and other trace elements in the form of enrichment or depletion relative to the unaltered rocks. The following examples provide whole-rock analytical evidence of this type: (1) hydrothermal REE-fluorite ore deposits (Williams-Jones et al., 2000), (2) REE-enriched iron-oxide copper gold deposits and REE deposits associated with alteration zones around carbonatites (Samson and Wood, 2005), (3) REE-Zr-Y anomalies in the alteration zones of uranium deposits (Fayek and Kyser, 1997; Mathieu et al., 2001; Rene, 2008), and (4) REE enrichments of certain alteration zones in a variety of (magmatic-) hydrothermal ore deposits (Salvi and Williams-Jones, 2005; Samson and Wood, 2005).

The inference here is that REE-bearing minerals can be precipitated from hot, oxidizing aqueous phases, which therefore must have had significant REE solubility. In other (non-ore forming) cases, one may find zirconolite, an HFSE, REE, and actinide-bearing mineral that was observed in lava vesicles (de Hoog and van Bergen, 2000), which suggests precipitation from magmatic vapor. Zirconolite is also found in other hydrothermal regimes, such as in contact-metamorphic aureoles (Gieré, 1986).

REE mobilization can also manifest as trace element depletion of hydrothermally altered rocks (e.g., Rubin et al., 1993; Salvi and Williams-Jones, 1996; Lewis et al., 1997; Cherniak, 2000). Different alteration zones are likely to have different REE characteristics. For example, garnets in proximal zones of skarn systems can have a notable REE and Y-Zr-Sc depletion (Nicoleescu et al., 1998; Gaspar et al., 2005). Thus, REE redistribution through water-rock interaction is common in hydrothermally altered rocks, especially by fluids that have temperatures  $>300^{\circ}\text{C}$ , low pH, and high halogen content, i.e., typical ore-forming fluids. These fluid properties will be discussed below.

#### Theoretical considerations

Element mobility in hydrothermal fluids is largely dependent on the stability of ligands available to form complexes. As the REE, Y, and Zr form small, highly charged cations in the sense of Pearson (1963), they prefer hard ligands like fluoride (e.g., Bau and Dulski, 1995), sulfate, and carbonate (e.g., Rubin et al., 1993; Douville et al., 1999). Fluoride may preferentially complex with more abundant elements such as calcium (Wood, 2005), and the previously mentioned Y/Ho fractionation, characteristic of hydrothermally altered rocks, is a consequence of preferential complexation of Y in halogen-rich fluids (Bau and Dulski, 1995). However, in the case of REE, recent experimental studies indicate that they form strong complexes with chloride, a ligand of intermediate

hardness (Migdisov and Williams-Jones, 2002; Migdisov et al., 2009). Indeed, these experiments show that for chloride-rich fluids such as those responsible for the formation of porphyry copper deposits (Seedorff et al., 2005), chloride complexes may control the transport of REE, as is also indicated by thermodynamic modelling (e.g., Douville et al., 1999). Since the stability of ligands is controlled by temperature, pressure, and pH and these factors may change rapidly and frequently in geologically realistic situations, caution is required when assessing the overall mobilization capacity of fluids.

The current lack of solubility data of REE- and trace-element-bearing minerals in geothermal fluids (Samson and Wood, 2005; Wood, 2005) prevents a quantitative assessment of REE mobilization using theoretical considerations. Note that the effects of sorption processes are also omitted from our discussion. However, the significant evidence that REEs are mobile in porphyry copper-type fluids reviewed above, in combination with the typically high fluid-rock ratios of porphyry copper deposits (Seedorff et al., 2005), supports our hypothesis that the observed REE variations in porphyry copper deposits can be explained by a combination of source rock (magmatically inherited) variations plus hydrothermal remobilization of the REEs.

#### Geologic Background of the Ok Tedi Deposit

The Ok Tedi deposit is situated in western Papua New Guinea (Fig. 1) close to the border with Indonesia, in a regional south-verging fold-and-thrust belt made up mostly of limestone and siltstone units. The belt is located south of the axis of the east-west-trending Papua New Guinean orogen. Deformation in the orogen has been ongoing since the Late Miocene collision of an island arc with the northern margin of the Australian plate on which Ok Tedi is situated (Hill et al., 2002). The fold-and-thrust belt has been intruded at various locations by Plio-Pleistocene monzodiorite and granite stocks (Bamford, 1972), among which is the 4-km-wide, U-shaped Ok Tedi Intrusive Complex (western half of complex, shown in Fig. 1A).

Copper-gold mineralization is centered on two adjoining stocks of monzonite-monzodiorite in the northwestern quadrant of the Ok Tedi monzodiorite complex (Fig. 1B). Disseminated, gold-bearing copper sulfides occur mostly within the strongly altered northern Fubilan monzonite porphyry, whereas subvertical and flat-lying magnetite- and Cu-Au-bearing sulfide skarns surround the adjacent southern Sydney monzodiorite stock, which is equigranular to locally porphyritic. Leaching and redeposition of copper minerals have produced a gold-enriched leached cap and underlying enriched copper zone carrying economic gold grade (Rush and Seegers, 1990).

The intensely altered and mineralized Fubilan monzonite porphyry contains a central core of barren quartz stockwork, roughly  $350 \times 150$  m in surface area, around which mineralization forms an annulus. The Fubilan intrusion has an assemblage of oligoclase, orthoclase, quartz, and hydrothermal biotite (sometimes after hornblende, as indicated by rare remnants). Apatite, rutile after titanite (Rush and Seegers, 1990), and magnetite, pyrite, and chalcopyrite are common accessories.

Rush and Seegers (1990) synthesized previous work on the alteration at Ok Tedi (Bamford, 1972) and listed two stages of

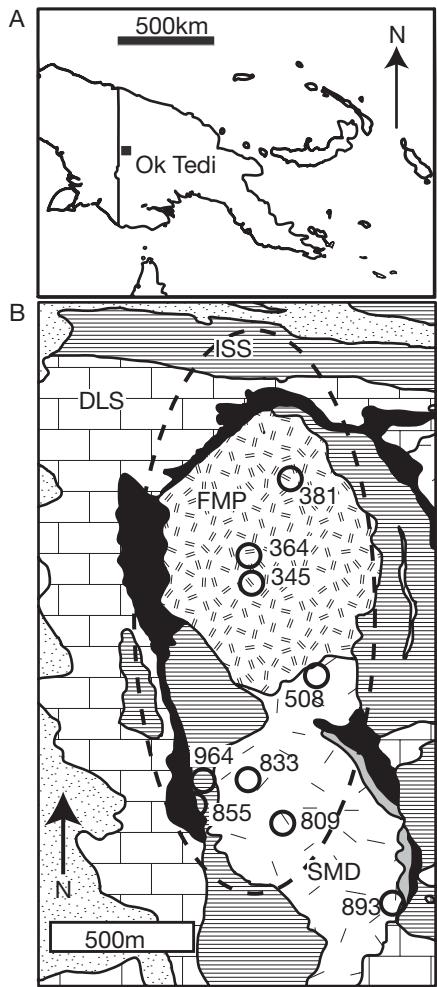


FIG. 1. A. Location of Ok Tedi in Papua New Guinea. B. Geologic map of Ok Tedi mine area and sample location, courtesy of Ok Tedi Mining Limited. Labels indicate drill holes used to obtain samples. Legend: DLS = Dara limestone, FMP = Fubilan monzonite porphyry, ISS = Ieru siltstone, SMD = Sydney monzodiorite. The mine area is indicated by a dashed line.

potassic alteration, surrounded by marginal advanced argillic alteration. They show that stage 1 is characterized by pervasive green-brown biotite, partly altered to fine-grained clay minerals, partial rutile replacement of titanite, and commonly accompanied by chalcopyrite and magnetite. Stage 2 is characterized by K-feldspar, pale-brown phlogopite that commonly forms aggregates after mafic minerals from both unaltered and altered rocks, and common rutile replacement of titanite. Chalcopyrite, bornite, molybdenite, and gold are associated with phlogopite. This stage 2 phase assemblage occurs both pervasively and near fractures. Argillic alteration (not sampled in this study) is characterized by kaolinite, montmorillonite, magnetite, other iron oxides, titanite, and rare sulfides.

In contrast, the southern Sydney monzodiorite is somewhat less altered and preserves plagioclase (An40–An10), orthoclase, and smaller proportions of mafic phenocrysts such as clinopyroxenes (diopside), hornblende, and biotite. Common accessory minerals are titanite, apatite, zircon, pyrite and magnetite.

### Nature of Hydrothermal Fluids at Ok Tedi

Large-scale, intense alteration and fluid flow at the Ok Tedi deposit is indicated by (1) the presence of massive, mineralized skarn bodies bordering the intrusions, (2) 20-m-wide polymict hydrothermal breccias within and surrounding intrusions, (3) alteration of igneous mineral assemblages (pyroxene, amphibole, plagioclase), (4) K-feldspar and biotite enrichment, and (5) the presence of quartz and K-feldspar veins and disseminated Cu- and Fe-sulfides.

The estimated 4.98 Mt of contained Cu metal (Ok Tedi resource statement 2007, [www.oktedi.com](http://www.oktedi.com)), in less than 1 km<sup>3</sup> of rock volume, coupled with a solubility of Cu in porphyry copper fluids of ~0.75 wt percent Cu (Ulrich et al., 1999) suggest that fluid-rock ratios must have been on the order of tens to hundreds of thousands. Such fluid-rock ratios can transport sufficient amounts of REE to change the REE patterns of the rocks, provided that REE-hosting minerals dissolve into these fluids (Bau, 1991). The alteration assemblages, including biotite and K-feldspar, suggest temperatures of >400°C (Seedorff et al., 2005), similar to other porphyry copper deposits (Dilles and Einaudi, 1992; Heathersay and Walshe, 1995). The widespread occurrence of magnetite and rutile (Doucette, 2000) suggest that conditions were oxidizing (Ishihara, 1981). The higher F concentration (>2.4 wt %) of hydrothermal biotite in the deposit (Doucette, 2000), as opposed to magmatic biotite (<2.0 wt %), suggests a high halogen content of the hydrothermal fluids (Kesler et al., 1975; Banks, 1976). Recent reviews on REE complexation (e.g., Samson and Wood, 2005; Wood, 2003) suggest that such oxidizing, halogen-rich, hot, acidic fluids would facilitate dominantly chloride and perhaps minor fluoride complexation of REE (Bau and Dulski, 1995; Wood, 2003). Considering the calculated fluid/rock ratios, such fluids would have the potential to mobilize REE when fluxed through the rocks at Ok Tedi, especially within the Fubilan monzonite porphyry.

### Methods

We collected a number of samples to test whether remobilization of REE did occur at Ok Tedi. Most drill core samples used for polished thin section and geochemical analysis were collected from the mine area (Fig. 1B). Some samples of igneous rocks from the Ok Tedi Intrusive Complex were collected from drill cores outside the mine area (Table 1). Textural criteria such as grain shape and proximity to and abundance of veins, following Gifkins et al. (2005), were used to

TABLE 1. Collar Data of Drill Core from Outside the Mine Area

Core	Easting (m)	Northing (m)	Altitude (m)	Position in intrusive complex
DDH848	316616	422031	1216	South
DDH825	316390	421730	1185	South
DDH814	316952	424960	1602	Northeast
GDH871	317536	423648	1536	East
DDH364	315161	424293	1755	Mine area

Notes: Data for DDH 364 are also given as a reference point to Figure 1B; the sample number digits before the dash correspond to drill hole number; the digits after the dash correspond to drill hole depth

identify and study alteration minerals in thin sections and to define a qualitative intensity index scaled from 1 to 3, with 3 indicating the most intense alteration. Mineral abbreviations follow Kretz (1983). Mineral separation with a 50- to 20- $\mu\text{m}$  siphoning mesh followed standard procedures.

A standard petrographic microscope and a scanning electron microprobe (SEM) were used to identify and photograph common and REE-rich minerals, and describe their textural and mineralogical relationships. Major element concentrations were determined from fused discs using X-ray fluorescence at the Commonwealth Scientific and Industrial Research Organisation laboratories in Adelaide, Australia. Trace-element concentrations for the majority of samples were determined at Monash University, School of Geosciences. Sample powders were dissolved in high-pressure Teflon bombs for 72 h in HF, evaporated, and redissolved in HCl and  $\text{HNO}_3$ . Solutions were analyzed for REE and trace elements using a quadrupole ICP-MS, following procedures outlined in Elburg et al. (2002). Measured REE concentrations of the standard BHV-01 (Eggins et al., 1997) were within 4 percent deviation of the recommended values. Analytical results were recalculated using the recommended values for BHV-01. A subset of the samples was analyzed at James Cook University (JCU), using normal HF dissolution and quadrupole ICP-MS. The results for control sample WZ1-237 analyzed in both labs showed that REE concentrations measured at James Cook University were on average 7 percent higher than at Monash University. These higher values were corrected for this inter-laboratory variation using individual element factors from the control run of WZ1-237.

REE concentrations were normalized to C1 chondrite values (Sun and McDonough, 1989).

## Results

### Mineralogy and texture

Both the Fubilan and Sydney altered stocks contain sub- to anhedral K-feldspar, quartz, biotite, sericite, and occasionally magnetite (Fig. 2, Table 2). These minerals are typical of, but not exclusive to, K-metasomatized rocks in porphyry systems (Evans, 1993). We observe a decrease in modal content of this K-rich assemblage with increasing distance from the main Cu bodies, while plagioclase, euhedral magnetite, hornblende and pyroxene modal abundances increase (Fig. 2, Table 2). Alteration intensity decreases outwards from the main center of alteration in the Fubilan Monzonite Porphyry (Fig. 3). The main difference between weakly altered and moderately to strongly altered rocks is the greater abundance of K-feldspar, quartz and anhedral biotite in altered rocks. The highly altered rocks also have a larger proportion of anhedral minerals. Full details are given in Table 2.

The style of alteration in the Ok Tedi deposit conforms to the diorite model (Hollister, 1975), which is based on a number of Cu-Au mineralized porphyritic monzonites. It is characterized by potassic and propylitic alteration zones and a notable occurrence of magnetite in all alteration zones. It generally lacks phyllitic and argillitic alteration zones. Significant amounts of gold may occur, whereas Mo/Cu ratios are low.

In the prominent alteration zones (intensity 2–3) at Ok Tedi, textures are consistent with reactions of magmatic

TABLE 2. Typical Petrographic Differences between the Three Levels of Alteration Intensity in Samples from the Ok Tedi Mine Area

Alteration intensity	Di	Ttn	Hbl	Pl	Kfs	Qtz	Bt	Zrn	Mag	Ccp	Py	Chl	Ms	Ap	Rt	Alteration textures
<i>Fresh to weak</i>						-	-	-		-	-	-	-	-	-	Occasional partial magnetite replacement of pyroxene, occasional selective mica replacement of hornblende, selective replacement of enclave material by biotite and magnetite
<i>Moderate</i>										-				-	-	Selective to pervasive replacement of plagioclase by K-feldspar, mafic phenocrysts by biotite, cryptocrystalline matrix with quartz infill, most crystals are fractured
<i>Intense</i>								-		-				-	-	Pervasive pseudomorphic replacement of plagioclase by K-feldspar and biotite, mafic phenocrysts by magnetite and biotite. Common micro-crystalline quartz and quartz infill near replacement textures. Texture destroyed for exoskarn samples; all crystals fractured

Abbreviations: Apt = apatite, Bt = biotite, Ccp = chalcopyrite, Chl = chlorite, Di = diopside, Hbl = hornblende, Kfs = K-feldspar, Mag = magnetite, Ms = muscovite, Ttn = titanite, Pl = plagioclase, Py = pyrite, Qtz = quartz, Rt = rutile, Zrn = zircon

common      abundant      dominant      — = sparsely present      - = present

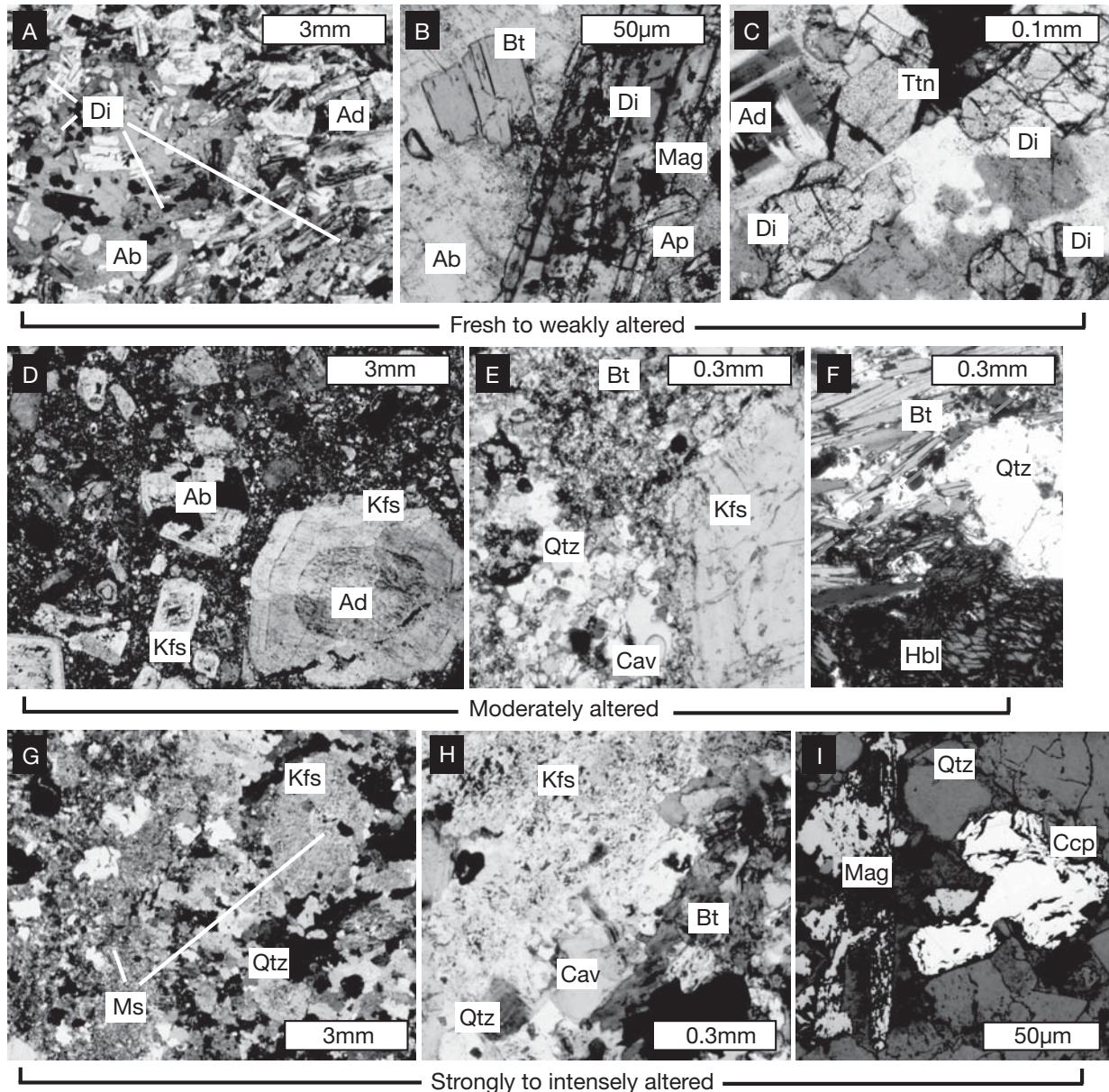


FIG. 2. Photomicrographs of the three characteristic alteration intensities observed in the Ok Tedi intrusive complex. The upper row (A-C) represents fresh to weakly altered rocks of intensity 1, the middle row (D-E) represents moderately altered rocks (intensity 2), and the lower row (G-I) represents intensely altered rocks (intensity 3). Images A-H are transmitted, cross-polarized light images, I is a reflected light image. A. Sample DDH 825-680m: fresh monzogabbro with seriate trachytic texture and albitic oikocrysts. The phenocryst assemblage consists of euhedral andesine (Ad), diopside (Di), titanite (Ttn), biotite (Bt), and minor hornblende (Hbl) and apatite (Ap). B. Sample DDH 825-680m: monzodiorite with euhedral biotite phenocrysts surrounded by albite (Ab), indicating a magmatic origin. Diopside is partially replaced by magnetite (Mag) along cracks, indicative of weak alteration. C. Sample DDH 848-453m: monzodiorite-monzogabbro with euhedral titanite surrounded by andesine. D. Sample DDH 381-356m: porphyritic monzonite with sub- to anhedral albite and K-feldspar (Kfs) crystals. Feldspar megacryst contains an andesine core overgrown by a rim of Kfs with microinclusions of chalcopyrite, hinting at the hydrothermal nature of this rim. Other plagioclase phenocrysts, which are mostly albite (Ab), have K-feldspar rims and contain fractured cores that are partially replaced by opaque minerals. E. Sample DDH 381-456m: monzonite porphyry with anhedral fine-grained biotite, anhedral quartz (Qtz), and cavities (Cav) and a groundmass of K-feldspar phenocrysts. Although the presence of quartz and cavities are not unambiguously hydrothermal features, their association with secondary biotite argues for a magmatic-hydrothermal origin. Unlike unaltered rocks, feldspar phenocrysts are not euhedral—the plagioclase crystals are especially corroded. F. Sample DDH 376-434m: monzonite porphyry with fine-grained biotite-quartz vein (upper part of image), next to a hornblende crystal that is partially replaced by opaque material and possibly biotite. G. Sample DDH 833-218m: the original rock texture is completely destroyed and the specimen now contains abundant, very fine grained muscovite (Ms), abundant fine-grained anhedral quartz, and K-feldspar that is partly replaced by muscovite. H. Sample DDH 833-218m: very fine grained biotite, quartz, cavities, and K-feldspar that is partially replaced by opaque material. I. Sample DDH 508-366m: fine-grained anhedral magnetite and chalcopyrite (Ccp) in association with quartz. The spongy magnetite texture is suggestive of a replacement reaction, rather than free crystal growth.

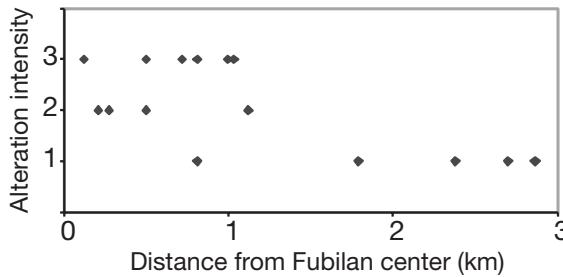


FIG. 3. Horizontal distance of drill hole location to the center of the Fubilan monzonite porphyry vs. alteration intensity. Zones of moderate to intense alteration generally occur within a radius of 1.5 km from the Fubilan center.

minerals with hydrothermal fluids (Fig. 2). Idiomorphic replacement of plagioclase by K-feldspar is common, as evidenced by the gradual substitution of plagioclase by K-feldspar through rim alteration. Other examples are remnant mafic minerals such as clinopyroxene and hornblende overgrown by biotite and sericite. Oxides such as rutile and magnetite commonly replace titanite and rare ilmenite. Chalcopyrite commonly occurs as overgrowths or adjacent to magnetite grains, indicative of “sulfidation” of iron oxides by hydrothermal fluids (Einaudi et al., 2003). The presence of these mineral reaction textures correlates with rocks containing abundant features indicative of the former presence of fluids, such as abundant microcracks, quartz fillings, vesicles and miarolitic cavities.

Strongly altered magmatic rocks (intensity 3) close to the contact with marble surrounding the Sydney Monzodiorite are characterized by Ca-garnet and Ca-pyroxene assemblages and termed “endoskarns”, in which magmatic textures can still be recognized. Other parts of these endoskarns consist of clay mineral assemblages. Magnetite  $\pm$  sulfide “exoskarns” occur in various parts of the mine area, especially in the country rock around the Sydney Monzodiorite. In most cases, the original composition and texture of this rock type are unidentifiable, but the occasional preservation of fossils and slump textures strongly suggests their origin is at least partly sedimentary. These exoskarns are economically important and are included for comparison but are not the main focus of this work.

As the assemblages change from primary magmatic Pl, Bt and Hbl in stage 1 to secondary, hydrothermally precipitated/ altered Kfs, Bt, Ms, Py, Mag in stage 3, the accessory minerals decrease in size and become increasingly anhedral (Fig. 4), except zircon. Correspondingly, the modal content of REE-rich accessory minerals change from apatite- and titanite-dominated assemblages to zircon-, rutile-, thorite-, monazite- and xenotime-dominated (Fig. 5).

Petrographic microscope and SEM images of zircon-bearing rocks reveal that zircon crystals are between 5 and 150  $\mu\text{m}$  in size. In contrast to other minerals, they are euhedral in moderately to intensely altered samples, and subhedral in weakly altered samples. Five zircon separates were investigated by transmitted light microscopy and compared with SEM images of thin sections (Fig. 6). All separated zircons showed characteristics typical of unaltered magmatic zircons (Fig. 6), such as elongate prismatic shapes and oscillatory zoning in cathodoluminescence images, and melt inclusions

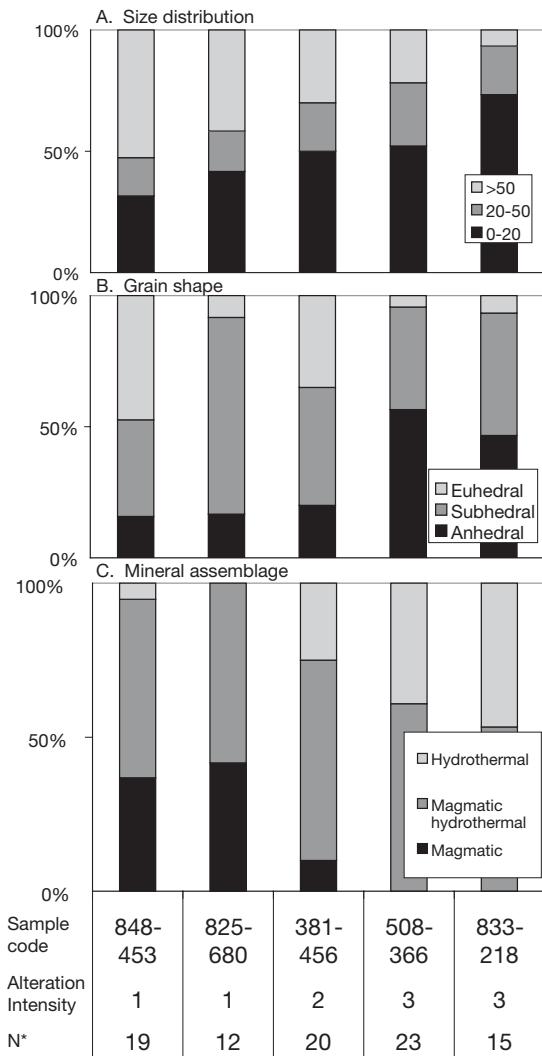


FIG. 4. Charts of accessory mineral percentages using three parameters from SEM analysis of selected samples. N\* is the number of documented grains. A. Size distribution of accessory minerals (in  $\mu\text{m}$ ). The percentage of small grain sizes ( $<20 \mu\text{m}$ ) increases with alteration intensity. B. The percentage of accessory minerals with anhedral grain shape increases with alteration intensity, whereas euhedral shapes decrease. C. Nature of the mineral assemblage: magmatic (andesine, pyroxene, titanite, magmatic biotite), magmatic-hydrothermal (replacement textures by quartz, K-feldspar, hornblende, biotite, and anhedral), or hydrothermal (magnetite, quartz, rutile, hydrothermal biotite, sulfides). Magmatic-hydrothermal assemblages dominate all intensities, indicating that the assemblages are transitional. The percentage of magmatic assemblages is highest for rocks of low alteration intensity, whereas the percentage of hydrothermal assemblages is highest for rocks of high alteration intensity.

(Corfu et al., 2003). This implies that hydrothermal remobilization of zircons was relatively limited. With increasing alteration intensity however, the surface of zircon crystals becomes increasingly pock-marked. For example, zircons from sample 508-366m (alteration intensity 3) show spongy, amorphous textures on the crystal faces, in some cases penetrating halfway to the crystal cores (Fig. 6C). We also found single and two-phase fluid inclusions in the zircons from this sample. We interpret these findings as evidence for some zircon-fluid interaction in highly altered samples.

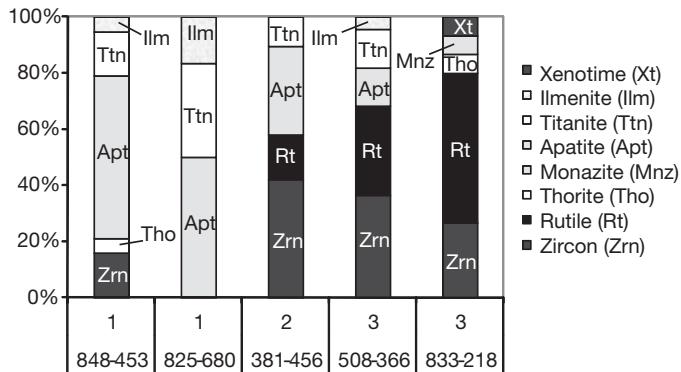


FIG. 5. Percentage chart of documented REE-rich accessory minerals per sample, for different alteration intensities. Titanite and apatite decrease with increasing alteration intensity, whereas rutile increases. The most altered samples also contain xenotime, monazite, and thorite. These minerals may have been formed as replacement products of zircons and scavenged their REEs, or they may have crystallized from the melt or fluids if zircon formation, which would have scavenged HREE, was unfavorable.

### Geochemistry

Silica contents vary from ~56 to ~69 wt % over the range of analyzed samples (Table 3), with the exceptions of sample 848 with 44 wt % silica (an enclave within the monzodiorite) and skarn samples 855-159m, 893-55m and 964-30m. All rocks, including the least hydrothermally altered samples, have high alkali and low iron and magnesium contents, are chemically classified as shoshonitic series, and modally as monzogabbros, monzodiorites, monzonites, and monzo-syenites (Bamford, 1972; Rush and Seegers, 1990).

Total REE concentrations at Ok Tedi vary from less than 0.7 to 239 ppm (Fig. 7 inset, Table 3). All samples are enriched in REE relative to chondrite values and are enriched in LREE relative to HREE. Excluding skarn samples, fresh to weakly altered magmatic rocks show higher concentrations of total REE (240–115 ppm) than moderately altered rocks (183–42 ppm) and intensely altered rocks (175–47 ppm). The REE content of endoskarns is high at 253 ppm, while the exoskarn has the lowest value of the set at 0.7 ppm. For the purposes of discussion, we separate analytical results of originally magmatic samples and skarn samples, because of their different original composition and mineralogy.

The broad decrease in total REE content with alteration is accompanied by an increase in chondrite-normalized REE slope. Average La/Yb ratios of ~20 for weakly altered samples change to up to 70 for moderately and intensely altered samples. The most strongly altered and REE depleted samples also have positive Ce anomalies. Sample 964-30m, taken from a weathered and clay-altered skarn with relict garnet, is the only sample with a positive Eu anomaly, whereas all other samples show no significant negative or positive Eu anomaly.

With increasing alteration intensity, K<sub>2</sub>O and SiO<sub>2</sub> contents increase, whereas P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, Zr and Y decrease (Fig. 8A-C). Moreover, alteration is accompanied by pronounced deviation from the chondritic Y/Ho ratio (Fig. 8D). In order to determine the relationship between REE content and accessory mineral breakdown, we defined a REE mineral index as the weighted total sum of Zr, Y, P<sub>2</sub>O<sub>5</sub> and TiO<sub>2</sub>, to test whether the bulk of the REE is hosted in zircon, xenotime, rutile or

apatite. The total REE content decreases with these elements' concentrations (Fig. 9), with three exceptions (shaded gray) that are discussed later. The total REE concentration and REE mineral index do not differ significantly for samples of moderate and high alteration intensity (Fig. 9).

Sample 833-218m is unique amongst the rocks studied, being more depleted in REE's than the other intensely altered samples (Fig. 7), consisting mainly of intense alteration minerals (Table 2) but yet having close to chondritic values of Y/Ho (Fig. 8D, Table 3). Another noticeable distinguishing feature of sample 833-218 is that its accessory mineral assemblage is dominated by rutile and lacking apatite (Fig. 5), in contrast to the other intensely altered samples which all contain apatite. The correlation between lack of apatite and lower concentrations of REE suggests that the bulk of REE are hosted by apatite. Furthermore, the chondritic Y/Ho of 833-218 suggests that other processes than apatite destruction are responsible for changing the Y/Ho. This is consistent with reviews that show that Y and Ho are not significantly hosted in apatite (Samson and Wood, 2005).

### Discussion

Here we discuss the evidence that suggests that hydrothermal alteration in porphyry Cu-Au systems causes REE depletion of magmatic host rocks. We also discuss the possible inconsistencies in our data and the implications of our results for the interpretation of trace-element data from similar magmatic-hydrothermal systems.

#### Hydrothermal alteration and REE depletion

At Ok Tedi, the change from a magmatic assemblage consisting of Di-Pl-Hbl/Bt- (Ttn) to an assemblage of Pl-Kfs-Bt-Qtz corresponds to the measured increase in alkali and silica contents (Table 2). This is similar to other porphyry copper deposit systems that formed from fluids exsolved due to decompression and crystal fractionation (Reed, 1979; Dilles and Einaudi, 1992). Fluid exsolution occurs at the late stages of magma fractionation and is therefore naturally associated with alkali- and silica-rich, fractionated magmas. Typical magma fractionation is associated with an increase in REE contents (Wilson, 1989; Candela and Piccoli, 2005). However, at Ok Tedi the observed relationship is decreasing REE content with increasing alkali and silica content of magmatic rocks. Thus, rather than being a feature of the original magmatic rocks becoming more fractionated, the cause for the observed REE depletion is an increase in hydrothermal alteration intensity.

Element mobility is further demonstrated by the strong deviation of many elements including REE from the line of constant mass (Grant, 1986), represented by the Al<sub>2</sub>O<sub>3</sub> isocion (Fig. 10), one of the few elements that does not change concentration after alteration and can therefore be considered immobile. Important gains of Cu, SO<sub>3</sub>, SiO<sub>2</sub> and K<sub>2</sub>O (Fig. 10) are consistent with the occurrence of chalcocite-quartz veins and K-feldspar alteration in the most altered samples. The loss of many elements including REE, Y, Ti, P and many of the major elements (Fig. 10) is interpreted as an effect of hydrothermal remobilization. This is supported by the following: a) decrease in size and increasing anhedral shape of the REE-rich accessory minerals with increasing degrees of alteration, including the presence of spongy

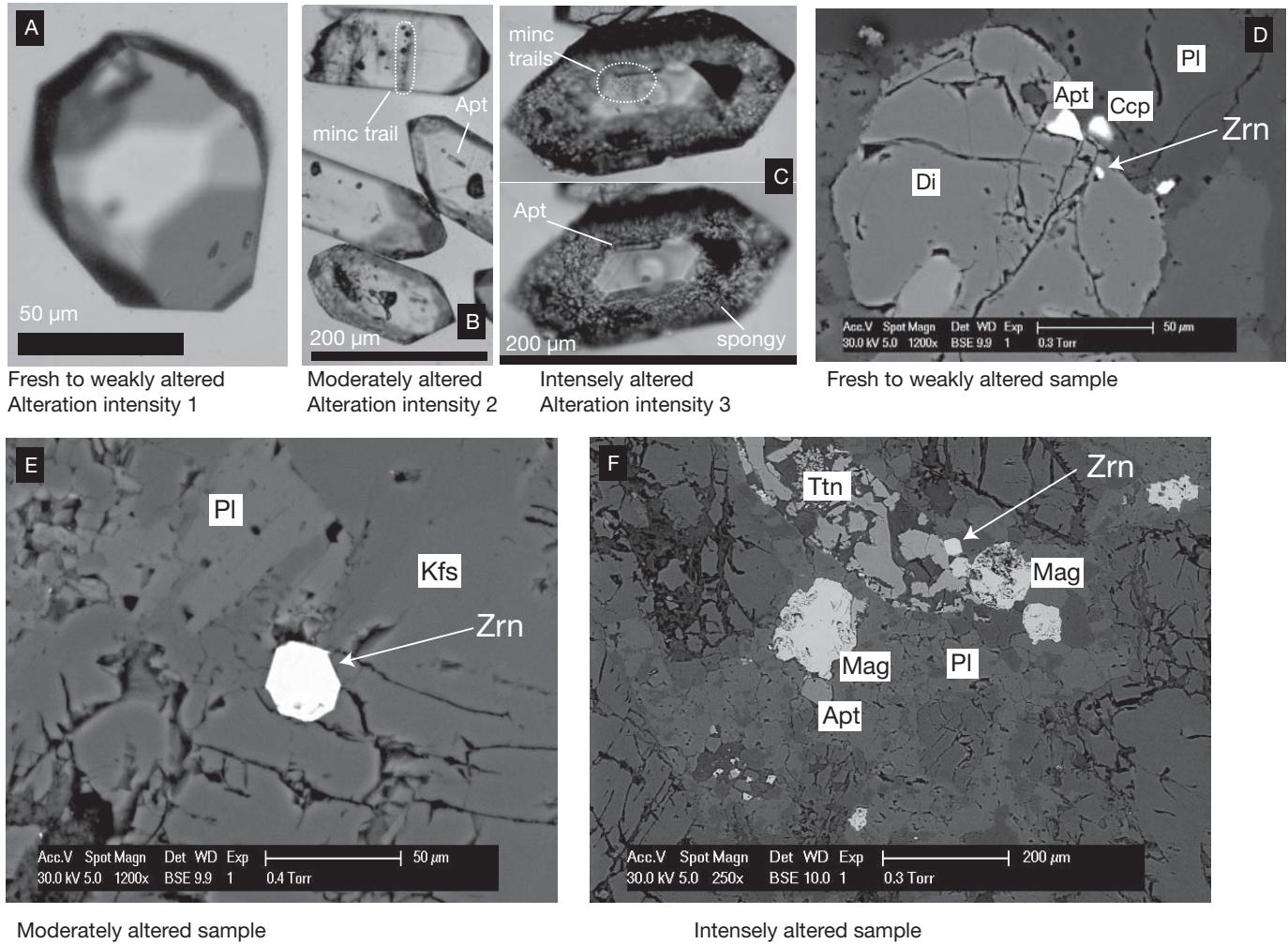


FIG. 6. Photomicrographs of zircon separates (A-C) and SEM images of in situ zircons (D-F) from samples of different alteration stages. Zircons (Zrn) crystals are indicated by a white arrow in SEM images. A. 848-419m: monzodiorite with alteration intensity 1. Zircon crystals are euhedral, planar-faced, contain few to no inclusions and no significant alteration. The maximum crystal size is 100  $\mu\text{m}$ . B. 381-399m: monzonite porphyry with alteration intensity 2. Zircon crystals are euhedral, and many contain mineral inclusions such as apatite (Apt), melt-inclusion (mine) trails and some contain fluid inclusions. There are a few spongy surfaces, such as the bottom zircon. C. 508-366m: monzonite porphyry with alteration intensity 3. Many zircon crystals have spongy textures. Two different focus depths from the same zircon are shown to illustrate the penetration of this texture into the crystal. In general, the zircon crystals are euhedral and contain mineral, melt, and fluid inclusions. D. 848-453m: monzodiorite, alteration intensity 1. This rock contains a subhedral zircon crystal of ~8- $\mu\text{m}$  width within a diopside (Di), and thus may have been shielded from any possible alteration. The small crystal size and subhedral shape, together with the relatively primitive composition of the rock, suggest this was one of the first zircons to crystallize. This zircon may have experienced some hydrothermal fluid flow, however, since chalcopyrite (Ccp) has been deposited close to the zircon and the nearby diopside and plagioclase (Pl) contain fractures. E. 381-456m: monzonite porphyry with alteration intensity 2. This rock contains a 25- $\mu\text{m}$ -wide euhedral zircon, which was located within K-feldspar (Kfs) surrounded by plagioclase. Cracks in the K-feldspar suggest that the zircon was within a zone of fluid-rock interaction that produced K-feldspar alteration and was thus subject to hot (>400°C), acidic fluids. F. 508-366m: monzonite porphyry with alteration intensity 3. This rock contains a 40- $\mu\text{m}$ -wide euhedral zircon bordering magnetite (Mag) and a large aggregate of small titanite (Ttn) crystals that suggest replacement or breakdown. The surrounding assemblage of anhedral K-feldspar, Na-plagioclase, magnetite, and apatite is typical of this alteration intensity.

zircons in altered rocks, 2) decrease in REE mineral index (P, Zr, Ti, Y), suggesting accessory minerals break down in regions of intense alteration, and 3) fractionation of Y from Ho in altered rocks, with strong deviations of Y/Ho values from chondritic ratios (Table 3, Fig. 8 D). Zr was mobilized from strongly altered sample 833-218, but mobility of Zr cannot be proven for the entire sample set due to the limited Zr data and the problem of a nugget effect discussed below.

A potential alternative explanation for the loss of many elements (Fig. 10) would be dilution by addition of K-feldspar and quartz. However, since  $\text{Al}_2\text{O}_3$  remains constant, addition of K-feldspar is unlikely. Silica gain is only 10 wt%, much lower than the calculated REE loss of 30% ( $\text{C}^{\text{A}}/\text{C}^{\text{0}} = 0.7$ , Fig. 10). Therefore, dilution can at best play only a minor role.

At the Northparkes porphyry deposit, vapor separation from magma during degassing, with concomitant partitioning

TABLE 3. Analytical Results of Whole-Rock Major and Trace Elements from Samples of the Ok Tedi Intrusive Complex (refer to Fig. 1 for sample locations)

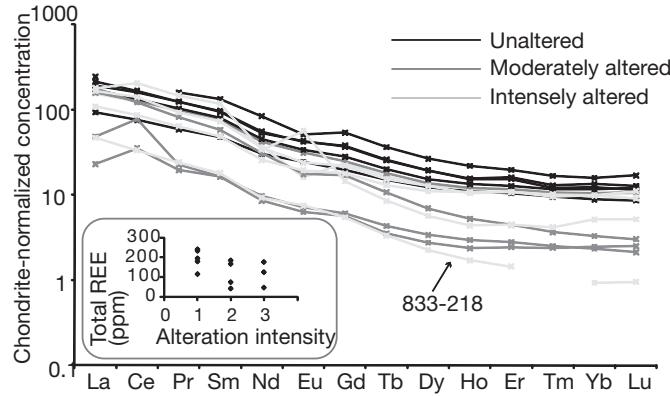


FIG. 7. REE concentrations normalized to C1 chondrite values (Sun and McDonough, 1989). Samples that are altered (intensities 2 and 3) generally have lower normalized REE values, and steeper slopes. The total REE concentration decreases with alteration intensity (lower left inset).

of REE into the vapor phase, was suggested by Lickfold et al. (2007) to explain the lower concentrations of REE and convex shape of REE patterns of intensely altered samples. Limited evidence from solubility experiments supports this explanation, e.g., Flynn and Burnham (1978). However, the solidus of typical intermediate magmas such as those of porphyry copper deposits ( $\sim 800^{\circ}\text{C}$ ) is above the upper limit ( $\sim 500^{\circ}\text{C}$ ) of measured fluid inclusion temperatures (e.g., Lickfold et al., 2003) and calculated alteration temperatures (e.g., Seedorff et al., 2005) from porphyry copper deposits. Therefore, it is reasonable to assume that most REE-rich accessories crystallized before or in the early stages of fluid exsolution.

Furthermore, more abundant rock-forming elements that easily complex with Cl, such as K and Na, would partition into such fluids to a larger extent than the REE. For example, in high T fluid inclusions the average NaCl equiv can be up to 40 wt percent (Heinrich et al., 1999). The alkali content of REE-depleted rocks is expected to decrease in parallel with

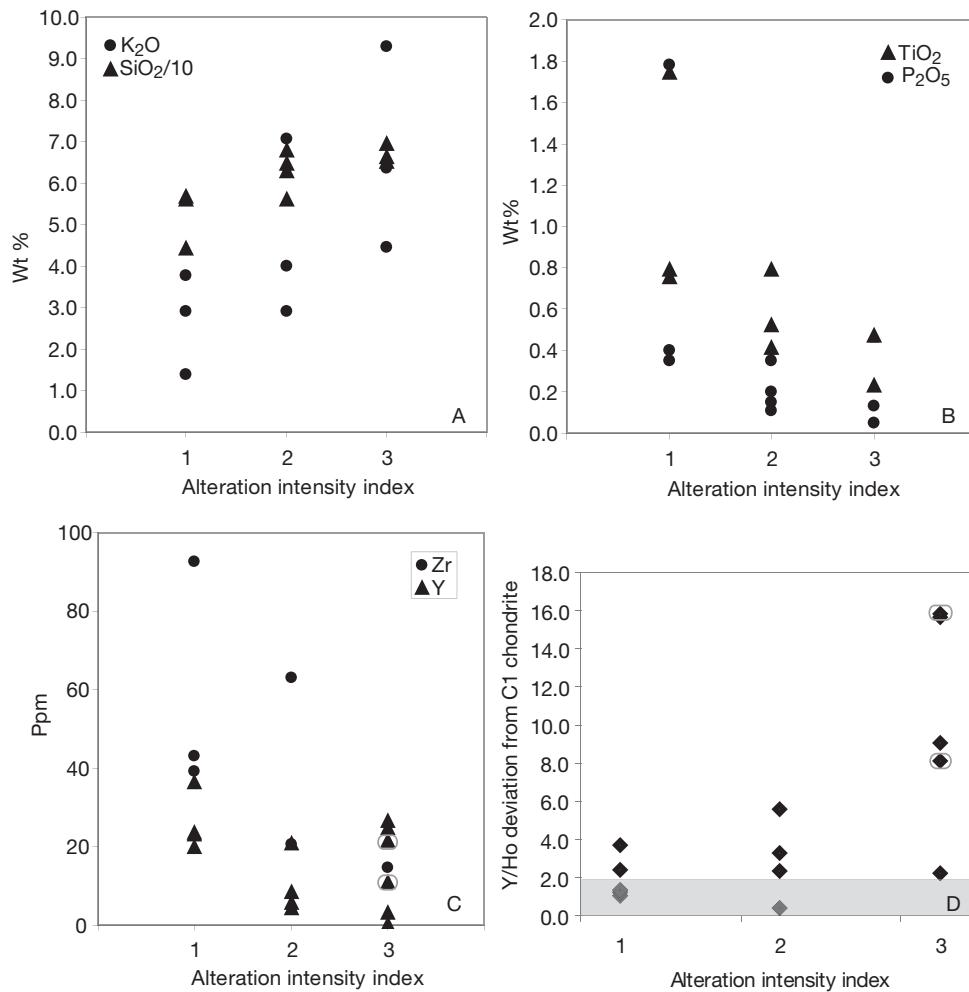


FIG. 8. Alteration intensity vs. different geochemical variables. A. Alteration intensity shows a positive correlation with  $\text{SiO}_2$  and  $\text{K}_2\text{O}$  content, suggesting K-metasomatism and quartz veining were responsible for the compositional shift. B. A negative correlation with  $\text{TiO}_2$  and  $\text{P}_2\text{O}_5$  content, suggesting removal of titanite and apatite. C. A negative correlation with Zr and Y, suggesting decreasing contents of zircon and Y-bearing minerals (monazite, garnet?), and D. A positive correlation of the deviation between chondritic Y/Ho ratio  $27.7 \pm 1.9$  (Bau, 1996) and the sample ratio, suggesting processes other than magmatic fractionation modified the REE content. Skarn samples are circled; major element data is not available for the skarns, hence they do not appear in A and B.

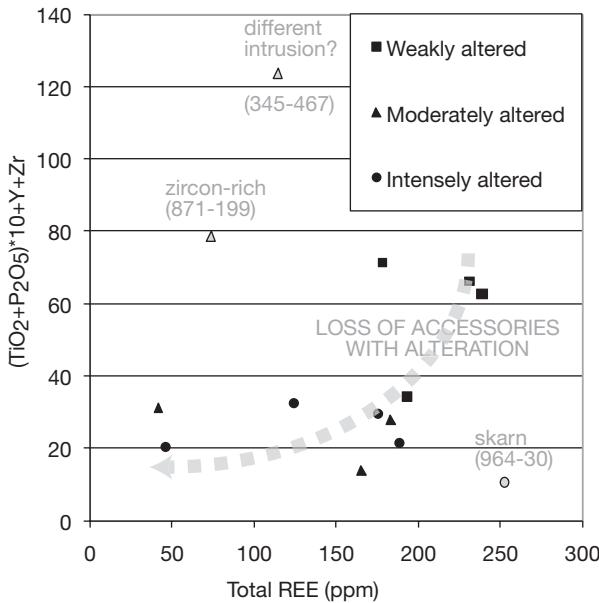


FIG. 9. Total REE concentration vs. REE mineral index (formula given on the axis). Samples of high alteration intensity (circles) have lower total REE and REE mineral index than those with low alteration intensity (squares). Exceptions to this trend are labeled and have gray symbols; they are explained in the text.

decreasing REE, as both REE and alkalis would be transported away. The absence of such a positive correlation between REE and alkali depletion in the rocks at Ok Tedi suggests the mechanism of REE fluid partitioning from a crystallizing magma was unlikely to have caused the trends observed.

Finally, we also discard magma mixing (Hattori and Keith, 2001) as a viable explanation for the distinctly depleted REE

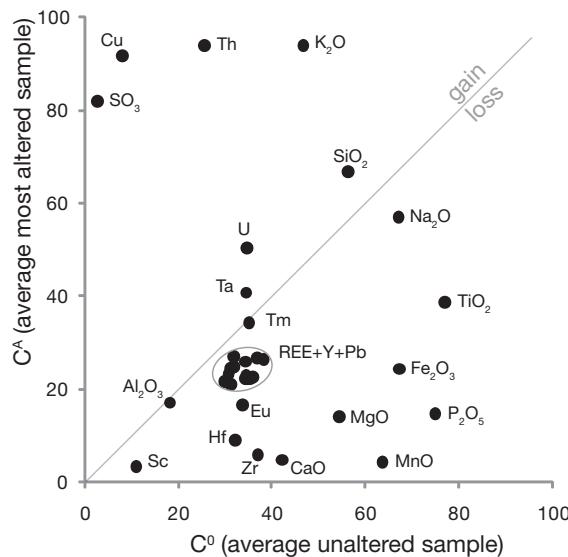


FIG. 10. Isocon diagram after Grant (1986), showing elemental gains and losses based on the immobility of  $\text{Al}_2\text{O}_3$ .  $\text{C}^0$  is the average of two analyses of relatively fresh samples (871-199 and 825-680) and  $\text{C}^A$  is the average of three analyses of intensely altered samples (833-218, 364-550, 508-366). Note that elemental and oxide concentrations are scaled to fit the diagram following methods similar to Grant's (2005).

concentrations at Ok Tedi because typical mixing and mingling features (e.g., mafic blobs or minerals in felsic melts, reaction textures, coronas, mafic magmatic rocks within the intrusive complex) are absent.

#### Possible inconsistencies

We noted that Fig. 9 has three exceptions:

1. Sample 345-467 is classified as moderately altered, but has trace and rare-earth element contents typical of intensely altered samples, except Zr, which is more typical of slightly to moderately altered samples. Petrographic inspection of this sample confirms the presence of numerous zircons, which implies that they do not contribute significantly to the REE content of the sample. Thus, this exception is best explained by a discrepancy between the results of textural and geochemical analysis.

2. Sample 871-199m contains 115 ppm total REE, which is the average for moderately altered samples. However, Zr is 2 times higher than average, which may be due to a cumulate or nugget effect of zircons, although not apparent in thin section. This sample was taken from a drill hole far from the mine site with little stratigraphic context and could belong to a different magmatic pulse than the Fubilan or Sydney intrusions, as suggested by the presence of large (3-mm) mafic crystals, which do not appear in other intrusive samples.

3. Sample 964-30, a skarn sample that is unusually high in REE, which may indicate a possible sink for remobilized REE.

Bau (1996) argued that, similar to Y-Ho, the Zr-Hf pair should not fractionate during magmatic differentiation. During experimental alteration of zircon by acidic solutions at  $>400^\circ\text{C}$ , Zr/Hf fractionation was observed in altered domains (Geisler et al., 2003), suggesting that this could happen in real hydrothermal systems. We tested five zircon-bearing samples, which yielded Zr/Hf ratios between 20 and 42. In contrast to Y/Ho, samples with low alteration intensity yielded the largest deviation from the chondritic Zr/Hf value of  $\sim 36.6$  (Bau, 1996). These results suggest that Zr/Hf fractionation is not coupled to Y/Ho fractionation for reasons that remain obscure.

#### Implications

Prior to this study, the extent to which REE can be remobilized by ore-related hydrothermal fluids in porphyry systems may have been underestimated. Our results suggest that the use of REE geochemistry to determine the origin of hydrothermally altered magmatic rocks is fraught with difficulties, and such studies should preferably focus on unaltered samples only. We discuss three particular implications of our results.

Firstly, the REE patterns observed at Ok Tedi are similar to those of other porphyry copper(-gold) deposits, which also show lower values of REE, Zr, Y, P, and Ti for the mineralized (and hydrothermally altered) portions of the magmatic rocks than for unmineralized portions. Examples are Northparkes, Cadia, and Copper Hill deposits in the Lachlan fold belt, Australia (Blevin, 2002; Lickfold et al., 2003), Sierrita, Safford, Ray-Christmas, and Baghdad deposits in Arizona (Anthony

and Titley, 1994; Lang and Titley, 1998), and deposits of the Kerman arc, Iran (Shafiei et al., 2009). We calculated Y/Ho and Zr/Hf ratios for the deposits in Arizona using data from Lang and Titley (1998) and approximately half of the Zr/Hf and Y/Ho ratios are outside the range of chondritic values, implying that REE concentrations in these rocks may no longer represent magmatic values. Similarly, six out of 15 mineralized porphyries from the Kerman arc (Shafiei et al., 2009) have nonchondritic Y/Ho. As such, some of the trends in REE patterns from the above-mentioned deposits can be explained by hydrothermal remobilization, rather than melt source characteristics.

Secondly, our results offer an explanation for the supposed link between porphyry copper deposits and K-rich magmatic rocks (Muller and Groves, 1997; Thiéblemont et al., 1997; Lickfold et al., 2007), and, particularly, adakites (Oyarzun et al., 2001), i.e., those with Sr/Y ratios up to 400 and low Y (<15 ppm) (Martin, 1999). Although unaltered rocks from Ok Tedi are K rich (shoshonitic), in the highly altered zones, K-enrichment (due to K-metasomatism) is accompanied by Sr enrichment and depletion of incompatible, supposedly immobile trace elements such as yttrium. Our results show that Y may be removed from the host rock by hydrothermal fluids, thus providing an alternative explanation for high Sr/Y and low Y of magmatic rocks related to porphyry mineralization. We also calculated that the majority of Y/Ho ratios from “adakitic” volcanic rocks in Ecuador (Chiaradia et al., 2004) are about 22, significantly below the chondrite ratio. We therefore agree with Richards and Kerrich (2007) who, in reviewing the relationship between adakites and mineralization, concluded that the correlation with mineralized porphyries is not unique.

Thirdly, the spongy textures, fractures, and melt and fluid inclusions in zircons in the most altered rocks in the Ok Tedi deposit, combined with the demonstrated mobility of REE and some Zr, raise the question of how to interpret zircon REE geochemistry in porphyry deposits. For example, distinct Ce anomalies have been found in zircons from mineralized porphyries (Ballard et al., 2002) and zircons are also used to obtain crystallization ages from porphyry deposits (e.g., Chuquicamata, Ballard et al., 2001; Ok Tedi, Van Dongen et al., 2010). Previous studies show that zircon geochemistry may be affected by hydrothermal alteration (Nesbitt et al., 1999; Woodhead et al., 2001; Geisler et al., 2003; Hoskin and Schaltegger, 2003; Schaltegger et al., 2005; Schaltegger, 2007; Rene, 2008) and there are a number of reports of hydrothermal zircon (Samson, 1990; Gieré, 1996; Rubatto et al., 2008), with a good example from magmatic-hydrothermal ore deposits in Spain, where zircons were preferentially associated with hydrothermal minerals in zones with the most intense alteration (Nesbitt et al., 1999). In contrast, Ok Tedi zircons are likely to have preserved their original magmatic composition. They have not developed metamict domains because of their young age (Van Dongen et al., 2010), and such domains are a key prerequisite for efficient re-equilibration of zircons in the presence of fluids (Balan et al., 2001; Geisler et al., 2007). Hence, when using zircon geochemistry to study porphyry deposits, petrographic characterization of the zircons in question should accompany the results and be consistent with their interpretation.

## Conclusions

At Ok Tedi, major and minor elements, including Y, P, Ti, and REE, have been remobilized from magmatic rocks through interaction with large volumes of hot, oxidizing, and chloride-rich fluids. REE-rich phases such as titanite, apatite, and zircon were partially destroyed, as evidenced by lower modal abundances of accessory minerals and distinct changes in their shape and size. The elements contained in the accessory minerals were remobilized from regions of high alteration intensity and possibly reprecipitated in nearby skarns. The process produces fractionation relative to unaltered rocks, characterized by whole-rock geochemical features such as nonchondritic Y/Ho and Zr/Hf ratios, lower REE concentrations, and steep or concave upward chondrite-normalized REE diagrams. Similar geochemical features have been observed in other porphyry deposits worldwide. Our results suggest that Y, Zr, P, Ti, and REE are mobile under the conditions that prevail in ore-forming magmatic-hydrothermal systems and extreme care should be taken when using trace and REE data to study the origin and evolution of the magmatic rocks from such ore-forming systems.

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