

Origin of the secondary REE-minerals at the Paratoo copper deposit near Yunta, South Australia

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ABSTRACT

The Paratoo copper deposit, located in the Neoproterozoic to Cambrian Adelaide Geosyncline, South Australia, produced around 360 tons of Cu between 1888 and 1967 from oxidized ores. The deposit is located in the core of a breached, doubly plunging anticline, near a zone of disruption containing brecciated Adelaidean sedimentary rocks and dolerite ('Paratoo Diapir'), and hosted in dolomitic shales of the Neoproterozoic Burra Formation. Near the surface, the mineralization resides mainly in deeply weathered quartz-magnetite-sulphide (pyrite, chalcopyrite) veins (≤ 10 cm wide). At depth, drill cores reveal disseminated magnetite, pyrite, chalcopyrite, copper sulphide and native copper associated with extensive potassic alteration. K-Na-rich fluids also affected the dolerite in the 'Paratoo diapir', resulting in the precipitation of K-feldspar, dravite and K-bearing chabazite-Na. The most likely scenario for the genesis of the Paratoo deposit involves circulation of basinal fluids, focusing into the 'Paratoo Diapir', and ore precipitation through neutralization by fluid-rock interaction with the dolomitic shales hosting the mineralization.

The Paratoo deposit is deeply weathered, with malachite and chrysocolla ($\pm$ tenorite and cuprite) containing the bulk of the copper recovered from the shallow workings. A diverse assemblage of secondary REE-bearing carbonate minerals, including the new species decrespignyite-(Y) and paratooite-(La), is associated with the weathered base metal and magnetite ores. Whole-rock geochemical analyses of fresh and mineralized host rock and of vein material reveals that the mineralization is associated with a strong, albeit highly variable, enrichment in light rare earth elements (LREE). This association indicates that REE and base metals were introduced by the same hydrothermal fluid. The strong negative Ce anomaly found in secondary REE minerals and mineralized rock samples suggests an upgrade of the REE contents in the weathering zone, insoluble Ce⁴⁺ being left behind.

The Fe-oxide-REE-base metal association at Paratoo is also characteristic of the giant Mesoproterozoic Fe oxide copper gold deposit of Olympic Dam, located 350 km to the NW. A similar association is found in the Palaeozoic deposits of the Mt Painter Inlier, 300 km to the NNE. The widespread occurrence of this elemental association in the Province probably reflects the geochemistry of the basement, which contains numerous Mesoproterozoic granites enriched in REE and U.

KEYWORDS: Paratoo copper deposit, South Australia; Adelaide Geosyncline; Rare Earth Elements; Fe oxide copper gold deposit.

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Introduction

THE Paratoo copper deposit is located 30 km SW of Yunta in South Australia (32°40'40" S, 139°19'50" E). Small-scale exploitation of supergene copper ores, including malachite, chrysocolla, and the recently described decrespignyite-(Y), took place between 1888 and 1890 (Brown, 1908). The mine also produced a total of 10 tons of ore containing 26.75% copper between 1899 and 1900. Further attempts to mine the site in 1912–1926 and later in 1965–1967 by heap leaching produced a total of 357 tons of copper. Most recently (2002–2003), Range River Gold Inc. conducted geological mapping and percussion drilling on the prospect for copper and gold.

Until recently, the Paratoo deposit was seen as a small, deeply weathered stratabound copper mineralization occurrence (Nixon, 1967). However, in 1998, an Adelaide collector, Mr John Toma, brought samples of an unidentified blue mineral to the attention of two of the present authors (AP and UK). The mineral was found to contain copper and large quantities of REE and yttrium. Subsequent fieldwork led to the discovery of a rich and unusual assemblage of REE minerals (Table 1), and the blue mineral was described as the new species decrespignyite-(Y), a hydrated copper-yttrium carbonate-chloride with the chemical formula $(Y,REE)_4Cu(CO_3)_4Cl(OH)_5 \cdot 2H_2O$ (Wallwork *et al.*, 2002). A further new, pale blue monoclinic Ca-La-Cu-carbonate was described as paratooite-(La) by Pring *et al.* (2006) with the empirical chemical formula $(REE,Ca,Na,Sr)_6Cu(CO_3)_8$. The other REE-bearing species identified so far include: bastnäsite-(La) (partly very Y-rich), calcio-ancylite-(Nd), caysichite-(Y), donnayite-(Y), kamphaugite-(Y), tengerite-(Y) (Table 1).

All the REE minerals noted to date are supergene weathering products, appearing only within 2 or 3 m of the surface. Decrespignyite-(Y) is the first carbonate mineral containing REE and Cu, reflecting the rarity of this geochemical association in nature. The only other report of a copper-Y carbonate is an unnamed Y-Ba-Cu mineral from the giant Olympic Dam Fe oxide Cu-Au-U-REE deposit (Lottermoser, 1987). This rare mineral occurs as grains $\leq 20 \mu m$, and is associated with primary (i.e. hydrothermal) bastnäsite-(Ce), synchysite-(Ce), florencite-(Ce), monazite-(Ce), xenotime-(Y), britholite-(Ce), apatite and with the U minerals uraninite, coffinite and brannerite. Little is known about the weath-

ering of the Olympic Dam orebody, and it is unknown whether this unusual Y-Ba-Cu phase represents a primary hydrothermal mineral or a weathering product of the Mesoproterozoic hydrothermal mineralization.

Two alternative mechanisms may be responsible for the genesis of the unusual mineral assemblage at Paratoo: (1) the REE were sourced outside the Paratoo copper deposit, transported in saline groundwater, and came into contact and reacted with the pre-existing copper mineralization. This possibility is supported by the fact that saline groundwaters occur in salt-laden Australian soils, and such groundwater is able to carry significant amounts of REE. For example, groundwaters in mineralized regions of the Yilgarn Craton of Western Australia containing between 46,000 and 306,000 ppm total dissolved salts carry up to 685 ppb Y, 803 ppb La and 1118 ppb Ce (see Carey *et al.*, 2003 for location of the samples and their geological and hydrological framework); (2) the REE and copper were transported by the same hydrothermal fluid, and were deposited simultaneously at Paratoo. During subsequent weathering, leaching of the unusual base metal-REE mineralization led to the formation of a unique assemblage of secondary REE-Cu-carbonate minerals.

In an attempt to resolve the origin of the Paratoo deposit and its suite of secondary REE minerals, we measured the concentrations of REE in 100 rock samples collected around the Paratoo prospect, and then studied the mineralogy of the REE in some anomalous samples with electron microscopy. In this report, we combine these results with new field mapping and observations from available diamond cores to establish a framework for the genesis of this deposit and its unique assemblage of secondary REE minerals. In particular, we investigate whether the REE found in secondary minerals were associated with the base metal mineralization, or were introduced well after the base metals. We also discuss the relationship between the elemental association found at Paratoo and that of the giant Olympic Dam Fe oxide copper gold uranium deposit, located 350 km to the NW (Lambert *et al.*, 1987).

Geological and metallogenic settings of the Paratoo Cu deposit

The Paratoo deposit is located in sedimentary rocks of the Adelaide Geosyncline, which is a Neoproterozoic to Middle Cambrian complex of

TABLE 1. Secondary minerals identified at the Paratoo copper deposit, South Australia.

Mineral	Chemical formula
<i>HREE</i> enriched	
Caysichite-(Y)	$(\text{Ca}, \text{Y}, \text{Er})_4 \text{Y}_4 \text{Si}_8 \text{O}_{20} (\text{CO}_3)_6 (\text{OH}) \cdot 7 \text{H}_2\text{O}$
Decrespignyite-(Y)	$(\text{Y}, \text{REE})_4 \text{Cu} (\text{CO}_3)_4 \text{Cl} (\text{OH})_5 \cdot 2 \text{H}_2\text{O}$
Donnayite-(Y)	$\text{NaSr}_3 \text{CaY} (\text{CO}_3)_6 \cdot 3 \text{H}_2\text{O}$
Kamphaugite-(Y)	$\text{Ca}_2 (\text{Y}, \text{Dy}, \text{Gd}, \text{Nd})_2 (\text{CO}_3)_4 (\text{OH})_2 \cdot 3 \text{H}_2\text{O}$
Tengerite-(Y)	$\text{Y}_2 (\text{CO}_3) \cdot 2 - 3 \text{H}_2\text{O}$
<i>LREE</i> enriched	
Bastnäsitate-(La)	LaCO_3F (partly very Y-rich)
Calcio-ancylite-(Nd)	$(\text{Nd}, \text{Ca}, \text{Sr}) \text{CO}_3 (\text{OH}, \text{H}_2\text{O})$
Paratooite-(La)	$(\text{REE}, \text{Ca}, \text{Na}, \text{Sr})_6 \text{Cu} (\text{CO}_3)_8$
Major secondary copper minerals (by abundance)	
Malachite	$\text{Cu}_2 \text{CO}_3 (\text{OH})_2$
Chrysocolla	$(\text{Cu}, \text{Al})_2 \text{H}_2 \text{Si}_2 \text{O}_5 (\text{OH})_4 \cdot n \text{H}_2\text{O}$
Tenorite	CuO
Cuprite	Cu_2O
Others	
Analcime	$\text{Na} (\text{AlSi}_2) \text{O}_6 \cdot \text{H}_2\text{O}$
Azurite	$\text{Cu}_3 (\text{CO}_3)_2 (\text{OH})_2$
Baryte	BaSO_4
Calcite	CaCO_3
Celestite	SrSO_4
Chalcedony	SiO_2
Connellite	$\text{Cu}_{19} \text{Cl}_4 \text{SO}_4 (\text{OH})_{32} \cdot 3 \text{H}_2\text{O}$
Gypsum	$\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$
Nontronite	$\text{Na}_{0.3} \text{Fe}_3^{3+} (\text{Si}, \text{Al})_4 \text{O}_{10} (\text{OH})_2 \cdot n \text{H}_2\text{O}$
Pseudomalachite	$\text{Cu}_5 (\text{PO}_4)_2 (\text{OH})_4$
Siderite	FeCO_3

rift and sag basins flanking the eastern margin of the Gawler Craton and western margin of the Curnamona Province (Fig. 1). The basins are underlain by Palaeoproterozoic to Mesoproterozoic cratonic basement. The Adelaide Geosyncline is filled with a thick sequence (up to 10 km) of sedimentary and minor volcanic rocks. Equivalent, but thinner (up to 800 m), sedimentary rocks were deposited over the Gawler Craton (Stuart Shelf; Lambert *et al.*, 1987; Preiss, 1990).

The oldest rocks of the Geosyncline belong to the Callanna Group (Willouran), and consist of basal clastics, carbonates and mafic lavas (Arkaroola Subgroup), followed by halite-bearing, mixed carbonate and clastic sediments deposited under evaporitic conditions (Curdimurka Subgroup). Basalts of the Woollana Volcanics, located near the base of the Callanna Group, have been dated at 827 ± 6 Ma

(Wingate *et al.*, 1998). Rare rhyolitic lavas and tuffs occurring probably near the top of the Callanna Group are dated at ~ 800 Ma (Rook Tuff, 802 ± 10 Ma; Oodla Wirra Volcanics, 798 ± 5 Ma). There are only limited exposures of Callanna Group rocks in the Adelaide Geosyncline; they are commonly observed in a disrupted state within diapiric structures that intrude younger Neoproterozoic and lower Cambrian sediments (Drexel *et al.*, 1993). The evaporite horizons played an important role in diapir formation (Paul *et al.*, 1999). Diapirism was probably initiated by sediment loading during the Neoproterozoic–Lower Cambrian and, along with associated faults, reactivated during the Cambro-Ordovician Delamarian Orogeny (Dyson, 2001).

The Burra Group (Torrensian) overlies the Callanna Group, and consists predominantly of shales and dolomitic sediments. The overlying Umberatana group includes a thick series of

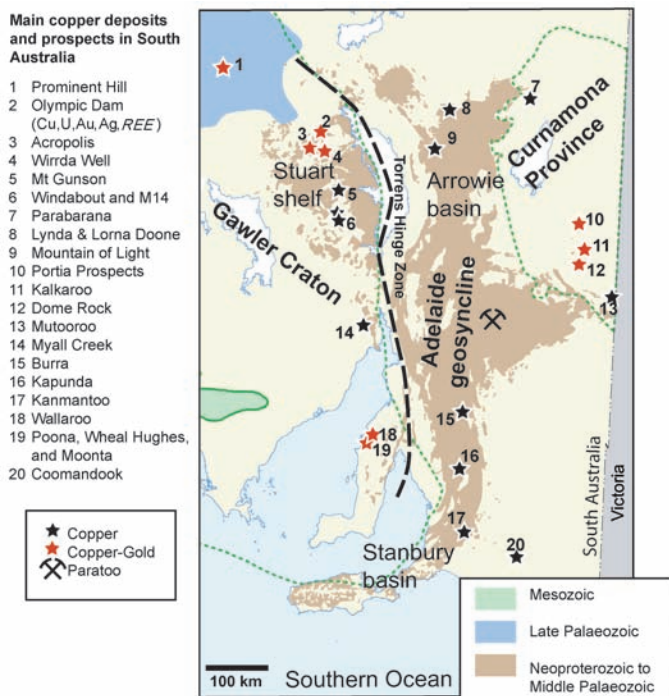


FIG. 1. Geological provinces of South Australia and location of the major copper deposits and prospects. Modified from data and maps provided by Primary Industry and Resources South Australia (PIRSA).

diamictite breccias, interpreted to be tillites (e.g. Young, 1992). The post-glacial Wilpena Group of late Marinoan age consists of siltstone, sandstone and minor carbonate, and the deltaic ABC Range Quartzite records the most extensive marine inundation of the Adelaide Geosyncline.

Sedimentation ceased at the onset of the Delamerian orogeny. The orogen resulted in folding and faulting of the Adelaide Geosyncline sediments and very low to low-grade (zeolite to lower greenschist facies) metamorphism over most of the basin. Deformation of the geosyncline has formed the Adelaide Fold Belt which is subdivided into four main structural domains: the southern Adelaide Fold-Thrust Belt, the Nackara Arc in the east, the central Flinders Ranges in the mid-north and the northern Flinders Ranges in the far-north (Marshak and Flöttmann, 1996; Paul *et al.*, 1999). Paratoo is located in the Nackara Arc in an area where the strike of Adelaidean strata swings from a north-northeasterly direction to an east-northeast orientation.

There is evidence of significant but small-scale, post-Delamerian igneous activity throughout the

Adelaide Geosyncline. Mesozoic lamprophyric intrusives, including kimberlites, some of which are diamond-bearing (e.g. Black *et al.*, 1993; Lindsay, 2003), are widespread, particularly near Terowie, 50 km southwest of Paratoo.

The Adelaide Geosyncline and Stuart Shelf provinces host a large number of stratabound and structurally-controlled copper, gold and lesser Pb-Zn deposits. Historically, copper has been the most important commodity mined. Copper mineralization is widespread in both Neoproterozoic sedimentary rocks and in underlying Palaeoproterozoic-Mesoproterozoic cratonic basement. Deposits can be divided into the following settings/genetic types (e.g. review by Lambert *et al.*, 1987; Fig. 1):

(1) Basement-hosted early Mesoproterozoic to late Palaeoproterozoic hydrothermal deposits related to bimodal alkali-rich igneous activity (~1.63 to 1.51 Ga; e.g. Pollard, 2006; Johnson and Cross, 1995). This includes the giant Fe oxide Cu-U-Au-REE deposit of Olympic Dam, containing in excess of 4,430 millions tons at 1.1 wt.% Cu, 0.4 kg/ton U₃O₈ and 0.5 g/ton Au,

as well as significant amounts of *REE* which are not recovered (BHP Billiton company presentation, September 2006). The Olympic Dam is located in the Stuart Shelf region, underneath ~350 m of Adelaidean sediments (Fig. 1). The major historical production centres of Moonta and Wallaroo (economic Cu, Au; traces of U, *REE*) are considered to be part of the early Mesoproterozoic Olympic Fe oxide Cu-Au province in the eastern Gawler Craton. These hydrothermal deposits are hosted in fracture zones in feldspar porphyry and schists (Parnell, 1989; Lambert *et al.*, 1987; Morales Ruano *et al.*, 2002).

(2) Copper mineralization related to transgressive unconformities on the Stuart Shelf. At Mt. Gunson, sulphides occur in a network of fracture-filling veins in periglacially brecciated sandstone of the Mesoproterozoic Pandurra Formation and in unconformably overlying Neoproterozoic Adelaidean sedimentary rocks (Tonkin and Creelman, 1990). Mining took place in several periods for a total production of ~142,000 tons of contained copper from ~8.4 Mtons of ore (average grade 1.7%).

(3) Hydrothermal copper mineralization associated with igneous activity in the Neoproterozoic Burra Group (Wright, 1975). The Burra mine occurs adjacent to a silicified 'diapir' characterized by intense alteration (talca, chlorite, mica $\pm$ feldspar, pyrite, tourmaline), and is hosted in shaley dolomites of the Burra Group proximal to a small quartz-feldspar intrusion.

(4) Sediment-hosted base metal mineralization found within or adjacent to major diapiric structures, e.g. the Arkaba, Beltana, Blinman, Spalding, Oraparinna and Paratoo Diapirs. Dyson (2001) grouped these deposits into five types – Mississippi valley type, sandstone-hosted type, redbed type, Kupferschiefer type and Green River type – based on the nature of the sediment host and geochemistry of the ore fluids. The relationship of diapirism to mineralization is controversial and poorly understood (Dyson, 2001). Deposits can have mineralization features which are syngenetic, diagenetic and/or epigenetic in nature. It appears likely that diapirs acted as conduits for circulating basinal fluids and metals were precipitated through fluid-rock interaction, e.g. reduction by black shales at the Willippa Diapir (Dyson, 2001); reaction with Cambrian dolomites at Beltana (Brugger *et al.*, 2003).

(5) Stratabound copper in the Neoproterozoic Adelaidean sedimentary rocks, in which sulphur was derived by bacterial reduction of sulphates

present in the sequence, and base metals were introduced by hydrothermal fluids (e.g. at Kapunda – Lambert *et al.*, 1980; at Kanmantoo – Seccombe *et al.*, 1985). Foden *et al.* (2000) interpreted a 586 ± 30 Ma Rb-Sr isochron in the Adelaide Geosyncline sedimentary rocks as representing a major intra-basinal fluid convection system related to an aborted rifting event, which may be associated with mobilization of copper in the Adelaide Geosyncline.

(6) The Mesoproterozoic Mount Painter Inlier (Fig. 1) contains a number of U-Cu-*REE* deposits of Palaeozoic age, which may be related to nearby granite intrusions (Bakker and Elburg, 2006; Elburg *et al.*, 2003; Lambert *et al.*, 1982). This Palaeozoic (~440 Ma) thermal event in the Mount Painter Inlier (Elburg *et al.*, 2003) may also be linked with hydrothermal circulation in the Adelaide Geosyncline, resulting for example in the formation of the non-sulphide Zn mineralization at Beltana (Brugger *et al.*, 2003).

Geology and mineralogy of the Paratoo copper deposit

Mineralization at Paratoo is hosted by shales and dolomites of the Torrensian Burra Group, below Umberatana Group tillite horizons (Fig. 2). The deposit occurs in the core of a breached doubly plunging anticline known as the Whydown Dome. The core of this structure is disrupted by several dolerite bodies and brecciated sedimentary material forming the 'Paratoo Diapir' (Holt, 1970; Preiss, 1987). Bedding in the sedimentary rocks becomes highly contorted in the immediate vicinity of the diapir (Fig. 2).

Outcrop to the east of the Paratoo mine is largely obscured by Quaternary sediments but SAEI (South Australia Exploration Initiative) regional aeromagnetic data suggest that the diapir extends over an area up to 4 km $\times$ 7 km. The outcropping dolerite bodies correspond to magnetic highs from these data, and a further three magnetic highs in the area of Quaternary cover suggest the presence of additional non-outcropping mafic igneous rocks.

The medium-grained dolerite is highly weathered in outcrop, consisting of amphibole (actinolite) and chlorite ($\pm$ hematite, magnetite) replacing a magmatic clinopyroxene; albite $\pm$ epidote, zoisite, sericite replacing a probable magmatic labradorite; and magnetite-ilmenite. The freshest surface samples preserve a porphyritic texture, and the dolerite probably

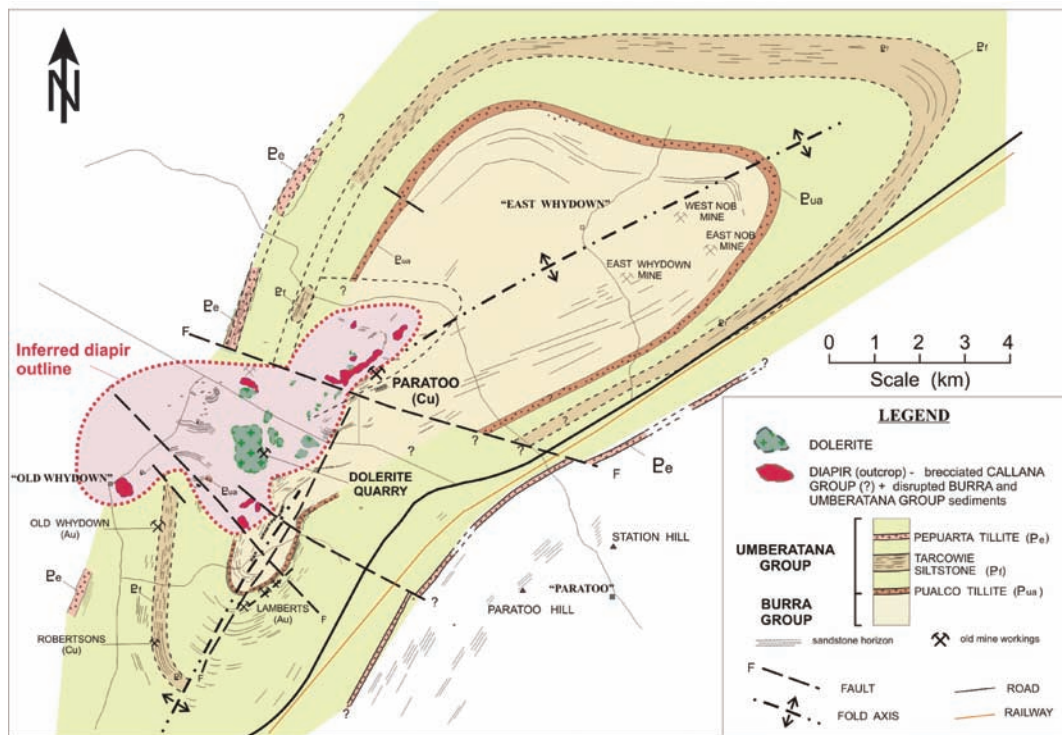


FIG. 2. Geological map of the Paratoo copper deposit, South Australia.

represents a high-level intrusion. The contact between the dolerite and the disrupted sedimentary rocks hosting mineralization is rarely observed; only one outcrop in one of the old dolerite quarries exposes a highly sheared contact. Locally, the dolerite contains abundant vuggy veinlets up to several cm thick consisting mainly of pink K-feldspar, hematite, epidote, and minor dravite (Table 2). The pink K-feldspar also occurs in porphyroblast-like textures along cleavage planes (Sample [03]). Rare aggregates of orange chabazite-Na (Coombs *et al.*, 1997) up to 2 cm in diameter also occur in the dolerite. This chabazite-Na is associated with disseminated pyrite and chalcopyrite. A single-crystal structure refinement of a well-crystallized fragment of this mineral (Nonius KappaCCD diffractometer, Mo- $K\alpha$ X-radiation, full Ewald sphere up to 70°) gave a rhombohedral unit cell with space group $R\bar{3}m$ and $a = 13.796(2)$, $c = 14.981(3)$ Å (hexagonal setting), and a structure model in good agreement with literature data (details are available on request; Mazzi and Galli, 1983). Compared with the chabazite-Na recently discov-

ered in late fractures postdating the main base-metal mobility at the Angas Zn prospect, Strathalbyn, South Australia (Table 2), the chabazite-Na from the dolerite at Paratoo is poorer in Na_2O but richer in K_2O , MgO and FeO . Compared with a chabazite from vacuoles in lavas, the chabazite-Na from Paratoo also has greater K_2O , MgO and FeO contents.

The breccia in which the dolerite bodies are hosted is dominated by recrystallized dolomite ($\pm$ talc, chlorite) containing detrital and diagenetic quartz with inclusions of pale green tourmaline; fragments of siltstones; and blocks of quartzite, which in places is feldspathic and displays heavy mineral banding. Nearly pure magnesite blocks have been encountered by drilling at 48 m depth (Holt, 1970). Some of the feldspathic sandstones with heavy mineral laminae have been identified as Rhynie Sandstone, which is derived from the Burra Group, at a stratigraphic level much lower than the exposed outcrop in the Whydown Dome. A rare stromatolite species found in clasts from this breccia (Preiss, 1987) has not been seen elsewhere

TABLE 2. Electron microprobe analyses of minerals related to potassic alteration in the Paratoo dolerite (quarry shown in Fig. 2). The chabazite-Na is compared with volcanogenic chabazite from NSW and hydrothermal chabazite-Na from the Angas Zn mine, SA. Fluorine was analysed, <0.1 wt.% in chabazite-Na and chabazite, and <0.14 wt.% in dravite. SrO and Cr₂O₃ are below detection limit for all minerals (<0.05 wt.%). *n* is the number of analyses, and 1σ is the standard deviation. Normalization: chabazite-Na, 12 oxygens (water excluded); dravite, 16 cations; K-feldspar, 5 cations.

Mineral	Chabazite	Chabazite-Na	Chabazite-Na	Chabazite-Na	Chabazite-Na	Dravite	K-feldspar
SA Museum #	G3108	G28316	G28314	G31056	G31057	G31057	G31057
Locality	Emmaville, NSW	Angas, SA	Angas, SA	Dolerite Quarry, Paratoo	Dolerite Quarry, Paratoo	Dolerite Quarry, Paratoo	Dolerite Quarry, Paratoo
<i>n</i>	8	8	5	7	6	1σ	1σ
Na ₂ O (wt.%)	1.48	8.38	10.22	6.42	2.40	(0.16)	0.17
MgO	<0.04	0.43	0.47	0.92	6.93	(0.12)	<0.04
Al ₂ O ₃	17.87	17.06	18.31	17.78	29.23	(0.65)	17.93
SiO ₂	47.96	49.13	53.28	51.73	36.29	(0.26)	64.87
K ₂ O	0.86	2.48	1.42	3.30	0.02	(0.01)	(0.47)
CaO	7.80	0.90	0.82	1.06	0.83	(0.19)	16.48
TiO ₂	≤0.07	0.04	<0.04	≤0.05	0.59	(0.19)	(0.30)
MnO	<0.04	≤0.07	≤0.04	≤0.06	≤0.05	(0.04)	<0.04
FeO	<0.04	≤0.05	0.57	1.14	9.86	(1.09)	≤0.06
Sum	75.97	78.41	85.09	82.35	86.15		0.08
Atoms per formula unit							99.63
Si ⁴⁺	4.17	4.22	4.21	4.23	6.09		3.01
Ti ⁴⁺	≤0.005	0.003	<0.002	≤0.003	0.08		<0.002
Al ³⁺	1.83	1.72	1.71	1.71	5.78		0.98
Sum	6.00	5.94	5.92	5.94	11.94		4.00
Mg ²⁺	<0.005	0.05	0.06	0.11	1.73		<0.003
Mn ²⁺	<0.005	≤0.001	≤0.003	≤0.004	≤0.007		≤0.002
Fe ²⁺	<0.005	≤0.001	0.04	0.08	1.38		0.003
Sum	<0.01	0.05	0.10	0.19	3.12		<0.01
K ⁺	0.10	0.27	0.14	0.34	0.00		0.98
Na ⁺	0.25	1.40	1.57	1.02	0.78		0.01
Ca ²⁺	0.73	0.08	0.07	0.09	0.15		0.005
Sum	1.08	1.75	1.78	1.45	0.93		1.00
Ca+(Na+K)/2	0.66	1.58	1.68	1.24			

Notes: Cameca SX50 electron microprobe, operated at 15 kV, 20 nA, with a tightly focused beam scanned over a 20 μm × 20 μm area to minimize sample damage. Counting time was 20 s per peak, and 10 s for the background on each side of the peak. The following X-ray lines, analyser crystals, and standards were used: K Kα, PET, Sanidine; Ca Kα, PET, Dolomite; Sr Lα, PET, Celestine; F Kα, PC0, Fluorite; Ti Kα, LIF, Rutile; Cr Kα, LIF, Cr₂O₃; Mn Kα, LIF, Rhodonite; Fe Kα, LIF, Almandine garnet; Na Kα, TAP, Albite; Mg Kα, Al Kα and Si Kα, TAP, Almandine garnet.

in the Adelaide Geosyncline, and is regarded as probably having been derived from Callanna Group rocks (Preiss, 1987).

The breccia has been interpreted as representing a diapir, in which salt-laden Callanna Group sediments rose through the overlying formations (e.g. Preiss, 1987). Mafic intrusive rocks are present in many diapirs in the Adelaide Geosyncline and have variously been interpreted as intrusions or as clasts (e.g. Preiss, 1987). Alternatively, the dolerites may have intruded during initial diapir formation and then became fragmented during later stages of diapirism or diapir reactivation (Preiss, pers. comm.).

Geological mapping and interpretation of SAEI aeromagnetic data has outlined two important structural trends within the Whydown Dome. The largest is a NW–SE trending structural corridor that bisects the dome and has partially localized the Paratoo Diapir (Fig. 2). The second important trend, parallel to the NE axial plane of the dome, appears to have focused low-grade Cu mineralization with anomalous Au (Fig. 2), including the Paratoo Mine which is located near the

intersection of this trend and the NW–SE corridor.

The mineralization at Paratoo occurs in two parallel zones (Fig. 3), which are roughly parallel to the axis of the anticline (ENE direction) and are centred along regional shear zones that contain low-grade Cu–Au mineralization extending over 3000 m (<http://www.rangeriver.com.au/docs/exploration/sa.htm>). The two zones are ~110 m apart and are labelled South and North ore zones (SOZ and NOZ, respectively; Fig. 3). At least four different vein sets observed in the open-cut excavations carry Cu mineralization. Three of these are discordant to lithology and carry no anomalous Au (Fig. 4a). They consist of quartz, weathered sulphides (pyrite and chalcopyrite mainly), and magnetite in varying proportions, and their thickness does not exceed 10 cm. The fourth vein type is magnetite-rich and parallel to bedding (≤ 5 cm in thickness); limited sampling by Havilah Resources Ltd (1998) has indicated anomalous Au mineralization of up to 0.93 g/ton Au. The best Au intersection reported by Range River Gold, obtained from a campaign of shallow

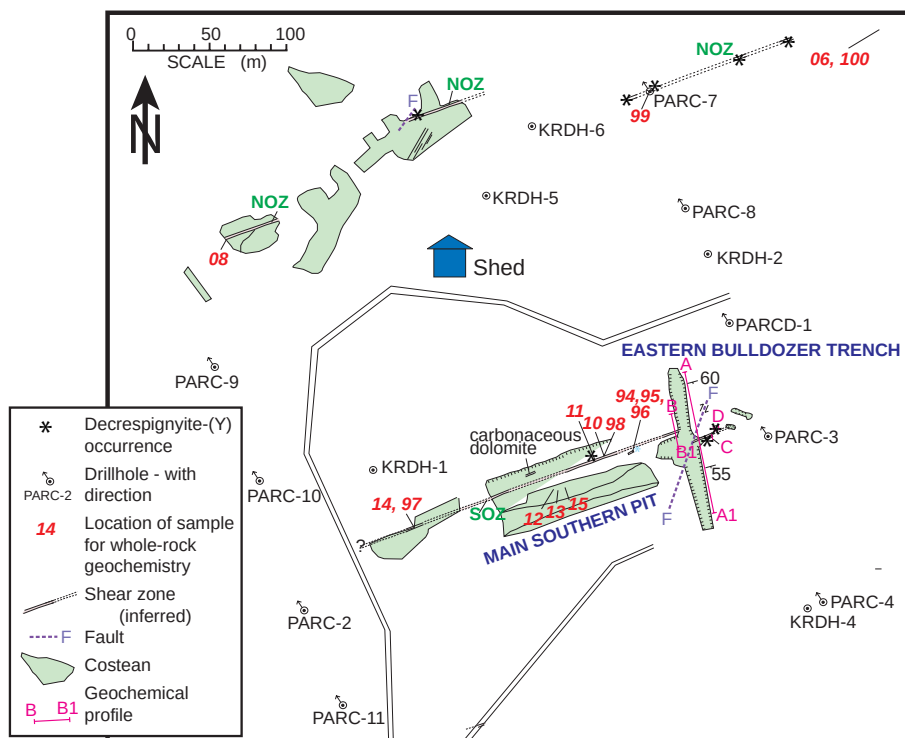


FIG. 3. Locations of samples and trenches at the Paratoo copper mine, South Australia.

rotary airblast drilling, is 0.21 g/ton over 8 m, supported by Cu grades of up to 0.4 wt.% over 20 m. A coarse-grained quartz-siderite vein (>50 cm thick) containing malachite staining and pyrite crystals occurs next to the contact with the dolerite (sample [05]).

At the surface, the shear zones are marked by small-scale folding and disruption in the dip of the bedding, associated with brecciation and silicification. A fibrous dolomite vein up to 30 cm in thickness marks the SOZ in the main trench (Fig. 4b). The bulk of the copper mineralization occurs in the quartz/magnetite veins, and as impregnations and fissure fillings of secondary copper minerals in shales and dolomites.

At depth (e.g. ~190 and 300 m in core KRDH-1; Fig. 3), drilling has intersected disseminated copper mineralization consisting of porphyroblast-like magnetite grains up to 3 mm in diameter (Fig. 5a), and fine-grained, dispersed

pyrite, chalcopyrite, a copper sulphide (probably digenite) and minor native copper located in hydrothermally altered shales (Holt, 1970). Macroscopically, the altered rocks are characterized by a white colour, contrasting with the grey to black shales. Powder XRD reveals that the most altered rocks consist mainly of K-feldspar and quartz. This type of mineralization probably represents the unweathered equivalent of the impregnations of secondary copper minerals observed at the surface.

The surface mineralization has been deeply weathered, with malachite, chrysocolla, tenorite and minor cuprite containing the bulk of the copper; relict pyrite and chalcopyrite are only rarely observed. The secondary Cu-REE mineralization, dominated by decrespignyite-(Y), generally occurs as thin coatings along bedding joints and fractures, and is most abundant near the surface (<3 m). At one location, decrespignyite-

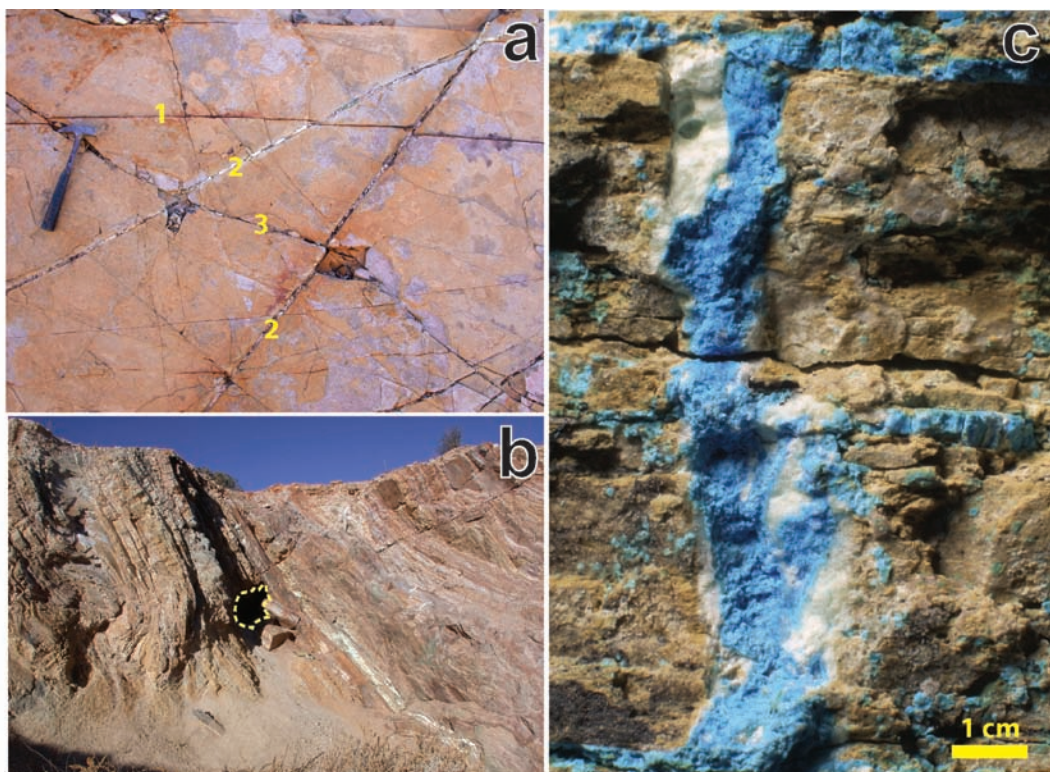
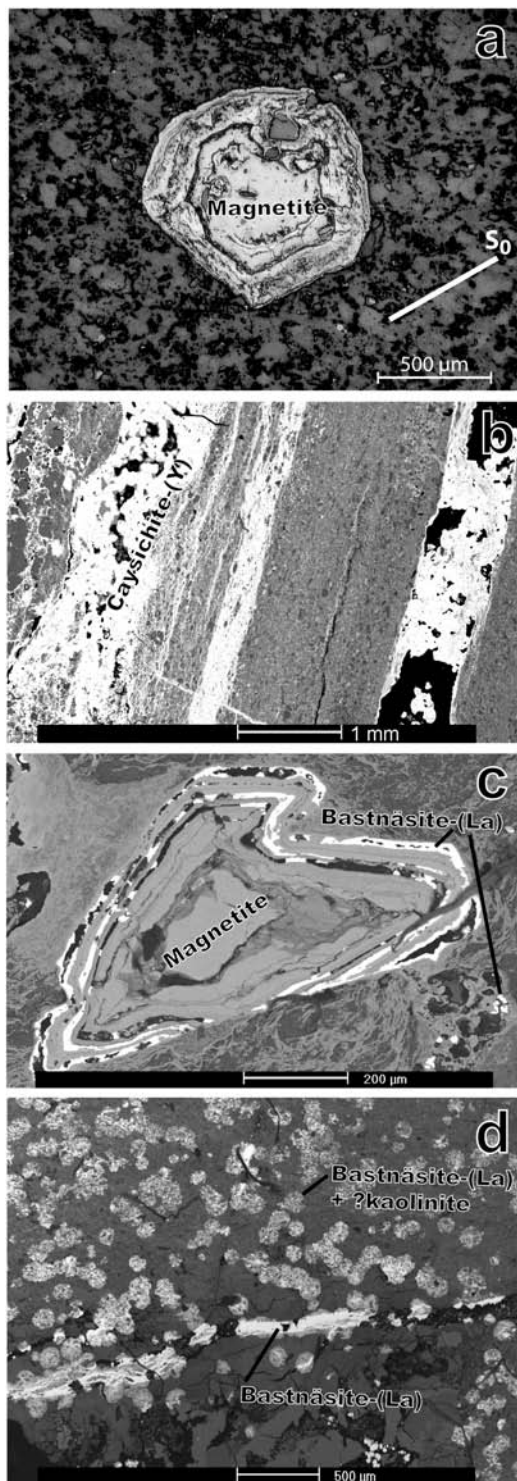


FIG. 4. Field views on the Paratoo copper mine: (a) Conjugate set of thin (<5 cm) quartz veins with magnetite and malachite ($\pm$ tenorite) in the Main Southern Pit (Fig. 3). Relative timing is highlighted. (b) Central part of the Eastern wall of the Eastern Bulldozer trench (Fig. 3 for location; see Fig. 6 for a schematic drawing of this face), showing the Southern Ore Zone shear zone, underlined here by a fibrous dolomite vein. The location of a small gallery (dating from the early 1900s) is highlighted. (c) Rich decrespignyite-(Y) vein in pit C (Fig. 3).



(Y) fills thick (up to 1 cm) veinlets, which are also both parallel and discordant to the bedding (Fig. 4a). These features are also observed at the microscopic level (Fig. 5b). A large amount of porosity remains, indicating crystallization near the surface in open space. Decrespignyite-(Y) can be very abundant locally, and some ancient shallow workings seem to have followed seams of this mineral. All the decrespignyite-(Y) occurrences are located on the NOZ and SOZ (Fig. 3).

Geochemistry

Samples for whole-rock geochemical analyses were collected in and around the Paratoo surface workings (Table 3, deposited with the Principal Editor, also available from http://www.minersoc.org/pages/e_journals/dep_mat.html). The sampling strategy emphasized lithological differences as well as vertical profiles through the weathering zone as exposed in the deepest bulldozed trench (Figs 3, 6). One hundred of these rock and ore samples were analysed for a suite of 31 elements including the following *REE*: La, Ce, Nd, Sm, Eu, Tb, Ho, Yb and Lu. Element abundances were determined by Neutron Activation Analysis at Becquerel Laboratories, using the Australian Nuclear Science and Technology Organization's HIFAR reactor in Sydney, Australia. Samples of 10 g were weighed accurately and sealed in polypropylene vials, each with a Re flux monitor label. The samples were activated in one batch at a flux of $\sim 4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. The samples were counted after 6.5–7.5 days' decay for between 15 and 30 min, depending on the detector-to-sample spacing. Second counts were done after 14 to 17 days' decay for 30 to 60 min. Due to the activity from the *LREE*, several smaller portions, ranging in size from 0.1 g to 0.7 g, were also activated

FIG. 5. Micro-images of *REE* mineralization at Paratoo. (a) Hypidiomorphic magnetite crystal in heavily hydrothermally altered shale (now consisting mainly of K-feldspar, quartz, and minor muscovite). Drillcore KRDH-1, 1002 ft level (305.4 m); reflected light photomicrograph. (b) Caysichite-(Y) crystallizing along bedding joints and late fractures. Sample [90], back-scattered electron image. (c) Weathered magnetite grain with bastnäsite-(La) in oscillatory zoning. Sample [10], SEM. (d) Bastnäsite-(La) finely mixed with an Al-silicate (kaolinite?). Sample [88], SEM.

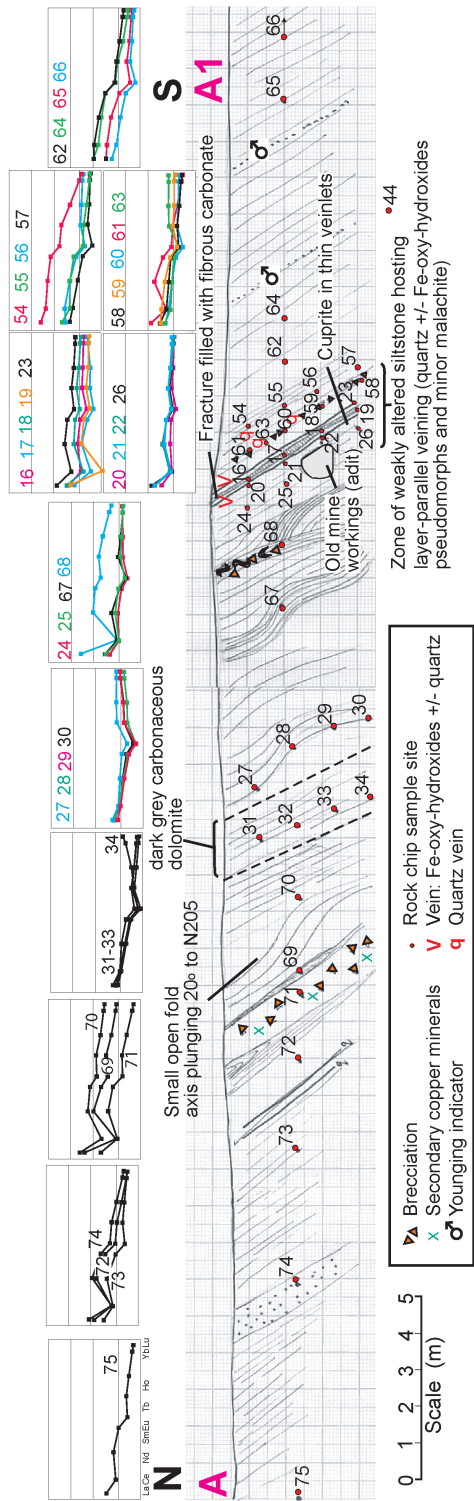


FIG. 6. Eastern wall of the Eastern Bulldozer trench (Fig. 3), showing sampling locations and chondrite-normalized REE patterns of the samples.

and counted after 7 and 14 days' decay for 30 to 60 min. Careful flux monitoring of each sample was necessary to account for neutron flux depressions caused by the high *REE* contents.

Gold grades are low, exceeding 100 ppb only in a few samples that are weakly mineralized in Cu (Table 3 deposited with the Principal Editor, also available from http://www.minersoc.org/pages/e_journals/dep_mat.html), and peaks at 391 ppb in sample [23], a red-purple shale containing bedding-parallel veins (Fe-oxy-hydroxides $\pm$ cuprite) and thin crosscutting veins (calcite + cuprite $\pm$ chrysocolla). In general, those samples showing evidence of intense hydrothermal alteration (veining; copper staining) have elevated As (up to 847 ppm) and Ba (up to 9540 ppm).

Chondrite-normalized (Evensen *et al.*, 1978) *REE* patterns for rocks and ores from Paratoo are shown in Figs 6 and 7. The dolerite retains a characteristic flat *REE* pattern (Fig. 7a). Retrograde veins within the dolerite are enriched in *LREE* by a factor of 2 compared to the most primitive dolerite (Fig. 7a). Siltstones are the most common lithology in the mine workings. These siltstones are characterized by relatively steep *LREE* enrichment and a negative Eu anomaly. This Eu anomaly is characteristic of post-Archaean Australian shales (McCulloch and Bennett, 1994). Most siltstones display a negative Ce anomaly as well, and some have none (Fig. 7b). Depth profiles from single beds (e.g. Fig. 6) do not show a clear trend in the evolution of the Ce anomaly. The unmineralized sandstone sample [56] (Fig. 7b) has a *REE* pattern similar to that of the siltstones, except for a small positive Ce anomaly. In contrast, the dolomites and silty dolomites are characterized by 'V-shaped' patterns and a negative Eu anomaly (Fig. 7c). A good example of this type of pattern is sample [34], a grey laminated dolomite, showing a decrease in chondrite-normalized *LREE* concentrations with increasing atomic number from Ce to Sm, but an increase for the *HREE* Tb to Lu (Fig. 7c).

The *REE* patterns from vein material are generally characterized by a highly variable *LREE* enrichment (Fig. 7d). The *HREE* contents are mostly similar to those of the siltstones. The most *LREE*-depleted veins have *REE* patterns similar to the siltstones, although some display extremely negative Ce anomalies. *LREE*-enriched vein samples contain up to 10 times more La than any siltstone. Vein samples [86] (from a

decrepsignite-(Y)-rich zone at the east of SOZ) and [14] (a S_0 -parallel vein west of the SOZ) also show enrichments in *HREE* by a factor of 5 relative to siltstones, while still retaining La/Lu_{CN} ratios >1 . In addition, three samples [82, 99 and 100] show enrichment in *HREE* relative to *LREE*. Another anomalous sample is [05], which corresponds to a coarse-grained quartz-siderite vein (>50 cm thick) containing malachite staining and pyrite crystals near the contact with the dolerite. This vein has a *REE* pattern that is essentially similar to that of the dolerite (Fig. 7a,d). In summary, veining and metasomatism generally result in large enrichment in *LREE* and in the development of a very large negative Ce anomaly relative to unaffected rocks.

The highest *REE* contents are associated with veining and shearing; however, high *REE* contents are not consistently associated with visible decrepsignite-(Y) or even with base metal mineralization. For example, sample [10] (Fig. 7e) contains an S_0 -parallel quartz vein with weathered magnetite crystals and no visible copper mineralization, but it has *REE* contents that are greater than a decrepsignite-(Y)-bearing sample ([99], Fig. 7e). The *REE* in the vein of sample [10] are hosted mainly by bastnäsite-(La). This bastnäsite-(La) occurs distributed among the many porous areas in this highly weathered vein, and also as rhythmic bands inside weathered magnetite crystals (Fig. 5c). The morphology of the magnetite in this S_0 -parallel vein is similar to that of the magnetite in the disseminated mineralization at depth (Fig. 5a), although no *REE* mineral was associated with the latter occurrence.

Sample [88] (Table 2; Fig. 5d) represents another type of cryptic secondary *REE* mineralization. It is a brown sandy siltstone with only traces of malachite; however, it contains 55,380 ppm *REE*, mainly in the form of bastnäsite-(La) in thin fractures, but more commonly as small spheres (~ 50 μ m in diameter) intimately mixed with an aluminium silicate (kaolinite?). Free-grown spherical bastnäsite-(La) aggregates were also observed on fissures along with paratooite-(La) (Pring *et al.*, 2006).

Discussion

REE mineralogy and weathering at Paratoo

All the *REE* minerals observed at Paratoo (Table 1) are late, secondary phases, occurring as coatings along joints and in fractures (Figs 4c,

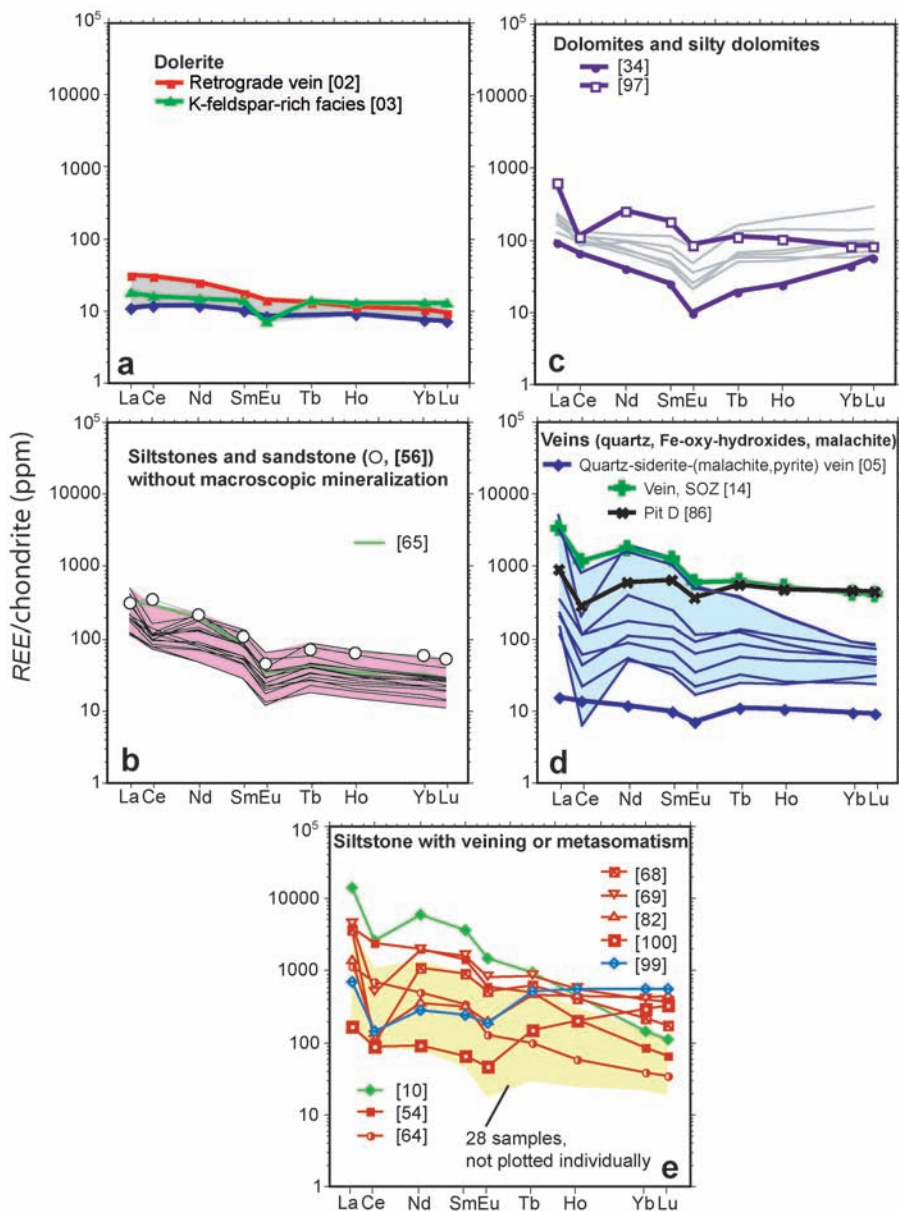


FIG. 7. Chondrite-normalized REE distribution in mineralized and un-mineralized rocks at the Paratoo copper deposit, South Australia.

5b–d), as impregnations in shales (Fig. 5d), or in open space left by the dissolution of unknown minerals (Fig. 5c). The assemblage of REE carbonate minerals at Paratoo appears to be unique among sediment-hosted base metal deposits not only in the province, but worldwide. This complex REE mineralogy contrasts with a

simple copper mineralogy, characteristic of deeply weathered deposits (Williams, 1990). Figure 8a illustrates the relationships among Cu minerals in the presence of sulphur and $\text{CO}_2(\text{g})$. The main weathering minerals (malachite, tenorite, cuprite) indicate precipitation from fluids with near-neutral to slightly basic pH. The

presence of chloride in decrespignyite-(Y) (Wallwork *et al.* 2002) suggests the involvement of saline groundwaters during weathering; hence, the absence of atacamite in the assemblage of weathering minerals also suggests a relatively high pH, as well as overpressure of $\text{CO}_2(\text{g})$ relative to modern atmospheric contents ($10^{-3.4}$ bar; Fig. 8a). The strong intensity of the weathering is demonstrated by the fact that no native copper is found in the weathering zone, and by the abundance of chrysocolla, often seen replacing malachite (Williams, 1990).

REE mobility in aqueous fluids and the Ce anomaly

REEs occur predominantly as trivalent cations in nature, and behave in a consistent manner through geochemical processes such as melting, fractional crystallization, transport in a fluid, phase separation, and coprecipitation. Fractionation among REE is caused by a slight systematic decrease in ionic radius from La^{3+} to Lu^{3+} , and by changes in oxidation states for some REE. Because of similar behaviour, Y is often treated together with REE (e.g. Bau and Dulski, 1995); the ionic radius of Y^{3+} is between those of Dy^{3+} and Ho^{3+} . In aqueous fluids, Eu^{2+} exists under reducing conditions at elevated temperature (Sverjensky, 1984), while Ce^{4+} is stable vs. Ce^{3+} under highly oxidizing conditions especially near room temperature. The REE are well established as petrogenetic indicators in magmatic systems

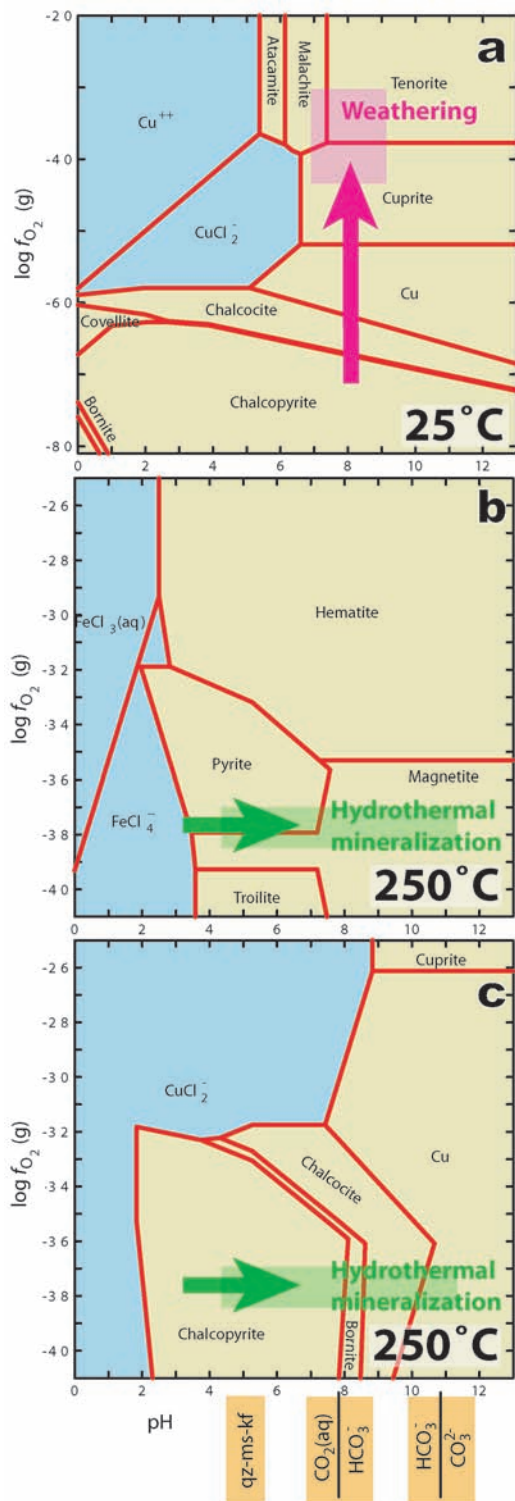


FIG. 8. Redox state (as $\log f_{\text{O}_2}(\text{g})$) vs. pH diagrams for the copper and iron mineralogy of the Paratoo copper deposit during weathering (a) and hydrothermal stage (b,c). The arrows indicate the main geochemical trend during weathering (a) and hydrothermal mineralization (b,c). The diagrams were calculated for the following conditions: aCu species = 10^{-4} ; aS species 0.001; $\text{aCl}^- = 1$. The pressure is one bar at 25°C and 39.7 bar at 250°C (liquid-vapour saturation) (b,c). At 25°C, $f_{\text{CO}_2}(\text{g})$ is 0.01 bar; values below 0.001 bar result in the disappearance of malachite in favour of atacamite (modern atmosphere are $p_{\text{CO}_2}(\text{g})$ of $10^{-3.4}$ bar). Diagrams (a) and (c) are built by assuming that Fe is controlled by the predominant phase in the Fe-O-H subdiagram, $a_{\text{Fe}} = 1$. qz-ms-kf stands for quartz-muscovite-K-feldspar. Thermodynamic data were taken from the Lawrence Livermore database (LLNL V8 R6), as delivered with the *Geochemist's Workbench* software (Bethke, 1996).

(e.g. Lipin and McKay, 1989). In contrast, the REE signature of hydrothermal minerals results from a complex interplay among a number of parameters (e.g. Gieré, 1996), including the REE contents of the fluid, the aqueous speciation (complexing) of the REE, the nature of the mineral (crystallographic control), and the mechanisms of crystal growth (e.g. equilibrium vs. non-equilibrium; Rakovan and Reeder, 1996). The REE contents of the fluid itself depend on the mineralogical and bulk REE contents of the source rock (e.g. preferential weathering of particular minerals) and on the chemistry of the fluid, in particular its redox state ($\text{Eu}^{2+}/\text{Eu}^{3+}$; $\text{Ce}^{3+}/\text{Ce}^{4+}$) and the availability of ligands to complex the REE. For example, HREEs (Gd-Lu) are complexed more strongly by fluoride, and less strongly by chloride, than the LREEs (La-Sm), whereas at basic pH conditions HREEs and LREEs strongly associate with hydroxide to an equivalent degree (Haas *et al.*, 1995). Ce^{4+} is highly insoluble, usually coprecipitating with Fe- and Mn-oxy-hydroxides (e.g. Takahashi *et al.*, 2000); hence Ce tends to be immobile at the centimetre level where Ce^{4+} is dominant. Taunton *et al.* (2000) show how this behaviour results in preferential leaching of trivalent REE in the top of the weathering profile in a granite; these REE are concentrated in the lower part of the profile in Ce-poor secondary minerals. At the surface, a positive Ce-anomaly developed in the soil because of extensive leaching of other elements and compaction during transformation of weathered rock to soil.

Origin of REE at Paratoo

The mineralized rocks at Paratoo are generally characterized by an enrichment in LREE when compared with non-mineralized equivalents (Fig. 7b,e). Most veins, which consist mainly of minerals deposited from the mineralizing fluid, present patterns that vary from being similar to that of unmineralized siltstones, to being extremely enriched in LREE (Fig. 7d). Only two samples [82,99] also show significant enrichment in HREE. The most REE-enriched samples contain a range of REE carbonate minerals, some enriched in LREE and others enriched in HREE due to crystallographic control (Table 1). Samples containing a large amount of the latter minerals, e.g. decrespignyite-(Y), can display an enrichment in HREE relative to LREE (e.g. sample [99]).

Most of these secondary REE minerals are characterized by a strong depletion in Ce. For minerals that preferentially incorporate LREE, this results in either La or Nd being the most abundant REE in their crystal structure (Table 1). The Ce-depletion characteristic of the Paratoo minerals is reflected in strong negative Ce anomalies for most mineralized samples (Fig. 7d,e). The sedimentary rocks, in contrast, display no or a much weaker negative anomaly, which may represent an original sedimentary feature or may result from weathering. Despite the large number of samples analysed for REE in this study, we did not find a Ce-enriched horizon. Only one sample (sandstone [56]) shows a slight positive Ce anomaly. Two possible scenarios may explain the consistent Ce depletion in the mineralized samples, depending on the timing and source of the REE:

(1) The REE were introduced into the Paratoo deposit by oxidized (i.e. near surface) groundwaters. Ce was present as Ce^{4+} and left behind during the transport from the unknown source rock to the Paratoo deposit. Interaction with the mineralized rocks at Paratoo caused the precipitations of the suite of REE carbonates, the Ce-depletion of which reflects the composition of the mother fluid.

(2) The hydrothermal fluid responsible for the magnetite and base-metals mineralization also deposited small amounts of REE in the mineralized veins. The remobilization of this anomalous mineralization during the deep weathering of the deposit resulted in the precipitation of secondary REE minerals, and in the enrichment of the REE contents at some level in the weathering or cementation zone. The Ce was left behind during the weathering, possibly in a soil zone that has since been washed away.

There are a number of problems related to the first hypothesis. (1) There is no obvious regional source for LREE-enriched groundwater. (2) The new minerals decrespignyite-(Y) and paratooite-(La) contain copper as an essential constituent, and this explains that they should be associated with the base-metal mineralization. However, there is no mechanism to explain the preferential precipitation of REE carbonates such as bastnäsite-(La) and calcio-ancylite-(Nd) in the ore-zone, as opposed to the host dolomitic shales. The special association between the SOZ and NOZ shear zones and the REE mineralization is the strongest argument in favour of a coeval enrichment of REE with base metals in these

structures. (3) Finally, scenario (1) does not provide any clue as to the reason for the uniqueness of the association of secondary *REE* minerals at Paratoo, whereas scenario (2) suggests that the combination of deep weathering with an unusual composition of the ore (*REE* together with base metals) resulted in this unique mineral assemblage.

Therefore, we conclude that the unusual association of *REE* minerals found at Paratoo results from the deep weathering of a primary, hydrothermal magnetite-copper-sulphides-*REE* mineralization, as this explains both the link between mineralization and high *REE* contents, and the exceptional character of the mineralogy at Paratoo. Paratoo is the only locality worldwide to have furnished base-metal-*REE*-carbonates (decrespignyite-(Y) and paratooite-(La)). Decrespignyite-(Y), in particular, is abundant in the deposit, and represents the main Cu and *REE* mineral at several locations along both the SOZ and NOZ. To our knowledge, the only other occurrence of this type of compound is an unnamed Y-Ba-Cu mineral from the Olympic Dam deposit (Lottermoser, 1987). The primary *REE* mineral at Paratoo may have consisted of fine-grained bastnäsite-(Ce), which is one of the main *LREE* carriers at Olympic Dam (Lottermoser, 1987). At the province scale, the uniqueness of the weathering mineralogy at Paratoo (prevalence of *REE*-carbonates) can be explained by the fact that Paratoo is the only Fe oxide-Cu-*REE* deposit of the region hosted by dolomitic sediments. Both the Proterozoic Olympic Dam-type deposits and the Palaeozoic Mt Painter-type deposits are associated with felsic magmatism, and occur within carbonate-poor basement sequences.

The genesis of the Paratoo deposit

Paratoo represents a hydrothermal deposit characterized by the deposition of magnetite and copper sulphides. The mineralization was associated with strong potassic alteration, and with an enrichment in *REE* (mainly *LREE*). The deposit is controlled by two shear zones oriented parallel to the axis of the regional anticline and originating from a dolerite-bearing breccia body (Figs 2, 3). The bulk of the ore occurs as veining and as well as disseminated sulphides and native copper in siltstones belonging to the Upper Burra group. The structures (shear zones, veins) hosting the deposit developed either during or after the

development of the Whydown Dome structure during the Cambro-Ordovician Delamerian orogen. The dolerite and the breccia of the 'Paratoo diapir' are also locally weakly mineralized (e.g. disseminated chalcopyrite). Significantly, the strong potassic alteration associated with the mineralization in the Burra group (K-feldspar) has also affected the dolerite (K-feldspar and K-bearing chabazite-Na).

The spatial relationship between the 'Paratoo diapir' and the mineralization and the evidence for potassic alteration in the dolerite bodies within the 'Paratoo diapir' provide strong arguments in favour of a model where the diapir acts as a channelway for the mineralizing fluids (Dyson, 2001; Brugger *et al.*, 2003). The quartz-siderite vein (sample [5]) found next to the contact with the diapiroic breccia, with its *REE* pattern similar to those recorded from the dolerite (Fig. 7a,d), may result from fluids which interacted strongly with the dolerite.

The association of primary minerals in the disseminated mineralization – magnetite, chalcopyrite, a copper sulphide (digenite?), and native copper – may have resulted from neutralization of an acidic hydrothermal fluid (e.g. buffered by quartz-feldspar-muscovite) by reaction with carbonate-bearing rocks. This is illustrated by the activity-activity diagrams in Figs 8b and 8c. These diagrams were built assuming a temperature of 250°C for the mineralizing fluids. Relatively high temperatures are suggested by the coarse nature of the magnetite. Neutralization of a fluid whose pH is buffered by muscovite + quartz + K-feldspar (e.g. siliciclastic sedimentary rocks of the Callanna Formation) would result in the precipitation of chalcopyrite, followed by a copper sulphide, followed by native copper, together with the precipitation of magnetite and/or pyrite depending upon the sulphur contents of the fluid and its redox state. Unfortunately, the limited data available on the disseminated mineralization does not allow us to assert a paragenetic sequence or mineralogical zonation that would help to better constrain the deposition mechanism.

Basinal brines from the Callanna Group represent the most likely mineralizing fluid. Much of the Adelaide Geosyncline represents a region of high heat flow derived from crustal heat sources within underlying Palaeo-Mesoproterozoic basement (Sandiford *et al.*, 1998). The conjunction of high heat flow from the basement, inversion tectonics reactivating deep-rooted struc-

tures, and evaporite lithologies able to supply the ligands and oxidizing conditions required for transport of metals all contribute to the prospectivity of the Adelaide Geosyncline. Evidence for large-scale fluid flow in the basin has been reported for the Neoproterozoic (Foden *et al.*, 2000; 586±30 Ma) and for the Palaeozoic (Groves *et al.*, 2003). The evidence for Ordovician (~440 My) mineralization through basinal brines in the Adelaide Geosyncline comes from K-Ar dating of coronadite that marks the collapse of the mineralizing system in the Beltana willemite deposit. In the latter case, base-metal mineralization (willemite) resulted from the interaction of acid, hot basinal brines travelling through siliciclastic, relatively oxidized sedimentary rocks of the Callanna beds and reacting with Cambrian carbonate rocks (Brugger *et al.*, 2003). In the case of Paratoo, fluid flow may also have been promoted by the development of the Whydown Dome during the Delamerian Orogen (Cambro-Ordovician).

The brines responsible for the formation of the Paratoo deposit may have interacted with underlying Callanna Group volcanics (Cu) and evaporite horizons (Cl). The high *LREE* enrichment of the Paratoo ores suggests that the mineralizing fluid was also enriched in *LREE*. This may have been achieved if the fluids interacted with Palaeo-Mesoproterozoic gneisses from the basement, though *REE* may also have been derived from the Callanna Group itself, for example from felsic volcanic rocks which are usually enriched in *LREE*, or by preferential dissolution of a detrital *LREE*-rich mineral such as monazite-(Ce).

The base metal-REE association in the Curnamona-Gawler craton province

The association of base metals with *REE* and Fe oxides at Paratoo is reminiscent of that found in the giant Olympic Dam Cu-U-Au-*REE* deposit, with the notable exception of uranium. However, the age of the mineralization (early Mesoproterozoic at Olympic Dam, but Palaeozoic at Paratoo) and the geological context (Mesoproterozoic granite of the Gawler Craton for Olympic Dam; Neoproterozoic sediments of the Adelaide Geosyncline for Paratoo) differ greatly. A similar association of Fe oxides, U, *REE* and minor Cu is found in the Palaeozoic magmatic and epithermal deposits in the Mt Painter Inlier (Drexel and Major, 1990). The

inlier is also well known for Mesoproterozoic granites enriched in incompatible elements such as U, Th and *REE* (e.g. Neumann *et al.*, 2000). The Paratoo deposit can, therefore, be considered as a further example of a *REE*±Cu±U system in the province that was active from the early Proterozoic and into the Palaeozoic. The wide distribution through time of the otherwise unusual *REE*-base metal association suggests that the occurrence of this elemental association in hydrothermal deposits of the province is not related to a particular tectonic or magmatic event, but rather reflects the unusual geochemistry of the Mesoproterozoic basement and of its *REE*-U rich granites. The mechanisms driving hydrothermal circulation appear to vary through time. Magmatic heat was probably important in the Mesoproterozoic (e.g. Olympic Dam) and possibly in the Palaeozoic (e.g. Mt Painter Province; Elburg *et al.*, 2003), whereas basinal fluid flow linked with the tectonic evolution of the Adelaide Geosyncline occurred during the Neoproterozoic (e.g. Foden *et al.*, 2000).

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