

Mobility of rare-earth elements and copper during shear-zone-related retrograde metamorphism

Geoffrey de Jong¹, Jackie Rotherham², G. Neil Phillips² & Patrick J. Williams³

¹ Pottenbakkersdonk 9, 7326 PA Apeldoorn, the Netherlands; ² Great Central Mines N.L., Melbourne, Australia;

³ National Key Centre in Economic Geology, Geology Department, James Cook University of North Queensland, Townsville Q 4811, Australia

Received 11 January 1996; accepted in revised form 19 February 1998

Key words: Australia, metadolerites, Mt Isa Inlier, REE mobility, sodic-calcic alteration

Abstract

In Mid Proterozoic crystalline rocks of the Mount Isa Inlier, around Cloncurry, Australia, 2000 km² of alteration and brecciation are the product of high-temperature (> 450 °C) concentrated saline solution activity. During retrogression, this fluid was locally responsible for mobility of V, Y, Nb and light rare-earth elements (15 × enrichment). Copper and S were leached during alteration and this may have been a significant source of components in nearby Cu-Au deposits. Similar rare-earth-element behaviour has been observed in the hematite breccias which host Cu-sulfides at the giant Olympic Dam Cu-Au deposit.

Introduction

In many situations rare-earth elements (REE) are immobile during metamorphism and are used as petrological classifiers (Rogers et al. 1984; Meschede 1986, Hellingwerf 1992). Other high-field-strength elements (HFSE) like Ti, Zr, Hf, Ta, V, Y and Nb are also regarded as immobile in metamorphic environments. In other situations, there is evidence that REE have been mobile during 'early' sea-floor alteration (Graf 1977, Hellman et al. 1979, Kwak & Abeysinghe 1987, Salvi & Williams-Jones 1990). Research in the Cloncurry terrain (NW Queensland, Australia) has revealed mobility of some HFSE and light rare-earth elements (LREE, La to Sm) during extensive albite-actinolite-dominated alteration (Phillips et al. 1994, De Jong & Williams 1995).

This paper focuses on the regional effects of fluid infiltration in mafic rocks at different crustal levels near Cloncurry. Mapping of 1000 km² during the National Key Centre's Cloncurry Project identified a zone of extreme brecciation and alteration for 100 km along strike. Well-exposed river sections were the sites of detailed mapping and sampling of mafic rocks. Mobility of LREE and some HFSE (V, Y, Nb) has

occurred on a scale of tens of centimetres in vein selvages. Geochemical considerations suggest an association between LREE, V, Y, Nb and Cl (and/or F) activity in the fluid (Oreskes & Einaudi 1990, Ramsden et al. 1993).

Considerable loss of Cu and S (and to a lesser extent Zn) from the mafic rocks has occurred during the albite-actinolite alteration. It is interesting to speculate that this leached Cu could be the source for some of the Cu in Cu-Au deposits found on north-south linear trends adjacent to the alteration and brecciation zone (Figure 1). Although REE behaviour and Cu leaching are described in the literature, few regional correlations are made between Cu leaching and REE mobility on the scale witnessed at Cloncurry (Taylor & Fryer 1983, Hannan et al. 1993).

Geological setting

Proterozoic rocks in the eastern part of the Cloncurry-Selwyn terrain, the eastern part of the Mount Isa Inlier, consist of psammopelitic gneisses and schists of the Maronan Supergroup, overlying profoundly reconstituted calc-silicate rocks of the Doherty For-

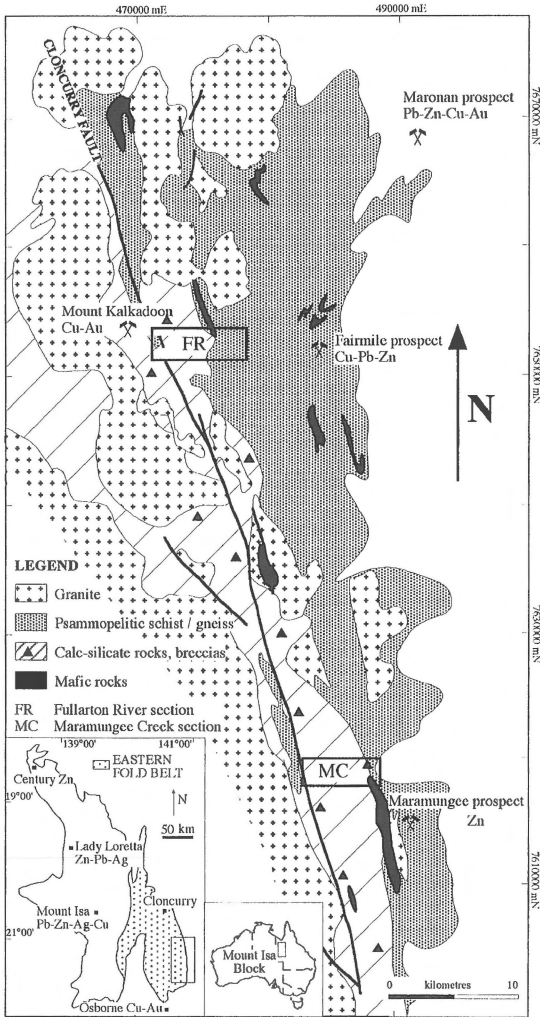


Figure 1. Simplified geology of the eastern part of the Cloncurry-Selwyn terrain. The Cloncurry Fault (partly illustrated, but extending towards Cloncurry) is central to the alteration and brecciation. Mafic rocks make up approximately 10% of the region. Boxes indicate the Fullarton River and Maramungee Creek locations.

mation. These reconstituted rocks are a result of large-scale post-peak-metamorphic fluid infiltration in deep-seated ductile shear zones. Episodic alteration was temporally and spatially associated with multiple phases of granitoid emplacement. The alteration style and mineralogical composition progressively evolved from ductile-shear-related alteration systems, to localized breccias, and finally to shallow fracture-controlled epithermal-style veining.

Multiple deformation phases affected the eastern part of the Cloncurry-Selwyn terrain. They are manifested in overprinting relationships such as refolded

folds, crenulations, rotation of lineations and development of high-strain zones, in which the latter caused juxtaposition of rocks with different metamorphic grades. The orientation and nature of the earlier ductile deformation phase(s) are somewhat speculative, due to the strong overprint of the pervasive D_2 deformation phase and the post- D_2 sodic-calcic alteration effect. However, D_1 appears to have produced a flat-lying fabric (S_1 foliation, Loosveld & Schreurs 1987, Loosveld 1989a, b). Prograde regional metamorphism reached the upper amphibolite facies (sillimanite-K-feldspar metamorphic grade, Beardsmore et al. 1988) during the main regional deformation phase D_2 (1580 ± 17 Ma, Page 1994). High-strain zones occur in the limb regions of regional D_2 folds, and are interpreted as thrust faults (Loosveld & Schreurs 1987). The general characteristic of D_2 is a pervasive north-south S_2 foliation, and an upright N-S to NW-SE trending 'tight' to 'close' asymmetrical west-verging fold style (Beardsmore et al. 1988, Loosveld 1989a, b).

Thinning of the earth's crust resulted in high geothermal gradients, associated with high-crustal-level granite intrusions, during the D_3 deformation. Thinning also caused reduction of the lithostatic pressure and increase of the fluid pressure. This resulted in the onset of regional brecciation by lowering of the effective differential stress, causing tensional failure to occur. The regional brecciation overprints the earlier ductile and brittle-ductile shear zones. This is evident by the occurrence of altered clasts with earlier high-strained fabrics and veins controlled by fold structures. The brecciation is spatially closely associated to the Cloncurry Fault and the high-level granite intrusions. Weak D_3 fabrics and partial brecciation in the granites are evidence for the synchronous nature of the brecciation with the D_3 deformation phase and granite emplacement.

Continuous unroofing resulted in a telescoping effect with juxtaposing and/or overprinting of the earlier sodic-calcic alteration assemblage by a later and shallower K-feldspar, quartz, chalcedony assemblage, and an epidote, prehnite, calcite assemblage. These assemblages are partly structurally controlled in extensional Riedel fractures attributed to post- D_3 sinistral movement of the Cloncurry Fault.

Regional scale of alteration

Large areas of the Cloncurry terrain have been affected by regional-scale alteration with reconstituted rocks

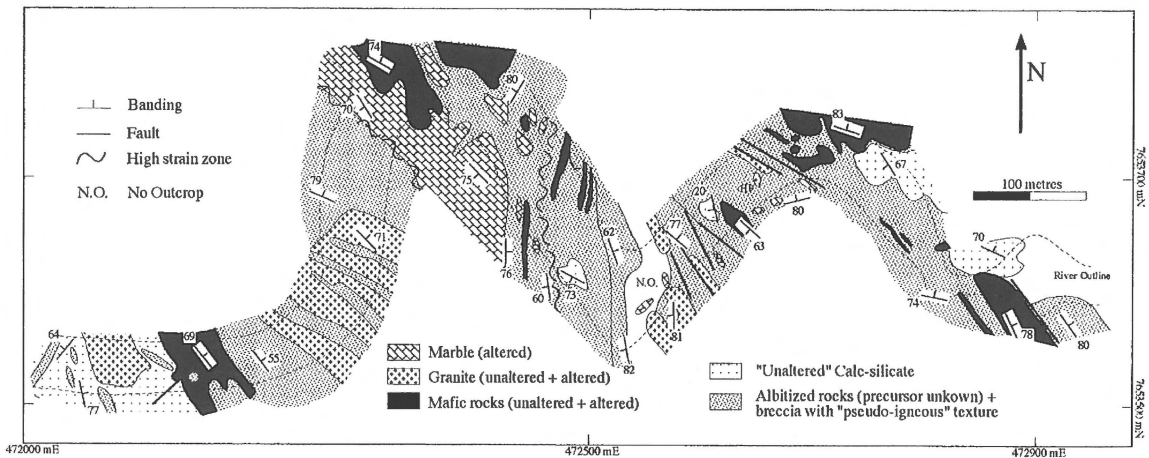


Figure 2. Mafic rock outcrops in the Fullarton River Gorge section. (For Maramungee Creek geology reference is made to Figure 6 of Phillips et al. 1994). Dashed lines outline the river bed.

exposed over hundreds of square kilometres (Phillips et al. 1994). Major fault zones with a complex reactivation history are the loci of the more intense alteration (Figure 1) and may have been the conduits for the large volumes of fluids responsible for the alteration (De Jong & Williams 1995). These fault zones have been traced over hundreds of kilometres (Figure 1).

The rocks affected by this alteration include psammitic to pelitic metasediments, calc-silicate rocks, granites, felsic and mafic intrusives and carbonate-rich metasediments. The overall result is one of high-variance mineral assemblages dominated by albite and actinolite in all rock types. Relicts of unaltered rocks are preserved within altered areas, providing a basis for paragenetic sequencing and for determining element mobility.

Sample sites

Regional alteration is studied in detail in two well-exposed river sections perpendicular to strike, the Maramungee Creek section and the Fullarton River Gorge (Figure 1). The Cloncurry Fault is just west of both sections. The Maramungee Creek section exhibits ductile late-D₂ shear zones which acted as channels for pervasive sodic-calcic alteration. In the Fullarton River Gorge (Figure 2), retrograde alteration is associated with brittle fractures and megabreccias. These deformation characteristics imply an early deep crustal level at Maramungee and a later higher crustal level at Fullarton River. Two suites of rocks (suites 1 and 2) were collected from the Fullarton River Gorge. Suite

3 was sampled in the Maramungee Creek. Samples analysed are from unaltered mafic rocks, and from selvages (the altered equivalents of the unaltered mafic rocks) of diopside-actinolite veins cross-cutting the unaltered mafic rocks.

Distribution of mafic rocks

Mafic rocks make up about 10% by volume of the Cloncurry terrain. They include intrusive bodies, varying in size from tens to hundreds of metres in thickness and a hundred metres in length (Figure 1). These were affected by D₂ structures and the dominant albite-actinolite alteration phase.

Within the alteration zone, virtually unaltered relicts consist of medium to coarse-grained green hornblende (80 modal %), coexisting with albite-oligoclase and titanite. In the centre of large mafic bodies, primary diopside is replaced by green hornblende, coexisting with oligoclase.

Analytical methods

A Siemens 303 Sequential X-Ray Fluorescence Spectrometer, at the Advanced Analytical Centre at James Cook University of North Queensland, was used for major and trace element analysis of whole-rock samples in this study. Major and minor elements were analysed on fused glass beads, using a lithiumborate flux as the oxidising agent. Duplicates were made of some samples to ensure the reliability of the analy-

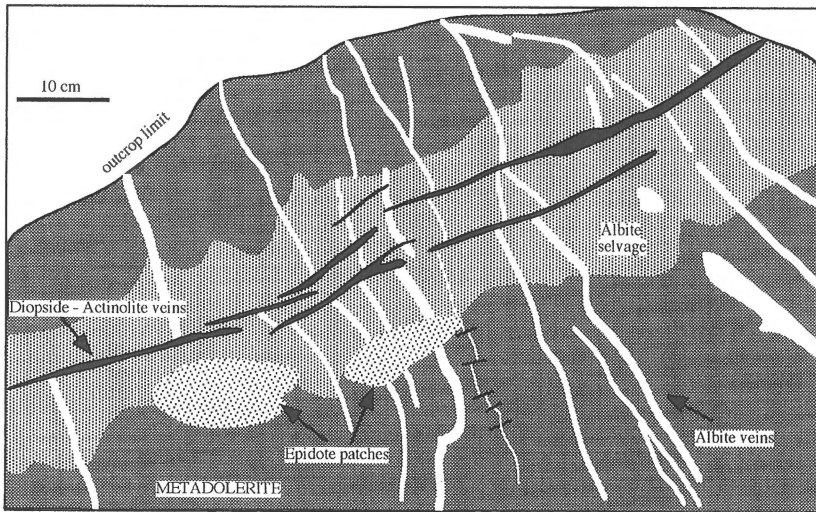


Figure 3. Schematic representation of an outcrop in the Fullarton River Gorge (most western outcrop of mafic rocks in Figure 2). Albite veins are cut by later diopside-actinolite veins, which have produced an intensely red albite alteration zone. Epidote occurs in sporadic, late-overprinting patches.

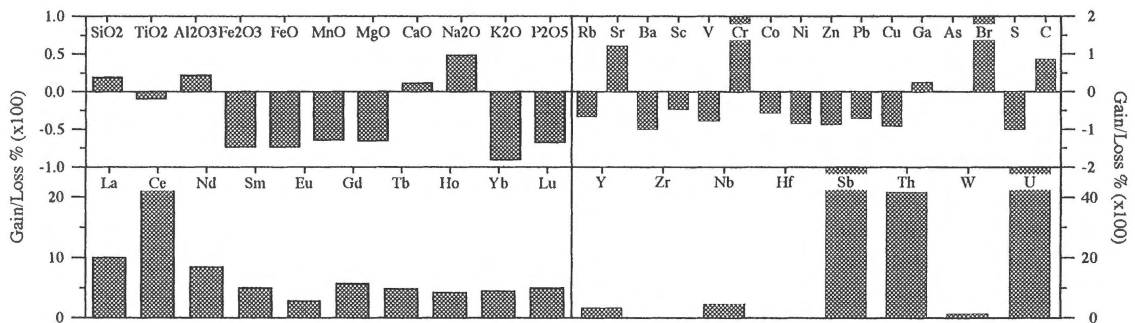


Figure 4. Gain/loss diagrams for an unaltered and an altered mafic rock (samples 1.1 and 1.2 respectively, see Table 1). The diagrams illustrate that Fe, base metals and S are lost, while REE are enriched (especially LREE). Elements that are immobile have zero gain/loss %.

ses. Whole-rock FeO determinations were performed by means of titration against potassium dichromate. Carbon and S were determined by a LECO analyser.

Rare-earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Ho, Yb, Lu), Hf, Ta, Sb, Th, W and U have been determined by instrumental neutron activation analysis (INAA) at Becquerel Laboratories Pty in Sydney, Australia.

Retrograde alteration

Pervasive albite-actinolite alteration occurred in and around high-strain zones during late to post-D₂ retrograde metamorphism. The greenschist-facies alteration

assemblage (i.e. albite and actinolite, locally diopside) overprints the regional metamorphic amphibolite-facies assemblage. This overprinting involved a vein-style alteration with greenschist-facies mineral assemblages (Figure 3, Phillips et al. 1994).

Widespread retrograde alteration assemblages include albite, and Mg-rich actinolite with or without magnetite, clinopyroxene, hematite, titanite, Na-scapolite, epidote, calcite, prehnite, quartz and K-feldspar. The overall paragenetic sequence is (Figure 3):

- 1) albite, actinolite, magnetite, titanite (\pm diopside \pm Na-scapolite \pm quartz) (first),
- 2) K-feldspar, quartz, hematite,

Table 1. Whole-rock analyses of unaltered and altered mafic rocks from the Fullarton River and Maramungee Creek localities.

Sample Type	Fullarton River					Maramungee Creek				
	Suite 1			Suite 2		Suite 3				
	1.1	1.2	1.3	2.1	2.2	3.1	3.2	3.3	3.4	3.5
Un	A	A	Un	A	Un	Un/A	Un/A	A/Un	A	
SiO ₂	47.31	56.39	45.61	46.90	52.89	49.05	48.59	50.45	49.23	54.01
TiO ₂	1.67	1.52	1.60	1.69	2.01	1.20	1.42	1.13	1.59	1.49
Al ₂ O ₃	12.50	15.28	14.08	13.23	11.94	14.89	13.97	15.90	12.32	14.12
Fe ₂ O ₃	8.16	2.16	8.62	7.13	2.52	11.35	7.49	8.32	12.55	7.55
FeO	7.58	2.02	2.30	8.15	2.34	0.75	4.89	2.27	1.34	2.33
MnO	0.14	0.05	0.01	0.18	0.10	0.14	0.12	0.13	0.14	0.13
MgO	5.72	2.01	4.14	6.45	4.77	5.44	6.27	6.55	6.18	5.49
CaO	8.85	9.84	19.93	8.30	14.05	10.22	10.13	10.36	11.25	7.74
Na ₂ O	4.49	6.64	1.83	3.76	3.75	3.96	4.84	3.25	2.94	2.57
K ₂ O	0.21	0.02	0.01	1.06	1.31	0.57	0.75	1.11	1.25	4.68
P ₂ O ₅	0.06	0.02	0.03	0.07	0.02	0.11	0.06	0.09	0.09	0.13
LOI	2.17	3.07	2.16	2.30	3.10	1.05	1.92	1.82	1.70	1.83
SUM	99.69	99.24	100.68	100.13	99.06	98.78	101.01	101.62	100.74	102.33
Rb	12	4	4	36	42	14	14	39	32	233
Cs	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.1	< 1.0	< 1.0	< 1.0
Sr	135	298	210	141	210	175	191	193	92	302
Ba	127	< 100	< 100	< 100	112	< 100	120	200	137	1450
Sc	50	27	42	50	45	36	38	38	49	35
V	789	182	449	799	257	310	291	277	378	329
Cr	0	8	2	0	6	96	179	149	96	62
Co	57	25	35	67	27	78	91	83	73	57
Ni	113	17	31	122	22	62	72	82	68	47
Zn	55	7	14	56	14	34	19	29	31	37
Pb	17	5	8	3	6	1	1	1	1	1
Cu	109	9	15	197	6	74	38	87	17	8
Ga	20	25	46	24	14	19	23	21	25	22
As	1	1	2	1	1	1	1	1	1	3
Br	< 1	1	2	2	1	17	21	< 1	< 1	2
S	1063	< 50	< 50	1132	< 50	486	570	75	< 50	< 50
C	1396	2596	2026	652	2847	806	979	< 500	514	651
La	4	44	49	4	62	10	9	9	10	45
Ce	6	144	150	6	204	19	19	18	19	65
Nd	7	66	65	6	88	13	13	11	11	43
Sm	2	12	12	2	16	3	4	3	3	8
Eu	0.7	2.6	3.1	0.9	3.4	0.7	0.9	1.0	0.6	1.9
Gd	2.0	13.3	13.5	2.4	18.0	2.8	3.8	3.3	3.0	8.2
Tb	0.4	2.3	2.3	0.4	3.1	0.5	0.7	0.6	0.5	1.4
Ho	0.6	3.1	3.0	0.6	3.9	0.7	0.9	0.8	0.8	1.9
Yb	1.4	7.6	7.2	1.7	9.3	1.8	2.3	1.9	2.2	4.7
Lu	0.2	1.2	1.0	0.2	1.3	0.3	0.4	0.3	0.3	0.7
Y	17	75	91	18	91	22	26	23	26	46
Zr	50	52	58	50	59	84	89	76	101	165
Nb	5	28	36	5	36	7	8	7	9	14
Hf	1.3	1.3	1.2	1.3	1.7	1.9	2.1	2.0	2.4	4.1
Ta	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	1.8	1.9	2.0	< 1.0	1.9
Sb	< 0.2	0.6	1.4	< 0.2	< 0.2	< 0.2	< 0.2	0.2	< 0.2	< 0.2
Th	0.3	12.8	10.4	0.3	13.8	2.7	2.0	2.4	2.8	4.3
W	51	129	124	51	91	204	410	345	192	233
U	< 2.0	13.5	13.3	< 2.0	14.3	< 2.0	< 2.0	< 2.0	< 2.0	< 2.0

Note: Un: unaltered, A: altered mafic rocks. FeO obtained by titration. Oxides in wt%, elements in ppm. Gold in all samples below 1 ppb.

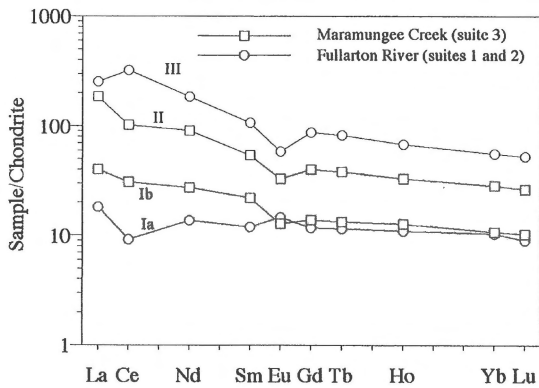


Figure 5. REE chondrite-normalized plot of Fullarton River and Maramungee Creek values. Trends Ia (Fullarton) and Ib (Maramungee) are of the least altered rocks. Trends II and III are of altered versions of Maramungee and Fullarton River respectively. This shows an enrichment of REE, particularly LREE, in altered mafic rocks.

3) epidote, calcite, prehnite, quartz, \pm monazite, \pm allanite, \pm fluorite (last).

Alteration temperatures obtained from fluid-inclusion studies of quartz indicate a temperature decrease from >450 to 270 °C from sequence 1 to sequence 3, and associated salinities of 40 down to 20 wt% NaCl (De Jong & Williams 1995).

Element mobility

In the Cloncurry terrain, unlike in many other terrains, there are no elements that, a priori, can be assumed to have been immobile, and we have to start with the premise that all REE and HFSE may have been mobile, until shown otherwise. This problem can be solved by comparison of the unaltered hornblende-plagioclase mafic rocks with the products of the alteration process. Geochemical data in Table 1 and the relative gain/loss diagrams in Figure 4 show that certain elements such as Ti, Al and Hf, and to a lesser extent Sc, Ga and Zr, are the only elements that have remained relatively immobile during alteration. These elements therefore can be used as reference for the relative mobility of other elements.

REE distribution

The REE concentrations in a solution which interacts with a rock will be controlled by several factors: 1) concentrations of REE in the rock, 2) the partitioning behaviour of the REE between the rock phase and

the interacting solution, and 3) the types of alteration reactions that take place (Graf 1977). The LREE have a larger radius than the HREE, and are included in the group of incompatible or large-ion lithophile (LIL) elements. HREE are, in general, more compatible with minerals such as zircon (Taylor & Fryer 1983), or with epidote (allanite) in a hydrothermal alteration system (Palacios et al. 1986). These features dictate which phases they are likely to partition into when crystallizing.

In mafic rocks in the Cloncurry region, enrichment is more pronounced in LREE than in HREE; an increase from 15 to 300 times chondritic values is seen in LREE, and one from 10 to 60 in HREE (Figure 5). The unaltered REE patterns are relatively flat compared to the altered REE patterns, with a chondrite-normalized $LREE_N/HREE_N$ ratio close to unity (Figure 5, trends Ia and b). Mineralogically, the unaltered rocks consist of plagioclase, hornblende, quartz and magnetite. The second REE trend shows a high increase in $LREE_N$, 15 to 100, and to a lesser degree in $HREE_N$, 10 to 30 (Figure 5, trend II). These patterns are from rocks with a pronounced epidote, clinopyroxene, calcite and scapolite alteration. The third trend (III) shows an even further increase in $LREE_N$, 100 to 300, and again to a lesser extent in $HREE_N$, 30 to 60. Mineralogically, these rocks are mainly affected by albite alteration. This last REE pattern has a distinct negative Eu anomaly, also seen in trend II.

Fluorine is present in a late-stage rare coarse purple fluorite (Fullarton River) and possibly also in the apatite-alteration minerals, which occur widespread in Maramungee and Fullarton River; chlorine is present in scapolite and apatite. The main host minerals for the REE are believed to be the late-stage-precipitated monazite and allanite, and additionally also apatite, titanite and actinolite. The REE host minerals favour LREE partitioning; this is partly reflected in the REE trends (Figure 5). The least altered trend I is reflected by samples from both localities; however, trend II was mainly obtained from the Maramungee Creek samples, while the most REE-enriched trend III is from the Fullarton River samples.

V, Y and Nb movement

Tholeiitic basic igneous rocks generally contain 150 to 350 ppm V (Wyllie 1967) depending on the magma evolution, and in particular on the separation of Ti-V-bearing magnetite (Mason & Moore 1982). In

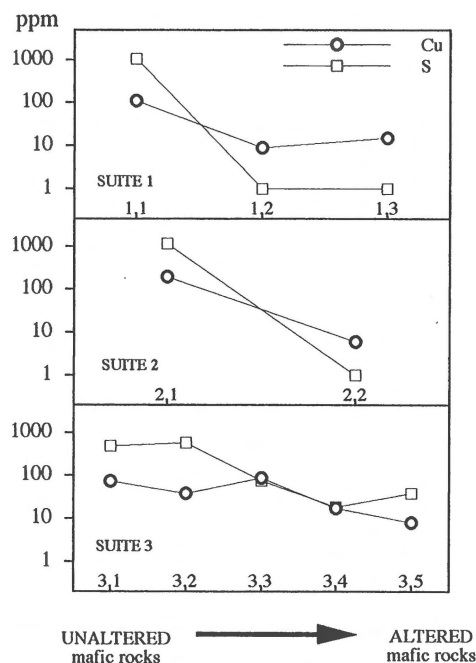


Figure 6. Copper and S values of suites 1 to 3 (1.1, 1.2 etc. are sample numbers, see Table 1). There is a strong depletion of both Cu and S in the altered mafic rocks.

the Cloncurry region, the unaltered mafic rocks are quite rich in V and values fluctuate considerably within suites of unaltered mafic rocks and their altered equivalents (Figure 4, Table 1). In the least altered rocks the V content tends to be quite high with a few samples exhibiting values much higher (799 ppm) than what is normal for an unaltered mafic rock. The altered zones corresponding to these suites show a strong depletion of V (257 ppm absolute). Generally the depletion of V in most samples is not this great; however, it is still very significant and is possibly related to the Na-rich alteration fluids which exert a mineralogical control on the Ti, and possibly V, content in magnetite.

Yttrium and Nb also show mobility between unaltered and altered suites of rocks (Figure 4, Table 1). The values for the unaltered rock (Y: 18 ppm, Nb: 5 ppm) are in line with those of mafic igneous rocks in general (Wyllie 1967). In the altered zones an increase occurs in these elements (Y: 91 ppm, Nb: 36 ppm). These are the extreme cases in the sample list (Table 1); however, the mobility of Y and Nb is demonstrated in all samples.

Leaching of Cu (S) and Fe related to regional sodic-calcic alteration

The Cu contents in the unaltered mafic rocks at Cloncurry average 116 ppm; this is typical of mafic rocks. The highest Cu value is 197 ppm (Table 1). A considerable drop in Cu (Pb, Zn, Co, Ni) and Fe is recorded in the altered rocks indicating that these elements have been leached (Figure 4, Table 1). Analyses indicate that 90% of the Cu has been leached during alteration and Fe values indicate a 70% loss. Williams (1994) calculated the loss of Fe_2O_3 (total) as 8.6 g per 100 g in mafic rocks from Maramungee Creek. If this is the case on a large scale then there are implications for the surrounding prospects and deposits (Osborne, Maronan, Fairmile, Eloise, Mount Kalkadoon). Williams (1994) also pointed out that the Fe in Fe-rich deposits could be derived from this leaching. The local overprinting of younger alteration styles influences the geochemistry; for example during sequence 2 of the paragenesis, samples are locally enriched in hematite-dusted K-feldspar. Sulfur behaves in a similar fashion to Cu, i.e. strong leaching occurs during alteration (Figures 4, 6).

Discussion

Peak metamorphism occurred during early D_2 (Page 1994). The fluids responsible for the alteration associated with the rock types of Cloncurry were possibly derived during metamorphism and deformation (D_1 to early D_3). The most intense alteration episode was during retrograde metamorphism which almost completely obliterated peak-metamorphic assemblages.

Gain/loss diagrams show the mobility of elements with respect to least altered rocks (Figure 4). For this to be effective, the pristine chemical composition of the mafic rocks acts as a reference frame for determining the mobility of elements. In the Cloncurry region, the saline fluids have been responsible for mobilizing all compatible, and nearly all incompatible elements. Three elements that have remained relatively immobile are Ti, Al and Hf. The general trend seen in Figure 4 is an increase in REE and incompatible elements, and a decrease in compatible elements.

The conditions during the alteration process became more oxidizing. This is indicated by an increase in $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio with intense alteration (Table 1), and by more pronounced negative Eu anomalies in trends II and III (Figure 5; Parr 1992).

The REE patterns also show an evolution of the fluid with depth. The unaltered starting material is uniform at both Maramungee Creek and Fullarton River (Figure 5, trends Ia and Ib). The alteration incurred at depth during the ductile regime, as seen at Maramungee Creek, involved fluids that show less enrichment in REE (trend II). By the time the fluids had moved up into the brittle regime, observed at Fullarton River, they had evolved more (trend III), and the mineralogy changed slightly to encompass more exotic minerals to host REE, e.g. monazite and allanite.

The presence of F and Cl in the alteration fluids has direct implications for the mobility of REE (particularly LREE), HFSE (V, Y, Nb) and the movement of Cu (and S) out of the system. This is not unlike the Olympic Dam deposit in South Australia, where REE mobility and F-rich hydrothermal fluids are associated (Oreskes & Einaudi 1990).

Large-scale sodic alteration, associated with brecciation, hematite and muscovite-alteration, and enrichment in REE, especially in LREE (La and Ce), are part of the Proterozoic Olympic Dam breccia complex (Oreskes & Einaudi 1990, Reeve et al. 1990, Hitzman et al. 1992). The suite of ore metals (Cu, U, Au-Ag) in this complex, with no significant Pb and Zn, and its associated elements (Fe, Ba, F and REE) are unique (Hitzman et al. 1992). The brecciation and the style of alteration and enrichment of LREE are similar to those of the Cloncurry terrain. However, unlike the Olympic Dam deposit, the Cloncurry region also has higher concentrations of incompatible elements (Figure 4), including LREE, over hundreds of square kilometres.

The minimum amount of Cu leached from the mafic rocks during the regional sodic-calcic alteration at Cloncurry matches the amount of Cu hosted in nearby deposits. For example, Osborne is one of the largest Cu-Au deposits in the district, and hosts 36 million tonnes of 2% Cu (Adshead & Keough 1993). An average of 100 ppm Cu in 10% of the mafic rocks at Cloncurry, in a 2000-km² zone, 200 m thick and with a specific gravity of 2.9 g/cm³, would give approximately 1.2 million tonnes of Cu. This is more than the total Cu at Osborne (0.7 million tonnes).

Conclusions

Some of the highest concentrations of REE in the Cloncurry region are associated with sodic-calcic alteration and Cu-Fe depletion. The alteration fluid was active over an area of 2000 km², and appears to have some

characteristics in common with Proterozoic deposits of iron oxide and of Cu-U-Au and REE, such as Olympic Dam (Hitzman et al. 1992).

Regional chondrite-normalized REE patterns in Proterozoic terrains can be a result of metallic sulfide mineralization. The alteration fluid in the Cloncurry terrain is LREE-enriched and causes Cu and Fe to be leached from the country rock. This could have implications for a possible source of the surrounding Proterozoic Cu deposits.

Oxidizing conditions, depletion of V, Cu, S and Fe, addition of Nb, Y and REE, the presence of F and Cl, and large volumes of hot highly saline fluids, all occurred during retrograde metamorphism. The evolution of this complex fluid is recorded in two crustal levels: ductile and brittle.

Acknowledgements

GdJ held the W.C. Lacy and Overseas Postgraduate Research scholarship at James Cook University. JR holds a James Cook University, National Key Centre of Economic Geology scholarship. Logistics were provided by the National Key Centre 'Cloncurry project'. Whole-rock, LECO and titration analyses were undertaken by Sharon Ness and Alan Chappell at the James Cook University Advanced Analytical Centre (AAC).

References

- Adshead, N.D. & D. Keough 1993 Exploration history and current status of the Osborne copper-gold project. Symposium on Recent Advances in the Mount Isa Block – Austral. Inst. Geosci. Bull. 13: 41–42.
- Beardmore, T.J., S.P. Newbery & W.P. Laing 1988 The Maronan Supergroup: an inferred early volcanosedimentary rift sequence in the Mount Isa Inlier, and its implications for ensialic rifting in the Middle Proterozoic of northwest Queensland – Precamb. Res. 40/41: 487–507.
- De Jong, G. & P.J. Williams 1995 A giant metasomatic system formed during exhumation of mid crustal Proterozoic rocks in the vicinity of the Cloncurry Fault, NW Queensland – Austral. J. Earth Sci. 42: 281–290.
- Graf, J.L. Jr. 1977 Rare earth elements as Hydrothermal traces during the formation of Massive Sulfide Deposits in Volcanic Rocks – Econ. Geol. 72: 527–548.
- Hannan, K.W., S.D. Golding, H.K. Herbert & H.R. Krouse 1993 Contrasting alteration assemblages in metabasites from Mount Isa, Queensland: Implications for copper genesis – Econ. Geol. 88: 1135–1175.
- Hellingwerf, R.H. 1992 Trace element zonation in marbles hosting Cu-Zn-Fe-Pb-As sulphides at Gruvasen, south central Sweden – Geol. Foren. Stockholm Förh 114: 17–27.

- Hellman, P.L., R.E. Smith & P. Henderson 1979 The mobility of the Rare Earth Elements – Evidence and implications from selected terrains affected by burial metamorphism – *Contrib. Min. Petrol.* 71: 23–44.
- Hitzman, M.W., N. Oreskes & M.T. Einaudi 1992 Geological characteristics and tectonic setting of Proterozoic iron oxide (Cu-U-Au-REE) deposits – *Precamb. Res.* 58: 241–287.
- Kwak, T.A.P. & P.B. Abeyinghe 1987 Rare earth and uranium minerals present as daughter crystals in fluid inclusions, Mary Kathleen U-REE skarn, Queensland, Australia – *Mineralog. Magazine* 51: 665–670.
- Loosveld, R.J.H. 1989a The Intra-cratonic evolution of the Central Eastern Mount Isa Inlier, Northwest Queensland, Australia – *Precamb. Res.* 44: 243–276.
- Loosveld, R.J.H. 1989b The synchronism of crustal thickening and high T/low P metamorphism in the Mount Isa Inlier, Australia 1. An example, the central Soldiers Cap belt – *Tectonophysics* 15: 173–190.
- Loosveld, R.J.H. & Schreurs 1987 Discovery of thrust klippen, northwest of Mary Kathleen, Mt Isa Inlier, Australia – *Austral. J. Earth Sci.* 34: 387–402.
- Mason, B. & C.B. Moore 1982 *Principles of geochemistry* – John Wiley & Sons, 4th ed., 350 pp.
- Meschede, M. 1986 A method of discriminating between different types of mid-ocean ridge basalts and continental tholeiites with the Nb-Zr-Y diagram – *Chem. Geol.* 56: 207–218.
- Oreskes, N. & M.T. Einaudi 1990 Origin of Rare Earth element-enriched hematite breccias at the Olympic Dam Cu-U-Au-Ag deposit, Roxby Downs, South Australia – *Econ. Geol.* 85: 1–28.
- Page, R.W. 1994 Mount Isa geochronology – 1993 Yearbook Austral. Geol. Sur. Organ., Canberra, 60 pp.
- Palacios, C.M., U.F. Hein & P. Dulski 1986 Behaviour of rare earth elements during hydrothermal alteration at the Buena Esperanza copper-silver deposit, northern Chile – *Earth Plant. Sci. Lett.* 80: 208–216.
- Parr, J.M. 1992 Rare-earth element distribution in exhalites associated with Broken Hill-type mineralisation at the Pinnacles deposit, New South Wales, Australia – *Chem. Geol.* 100: 73–91.
- Phillips, G.N., P.J. Williams & G. De Jong 1994 The nature of metamorphic fluids and significance for metal exploration – In: Parnell, J. (ed.) *Geofluids: Origin, migration and evolution of fluids in sedimentary basins.* Geol. Soc. Spec. Publ. 78: 55–68.
- Ramsden, A.R., D.H. French & D.I. Chalmers 1993 Volcanic-hosted rare-metals deposit at Brockman, Western Australia. Mineralogy and geochemistry of the Niobium Tuff – *Mineralium Deposita* 28: 1–12.
- Reeve, J.S., K.C. Cross, R.N. Smith & N. Oreskes 1990 Olympic Dam copper-uranium-gold-silver deposit – In: Hughes, F.E. (ed.) *Mineral Deposits of Australia and Papua New Guinea.* Austral. Inst. Mining Metallurgy, Melbourne 2: 1009–1035.
- Rogers, J.J.W., E.B. Suayah & J.M. Edwards 1984 Trace elements in continental-margin magmatism: Part IV. Geochemical criteria for recognition of two volcanic assemblages near Auburn, western Sierra Nevada, California – *Geol. Soc. Am. Bull.* 95: 1437–1445.
- Salvi, S. & A.E. Williams-Jones 1990 The role of hydrothermal processes in the granite-hosted Zr, Y, REE deposit at Strange Lake, Quebec/Labrador: evidence from fluid inclusions – *Geochim. Cosmochim. Acta* 54: 2403–2418.
- Taylor, R.P. & B.J. Fryer 1983 Rare earth element litho-geochemistry of granitoid mineral deposits – *Canad. Inst. Mining Bull.* 76: 74–84.
- Williams, P.J. 1994 Iron mobility during synmetamorphic alteration in the Selwyn Range area, NW Queensland: implications for the origin of ironstone-hosted Au-Cu deposits – *Mineralium Deposita* 29: 250–260.
- Wyllie, P.J. 1967 (ed.) *Ultramafic and related rocks* – John Wiley & Sons, Inc., 464 pp.