Granitoids Associated with Porphyry Cu Deposits in the Central Asian Orogenic Belt – Characteristics and Oxygen Fugacity

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ABSTRACT

Ore-bearing intrusions in the Central Asian Orogenic Belt (CAOB) were examined from nine mines: Boshekul, Nurkazgan, Kounrad, Borly, Aktogai, Koksai, Baogutu, Tuwu and Erdenet. The intrusions are diorite, granodiorite and tonalite with SiO_2 contents ranging from 58 to 75 wt per cent, and show mildly fractionated rare earth elements (REE) ($[LREE]_N/[HREE]_N$ = 2.7–4.7) – light REE and heavy REE – and varying Eu anomalies ([Eu]/[Eu]* = 0.58–1.4). The ratios of Sr/Y vary from 7.9 to 115 and the contents of Y from 4.6 to 23.9 ppm. The parental magmas of the intrusions are intrinsically oxidised. Zircon grains in the ore-bearing rocks from large- and intermediate-sized porphyry Cu deposits show high Ce^{4+}/Ce^{3+} ratios characterised by 65–422 at Boshekul (>4.1 Mt Cu), 76–480 at Kounrad (>4.8 Mt Cu), 90–280 at Aktogai (>12 Mt Cu), 80–250 at Erdenet (>11 Mt Cu) 74–370 at Nurkazgan (>3.9 Mt Cu), 100–210 at Koksai (>1.6 Mt Cu), and 71–340 at Tuwu (~2.0 Mt Cu). In two small deposits, the ore-bearing rocks display low values of Ce^{4+}/Ce^{3+}; Borly (0.6 Mt Cu) ranging from 28 to 158, and Baogutu (0.6 Mt Cu) from 29 to 113. The Ce^{4+}/Ce^{3+} ratio of 120 distinguishes large intermediate-size deposits from small-size deposits. This information is potentially useful in exploration for porphyry Cu deposits in the belt.

INTRODUCTION

Porphyry Cu deposits are associated with oxidised, calc-alkaline intermediate to felsic intrusions (Hedenquist and Lowenstern, 1994; Hattori and Keith, 2001; Cooke, Hollings and Walshe, 2005; Sillitoe, 2010). Ce is 4+ in oxidised conditions and readily incorporated into zircon crystal structure and produces high ratios of Ce^{4+}/Ce^{3+}. Since the rest of rare earth elements (REE) are 3+, zircon crystallised in oxidised magmas displays positive Ce anomalies. Previous studies show that zircons with high Ce^{4+}/Ce^{3+} ratios are found in igneous rocks hosting large porphyry Cu deposits in Chile (Ballard, Palin and Campbell, 2002), Tibet (Liang *et al*, 2006) and other areas in China (Qiu *et al*, 2013; Han *et al*, 2013). The Central Asian Orogenic Belt (CAOB) contains Palaeozoic porphyry Cu deposits of various sizes (Figure 1). The CAOB,

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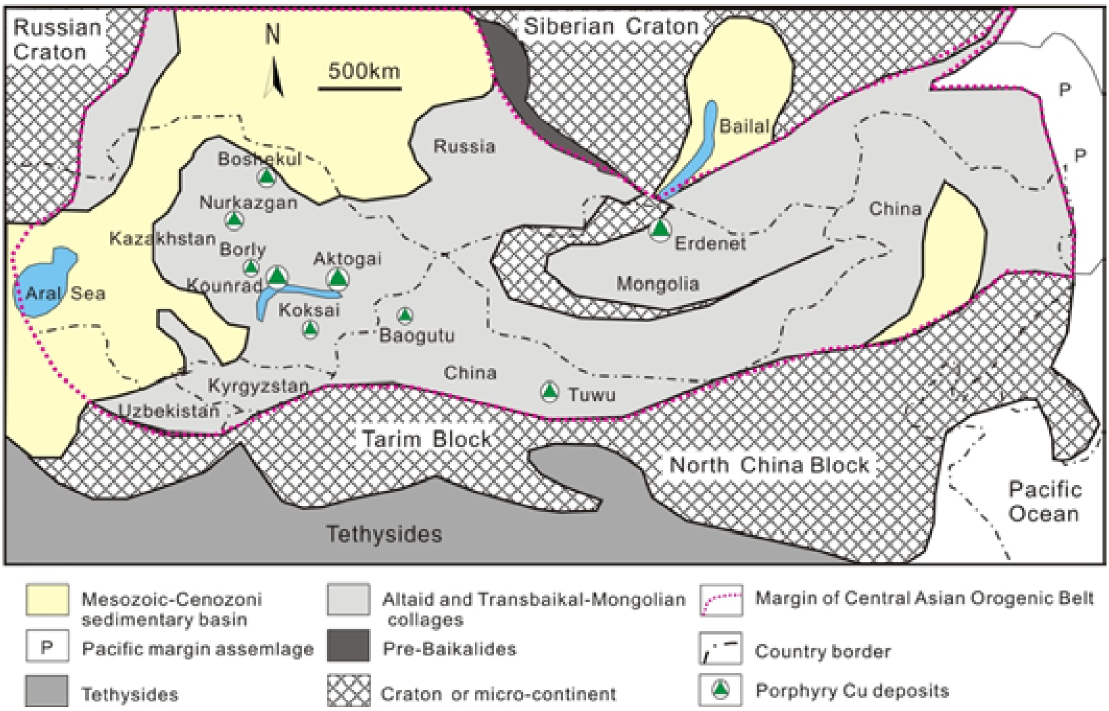

FIG 1 – Map showing the principal tectonic elements of the Central Asian Orogenic Belt and the porphyry Cu deposits studied in the paper (modified after Xiao *et al*, 2009; Seltmann, Porter and Pirajno, 2014).

therefore, presents an opportunity to study the relationship between tonnage of metals and oxygen fugacity of magmas of ore-bearing granitoids.

SAMPLES AND METHODS

We selected 12 ore-bearing intrusions from nine deposits: Boshekul, Nurkazgan, Kounrad, Borly, Aktogai, Koksai in Kazakhstan, Baogutu and Tuwu in China and Erdenet in Mongolia (Figure 1). All rocks in mineralised rocks show variable degrees of hydrothermal alteration characterised by illite replacing plagioclase and chlorite replacing hornblende, but we selected least altered rocks in active mining areas for whole-rock chemical analysis and zircon separation at the State Key Laboratory of Lithospheric Evolution, Chinese Academy of Sciences. Approximately 50–100 zircon grains per sample were separated and mounted in Epoxy resin. After examination of grains with CL-SEM, representative grains were selected for trace-element analysis with LA-ICP-MS at the Geological Survey of Canada. As the concentrations of La and Pr in zircon are very low and close to detection limits, we calculated Ce^{4+}/Ce^{3+} following the method described by Ballard, Palin and Campbell (2002). In our calculation, Ce^{3+} was evaluated from the concentrations of Nd, Sm, Gd, Tb, Dy, Y, Ho, Er, Yb, Lu in zircon grains and whole rock analyses.

RESULTS AND DISCUSSION

The ore-bearing granitoids selected for this study are diorite, granodiorite and tonalite (Figure 2 and Table 1). They show similar mineralogy but different proportions and the mineralogy and lithology of granitoid rocks are listed in Table 1. Representative rocks are shown in Figure 2. The ore-bearing rock at Boshekul is a tonalite porphyry containing phenocrysts of plagioclase, hornblende and quartz in a groundmass of quartz, plagioclase and minor magnetite. In

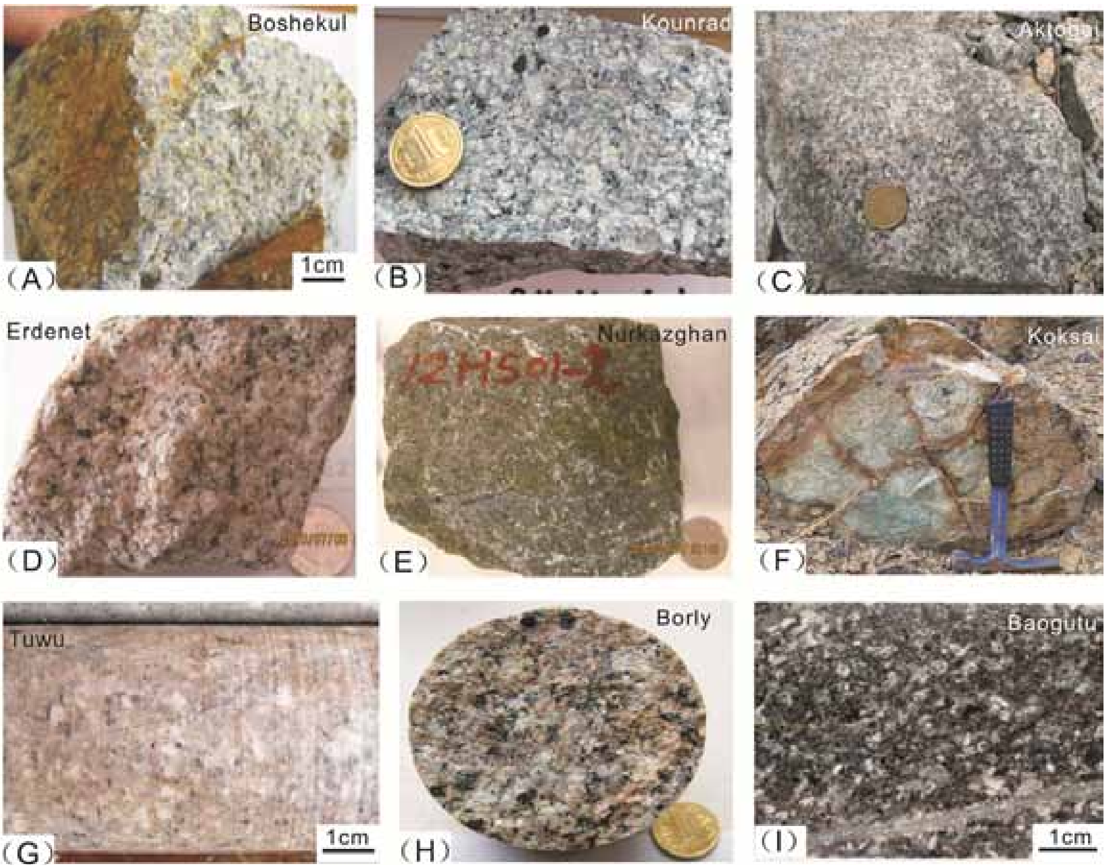

FIG 2 – Photographs of ore-bearing granitic rocks from the porphyry Cu deposits in the Central Asian Orogenic Belt. (A) Tonalite porphyry at Boshekul; (B) Granodiorite porphyry at Kounrad; (C) Tonalite porphyry at Aktogai; (D) Granodiorite at Erdenet; (E) Diorite at Nurkazgan; (F) Granodiorite porphyry at Koksai; (G) Tonalite porphyry at Tuwu; (H) Granodiorite porphyry at Borly; (I) Diorite at Baogutu.

Kounrad, the ore-bearing rocks are granodiorite porphyry (Figure 2b) and granodiorite. The former contains phenocrysts of plagioclase, K-feldspar, hornblende, and quartz in a groundmass of quartz, plagioclase and minor magnetite. The latter contains plagioclase, K-feldspar and minor hornblende, quartz and magnetite. In Aktogai, the ore-bearing tonalite porphyry (Figure 2c) contains phenocrysts of plagioclase and minor hornblende in a groundmass of a plagioclase, quartz and minor magnetite. In Erdenet, the mineralised granodiorite (Figure 2d) contains plagioclase, K-feldspar, hornblende, biotite, quartz and minor magnetite and titanite. In Nurkazgan, the ore-bearing diorite (Figure 2e) contains plagioclase, hornblende, quartz and minor magnetite. In Koksai, the ore-bearing granodiorite porphyry (Figure 2f) contains phenocrysts of plagioclase and minor K-feldspar and biotite in a groundmass of plagioclase, quartz and minor magnetite. In Tuwu, the ore-bearing tonalite porphyry (Figure 2g) contains phenocrysts of plagioclase, quartz and minor biotite in a groundmass of plagioclase, quartz and minor magnetite. The granodiorite porphyry (Figure 2h) at Borley contains phenocrysts of plagioclase, minor K-feldspar and biotite in a groundmass of plagioclase, quartz and minor magnetite. In Baogutu, the diorite (Figure 2i) contains plagioclase, hornblende, biotite, quartz and minor ilmenite, magnetite and titanite.

Samples show SiO_2 contents ranging from 58 to 75 wt. per cent. In the Zr/TiO_2 versus Nb/Y diagram (Figure 3a), most samples plot in the fields of diorite and granodiorite, which confirm

TABLE 1

Tonnage and mineralogy of studied granitic rocks hosting porphyry-type deposits.

Deposit name	Tonnage Cu (Mt)[a]	Lithology	Photograph	Primary mineralogy	Ce^{4+}/Ce^{3+} in zircon
Boshekul	>4.1	tonalite porphyry	2A	Phenocrysts: Pl, Hbl, Qz; Groundmass: Qz, Pl, Mag	65–422 (av 239)
Kounrad	>5.8	granodiorite porphyry	2B	Phenocrysts: Pl, Kfs, Hbl, Qz; Groundmass: Qz, Pl, Kfs, Mag	76–483 (av 241)
		granodiorite		Pl, Kfs, Hbl, Qz, Mag	
Aktogai	>12	plagiogranite porphyry	2C	Phenocrysts: Pl, Hb; Groundmass: Qz, Pl, Mag	90–279 (av 182)
Erdenet	>11	granodiorite	2D	Pl, Kfs, Hbl, Bt, Qz, Mag, Ttn	80–249 (av 150)
Nurkazgan	>3.9	diorite	2E	Pl, Hbl, Qz, Mag	74–374 (av 174)
Koksai	>1.6	granodiorite porphyry	2F	Phenocrysts: Pl; Kfs, Qz; Groundmass: Qtz, Pl, Mag	100–214 (av 166)
Tuwu	>2	tonalite porphyry	2G	Phenocrysts: Pl; Qz; Bt; Groundmass: Pl, Qz, Mag	71–344 (av 188)
Borly	>0.6	tonalite porphyry	2H	Phenocrysts: Pl, Kfs, Bt; Groundmass: Pl, Qz, Mag	8–158 (av 68)
Baogutu	>0.6	diorite	2I	Pl, Hbl, Bt, Qz, Ilm, Mag, Ttn	29–113 (av 56)

[a]past production plus reserves.

Abbreviations for minerals: Pl = plagioclase; Qz = quartz; Kfs = K-feldspar; Hbl = hornblende; Bt = biotite; Mag = magnetite; Ilm = ilmenite; Ttn = titanite.

the petrographic identification of rock types. Zirconium contents vary from 51 to 176 ppm. REE are moderately fractionated with high light REE relative to heavy REE ($[LREE]_N/[HREE]_N$ = 2.68–4.69) with very weak negative Ce anomalies ([Ce]/[Ce]* = 0.93–1.01), and negative or positive Eu anomalies ([Eu]/[Eu]* = 0.58–1.42) (Figure 3b). The ratios of Sr/Y vary from 7.9 to 115 and the contents of Y range from 4.6 to 23.9 ppm. High Sr contents of several samples may be partially attributed to hydrothermal alteration.

All zircon grains show oscillatory zoning due to varying Th and U in backscattered electron images and CL-SEM images. Sector zoning was rare in samples, and grains with apparent sector zoning were avoided for further analysis. The zircons are magmatic in origin with high Th/U ratios (from 0.3 to 0.9). The zircons show low contents of LREE and high HREE and are characterised by positive Ce anomalies with variable negative Eu anomalies. Zircon grains from large porphyry Cu deposits show variable, but high Ce^{4+}/Ce^{3+} ratios (Table 1). Boshekul (>4.1 Mt Cu) yields values that range from 65 to 422 (av 239), Nurkazgan (>3.9 Mt Cu) from 74 to 374 (av 174), Kounrad (>4.8 Mt Cu) from 76 to 483 (av 241), Aktogai (>12 Mt Cu) from 90 to 279 (av 182) and Erdenet (>11 Mt Cu) from 80 to 249 (av 150). In two intermediate-size deposits, the ore-bearing porphyry intrusions show intermediate to high Ce^{4+}/Ce^{3+} ratios; Koksai (>1.6 Mt Cu) shows values ranging from 100 to 214 (av 166), and Tuwu (~2.0 Mt Cu) from 71 to 344 (av 188). In two small deposits, the ore-bearing porphyries display a narrow range and low values of Ce^{4+}/Ce^{3+}; Borly (0.6 Mt Cu) range from 28 to 158 (av 68), and Baogutu (0.6 Mt Cu) from 29 to 113 (av 56). The results suggest that higher Ce^{4+}/Ce^{3+} ratios in zircon are associated with greater tonnage of Cu (Figure 4). The Ce^{4+}/Ce^{3+} ratios greater than 120 are the values associated with large and intermediate-size deposits in this belt.

Ce^{4+}/Ce^{3+} values of zircon grains are controlled by fO_2, temperature and the compositions of magmas. Our studied granitoids have similar mineralogy and comparable Al and alkali contents. The ratios of Al/(Na+K) range from 1.40 to 2.80 (av 1.87). Temperatures of

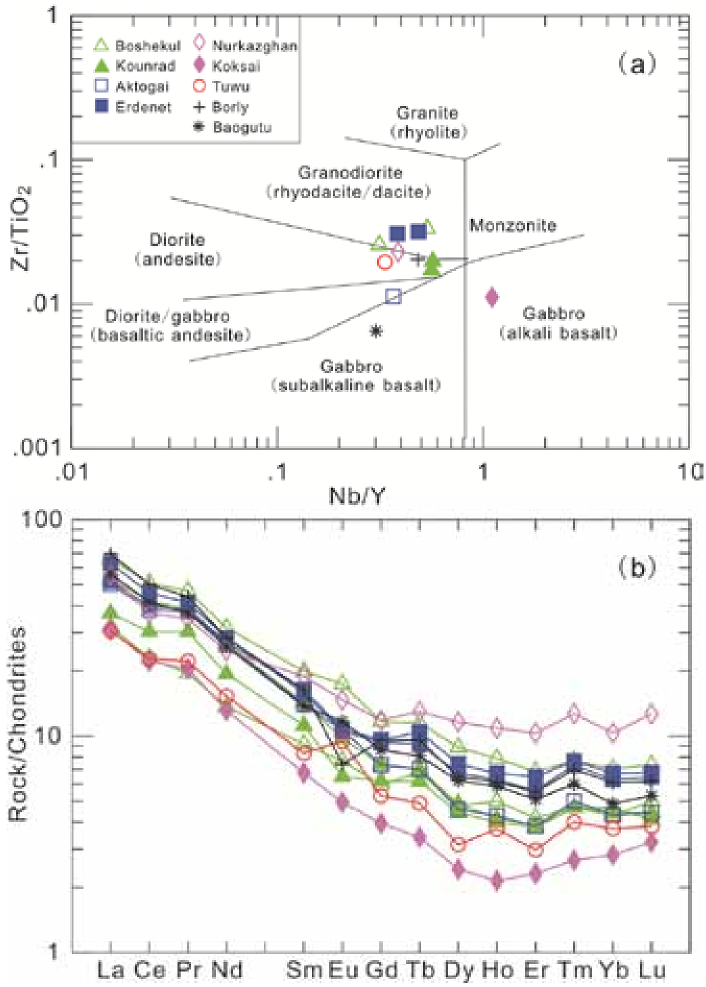

FIG 3 – (A) Zr/TiO_2 versus Nb/Y classification diagrams (Vry *et al*, 2010) of studied ore-bearing granitic rocks in the Central Asian Orogenic Belt; (B) Chondrite-normalised rare earth element patterns for the mineralised granitic rocks in the CAOB.

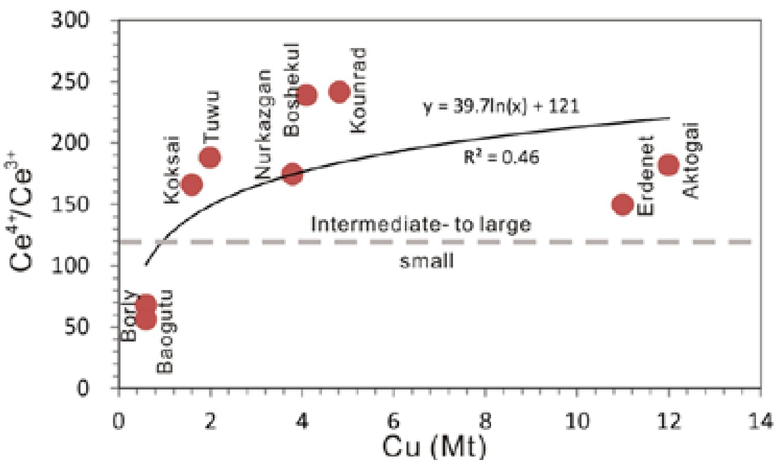

FIG 4 – Average zircon Ce^{4+}/Ce^{3+} ratios versus Cu reserves of porphyry Cu deposits in the Central Asian Orogenic Belt.

crystallisation evaluated from Ti in zircon grains are also comparable. Therefore, fO_2 is the main contributing factor to Ce^{4+}/Ce^{3+} in zircon. The Higher Ce^{4+}/Ce^{3+} values from the larger deposits suggest that the zircons in these deposits crystallised from more oxidised magmas. The information can potentially be used in exploration for porphyry Cu deposits in the CAOB.

CONCLUSIONS

- The ore-bearing rocks from porphyry Cu deposits in the CAOB are diorite, granodiorite and tonalite.
- The Ce^{4+}/Ce^{3+} ratio of 120 in zircon distinguishes granitoids hosting large intermediate-size deposits from those associated with small-size (Cu<1Mt) deposits in the CAOB.

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REFERENCES

Ballard, J R, Palin, J M and Campbell, I H, 2002. Relative oxidation states of magmas inferred from Ce(IV)/Ce(III) in zircon: application to porphyry copper deposits of northern Chile, *Contrib Mineral Petrol*, 144:347–364.

Cooke, D R, Hollings, P and Walshe, J L, 2005. Giant porphyry deposits: characteristics, distribution, and tectonic controls, *Econ Geol*, 100:801–818.

Han, Y G, Zhang, S H, Pirajno, F, Zhou, X W, Zhao, G C and Qü, W J, 2013. U–Pb and Re–Os isotopic systematics and zircon Ce^{4+}/Ce^{3+} ratios in the Shiyaogou Mo deposit in eastern Qinling, central China: insights into the oxidation state of granitoids and Mo (Au) mineralization, *Ore Geol Rev*, 55:29–47.

Hattori, K H and Keith, J D, 2001. Contribution of mafic melt to porphyry copper mineralization: evidence from Mount Pinatubo, Philippines and Bingham canyon, Utah, USA, *Mineral Deposita*, 36:799–806.

Hedenquist, J W and Lowenstern, J B, 1994. The role of magmas in the formation of hydrothermal ore deposits, *Nature*, 370:519–527.

Liang, H Y, Campbell, I H, Allen, C, Sun, W D, Liu, C Q and Yu, H X, 2006. Zircon Ce^{4+}/Ce^{3+} ratios and ages for Yulong ore-bearing porphyries in eastern Tibet, *Mineral Deposita*, 41:152–159.

Qiu, J T, Yu, X Q, Santosh, M, Zhang, D H, Chen, S Q and Li, P J, 2013. Geochronology and magmatic oxygen fugacity of the Tongcun molybdenum deposit, northwest Zhejiang, SE China, *Mineral Deposita*, 48:545–556.

Seltmann, R T, Porter, M and Pirajno, F, 2014. Geodynamics and metallogeny of the central Eurasian porphyry and related epithermal mineral systems: a review, *Jour Asian Earth Sci*, 79:810–841.

Sillitoe, R H, 2010. Porphyry copper systems, *Econ Geol*, 105:3–41.

Vry, V H, Wilkinson, J J, Seguel, J and Millán, J, 2010. Multistage intrusion, brecciation, and veining at El Teniente, Chile: evolution of a nested porphyry system, *Econ Geol*, 105:119–153.

Xiao, W J, Windley, B F, Huang, B C, Han, C M, Yuan, C, Chen, H L, Sun, M, Sun, S and Li, J L, 2009. End-Permian to mid-Triassic termination of the accretionary processes of the southern Altaids: implications for the geodynamic evolution, Phanerozoic continental growth, and metallogeny of Central Asia, *Int J Earth Sci*, 98:1189–1217.