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

P Shen¹, K Hattori², H Pan³, S Jackson⁴ and E Seimuratova⁵

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 SiO₂ 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 Ce⁴+/Ce³⁺ 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 Ce⁴+/Ce³⁺; Borly (0.6 Mt Cu) ranging from 28 to 158, and Baogutu (0.6 Mt Cu) from 29 to 113. The Ce⁴+/Ce³⁺ 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 Ce⁴+/Ce³⁺. 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 Ce⁴+/Ce³⁺ 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,
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\textsuperscript{4+}/Ce\textsuperscript{3+} following the method described by Ballard, Palin and Campbell (2002). In our calculation, Ce\textsuperscript{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.
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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 SiO₂ contents ranging from 58 to 75 wt. per cent. In the Zr/TiO₂ versus Nb/Y diagram (Figure 3a), most samples plot in the fields of diorite and granodiorite, which confirm
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 Ce4+/Ce3+ 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 Ce4+/Ce3+ 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 Ce4+/Ce3+; Borly (0.6 Mt Cu) range from 8 to 158 (av 68), and Baogutu (0.6 Mt Cu) from 29 to 113 (av 56). The results suggest that higher Ce4+/Ce3+ ratios in zircon are associated with greater tonnage of Cu (Figure 4). The Ce4+/Ce3+ ratios greater than 120 are the values associated with large and intermediate-size deposits in this belt.

Ce4+/Ce3+ values of zircon grains are controlled by fO2, 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

### Table 1

<table>
<thead>
<tr>
<th>Deposit name</th>
<th>Tonnage Cu (Mt)*</th>
<th>Lithology</th>
<th>Photograph</th>
<th>Primary mineralogy</th>
<th>Ce4+/Ce3+ in zircon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boshekul</td>
<td>&gt;4.1</td>
<td>tonalite</td>
<td>2A</td>
<td>Phenocrysts: Pl, Hbl, Qz; Groundmass: Qz, Pl, Mag</td>
<td>65–422 (av 239)</td>
</tr>
<tr>
<td>Kounrad</td>
<td>&gt;5.8</td>
<td>granodiorite porphyry</td>
<td>2B</td>
<td>Phenocrysts: Pl, Kfs, Hbl, Qz; Groundmass: Qz, Pl, Kfs, Mag</td>
<td>76–483 (av 241)</td>
</tr>
<tr>
<td>Aktogai</td>
<td>&gt;12</td>
<td>plagiogranite porphyry</td>
<td>2C</td>
<td>Phenocrysts: Pl, Hb; Groundmass: Qz, Pl, Mag</td>
<td>90–279 (av 182)</td>
</tr>
<tr>
<td>Erdenet</td>
<td>&gt;11</td>
<td>granodiorite</td>
<td>2D</td>
<td>Pl, Kfs, Hbl, Bt, Qz, Mag, Ttn</td>
<td>80–249 (av 150)</td>
</tr>
<tr>
<td>Nurkazgan</td>
<td>&gt;3.9</td>
<td>diorite</td>
<td>2E</td>
<td>Pl, Hbl, Qz, Mag</td>
<td>74–374 (av 174)</td>
</tr>
<tr>
<td>Koksai</td>
<td>&gt;1.6</td>
<td>granodiorite porphyry</td>
<td>2F</td>
<td>Phenocrysts: Pl, Kfs, Qz; Groundmass: Qtz, Pl, Mag</td>
<td>100–214 (av 166)</td>
</tr>
<tr>
<td>Tuwu</td>
<td>&gt;2</td>
<td>tonalite porphyry</td>
<td>2G</td>
<td>Phenocrysts: Pl; Qz; Bt; Groundmass: Pl, Qz, Mag</td>
<td>71–344 (av 188)</td>
</tr>
<tr>
<td>Borly</td>
<td>&gt;0.6</td>
<td>tonalite porphyry</td>
<td>2H</td>
<td>Phenocrysts: Pl, Kfs, Bt; Groundmass: Pl, Qz, Mag</td>
<td>8–158 (av 68)</td>
</tr>
<tr>
<td>Baogutu</td>
<td>&gt;0.6</td>
<td>diorite</td>
<td>2I</td>
<td>Pl, Hbl, Bt, Qz, Ilm, Mag, Ttn</td>
<td>29–113 (av 56)</td>
</tr>
</tbody>
</table>

*past production plus reserves.

Abbreviations for minerals: Pl = plagioclase; Qz = quartz; Kfs = K-feldspar; Hbl = hornblende; Bt = biotite; Mag = magnetite; Ilm = ilmenite; Ttn = titanite.
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**FIG 3** – (A) Zr/TiO₂ 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 Ce⁴⁺/Ce³⁺ ratios versus Cu reserves of porphyry Cu deposits in the Central Asian Orogenic Belt.
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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