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Pb and Zn Behaviour during LP/HT Metamorphism: Implications for Pb-Zn Ore Genesis

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1 Introduction

Studies on zinc and lead mobility during regional metamorphism are rare and contentious (e.g., Haack et al., 1984; Pitcairn et al., 2006) as we currently lack information on controlling factors for Zn and Pb enrichment or depletion during regional metamorphism. Better understanding of Pb and Zn behaviour will help to shed light on the long-standing discussion on the original source of base metals that feed Pb-Zn ore systems. In this study, we systematically studied Zn and Pb behaviour on a mineral whole-rock and scale during prograde metamorphism using a set of well-characterised psammopelite samples. The combination of bulk-rock and mineral geochemistry with Zn isotope data allows а comprehensive understanding of Pb and Zn migration in metamorphic systems. The study site is the Eastern Mount Lofty Ranges, South Australia, metamorphosed during the Delamerian orogeny at ~ 500 Ma (e.g. Hammerli et al., 2014; Fig. 1).

Metamorphic conditions range from \sim 350 °C to the onset of partial melting in the presence of excess aqueous fluid at \sim 650–700 °C (3 to 5 kbar). Stable isotope studies indicate widespread up-temperature fluid flow during metamorphism, which may have triggered significant element mobility (e.g., Oliver et al., 1998).

2 Results

Our results show that in staurolite-absent rocks, biotite contains >90 % of the bulk rock Zn inventory, and therefore controls the Zn budget during metamorphism. Fe-Ti oxides can contain relatively high amounts of Zn, but due to their small modal fraction they only represent a

Fig. 1. Map of the Eastern Mount Lofty Ranges, South Australia, with sample locations and metamorphic gradients (modified after Hammerli et al., 2014).

small proportion of the bulk rock Zn content. We observe that biotite in low-grade (<450 °C) samples have a wide range of Zn concentrations (e.g., 200–900 ppm), which greatly contracts at temperatures \geq 450 °C. Moreover, the Zn content of biotite decreases upon prograde metamorphism and reaches its lowest values in migmatitic rocks. This leads to an overall loss of ~80 % of the bulk rock Zn content during prograde metamorphism.

Bulk-rock Pb concentrations also decrease with prograde metamorphism, although the trend is less pronounced than for Zn, where a total of ~50% of the bulk-rock Pb is lost during metamorphism. In low-grade rocks, substantial amounts of Pb can be hosted in mica and carbonates whereas in higher-grade-rocks, Pb is mainly hosted in feldspars. At the mineral-scale, a very similar picture is observed with systematic Pb loss form micas

oo Group Australia -350 °C Biotite Garnet ~450 °C 20 km A 500 °C ADELAIDE ~550 °C Sill ~600 °C Mia Rathjen Biotite-Garnet Sillimanite ≥650 °C Andalusite-Staurolite Migmatite Sample Fibrolite + Granite

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during metamorphism.

Biotite and apatite show elevated Cl concentrations in high-grade samples. We followed the same approach as Coulson et al. (2001) to calculate HCl/H₂O and HF/HCl activity ratios in the coexisting fluid from the biotite compositions. Activity ratios HCl/H₂O spread between - 3.8 and -2.2 in low-grade rocks and from -3.2 to -2.5 in migmatites, although individual migmatite samples cover smaller ranges.

Zinc isotope (δ^{66} Zn) values at low temperatures are near those of basaltic igneous rocks ($\approx 0\%$ vs. IRMM-3702) increasing to slightly 66 Zn-enriched compositions (+0.2‰) at higher temperatures. This shift is mirrored by a decrease in Zn concentration, where the highest temperature, Zn-depleted samples also exhibit the heaviest δ^{66} Zn.

3 Discussion and Implications

Mobility of Zn during LP/HT metamorphism may represent a significant metal source for hydrothermal Zn mineralization, such as some SEDEX deposits. In the Kanmantoo Group metasediments, pervasive fluid flow caused a Zn decrease of ~50 µg/g and a Pb decrease of ~ 5 µg/g between protoliths and their migmatitic equivalents. The process of Pb loss in low-grade rocks can partially be explained with decarbonatization reactions when Pb is released from calcite and subsequently removed by metamorphic fluid. Another mechanism that explains Pb loss on a bulk rock and mineral scale is the interaction of Cl-rich fluids with micas where Pb is leached out and transported fluid as Pb–Cl species. This is consistent with the negative correlation between the Cl content in biotite and the bulk rock and Pb content (Fig. 2).

Our results show that the continuous decrease of Zn concentration on a bulk rock scale with metamorphism is strongly linked with Zn loss from biotite and muscovite. Upon fluid/rock interaction, Zn strongly partitions into Cl-rich fluids compared to Fe and Mg (for which Zn substitutes in silicate minerals; e.g. Ilton and Eugster, 1990).

Since more than 85 % of the bulk rock Zn is hosted in biotite, Zn loss from biotite is primarily responsible for the bulk rock Zn loss during metamorphism. Our calculations show that ~27 Mt of Zn and ~2.7 Mt of Pb were mobilized during prograde metamorphism in the Mt. Lofty Ranges, which is comparable to the amounts of base metals found in world class Pb-Zn deposits (e.g., Howards Pass deposit). Metal mobility is likely only achieved because of the elevated Cl content of the metamorphic fluids and pervasive nature of fluid flow that allowed fluid access to large rock volumes. If the chlorine-bearing fluids evolved during metamorphism can interact with shallower parts of the crust in which sedimentation, diagenesis or vein formation is occurring, there is major potential for metal



Fig. 2. Bulk rock Zn and Pb vs. molar Cl content of biotite. Individual samples are vertically separated.

contribution into these shallower ore systems.

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