

## Release of uranium from highly radiogenic zircon through metamictization: The source of orogenic uranium ores

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We recently presented a model for syn-orogenic U mineralization enriched in Zr and rare earth elements (REEs), which invoked scavenging of these elements from the sheared margin of unusually U- and Th-rich granite by highly saline fluids (McGloin et al., 2016). We appreciate the debate of this paper provided by Cuney (2016), and welcome this opportunity to further discuss our work.

A key overarching point that we made in our paper is that to improve our understanding of ore deposit genesis in general, elements other than the metals of economic interest can be used to trace the source of metals; in this case, Zr was used to trace the source to granites in which the zirconium minerals were highly metamict. A similar approach could be used to improve our understanding of other deposit types; for example, Ag and As in orogenic gold systems, or platinum group elements in porphyry Cu-Au systems.

Cuney's Comment does not challenge this point, but rather, focuses on the mineralogy of the U-bearing minerals in the granite. He rightly points out that U is contained in a series of minerals, not just zircon. We agree completely, and in the primary manuscript, provided a series of element and mineral maps showing that U, Zr, and REEs are contained in complex clusters of metamict minerals including zircon; several U-Th-Zr, Th-Zr, and Th-Zr-K silicate minerals; and REE fluorocarbonate, coexisting with fluorite and fluorapatite (our figures 3 and 4). Possibly the best source to understand the mineralogy in these clusters is provided by Förster (2006), who points out that there is a complex array of solid solutions in the system zircon (ZrSiO<sub>4</sub>)–coffinite [U(SiO<sub>4</sub>)]<sub>2</sub>; can be hydrous–thorite (ThSiO<sub>4</sub>)–xenotime [(Y,HREE)PO<sub>4</sub>], and that the understanding of the mineralogical variation in this system is far from complete. Cuney is not accurate in his analysis of the mineralogy in our figures, suggesting that the orange-colored Th-Zr silicate mineral in figures 4B and 4C is thorite; it is instead clearly a member of the zircon-coffinite-thorite solid solution. In any case, the exact trace-element mineralogy and their relative contribution to the whole-rock U budget is, in the context of our model, irrelevant; the key point is that the high U and Th contents of these minerals causes them to become metamict in a short period of time (~100 m.y. in the present case), allowing U, Zr, and REEs to become susceptible to mobilization by subsequently infiltrating fluids, provided that appropriate ligands exist.

Cuney's final query relates to the composition of the fluids responsible for U, Zr, and REE mobilization, suggesting that the sodic alteration may not indicate a saline fluid, and that CO<sub>2</sub> has limited solubility in orogenic saline fluids (citing a paper that conducted experiments at 90 °C and 0.13 kbar; Carvalho et al., 2015). The latter point is quickly dismissed; it has been well established that at the relevant greenschist to amphibolite facies conditions, metamorphic fluids can contain appreciable concentrations of both NaCl and CO<sub>2</sub> (Heinrich, 2007). In this system, phase separation into a highly saline brine and CO<sub>2</sub>-dominated fluid is controlled primarily by pressure decrease and, to a lesser extent, by temperature decrease. Although the fluid responsible for U-REE-Zr

mineralization at Valhalla has not been characterized by analysis of fluid inclusions (there are no quartz veins), the Mount Isa region is one of the most highly metasomatized regions known on Earth, and it has been well established that the fluids responsible for the widespread sodic alteration throughout the region were highly saline (Kendrick et al., 2011; Oliver et al., 2008, and references therein). The sodic alteration of the sheared granite margin (albite) and at the Valhalla deposit (albite and riebeckite), and abundant carbonate veins at Valhalla, are consistent with metasomatism driven by a highly saline brine and elevated CO<sub>2</sub>. It is plausible, even likely, that the primary fluid had separated into brine- and CO<sub>2</sub>-dominated phases at Valhalla. Such phase separation is likely to generate high pH conditions in the brine, promoting alkali metasomatism (Yardley, 2013) and quartz dissolution, consistent with the metasomatic assemblage at Valhalla.

One of the key points in our paper is that the high salinity of the regional fluid allowed enhanced dissolution of carbonates regionally, and phosphates and fluorite from the granite (see Tropper and Manning, 2007, their figures 5 and 6), providing a broad range of ligands for complexation with the unusual suite of elements that were eventually deposited in the U-REE-Zr mineralization at Valhalla and elsewhere.

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