

## The fluorine link between a supergiant ore deposit and a silicic large igneous province

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I welcome the description by McPhie et al. (2011) of the major role played by fluorine in the genesis of mineral deposits at Olympic Dam (Australia), and more broadly in the Gawler Range Volcanics. It is important to recall that intrusive granitic rocks with 1%–2% fluorine (F) are a characteristic of much of the European Hercynian province, associated with tin mineralization in particular (e.g., Stein and Hannah, 1990; Aiuppa et al., 2009). Extensive brecciation and greisenization (wall-rock alteration of granite to produce a topaz-quartz-mica assemblage) is commonly associated with these mineral deposits.

In their description of Olympic Dam, McPhie et al. claim in their discussion that dissolution of rock fragments is due to the action of hydrofluoric acid (HF). I question this, partly on the basis of experience gained in experimental work using HF at temperatures from 500 °C to 800 °C at 100 MPa (1 kbar) pressure (Manning, 1981). Solutions of up to 10% HF were added to gold capsules, then a synthetic aluminosilicate gel of granitic composition (Hamilton and Henderson, 1968) was added, and the capsule sealed by welding. Following quenching after 1–2 weeks at up to 800 °C in a cold-seal pressure vessel, the capsule was opened to reveal the formation of a solid charge with a marked compositional gradient: at the end closest to the HF, the charge was an Al-F-rich “glass,” and F contents decreased progressively to more normal granitic compositions. Although spatially tiny in comparison to the phenomena described by McPhie et al., there was no evidence of dissolution, but abundant evidence of reaction, stripping alkalis from the solid to leave a quartz-aluminum fluoride-rich residue, under magmatic and near magmatic pressure-temperature (PT) conditions.

Other early work on the effect of F on phase equilibria in the granitic system (also cited by Aiuppa et al., 2009) reported similar reaction products (Anfilogov et al., 1973; Glyuk and Anfilogov, 1973a, 1973b; Kovalenko, 1978; Wyllie and Tuttle, 1961) when NaF or HF solutions were used. Indeed, Kovalenko (1978) showed that products of reaction between ground granite and 2% HF at 550 °C were completely crystalline. The Russian experimental work consistently reported a field of quartz + topaz + vapor for charge F contents in excess of 2%, when using NaF or HF solutions, and Wyllie and Tuttle (1961) report the formation of quartz by reaction between granite and 8% HF solutions. The experimental problem of how to introduce F to a synthetic granite charge without premature reaction was initially solved by Manning (1981) through the addition of  $AlF_3$  to Al-deficient gels, and other approaches have since followed (e.g., Jago and Gittins, 1989). There is clear evidence from this experimental work (Manning et al., 1980) that Al-F complexing is important in granitic melts.

These early experimental studies are highly relevant to the claims made by McPhie et al., who state that the Gawler silicic large igneous province (SLIP) magmas became “saturated in F” (p. 1004; to be pedantic, that would imply that gaseous fluorine exsolved from the magma, and they present no evidence of this). High F contents in low-Ca mag-

mas lead to topaz saturation and precipitation, as observed in the southwestern England topaz granites (Pichavant and Manning, 1984). High F contents in high-Ca magmas will lead to fluorite precipitation (in contrast to southwestern England, where fluorite is hydrothermal; Manning and Exley, 1984). In their discussion, McPhie et al. speculate that HF was involved in rock dissolution during brecciation, without presenting unambiguous supporting evidence, and this speculation is repeated in the abstract. Given the widely observed experimental evidence that reaction with fluoride in solution gives a quartz + topaz product, and the field evidence that this reaction takes place (topaz greisens are common in tin mineralized granites), at the very least one would expect to see topaz as a product of reaction with an HF-rich fluid, and also the formation of a quartz-rich reaction product. I remain to be convinced that dissolution during brecciation described in this interesting paper could be attributed primarily to reaction with HF, as is proposed.

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