

## **The role of fluorine on the formation of Iron Oxide Cu-Au (IOCG) deposits: Insights from in-situ XAS experiments and thermodynamic calculations**

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Fluorine enrichment is an important feature of many IOCG and REE deposits, forming fluorite and many F-bearing minerals such as fluorapatite, and REE minerals such as bastnäsite. For example, fluorine is enriched throughout the breccia complexes at the giant Olympic Dam deposit – the biggest IOCG deposit yet discovered. The extracted ores contain up to 2.5 wt.% fluorite, indicating the F-rich nature of ore-forming fluids.

The fluoride ( $F^-$ ) anion is a hard ligand, and as such it forms strong complexes with hard metals such as  $Fe^{3+}$ ,  $REE^{3+}$  and  $U^{6+}$ , suggesting an exceptional ability of F-bearing fluids to transport these metals. Fluorine can also exist in hydrothermal fluids as  $HF(aq)$ , which is highly corrosive and able to dissolve silicates and oxides. Therefore, the existence of  $HF(aq)$  in fluids may help to extract metals from wall rocks and enhance porosity and permeability of the breccia complexes, although this is yet to be confirmed by either experiments or theoretical studies.

The generation link between IOCG deposits and magmatic events has long been discussed since igneous rocks are direct host for many IOCG deposits and temporally overlapped with mineralization. Examples such as the Olympic Dam in Australia, the Lala deposit in SW China and the Kiruna district in Sweden are all hosted by intermediate to felsic igneous rocks. The Olympic Dam deposit, for instance, is hosted by the 1590 Ma Roxby Downs granite. Recently it was proposed that the Roxby Downs granite have superior potential for providing the fluids for the Olympic Dam breccia complexes because they are highly F enriched. Moreover, the Roxby Downs granite could also be a good source for U and REE, as these are also relatively enriched.

Here we report the results from *in-situ* X-ray Absorption Spectroscopy (XAS) experiments on Fe(II/III)-F complexing at 25-400°C, 600 bar. The data show that Fe solubility decreases with increasing T in F-bearing solutions; above 200°C, there was no detectable Fe in the solution. We also performed thermodynamic simulations at 25-600°C with fluid salinity of 0-40 wt.% NaCl to test the efficiency of fluid-rock interaction on generating F-bearing fluids and extracting metals from granites, taking advantage of recent improvement in our understanding of the speciation of REE in Cl- and F-bearing fluids. The results show that Fe and REE chloride complexes dominate the solution at elevated temperatures (>200°C). The main aqueous species of U are their uranyl ( $U^{6+}$ ) hydroxyl complexes. The low solubility of metal-F complexes indicates that  $F^-$  is not a good transporting ligand for Fe(II/III), REE(III) and U(IV/VI) under hydrothermal conditions.

Our simulations show that fluids with higher temperatures (>300°C) are more enriched in F, and  $HF(aq)$  becomes the predominant aqueous F species at 300-500°C. Silicon concentration increases with increasing F:Cl ratio as a result of increasing stability of Si-F species at 300-500°C, indicating that  $HF(aq)$  in high-T fluids does play a role in dissolving more silicates and enhancing porosity in IOCG-forming hydrothermal systems.