

Occurrence of reduction induced sulfide saturation in oxidised arc magmas

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It has been previously well documented that solubility of sulfur in silicate melts increases by order of magnitude as the sulfate (SO₄)₂ compared to the sulfide (S₂) species [1]. Also established is magnetite saturation, the first phase to appear on the liquid line of descent during fractional crystallisation that subtracts significant amounts of total Fe and also lowers the Fe₃₊/Fe₂₊ of the residual magma, may trigger reduction in the evolving silicate melt [2]. This process of reduction induced sulfide saturation (RISS) can lead to a melt attaining sulfide saturation in a closed system, without the need of any external input i.e., crustal assimilation of sulfur or an enriched slab component.

We have explored the details of the processes subsequent to magnetite saturation in arc magmas. For example, preliminary analysis of melt inclusions contained within titanomagnetite separated from a suite of subaqueous quenched volcanic glasses from the Pual Ridge recovered during Marine National Facility Voyage (FR08-1991), while confirming predicted Cu and S abundances at peak enrichment of these elements, require some finite amount of magnetite fractionation before sulfide saturation is achieved.

Relatively oxidised sulfate-saturated, representative basaltic andesite compositions doped with a suite of chalcophile trace elements, have been experimentally equilibrated under reducing conditions to simulate RISS. The experiments yield Cu-Ag-Au rich sulfides, experimentally validating for the first time the plausibility of this process in evolving arc magmas.

[1] Jugo, P. J., R. W. Luth & J. P. Richards (2005a). *Journal of Petrology* **46**(4): 783-798. [2] Jenner, F. E., O'Neill, H. ST. C., Arculus, R. J., Mavrogenes, J. A. (2010) *Journal of Petrology* **51**(12): 2445- 2464.

Fluid pressure versus rock pressure: Their influence on metamorphic reactions

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In the upper part of the Earth aqueous and other fluids interact physically and chemically with their surroundings, naturally or during fluid disposal and extraction. Differences between rock and fluid pressure are common in the upper few km of the crust. Pressure affects chemical equilibrium: so how do these two different pressures affect chemical processes? Despite the fundamental nature of this question, there are no agreed answers and systematic tests are lacking. Here we discuss results from a set of experiments on gypsum dehydration, where confining and fluid pressure are independently varied.

Because they involve significant volume change, dehydration reactions are sensitive to pressure. Most dehydration reactions involve a net volume increase; hence in confined conditions overpressure develops unless the fluid can drain away. Thus, porosity and permeability development are key processes in nature and experiment. In addition, when confining pressure is greater than fluid pressure, the solids may compact. Reaction, fluid flow and compaction will all influence the evolving fluid pressure field and feedbacks are inevitable. Despite this we show how we can distinguish the effects of reaction rate from those of other processes.

We have run an extensive set of experiments on gypsum dehydration (to bassanite) and, in parallel, have developed a numerical model for dehydration. We show two results.

1. Experiments show that the rate of gypsum dehydration is strongly influenced by pore fluid pressure and not by confining pressure. This means that, even as the bassanite becomes the dominant load supporting phase, the confining pressure it supports is not influencing the thermodynamics of the reaction.

2. Experiments and the numerical model both show that under some conditions a reaction *front* develops, separating unaltered gypsum from substantially reacted regions. Such fronts, if they develop, exert a strong influence on behaviour in experiments and will equally influence natural systems.