Carbonation of Ca- and Mg-rich silicates: Experimental investigations and kinetic modeling

D. DAVAL[1,2], I. MARTINEZ[1], B. GOFFE[2] AND F. GUYOT[1,3]

[1]IPGP, Paris, France (daval@ipgp.jussieu.fr, martinez@ipgp.jussieu.fr, guyot@ipgp.jussieu.fr)
[2]Laboratoire de Géologie, ENS, CNRS, Paris, France (bruno.goffe@cnrs-dir.fr)
[3]IMPMC, Paris, France.

Among the different ways considered to store CO_2, the safest one involves the conversion of CO_2 to its geologically stable carbonate form. The corresponding reaction (where M is a divalent species):

$$M_xSi_yO_{x+2y-t}(OH)_{2t} + xCO_2 \leftrightarrows xMCO_3 + ySiO_2 + tH_2O$$

is thermodynamically favoured for Ca- and Mg-rich silicates like (ultra)basic minerals (e.g. olivine, serpentine) (Robie & Hemingway, 1995). The efficiency of this method to store large amounts of CO_2 essentially depends on the overall reaction rate of carbonation, for which experimental data are scarce.

Recent studies (e.g. Giammar *et al*., 2005; Huijgen *et al*., 2006; McGrail *et al*., 2006) have demonstrated that such a reaction could occur relatively rapidly in hydrothermal conditions. However, kinetic modeling remains absent in most of those investigations.

Our ongoing work both combines laboratory experiments and kinetic modeling, at conditions relevant for geological storage (T=363 K, pCO_2 = 25 MPa). Experiments are performed in separated batch capsules filled with monomineral powders and water, introduced in a Ti-autoclave. Different reactions times (from few hours to months) are tested to follow the reaction advancements. Reaction products are identified using SEM, TEM and Raman spectroscopy, and carbonation rates are determined by different analytical methods (Rietveld refinement of X-Ray diffractograms, mass balance, and selective acid attack of carbonates followed by dosage of produced positive ions). These investigations are coupled with kinetic modeling (CHESS, van der Lee, ENSMP, Paris) using data from the literature for each main step of the reaction (silicate dissolution, carbonate precipitation).

We will present our results, focusing on the carbonation of wollastonite ($CaSiO_3$). Then we will discuss some causative factors to explain discrepancies between modeling and our experimental results, such as the general form of kinetic rate laws or armouring effect.

References

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Amphibole control in the differentiation of arc magmas

J. DAVIDSON[1], C. MACPHERSON[1] AND S. TURNER[2]

[1]Department of Earth Sciences, University of Durham, DH13LE, UK (j.p.davidson@durham.ac.uk and colin.macphesron@durham.ac.uk)
[2]Department of Earth Sciences, Macquarie University, Sydney, Australia, (sturner@els.mq.edu.au)

Subduction-related volcanic rocks are commonly porphyritic, with a typical gabbroic assemblage of plag + px ± ol. Rock suites from arc volcanoes, can, in terms of major elements, be modelled as due to extraction of this assemblage. However, three observations mitigate against this simple interpretation;

1. Petrographic observations suggest that many of the “phenocryst” phases are not in equilibrium with the liquid in which they were erupted – these phases are, in many cases, more appropriately referred to as antecrysts.
2. A significant amount of crystallisation (microlites, rims on antecrysts) occurs rapidly in response to decompression during ascent, and this material is not efficiently removed/ fractionated from the liquid, and
3. Trace element characteristics are difficult to reconcile with simple gabbro fractionation

We compiled REE data from several cogenetic arc suites, and found compelling evidence for a significant role for amphibole in the majority of cases (Fig. 1). A significant decrease in Dy/Yb with SiO_2 can only be attributed to amphibole partitioning, either as a directly fractionating phase, or as a residual phase in more complex melting-mixing mechanisms. The implication is that there is a major amphibole–bearing reservoir formed in the arc crust as a result of differentiation of ascending magmas. This reservoir can 1) sequester a fraction of the mantle-derived water from primary magmas, and 2) provide a potentially fertile source for intracrustal melting, producing hydrous silicic magmas.

Note that trends in Fig 1 do not back-project to a common parent, implying that parental compositions are defined by another control (deep early differentiation, possibly with garnet, or mantle source variation with different slab components)

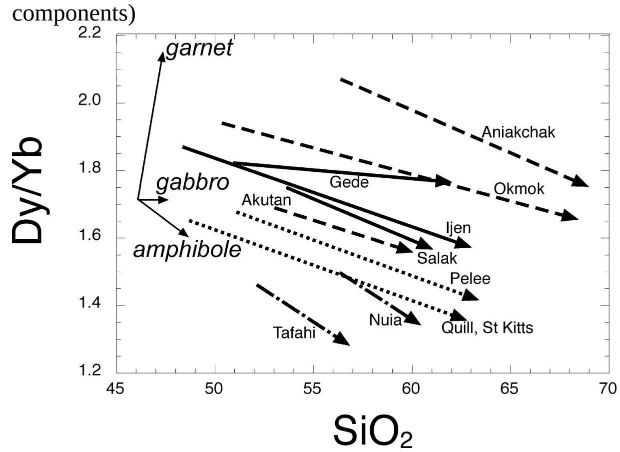

Figure 1. Compilation of differentiation suites from arc volcanoes showing evidence for amphibole fractionation.