

Effects of water on the nucleation of Li-rich granitic melts

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The amount of dissolved water controls the nucleation and crystallization of granitic melts by lowering their liquidus and glass transition temperature, their free energy relative to crystals, and viscosity. Although pegmatites and rhyolites are similarly affected by undercooling and cooling rate, they are at the opposite ends of the spectrum of igneous texture because pegmatite melts have incorporated and retained H₂O whereas rhyolites have lost H₂O [1].

Sixty nucleation-crystallization experiments on Li-B-haplogranite-H₂O compositions confirm that igneous texture is strongly controlled by the concentration of water. Time-series, isothermal runs (from 1 to 30 days) were performed at temperatures ranging from 400 to 700°C at 300 MPa, corresponding to variable degrees of undercooling between liquidus and glass transition. H₂O contents ranged from 2.6 to 8.3%, and kept below fluid saturation. Although metastable, mineral assemblages are reproducible. Viscosity data collected via the parallel-plate method indicate that the glass transition of both melts containing 6.5 % H₂O is just under 300°C, indicating that nucleation and crystallization took place in a liquid not in glass.

Clearly, H₂O concentration influences the time of incubation, nucleation densities, and crystal growth rates, but the effects are a nonlinear function of dissolved H₂O. For example, at 600°, nucleation delays are >5 days for a concentration of 8.3 % H₂O, decrease to a minimum of only one day for 6.5 % H₂O, and increase again to 2.5 days at 3.0 % H₂O. Growth and nucleation rates follow a similar parabolic behavior, as a consequence of the double role played by H₂O. On one hand, H₂O stimulates development of large crystals because of increased diffusion rate. On the other hand, H₂O decreases the liquidus temperature of the melt, therefore reducing the value of effective undercooling, which has the opposite effect of slowing down crystal growth. A “Goldilocks” behavior rules the development of pegmatite texture including large, skeletal crystals, graphic intergrowth, and low nucleation density. Ultimately, the value of effective undercooling has to be “just right”.

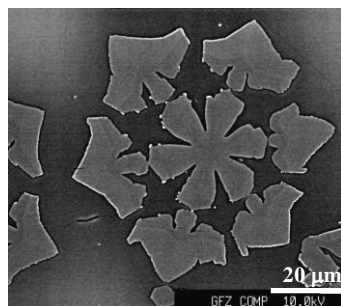


Figure 1: Skeletal “stuffed” beta-quartz produced in 30-day long run, at 500°C, in a haplogranitic melt with 3.0% (g/g) H₂O, 1% Li₂O, and 2.3 % B₂O₃

[1] Nabelek et al. (2010) *Contrib. Min. Pet.* **160**, 313-325.

Feedback effects of clay minerals formation on the kinetics and mechanisms of olivine carbonation within tholeiitic basalt

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Geological storage of CO₂ in basic rocks relies on the dissolution of its silicate components, followed by the precipitation of carbonates. However, the slow dissolution kinetics of Mg-rich silicates has proven a critical issue. Previous batch carbonation studies on separated olivine grains^[1] ((Mg,Fe)₂SiO₄), have emphasized the deleterious role of secondary phases, such as amorphous silica layers (SiO₂(am)) in controlling the dissolution rate of the parent mineral and the transport of reactants from and to the reactive surface.

We show here that carbonation processes and kinetics are strongly different for olivine within a tholeiitic basalt than for separated olivine. Batch experiments were conducted (at 150°C and P_{CO2} = 280 bars) on an Mg-rich (9.3 wt.% MgO and 12.2 wt.% CaO) tholeiitic basalt from Iceland, composed of olivine, Ti-magnetite, plagioclase and clinopyroxene. After 45 days of reaction, carbonation rates were quantified by CO₂ extraction with phosphoric acid, yielding up to 60 wt.% carbonation of Mg-rich phases as MgCO₃, but less than 0.5 wt.% of Ca-rich phases as CaCO₃.

Such observations diverge noticeably from those previously reported in lower T carbonation studies on Ca-rich, Mg-poor basalts^[2]. In addition, X-ray diffraction analysis on the reaction products reveals a substantial decrease in olivine content, supporting the idea that magnesite formation mainly follows from olivine dissolution. Therefore, these results suggest that in our experiments, no passivating silica layer was formed on the surface of olivine. Instead, investigations by transmission electron microscopy reveal that a thin layer (~100 nm) of porous, iron-bearing, aluminous phyllosilicate has formed on the surface of the remaining primary silicates. Taken together, these observations suggest that, in an Al rich-medium, the formation of clay minerals may consume the silicon of potential silica-rich surface layers, or directly inhibit their formation. Those phyllosilicates would therefore represent the ultimate sink for Si, with lesser impact on the transport of reactants than SiO₂(am). By providing a constant driving force for Si removal, we eventually propose that such phases allow olivine to dissolve as rapidly as it is known to occur in open natural systems, and therefore to reach higher carbonation rates^[3].

[1] Daval et al (2011), *Chemical Geology*, v.284, p.193-209

[2] Schaefer et al (2010), *IJGGC*, v.4, p.249-261

[3] Matter and Kelemen (2010), *Nature Geoscience*, v.2, p.837-841