Does diopside dissolve like glass? Insights from measurements of nano- to macroscale dissolution rates

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Whereas the dissolution rate of silicate minerals has been extensively studied at far-from-equilibrium conditions, extrapolating such rates over a broad range of solution compositions has proven challenging. In particular, a growing amount of studies have pointed out that the simplest TST-based rate-affinity dependence commonly implemented into most of geochemical codes was the source of dramatic overestimations of the actual fluid-rock interaction rates [1, 2]. Such limitations acted as a driving force for developing alternative dissolution models of solids over the past 10 years [3, 4].

Diopside was shown to belong to that category of minerals for which rate-affinity relationships do not follow a simple TST-like model, since an unexpected drop of the rate was evidenced at ΔG_r(diopside) as low as -76 kJ.mol^{-1} [5]. An examination of these data led us to envisage that two different, non-exclusive aspects were worth investigating: (i) the possible passivating ability of interfacial, nm-thick Si-rich layers developed on weathered silicate surface, and (ii) the stop of etch pits formation on crystal surface, which were found to be responsible for drops of olivine [2] and albite [3] dissolution rates, respectively. The former mechanism should be evidenced by the dependence of diopside dissolution rate on [SiO_2(aq)], whereas the latter should verify a strong anisotropy of diopside dissolution, with ($h\ k\ l\neq0$) faces dissolving noticeably faster than ($h\ k\ l=0$) faces. Both of these models were tested by running either classical flow-through experiments with controlled [SiO_2(aq)], and face specific dissolution experiments. In this latter case, single crystals were immersed in solution. The dissolution features were monitored by AFM imaging and the dissolution rates were calculated by measuring the global surface retreat between masked and unmasked regions using VSI [1].

Our results show that the dissolution rate of diopside drops as SiO_2(aq) is added to the solution, consistently with a dissolution mechanism controlled by the stabilization of a passivating, interfacial Si-rich layer, as already suggested for glass [6]. On the other hand, our preliminary results on the face-specific dissolution of diopside show that the dissolution rate of faces varies following: (021) >> (110) ~ (1$\bar{1}$0)>> (010) ~ (100), which does not invalidate the etch pit nucleation control of diopside dissolution kinetics. The results of the ongoing experiment on (001) face, as well as upcoming investigations of the interfacial layers by TEM, will help to make a final decision between the two proposed models.

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Differentiation and source controls along the Lesser Antilles arc

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The fluxes of elements into, and out of, subduction zones dictate both the composition of the crust and the heterogeneity of the mantle. Most flux estimates are predicated on the basis of the compositions of magmas erupted from arc volcanoes. However, volcanic rocks represet only 10-20% of the total magma flux from the mantle at arcs, and these magmas have undergone the maximum amount of filtering, having passed through the entire thickness of the upper plate lithosphere. In order, therefore, to realistically determine the contributions from the mantle wedge and slab (sediments and fluids) to arc magmas, it is critical to account for the effects of differentiation.

We have done this at the Lesser Antilles arc for two volcanoes; The Quill (Statia) in the north and Mt Pelee (Martinique) in the central part of the arc. An evaluation of the volcanic rocks, their constituent minerals and associated cumulate blocks allows us to show that 1) differentiation was controlled by an amphibole-plagioclase-dominated assemblage, as reflected in the cumulate blocks, and 2) differentiation was open system, involving assimilation of the arc crust.

Even though amphibole is not present in the phenocryst assemblage of the volcanic rocks, it is common in the cumulate xenoliths. Thus fractionation control is cryptic, with compositions determined largely by mineral assemblages not represented in the erupted fractionates. Indeed amphibole may be more common as a fractionating phase at arcs than has previously been appreciated [1]: By increasing SiO_2 and generating LREE enrichment, amphibole might have an important role in generating crust-like differentiates at arcs. The inferred assimilation of the arc crust modifies Pb and Sr isotope compositions in the magmas, suggesting that even at intra-oceanic arcs the isotopic compositions of erupted magmas cannot a priori be taken as indicative of their mantle source.

Once differentiation trends are established they can be back-extrapolated. When this is done, differentiation trends for The Quill and Mt Pelee do not converge on a common primitive/ parental composition, suggesting that mantle source compositions vary along the arc. The mantle sources of both volcanoes can be modlled by addition of <5% sediment or <1% sediment melt, along with LILE-bearing fluid. The differences between the sources of the two volcanoes can be explained by different sediment compositions delivered along the arc, or a slightly greater sediment contribution at Mt Pelee [2].

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