The arc delaminate: a geochemical reservoir twice the size of the continental crust

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Most primitive melts in arcs are basaltic in composition but the continental crust or arc average is andesitic. To evolve from a primitive basalt to an andesitic composition, cumulates have to be fractionated and, if gravitationally unstable, can be delaminated. Such lower crustal cumulates are exposed in the Kohistan arc (N Pakistan) in a 10 km section through dunites, wehrlites, websterites, cpx-bearing garnetites and hornblendites, and garnet gabbros. We have compiled primitive melts for nine island arcs from the literature and fitted these with the bulk Kohistan arc [1] or average bulk continental crust [2] and the Kohistan cumulates. By average, ~15 wt% wehrlite + ~20% garnet hornblendite + ~35% garnet gabbro complement ~30% arc or continental crust and explain very well (r^2~2) the evolution from a tholeiitic/calc-alkaline primitive high-Mg basalt to the continental crust. The bulk delaminate has 44-48 wt% SiO_2, total alkalis of 1.1-1.4 wt% and an X_{Mg} of 0.67-0.69. Mass fractions derived from major elements were employed to compare trace elements: cumulates+crust deviate on average only by 25-30% from primitive melts, with the biggest deviations on the subduction-added traces. Relative to the continental or arc crust, the delaminate mass results to 1.8-2.5 times that of the continental crust.

The delaminates have ρ=3.2-3.5 g/cm^3 and V_P=7.9-8.2. At the base of the crust, they are thus difficult to distinguish seismically. Once reaching a critical thickness, they may sink into the deeper mantle where they form a geochemical reservoir twice the size of the continental crust. With respect to primitive mantle, the delaminate is enriched in Ba, K, Sr, and P and REE with LREE<HREE. The delaminate reservoir would develop highly unradiogenic Pb over time and would counterbalance the radiogenic MORB and OIB reservoirs. Delamination of twice as much material as remains in the arc crust increases the flux of primitive melt in arcs threefold. This places the magma production rate at arcs (per km arc length) slightly above that at mid-ocean ridges indicating that global fluxes and magmatic heat loss need to be revised.

[1] Rudnick R.L., Gao S. (2003) *Treatise of Geochemistry* **3**, 1-64.
[2] Jagoutz O. Schmidt M.W. (2012) *Chem.Geol.* doi:10.1016/j.chemgeo.2011.10.022

Structural changes on dehydration of amorphous calcium carbonate

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Introduction and Methods

Amorphous calcium carbonate (ACC) is a common transient precursor to biogenic calcium carbonate, but the transformation and stabilization mechanisms remain unknown. Studies have shown that the calcium carbonate biomineralization pathway for two different biogenic ACC samples follows the progression of hydrated ACC ➔ anhydrous ACC ➔ calcite, aragonite and/or vaterite.[1][2] In this study, we present a structural analysis and comparison of hydrated and partially-dehydrated, synthetic ACC applying novel synthesis techniques to examine the under-studied first transformation step in the biomineralization pathway.

ACC was synthesized using three different methods and then partially-dehydrated by heating to temperatures below the crystallization temperature (ca. 185 °C or 330 °C depending on the synthesis method).[3][4] Hydrated and partially-dehydrated ACC samples were analyzed by X-ray absorption fine structure (XAFS) spectroscopy, pair distribution function (PDF) analysis from X-ray total scattering, FT-IR spectroscopy, thermal analysis, and nuclear magnetic resonance (NMR) spectroscopy.

Results and Conclusions

Thermal analysis showed total mass losses averaging 10% (46% loss of total water) with dehydration to 115 °C (16% and 75%, respectively for heating to 150 °C). XAFS and total scattering results showed no evidence of significant structural changes with heating, suggesting that the effects of dehydration relate primarily to the water component in ways that are largely insensitive to the X-ray based techniques. FT-IR spectra show a loss of structural water as evidenced by decreases in the intensity of the O-H bending and stretching bands at 1630 and 3300 cm^{-1}, respectively. The ^{1}H NMR spectra of hydrous ACC, obtained indirectly via ^{13}C-detection, contain signals from three principal hydrogen environments: a broad spinning sideband envelope from rigid structural water, a narrow peak near +5 ppm from restrictedly mobile water, and a small narrow peak at +0.2 ppm due to hydroxyl. Dehydration of ACC leads to a reduction in signal intensity from both rigid and mobile water that increases with increased dehydration temperature but with little change in their relative proportions. No significant change in the intensity of the hydroxyl peak was observed in samples heated up to 200 °C. The retention of some restrictedly mobile water and lack of change in the PDFs from X-ray total scattering in dehydrated ACC suggest that thermal dehydration does not significantly disrupt the calcium-rich framework of the ACC [5].

[1] Radha (2010) *PNAS*, **107**, 16438-16443. [2] Politi (2008) *PNAS*, **105**, 17362-17366.[3] Koga (1998) *Thermochim. A.* **318.** 239-244. [4] Faatz (2004) *Adv. Mater.* **16** 996-1000. [5] Goodwin (2010) *Chem. Mater.* **22.** 3197-3205.