The role of disseminated calcite in rates of calcium release and CO_2 consumption during the weathering of granitoid rocks

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Although Ca and Na reside predominately in plagioclase feldspar in granitoid rocks, recent studies have demonstrated that excess Ca often exits in surface and ground waters relative to plagioclase stochiometry. Explanations advanced to explain the Ca excess have included selective loss of Ca in soils due to watershed acidification (Hyman *et al.*, 1998), selective weathering of the anorthite component of plagioclase (Clayton 1986), and the rapid weathering of trace mineral phases such as calcite (Mast and Drever 1990). Chemical hydrolysis of Ca-silicate rocks is recognized as impacting long term atmospheric CO_2 consumption and global climate through silicate hydrolysis reactions (Berner and Caldeira 1997). In contrast, carbonate mineral dissolution does not have a corresponding impact because the CO_2 consumed in weathering is reintroduced back into the atmosphere by precipitation of carbonates in the ocean. Thus, the solute Ca/Na ratio in watersheds and rivers, reflecting proportions of silicate and carbonate weathering, is important in understanding long term global CO_2 balances.

Experimental weathering of disseminated calcite

This study investigates the distribution of disseminated calcite in granitoid rocks and quantifies the dissolution rates based on aqueous Ca and alkalinity concentrations in effluents from long-term column experiments. Pairs of fresh and weathered granitoid samples were obtained from the following research watersheds: the upper Merced River in Yosemite National Park, California, USA, the Loch Valle watershed in Rocky Mountain National Park, Colorado, USA, the Panola Mountain Research Watershed near Atlanta Georgia, USA and the Rio Icacos watershed in the Luquillo Mountains of Puerto Rico. Crushed samples were reacted with deionized water initially saturated at 0.05 atm. CO_2.

Cathode luminescence of polished thin sections indicates that trace amounts of microcrystalline calcite occur within silicate grains, along grain boundaries and in micro-fractures in the fresh granitoid samples. Acid digestion of the rocks and CO_2 analyses of head space by gas chromatography showed that calcite concentrations ranged between 0.026 and 0.28 wt.%. Microprobe analyses of disseminated calcite grains indicated essentially pure $CaCO_3$ with trace amounts of Fe, Mg, Mn and Sr (<1000 ppm). Weathered granitoid samples contained little or no observable calcite.

The relative amounts of disseminated calcite had a marked effect on the column effluent chemistry. In all cases, Ca dominated the initial solution chemistry of the fresh granitoids relative to other cations. The Ca/Na ratios after a 100 hrs of reaction ranged between 10 and 200, which greatly exceed the respective plagioclase stochiometries. As shown for the Panola Granite in Fig. 1, the micro-equivalents of Ca in the effluent from the fresh granitoids are balanced closely by alkalinity originating from calcite dissolution. After reaction times of 10,000 hrs, the Ca/Na ratios decrease significantly to between 2 to 30, indicating decreases in weathering portions of calcite relative to plagioclase. The Sr/Ca ratios in the effluents increased with time reflecting lower Sr concentrations in calcite (100 to 400 ppm) relative to that in the plagioclase (3,000 to 10,000 ppm).

Solubility calculations indicate that the column effluents were initially saturated with respect to calcite and became progressively more undersaturated as the pH and Ca decreased with time. Mass balances, based on initial calcite present in the fresh granitoids and total Ca lost to the effluents, indicate that between 65 and 100% of the calcite had been leached out of the granitoids after 10,000 hrs. Relative to the fresh granitoids, effluents from the naturally weathered counterparts were much lower in Ca and alkalinity (Fig. 1) and higher in Si and K, suggesting that weathering is dominated by biotite rather than calcite. This finding is supported by the significantly higher $^{87}Sr/^{86}Sr$ ratios in the initial

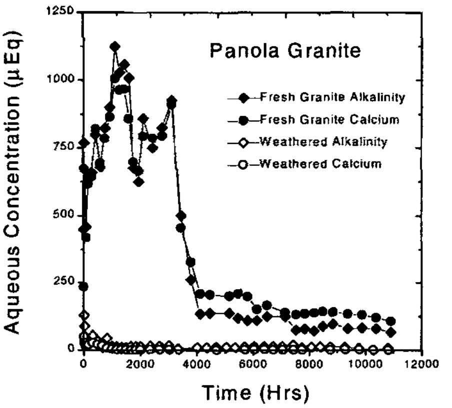

FIG. 1. Effluent Ca and alkalinity concentrations from column experiments using fresh and weathered Panola Granite.

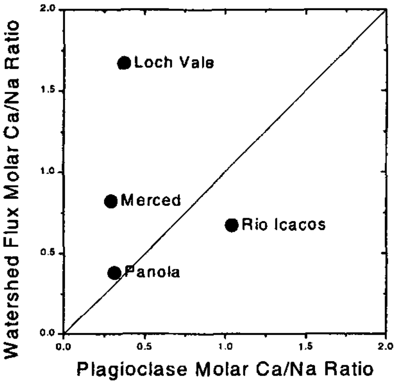

FIG. 2. Comparison of average Ca/Na ratios in plagioclase and annual discharge fluxes for watershed studies. Diagonal line represents stochiometric dissolution of plagioclase.

column effluents of the weathered compared to the fresh granitoids.

Watershed-scale weathering of calcite

Experimental results predict that trace amounts of calcite will play an important role in Ca and alkalinity release during the earliest stages of granitoid weathering. This prediction is confirmed in studies characterizing chemical weathering in the four watersheds from which the granitoids were sampled. In Fig. 2, the Ca/Na ratio based on the average plagioclase stochiometry for each watershed is plotted against the ratio of the average annual Ca and Na discharge fluxes. The diagonal line is the one-to-one correspondence in which the watershed solute flux directly reflects plagioclase weathering. As indicated, both the Loch Vale and Merced watersheds plot above this line indicating excess Ca attributed to calcite dissolution. Both these high elevation watersheds have extensive fresh bedrock surfaces exposed by glaciation during the last 15k yrs. In contrast, solute discharge from the geomorphologically older, non-glaciated Panola and Rio Icacos watersheds fall on or below the diagonal line indicating the lack of an excess Ca contribution from calcite.

Differences in these Ca/Na ratios in discharge fluxes correlate with the relative extent of calcite and plagioclase weathered from granitoid profiles in the watersheds. Detailed analyses of an exfoliated granitoid section in the glaciated Merced watershed indicate that the Ca and Na concentrations are essentially constant with depth while carbonate concentrations are significantly depleted in the upper two thirds of the profile. These contrasting distributions imply that trace amounts of the calcite are lost much more rapidly in recently exposed granitoid rocks than is plagioclase. In contrast, in a deep weathering profile through the surfically old Panola granitoid (>250 k yrs), both plagioclase and calcite were coincidentally lost implying that advancement of the weathering front is controlled by rates of fluid penetration and not by differences in the respective plagioclase and calcite weathering rates.

Ongoing studies on a large suite of granitoid rocks from around the world indicate that calcite is an ubiquitous trace phase associated with late stage magmatic cooling and hydrothermal alteration. The results described in this paper imply that rapid dissolution of calcite during the initial exposure and weathering of granitoids will have a major impact on solute Ca and alkalinity in watershed discharge. Variability in the weathering of disseminated calcite may account the apparent discrepancies observed in climatic comparisons between watersheds (White and Blum, 1995). On a global scale, during periods of glaciation and tectonism, weathering of trace amounts of calcite will have a significant impact on estimates of the rates of silicate hydrolysis and CO_2 drawn down from silicate terrains.

References

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