Field weathering rates versus laboratory dissolution rates: an update

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Introduction

Several previous studies have reported that the rate of weathering of silicate minerals in the field is 1 to 3 orders of magnitude slower than would be predicted by rates of dissolution of the same minerals in laboratory experiments (Paces, 1983; Velbel, 1985: Schnoor, 1990; Brantley, 1992; Swoboda-Colberg and Drever, 1993). Proposed reasons for the discrepancy include: differences in reactivity between freshly-crushed and weathered minerals, errors in estimating the exposed surface areas of minerals in the field, and differences in solution composition, particularly degree of undersaturation, between the field and laboratory. We report here some experimental results that constrain some of these mechanisms.

Results and discussion

As part of a field study of weathering in a small catchment in Colorado, we (Clow, 1992) measured the dissolution rates of uncrushed minerals from the soils in flow-through reactors and compared them to rates from crushed underlying bedrock. The steady-state rates of equivalent grain sizes were indistinguishable, confirming our previous conclusion (Swoboda-Colberg and Drever, 1993) that 'aging' of surfaces was not a cause of decreased rates in the field. Also, treatment of the soil minerals with hydrogen peroxide and citrate-dithionite-bicarbonate had essentially no effect on dissolution rate, suggesting that, in these soils at least, coatings on the mineral surfaces had no significant effect on dissolution rate.

We (Murphy, 1993) investigated the relationship between BET surface area and dissolution rate for albite at pH 4. We found that, contrary to previous results (Holdren and Speyer, 1985, 1987), dissolution rate scales perfectly with pre-reaction surface area. Slow apparent rates in the field are thus not a consequence of anomalous behavior of small grain-size material. BET surface area changes during dissolution experiments and during weathering (Anbeek, 1992a, b), but this does not directly affect field-lab comparisons because the comparisons are generally based on geometric surface area calculated from grain-size distribution and not from BET area.

The effect of solution composition on dissolution rate is complex. Comparisons between field and lab are usually based on a single parameter such as pH, and it is assumed that solutions are sufficiently far from saturation with primary phases that back reactions can be ignored (Velbel, 1989). Dissolution in the field may be inhibited either by the accumulation of a solute (such as Al) that reduces dissolution rate (Chou and Wollast, 1985), or by approach to saturation (the chemical affinity effect). Burch *et al* (1993) proposed that decreased rates due to the chemical affinity effect occurred at much greater degrees of undersaturation than predicted by the simple models that had been used previously. In our batch experiments at pH 4 on albite dissolution, a marked decrease in reaction rate was observed, typically after about 5–7 months. The decrease did not, however, correspond to a particular degree of undersaturation and the underlying mechanism is unclear.

Conclusions

The discrepancy between field and laboratory rates is real. In water-saturated or nearly saturated environments it is best explained by a combination of two effects: (1) at low flow rates (i.e. long residence times), dissolution in the field is inhibited either by the accumulation of a solute (such as Al) that reduces dissolution rate, or by approach to chemical saturation (the chemical affinity effect). (2) at high flow rates, flow takes place preferentially through high-permeability channels ('macropores'), so much of the mineral surface area is effectively out of contact with 'fresh' solution. Solution in lower permeability regions ('micropores') has a long residence time and so dissolution rates decrease for chemical reasons. In reality, these explanations represent a continuum. At very slow flow rates, there should be little difference between the compositions of solutions in macropores and micropores, the time available for reaction will be long, and dissolution will be inhibited for chemical reasons. As flow rate increases, the rate-limiting process will progressively shift from a purely chemical process towards diffusional transport between micropores and macropores. In the vadose zone, the situation is further complicated by increased water saturation and hence 'wetting' associated with high flow rates.

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