

Surface area and porosity of primary silicate minerals

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The rates of many heterogeneous reactions are dependent upon the mineral-water interfacial area. Along with the permeability, the reactive surface area is one of the most difficult physical parameters to quantify in extrapolating from the laboratory to the soil plot to the watershed (White and Peterson, 1990; Brantley *et al.*, 1998). Most models of solute transport ignore the mineral-water surface area term by combining it with the kinetic rate constant, despite the fact that the specific surface area may vary over several orders of magnitude – 10^2 – 10^6 cm²/g. Little systematic effort has been expended to understand or predict either surface area or reactive surface area for primary silicates, or to correlate surface area with porosity of weathered samples. A review of data from the literature, along with new BET measurements and observations concerning internal porosity, yields some insights into the controls on surface area as a variable in chemical weathering.

Examples of porosity in natural samples

The measured surface area is comprised of both external and internal contributors, where internal surface area can be described as all cracks or connected pores which are deeper than they are wide. While porosity in soils and sediments has been documented in the literature, only a few samples have been well studied. Pores in natural samples may become occluded during precipitation (see Cape Cod example, below), or may etch out during dissolution (see hornblende example, below).

For example, glacial outwash sediments such as quartz and feldspar from the Cape Cod USA saturated zone contain between 4–19% porosity, as measured by mercury porosimetry (Yau, 1998). Gas adsorption hysteresis for these samples also reveals the presence of internal porosity. Smectite, illite, and kaolinite have been observed within the pores in the feldspar, but not in the quartz. Calculated volume and surface area of pores ranging in diameter from 2 to 300 nm, using a standard method, reveal that most of the porosity of both the quartz and feldspar grains is present as mesoporosity. The presence of clay minerals only inside pores in this aquifer suggests a different chemistry in the porosity as compared to the

intergranular pores.

Porosity in minerals may also increase with time as a function of weathering duration and chemistry, although this effect has not been well-documented. For example, the presence of porosity in hornblende samples from Gore Mountain, NY (USA) is documented by adsorption-desorption isotherms for 75–150 µm hornblende grains. Three model calculations of pore volumes suggest that this hornblende has pore diameters in the range of 25 to 40 Å. Such mesoporosity may be related to etching along cleavage planes as observed in soil hornblendes (Brantley and Chen, 1995). Laboratory etching of the hornblende samples in batch experiments with HCl-H₂O solutions (starting pH 2.2) over a period of 5 weeks also increased the mesoporosity of the grains measurably.

Clearly, estimation of reactive surface area for samples such as the Cape Cod feldspar, where clay surface area within pores contributes to measured surface area, and for samples such as hornblende, where porosity increases during low pH dissolution, is problematic at best.

BET surface area and roughness

Reactive surface area is usually approximated by the BET surface area. Surface areas measured in the laboratory are presented as specific surface area, or the surface area per gram of solid. Thus, the specific geometric surface area, A_{geo} , can be expressed:

$$A_{geo} = a' \rho^{-1} r^{d-3} \quad (1)$$

where r is radius of the particle, ρ is the density of the solid and a' is a geometric parameter (= 6 for a cube, 3 for a sphere). For Euclidean solids (i.e. solids with no fractal properties), $d = 2$ and the exponent for r equals -1 .

Specific surface areas of ground mineral powders have commonly been reported as a function of powder particle size. Variations among specific surface area measurements reflects density, fracturing, cleavage, and porosity. Reviewing data from the literature and our own laboratory, the specific surface area of laboratory-ground silicates generally increases (for the 75–150 µm fraction) from olivine

\approx quartz \leq albite $<$ diopside \leq alkali feldspar \leq microcline \approx oligoclase \leq andesine \approx wollastonite \approx labradorite \leq bytownite $<$ hornblende $<$ anorthite (Table 1). A similar trend has been observed by White (1995) for soil grains weathered for several tens of thousands of years: quartz $<$ K feldspar $<$ plagioclase $<$ hornblende. These trends generally follow increasing weatherability (except for a few notable contradictions, such as olivine). Possibly, increasing weatherability relates to increasing concentration of internal pores (see discussion below and Table 1) and increasing surface area.

When equation (1) is used to fit BET surface area to particle size, the value of d calculated may or may not equal 2. White and Peterson (1990) compiled data for a suite of unweathered, laboratory-ground minerals over a large range in particle size, and concluded that $d = 2.0$ for the whole set. A similar conclusion has been reached concerning ground quartz. A compilation of surface area vs. grain size for other minerals reveals that data for other minerals are not as comprehensive (Table 1). For minerals such as albite, slopes of -1 on the $\log A$ - $\log r$ plot are consistent with a lack of porosity. Conversely, plotting surface area data for Gore Mountain hornblende yields a slope of -0.5 . For plagioclase compositions, the slope of the $\log A$ - $\log r$ plot of all published data generally becomes shallower as the composition changes from albite to anorthite.

Shallower slopes could correlate with increasing porosity (the relative contribution of the internal surface area decreases as particle size decreases). According to these observations and published data, the albite, alkali feldspar, and microcline samples previously investigated by geochemical researchers have little porosity while the other feldspar phases and hornblende discussed in the literature have some porosity.

In contrast to lab-ground samples, the surface area data for weathered grains apparently always exhibit slopes shallower than -1 on $\log A$ vs $\log r$ plots. For example, soil grains from soils as young as 9000 y show a slope shallower than -1 (Brantley, unpub. data; Table 1), and particle size distributions plotted against BET surface areas for the aluminosilicate fractions in soils of substantially greater ages show similar slopes (White *et al.*, 1996).

Conclusions

In order to model kinetics of natural geochemical systems, mineral-water surface area must be

quantified and predicted. However, little research has focussed upon surface area. A comparison of values of specific surface area (A) (cm^2/g) of primary silicate minerals reveals that A generally increases for a specific grain size as weatherability of the mineral increases (e.g. quartz $<$ kspars $<$ plagioclase) for both laboratory-ground and naturally weathered samples. This trend may be related to increasing porosity, as inferred from $\log A$ $\log r$ plots (Table 1). Many of the primary silicates contain intragranular porosity (Table 1).

Field studies show that specific surface areas of silicates increase significantly with duration of weathering. Much of this increased surface area (at least for hornblende and feldspar) is probably due to the development of internal porosity present as mesoporosity (pore radii in the range of 2 to 50 nm). Similarly, the porosity of some silicates has been documented to increase in the laboratory during etching, albeit over the period of weeks. For other samples, dissolution within the pores may cause precipitation of secondary phases such as clays and Fe-oxides. Surface area related to porosity may create problems in extrapolating laboratory kinetics to the field, in that some measured internal surface area may be dominated by secondary phases within pores, or may have a different reactivity. Better understanding of all these phenomena is needed.

References

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