Phase shift interferometry, near-atomic scale surface data, and a new view on fluid-rock reactions

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Mineral, metal and glass surfaces in contact with a fluid are involved in several key processes governing many geologically and technically important reactions. Such processes include weathering and global change, sedimentary basin dynamics, reactions in subduction zones, metamorphism, environmental pollution, formation of ore deposits, radioactive waste containment, and even corrosion of materials used in a large number of technical processes. Kinetic data on mineral surface processes during dissolution and growth are of central importance to any attempt to model such complex systems. Most experimental work to date has used mineral powders, which yield dissolution/precipitation kinetic data that average the rates on a variety of different surface sites. To understand the role of reactive surface area on the whole mineral-fluid reaction field, therefore, it is critical to begin to look at the atomic dynamics taking place on the mineral surfaces themselves.

Method

An optical interferometry system has been built for studies of the dynamics of dissolving (and precipitating) mineral surfaces. Vertical scanning white light interferometry (VSWLI) provides about 0.5 micron lateral resolution and near atomic scale vertical resolution on the order of $1-10$ nm for surface features up to 100 microns high. Reaction rates are determined from the surface-normal retreat or advance of the mineral surface over time. A flattened Pt-wire is glued to the surface as a reference surface. The slow rates of growth/dissolution for many minerals, e.g. aluminosilicates or dolomite, require hydrothermal conditions for the application of this method. We have developed a hydrothermal recirculating system that operates up to 300°C and 200 bar and includes an internal pump that provides solution flow rates exceeding 10 ml/min. The solution chemistry is controlled by injecting reagent solutions with HPLC pumps.

Results and discussion

An important example of the application of the method is provided by dissolution experiments on a near endmember anorthite (An_{98}) from Miyake-jima, Tokyo, Japan. Kinetic interferometric measurements at pH 3 and 25°C were made on 15 different locations on the surface up to 168 hours. The originally 'flat' surface develops into an array of flat-bottomed etch pits, but some areas of pristine cleavage surface remain even after 168 hours. The etch pits exhibit a bimodal size distribution, with larger etch pits increasing in size, but more numerous small etch pits reach a steady-state size after about 84 hours. Measurements of surface-normal retreat of individual etch pits yield rates of about 2.7×10^{-8} and 6.6×10^{-8} moles/m²/sec. The bulk volume removed from the pits over an area of 3563 square microns gives a maximum bulk rate of 1×10^{-8} moles/m²/sec. This value is in very good agreement with the rates calculated from the rate law obtained from powder experiments, 9.4×10^{-9} moles/m²/sec, (Oelkers and Schott, 1995). The close agreement of our global kinetic rate (i.e. averaged over the entire surface) with that from flow-through experiments bodes well for the use of BET surface area by most previous laboratory studies. However, it is important to note that there is a range of more than one order of magnitude in the individual reactivity observed on the anorthite mineral surface. Nonetheless these new studies emphasize the need to obtain a realistic reactive surface area to enable extrapolations of the lab data to the field. Current work needs to take into consideration (1) the variation in rates for surfaces cleaved or fractured in different crystallographic orientations and (2) the evolution of the etch pit size distribution. Similar studies at high temperature are now being carried out on the dolomite surface.

Kinetic data from the dolomite reaction will also be presented.

References

Oelkers, E.H. and Schott, J. (1995) *Geochim. Cosmochim. Acta*, **59**, 5039–53.