

# Experimental simulations of fluid-rock interaction: the effect of surface area on the rate of alteration

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## Introduction

Despite our extensive, although incomplete, knowledge of the chemical aspects of fluid-rock interaction, our understanding of how these are linked to physical properties to produce wallrock alteration is still limited. Mathematical models can provide some insight into the connection between spatial and chemical aspects, but, at present, they are still inadequate. Experimental analogs may help to re-create some of the unknown fluid dynamic and kinetic parameters that, at this time, cannot be incorporated into mathematical

models of fluid-rock interaction. We report here results from such an experiment analog in which the evolution of the fluid over time was shown to be dependent not only on rock composition but also on the changing physical properties of the rock during alteration.

## Methods

A single pass, continuous-flow system was used to simulate the reaction of pure water with quartz diorite at 350°C, 480 bars. The rock was composed of quartz, oligoclase, albite, chlorite, sericite, ankerite and calcite, with lesser amounts of magnetite, rutile, ilmenite and pyrite. The hydrothermal solution was doubly-distilled water, equilibrated with atmospheric CO<sub>2</sub>, which was passed through the rock at a rate of 1 ml/hr. Effluents were analyzed for Al, Ca, Mg, Mn, Fe, Cu, Ni, Zn, Ti, P, Na, K, Si, SiO<sub>2</sub>, and room temperature pH. Run products were studied using SEM, XRD and electron microprobe. For experimental and analytical details, refer to Mountain (1993).

## Results

Figure 1 shows the concentration profiles for selected elements as a function of time. For the first 420 hours, temperature was maintained at 22°C. During this period, the fluid composition was dominated by the dissolution of carbonate minerals explaining the presence of Mg, Ca and dissolved CO<sub>2</sub> in the effluent. At 420 hours, the temperature was shifted to 350°C, after which there was an immediate increase in SiO<sub>2</sub> concentration which reached quartz saturation within two days. At the same time there were also immediate increases in the contents of Na, CO<sub>2</sub>, and more gradual increases in K and Al contents. Ca concentration decreased to below detection limit. SiO<sub>2</sub> concentration remained at quartz saturation for the succeeding 500 hours, and then dropped precipitously due to the complete dissolution of quartz. During this period, the

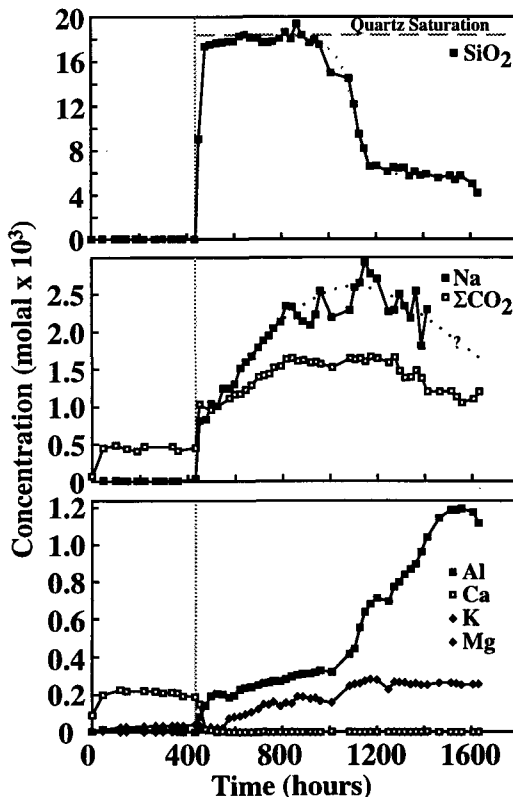


Fig. 1. Concentration profiles of selected elements versus time.

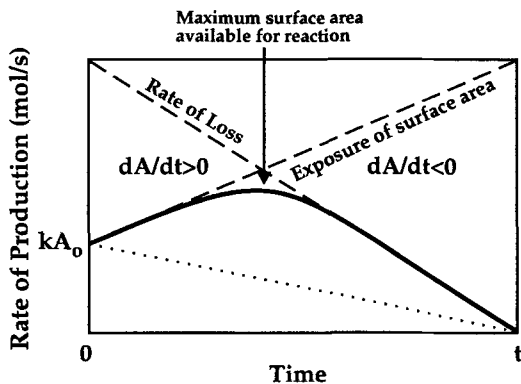


FIG. 2. The effect of changing surface area on the rate of production of a component.

concentrations of Na, CO<sub>2</sub>, Al, Ca and K all increased gradually.

During the next 200 hours, SiO<sub>2</sub> concentration continued to decrease, but at a much slower rate; Al continued to increase, but at a rate much faster than previously. Na and CO<sub>2</sub> also started to decrease.

Analysis of the run products showed the presence of abundant newly-formed anorthite, chlorite and lesser titanite. Much of the original chlorite, sericite, carbonate and opaques remained in the rock. Quartz, oligoclase and albite were not present.

### Discussion

The rate of production of an aqueous component *i* from a dissolving mineral can be expressed simply as:

$$\frac{dc_i}{dt} = \frac{\nu_i k}{V} \quad (1)$$

where *c<sub>i</sub>* is the concentration of *i* in molar units, *v<sub>i</sub>* is the stoichiometric coefficient of component *i* in that mineral, *k* is the dissolution rate constant (mol cm<sup>-2</sup>s<sup>-1</sup>), *A* is the surface area (cm<sup>2</sup>) and *V* is the volume of solution (*l*). This is only valid if, over time *t*, the surface area of the dissolving phase is constant, *i* is dissolving congruently from that phase (i.e. no other phase containing *i* begins to precipitate). If the surface area of the dissolving phase is changing over time, equation (1) must be modified to:

$$\frac{dc_i}{dt} = \frac{\nu_i k}{V} \left[ A + \frac{dA}{dt} t \right] \quad (2)$$

which incorporates the change in surface area with respect to time. At time = 0, *A* = *A*<sub>0</sub>, the initial surface area, and equation (1) reduces to equation (2). Therefore equation (2) can be written as:

$$\frac{dc_i}{dt} = \frac{\nu_i k}{V} \left[ A_0 + \frac{dA}{dt} t \right] \quad (3)$$

The integration of any of these equations would give the concentration in the fluid at time *t* for a static experiment and the concentrations in Figure 1 would thus represent cumulative concentrations. However, the experiment is of the single-pass flow-through type therefore the concentrations in Figure 1 are more representative of the rate of production (*dc<sub>i</sub>/dt*).

Upon the temperature shift, the sharp increases in SiO<sub>2</sub>, Na, CO<sub>2</sub> are linked to the first term of equation (3), i.e. the first exposed accessible surface area (*A*<sub>0</sub>). SiO<sub>2</sub> reaches a maximum rate of production dictated by saturation with respect to quartz. The high solubility of quartz (~0.1 wt. % in solution), and thus the significant outflux of SiO<sub>2</sub> results in the continuous exposure of the surface areas of other less soluble minerals (*dA/dt* > 0). Once quartz has completely disappeared, the accessible surface area of these minerals reaches a maximum and then begins to decrease as they are dissolved (*dA/dt* < 0). As a consequence, the rate of production of components from these phases begins to decrease. This is particularly evident for Na and CO<sub>2</sub> which are not involved in the precipitation of newly-formed minerals. These relationships are summarized in Figure 2.

Upon opening of a fluid conduit, an initial accessible surface area is available. If temperature is low, or flow rate is fast, kinetics may preclude attainment of local equilibrium between fluid and the rock. In this case, fluid composition will be sensitive to increases in accessible surface area and thus the actual rate of alteration will increase. Note that the opposite case is also true, in that, if pore space is filled by a precipitating phase, the rate of alteration will decrease as accessible surface area of other phases decreases.

### References

- Lasaga, A.C. (1984) *J. Geophys. Res.*, **89**, 4009–25.  
 Mountain, B.W. (1993) Fluid–rock interaction paths: Natural and experimental examples: Unpub. Ph.D. Thesis, McGill University, 352 p.