

LETTER REPORT

TITLE: Review of "Surface Oxidation-Reduction Kinetics Associated with Experimental Basalt-Water Reaction at 25°C," by A. F. White, A. Yee, and S. Flexser (1985). Chemical Geology 49, 73-86.

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REVIEW

The weathering of iron-containing silicates and oxides in an aquifer may have significant effects on speciation of multivalent ions and on the rates of chemical migration. Such weathering processes have long been of interest as major sources for the cycling of iron. The work reported in this paper addresses ways in which weathering may also affect aqueous oxidation-reduction reactions, dissolved oxygen (D.O.) concentrations, and the formation of secondary Fe-oxyhydroxides.

At low values of pH it has been shown that the Fe^{3+}/Fe^{2+} couple may have a strong influence on the redox conditions of geochemical systems. However, the effects of Fe on the redox conditions of neutral to alkaline groundwaters are generally not well understood. The situation has become more complicated with the recent finding by Winograd and Robertson (1982) that appreciable D.O. may exist even in old groundwater systems. Transport of trace elements, including some radionuclides, has been shown to be strongly influenced by sorption and coprecipitation with Fe-oxyhydroxides.

This paper is concerned with mechanisms of Fe oxidation-reduction reactions associated with rock-water interactions at 25°C. The present investigation is concerned with basalt-water interactions and uses an experimental approach similar to that of a study of Fe-containing silicates by some of the same authors (White and Yee, 1985).

Basalt was chosen for this study because it is the most common rock with high Fe concentrations. The particular basalts selected were from the Grande Ronde formation of the Pasco, Washington basin. The interest in this formation was, of course, its role as a candidate site for emplacement of high-level nuclear waste. Samples from the Umtanum and

Cohasset units were investigated. Although the total iron content of samples from the two units is similar, Fe(III) was found to be higher in Umtanum basalt.

Samples of Umtanum basalt were obtained from drill cores, while the source of Cohasset basalt was outcrop material. The mineralogy of representative samples was determined by a variety of techniques and appears to have been thoroughly characterized. Processing of samples for chemical experiments took precautions to avoid Fe contamination, and oxygen was excluded during the final cleaning, drying, and storage. It is not clear that oxygen was excluded at all stages of sample preparation, which would have been desirable.

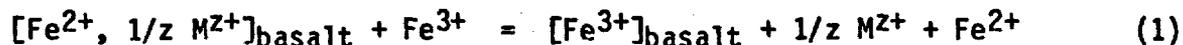
As in the authors' companion study on Fe-containing silicates, basalt-water reactions were carried out under open-system and closed-system conditions. For the experiments under open-system conditions, solutions were buffered and exposed to a flow of an O₂ and CO₂ mixture with carefully controlled composition. Closed-system conditions were used to monitor O₂ uptake. For such experiments, samples of basalt and an appropriate aqueous medium were sealed and allowed to react for several months. Periodically, the flasks were opened and D.O., Eh, Fe(II), and total Fe were determined. Other dissolved components were measured later. Both in the aqueous solutions and in the solid basalt, concentrations of Fe(III) were determined by the difference in concentration between total Fe and Fe(II). As in their related study on iron-containing silicates (White and Yee, 1985), the authors employed an impressive array of physical and chemical methods to study the products and effects of the basalt-water reaction.

Studies by x-ray photoelectron spectroscopy (XPS) showed the presence of large amounts of Fe(III) on the surfaces of the basalt phase assemblage as well as on minerals, to depths of a few nm. However, despite the presence of significant surface and bulk Fe(III), solutions in contact with basalt showed greatly suppressed amounts of oxidized iron at all values of pH, and at low pH Fe(III) was undetectable. During the same time interval, concentrations of Fe(II) showed significant increases. At pH 3.0, the final Fe(II) concentration greatly exceeded the initial Fe(III) concentration, indicating a contribution to the total Fe concentration from basalt dissolution. An obvious interpretation for this behavior is that Fe³⁺ is reduced in solution to Fe²⁺ in the presence of basalt. The present study attempted to determine the mechanism of this reduction by employing methods similar to those of White and Yee (1985).

Experiments with ⁵⁹Fe³⁺ suggested that reduction of iron occurred predominantly in solution. At values of pH > 6, concentrations of Fe are controlled by precipitation of oxyhydroxides. The rate of oxidation of Fe(II) was shown to exhibit the well-known, first-power dependence on the concentration of Fe(II), which was accelerated by addition of basalt to the system. In testing the effect of oxyhydroxide precipitation on dissolved Fe(II) and O₂ concentrations at near-neutral values of pH,

synthetic, blank solutions showed evidence for oxidation of Fe(II) to Fe(III), with precipitation of either Fe(OH)₃ or FeO(OH), goethite. Addition of basalt to such solutions caused a loss of Fe(II) not associated with the formation of ferric hydroxide or goethite. The decrease in oxygen concentration over long periods of time followed a diffusion-controlled reaction with basalt. The magnitude of the diffusion coefficient required to fit a simple, one-dimensional model, 10⁻¹⁴ cm² s⁻¹, suggests relatively rapid diffusion of O₂ at grain boundaries rather than solid-state diffusion, which would be slower. Generally, the rates of O₂ uptake for basalt are much faster than for separated silicate phases of the kind investigated by White and Yee (1985).

It is not surprising that the results indicate significant interaction between the basalt mineral assemblage and dissolved Fe(II), Fe(III), and O₂. However, it is surprising that, although the loss of Fe from the basalt with increasing pH correlates with an increase of Fe in aqueous solution, no increase in surface iron occurs, as would be expected for deposition of a surface oxyhydroxide coating. In solutions with pH less than 5.5 and undersaturated with oxyhydroxide phases, Fe was found to exist predominantly as Fe(II). By analogy with a similar situation observed by White and Yee (1985) for reduction of Fe(III) in aqueous systems containing silicate minerals, the authors propose that Fe(III) in solution is reduced by electron transfer during the oxidation of Fe(II) in the basalt surface, represented as follows:



Here, M denotes a cation of charge z+, and species in solution are shown without subscripts. The dissolution of a cation of charge z+ from the basalt phase serves to balance the charge exchanged when Fe(III) in solution is reduced.

At neutral to basic values of pH, the mechanism in eq. (1) is countered by the precipitation of Fe(OH)₃ and FeO(OH), such that Fe(II) is not observed at pH > 5.5. In solutions without a basalt phase present, oxyhydroxide precipitation controls the loss of Fe(II) by oxidation processes. When basalt is present, deviations in the final O₂ concentrations imply that aqueous Fe(II) is sorbed on the basalt surface, in addition to its oxidation and precipitation as Fe(III) hydroxide and oxyhydroxide. Finally, insufficient Fe is precipitated from the bulk solution to account for the quantities of O₂ consumed. The data presented appear to show that oxygen continues to diffuse into interior pore spaces and along grain boundaries dominated by iron oxides. The mechanism for consumption of oxygen at these sites is not defined but probably involves oxidation of interior ferrous iron and formation of ferric hydroxides and oxyhydroxides.

EVALUATION

This paper is a very detailed study of the basalt-water interaction, with emphasis on kinetic effects, using a variety of physical and chemical methods. It is not possible to evaluate all aspects of the experiments, since relatively little detail about experimental techniques was included. For example, oxygen was excluded during the final cleaning, drying, and storage, but it is not clear from the paper that oxygen was excluded at all stages of sample preparation, which would have been desirable. With these reservations, the experimental work appears to be of high quality, and a large number of analytical methods were employed to investigate the details of the various reactions which appear to be involved.

The general conclusions of this paper are interesting and relevant to problems which might be encountered in a basalt nuclear waste repository flooded with water. However, the series of reactions concerned with the basalt-water interaction are so complex that the conclusions of the paper tend to be qualitative and do not form an adequate basis for quantitative modeling. This comment is not intended to be critical of the research under discussion but, rather, is intended to suggest the work described in this paper serves as an excellent foundation for future studies of this type which are needed before a quantitative understanding of these processes can be reached. An obvious example of such future work is the acquisition of data at elevated temperatures and pressures.

It would have been helpful if the authors had recorded their views on the implications of the redox behavior of basalt-water systems on the speciation of multivalent ions and on radionuclide migration. The subject was mentioned briefly in the introduction and was not discussed further.

REFERENCES

White, A. F. and Yee, A. (1985). "Aqueous Oxidation-Reduction Kinetics Associated with Coupled Electron-Cation Transfer from Iron-Containing Silicates at 25°C," Geochim. et Cosmochim. Acta 49, 1263-1275. See also letter report on this paper by G. D. O'Kelley, LR-287-27, January, 1986.

Winograd, I. J. and Robertson, F. N. (1982). "Deep Oxygenated Groundwater: Anomaly or Common Occurrence," Science 216, 1227-1229.