Precipitation-Front Modeling: Issues Relating to Nucleation and Metastable Precipitation in the Planned Nuclear Waste Repository at Yucca Mountain, Nevada

J.A. Apps and E.L. Sonnenthal
Lawrence Berkeley National Laboratory, Berkeley, CA, jaapps@lbl.gov.

1 INTRODUCTION

The focus of the presentation is on certain aspects concerning the kinetics of heterogeneous reactions involving the dissolution and precipitation of unstable and metastable phases under conditions departing from thermodynamic equilibrium. These aspects are particularly relevant to transient thermal-hydrological-chemical (THC) processes that will occur as a result of the emplacement of radioactive waste within the Yucca Mountain Repository. Most important of these is a phenomenon commonly observed in altering soils, sediments and rocks, where less stable minerals precipitate in preference to those that are more stable, referred to as the Ostwald Rule of Stages, or the Ostwald Step Rule.

W. Ostwald (1897) described the phenomenon characterizing his rule (as cited in Schmeltzer et al., 1998), thus:

> "...in the course of transformation of an unstable (or metastable) state into a stable one the system does not go directly to the most stable conformation (corresponding to the modification with the lowest free energy) but prefers to reach intermediate stages (corresponding to other metastable modifications) having the closest free energy to the initial state".

This phenomenon is so widespread in natural geochemical systems, particularly under hydrothermal or low temperature conditions, that few geochemical parageneses involving the subcritical aqueous phase can be described without invoking the Ostwald Rule of Stages. Commonly observed systems where this phenomenon occurs include carbonates, silica, clay minerals, iron and manganese oxides, iron sulfides and zeolites (Morse and Casey, 1988). Simulations involving natural or anthropogenically modified reactive chemical transport must therefore be consistent with field observations describable by the Ostwald Rule.

Geochemists have long been familiar with the Ostwald Rule, but, with one exception (Steefel and Van Cappellen, 1990), have not incorporated the underlying chemical principles justifying the Rule in reactive chemical transport simulations, other than through arbitrary fixes involving the suppression of the thermodynamically more stable phases, and by prohibiting the re-dissolution of minerals.

Another issue relating to mineral metastability is the contribution of interfacial free energy to the total free energy of a geochemical system. The interfacial free energy contribution is trivial for crystal sizes in excess of 1 micrometer. However, the alteration of soils and sediments entails both the dissolution of finely crystalline products of diagenesis and heterogeneous nucleation and precipitation of new phases. The latter phases are commonly microcrystalline or amorphous, with substantial contributions of surface free energy to the total Gibbs free energy of the phase. Such contributions must be taken into account when modeling the chemical evolution of such systems, as they stabilize metastable phases and can modify aqueous species concentrations by up to two orders of magnitude. This condition is especially relevant to anthropogenically driven geochemical processes involving extreme levels of supersaturation where nucleation processes are dominant. Furthermore, by a process known as Ostwald Ripening, larger crystallites, usually possess a lower surface free energy

contribution, and being more stable, destabilize smaller coexisting crystallites of the same phase, leading to a decreased crystal size distribution, and the growth of progressively fewer crystals.

2 THEORETICAL BASIS FOR THE OSTWALD RULE OF STAGES

Ever since Ostwald stated his Rule of stages in 1897, attempts have been made to derive a theoretical basis for the rule. Now, even after 100 years, an undisputed theoretical basis for the rule has not been formulated successfully, even though field and laboratory observations supporting the rule are now too numerous to mention. A general consensus is that the rule can be explained through an understanding of nucleation theory and reaction kinetics. However, there is no rigorous basis for the rule in fact, i.e., in principle, there is no reason for the rule not to be violated, and occasional exceptions to the rule have been cited. In fact, one school of thought has attempted to formulate the rule on the basis of irreversible thermodynamics.

In natural systems, manifestations of the Ostwald rule, may in fact contain components both of kinetics, irreversible thermodynamics, and equilibrium thermodynamics. (See, for example, Duffy, 1993). Because quantitative evaluations of alteration rates in complex natural systems have hardly ever been made, it is not possible at this time to comment further on the applicability of each approach, and whether or not they can be reconciled, particularly when the complexity of the problem is fully appreciated. Perhaps, the strongest argument for preferring a kinetic treatment for the Ostwald rule, is evidence for the simultaneous growth of two or more phases of the same composition. Experimental results on a zeolitic system, cited by Barrer (1982), provide substantiation, although further examples are needed to lend credibility to this position.

3 ISSUES RELATING TO PRECIPITATION KINETICS AT YUCCA MOUNTAIN

At Yucca Mountain, Nevada, the site of a planned nuclear waste repository, metastable phase assemblages resulting from the low temperature hydrolysis of vitroclastic tuffs provide ample illustration of the Ostwald Rule of Stages. The occurrence of opal-A, and opal-CT in fractures (Carlos, 1989; Carlos et al., 1991; Vaniman, 1994; Carlos et al., 1995) and in the rock matrix (Bish and Vaniman, 1985; Chipera and Bish, 1988; Duffy, 1993: Carey et al., 1997) as products of glass alteration and possibly of devitrified tuff is evidence of metastability in the subsystem SiO_2-H_2O. Metastability in this system is widespread (Kastner, 1979; Williams et al., 1985; Barrer, 1982; Parks, 1990; Chang and Yortsos, 1994). The low temperature silica polymorphs follow the sequence opal-A - opal-CT - chalcedony (a microcrystalline form of quartz) - quartz (the stable end product) at near surface ambient temperatures. The rates of silica polymorph conversion under these conditions are extremely slow, taking millions of years (Kastner, 1979; Duffy, 1993). Because of the slow rate of silica phase transformation at near earth-surface temperatures, the silica activity in solution may be controlled by the silica polymorphs, thereby stabilizing other kinetically favored metastable phases such as the clays (Abercrombie et al., 1994) or zeolites.

Zeolite parageneses in the vitroclastic deposits at Yucca Mountain also provide evidence of adherence to the Ostwald Rule of Stages, as supported by independent observations elsewhere (Dibble and Tiller, 1981; Barrer, 1982; van Santen, 1984; Morse and Casey, 1988). Smyth (1982) noted the following zeolite sequence at Yucca Mountain:

(clinoptilolite (+ mordenite) + opal-CT) $\Rightarrow$ (analcime + quartz) $\Rightarrow$ (low albite + quartz)

Analysis of this sequence in terms of the Ostwald rule of stages is complicated, because of the complex chemistry of clinoptilolite in natural systems. The transformation rate of the assemblage (clinoptilolite (+ mordenite) + opal-CT) to (low albite + quartz) progresses very slowly within the YM stratigraphy. The time frame is of the order of millions of years, in conformity with independent reasoning by Dibble and Tiller (1981). However, with elevation of temperature, the kinetics of transformation is drastically accelerated as cited by Barrer (1982) in an analogous synthetic zeolitic system at 175°C, where metastable intermediates persisted for only 48 hours.

3.1 *Effects Related to Emplacement of Heat-Generating Nuclear Waste*

At Yucca Mountain, the emplacement of radioactive waste will lead to transient desiccation of the host rocks surrounding the emplacement drifts due to the release of heat during radioactive decay of the waste. Eventually, the desiccated region will be rehydrated. Thermal-hydrological-chemical processes involving the desiccation, condensation, and wetting fronts in this system produces conditions involving supersaturation with respect to siliceous phases and carbonates. The distribution of precipitating mineral phases in this system is strongly related to differences in solubility as a function of temperature. Precipitation of amorphous silica is expected to be confined to a narrow zone where evaporative concentration from boiling exceeds its solubility. In contrast, calcite may precipitate in fractures over a wider zone of elevated temperature, because of its lower solubility at higher temperatures. It is anticipated that the system will respond according to the Ostwald Rule of Stages.

In an experiment set up as an analogy to THC processes in the fractured tuff at Yucca Mountain, rapid precipitation of amorphous silica precipitation was produced by passing water through crushed tuff at 80°C and then allowing it to drain into an artificial fracture where the temperature was held in a gradient from 80°C to 130°C (Dobson et al., 2003). Results of ractive transport modeling of the experiment indicated that extremely high reactive surface areas were required (approximately equivalent to that characteristic of colloidal silica) to capture precipitation rates in this system.

Precipitation of amorphous silica, calcite, and gypsum (possibly anhydrite initially) have also been observed as products of boiling in the deep underground thermal tests at Yucca Mountain (e.g., Levy et al, 1998). Modeling the distribution of mineral precipitation in the fractures in the experiments also requires extremely high surface areas to capture rapid nucleation at the boiling front. Because the rock becomes completely dry thus resulting in complete precipitation of all silica, and the rate of advance of the boiling front is captured by temperature measurements and modeling quite accurately, the rates of silica precipitation can be estimated. However, the extent to which aqueous silica becomes supersaturated with respect to amorphous silica is unknown because fluid samples extracted from rocks by ultracentrifugation have equilibrated with a lower solubility silica polymorph at lower temperatures.

4 CONCLUSIONS

In summary, the issues requiring quantification and development of a realistic treatment in reactive chemical transport models are:

- A process incorporating the Ostwald Rule of Stages, thereby allowing the model to select automatically that phase (or those phases) that should precipitate from solution under specific conditions, rather than forcing the model to precipitate an arbitrarily selected phase. This feature is particularly important when two or more phases with differing thermodynamic stabilities may be precipitating simultaneously.

- A model that incorporates nucleation, growth, and Ostwald ripening. The model should allow for varying rates of precipitation, and the progressive reduction of growth sites with time.

5 REFERENCES

Abercrombie, H.J., Hutcheon, I.E., Bloch, J.D. & de Caritat, P. 1994. Silica activity and the smectite-illite reaction. *Geology* 22:539-542.

Barrer, R.M. 1982. *Hydrothermal Chemistry of Zeolites*. Academic Press, New York, 360 p.

Bish, D.L. & Vaniman, D.T. 1985. Mineralogic summary of YM, Nevada. *Los Alamos National Laboratory Report LA-10543-MS*, 55 p.

Carey, J.W., Chipera, S.J., Vaniman, D.T., Bish, D.L., Viswanathan, H.S., & Carter-Krogh, K. 1997. Three-Dimensional Mineralogic Model of Yucca Mountain, Nevada, Rev. 1. Report SP344BM4. Los Alamos National Laboratory.

Carlos, C., 1989. Fracture-coating minerals in the Topopah Spring member and upper tuff of Calico Hills from Drill Hole J-13. Los Alamos National Laboratory Report LA-11504-MS, 20 p.

Carlos, C., Bish, D.L. & Chipera, S.J. 1991. Fracture-lining minerals in the lower Topopah Spring tuff at YM. *IHLWC'91*.

Carlos, C., Chipera, S.J. & Bish, D.L 1995. Distribution and chemistry of fracture-lining minerals at YM, Nevada. *Los Alamos National Laboratory Report LA-12977-MS,* 92 p.

Chang, J. & Yortsos, Y.C. 1994. Lamination during silica diagenesis-effects of clay content and Ostwald ripening. *Am. J. Sci.* 294:137-172.

Chipera, S.J. & Bish, D.L. 1988. Mineralogy of Drill Hole UE-25p#1 at YM, Nevada. *Los Alamos National Laboratory Report LA-11292-MS,* 24 p.

Dibble, W.E. Jr. & Tiller, W.A. 1981a. Non-equilibrium water/rock interactions. I. Model for interface-controlled reactions. *Geochim. Cosmochim. Acta* 45:79-92.

Dibble, W.E., Jr. & Tiller, W.A. 1981b. Kinetic model of zeolite paragenesis in tuffaceous sediments. *Clays & Clay Minerals* 29:323-330.

Dobson, P.F., T.J. Kneafsey, E.L. Sonnenthal, N.F. Spycher, and J.A. Apps 2003. Experimental and numerical simulation of dissolution and precipitation: Implications for fracture sealing at Yucca Mountain, Nevada. *Journal of Contaminant Hydrology* 62-63:459-476.

Duffy, C.J., 1993. Preliminary conceptual model for mineral evolution at YM. *Los Alamos National Laboratory Report LA-12708-MS,* 46 p.

Kastner, M. 1979. Silica Polymorphs. In R.G. Burns (ed.), *Marine Minerals, Chapter 3, Mineralogical Society of America Short Course Notes* 6:99-109. Mineralogical Society of America, Washington, DC.

Levy, S., Chipera, S., & Snow, M. 1998. Mineralogical products of the ESF Single-Heater Test. *YMP Milestone SPY147M4*. Los Alamos National Laboratory.

Morse, J.W. & Casey, W.H. 1988. Ostwald processes and mineral paragenesis in sediments. *Am. J. Sci.* 288(6):537-560.

Ostwald, W. 1897. Studien über die Bildung und Umwandlung fester Körper: *Zeitschrift für Physikalische Chemie* 22:289–330.

Parks, G.A. 1990. Surface energy and adsorption at mineral-water interfaces: An introduction. *Rev. Mineral.* 23(Mineral-Water Interface Geochem.):133-75.

Schmelzer, J. 1998. Ostwald's rule of stages. The effect of elastic strains and external pressure.: Moeller, Joerg; Gutzow, Iwan. *Z. Phys. Chem. (Munich)* 204(1/2):171-181.

Smyth, J. R. 1982. Zeolite stability constraints on radioactive waste isolation in zeolite-bearing volcanic rocks: *J. Geol.* 90:195-202.

Steefel, C.I. & Van Cappellen, P. 1990. A new kinetic approach to modeling water-rock interaction: The role of nucleation, precursors, and Ostwald ripening. *Geochim. Cosmochim. Acta* 54:2657-2677.

Vaniman, D.T. 1994. Calcite deposits in fractures at YM, Nevada. *HLRWM-94.*

Van Santen, R. A. 1984. The Ostwald step rule. *J. Phys. Chem.* 88(24):5768-5769.

Williams, L.A., Parks, G.A. & Crerar, D.A. 1985. Silica diagenesis, I. Solubility controls. *J. Sed. Petrol.* 55(3):301-311.