

EXPERIMENTAL TESTS OF MICRO-CONCRETION NUCLEATION IN POROUS MEDIA. L. M. Barge¹ and J. Petruska², ¹University of Southern California, Dept. of Earth Sciences (3651 Trousdale Parkway, Los Angeles CA 90089, barge@usc.edu), ²University of Southern California, Dept. of Biological Sciences (1050 Childs Way, Los Angeles, CA 90089, petruska@usc.edu)

Introduction: Here we examine nucleation of self-organized spherical precipitates in porous and permeable media. Spheroidal concretions are common in geological environments and can arise through various geological or biological mechanisms, such as growth around an already existing nucleus (e.g. organic matter). Iron oxide concretions, however, often lack any obvious nucleus [1] and their presence in sandstone environments may result from self-organized nucleation and precipitation. Spherical iron oxide concretions with a self-organized distribution have also been observed at the MER Opportunity landing site at Meridiani Planum, Mars. These "blueberries" are found distributed throughout the section and their distribution and chemistry indicates that they were formed through aqueous diagenetic processes [2].

The growth of concretions via advection or diffusion of additional reactants has been studied theoretically [3] and experimentally [1], and much previous work, both experimental and theoretical, exists regarding the formation of periodic precipitates in diffusion-controlled systems [4]. The mechanisms that lead to the formation of periodic bands in gels are well understood, and the positions of the bands of precipitate in a homogenous medium can be derived from solutions of Fick's laws of diffusion, assuming certain boundary conditions [4, 5]. A similar approach can be taken for calculating the formation of periodically distributed spherical precipitates in a heterogeneous sandstone, and this has been modeled by [1].

Experimentally, however, the nucleation and growth of spherical concretions in porous media requires further investigation. We have performed diffusion experiments in combined glass beads and gel media, to study the effects of grain size, pore size, and pore distribution on the morphology of silver chromate precipitates. Precipitates in our experimental systems range from spherical to "finger fluid fronts", and these resemble various types of iron precipitation morphologies that are also observed in natural environments (e.g., the Navajo Sandstone [1]).

Experimental: Our approach involves diffusion of silver and chromate ions through different types of gels and glass beads. The silver ion (Ag^+) was chosen because it forms insoluble precipitates with many anions, and its simple monovalent character allows us to study precipitation morphologies independent of the effects of oxidation. The chromate ion (CrO_4^{2-}) was chosen

because its red color allows easy observation of precipitates in a column of glass beads (unlike many iron precipitates, which are colorless). Glass beads are used to simulate a sand/sandstone environment in which ions can diffuse from one pore to another and fluid convection or flow can occur when pore sizes are large enough. Four sizes of glass beads were used (106, 150-212, 212-300, and 450-600 μm) to represent porous sandstone. Gels are used to fill the pore spaces in a column of glass beads because their smaller pore size prevents bulk movement of fluid while allowing diffusion of small molecules and ions, and prevents product particles greater than a certain size from moving from their sites of formation. In this work we use a variety of gels (agarose, gelatin, agar, and silica hydrogel). Potassium chromate was distributed evenly throughout the diffusion medium, and the silver ion was introduced in a concentrated solution that was applied to the top of the gel/bead column. The reaction then proceeds as $\text{CrO}_4^{2-}(\text{sol.}) + 2\text{Ag}^+(\text{sol.}) \rightarrow \text{Ag}_2\text{CrO}_4(\text{insol.})$, yielding an insoluble compound that precipitates out of solution.

Results/Discussion: In this work varying types of self-organized silver chromate precipitates were produced in compact glass beads saturated with either pore fluid or gel. When the glass bead column was saturated with gel, randomly distributed spheroidal precipitates of silver chromate ranging from 1-3mm in diameter formed, morphologically resembling the mm-size spheroidal HFO concretions that are found in certain field localities in the Navajo Sandstone [6]. Finger-like fluid fronts were observed when the pores were filled with solution (not gel). Precipitation of silver chromate in our experiments was rapid, and the formation of patterns (spherules, etc) was complete within days.

Effects of grain size and pore size on precipitate morphology: When the glass bead column was saturated with pore fluid only (not gel), the size of the grains had a pronounced effect on the morphology of precipitate. Experiments with glass beads of intermediate size (150-212 μm , 250-300 μm) often produced fingered precipitation fronts, and in columns of 100 μm beads spheroidal precipitates with blurred edges were produced. When the glass beads were very small (100 μm) the sand-like matrix behaved somewhat like a gel in that its pores were small enough to prevent immediate convection of fluid and diffusive motion of ions between pores was possible. However, in contrast

to a tube of gel where the matrix is mostly homogeneous and diffusion of ions proceeds more or less in the vertical direction, this matrix composed of glass spheres of varying size likely broke up the initially planar reaction front. Liesegang-type processes operating in the glass bead column would lead to 3-dimensionally distributed spherical precipitates rather than the rhythmic banding commonly observed in gel diffusion experiments of this nature [4], since precipitation is centered around the pore where initial nucleation took place [1].

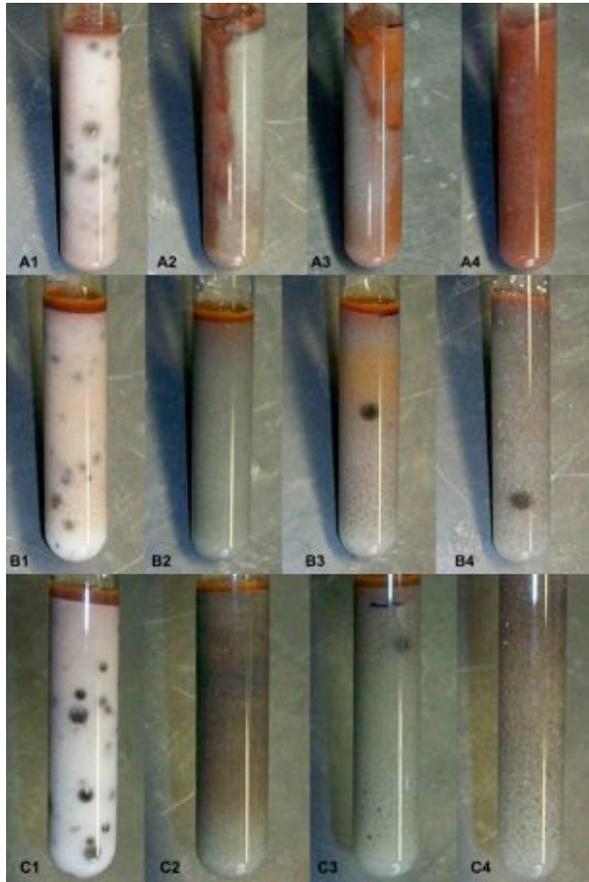


Figure 1: Silver chromate precipitation in glass beads and gel. A - Compacted glass bead matrix saturated with chromate solution. B - Compacted glass beads saturated with agarose gel. C - Compacted glass beads saturated with agar gel. Bead sizes are as follows: 1 = 100µm, 2 = 150-212µm, 3 = 250-300µm, 4 = 450-600µm. Test tubes are 13mm diameter.

The observation that smaller grain sizes (and therefore pore sizes) led to more structured precipitates led us to perform the experiments in which the glass bead matrix was saturated with gel. Including gel in the pores of the glass beads decreased the pore size and held it constant for all bead sizes, but allowed observation of the effects of pore connectivity on precipitate

morphology. In larger bead sizes, the inclusion of gel noticeably changed the morphology of precipitates. In the 212-300µm glass bead columns, fingered fluid fronts did not form and instead larger single spherules formed at some distance from the gel-air interface (Fig. B3, C3), and in the 425-600µm beads saturated with agarose gel a single large spherule formed near the bottom of the tube (Fig. B4).

The inclusion of gel in the pores of glass beads ensures that the only movement of reactive ions is through diffusion [4], but the actual flux of reactants into the system will be determined by the concentration gradient with distance (dC/dx) as well as the diffusion coefficient. It has been experimentally shown that the inclusion of glass beads in a gel decreases the diffusion rate of ions through that gel [7], and that in a compacted glass bead column the diffusion rate decreases with decreasing bead size [8]. Slower diffusion through the 100µm glass bead + gel column probably results in more rapidly increasing concentrations in the pores (since ion movement is slower), which may explain the nucleation of many smaller concretions as opposed to fewer larger ones. This is consistent with numerical model results from [1], which predicted formation of many small spherical precipitates closer to the fluid inlet at lower reactant fluxes, and fewer larger spherules at a greater distance from the fracture at higher fluxes.

Conclusion: We have produced spheroidal precipitates in porous media under a variety of conditions. These mm-size spherules have morphological similarities to "mini"-concretions in the Navajo Sandstone and the hematite concretions on Mars, including self-organized distribution, lack of an obvious macro nucleus, size, and ability to form "twin" morphologies. In all cases, spherical precipitates nucleated under diffusion-controlled conditions, and some growth occurred although advection was not present. Although the chemical conditions in our precipitation experiments are obviously very different from what would be expected in the Navajo Sandstone or on Mars, this experimental work shows how physical and chemical effects of a porous/permeable medium can greatly affect the morphology of precipitates produced.

References: [1] Chan, M.A. et al. (2007) *Geofluids* 7, 1-14. [2] Author A. B. and Author C. D. (1997) *JGR*, 90, 1151-1154. [2] Squyres, S.W. et al. (2004) *Science* 306: 1709-1714. [3] Berner, R.A. (1968) *Geochimica et Cosmochimica Acta*, 32, 477-483. [4] Henisch, H.K. (2005) Cambridge University Press. [5] Ortoleva, P. (1994) Oxford University Press. [6] Barge, L.M. et al. (2007) *LPSC XXXIX*, Abstract #1414. [7] Manley, D.R. and Stern, K.H. (1955) *J. Colloid Sci.* 10, 409-412. [8] Stern, K.H. and Shniad, H. (1958) *J. Colloid Sci* 13, 24-31.