REACTIVE TRANSPORT MODELING OF PHOSPHATE MOBILITY UNDER MARS-LIKE CONDITIONS. E. M. Hausrath[1] and V. Tu[1] [1]University of Nevada, Las Vegas 4505 S. Maryland Parkway, Las Vegas, NV 89154 Elisabeth.Hausrath@unlv.edu

Introduction: Phosphate is an important nutrient on Earth, used by life for ATP, DNA, RNA and phospholipid membranes [1]. Phosphate has recently been proposed as essential in the prebiotic formation of RNA on Earth [2], and therefore, if life is or ever was present on Mars, it may have started in a phosphate-rich environment. In addition, phosphate may be present in preserved biosignatures on Mars. For example, some of the ways that biota perturb the phosphate cycle on Earth is by greatly increasing the dissolution of apatite by releasing organic acids [3]. Biogenic phosphate minerals have also been identified, and may be valuable as biosignatures [4].

Phosphate has also been postulated as an important indicator of previous aqueous conditions on Mars [5]. Phosphate behaves differently under different conditions of pH, water: rock ratio, time and oxidation state. Under different conditions, phosphate adsorbs onto mineral surfaces, substitutes as a trace element into other mineral phases, forms amorphous precipitates, and forms secondary crystalline phases, recording the conditions under which these phases form.

Understanding the behavior of phosphate on Mars is therefore crucial in the search for life on Mars, and the interpretation of the climate history of that planet. To explore the behavior of phosphate under Mars-like conditions, we are using the reactive transport model CrunchFlow. Reactive transport modeling has great strengths in interpreting evidence of aqueous alteration on the surface of Mars. Recent work has shown that when secondary mineral precipitation rates can be quantified, primary mineral dissolution rates in the field on Earth can be successfully modeled using reactive transport modeling [6]. Duration of liquid water on Mars is a very important component of habitability, and mineral dissolution kinetics as modeled by reactive transport modeling may therefore be useful in quantifying habitability on Mars. CrunchFlow has been previously used to model olivine alteration on Mars, yielding a quantitative duration of alteration based on weathering profiles through weathering rinds [7].

Here, to groundtruth phosphate mobility for modeling of Mars, we report on reactive transport modeling of Mars analog experiments [8, 9], as well as dissolution experiments of amorphous secondary Al- and Fe-phosphate minerals.

Methods:

Modeling

Previously performed laboratory column dissolution experiments [8, 9] were modeled using the reactive transport code CrunchFlow. Experiments contained a mixture of fluorapatite, basalt glass, and olivine, to simulate likely quickly dissolving phases present in the Columbia Hills, Mars. CrunchFlow, written by Carl Steefel at Lawrence Berkeley National lab, simulates kinetic multicomponent reactive flow in porous media. CrunchFlow allows kinetically controlled mineral reactions; it incorporates advective, diffusive, or dispersive flow; and it contains reaction-induced porosity and permeability feedback. Surface complexation in CrunchFlow allows either a double layer or non-electrostatic model, after [10]. CrunchFlow has previously been used to simulate a variety of weathering conditions on Earth [6, 7, 11-13] and Mars [7]. Some of this work has focused specifically on adsorption of phosphate to sediments reacting with hydrothermal fluids [11]. Additional work has focused on Ostwald ripening from amorphous phosphate-precursors to crystalline phosphate phases [14].

Inputs to the code in this work include parent minerals (fluorapatite, forsterite, and basalt glass) with surface areas. Laboratory mineral dissolution rates from the literature were used [15]. Reacting solution chemistry consisted of the measured acid solutions with measured advective flow rates, and the model was run for the duration of the experiments. Model outputs were compared to experimental values.

Dissolution of amorphous Al- and Fe- phosphates

Amorphous Al- and Fe- phosphates have been formed in Mars-analog laboratory experiments [8] as well as the phosphate-rich Mars-analog environment Craters of the Moon, Idaho [16], and may therefore be important on Mars. Few dissolution rates of amorphous Al- and Fe- phosphates exist in the literature. We therefore synthesized amorphous Al- and Fe-phosphates using published methods [17] except that experiments were run for 24 hours and shaken continuously. Dissolution experiments are currently being performed reacting synthesized amorphous Al- and Fe-phosphates with constant ionic strength solutions at a variety of pH values.

Results and Discussion: Reactive transport modeling of the pH = 3 laboratory dissolution columns indicates that experimental results can be reasonably matched with model outputs once the system has reached steady state (Figure 1). The column dissolution experiments reach steady state after about 100 hours – before that concentrations decrease, possibly due to factors such as dissolution of fine particles or high energy sites.

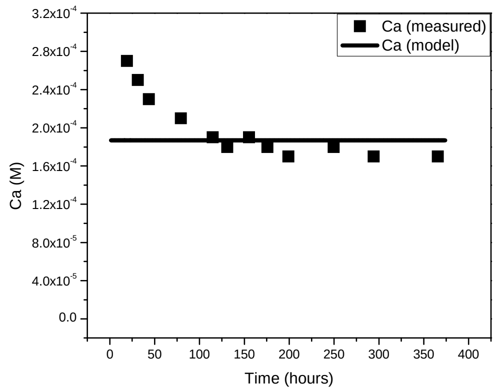

Figure 1. Modeled Ca concentrations compared to measured Ca concentrations from previous experiments [8,9]

Developing a rate law for amorphous Al- and Fe-phosphate dissolution under Mars-relevant conditions will provide useful information for reactive transport modeling of phosphate-rich Mars environments such as Watchtower and Wishstone.

Conclusions: Phosphate is an important indicator of water-rock interactions, as well as crucial for biological activity. Reactive transport modeling of Mars-analog experiments builds confidence for future work using dissolution rates of Mars important minerals such as chlorapatite and merrillite [18]. Future work includes modeling of the Mars-analog environment Craters of the Moon, Idaho as well as phosphate-containing environments on Mars such as Watchtower and Wishstone.

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