

USING A REVERSE OSMOSIS REACTOR TO MODEL THE CRYSTALLIZATION OF SECONDARY MINERALS IN MARS DURING LONG-TERM EVAPORATION PROCESSES. E. Losa-Adams¹, A.G. Fairen², C.Gil-Lozano², V.F. Chevrier³, A.F. Davila⁴ and L.G. Duport¹. ¹Dept. Geociencias Marinas. Universidad de Vigo36200 Vigo, Spain. (elosa@uvigo.es). ²Centro de Astrobiología (CSIC-INTA), Madrid 28850, Spain., ³Arkansas Center for Space and Planetary Sciences University of Arkansas Fayetteville, AR 72701, ⁴ SETI Institute, Mountain View, CA 94043, USA.

Introduction: In this study we explored the sequences of crystallization of secondary minerals resulting from basalt dissolution through experiments performed by batch reactors connected to reverse osmosis (RO) membranes, enabling us to understand the mechanism and rates of supersaturation.[1] The results could be further used to set up strategies to model long-term evaporation process on Mars.

One of the goals of our work is to show how different rates of generation of supersaturation (and not only a particular level of supersaturation) can greatly influence the sequence and type of phases in the system when a kinetic approach is considered. If different rates of supersaturation are employed, new evolutionary pathways for the phase crystallization sequence are expected to be obtained.

One of main technical problems to analyze the formation of secondary minerals from basalt dissolution is, how to get enough cations in solution to reach sulfates or chlorides saturation. This is due to the low solubility of basalt bearing minerals. Even if the atmospheric volatiles can sufficiently acidify the solution, reached near-to-equilibrium conditions -when dissolution of basalt is arrested- lead to low values of ionic strength (i.e.: the measured conductivity is in the range of 10-20 $\mu\text{S cm}$).

In principle, supersaturation for a given phase can be obtained in two ways: either increasing the amount of ions in dissolution involved in the stoichiometry of that phase (this is not only true for cations, it is also true for anions) or decreasing the amount of water. In our case the cations in solution derive primarily from the dissolution of basalt minerals under low concentration conditions. In one scenario with continuous evaporation, the concentration increases continuously due to the loss of water

In kinetic experiments the rate of both, acidification and the generation of supersaturation, are time-dependent and may greatly influence the sequence of phases within a multicomponent system. As supersaturation evolves with time, together with the pH, there is a sequence of intermediate (metastable or transient) phases that can precipitate and/or re-dissolve over the time course of the process driving the composition of the systems in several directions depending on varia-

bles such as reactive surface that are not considered in equilibrium models [2].

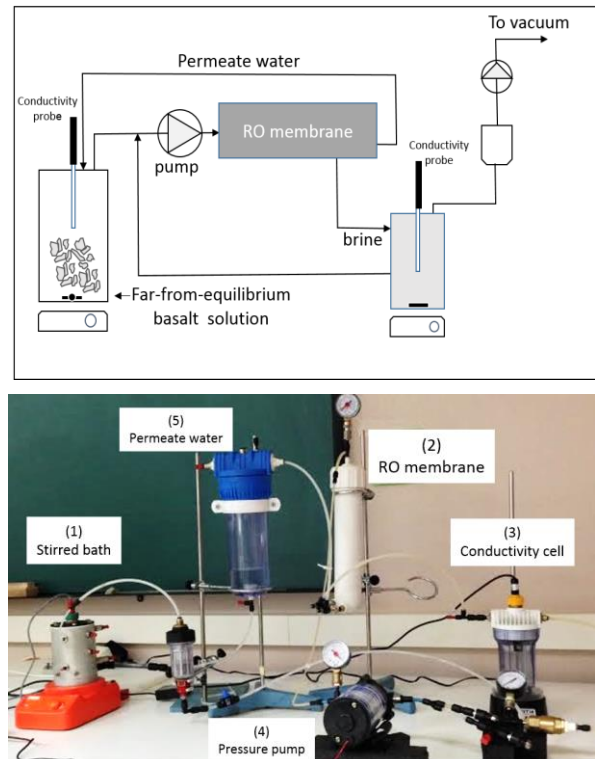


Figure 1. (a) Circuit scheme and (b) experimental arrangement of the flow-through batch reactor with Reverse Osmosis membrane employed to produce concentrated brines from far-from-equilibrium dissolution of basalt. This procedure can be used to set up strategies to model the formation of secondary phases during long-term evaporation process on Mars.

Reactor description and operation: We use the reactor circuit described in figure 1. Dissolution of basalt fragments (0.1-5cm in diameter) was allowed to take place in an stirred (750 rpm) batch reactor connected to a RO radial membrane through a pressure pump (8 bars). The brine was produced at the high pressure side of the membrane and its conductivity was continuously recorded in a second stirred tank.

Permeate water (i.e deionized water) resulting from the low pressure side of the RO membrane was recirculated back to the flow-through batch containing the basalt fragments (left side of the figure) to provide a continuous far-from equilibrium dissolution rate of ions.

Both concentrate and far-from-equilibrium dissolution streams were recirculated until the maximum concentration was reached.

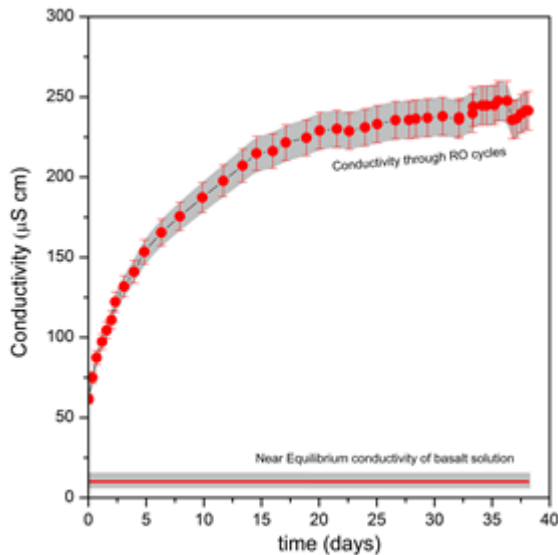


Figure 2. Conductivity ($\mu\text{S cm}$) of the concentrated stream resulting from continuous recycling of the basalt dissolution products through a RO membrane (upper curve) compared with the conductivity measured in a dissolution of basalt at near-equilibrium conditions.

Results and conclusions: As is shown in figure 2, the use of a RO membrane attached to a continuous flow-through batch reactor allows the initial solution - equilibrated with basalt (conductivity $\approx 10 \mu\text{S cm}$) - to be concentrated by a factor of twenty ($\approx 250 \mu\text{S cm}$).

This concentration can be related to evaporation processes by considering that the net amount of water released or -more precisely- the remaining fraction of water at each instant is the relevant quantity when calculating the evolution of supersaturation in the system and the kinetics of phase development. In the case of reverse osmosis the rate of water passage through the semipermeable membrane is defined as:

$$Q_w = (\Delta P - \Delta\pi_{\text{osm}}) * K_w * S/d$$

where Q_w is the rate of water flow through the membrane, ΔP is the hydraulic pressure differential across the membrane, $\Delta\pi_{\text{osm}}$ is the osmotic pressure differential across the membrane, K_w is the membrane permeability coefficient for water, S is the membrane area, and d is the membrane thickness. Inducing variations of these parameters as well as in the flow velocity of the reactor, will simulate different rates of water lost in the system and therefore different evaporation processes. Finally as brine is concentrated along the process, the potential precipitation of brine components can be evaluated. The saturation index of minerals whose precipitation could limit the concentration step may be calculated with the PHREEQC code using the Pitzer database.

References: [1] Casas et al (2012) Solvent Extraction and Ion Exchange, 30: 322–332, [2] Zolotov et al. (2005) Mars. Geophys. Res. Lett. 32, L21203