

Using a Reverse Osmosis Reactor to Model the Crystallization of Secondary Minerals in Mars during Long-term Evaporation Processes

E. Losa-Adams^{1*}, A.G. Fairen², C.G. Lozano², V.F. Chevrier³, A.F. Davila⁴, and L.G. Duport¹.

Dept. Geociencias Marinas, Universidad de Vigo. 36200 Vigo. Spain, *elosa@uvigo.es, ²Centro de Astrobiología (CSIC-INTA), Madrid 28850, Spain, ³Center for Space and Planetary Sciences, University of Arkansas, AR 72701 Fayetteville, Arkansas, ⁴SETI Institute, Mountain View, CA 94043, USA.

Universidade de Vigo



Introduction

One of the main technical problems concerning the development of experimental strategies to model long-term evaporation processes on Mars is how to get enough cations in solution to reach sulfates or chlorides saturation, because the solubility of basalt-bearing minerals is very low. Even if the atmospheric volatiles could sufficiently acidify the solution, near-to-equilibrium conditions are rapidly reached and dissolution tends to be arrested, leading to low values of ionic strength with measured conductivities in the range of 10-20 $\mu\text{S}/\text{cm}$.

This study focuses on analyzing 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 saturation [1], [2] and used to set up strategies to model long-term evaporation processes on Mars.

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 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 variables such as reactive surface that are not considered in equilibrium models [3].

Reactor description and operation

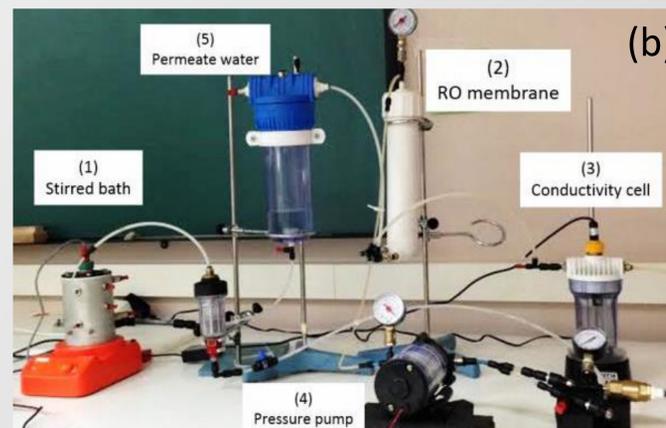
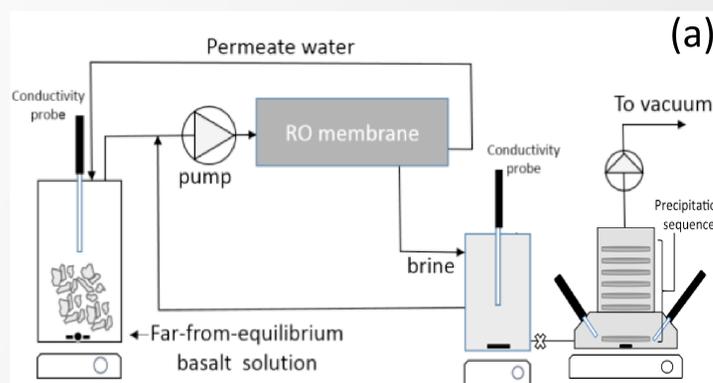


Figure 2

Results and Conclusions

The use of a RO membrane attached to a continuous flow-through batch reactor allowed the initial solution equilibrated with basalt (conductivity $\approx 10 \mu\text{S}/\text{cm}$) to be concentrated by a factor of about twenty (conductivity $\approx 250 \mu\text{S}/\text{cm}$). These concentration values agree fairly well with the equilibrium calculation of conductivity made by phreeqc during the evaporation of a dissolution of basalt minerals (fig. 3 (b)).

The increase in concentration derived from RO-Batch experiments 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:

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

Q_w = rate of water flow through the membrane
 ΔP = hydraulic pressure differential across the membrane
 $\Delta \pi_{osm}$ = osmotic pressure differential across the membrane
 K_w = membrane permeability coefficient for water
 S = membrane area
 d = membrane thickness

Inducing variations of these parameters -as well as in the flow velocity of the reactor- enables us to simulate different rates of water lost in the system and therefore to simulate different evaporation processes.

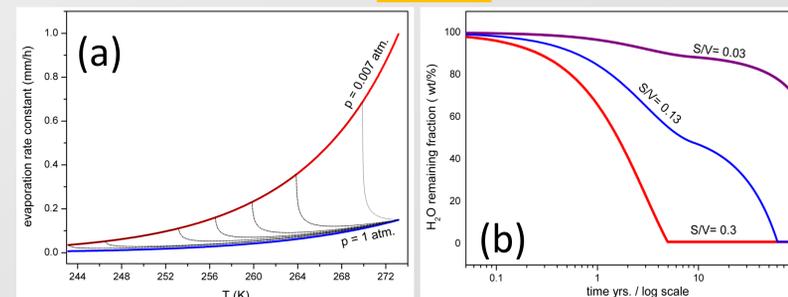
Finally, as brine is concentrated along the process, the potential precipitation of brine components can be evaluated. The saturation index of minerals whose precipitation could limit the concentration step may be calculated with the PHREEQC code and employing the Pitzer database.

From the point of view of a liquid-vapor phase transition, the rate of evaporation in Mars terms can be expressed as:

$$\frac{dM_w}{dt} = \frac{S}{V} \cdot E_v \left(1 - \frac{P}{P_0}\right)$$

M_w = stand for the moles of H_2O evaporated (mol/kgw)
 S/V = surface to volume ratio (m^2/dm^3) [depends on the geometry and size of the basin]
 E_v = specific rate constant (mol/ m^2s)
 $(1 - P/P_0)$ = saturation term [represents the distance from the equilibrium]

Figure 1



The temperature dependence of the specific rate constant for evaporation, under the consideration of a free convection mechanism is shown in Figure 1(a), where E_v is expressed in mm/h. The remaining fraction of H_2O , which is the relevant parameter to evaluate the time dependence of the supersaturation, depends on temperature and pressure through the variations of E_v with these parameters and, also, depend on an additional factor, the surface to volume ratios (S/V) of the reservoir. This variation is illustrated in Figure 1(b) which represents the time evolution of the mass of H_2O for various S/V ratios (0.3, 0.13 and 0.03) respectively.

We designed a circuit to perform this study using a RO radial membrane connected to a pressure pump (8 bars) and to two stirred (750 rpm) batch reactors.

In one of them, we placed the dissolution of basalt fragments with the deionized water resulting from the low pressure side of the RO membrane providing a continuous far-from-equilibrium supply of ions that return to the membrane. And in the other, the brine resulting from the high pressure side of the RO membrane was accumulated.

Both, concentrated and far-from-equilibrium dissolution streams were recirculated until the maximum concentration was reached and its conductivities were continuously recorded.

Finally, concentrated solution was evaporated completely by vacuum and the secondary phases were collected on a sequence of filters for future analysis.

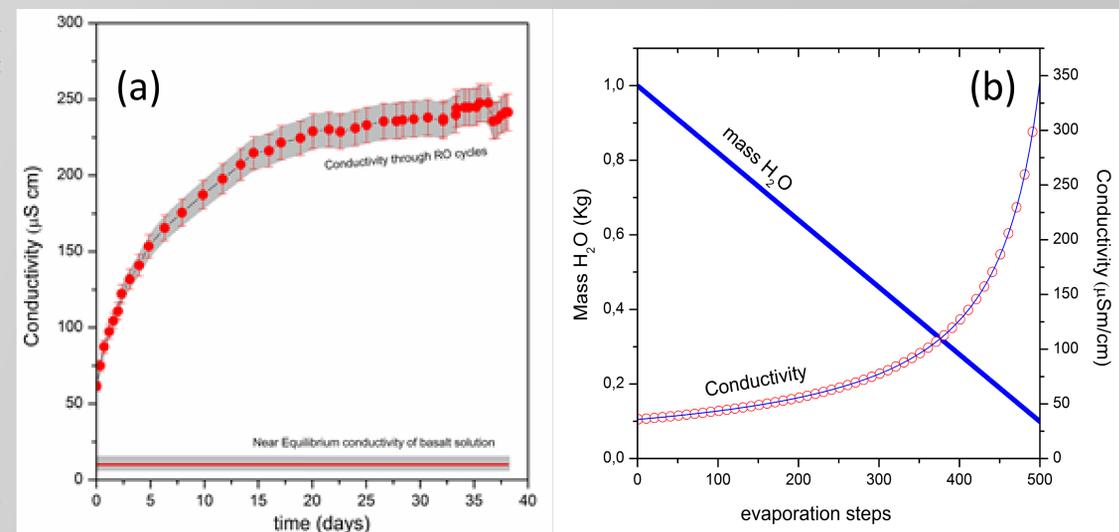


Figure 3

References

[1] Waly *et al.*, (2011) *Desalination*, 280, 27-32 [2] Casas *et al.*, (2012) *Solvent Extraction and Ion Exchange*, 30: 322-332, [3] Zolotov *et al.*, (2005) *Mars. Geophys. Res. Lett.* 32, L21203