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The morphology of gypsum precipitated under hyper-saline conditions – preliminary results from Dead Sea - Red Sea mixtures

A.G. Reiss[a,b,1], I. Gavrieli[b], J. Ganor[a]

[a]Department of Geological and Environmental Sciences – Ben-Gurion University of the Negev, post office box 653, Beer-Sheava 8410501, Israel
[b]Geological Survey of Israel, 30 Malkei Israel, Jerusalem 9550161, Israel

Abstract

Solutions of different chemical compositions will precipitate gypsum crystals with different morphology. The dependence of gypsum morphology on the chemical composition can therefore be a tool for interpreting the paleo-chemistry and environments of solutions from which gypsum in the geological record precipitated. In addition, the morphology of the gypsum that will precipitate in the Dead Sea once the Red Sea-Dead Sea conduit is built will determine if the crystals will remain in suspension in the surface brine, thereby leading to "whitening" of the lake. Despite its importance, little is known about the impact of the different parameters on the morphology of gypsum precipitated from natural brines. In the present study we conducted single point batch experiments with mixtures of Dead Sea - Red Sea brines and utilized image processing techniques to study the morphology of the gypsum that precipitated from different solution compositions at different degrees of oversaturation. The results from the first data set towards the understanding of what controls the morphology of gypsum while providing a preliminary tool for the forecast of the future of the Dead Sea are presented here.

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Keywords: gypsum; gypsum morphology; Dead Sea

1. Introduction

1.1. General introduction

Gypsum ($CaSO_4*2H_2O$) is a common mineral precipitated in both geological and industrial processes. While the

* Corresponding author. Tel.: +972-8-6477517; fax: +972-8-6477655.
E-mail address: reissam@poat.bgu.ac.il

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precipitation kinetics of gypsum was extensively studied, there are fewer studies on the morphology of the forming crystals[1-3]. The knowledge about the effects of the solution composition (either dissolved ions or organics) on the morphology is mostly derived from industrial processes and synthetic solutions and there is a lack of data from natural brines. A full understanding of the effects that dictate gypsum crystal morphology can help in understanding paleo-chemistry of various water bodies as well as contemporary environmental problems. One such example is the possible "whitening" of the Dead Sea following the implementation of the Red-Sea Dead Sea conduit and the mixing of Red Sea water in the Dead Sea[4].

1.2. Case study

The Dead Sea is a hyper-saline (~280 g/kg) terminal lake situated along the Dead Sea valley. Since the mid-20th century the lake has been experiencing a negative water balance causing a drop in the water level (~30 m drop) to the contemporary level of 429 m below sea level[5]. The dehydration of the lake has resulted in brine that is oversaturated with respect to gypsum (Ω_{gyps} ~1.5) as well as other minerals. Due to the ongoing negative water balance, the oversaturation with respect to gypsum has been increasing with time, yet while gypsum precipitation is relatively minor[6] Any gypsum precipitation that does occur in the lake is masked by precipitation of halite ($1.0 < \Omega_{halite} < 1.1$)[7].

In addition to the increase in salinity, the declining level of the lake has affected the lake and its environment both chemically and physically. Some of those changes, the creation of sinkholes for example, endanger infrastructure and human lives[8]. In order to mitigate the environmental changes as well as to produce potable water for the surrounding countries, a Red Sea-Dead Sea conduit was proposed. Under the proposed project, water from the Red Sea will be desalinated and the reject brine will be transferred to the Dead Sea[4]. A major concern is that this will cause a rise in turbidity of the Dead Sea, leading to "whitening" of the water due to the formation of minute gypsum crystals that will stay afloat. The latter will be determined by the crystal size distribution (which is determined by kinetics), crystal morphology, and the change of the size and morphology with time. The kinetics of gypsum precipitation in Dead Sea-Red Sea mixtures was extensively studied by[9-11] but there is no data about the morphology of the forming crystals and how this morphology changes under different mixing conditions. Thus, understanding how the chemical composition of brine controls the morphology of gypsum will allow to predict the potential of Dead Sea whitening events while also providing a tool for studying the composition of paleo-brines that have precipitated gypsum.

2. Methods

Experimental solutions were prepared by mixing Dead Sea brine, evaporated Red Sea brine containing Na_2SO_4 and $CaCl_2*2H_2O$ dissolved in DDW (Double deionized water). The DDW is added in an amount that together with the H_2O added from the $CaCl_2*2H_2O$ would equal the amount of water evaporated from the Red Sea waters used. The salts are added in amounts that keep the molar Ca^{2+}/SO_4^{2-} ratio (molar Ca^{2+}/SO_4^{2-} is 115 and 0.37 in Dead and Red seas respectively) as well as the concentrations of other dissolved ions. The contribution of sodium and chloride to the mixture are negligible compared to those already in solution.

At the onset of each experiment the mixed solution is divided into several bottles, containing a 200 g aliquot each. The bottles are then placed in a thermostatic shaking bath, set to 25.0±0.1 °C. One of the bottles is sampled routinely to follow the change in SO_4^{2-} concentration as a measure of the amount of gypsum that precipitated. The other bottles are intended for solid-liquid separation. At designated times a sample for chemistry analysis is taken and one of the bottles is removed from the thermostatic bath, and its crystals are separated from solution for measurement. For the chemical analysis ~ 1g solution is filtered (0.22 μm) into a bottle and diluted by weight to a factor of ~100, in order to stop further precipitation. The crystal-solution separation is done by filtration through a 0.22 μm polycarbonate filter using a peristaltic pump. In order to collect all crystals, the solution separated is then used to rinse the bottle from which the crystals were separated. This solution is then re-filtered through the same filter.

Images of the filters containing the precipitated gypsum crystals are taken using a binocular. Images are taken across the entire filter so that crystals from various parts of the filter would be recorded. The crystals on the images