



Magnesium isotopic fractionation between Mg salts and brine in the course of evaporation of marine derived brines

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The Mg isotopic compositions ($\delta^{26}\text{Mg}$) of seawater-derived-brines and Mg-salts that precipitate from such brines during the course of evaporation were measured in laboratory experiments, in Mg-salts from the geological record and in the Dead Sea brine system. Mg evaporites are one of the sink fluxes in the global Mg geochemical cycle and play an important role in the evolution of hypersaline water bodies during the Phanerozoic including the modern Dead Sea and its predecessors, from the Pliocene Sedom Lagoon to the Late Pleistocene brine lakes^{1,2}.

The advanced evaporative evolution of marine derived brines includes precipitation of a series of Mg minerals³: epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), hexahydrite ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), kainite ($\text{MgSO}_4\text{KCl} \cdot 3\text{H}_2\text{O}$), carnallite ($\text{KMgCl}_3 \cdot 6\text{H}_2\text{O}$), bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$) and in some cases polyhalite ($\text{K}_2\text{MgCa}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$). To the best of our knowledge, just two Mg isotopic fractionation factors between Mg salts and brines ($\Delta^{26}\text{Mg}_{\text{salt-brine}}$) were determined up to date: the equilibrium fractionation between epsomite and MgSO_4 solution was found to be about 0.6‰⁴ and the fractionation between carnallite and Dead Sea brine was found to be 0.6‰⁵.

Here we provide Mg isotope fractionation factors based on $\delta^{26}\text{Mg}$ measurement in brines and precipitating Mg-salts during the evaporation path of seawater. The sequence of Mg salts precipitated in our evaporation experiments was as follows: Mg-sulfate salts started to precipitate at Li scale degree of evaporation (DE_{Li}) of >50 . The next salts to precipitate were Mg-K-sulfate salts at $\text{DE}_{Li} \approx 90$, followed by Mg-K-chloride salts at $\text{DE}_{Li} > 150$ and by Mg-chloride salt at $\text{DE}_{Li}=195$ (the end of the experiment). Our isotopic measurements show that Mg isotopes fractionate significantly and in different directions depending on the Mg mineral phase. The $\Delta^{26}\text{Mg}_{\text{salt-brine}}$ for carnallite was greater than 0.6‰ and the $\Delta^{26}\text{Mg}_{\text{salt-brine}}$ for kainite was about -1.2‰. These results were corroborated by the $\delta^{26}\text{Mg}$ values measured on Mg minerals from the geological record on which we measured a value of 1.72‰ for Permian carnallite from Klodawa, Poland and -2.02‰ for Messinian kainite from Sicily, Italy.

The opposite fractionations during the precipitation of different Mg mineral phases in the course of evaporation of seawater reveal a rather complex evolution of the $\delta^{26}\text{Mg}$ value in marine derived brines. The present day seawater $\delta^{26}\text{Mg}$ is -0.83‰ and it increased to -0.6‰ when brine evaporation reached the kainite facies and decreased down to -1.0‰ when brine evaporation reached the bischofite facies. These new data may provide the evaporite signal for models reconstructing the evolution of the Dead Sea and the secular variations in the marine $\delta^{26}\text{Mg}$ record in general.

References:

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