

Mg isotope fractionation during precipitation of marine Mg-evaporites

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Mg isotope fractionation between Mg-evaporites and marine derived brines was studied along the course of seawater evaporation. The sequence of Mg-salt included epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), kainite ($\text{KMgClSO}_4 \cdot 3\text{H}_2\text{O}$), carnallite ($\text{MgKCl}_3 \cdot 6\text{H}_2\text{O}$), kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$) and bischofite ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). These Mg-salts typically precipitate only in nearly closed evaporitic basins, such as the Permian Zechstein sections in northern Europe and the Messinian sections around the Mediterranean. As chemical deposits, they represent a direct record of the chemistry of their precipitating brines and hence serve as an archive for the compositions of ancient brines and past seawater. In addition, Mg removal by precipitation of these minerals may affect the $\delta^{26}\text{Mg}$ value of the brine, provided the process involves significant Mg-isotope fractionation.

The results show mineral-dependent Mg-isotope fractionation in both directions, during Mg-evaporites precipitation. The following fractionation factors were established: $\epsilon_{\text{epsomite-brine}} = +0.59 \pm 0.31\%$, $\epsilon_{\text{kainite-brine}} = -1.3 \pm 0.43\%$ and $\epsilon_{\text{bischofite-brine}} = +0.33 \pm 0.19\%$. The ranges for $\epsilon_{\text{carnallite-brine}}$ and $\epsilon_{\text{kieserite-brine}}$ are $+0.92\%$ to $+5.5\%$ and -1.8% to -0.37% , respectively. $\delta^{26}\text{Mg}$ values determined on minerals from the geological record corroborate these results. The fractionation factors are shown to correlate with the number of water molecules in the mineral formula, suggesting that Mg isotope fractionation occurs during both the dehydration of the aquo-ion $[\text{Mg}(\text{OH}_2)_6]^{2+}$, whereby ^{24}Mg is preferentially dehydrated, and during the incorporation of Mg into the mineral lattice, whereby ^{26}Mg is preferentially incorporated.

Despite the significant fractionations and considerable Mg removal, $\delta^{26}\text{Mg}$ of the brine changed only slightly along the course of evaporation. This is due to the precipitation of multi-mineral assemblages having opposite fractionations. Thus, given the fractionation factors established in this work for the different Mg-salts, $\delta^{26}\text{Mg}$ recorded in ancient Mg-evaporite sequences may serve as a tool to reconstruct the Mg budget of ancient evaporitic environments and the $\delta^{26}\text{Mg}$ of past seawater.