

Establishing the Magnesium isotope ($\delta^{26}\text{Mg}$) signature of early and late diagenetic dolomite types

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The Magnesium isotopic composition has been established as a paleo-climate/paleo-weathering proxy in marine and terrestrial carbonate precipitation environments. Precipitation kinetics of dolomites and dolomite precipitation models, which relate to their diagenetic environments and the commonly complex fluid chemistry, are under debate. Any independent geochemical evidence, such as specific dolomite $\delta^{26}\text{Mg}$ signatures characterizing specific dolomite formation realms, has the potential to add a valuable additional interpretation tool. This study represents a considerable advance in dolomite Mg isotope research and reviews data from previous research studies. In addition, we took advantage of well-established isotope systems in order to establish a detailed diagenetic history of each sample investigated. Proxies included oxygen ($\delta^{18}\text{O}$), carbon ($\delta^{13}\text{C}$) and strontium ($^{87}\text{Sr}/^{86}\text{Sr}$) isotopes as well as main and trace element abundances. Our data indicate that there is no unambiguous Mg isotopic pattern that characterizes specific dolomite types. At present, it seems obvious, that magnesium isotope values of different dolomite types are controlled by a complex array of factors. Burial dolomites display the widest isotope range observed. Obviously, in the burial domain, the temperature of the precipitating fluid is of interest. Therefore, we applied clumped isotope thermometry (Δ_{47}) to burial dolomites displaying end-member Mg isotope values. Our preliminary data set reveals a fair correlation between burial fluid temperature and dolomite Mg isotope signature. As the clumped isotope closure temperature for dolomite is not established yet, this could represent an interesting contrast to recent work [1] documenting that earliest diagenetic sabkha dolomites homogenized under burial temperatures of up to 450°C. The tentative working hypothesis is that the temperature of the precipitating burial fluid affects, amongst other factors, dolomite $\delta^{26}\text{Mg}$ signatures.

[1] Geske *et al* (2012) *Chem. Geol.* **332-333**: 45-64.

Natural $\text{BaCa}_6[(\text{SiO}_4)(\text{PO}_4)](\text{PO}_4)_2\text{F}$ with a new modular structure type

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$\text{BaCa}_6[(\text{SiO}_4)(\text{PO}_4)](\text{PO}_4)_2\text{F}$ (space group $R\bar{3}m$ (No.166) $a = 7.09660(10)$ Å, $c = 25.7284(3)$ Å, $Z = 3$), a not yet approved new mineral, has recently been found enclosed in paralavas confined to pyrometamorphic rocks of the Hatrurim formation, Israel.

The structure of it is easiest described as a 1:1 stacking of the two modules (1) $\{\text{Ca}_6(\text{T}^{4.5+}\text{O}_4)_2\text{F}\}^{4+}$ and (2) $\{\text{Ba}(\text{T}^{5+}\text{O}_4)_2\}^{4-}$ along the c -axis. Module (1) consists of close packed sevenfold coordinated Ca with (SiO_4) and (PO_4) tetrahedra filling the gaps. F is surrounded by 6 Ca atoms forming almost perfect octahedra. Module (2) is characterized by (PO_4) tetrahedra connected to sixfold coordinated Ba.

The modular stacking of $\text{BaCa}_6[(\text{SiO}_4)(\text{PO}_4)](\text{PO}_4)_2\text{F}$ presents a new structure type. The only mineral with related structure we are aware of is nabimusaite $\text{K}(\text{Ca}_{12}(\text{SO}_4)_2(\text{SiO}_4)_2)\text{O}_2\text{F}$ (space group $R\bar{3}m$, $a = 7.1905(4)$, $c = 41.251(3)$ Å, $Z = 3$) [1]. The structure of its synthetic analog has been reported before and is characterized by a 2:1 stacking of modules similar to those of $\text{BaCa}_6[(\text{SiO}_4)(\text{PO}_4)](\text{PO}_4)_2\text{F}$ but with different cations [2].

[1] Galuskin, E.V. *et al* (2013) *Min. Mag.*, **77**, 1-12. [2] Fayos, J. *et al* (1985) *Acta Cryst.*, **C41**, 814-816.