

## Be-silicates: New minerals, structure topologies, classification and uses

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In minerals only Be in tetrahedral coordination is known. In beryllium silicates  $[\text{BeO}_4]$  and  $[\text{SiO}_4]$  are well ordered and polymerization is highly developed. Of the 61 Be-silicate species most are sheet structures (20 species) or framework structures (29 species). There are 7 chain structures and 5 undetermined. The high degree of polymerization is due to the high bond valence of  $[\text{BeO}_4]^{6-}$  (0.50 v.u.) which is even higher than that of  $[\text{SiO}_4]^{4-}$  (0.33 v.u.).

Improved laboratory instrumentation has led to the discovery of several new Be-silicate minerals and the determination of their crystal structures. Sheet structures are typically constructed of 4-, 5-, 6-, and 8-membered rings. The new mineral bussyite-(Ce),  $(\text{Ce,Ca})_3\text{Na}_3[\text{Be}_2\text{Si}_5\text{O}_{15}\text{F}_2]$ , is typical of this with net topology;  $(458)_2(5^28)_2(5^28^2)$  as is the sheet for the new mineral ciprianiite,  $\text{Ca}_4(\text{Ce,Th})_2\text{Al}[\text{BeB}_4\text{Si}_4\text{O}_{22}(\text{O,OH})_2]$ ;  $(48^2)_2(8^2)(8^3)$ . The frame-work structures are varied and complex. New minerals such as telyushenkoite,  $\text{CsNa}_6[\text{Be}_2\text{Al}_3\text{Si}_{15}\text{O}_{39}\text{F}_2]$  and eirikite,  $\text{KNa}_6[\text{Be}_2\text{Al}_3\text{Si}_{15}\text{O}_{39}\text{F}_2]$  have 5-, 6- and 7-membered rings with the Be-site centring the  $(7^3)$  topology. Higher orders of polymerization are often unique, zeolite-like structures; nabesite with 9-membered rings, chiavennite and roggianite with 12-membered rings, and odintsovite with a giant, ovoid 22-membered ring. In each of these structures the Be-site(s) is a facilitator in augmenting the degree of polymerization.

## Evidence for a dynamic marine calcium cycle during the past 30 million years from a record of Calcium isotopes in marine barite

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The marine calcium (Ca) cycle is related to processes that control oceanic alkalinity and atmospheric  $\text{CO}_2$  playing an important role in earth's climate. Fluctuations and imbalances in the marine calcium carbonate reservoir, the largest carbon reservoir in the atmosphere, biosphere, and ocean, likely represent changes in the carbon cycle and may be related to global changes in climate and tectonics. The amount of  $\text{Ca}^{2+}$  in the modern oceans and its isotopic composition are determined by the balance between riverine and hydrothermal input and removal via calcium carbonate deposition and alteration of oceanic crust and their respective isotopic compositions.

Recent work using Ca isotope ratios measured in marine carbonates has suggested that the biogeochemical cycling of marine calcium is more dynamic than previously assumed given its long residence time  $\sim 1\text{Ma}$ . However, multiple processes may control the Ca isotope composition measured in marine carbonates, complicating their interpretation. Here, we present a new high-resolution, continuous seawater Ca isotope curve from marine barite ( $\text{BaSO}_4$ ). Marine barite precipitates inorganically in seawater incorporating  $\text{Ca}^{2+}$  with a constant isotopic offset from seawater (isotopic fractionation) that is not strongly related to any measured present day oceanic environmental parameter.

Our seawater Ca isotope record displays a long term increasing trend over the past 30 Ma towards more positive values at the present, in general agreement with existing records. However, our data reveals new features that correspond with shifts in marine carbon and oxygen isotope records, most notably at the middle Miocene climatic transition ( $\sim 15\text{Ma}$ ). We used a numerical model to investigate what the Ca isotopic record suggests about the marine Ca biogeochemical cycle in relation to perturbations in the carbon cycle and major climate events.