

### 3 stages of Earth evolution — Core formation, ocean emergence and the 2.3 Ga rise of atmospheric oxygen: How are they linked?

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Recognized nearly a century ago [1], the mean specific angular momentum (a. m.) of SS planetary materials is  $>10^5$  times the Sun's, so it is an important constraint upon how the planets were built. Nebula is the only conceivable agent for this partition. And it must do this for both the protoplanet and all of its feedstock, so planetary growth must be essentially complete before it departs ( $<5$  Ma?). This rules out the post-nebula growth in cores-by-Fe-percolation models, for which isotopic (Hf-W, etc) data have been interpreted as needing upwards of 30 Ma for completion, though this interval may actually relate to post-core-completion exchange at the CMB.

Those models also do nothing for the origin of SS water. Ringwood's model (1960-1978) invokes a cool nebula, achievable with other advantages [2-4], to give high- $f_{O2}$  accretion. It then uses the nebula to reduce hot erupted FeO at the protoplanet's surface; the Fe then being 'subducted' to form the core. Nebular departure halted this, leaving some FeO in the mantle. Incorporation into its mineral structure of a few of the  $>400$  Earth-ocean volumes of reaction water thus generated greatly water-weakened it, facilitating convective loss of early heating.

But at  $\sim 2.49$  Ga, ocean production caused parts of the upper mantle to reach a critical loss of water-weakening in the presence of interstitial melt [5], halting convective motion for  $\sim 270$  Ma [6, 7]. MOR collapse lowered sea-level by  $>3$  km, exposing cratons to erosion, unroofing TTG, lowering atmospheric CO<sub>2</sub> and causing Huronian glaciation (2.4 Ga). During this hiatus, oxygenic life, previously confined to the top 200 m of oceans, won its battle against MOR effusions, depositing BIF and oxygenating the atmosphere, which is why we are here [5, 7]. The restart after 2.22 Ga left cratons with the deep-keeled tectospheres of stiffened mantle, manifest in plate dynamics behaviour for at least the past 90 Ma [8].

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### Experimental study of nucleation and phase stability of calcium sulfate

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Calcium sulfate presents three common phases when precipitated from aqueous solution in nature or in the laboratory: gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), bassanite (CaSO<sub>4</sub>·0.5H<sub>2</sub>O) and anhydrite (CaSO<sub>4</sub>) [1]. The conversion of these phases into each other takes place in nature but also represents the basis of gypsum-based building materials. Therefore many studies have been performed on the phase stability of calcium sulfate in solution, as a function of temperature but, at present, the mechanisms by which precipitation, phase transition and phase stability occur in solution are not well defined [2].

We performed an experimental study in order to identify the factors that influence the nucleation, growth and phase stability of calcium sulfate at laboratory scale. The crystallization was carried out by chemical reaction by varying temperature (40°C-120°C), salinity (0.8, 2.8, 4.3 M NaCl) and duration of the experiments (2 min – 3 months). The reaction products were characterized by Powder X-Ray Diffraction, SEM and TEM.

Our results show a clear dependence on temperature and salinity of the precipitated phase of calcium sulfate; at low temperatures, gypsum is the most stable phase ( $<60$ °C). As temperature increases, direct precipitation of bassanite (80-110°C) and anhydrite (120°C) occurs. The temperature at which primary bassanite appears decreases with increasing salinity (110-80°C) while anhydrite shows a more complex dependence. Besides primary precipitation phase transition of calcium sulfate in contact with the mother solution occurs over time ( $>$ days). With time the temperature at which bassanite and anhydrite appear decreases. This behavior is generalized for the three salinities studied but at the highest salinity this phase transition occurs faster.

A plausible explanation for the mechanism of phase transition is the dissolution of the phase that precipitates first (less stable) and subsequent 'recrystallization' of the more stable phases with passing time. The kinetics of dissolution/precipitation of these compounds plays a decisive role in the transition rates of calcium sulfate phases and are mainly controlled by temperature and solution salinity.

[1] Christensen *et al.* (2008) *Chem. Mater.* **20**, 2124-2132  
[2] Freyer & Voigt (2003) *Monatshfte für Chemie* **134**, 693-719.