

Secular geochemical evolution linked to atmospheric oxidation

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Secular geochemical evolution of the Earth's crust has typically been obscured by the geochemical heterogeneity of the rock record along with imperfect sampling¹. In order to ameliorate this problem, we have taken a new approach: weighted bootstrap resampling Monte Carlo analysis of a ~70,000 sample igneous rock database. In addition to gradual trends in compatible and incompatible elements expected from secular cooling, the results reveal a period of dramatic geochemical change near the Archean/Proterozoic boundary. Temporal correlation of this event with stepwise atmospheric oxidation circa 2.4 Ga² may suggest a link between deep earth geochemical processes and the rise of atmospheric oxygen on Earth.

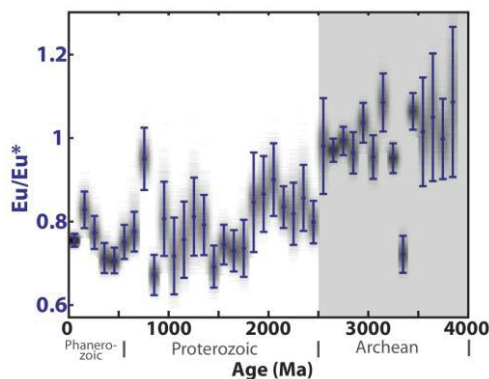


Figure 1: Monte Carlo analysis of mean europium anomaly in felsic (62-73% SiO₂) samples through time. Error bars: 2 σ standard error.

Notable changes across the boundary include decreases in deep melting/fractionation indicators such as La/Yb and Eu/Eu* of felsic rocks (Figure 1), as well as decreases in mantle melt fraction in basalts. In the context of observed increases in preserved crustal thickness across the Archean-Proterozoic boundary^{3,4}, these data suggest a model where high degree Archean mantle melting produced a thick, mafic lower crust, leading to deep crustal delamination; delamination and associated lower crustal anatexis in turn resulted in abundant tonalite-trondhjemite-granodiorite (TTG) magmatism and a thin preserved Archean crust.

Since higher pressure restitic assemblages may contain substantial Fe³⁺, we speculate that deep melting or deep fractionation in the Archean may have resulted in magmas with lower Fe³⁺/Fe²⁺, and consequently larger budgets of reduced volcanic volatiles. Cessation of abundant deep crustal melting at the end of the Archean may therefore have resulted in decreased reducing flux to the atmosphere, contributing to the atmospheric Great Oxidation event.

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The role of pre-nucleation clusters in the crystallization of CaCO₃

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Introduction

Recent studies have revealed that stable pre-nucleation clusters exist in both super- and undersaturated solutions of calcium carbonate prior to the formation of a solid phase [1]. Computer simulation data indicate that the thermodynamic stability of these species is based on strong hydration in combination with a distinct entropic contribution, resulting from the high degree of disorder inherent to their dynamic chain-like structure [2]. Nucleation of solid particles from this solute form appears to occur through aggregation of the clusters, rather than by the stochastic assembly of ions into metastable nuclei envisaged in classical theories [3,4]. However, direct insight into these processes has not yet been gained.

The phase initially precipitated from these pre-nucleation clusters was found to be amorphous calcium carbonate (ACC) exhibiting distinct short-range structural features, which resemble the long-range order in calcite or vaterite [5] and moreover seem to be already encoded in the clusters [1]. Transformation of ACC into more stable crystalline polymorphs usually takes place within minutes unless kinetic stabilization is provided, as for instance achieved by coating the nanoparticles with silica [6].

Results and Conclusions

In the present contribution, we outline the concept of non-classical nucleation via stable ion clusters and highlight experimental evidence supporting this scenario for the case of calcium carbonate as well as other important minerals. It is furthermore demonstrated that silica can be used as an additive slowing down or impeding the nucleation process due to colloidal shielding of the clusters [7]. In this manner, details of the transformation of ion clusters into ACC nanoparticles could be resolved experimentally. Results corroborate that nucleation of ACC relies on aggregation and coalescence of the clusters, yielding primary particles that exceed a certain critical size. In addition, our methodology facilitates preparation of solutions rich in pre-nucleation clusters, which – despite high supersaturation – do not nucleate even after periods of more than a year, as the classical ion-by-ion pathway is obviously not accessible under the given conditions. Colloidal stabilization with silica even allows for a direct isolation of these elusive species, which may be a key step for the analysis of their structure. Our findings are likely to be relevant for crystallization phenomena in various geological settings.

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