

$\delta^{15}\text{N}$ chemostratigraphy of Ediacaran-Cambrian sections of South China

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Marine productivity and biogeochemical processes may be inferred from the isotopic compositions of sedimentary rocks. Isotopic trends of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\delta^{13}\text{C}$ can also be useful for stratigraphic correlation. The use of $\delta^{15}\text{N}$ data for such purposes has been debated for a long time in the literature, resulting in its still ambiguous utility as a geochemical tracer and stratigraphic tool. Here, we compare nitrogen isotope trends for five sections in South China that straddle the Ediacaran-Cambrian boundary. Nitrogen isotope values for bulk samples range from +8‰ to -3‰, showing highly systematic variability during the period of interest and testifying to changes in the biogeochemical cycle of the ancient ocean. Negative values might reasonably be ascribed to the action of purple bacteria in the euphotic zone. Many sections show the same general trend, with positive values in upper Ediacaran strata and a strong negative shift in Cambrian strata (more pronounced in black-shales). If these isotopic trends are confirmed, at least two conclusions may be drawn. On the one hand, this evidence is a clear demonstration of nitrogen isotopic signal conservation, thus excluding diagenetic alteration or isotopic contamination during the time elapsed since marine sedimentation. On the other hand, the use of $\delta^{15}\text{N}$ profiles could then be considered a genuinely useful chemostratigraphic correlation tool, especially where biostratigraphy is of limited usefulness.

Alkaline earth metal adsorption to gibbsite as a function of temperature

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Surface potential of mean force (PMF) calculations between the alkaline earth metal cations and the gibbsite basal surface suggest that the alkaline earth metals do not form inner-sphere surface complexes at 298K because of the activation energy barriers associated with the removal of the hydration water around the cations as they near the surface. The activation energy barriers between outer- and inner-sphere complexes increase in height with decreasing cation radii. Consistent with the PMF calculations, molecular dynamics simulations at higher temperatures resulted in the formation of inner-sphere complexes. The temperature at which inner-sphere complexation occurs in the simulations decreases with increasing ionic radii. Barium forms both inner- and outer-sphere surface complexes at 298K; however, Mg only forms inner-sphere complexes at temperatures over 500K.

To investigate these results further, macroscopic experiments were performed to examine alkaline earth metal cation adsorption in different electrolyte solutions as a function of temperature and ionic strength. The trends in alkaline earth metal ion adsorption follows that predicted for a low dielectric constant surface such as gibbsite ($\text{Mg} > \text{Sr} > \text{Ba}$) over the range of temperature studied. The experimental findings are consistent with the modeling results; the ionic strength dependence of alkaline earth adsorption decreases with increasing temperature suggesting an increase in inner-sphere complexation, and the temperature at which the ionic strength dependence on adsorption is no longer evident decreases with increasing ionic radius. Indeed, no ionic strength dependency was observed for Ba adsorption onto gibbsite at ambient temperature.

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