## Freeze-fry cycles in the Paleoproterozoic Turee Creek Group, Western Australia

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Previous research has suggested a Paleoproterozoic Snowball Earth consisted of up to three glaciations from 2.42–2.22 Ga, coincident with the timing of the inferred rise in atmospheric oxygen [1, 2]. Supporting geological and isotopic data from North America, Fennoscandia, and South Africa are supported by the occurrence of glacial rocks in the Turee Creek Group (TCG), Australia, and their geochemical characteristics [3, 4].

New  $\delta^{13}$ C and  $\delta^{18}$ O isotope data on bedded and stromatolitic dolomites, combined with previously available results [5] - recast in the light of corrected stratigraphic assignation - suggest that three freeze-fry cycles are recorded in the TCG. The first cycle is preserved in the lowest Kungarra Formation, reflected by a decrease and subsequent increase in  $\delta^{13}$ C upsection, from  $0-2\% \rightarrow -6\% \rightarrow 0\%$ , associated with a decrease in  $\delta^{18}$ O from  $0 \rightarrow -4\%$ . Part of a second cycle is recorded in rocks of the glaciomarine Meteorite Bore Member and immediately overlying rocks of the upper Kungarra Formation ( $\delta^{13}$ C from -2.5 to  $-6\% \rightarrow -1\%$ , and  $\delta^{18}$ O from 0 to  $-3 \rightarrow -12\%$ ), whereas a third cycle is recorded in rocks of the overlying Kazput Formation ( $\delta^{13}$ C from  $-3 \rightarrow 1\%$ , and  $\delta^{18}$ O from  $0 \rightarrow -16 \rightarrow 5\%$ ).

The low-grade TCG carbonates are considered to have escaped significant post-depositional resetting.  $\delta^{18}$ O variability and trends are interpreted to reflect changes in the temperature of basinal diagenetic fluids across cooling and warming periods, while mantle-like  $\delta^{13}$ C values support periodic global collapse of the biosphere.

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## Ion diffusion in argillaceous materials

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Molecular diffusion is the dominant transport process of radionuclides which needs to be considered when evaluating the safety of radioactive waste repositories in argillaceous host rocks. The diffusive behaviour of radionuclides depends both on the properties of the porous medium and on the diffusing species.

Clay minerals (notably montmorillonite and illite) have a permanent negative surface charge which attracts cations and repulses anions leading to the formation of a diffuse double layer (DDL). The net positive charge of the DDL compensates the negative charge of the clay surface [1]. In the case of the diffusion of neutral species, no interaction between the electrostatic field and the species occurs and diffusion can be described by Fick's law [2]. The concentration gradient in the pore water is the driving force for diffusion of neutral species. In this case, only geometrical factors such as constrictivity and tortuosity are important. In the case of charged species, the situation is different. Because cations are attracted by the negative surface charge, the concentration gradients in the DDL and in the interlayers of the clay grains are larger than in the free pore water and consequently the diffusive flux is also larger. The electrostatic field thus enhances cation diffusion. Unlike cations, anions are repulsed from the surface leading to anion exclusion from the interlayers and the DDL. Anion exclusion leads to a lower accessible porosity for the anions, resulting in lower diffusive fluxes. All factors directly influencing the DDL thus also affect the diffusive behaviour of cations and anions.

This study gives an overview of the state-of-the art of knowledge on diffusion processes in dense argillaceous materials. Focus will be on tracer diffusion of ion exchanging cations, anions and neutral species in a constant electrolyte background and in different argillaceous materials [3]. The diffusive behaviour of cations which.. sorb via surface complexation is expected to be different and a brief outlook on current activities will be discussed.

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