Ice nucleation in supercooled nano water droplets

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Abstract

The prediction of contribution to global radiative budget and future climate change by cirrus clouds requires computation of the formation rates, growth rates, shape evolution and size distribution of small ice particles. The formation of ice particles under various thermodynamic, dynamic, and chemical environments still remains very poorly understood. Here we report a large-scale numerical study of spontaneous ice nucleation from supercooled nano water droplets, with the size of droplets ranging from 6 nm to 12 nm at 230K. In this study, we combined forward flux sampling method [1] with molecular dynamics simulations, and employed a recently developed coarse-grained water model [2]. The large number of nucleation trajectories (500) sampled in this study allowed obtaining nucleation rates directly from molecular simulations and identifying ensembles of various crystal structures and morphology of the fully crystallized ice clusters. The calculated nucleation rates show strong size dependence below 10 nm: it increases from $1.97\pm0.92\times10^{8}$ m^{-3}s^{-1} to $1.08\pm0.47\times10^{14}$ m^{-3}s^{-1} as the size of water droplets increase from 6 nm to 9.5 nm. When the size of water droplets is beyond 10 nm, the calculated ice nucleation rates become indistinguishable from the calculated ice homogenous nucleation rates in bulk supercooled water at the same temperature [3]. The preferential location of the formation of ice embryos also shows variation with the size of water droplets, with a strong preference for the location identified within the subsurface (1~1.5 nm below the immediate surface) for larger water droplets (>7.6 nm). The fully crystallized ice clusters are found to be mixtures of both hexagonal ice (I$_h$) and cubic ice (I$_c$), and display a variety of structures and shapes. In consistent with previous study in bulk water [3], we also identified the five-fold twin boundary (FFTB) structure in ice cluster. A single FFTB per ice cluster yields a nearly decahedral shape of crystallized ice cluster. In addition, we have also identified a more complex and highly symmetrical defect structure that is composed of 12 FFTB merging and forming a 512 water cage at the center of the defect. Such defect structure results in a nearly icosahedral shape, which also displays nearly 5 fold rotational symmetry.

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Fe isotope and U-Th-Pb evidence for a reduced 3.4 Ga Archean ocean

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Evolution of Earth's early atmosphere is critical to understanding the geologic history of the Earth, yet the levels of oxygen in Earth's atmosphere in the Archean continue to be debated. The hematite-bearing 3.4 Ga Marble Bar Chert (MBC) at Marble Bar area of the Pilbara Craton, NW Australia, has been used to argue that Earth's early atmosphere contained significant amounts of oxygen [1]. We measured Fe and U-Th-Pb isotope composition of the MBC samples. Our results indicate that the Marble Bar Chert was deposited from a Fe-rich, but U-poor ocean. The δ^{56}Fe values of hematite in MBC range between 1.71‰ and 2.63‰, which are the most positive δ^{56}Fe dataset that has ever been reported from natural rocks (Figure 1). Given that hydrothermal sources of aqueous Fe^{2+} should have had a δ^{56}Fe value of around 0‰ [2], and that Fe isotope fractionation between hydrous ferric oxides and aqueous Fe^{2+} is ~3-4‰ [3][4], the high δ^{56}Fe values of hematite in MBC requires partial oxidation of aqueous Fe^{2+}. This suggests that the oxidant was extremely limited and the main body of ocean water was reduced and rich in Fe^{2+}. In addition, U concentrations of the MBC samples are over one order of magnitude lower than those of Phanerozoic cherts, indicating lower U content of Archean ocean water than modern ocean water. Moreover, U-Th-Pb isotope analysis shows that the MBC samples has actually undergone U addition during the Phanerozoic, which further attests to low U contents during deposition at 3.4 Ga. This indicates low O$_2$ levels in Archean atmosphere.

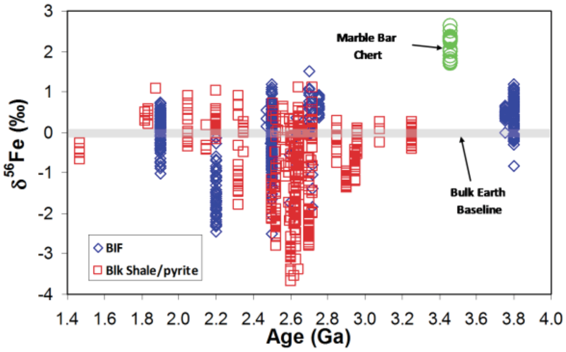

Figure 1. Compilation of δ^{56}Fe values for minerals and rocks from the Archean and Proterozoic sedimentary rocks

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