Controlled synthesis, manipulation of surface hydrophobicity, and self-assembly of hematite nanocrystals

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The preparation of uniform iron oxide monolayer thin films is of great interest not only in advanced materials synthesis but also in studies of microbial cell and iron oxide mineral interface interactions by techniques such as neutron reflectometry, which requires the use of uniform thin films of the mineral on a substrate. Here we report three techniques for fabricating such uniform hematite (α-Fe_2O_3) nanocrystal thin films. The nanocrystals with controlled sizes and morphologies were first synthesized by thermal hydrolysis of Fe^{3+} ions in acidic aqueous solution. Three methods were tested to enhance the surface hydrophobicity of the synthesized nanoparticles, including thermal dissociation of surface hydroxyl groups, stepwise solvent exchange, and surfactant-assisted phase transfer. FTIR and Raman spectroscopic analyses were used to elucidate the mechanisms of surface hydrophobicity changes on hematite nanoparticles. Results indicate that techniques of thermal treatment and stepwise solvent exchange caused the dissociation of surface -Fe–OH groups into –Fe-O-Fe structures, whereas surfactant-assisted phase transfer gave rise to surface hydrophobicity due to sorbed hydrocarbon chains. These surface modified hematite nanoparticles were found to readily self-assemble into monolayers at the water-air interface, which provided an effective means to obtain hematite nanoparticle thin films with controlled packing density and layer thicknesses in a Langmuir-Blodgett trough. Langmuir isotherm, SEM, TEM, AFM, UV-visible spectroscopy, and neutron reflectometry were used to characterize these thin films for their stability and uniformity before they were used for studies of the interactions between hematite and macromolecules.

Rapid Amazonian moisture changes during the last glacial period

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Terrestrial paleoclimate records on abrupt climate events from the tropics are still rare, in particular, from Amazonia, which contains the largest tropical rainforest in the world. We have obtained a high-resolution oxygen isotopic record of cave calcite from Caverna Paraíso, Amazonia, Brazil. The chronology was determined by 86 U-Th ages from 7 stalagmites. Tests for equilibrium conditions show that their oxygen isotopic variations are primarily caused by climate change. We thus interpret the Paraíso record, spanning the last 50 thousand years, in terms of meteoric precipitation changes at this equatorial location. The oxygen isotopic profile shows significant abrupt millennial-scale variations during Marine Isotope Stage (MIS) 3, with amplitudes as large as 2 per mil. Using independent age scales, we compare the record to contemporaneous records from caves in eastern China and high-latitude ice cores. During MIS 3, the PAR calcite oxygen isotopic profile anti-correlates remarkably with the Hulu Cave record [1], indicating that precipitation histories at the two sites are asynchronous, similar to our previous observations from northeastern and southern Brazil speleothems [2, 3]. During MIS 3, Paraíso precipitation also broadly anti-correlates with Greenland D-O events [4] and positively correlates with Antarctic warm events [5]. Our record adds further support to the idea that abrupt climate events have a worldwide distribution during MIS 3. The observed correlations between the records support an oceanic meridional overturning circulation mechanism for driving the abrupt millennial-scale events of the last glacial period, coupled with strong air-sea feedbacks from the tropics. In combination with Andean ice core and lake records, knowledge of the meteoric precipitation oxygen isotope and moisture history of the central Amazon may shed new light on the role of the tropics in abrupt climate change.

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