

Fate of magnetite nanoparticles in leachate-impacted groundwater

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Nano-scale iron oxides, particularly magnetite, have been suggested as potential reductants for a number of environmental contaminants such as heavy metals, radionuclides, and volatile organics. Experiments have generally shown that magnetite is a viable reductant of a number of contaminants in a laboratory setting [1], though effectiveness is influenced by iron-oxide particle size and the presence of additional cationic and anionic species [2]. However, key questions remain about the fate of magnetite nanoparticles in groundwaters with complex chemistry.

Magnetite nanoparticles were synthesized in the laboratory by partial oxidation of ferrous iron sulfate in a basic medium. A combination of TEM and XRD were used to characterize the reaction products. A custom-made nanoparticle holder was designed to be compatible with the existing 1" OD groundwater wells at the USGS Norman Landfill Site. By means of this nanoparticle holder, magnetite nanoparticles were deposited on TEM grids and then inserted into a groundwater monitoring well at the USGS Norman Landfill Site. The particles were reacted for 10 days, retrieved from the site, and then stored in an anaerobic chamber prior to analysis. The reaction products were analyzed via TEM and compared to the initial characterization. Total volumes were calculated for both the initial synthesis products and the reacted magnetite particles. These volumes were compared to determine the volume of material lost and to calculate an approximate dissolution rate.

TEM characterization of the synthesis products indicated euhedral magnetite with a size range of 250 to 11 nm, along with euhedral goethite particles. Mineralogies identified in synthesis products via TEM were confirmed by XRD analysis. TEM analysis of the reacted particles revealed that the particles were subhedral, indicating dissolution of the magnetite particles, primarily at the corners and edges. Bright field images also indicated a textured surface on the reacted magnetite surfaces, which is also indicative of dissolution of the iron oxide particles.

Experimental results indicate that the magnetite particles lost 10 to 30 percent of their total volume over the 10 day time period. Interestingly, no clear trend between particle size and total volume lost was apparent in the data. An approximate dissolution rate of $2.9 (0.9) \times 10^{-9}$ nmol/m²*day was obtained using the TEM images.

[1] Roh (2003) *Clay and Clay Minerals* **51**, 83-95. [2] Roonasi (2010) *Surface and Interface Analysis* **42**, 1118-1121.

Implications of noble gases in Stardust samples for the source of Earth's water

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Comets as the Source of Earth's Water

Comets have long been considered a possible source of Earth's water. The compositions of comets would provide an obvious constraint, but the only compositional parameter that has been widely applied is the D/H ratio. Although most comets in which D/H have been measured have ratios a factor of two higher than Earth's oceans, a recent measurement of Comet Hartley 2 gave an Earth-like ratio [1], reviving interest in the idea of a cometary source.

Another compositional parameter that could prove powerful is the noble gas abundance in comets. Based on a spectroscopic measurement of the Ar/O in the coma of Comet Hale-Bopp [2], Swindle and Kring [3] argued that if comets had brought in the Earth's water, orders of magnitude more noble gas would be in Earth's atmosphere than there presently is. However, that measurement has not been replicated, and other measurements suggest much lower noble gas abundances in comets, giving only upper limits [4].

More recently, noble gases have been measured in samples returned from the coma of Comet Wild 2 by the Stardust mission, so it is appropriate to revisit the argument, considering only the noble gases in the dust.

Extrapolating Stardust measurements to Xe in comets

Marty et al. [5] measured He and Ne in Stardust samples, and concluded that the dust contained ~ 0.1 cm³STP of Q-type ²⁰Ne per gram of dust ($\sim 9 \times 10^{-5}$ g_{Ne}/g). If we conservatively assume that comets are 10% dust, that would mean that to bring in an amount of H₂O equivalent to the Earth's oceans, 3×10^{-4} of Earth's mass [6] would also bring in more than 1000 times as much Ne as is currently present in the atmosphere ($\sim 10^{-12}$ g_{Ne}/g). However, Ne is light enough that it is possible that it would not be retained during cometary impacts (although its molecular weight is higher than that of H₂O). If we consider Xe instead, the ²⁰Ne/¹³²Xe (molar) ratio in Q-type gas is 3.2, which would mean that an ocean's worth of cometary water would contain more than 10,000 times as much ¹³²Xe as the present atmosphere. It is difficult to envision ways to lose that amount of Xe, although the argument does depend on the identification of the Stardust Ne as Q-type. Furthermore, this argument only applies to the dust, and does not even consider the ice, which could have large amounts of noble gases as well.

Once again, noble gas abundances appear to be a problem for arguing for a cometary source for Earth's water, but more definitive measurements are clearly needed.

[1] Hartogh et al. (2011) *Nature* **478**, 218-220. [2] Stern et al. (2000) *Astrophys. J.* **544**, L169-L172. [3] Swindle and Kring (2001) *11th Goldschmidt Conf.*, Abstract #3785. [4] Weaver et al. (2002) *Astrophys. J.* **576**, L95-L98. [5] Marty et al. (2008) *Science* **319**, 75-78. [6] Abe et al. (2000) *In The Origin of the Earth and Moon*, 413-433.