Nanogeochemistry: Geochemical reactions in nanopores

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Nanopores are ubiquitous in porous geologic media and constitute an integral part of total porosity of rocks. Existing data indicate that the contribution of nanopores to the total surface area in geologic materials can be very high, probably over 90 percents. To clarify the effect of nanopore confinement, acid-base titration and metal adsorption experiments were performed on both nanoporous alumina and alumina particles under various chemical conditions. The experiments have demonstrated that the nano-scale confinement has a significant effect, most likely via the overlap of the electric double layer, on ion sorption onto nanopore surfaces. Under the same chemical conditions, the surface charge per mass on nanoporous alumina was as much as 45 times higher than that on alumina particles. The nanopore confinement leads to a shift of ion sorption edges and enhances ion sorption on nanopore surfaces for both cations and anions. As a result, trace elements in natural systems tend to be preferentially enriched in nanopores. This effect cannot be adequately modeled by existing surface complexation models. To understand the state of water in nanopores, the experiment of water adsorption under various relative-humidity conditions were performed in combination with H magic-angle spinning nuclear magnetic resonance (MAS NMR) and Fourier transform infrared (FTIR) spectroscopic analyses. The experimental results show that water molecules in nanopores form more rigid structures than those in bulk solutions. The observed nanopore confinement effects will shed a light on many important geochemical phenomena.

Relationship between Freundlich equation constants for zinc sorption on nanocrystalline calcite

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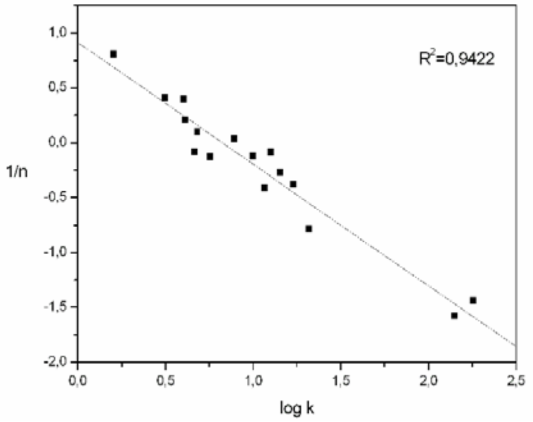
The solid state properties of nanocrystalline particles obtained by high-energy milling with a high surface area has led recently to their utilization as reactive minerals and heavy metal sorbents [1]. The nanoparticles have been shown to possess a much greater number of defect sites per unit surface area, which are believed to be responsible for the observed chemistry [2,3]. The aim of this work was to examine the sorption behaviour of zinc ions on calcite whose solid state properties were modified by high-energy milling. Freundlich equation has been applied for the description of sorption process. A good relationship has been found between the Freundlich equation constants logk and 1/n for zinc sorption on 16 samples of nanocrystalline calcite modified by high-energy milling (Fig.1).

Figure 1 Freundlich isotherm



The different solutes applied for the adsorption on one sample of carbon described in paper [4] and the different calcites (as for origin and solid state properties) applied for the adsorption of one solute (zinc ions) in our work has led to the same character of relationship between constants of Freundlich equation which demostrates its universal character.

References

[1] Baláž, P. (2000) Extractive Metallurgy of Activated Minerals, Elsevier, Amsterdam
[2] Banfield, J.F., Navrotsky, A., Eds. (2001) Nanoparticles and the Environment, Reviews in Mineralogy and Geochemistry, Vol. 44, Washington
[3] Klabunde, K. J.: (2001) Nanoscale Materials in Chemistry, Wiley-Interscience, New York
[4] Abe, I., Hayashi, k., Hirashima, T.: Am. Chem. Soc. 1982, 104, 6452-6453