

Nanogeochemistry: Geochemical reactions and mass transfers in nanopores

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ABSTRACT

Nanopores are ubiquitous in porous geologic media and may account for >90% of total mineral surface areas. Surface chemistry, ion sorption, and the related geochemical reactions within nanopores can be significantly modified by a nanometer-scale space confinement. As the pore size is reduced to a few nanometers, the difference between surface acidity constants ($\Delta pK = pK_2 - pK_1$) decreases, giving rise to a higher surface charge density on a nanopore surface than that on an unconfined mineral-water interface. The change in surface acidity constants results in a shift of ion sorption edges and enhances ion sorption on nanopore surfaces. Also, the water activity in a nanopore is greatly reduced, thus increasing the tendency for inner sphere complexation and mineral precipitation. All these effects combine to preferentially enrich trace elements in nanopores, as observed in both field and laboratory studies. The work reported here sheds new light on such fundamental geochemical issues as the irreversibility of ion sorption and desorption, the bioavailability of subsurface contaminants, and the enrichment of trace metals in ore deposits, as well as the kinetics of mineral dissolution and/or precipitation.

Keywords: nanostructured material, nanopore confinement, ion sorption, bioavailability, interface chemistry.

INTRODUCTION

The emergence of nanotechnology has not only made it possible to purposefully manipulate material structures at nanometer scales but has also greatly advanced our understanding of how nanometer-scale structures give rise to novel physical and chemical properties of materials (e.g., Hummer et al., 2001; Klambunde, 2001). Nanometer-scale bimetallic particles have been shown to have an enhanced capability for the reduction of chlorinated hydrocarbons in the environment (Wang and Zhang, 1997). Mesoporous materials modified with specific surface functional groups are found to have high sorption capacities for removing mercury (Feng et al., 1997), chlorinated organic compounds (Zhao et al., 2000), and copper, lead, and uranyl ions (Xu et al., 1999; Shin et al., 1999; Jung et al., 2001) from aqueous solutions. The study of nanometer-scale mineral-water interface phenomena is a necessary step to bridge the existing gap between the molecular level understanding of a geochemical process and the macro-scale laboratory and field observations (Hochella, 2002). Here we report that the space confinement within nanopores—pores of nanometer scale—can significantly modify geochemical reactions in porous geologic media and can lead to a preferential enrichment of trace ele-

ments in nanopores. This effect has a wide range of implications for many fundamental geochemical issues.

NANOPORES IN GEOLOGIC MEDIA

Nanopores are ubiquitous in porous geologic media and constitute an integral part of total porosity of rocks. A listing of typical examples, illustrated in Figure 1, follows.

Diatomaceous Materials

Transmission electron microscopic (TEM) observations reveal that diatomaceous materials display both micrometer-scale and nanometer-scale pore structures. The nanopores are regularly distributed, with a pore size of ~ 3 nm (Fig. 1A). The nanopore structure may have been formed by organic molecules (probably a specific protein) in template fashion (Ollver et al., 1995; Lobel et al., 1996; L. Wang et al., 2002), similar to a process used by material scientists to synthesize mesoporous materials (Kresge et al., 1992).

Mesoporous Iron Oxyhydroxides

Nanopores are commonly associated with Fe-oxyhydroxides in soils (Fig. 1B).

Grain Boundaries

Figure 1C shows nanometer-scale channels at a grain boundary. It has been postulated that these nanometer-scale channels provide necessary passages for mass transport during

mineral reactions, such as polysomatic reactions, and could possibly limit overall geochemical processes (Veblen, 1991). A quantitative evaluation of mass transport in these channels requires a mechanistic understanding of fluid movement and chemical diffusion within nanopores.

Nanometer-Scale Inclusions

Figure 1D shows the presence of nanometer-scale copper inclusions in partially weathered illite (Ahn et al., 1997), pointing to the control of nanostructures on geochemical reactions. Similarly, our TEM studies on samples from Changken cataclastic gold ore deposit in southern China indicate that gold is mainly present as nanoparticles with microfractures of quartz crystals or along quartz-illite grain boundaries, indicating that the nanopore confinement may have enhanced gold enrichment.

Surface-Area Effects

Data indicate that the contribution of nanopores to the total surface area in geologic materials can be very significant. In B-horizon soils, the pores with diameters smaller than 100 nm account for 10–40% of the total porosity (Görres et al., 2000). The porosity of a Georgia kaolinite was dominated by pores smaller than 10 nm (Tardy and Nahon, 1985). Because the specific surface area for a given pore volume is inversely proportional to the pore diameter, the contribution of nanopores to the total surface area in those materials is very high, probably >90%. This estimate is consistent with our TEM observations (Fig. 1) and other data (Tachi et al., 1998; Trivedi and Axe, 2001).

EXPERIMENTS

To isolate the effect of nanopore confinement, we chose to use synthetic mesoporous materials, which can be synthesized using a process involving a self-assembled supramolecular template (Kresge et al., 1992). The material we used was the synthetic mesoporous alumina purchased from the Aldrich Chemical Company, Inc. This material has an irregular pore structure with a pore size of ~ 2 nm \times 2 nm \times 10 nm and a surface area of ~ 284 m²/g. For a comparison with a nonmesoporous material, 80–200 mesh activated alumina par-

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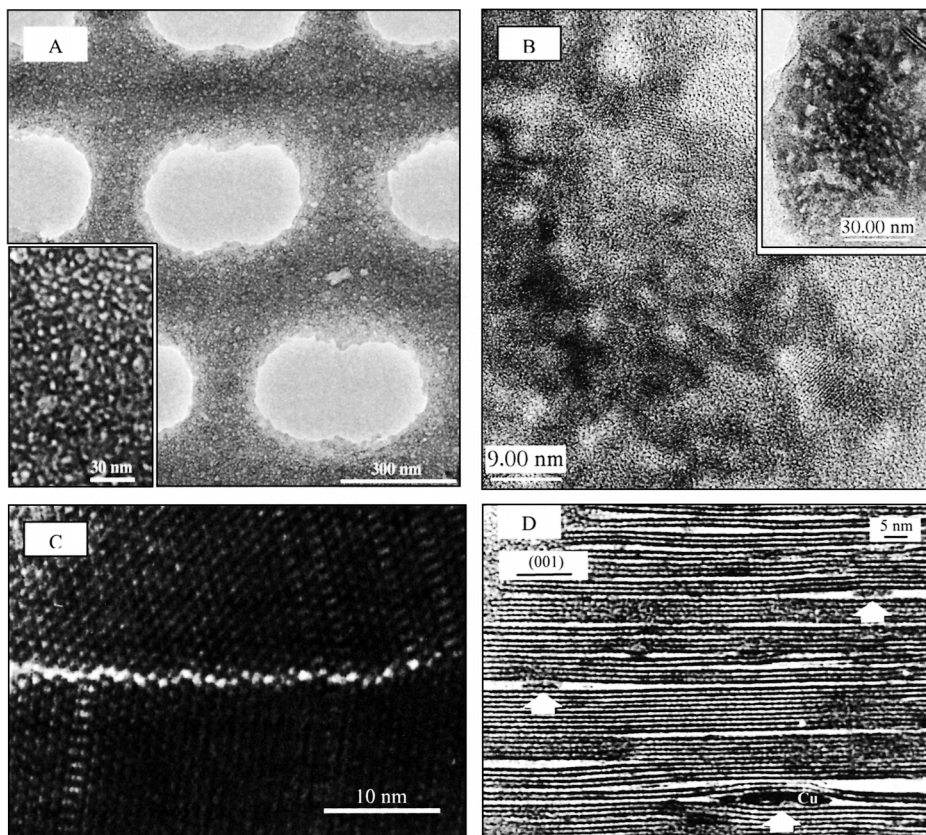


Figure 1. Transmission electron microscope (TEM) images of mesoporous structures in geologic materials. **A:** Diatomaceous material displaying both micrometer-scale and nanometer-scale pore structures (pore size of ~ 3 nm) (see insert). **B:** Mesoporous Fe-oxyhydroxide from paleosol with inserted low-magnification TEM image showing nanometer-scale pores. **C:** Nanometer-scale channels (large white dots on image) along grain boundary between two amphibole crystals. **D:** Partially weathered illite containing nanometer-scale elemental copper inclusions (modified from Ahn et al., 1997), indicating preferential enrichment of heavy metal in nanometer-scale pores.

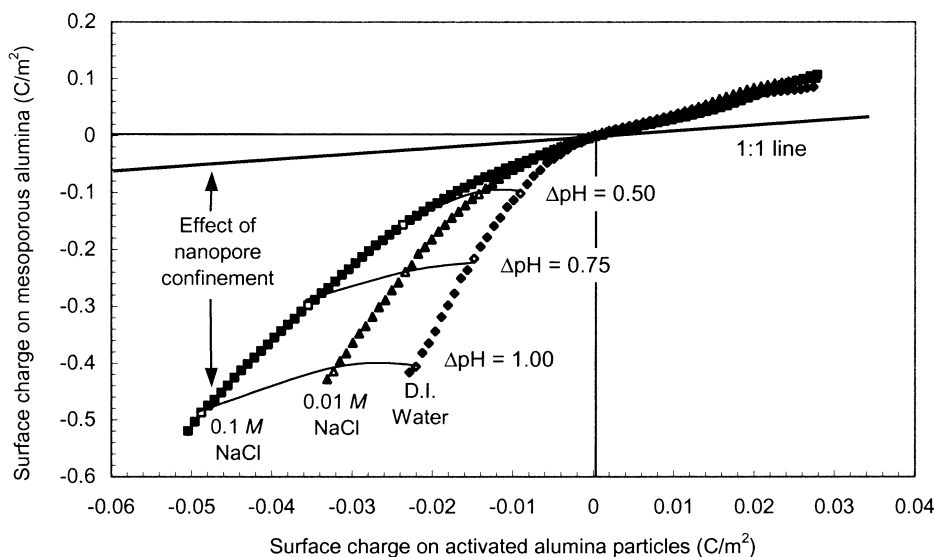


Figure 2. Surface charge on mesoporous alumina vs. surface charge on alumina particles for corresponding ($\text{pH} - \text{PZC}$ [points of zero charge]) values and ionic strengths. If surface-charge difference between two materials were controlled only by surface-area difference, all data points would fall on 1:1 straight line. Deviation from straight line is due to effect of nanopore confinement. D.I. is deionized.

ticles from Fisher Chemicals were also used. The activated alumina particles have a surface area of $118 \text{ m}^2/\text{g}$. The large surface area in this material is due to the presence of microfractures on particle surfaces. The surface areas of both materials were measured with a N_2 BET method using a Micromeritics Gemini 2360 surface analyzer. Our TEM observation indicates that the outer rims of the particles consist of an amorphous Al_2O_3 phase and very closely resemble the mesoporous alumina in chemical composition and crystallinity. Acid-base titration and Zn sorption experiments were conducted on both materials with procedures developed by Y. Wang et al. (2002).

RESULTS

From the pH titration data, the points of zero charge (PZC), corresponding to the cross points of titration curves for different ionic strengths (Stumm, 1992), are determined to be 9.1 for mesoporous alumina and 8.7 for activated alumina particles; both are close to each other and within the range reported for alumina oxides (Stumm, 1992), thus indicating that the nanopore confinement has little effect on the PZC of pore surfaces. We also calculated surface charges as a function of ΔpH ($= \text{pH} - \text{PZC}$) from pH titration data. In Figure 2, the surface charge per unit of surface area on the mesoporous alumina is plotted against that on the activated alumina particles for given ΔpH values. If the surface-charge difference between the two materials were controlled only by the surface area difference, all the experimental data points in the plot would fall on a 1:1 straight line. Apparently this is not the case; the surface charge density on mesoporous alumina is much higher than that on alumina particles. We thus postulate that this high surface charge density is likely caused by the nanopore confinement. Figure 2 also indicates that, for a given ΔpH , the surface charge density on a nanopore surface is less sensitive to ionic strength changes than that on an unconfined surface.

The attainment of a high surface charge density by a mesoporous material is attributed to the modification of surface acidity constants by the nanopore confinement. If five sorption sites per square nanometer of alumina surface (Stumm, 1992) are assumed, the acidity constants for both materials, which characterize the ability for surface protonation and deprotonation, are calculated to be: $\text{pK}_1 = 9.0$, $\text{pK}_2 = 10.3$ for mesoporous alumina, and $\text{pK}_1 = 7.7$, $\text{pK}_2 = 11.0$ for activated alumina particles (Y. Wang et al., 2002). (A slight difference between the PZC values determined from the crossing point of titration curves and those calculated from the relationship $\text{PZC} = [\text{pK}_1 + \text{pK}_2]/2$ may be due to the uncertainty as-

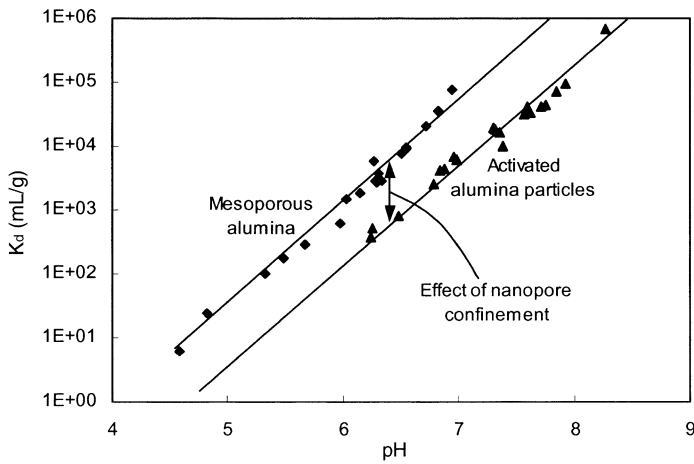


Figure 3. Sorption coefficients (K_d) of Zn on both mesoporous alumina and activated alumina particles, measured as function of pH.

sociated with a linear extrapolation of acidity constants from a highly charged surface to a neutral environment.) Thus, owing to the nanopore confinement, the separation between the two acidity constants, ΔpK ($= pK_2 - pK_1$), becomes significantly narrowed for the mesoporous alumina ($\Delta pK = 1.3$) as compared to that for the alumina particles ($\Delta pK = 3.3$). As a result, within nanopores, neutral-surface species become depleted, and the pore surface tends to be either positively or negatively charged, giving rise to a high surface charge density on mesoporous materials. The resulting change in surface acidity constants is expected to shift ion adsorption edges and consequently enhance both cation and anion sorption on nanopore surfaces.

We measured the sorption coefficients (K_d) of Zn on both mesoporous alumina and activated alumina particles as a function of pH (Fig. 3). In these experiments, we added 0.1 g of mesoporous alumina or 0.25 g of activated alumina particles to 20 mL deionized water in each sample, resulting in the same ratio of solid surface area to liquid volume in both systems. The equilibrated pH of each sample was adjusted by adding a concentrated HCl or NaOH solution. It is interesting to note that, at a given pH value, the sorption coefficient (K_d) for mesoporous alumina was ~ 10 -fold higher than that for activated alumina particles (Fig. 3). To our knowledge, this is the first set of data that convincingly demonstrates the effect of nanopore confinement on cation sorption on nanopore surfaces. Two factors may contribute the observed high sorption capability of nanopore surfaces. First, the confinement-induced change in ΔpK shifts cation sorption edges to a lower pH range and therefore enhances cation sorption. The increase in K_d for Zn seems comparable in magnitude with the shift in surface acidity constants. Second, as demonstrated here, the low

water activity in nanopores reduces ion hydration and thus increases the possibility for inner-sphere complexation. As a result of the pore space confinement, trace elements in natural environments tend to be enriched in nanopores.

This enrichment is further enhanced by water activity (a_w) changes in nanopores. The nanopore confinement modifies water properties (Denoyel and Pellenq, 2002). The behavior of confined water is similar to that of supercooled water at lower (~ 30 K) temperatures (Teixeira et al., 1997), implying a low water activity in nanopores. According to Kelvin's equation (e.g., Hiemenz, 1986), $\ln(a_w)$ in a pore of radius r is roughly proportional to $-r^{-1}$. Therefore, the water activity in nanopores can be much lower than that of bulk water (Tardy and Nahon, 1985). The reduction in water activity has two fundamental impacts on ion sorption and mineral precipitation. First, it reduces the hydration of aqueous species and therefore increases the possibility for inner-sphere complexation on nanopore surfaces. Second, it forces solutes to precipitate out from solutions and therefore results in preferential precipitation of minerals in nanopores (e.g., $H_4SiO_4[aq] \rightarrow SiO_2[s] + H_2O$). A similar mechanism has been proposed for nonelectrical exclusion of ions in thin water films (Zilberbrand, 1997).

DISCUSSION

The work reported here sheds new light on our understanding of the irreversibility of ion sorption and desorption and the bioavailability of contaminants in natural environments. Typically, metal ion desorption from geologic materials occurs in two phases. One fraction desorbs rapidly, whereas the rest desorbs only slowly, and the proportion of slowly desorbing metal ions increases with sorption time (e.g., McLaren et al., 1998; Glover et al., 2002). Figure 4 shows the desorption behavior

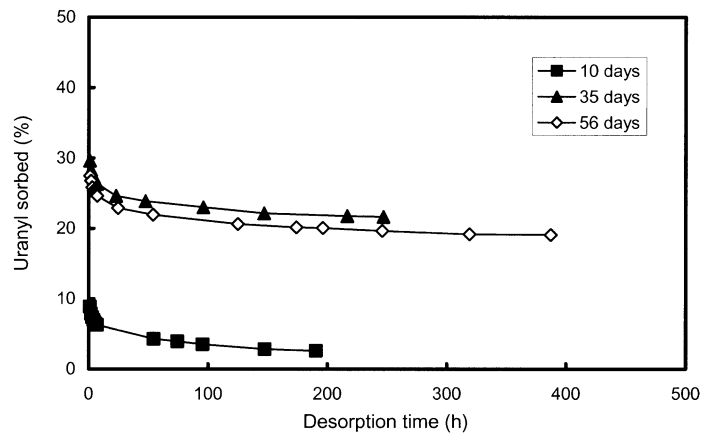


Figure 4. Uranyl desorption from synthetic porous goethite materials for uranyl-goethite contact times of 10, 35, and 56 days. Slow-release phase may result from preferential metal adsorption and precipitation within nanometer-scale pores, whereas initial fast-release phase is related to desorption from outer surfaces of material.

of uranyl from a synthetic goethite material, which contains a large number of intragrain and intergrain nanopores, as revealed by our TEM observation. Note that intraparticle diffusion could be a rate-limiting process in the sorption of metal ions to amorphous iron oxyhydroxides (Axe and Trivedi, 2002). We postulate that the slow-release phase may result from preferential metal sorption and precipitation in nanopores, whereas the initial-release phase is related to the metal desorption from outer surfaces of the material. The dependence of desorption kinetics on sorption times may arise from the slow migration of uranyl from large pores (and outer surfaces) to nanopores owing to a chemical potential gradient created by the pore-space confinement. Such a mechanism can greatly reduce the bioavailability of contaminants in natural environments, because nanopores are generally too small to be accessible by microorganisms.

Our work suggests that the ion sorption measurements on disaggregated geologic materials may not represent chemical conditions in actual systems, because they may not be able to capture the effect of nanopore confinement. This possibility is consistent with the measurement of apparent distribution coefficients of radionuclides in saturated bentonite as a function of compaction density (Conca and Wright, 1992). It was found that physical compaction could change retardation behaviors of radionuclides and even enhance retardation capability. Such behaviors can be readily explained by the nanopore confinement effect we observed. Because of this effect, the surface sites on the same mineral surface can exhibit different sorption affinities in porous geologic media, and the sorbed ions in nanopores are more strongly bound than those outside the nanopores.

Our pH titration results suggest that the existing surface-complexation models (e.g., Da-

vis and Kent, 1990; Dzombak and Morel, 1990), which have been developed mostly for unconfined surfaces, might not be adequate for modeling ion sorption on nanopore surfaces without taking into account the effect of pore-space confinement. Zhmud et al. (1997) attempted to develop a charge-regulation model for the surface of porous matrices, in which a pore is represented by a cylindrical cavity and the overlap of the electrical double layer is taken into account by diminishing the radius of the cylinder. The model predicts a decrease in surface charge density with decreasing pore size, which seems inconsistent with our experimental results.

The modification of surface chemistry and pore-water activity by the nanopore confinement effect also has an impact on mineral dissolution and precipitation kinetics. It was observed that diatomaceous materials display unique nonlinear dissolution kinetics (Van Cappellen and Qiu, 1997): in the vicinity of the equilibrium point, the dissolution rates are nearly linear. With increasing distance from equilibrium, there is a pronounced transition in the functional dependence on the relative degree of undersaturation. Beyond the transition, the dissolution rate rises much faster with increasing degree of solution undersaturation. On our TEM observations (Fig. 1A), this nonlinear behavior is probably due to the presence of nanopore structures in biogenic materials. The water inside the nanopores has a low activity and so is less undersaturated than the unconfined fluid; thus nanopore surfaces have less of a tendency to dissolve than unconfined outer surfaces. A similar process can be used to explain the large discrepancy between laboratory measurements and field observations in weathering rates (e.g., Brantley, 1992), considering that nanopores in soils can account for >90% of their total surface area. The work summarized herein also sheds new light on dolomite formation. Dolomite formation is inhibited by strong Mg^{2+} hydration (de Leeuw and Parker, 2001). The decrease in water activity and the resulting reduction in Mg^{2+} hydration in nanopores can possibly enhance dolomite formation in natural systems.

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