Influence of the bound water on molecular migration of CO_2 and noble gases in clay media

SOPHIE GIANNESINI[1,2]*, ALAIN PRINZHOFER[1,2], MANUEL MOREIRA[1] AND CAROLINE MAGNIER[2]

[1]Geochimie-Cosmochimie, Institut de Physique du Globe de Paris, 4 pl. Jussieu, 75005 Paris, France (*correspondence: giannesini@ipgp.jussieu.fr)
[2]IFP, 1 av. de Bois Préau, 92500 Rueil Malmaison, France

In claystones, the so-called "bound water" could reach 25 to 50% of the total interstitial water. It concerns the water adsorbed on the charged clay surfaces. As some properties of the water are modified at this interface, like viscosity [1] or density, the migration parameters should also be modified. For solute migration modelling in aquitards, typically only diffusion coefficients in free water are considered, biasing results and interpretations about safety of hazardous waste geological storage or valuation of intra-basinal migration.

We used the combination of diffusion experiments and modelling to evaluate the efficient diffusion coefficients of CO_2 and noble gases in different sedimentary porous rocks. For this purpose, we conducted gas migration experiments with a stainless steel cell composed by two gas tanks separated by a water saturated porous clay medium. The comparison between the experimental data and the solubilization/diffusion modelling allows constraint of the influence of the clay properties and then the migration parameters for each gas. At the water/clay interface, the efficient diffusion coefficients decrease with increasing masses for noble gases, due to adsorption processes.

The gas patterns obtained by solubility-diffusion processes through water saturated clay media differ from those that could be assessed with only solubility and diffusion processes in free water from the literature. The influence of clay mineralogy on migration through porous clay material is investigated, taking into account that it induces different bound water contents and the possible presence of interlayer water, with specific properties. Since isotopic fractionation of the light hydrocarbons have been shown by diffusion through shales [2, 3], the possible isotopic fractionations of noble gases during molecular migration through clay media are also investigated.

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Anthropogenic metal sulfates in atmospheric particulate matter

R. GIERÉ[1]*, A. OEHLER[1] AND K. SMITH[2]

[1]Universität Freiburg, Germany (*correspondence: giere@uni-freiburg.de)
[2]Australian Nuclear Science and Technology Organisation, Menai, Australia

Sulfate minerals play an important role in metal cycling, especially in acid mine drainage environments and closed sedimentary basins in arid climates. In these environments, they form primarily through dissolution and precipitation reactions involving a liquid phase. However, sulfate minerals can also precipitate from the gas phase, a process that is important in some surficial geological environments. Metal sulfates, for example, precipitate when hot volcanic gasses, which transport both sulfur and metal species, are emitted into the atmosphere [1]. Similarly, metal sulfates precipitate from the burning of coal seams, coal dumps and tailings from ore-processing facilities [2, 3].

Recently, various metal sulfates have been detected in the particulate emissions from a coal-fired power station [4]. Phases identified include anglesite ($PbSO_4$), anhydrite ($CaSO_4$), several types of Al-sulfate, gunningite ($ZnSO_4·H_2O$), yavapaiite ($KFe(SO_4)_2$), and members of the voltaite group ($K_2Me^{2+}{}_5Fe^{3+}{}_3Al(SO_4)_{12}·12H_2O$). Various types of alkali and base metal sulfates have now also been identified (using qualitative EDS spectroscopy) in atmospheric particulate matter (PM_{10}) collected in Strasbourg, France. The air in this urban environment is polluted by road, train, and boat traffic as well as by emissions from several industrial point sources (e.g., steel plant, waste incinerator, biomass combustion plant). At Strasbourg, almost all sulfates have circular diameters <1 µm. They account for a total of up to 20% of all individual particles studied by automatic SEM (Genesis, EDAX) single-particle analysis [5].

We conclude that metal sulfates are common particulates in urban and industrial environments and that a large fraction is formed as a result of combustion processes. It is important to characterize these phases in order to understand better the interactions with atmospheric gases, moisture and radiation as well as with the cells and fluids present in our respiratory system.

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