Geochemistry of capillary hydrogeochemical systems in arid environments.

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Abstract.

In arid environments, porous media are unsaturated with water which is submitted to capillary constraints. The present chapter focuses on the geochemical impacts of such physical constraints and how theoretical analysis can help interpreting field or laboratory observations. The basic principles of capillary geochemistry suggest that the fate of contaminants, either organic or inorganic, can be significantly impacted in terms of reactive mass transfer in addition to flow and transport processes. All these mechanisms are closely interconnected, what makes the description of the behavior of such systems very complicated. An important work still has to be done in order to achieve such a goal: a number of mechanisms are not taken into account in the current state of development of the capillary geochemistry, namely mechanisms that occur in the thinnest confining geometries, like disjoining pressures, surface forces, etc.

1. INTRODUCTION

Porous media containing water in dry or arid contexts are only partially saturated, which means that water is strongly bounded to the solid matrix either in a capillary state or as thin hydration films on mineral surfaces. These particular features modify the thermo-physical properties of the confined water compared to the free bulk water (see previous chapters). This, in turn, leads to dramatic modification of the geochemical behavior of water-rock-gas systems compared to what is classically observed in saturated porous media. Then questions arise: i) how much different and specific are these behaviors? ii) What are their effective roles on mass and heat transfers from the soil surface to the underlying aquifers and on the water quality of these aquifers? iii) In particular, what can be their role in the fate of pollutants and pesticides? iv) Could they also play a role in the response to the global warming and the fate of greenhouse-effect gases?

In order to interpret observations made on the field or in the laboratory (§ 2), theoretical developments have been performed (§ 3) for dealing with such systems and for starting bringing some tentative answers to questions above (§ 4).

2. OBSERVATIONS FROM FIELD AND LABORATORY EXPERIMENTS

The first major field observations leading to the idea that the peculiar state of water in unsaturated porous media could shift chemical equilibria were performed by Yves Tardy and his collaborators [1-3]. These authors pointed out the coexistence of local mineralogical heterogeneities in old lateritic profiles, where thermodynamic equilibrium was expected. More precisely, they observed that hydrated minerals (like gibbsite or goethite) preferentially precipitate in large pores while anhydrous or less hydrated minerals (e.g. kaolinite, hematite) rather formed in smaller pores.

Recently, specific experiments have been performed in order to explore more deeply the underlying mechanisms. Bouzid *et al.* [4] observed the formation of differently shaped salt crystals in the pores of polycarbonate filters, depending on the ambient relative humidity (RH) and the water repartition/dynamics in the porosity. Using NMR technics, Rijniers *et al.* [5] measured the solubility of sodium carbonate in a natural porous medium. They observed that this solubility varied as a function of pore size on model porous materials of known pore sizes. The authors recorded that the solubility of sodium carbonate increased with decreasing pore size while sodium sulfate was not sensitive to pore size. Lassin et al. [6] monitored the partial pressure of CO_2 (pCO_2) at equilibrium with samples of an argillaceous rock at various RH. They observed that the equilibrium pCO_2 was decreasing with decreasing RH.

All these observations indicate that capillary and/or confined porous media exhibit specific complex chemical behaviors compared to bulk water-mineral-gas systems. Therefore, in parallel to these experimental works, theoretical developments have been performed, as described in the following for capillary systems.

3. THEORETICAL BACKGROUND

3.1. Thermodynamics of chemical reactivity in capillary systems

The chemical behavior of capillary systems has been studied for more than ten years, and the theoretical framework is now well established for calculating the standard thermodynamic properties of chemical compounds submitted to capillary pressure [7-9]. Briefly, the Young-Laplace and Kelvin laws imply that pore water at physical equilibrium with a given relative humidity is subjected to a pressure lower than in the surrounding gas phase. For sufficiently low relative humidity, the internal pressure of water – below the gas-water meniscus – can be negative. The corresponding impact on the thermodynamic properties of water, dissolved species and minerals, and therefore on operant chemical reactions can be calculated using the Thermo-ZNS calculation code [9]. The latter includes the equations of state (EoS) of water and aqueous species after Wagner and Pruss [10] and Helgeson *et al.* [11,12], respectively. The extended use of these equations to capillary systems and negative pressures can be discussed (see Chapter XX [12]). Their limit of validity, in terms of pressure, is not known and specific studies would be necessary to check or improve existing equations.

However, using the state-of-the-art EoS, one can show that capillary constraints can significantly impact water thermodynamic and electrostatic properties like the dielectric constant, ε, and its derivatives with respect to pressure and temperature. As an illustration, the Born function Z ($= -1/\varepsilon$) is plotted on Fig. 1-a as a function of temperature, at different pressures. This affects the thermodynamic properties of aqueous species too, which depend on temperature and pressure, but also on the dielectric properties of the solvent, namely water [11]. The apparent standard Gibbs free energy of Na^+, $SO_4^=$ and Cl^- are plotted on Fig. 1-b,c,d, respectively, as a function of pressure, at different temperatures. They show very different behaviors from one aqueous species to another, and from positive to negative pressures. Since, for every chemical reaction, the mass action law involves activity of aqueous species rather than concentration, another parameter related to aqueous species may be affected by capillary pressure. This is the activity coefficient by the means of the Debye-Hückel coefficients A_γ and B_γ [9] which are functions of water density and dielectric constant, and of temperature.

Consequently, the thermodynamic impact of capillary pressure on homogeneous chemical equilibria (*i.e.* in water) cannot be foreseen easily. Obviously, this also concerns heterogeneous equilibria (*i.e.* mineral-water and gas-water systems). Furthermore, in addition to the single pressure effect, the chemistry of capillary systems offers specific features called the anisobar contexts (i.e., where phases can undergo different pressures). They apply particularly to gas-aqueous solution equilibria since a gaseous compound cannot undergo negative pressures whereas its aqueous equivalent undergoes the internal capillary water pressure. A similar situation can be envisioned for minerals initially present in the rock matrix. They are submitted to the local pressure constraint when the porosity is saturated with water and the same pressure applies to these minerals during desaturation regardless of water content. On the other hand, if the capillary aqueous solution is supersaturated with respect to a mineral, the latter should precipitate at the capillary water pressure. Some evidence for this isobar/anisobar situation was obtained experimentally [4] as explained in § 4. According to the theoretical developments described above, thermodynamic properties and thus solubility of a mineral differ according to the isobar or anisobar context. As a general trend, anisobar conditions are less favorable to mineral stability than isobaric ones, which is physically consistent. The difference between these two contexts depends on the volumetric properties of the mineral. In particular, hydrated mineral phases are generally more affected by pressure than anhydrous ones. On the other hand, gases are expected to be more soluble in capillary conditions.

1.1. Thermodynamic database

In order to simulate the behavior of hydro-geochemical systems, we use the well-known PhreeqC-2 geochemical calculation code [14]. It allows calculating the aqueous speciation of solutions, saturation indices of minerals, partial pressures of gases, amounts of precipitated or dissolved minerals, etc. The use of this code at temperatures and pressures far from the liquid-vapor saturation curve is possible if appropriately adapted thermodynamic databases are available. Such databases including both isobar and anisobar mineral

dissolution/precipitation reactions were generated using the Thermo-ZNS code indicated above. The reference thermodynamic database implemented in Thermo-ZNS is the Thermoddem database [15] which provides information on critically selected standard thermodynamic properties of chemical compounds and reactions necessary for their calculation at various temperatures and pressures.
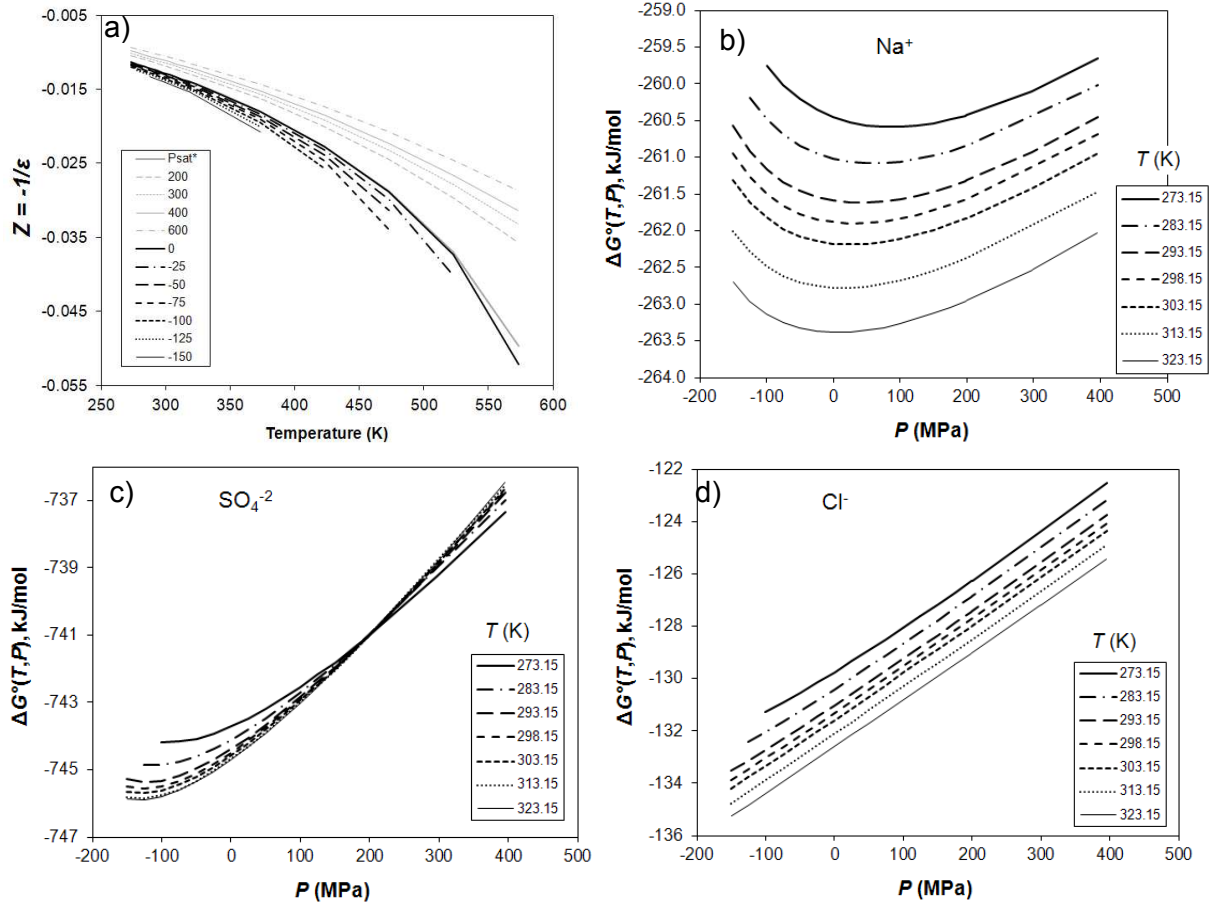

Figure 1: temperature and pressure dependence of various thermodynamic and electrostatic properties of water and aqueous compounds: a) Born function Z of water, and apparent standard Gibbs free energy b) of Na^+, c) of $SO_4^=$, and d) of Cl^-.

2. INTERPRETATIONS

Once the theoretical framework is defined, experimental observations evoked previously can be interpreted quite simply. In this section we focus on experiments from Bouzid *et al.* [4] and from Lassin *et al.* [6]. In the former work, the pores of a polycarbonate filter were initially filled with a NaCl aqueous solution slightly under-saturated with respect to halite. During the progressive drying of the filter, different stages were observed and, applying the principles of capillary geochemistry, Bouzid *et al.* [4] could provide the interpretation summarized hereafter (Fig. 2).

a- Precipitation of (cubic) halite while porosity is still saturated with water. Part of the volume of water which has evaporated is occupied by the salt. In some cases the corners of the precipitated salt can touch the pore wall, thus modifying the pore geometry.

b- As evaporation proceeds, de-saturation occurs and capillary water goes in the angular spaces created between the pore wall and the salt. A typical anisobar context thus takes place between water and solids. The less soluble and most supple solid (the polycarbonate pore wall) deforms while the most soluble and less supple solid (halite) dissolves, its destabilization being predicted by thermodynamics. The corners of the crystal are eroded.

c-　　　On the contrary, the isobar polymorph of halite, probably a nano-crystalline or an amorphous halite, is stabilized and thus massively precipitates under the capillary meniscus before water has totally evaporated.

All of these successive stages are fully consistent with the theoretical interpretation of the geochemical mechanisms in capillary context. They cannot be explained by the classical geochemistry applied to water-saturated porous systems.

The second series of experiments [6] recorded the CO_2 partial pressure at equilibrium with a clay rock in a closed system at various relative humidity values. The rock (the Callovo-Oxfordian argillite) and its pore water are well known. A geochemical model has been developed, involving mineral dissolution/precipitation and cation exchange reactions at thermodynamic equilibrium [16], and is used as a reference for describing this water-rock system. In particular, this model calculates the correct in situ pCO_2. By simply applying the principles of capillary geochemistry and without any parameter adjustment, Lassin *et al.* [6] could reproduce with a good accuracy the observed decrease of the equilibrium pCO_2 with decreasing relative humidity, from 8 down to less than 1 mbar and from 100 down to 50%, respectively. The authors took into account the evaporation of water from porosity and the consequent increase in salinity. They considered that anisobar alumino-silicates could only dissolve according to the time scale of the experiments (from 6 to 18 months). On the other hand, more reactive minerals, like carbonates, were initially present as anisobar phases and could evolve to their isobar polymorphs. Here again, the observed equilibrium pCO_2 could be reproduced only if principles of capillary geochemistry were applied.
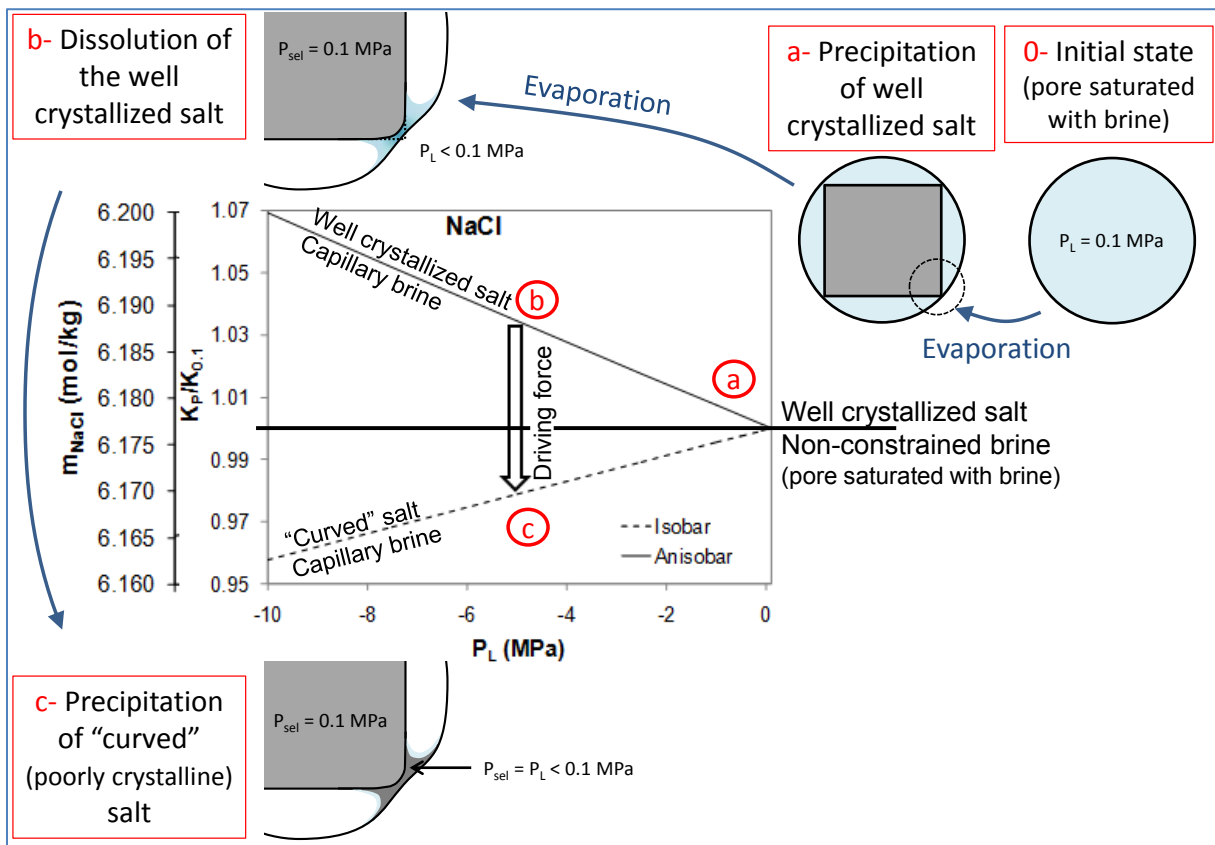

Figure 2: Successive reactive steps during the evaporation of a NaCl brine from the porosity of a polycarbonate filter and calculated solubility product of halite as a function of capillary pressure, both in the isobar and the anisobar contexts. a) Precipitation of well crystallized cubic halite; b) establishment of capillary conditions and dissolution of the cubic (anisobar) halite angles; c) precipitation of isobar poorly crystallized halite under the capillary meniscus. Modified after [4].

3. CONCLUDING REMARKS

These results were obtained in very different porous hydro-geochemical systems thus illustrating the wide applicability of the capillary geochemistry approach. Consequently, a new interpretation of the observations of Rijniers *et al.* [5], amongst others, could be done in the light of the principles of capillary geochemistry. Applications to other domains can therefore be envisioned quite straightly. They are related to industrial activities like CO_2 (or more generally: non-wetting phases) geological storage as well as nuclear waste repository in argillaceous rocks. They are also related to natural environments which have been impacted by human activity, in particular for studying the fate of inorganic and organic pollutants in arid environments.

Results above also illustrate the significant impact that capillary pressure can have on geochemical equilibria in arid environments. However, the obvious question to ask concerns the volume of water involved and the consequences on the mass/heat transfers through the porous medium. According to Pettenati *et al.* [17] significant amounts of water can remain held in the porosity for low relative humidity, depending on the pore network structure and petrophysical properties of the soil.

On the other hand, the different chemical compounds present in the pore solution can play a significant role on the air-solution interfacial tension and on the wettability of the pore walls depending on their affinity to interfaces and on their concentration in water. This may in turn affect the water content versus relative humidity relationship, but also the relative permeabilities in multiphase systems as well as the hysteresis and memory effects, etc., and thus the mass/heat transfers.

The principles on which capillary geochemistry is based are fairly consistent with approaches focused on other processes like crystallization pressure (see chapter YY [18]) and solution pressure phenomena (see chapter XX [19]). In such processes, anisobar conditions are also encountered in confined porous media, with strong relationships with pore water chemistry and shapes of interfaces. These similarities suggest that a single and general formalism able to describe all the above systems can be developed. An important work remains to achieve such a goal since a number of mechanisms are not taken into account in the current state of development of the capillary geochemistry. In particular, this approach only deals with bulk properties of capillary water. It does not take yet into account mechanisms that occur in the thinnest confining geometries, like disjoining pressures or surface forces (see chapters ZZ [20] and VV [21]). Works are under progress in this direction (see chapters of [22], [23], [24]).

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