The influence of natural trace element distribution on the mobility of radionuclides. The exemple of nickel in a clay-rock

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ABSTRACT

The natural distribution of nickel (Ni) in the Callovian–Oxfordian clay-rich rock of Bure (France) was investigated, together with that of cobalt (Co), zinc (Zn) and lead (Pb). The most Ni-enriched phases are pyrite ($\sim$400 $\times$ 10^{-6} g g^{-1} Ni), sphalerite ($\sim$300 $\times$ 10^{-6} g g^{-1}), chlorite ($\sim$285 $\times$ 10^{-6} g g^{-1}), organic matter ($\sim$300 $\times$ 10^{-6} g g^{-1}), muscovite (100–200 $\times$ 10^{-6} g g^{-1}) and possibly carbonate minerals (mainly calcite and minor dolomite, $\sim$10 $\times$ 10^{-6} g g^{-1}). Despite their high abundance (up to $\sim$80% in the upper part of the formation), carbonate minerals are quantitatively a minor Ni reservoir; most of the Ni is borne by chlorite and pyrite, which are minor mineral phases. Co and Ni have a similar distribution, whereas Pb and Zn have partly different reservoirs (e.g. sphalerite – ZnS).

In parallel, the equilibrium between rock and pore water was investigated, and importance of pyrite (or reduced sulfur minerals) as Ni reservoir in the formation was confirmed from an in situ experiment perturbed by oxidation processes. Under unperturbed conditions (laboratory kinetics experiments and in situ pore water sampling), Ni solubility ranges from $\sim$0.2 to 1 $\times$ 10^{-6} mol L^{-1}. The rock sorption capacities with regards to radioactive Ni (in the range of $\sim$1.5 $\times$ 10^{-10} mol L^{-1} to $\sim$1.5 $\times$ 10^{-9} mol L^{-1} of spiked ^{63}Ni) were also tested using batch experiments. Sorption kinetics of ^{63}Ni on the Callovian–Oxfordian clay-rich rock was explained by two mechanisms: fast and reversible sorption onto clay minerals and slow incorporation in another phase. Indirect evidences point out the likely major role of calcite in this latter process albeit pyrite and organic matter may also be involved. Reversible sorption of Ni onto clay minerals surfaces is shown to be hindered by competition processes with other naturally occurring bivalent metals (e.g. naturally-occurring Ni and Zn), thus decreasing the ^{63}Ni Rd value as compared to the value predicted from a bottom-up approach considering only ^{63}Ni sorption on clay minerals. At longer time scale, irreversible ^{63}Ni trapping is observed and compensates the competition processes. These two mechanisms were implemented in a reactive transport model to illustrate their influence on the prediction of long-term behavior of radioactive Ni. Migration distances are increased by the effect of cation competition, and reduced in a comparable extent by irreversible trapping in the time frame investigated.

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1. Introduction

Mineralogical and chemical characterization of clayey formations is of particular interest in the perspective of confinement of toxic and radioactive wastes. Nuclear waste disposal in such formations is currently being studied by different nuclear agencies in Europe. France has established its underground research laboratory in a Callovian–Oxfordian clay-rich rock, whereas Switzerland and Belgium conduct their experiments in Opalinus and Boom clay formations, respectively (see for example Altmann, 2008; Barnichon and Volckaert, 2003; Bennett and Gens, 2008; Bossart et al., 2002). The confinement properties of such geological environments are mainly driven by clay minerals, which have low permeability, are self-healing/self-sealing and have high sorption

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capacities, the latter effect resulting from their high specific surface and negative layer charge. All of these properties retard pollutant migration and are advantageous for the confinement of hazardous materials.

Clay minerals are most efficient for fast sorption and immobilization of pollutants via formation of inner- or outer-sphere surface complexes and via cation exchange, but these phenomena are mostly reversible on a fast time-scale (Tournassat et al., 2013). On the other hand, other solid phases present in clay-rich rocks participate in solid/water exchanges and can trap (or release) elements present in their structure, both through structural incorporation (or dissolution) and surface reactions. Despite its low specific surface, calcite is especially of interest because it is often present as one of the major minerals in clayey formations and because its equilibration kinetics with water is fast. As a result of its reactivity, this mineral traps a wide range of elements under environmental conditions (e.g. Curti, 1999; Fernandes et al., 2008; Lakshtanov and Stipp, 2007; Pingitore and Eastman, 1986; Reeder, 1996; Rimstidt et al., 1998; Stumpf and Fanghänel, 2002).

In the case of radioactive elements, isotopic exchange may also significantly contribute to retarding pollutant migration. Note that, in the whole present study, "isotopic exchange" is used in the sense defined by the IUPAC (International Union of Pure and Applied Chemistry; IUPAC, 2014), and refers to the incorporation of a radioactive atom in the lattice of a given mineral through replacement of a stable, naturally occurring, isotope. As a consequence, it includes all phenomena that may occur at equilibrium albeit adsorption on clay minerals will be considered separately. Isotopic fractionation between natural Ni (mainly ^{58}Ni) and radioactive Ni is assumed to be 1.

Prediction of pollutants retention and migration in a clay-rich rock requires a sound understanding of the distribution from all naturally occurring and possibly competing elements within the formation, i.e. identification of the main reservoirs and discrimination between the main and most reactive ones. It also requires the use of kinetic experiments. However, such a methodological approach is seldom applied in studies aiming at determining the retention capacities of rocks with regards to the elements of concern. A few studies investigated the effect of contact time on retention capacities of different minerals constituting a soil of interest (e.g. Freedman et al., 1994) and demonstrated that the fraction of the metal of interest that is reversibly bound to clay minerals decreases with time (e.g. Almås et al., 2000; Lu et al., 2005). However, most laboratory experiments typically last a few days (one week or less, e.g. Joseph et al., 2011, 2013; Tertre et al., 2009; Van Loon et al., 2009) and results thereof are extrapolated in a "blind modeling approach", assuming sorption control by clay minerals (e.g. Pfingsten et al., 2011). Although this modeling method accurately describes experiments with short solid/liquid interaction time, it may not be complete enough to describe for long-term experiments, because the influence of minerals having equilibration kinetics lasting more than a few days is not considered, which may induce an over-estimation of the migration distance for the metal of interest.

Among trace elements of interest, nickel (Ni, which in the present study will refer to the element, whatever its speciation) is of special concern, because both its stable and radioactive isotopes may pose a threat to the environment. Stable Ni is potentially toxic to plants and animals (Babich et al., 1982; Baccouch et al., 1998, 2001; Berton et al., 2006; Blaylock and Frank, 1979; Fuentebella and Kerner, 2010; Wang, 1987). Its radioisotope (^{63}Ni – pure-β emitter, 66 keV maximum energy, Cassette et al., 1998) is of concern in the perspective of long-term geological disposal of nuclear waste (Hou et al., 2005; Lee and Tank, 1985) and its behavior may be assumed to be a relevant analogous of that from ^{59}Ni, which is another radioelement of major interest in the perspective of

nuclear waste storage (Andra, 2005), but does, in contrast to ^{63}Ni, not result from activation processes and has a much longer half-life (about 75 000 years as compared to about 100 years for ^{63}Ni).

The present study aims at unraveling the main natural nickel reservoirs and the importance of solid/water exchanges in the Callovian–Oxfordian rock of Bure (France) with respect to this element. The main Ni host minerals were identified using a combination of physical and chemical methods. Laboratory experiments were conducted to quantify the kinetics of Ni equilibration between water and rock and the results were compared to concentrations obtained by in situ sampling. The sorption kinetics of ^{63}Ni on a Callovian–Oxfordian sample, under unperturbed conditions, was investigated, and the degree of sorption reversibility as a function time was quantified. The results were then merged to identify which Ni-bearing phases can control or impact aqueous Ni concentrations under various chemical perturbations and at different time scales. These data are used to critically evaluate the relevance and accuracy of the blind modeling approach for prediction of radioactive element long-term migration in a clayey formation. Insights into the occurrence and distribution of other trace metals that could influence Ni migration through sorption competition on clay surfaces is also investigated to better constrain future modeling exercises.

2. Materials and methods

2.1. Origin of solid samples

All samples (Fig. 1) were collected from the Callovian–Oxfordian clay-rich rock in the eastern part of the Paris basin (France). They originate from different boreholes (EST205, EST212, EST423, PAC1002, PAC2001, PAC2002 – Claret et al., 2010) drilled by Andra (French Radioactive Waste Management National Agency) from the surface and from the drifts of the Meuse/Haute-Marne Underground Research Laboratory (URL – Delay et al., 2007a,b, 2014).

Sequential extractions and granulometric separation were performed on a sample (K100) originating from a carbonate-rich level (C2d) and on another one (K119) from a deeper, clay-rich level (C2b1). Their mineralogy was determined previously (Tournassat et al., 2007).

For scanning μ-XRF and (or) microprobe experiments, two types of samples were prepared. Pyrite nodules and pyritous ammonites were collected in sediments excavated from the URL in the C2b1 lithologic sub-unit and polished prior to use. They are mostly built up from aggregated framboidal and euhedral sub-micrometric pyrites. Thin rock sections from different boreholes were selected in sub-units C2d, C2c, C2b2, C2b1 and C2a, so as to be as representative as possible of the Callovian–Oxfordian rock (Fig. 1). Different samples from the same horizon were analyzed to minimize potential artifacts induced by the sampling procedure (e.g. specific enrichment in a given rock sample). Results from analyses of samples from a same unit were always mixed so as to enhance statistical robustness.

Sample used for all batch sorption experiments (EST25691) was collected in the C2b1 lithographic unit during a drilling operation (PAC1002) performed by Andra (Vinsot et al., 2008). Immediately after collection, this sample was stored in a sealed bag filled with N_2 and transferred into an O_2-free glove box, where it was crushed to $d < 500$ μm. The mineralogical composition of this sample was assumed to be similar to that of two other samples previously characterized in detail, collected in the same borehole at ~1 m distance. As a support to this hypothesis, BET surface measured on this sample (36.7 $m^2\,g^{-1}$) was similar to that of the two other samples (35.9 ± 2.0 $m^2\,g^{-1}$) whose mineralogical composition is given in Table 1.