NATURAL Ni SPECIATION
IN THE CALLOVO-OXFORDIAN CLAY ROCKS:
IMPLICATIONS FOR POTENTIAL [63]Ni ISOTOPIC
EXCHANGE AND RETENTION MECHANISMS

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In the perspective of deep underground long-term nuclear waste storage, [63]Ni is considered as a priority radio-element to be studied (ANDRA, 2005). [63]Ni behaviour prediction is made difficult mainly because its geochemical behaviour is still subject to debate. For instance, the solubility of Ni simple compounds at high pH is ill-defined (Hummel and Curti 2003), and the knowledge on solubility control phases is still pending. Clay rocks such as Callovo-Oxfordian (COx) contain non negligible amounts of natural and stable isotopes of Ni. As a consequence, a good understanding of the natural speciation of Ni in the formation could help to understand [63]Ni controls in this environment, including long term isotopic exchange with naturally present Ni.
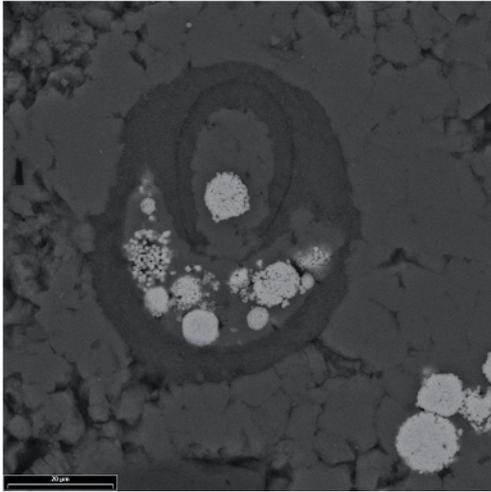
We focused our study on the COx formation, where the Bure (France) ANDRA underground research laboratory is located. Speciation of naturally occurring Ni was studied by combining chemical, microscopic and spectrometric methods. Chemical methods consisted of total rock analyses and sequential extractions (Tessier *et al.*, 1979) on various COx samples representative of the variability of the formation (from carbonate rich samples to clay rich samples). This method enabled quantifying the main Ni reservoirs. Physical methods were used to get a closer look at the Ni-bearing phases. Optical and scanning electron microscopy techniques were used to identify and isolate minerals from thin rock sections, originating from different geological horizons.

Chemical results indicate that the mean Ni concentration in the Callovo-Oxfordian clay rock is of ~30 ppm (10^{-6} g/g – Figure 1). Identified Ni-bearing minerals were mainly primary minerals (biotite, chlorite, muscovite), calcite and pyrite; organic matter being also observed. Electron microprobe and X-ray fluorescence analyses were performed in order to quantify the amounts and variability of Ni contents in these different Callovo-Oxfordian components. Ni is occasionally present in primary minerals with concentrations that can reach up to ~ 800 ppm, but its occurrence in these minerals remains limited. Ni occurrence in carbonates also remains limited, with respect to the analytical detection limit. On the contrary, Ni was frequently observed in pyrite, both massive and framboidal (*e.g.* Figure 2), with concentrations as high as ~ 2000 ppm. With a total concentration of ~1% in the Callovo-Oxfordian formation (Gaucher *et al.*, 2004), pyrite may thus be the main Ni reservoir. Thus, its isotopic exchange capacities will be studied with special care, so as to determine if naturally occurring Ni is readily available for exchange or not.

Finally, the presence of accessory small metal particles, mainly Ag, was also detected. In these particles, Ni-rich zones, with concentrations that can be as high as 100%, have been detected. The
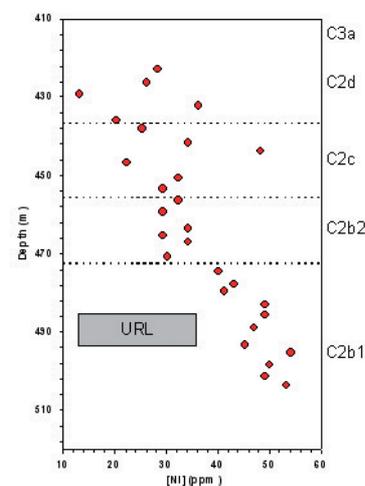
Figure 1: Total Ni concentration in the Callovo-Oxfordian rock (drillhole EST205) as a funcion on depth (solid circles). Dotted lines represent the formation limits. Name of the formations on the right of the figure. URL stands for Underground Research Labortory (position is approximate).

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Figure 2: Backscattered electron (BSE) view of a carbonated fossil (dark central area), containing framboidal pyrite (light gray zones). No Ni was detected by microprobe in the carbonated zone, whereas pyrite-rich zones contain about 1000 ppm Ni. Approximate fossil and pyrite sizes: $\sim 40 \times 40$ mm and $\sim 0.3 \times 0,3$ mm, respectively.

occurrence of these particles is however uneven in the formation; when detected, their presence is very limited and thus, despite their potentially very high Ni content, they are not expected to contribute significantly to the total Ni reservoir.

References:

ANDRA, 2005. Référentiel du comportement des radionucléides et des toxiques chimiques d'un stockage dans le Callovo-Oxfordien jusqu'à l'Homme. Châtenay-Malabry, France: Agence Nationale pour la gestion des déchets radioactifs. Report no. Dossier 2005 Argile.

Gaucher, E., Robelin, C. *et al*., 2004. "ANDRA underground research laboratory: interpretation of the mineralogical and geochemical data acquired in the Callovian-Oxfordian formation by investigative drilling." *Physics and Chemistry of the Earth, Parts A/B/C* **29**(1): 55-77.

Hummel, W. and Curti, E., 2003. "Nickel Aqueous Speciation and Solubility at Ambient Conditions: A Thermodynamic Elegy." *Monatshefte für Chemie / Chemical Monthly* **134**(7): 941-973.

Tessier, A., Campbell, P.G.C. *et al*., 1979. "Sequential extraction procedure for the speciation of particulate trace metals." *Analytical Chemistry* **51**(7): 844-851.

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