

STRONTIUM DISTRIBUTION AND ORIGINS IN A NATURAL CLAYEY FORMATION (CALLOVIAN-OXFORDIAN, PARIS BASIN, FRANCE): A NEW SEQUENTIAL EXTRACTION PROCEDURE

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Strontium is a minor element in the Callovian-Oxfordian clayey formation of Bure (ANDRA Underground Research laboratory, France) and may be interesting as a natural analogue of cationic radionuclides. The objective of our study was to better understand the chemical behaviour of this element since the sediment deposition. Previous mineralogical work showed that main strontium-bearing minerals in the claystones, in addition to clay minerals, are celestite, carbonates and accessory micas and K-feldspars. In order to establish the strontium distribution and determine its origins across the clayey formation and establish a strontium diffusion profile, a four step sequential extraction procedure (Table 1) combined with strontium isotopes was developed and adapted to the mineralogy of the Bure claystones.

Table 1: Description of the four steps of the sequential extraction procedure

Step	reagent	Reagent/ solid ratio	time	Extracted fraction
1	Cobaltihexamine trichloride	20	30 min	Exchangeable fraction
2	Na acetate (+ acetic acid, pH 5)	20	4 h	Calcite fraction
3	EDTA	20	1 h	Others carbonates
4	HNO ₃ + HF + HClO ₄ / HCl 6N	20	Two weeks	Residue (dominant silicates)

The four-steps sequential extraction developed and applied to sixteen samples of Callovian-Oxfordian claystones showed that the exchangeable fraction (27 to 48% of the total strontium) and the carbonate fraction (38-47% of the total strontium) are the two main fractions carrying the strontium, the detrital fraction being secondary (< 15%). Celestite is the major strontium-carrier mineral that can perturb the results of the sequential extraction but not significantly modify the distribution of strontium at the scale of the formation. The celestite was studied on micronic to centimetric crystals, separated by handpicking on core samples. The development of this sequential extraction procedure for the Callovian-Oxfordian formation shows the importance of the first cobalt hexamine trichloride step to extract the exchangeable strontium adsorbed on clay minerals and block the exchangeable sites with cobalt for the following steps, allowing a good separation of exchangeable fraction and carbonates. However the reagent/solid ratio of 20 seems to be less adapted to carbonate-rich samples. The good separation between exchangeable strontium and strontium incorporated by carbonates allowed having a strontium isotopic composition representative of each one. The isotopic signature of exchangeable Sr (0.70745) is in equilibrium with the present-day porewaters (0.7074-0.7076), and is significantly different from the strontium isotopic signatures of the carbonate fraction (0.7070-0.7072) and celestite (0.07070-0.7073) which are quite similar to Callovian-Oxfordian seawater. The small detrital fraction (K-micas and feldspars) shows high strontium values, in agreement with their Hercynian continental origin, providing evidence of low exchange with other main strontium fractions. This demonstrates the low contribution of the detrital minerals in the establishment of the present porewater chemistry of this formation as it has been demonstrated by (GAUCHER *et al.*, 2009) using thermodynamic and kinetic arguments.

The slight ^{87}Sr enrichment of the exchangeable fraction relative to the Callovian-Oxfordian seawater is possibly due to a low support of radiogenic strontium by alteration of the detrital fraction or to slow diffusion of Dogger formation waters into the clay formation. However, if it is clearly demonstrated that the chloride content of the COx porewater diffuses from the Dogger formation, the homogeneous exchangeable strontium isotope composition across the clayey formation (Figure 1) have not shown a diffusion profile of strontium between the overlying Oxfordian and the subjacent Dogger aquifers. Consequently the clay formation is a strong buffer considering the diffusion of the alkaline-earth cations and that the ion exchange processes limit the diffusion of the Sr for very long periods, and confirms the efficient aquitard role of the Callovian-Oxfordian clay formation between the Dogger and the Oxfordian limestones (BUSCHAERT *et al.*, 2007).

Future developments of this research will be focused on an eventual enrichment of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio at the limit between the Dogger and the Callovian-Oxfordian. Experimental study of the transformation of Sr-rich biogenic carbonates in diagenetic Sr-poor calcite associated with celestite will be interesting in order to understand the formation of the celestite.

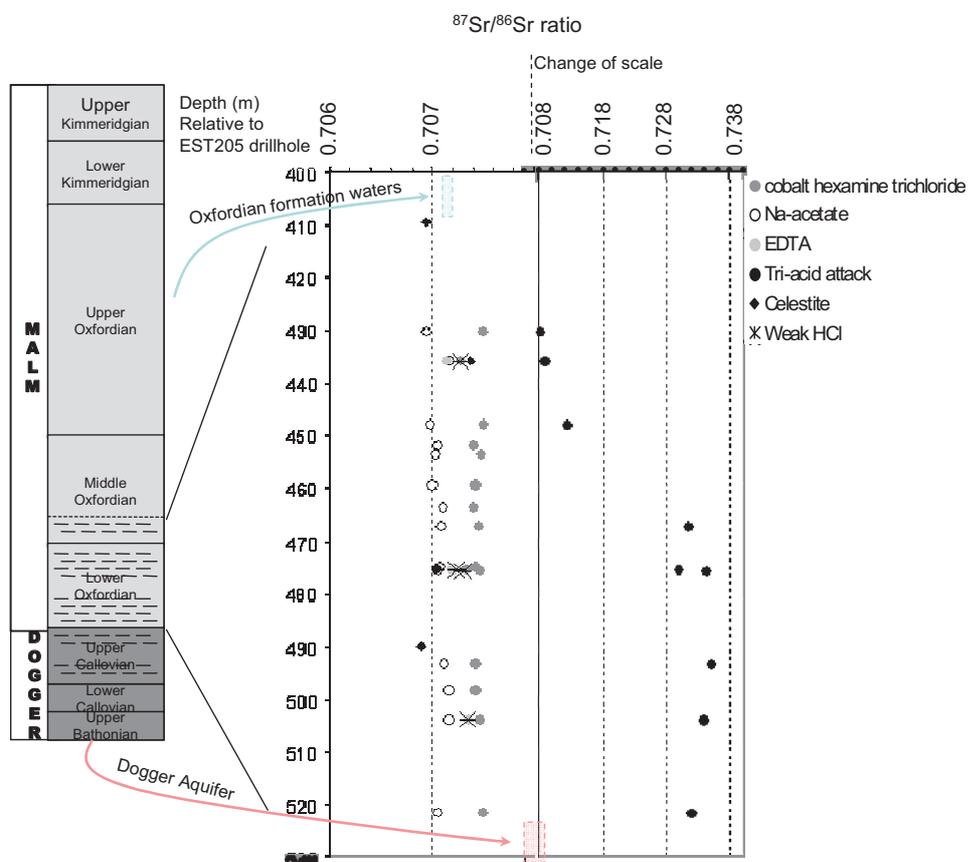


Figure 1: Profile of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the four successive fractions extracted by sequential extraction in the Callovian-Oxfordian clayey formation of Bure.

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