



## **(S, C, O, Sr) isotopic constraints on the diagenetic evolution of the COX clay formations at the Bure URL site, Paris Basin)**

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The Underground Research Laboratory of Bure, located in the Eastern part of the Paris Basin, was selected by ANDRA (French Agency for Nuclear Management) in order to study the feasibility of a nuclear waste disposal in the Callovian-Oxfordian thick clayey formation at 400 meters depth. Since 1994's, numerous investigations have been initiated to understand and predict the behaviour of the clay formation in time and in space, by constraining its stability, the chemical evolution of the porewaters, and solution transfers between the clayey formation and its adjacent limestone sequences during geological times (ANDRA, 2005). In that way, this study presents combined new mineralogical and isotopic data of the diagenetic mineral sequence to constrain the porewater chemistry of the rock at different stages of the sedimentary then burial history of the clayey formation.

The petrological study of Callovian-Oxfordian claystones provided evidence of the following diagenetic mineral sequence: 1) Framboidal pyrite  $\pm$  micritic calcite in replacement of carbonate bioclasts and in bioturbations, 2) Iron-rich euhedral carbonates (ankerite, sideroplesite), Glauconite, 3) Sparry dolomite, celestite in residual porosity, 4) Chalcedony 5) quartz/calcite. Pyrite in bioturbations shows a wide range of  $\delta^{34}\text{S}$  (-38 to +74 permil/CDT), providing evidence of bacterial sulphate reduction processes. The lowest negative values (-38 to -22 permil) indicate precipitation of pyrite in a marine environment with a permanent recharge in sulphate, whereas the higher pyrite  $\delta^{34}\text{S}$  values (-14 up to +74 permil) show that pyrite precipitated in a system that closed for sulphate. Consequently the variations of pyrite  $\delta^{34}\text{S}$  in bioturbations along the lithostratigraphic profil indicate a change of sedimentation conditions from a deep marine environment to an environment with alternative recharge of marine sulphates; that is consistent with the transgression/regression cycle observed in the middle sequence of the formation. The  $\delta^{34}\text{S}$  values of celestite (+ 22 to +31 permil /CDT) reflect the last evolution stage of the system at which the bacterial activity ends, the celestite corresponding to the deposition of the residual dissolved sulphate anions in the diagenetic porewaters. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of celestite (0.706872-0.707040) is consistent with a deposition from Jurassic marine-derived waters. Carbon and oxygen isotopic compositions of bulk calcite and dolomite are consistent with marine carbonates ( $\delta^{13}\text{C} = +0.2$  to +2.3 permil/PDB,  $\delta^{18}\text{O} = +27.7$  to +28.7 permil/SMOW) whereas late diagenetic siderite is slightly  $^{13}\text{C}$ - depleted. The  $^{13}\text{C}$ -depletion could be attributed to a partial contribution in diagenetic porewaters of carbonate ions derived partially from the degradation of organic matter issue of the bacterial sulphate reduction. The  $\delta^{18}\text{O}$  values of late diagenetic chalcedony range between +27 and +31 permil/(SMOW), suggesting precipitation from marine-derived porewaters at temperatures of maximum burial ( $\sim 40\text{-}50^\circ\text{C}$ ). Late calcite in veinlet reworking with chalcedony and celestite, and late euhedral quartz in a limestone from the top of the formation have lower  $\delta^{18}\text{O}$  values ( $\sim +19$  permil/SMOW), suggesting they precipitated from meteoric fluids ( $\delta^{18}\text{O} \sim -6$  permil), whose signature is close to present-day porewaters of the formation.

To conclude, combined mineralogical and isotopic data show that pyrite, sulfates, calcite cement, euhedral iron-bearing carbonates and probably chalcedony are diagenetic phases precipitated from marine-derived porewaters in conditions controlled by bacterial sulphate reduction. A calcite veinlet reworking chalcedony and celestite (in the middle sequence of the formation) and euhedral quartz encrusting a vug in a limestone from the top of the clayey formation are the only mineral records of the introduction of meteoric fluid in the clay formation, and the only phases at isotopic equilibrium with present-day porewaters.