U/Pb dating of geodic calcites: A tool for paleohydrological reconstructions

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This study presents U/Pb dating of secondary geodic calcites carried out to provide chronological constraints on diagenetic processes and past fluid circulations that affected the deep sedimentary formations of the East of the Paris Basin. It is part of projects developed by the French Agency for Nuclear Waste Management (ANDRA) in order to test the feasibility for nuclear waste storage in the Callovo-Oxfordian argillite. This layer is embedded between two carbonated shelf formations, Dogger and Oxfordian in age, characterized by very low porosity due to secondary sparite precipitation. These calcites are thougth to reflect main diagenetic events and phases of fluid circulation within the sedimentary basin since the early Cretaceous period. But the absolute ages of these events are uncertain and still subjet to debate. The aim of this project was thus to date secondary geodic calcites related to these fluid circulations in order to reconstruct the diagenetic and palaeohydrological history of the site.

The U/Pb dating method was optimized to large secondary calcites samples with very low concentrations of lead (from 3 to 26 ppb) and uranium (from 22 ppb to 1ppm). Geodic calcites from Oxfordian and Dogger formations were sampled from drilling cores and were analyzed by TIMS (VG 54 Sector at CEREGE) using a ^{205}Pb-^{236}U-^{233}U-^{229}Th spike.

Results depict clear isochrons and several phases of secondary calcite precipitation were identified. Two ages were obtained on 4 geodes from the Dogger formations at -149.2±5.8Ma and -99.1±1.9Ma. They strongly suggest two phases of sparite precipitation: (1) during early diagenetic processes and (2) during a later recristallization process. On the contrary, 6 geodes from the Oxfordian formations gave a unique age at -33.2±5.5Ma indicating a more recent and unique phase of porosity infilling. This precipitation phase is very likely related to a major fluid circulation event synchronous with the Late Eocene/Oligocene tectonic extension responsible for the formation of major rifts in northern Europe (e.g. Rhine graben). This event affected the whole Oxfordian formations in the eastern part of the basin but did not affect the Dogger formations.

U/Pb dating of geodic calcites thus offers a new powerful way for reconstructing the coupled palaeohydrological and tectonic history of sedimentary basins.

Iron and other metals in the Proterozoic oceans

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The chemical composition of the ocean changed dramatically with the oxidation of the Earth's surface, and this process has profoundly influenced the evolutionary and ecological history of life. The early Earth was characterized by a reducing ocean-atmosphere system, while the Phanerozoic Eon (<542 million years ago) is known for a stable and oxygenated biosphere conducive to the radiation of animals. The redox characteristics of surface environments during the Earth's middle age (1.8 to 1 billion years ago) are less well known, but over the past decade it has been commonly assumed that the mid-Proterozoic was home to a globally sulfidic (euxinic) deep ocean. Here, we present iron data from a suite of mid-Proterozoic marine shales. Contrary to the popular model, our results indicate that ferruginous (anoxic and Fe^{2+}-rich) conditions were both spatially and temporally extensive across diverse paleogeographic settings in the mid-Proterozoic ocean, inviting new models for the temporal distribution of iron formations and the availability of bioessential trace elements during a critical window for eukaryotic evolution. We suggest that ferruginous shales are not large sinks for bioessential chalcophile elements. In this light, the presence of widespread Fe^{2+}-rich conditions may allow for substantial redox-sensitive trace metal reservoirs in a largely reducing ocean.