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Evolution of porewater composition through time in limestone aquifers: Salinity and D/H of fluid inclusion water in authigenic minerals (Jurassic of the eastern Paris Basin, France)

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ABSTRACT

Past water circulations can significantly reduce the porosity and permeability of marine limestones. This is particularly the case in the Middle (Bathonian/Bajocian) to Upper (Oxfordian) Jurassic limestones from the eastern border of the Paris Basin. The knowledge of the timing, the temperature and composition of paleowaters is essential to model the hydrological evolution in this area where the Callovian–Oxfordian claystones are studied for the storage of nuclear wastes. In this way, fluid inclusions hosted in low-temperature (<60°C) authigenic calcite, quartz and celestite crystals were analyzed by Raman spectroscopy and mass spectrometry to determine the chlorinity and D/H ratios. Chlorinity measurements (mmol Cl per liter of water) in fluid inclusions trapped in authigenic crystals during the late Jurassic/early Cretaceous period revealed unexpected high values, up to 3800 mmol l^{-1}, indicating that brines were involved in some of the diagenetic crystallization processes. By contrast, fluid inclusions in calcite cements of Cenozoic age within the Oxfordian limestones have low Cl concentration (less than 150 mmol l^{-1}), thus showing that a dilution event caused by water infiltrations during the Cretaceous uplift of this part of the basin has flushed out the original saline porewater. By coupling δD of fluid inclusion with $\delta^{18}O$ of calcite crystals, we estimate that calcite precipitation occurred at temperatures between 25 and 53°C. The hydrogen isotope composition of calcite-forming water is different between the Middle Jurassic (δD ranging from −20 to −35.8‰$_{\text{V-SMOW}}$) and the overlying Oxfordian limestone (δD from −59.5 to −44.8‰$_{\text{V-SMOW}}$). Present-day groundwaters are also of distinct composition on both sides of the Oxfordian claystones, indicating that limestone aquifers underwent independent hydrologic evolutions since the early diagenetic Jurassic cementation.

1. Introduction

In the upper part of sedimentary basins, low-temperature diagenetic processes (<60 °C) may significantly modify the original porosity and permeability of the sediments through precipitation of authigenic cements. In such conditions, the chemical and isotopic composition of the fluids involved can be either characterized indirectly (e.g., chemical and isotopic analyses of authigenic minerals) or directly through the study of fluid inclusions (e.g. Shepherd et al., 2000; Sandström and Tullborg, 2009; de Haller et al., 2011). The latter approach is somehow challenging in low-temperature systems. Indeed, fluid inclusions trapped at temperatures lower than ~50 °C are generally very scarce, metastable and composed of one phase (liquid) at room temperature (Goldstein, 2001), making impossible accurate microthermometric measurements (excepted by forcing the nucleation of a vapor phase, see Krüger et al., 2011). The evolution of the paleofluid chemistry from ancient hydrologic conditions up to present day is however of critical importance for the understanding of the regime of element mobility in modern aquifers (Hendry et al., 2015).

This is particularly the case for the aquifer–aquiclude system of the eastern part of the Paris basin, for which models of fluid circulation are needed. Indeed, since 1994, the French national radioactive waste management agency (Andra) has been studying the feasibility of a long-term geological disposal of intermediate to high level long-lived nuclear wastes. In this framework, an underground research laboratory (URL) was built in the East of the Paris Basin (Meuse/Haute-Marne) in a

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150 m thick succession of Callovian - Oxfordian (COx) clay-rich rocks (present day depth between ~400 and 550 m). This formation is sandwiched between two limestone-dominated units: the overlying Oxfordian to Tithonian (Upper Jurassic) and the underlying Bathonian and Bajocian (Middle Jurassic) formations. Exchanges of gas and solutes through the Callovian–Oxfordian claystones occurred by diffusion (Lavastre et al., 2005), this process being responsible of the entire replacement of the original porewater at the Ma scale (Giannesini, 2006). Hence, the characterization of geological paleofluids related to the main fluid events helps understanding present porewater composition.

Both Oxfordian and Middle Jurassic limestones have been intensively cemented by ancient water circulations (Clauer et al., 2007; Brigaud et al., 2010; Lavastre et al., 2011). With the exception of early cementation in phreatic or vadose environments, most of the porosity is filled by successive stages of calcite spars (Buschaert et al., 2004; Vincent et al., 2007; Brigaud et al., 2009a; Carpentier et al., 2014).

Analyses were performed during the past decade on calcite cements, particularly oxygen and carbon stable isotope data (Buschaert et al., 2004; Hibsch et al., 2005; Vincent et al., 2007; Brigaud et al., 2009a; Carpentier et al., 2014), strontium isotope data (Maes, 2002; Hibsch et al., 2005; Brigaud et al., 2009a), and Rare Earth Elements (Carpentier et al., 2014). These studies highlighted several stages of calcite cementation inferred to Early Cretaceous uplift phases and Cenozoic tectonic stress periods. According to their $\delta^{18}O$ values and considering temperatures below 60 °C, Early Cretaceous calcite cements have likely originated from mixed marine and meteoric waters, whereas Cenozoic cementations are of meteoric origin (Buschaert et al., 2004; Brigaud et al., 2009a; Carpentier et al., 2014). Cenozoic cementation in the Oxfordian limestones filled most of the pore space and constitutes the only macroscopic crystals in geodes and vugs. Despite numerous available isotopic data on these cements, the precise origin of the calcite-forming water remains uncertain, as the temperature of crystallization derived from only six homogenization temperatures of primary fluid inclusions in calcite cements within the Oxfordian. Buschaert et al. (2004) estimated trapping temperatures between 32 and 42 °C after pressure correction.

Although somehow challenging, the measurements of fluid inclusion stable isotope compositions (δD and $\delta^{18}O$) might be of primary importance in the discussion of fluid–rock interactions (e.g., Mazurek, 1999; Tarantola et al., 2007; Dublyansky and Spötl, 2010). However, with the exception of the preliminary study of Buschaert et al. (2004), no chemical and isotopic analyses of fluid inclusions were carried out and thus, the paleohydrological evolution of the studied area is still not fully understood (Dubliansky, 2004).

This paper presents a detailed investigation of fluid inclusions trapped in calcite, celestite and quartz cements in the Middle to Upper Jurassic limestones and marls formations in the eastern Paris Basin. It explores 1) how the analysis of fluid inclusions trapped in authigenic crystals provide information regarding the composition and temperatures of paleo-groundwaters in a low-buried sedimentary basin, and 2) how to reconstruct the timing and origin of fluid circulations in relation to regional geodynamic events from deposition time to present.

2. Geological setting

The intracratonic Meso-Cenozoïc Paris Basin was initiated after a general collapse of the Variscan massif during Permian times (e.g., Mégnien et al., 1980). A westward shift of the subsidence towards the present day center of the Basin occurred during late Triassic (Carnian), which lead to the observed monocline structure. The eastern Paris Basin sedimentary formations gently dip to the West and show only local evidences of deformation.

Triassic sediments consist of fluvial siliciclastic deposits (Buntsandstein facies) grading into shallow-water marine carbonates (Muschelkalk facies) and evaporites (Keuper facies). The Lower Jurassic sedimentary formations consist mainly of marls and shales deposited during the Carnian to Toarcian stratigraphic cycle (Guillocheau et al., 2000). This period corresponds to a large opening of the Basin and to a transgression of the Tethys sea from the East. The early Bajocian marked the transition to a vast carbonate environment (Durlet and Thierry, 2000), with the deposition of oobioclastic sediments together with coral buildups. A major change of facies occurred at the early/late Bajocian transition, with mixed carbonate (ooid-dominated) and siliciclastic sedimentation (Brigaud et al., 2009b). A new carbonate ramp then developed in the northeastern Paris Basin during the Bathonian, with typical inner ramp depositional environment (oolitic shoal or lagoon). A general drowning of the platform resulting in deposition of clay-rich sediments started during the Callovian and lasted until the early Oxfordian. The depositional environment gradually returned to carbonate sedimentation during the Middle Oxfordian, with reefal-dominated and oolitic limestones. Lowstand relative sea-level favored the increase of siliciclastic inputs at the beginning of the late Oxfordian (Carpentier et al., 2010). A major carbonate crisis occurred at the Oxfordian/Kimmeridgian transition (Lefort et al., 2011), with marl dominated sedimentation, coming next with a mixed carbonate and siliciclastic ramp environment during the Tithonian. During late Cimmerian and late Aptian, two stages of emersion associated with erosion occurred (Quesnel, 2003), as a result of both eustatic sea-level drop and distant influence of uplift of rift shoulder linked to the North Atlantic rifting (Ziegler, 1990). A large transgression occurred in late Cretaceous times resulting in the deposition of chalk. The eastern basin margin definitively emerged and experienced weathering and erosion during the Cenozoic, allowing the exhumation of the underlying Jurassic and Triassic sediments, which presently crop out in the area.

The tectonic agenda in this part of the Basin was summarized by André et al. (2010). Two main stages have been distinguished:

i) Early stages, as recorded by the formation of discrete clay minerals (I/S minerals dated around 150 ± 10 Ma (Rousset and Clauer, 2003). Several episodes of thermal anomalies linked to the rifting of the central Atlantic Ocean are well known in Western Europe. Major hydrothermal events occurred during the Jurassic (190–170 Ma and ~150 Ma) resulting in Pb–Zn–Ba–F and U mineralizations along the margins of the basin, and in the Armorican, Central and Morvan massifs (Lancelot et al., 1984; Bonhomme et al., 1987; Respaut et al., 1991; Cathelineau et al., 2004, 2012), as well as widespread illitization in Permian and Triassic sandstones (Clauer et al., 1995). Other major extensional events favoring fluid circulations are known at ~120 Ma and 80 Ma (Clauer et al., 1995, 1996). All these events coincide with an increase in the subsidence rate in the Paris Basin (Ferry et al., 2007).

ii) Main tectonic events occurred during the Cenozoic, as the basin was submitted to the Pyrenean and Alpine orogenies, as well as extensional movements symmetric and synchronous of the continental rifting of the Rhine graben, such as the Gondrecourt graben delimiting the URL area (Fig. 1). Major faults, inherited from the Hercynian orogeny may also have been active during the Mesozoic and then reactivated by the Pyrenean and Alpine events (André et al., 2010).

The geothermal gradient in the URL area is around 3 °C/100 m (Landrein et al., 2013). The burial and thermal history of the Mesozoic series was reconstructed by the study of several independent geothermometers (Blaise et al., 2014). Maximum burial temperatures, reached during the Late Cretaceous, were estimated of 40 ± 5 °C in the Upper Oxfordian and 60 ± 5 °C in the Middle Jurassic limestones (Fig. 2).

3. Sampling

3.1. Core samples

The macroscopic evidences of water–rock interactions during burial diagenesis and telogenesis are the diagenetic/hydrothermal cements