



Evidence for long term deep CO₂ confinement below thick Jurassic shales at Montmiral site (SE Basin of France)

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Studies of natural CO₂ analogues bring key information on the factors governing the long term (>1My) stability/instability of future anthropogenic CO₂ storages. The main objective of this work is to trace the deep-origin CO₂ migrations in fractures in the Montmiral CO₂ deep natural occurrence (Valence Basin, SE France). The final objective is to document the reservoir feeding and the possible leakages through overlying series. The CO₂ reservoir is hosted within a horst controlled by a N-S fault network.

From the Triassic to Eocene, the Montmiral area was part of the South-East Basin of France. This period is marked by the Tethysian extension phase (Triassic-Cretaceous) followed by the closure of the basin which culminated during the Pyrenean compressive phase (Eocene). Then, from the late Eocene, the Valence Basin was individualised in particular during the Oligocene E-W rifting affecting the West of Europe. Finally the eastern border of the Basin was overthrust by Mesozoic formations during the Alpine orogenesis (Miocene).

The Montmiral CO₂ reservoir is intersected by the currently productive V.Mo.2 well, drilled through Miocene to Triassic sedimentary formations, and reaching the Palaeozoic substratum at a depth of 2771 meters. The CO₂ is trapped below a depth of 2340 meters, at the base of sandy, evaporitic and calcareous formations (2340-2771m), Triassic to Sinemurian in age. These units are overlain by a 575 m-thick Domerian to Oxfordian marly sequence which seals the CO₂ reservoir. Above these marls, calcareous strata (1792-1095 m), Oxfordian to Cretaceous in age, and sandy clayey formations (1095-0 m), Oligocene and Miocene in age, are deposited. The various stratigraphic levels from the Miocene to the basement were cored over a total length of ~100m.

From bottom to top, three lithological units, which exhibit well characterised contrasted diagenetic evolution, record various stages and effects of the CO₂ migration:

- Lower unit: Palaeozoic metamorphic basement;
- Middle unit: Triassic-Liassic reservoir;
- Upper unit: late Jurassic to Cretaceous.

The middle unit (reservoir) and the upper unit are separated by the thick, tight seal, Domerian to Oxfordian in age. The definition of these lithological units was made using combined petrographic techniques (cathodoluminescence CL, fluorescence, Raman spectroscopy, crushing tests), geochemical techniques (C and O isotopes) and microthermometry.

Lower unit: Paleozoic basement - In the metamorphic basement, aquo-carbonic and CO₂-dominant fluids are trapped as primary fluid inclusions in hydrothermal barite and fluorapatite, and as secondary fluid inclusions in extensional microcracks crosscutting metamorphic quartz. All these fluids, trapped in the two-phase stability field, indicate firstly a limited phase separation at 300°C and 400-500 bars evolving toward wider CO₂-H₂O unmixing at 200°C and 200 bars. Basinal saline brines (10 and 15-25 wt % eq. NaCl and 70<T<95°C) are trapped in the same extensive microcrack system. These fluid circulations are coupled with a precipitation of K-feldspar and fluorapatite followed by an intense illite-ankerite alteration and late veins of ankerite and barite in a continuous deformation system.

Middle unit: Triassic-Liassic reservoir - The fracture fillings of this unit is marked by polymineral fillings which trapped aqueous, oil, CO₂ and/or CH₄ (calcite, ankerite, pyrite, barite...). Microthermometric measurements and isotopic data provide evidence for a first circulation of a moderate temperature (80°C) marine origin fluids equilibrated with surrounding rocks (Delta18O ~ 0,5 permil SMOW) and a late circulation of lower temperature (52°C) meteoric fluids also equilibrated with limestones (Delta18O ~ -7 permil SMOW). CO₂ inclusions belong to the latest phase of fracturing, occurring during the meteoric fluids circulation phase. These open fractures, with

dog-tooth style euhedral calcite, exhibit, by comparison with the outcrop, a fabric of typical Pyrenean type.

Upper unit: late Jurassic to Cretaceous - Above the seal, the fractures are exclusively filled with carbonates (calcite and dolomite) trapping aqueous fluid inclusions only. CL, microthermometry and isotopic data provide evidence for low temperature meteoric fluids ($\Delta^{18}\text{O} \sim -5$ permil SMOW) with numerous karstic features in Cretaceous strata.

In conclusion, the CO_2 feeding phase occurred under high pressure conditions requiring the presence of a thick sedimentary cover. The cement phases in the reservoir and in the cover rock, which exhibit different geochemical characteristics, demonstrate that, in spite of the several fluid circulation phases, upper and middle units were disconnected. This provide in particular, evidence that the seal prevented upward CO_2 migrations from the Montmiral reservoirs and that the natural CO_2 reservoirs of Montmiral seem to have been stable through time even the complex tectonic history of the Valence basin.