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CO_2–Pore Water-Rock Interactions From Natural CO_2 Gas Pools – A Case History from the Southeast Basin of France.

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Abstract

To build confidence in the viability of CO_2 sequestration it is necessary to demonstrate an understanding of the long-term geochemical changes that may occur following CO_2 injection. Ideally, these changes will result in the permanent trapping of CO_2 as precipitated carbonate minerals. Although these processes will be reservoir-specific, some generic reactions may be predicted. One way of confirming these predictions is to study analogous natural CO_2-rich reservoirs where long-term geochemical processes may be observed.

We present a case history from the Southeast Basin of France, where CO_2 gas accumulates in small traps in Triassic sandstones and Early Jurassic limestones. This area, bounded by the Massif Central to the west and Alpine foreland to the east, is well known for many CO_2-rich springs that indicate CO_2 migration to the surface. The caprocks are siliceous Sinemurian clayey limestone and evaporites. Moderate reservoir properties are enhanced by a network of well-connected open fractures that maintain reservoir productivity.

Diagenetic studies indicate significant differences between reservoirs containing CO_2 and those not exposed to CO_2-rich fluids. This therefore allows identification of the effects of CO_2-rich pore waters on reservoir lithologies. In addition, fracture paragenesis and fluid inclusion analyses reveal the history of CO_2 migration and its effects above the reservoir.

CO_2 migration into the reservoir increased porosity through dissolution of feldspars and carbonate cements. Fracture reactivation in overlying limestones allowed further CO_2 migration with partial self-sealing through additional carbonate mineralisation. CO_2-rich fluid inclusions indicate the CO_2-rich fluid mobilised and transported hydrocarbons.

Geological setting

Several CO_2-rich gas pools occur throughout the Ardèche palaeomargin of the Southeast Basin of France (Figure 1), which is located to the southeast of the Massif Central and bounded on the east and south by the Tertiary thrust belts of the western Alps and the Pyrenees-Provence. From the Late Triassic to the end of the mid-Jurassic, this area underwent major extension as part of the Tethyan rifting that preceded the opening of the Ligurian ocean (Razin et al., 1996). A major rifting event in Oligocene to Aquitanian time produced NE-SW trending half-grabens. From the Late Miocene to the present an E-W compressional regime has been established, corresponding to the main Alpine orogen, with the sedimentary beds undergoing vertical fracturing with the formation of horsts and grabens. In the Neogene, uplift of the Massif Central was accompanied by three magmatic events of increasing scale - the latest starting about 15 Ma.

Oil exploration in the Southeast Basin has been accompanied by the discovery of CO_2, eight accumulations being discovered in total (Figure 1). This CO_2 is now extensively exploited by the sparkling mineral water industries centred around Vichy, Badoit and Perrier. As with other significant CO_2 occurrences throughout Europe, much (though not all) of this CO_2 appears to be of mantle or deep crustal origin (Arthaud et al., 1994). Although previous chemical and isotopic analyses of the many carbonated springs found throughout the Massif Central and Southeast Basin area indicate that the CO_2 and associated noble gases are predominantly of mantle or deep-crustal origin, $\delta^{13}C$ measurements at Montmiral indicate significant enrichment. This suggests that the CO_2 is not exclusively of magmatic origin and that storage in a carbonate containing reservoir has resulted in re-equilibration with dissolved carbonate.

Montmiral
One of the CO_2 gas accumulations, currently being exploited at Montmiral, is being studied within the NASCENT project. CO_2 occurrences are observed below 2400 m depth in both Early Jurassic Hettangian marine deposits, and Late Triassic Rhaetian and earlier, terrestrial or continental shelf evaporitic sediments. Layers of Late Triassic anhydrite, clays and dolomite separate the two CO_2 occurrences. Nevertheless, it is assumed that open fractures seen on the cores can maintain a connection from basal Hettangian down to the basement. The main CO_2 reservoir is within the lower Triassic sandstone that was deposited in an increasingly continental fluviatile system in a flood-plain environment with periodic sheet flooding, subaerial erosion and pedogenesis. The caprocks are siliceous Sinemurian clayey limestone. The Hettangian-lowermost Sinemurian comprises black shales overlain by massive doomite deposited in a restricted marine shelf environment.

Mean reservoir sandstone porosity and permeability is variable. Between 2455 and 2462 m depth, moderate reservoir properties of 6 % porosity and 0.5 md permeability are enhanced by a network of well-connected open fractures that maintain reservoir productivity. The CO_2 content is estimated at about 70%. Deeper, between 2462 and 2471 m depth, matrix porosity varies between 8 and 12 % with corresponding permeabilities of 0.3 to 120 md. In this zone, CO_2 saturation reaches 30 to 60 %. Over the 10 years of exploitation, average fluid composition is 1.33 % water, 0.12 % oil and 98.55 % CO_2.

The CO_2 is locally trapped below Triassic sequences of claystones, limestones and evaporites (mainly anhydrite but also halite). However, throughout this area, the many CO_2-rich springs and mineral waters provide evidence for CO_2 migration to the surface, through these caprock sequences. It is assumed that migration occurs along fractures and faults.

Reservoir Quality in a CO_2-Rich Fluid
Reservoir core has been characterised from three 1960's exploration boreholes, one at Montmiral (VM02) and two at nearby Saint Lattier (SL01 and SL02). VM02 is still producing CO_2 for industrial gases. SL02 contains small CO_2 gas shows whereas the adjacent SL01 well contained no CO_2 and therefore acted as a control, against which diagenesis in VM02 can be compared.

The main Triassic reservoir varies from fine arkosic sand to microconglomerate. Total quartz content varies between 62-79%, K-feldspar 20-24%, and up to 12 % mica (Figure 2a). In addition, variable amounts of albite (up to 13 %), dolomite (up to 31 %) and anhydrite (up to 18 %) occur in some samples. A detrital clay matrix infills porosity in some horizons towards the base of the unit, where its presence inhibits both development of other cements such as quartz overgrowths, dolomite and ankerite described below and also inhibits development of secondary porosity.

Early minor fracturing of coarser grains through compaction was followed by minor quartz and feldspar cementation as euhedral overgrowths developing into open primary porosity. Pore-lining dolomite forms isolated crystals and may pre-date quartz overgrowths in some cases. Much of the remaining primary porosity is subsequently infilled by pore-filling quartz, dolomite and poikilotopic anhydrite cement. Fractures that cross-cut the reservoir are also mineralised by this assemblage. The preservation of secondary porosity from K-feldspar dissolution (Figure 2b) would suggest that this dissolution event post-dates anhydrite formation. Indeed, anhydrite and dolomite are subsequently corroded with extensive removal in some areas. Minor kaolinite precipitation, through feldspar alteration, may post-date anhydrite corrosion. Later barite (Figure 2b) and Mn,Fe-rich dolomite, associated with mineralised veining, infills some of this secondary porosity. The barite is closely associated with feldspar dissolution.

K-feldspar, dolomite and anhydrite are corroded in all three wells. However, in VM02, where the reservoir contains CO_2, K-feldspar, anhydrite and dolomite corrosion is more extensive. In addition, kaolinite is more commonly developed in secondary porosity associated with the K-feldspar dissolution in VM02.

In addition to the reservoir itself, fluid inclusions within late calcites that mineralise open fractures (Figure 2c) that lie above the main reservoir, principally in Hettangian Limestones, reveal that they have acted as conduits for CO_2

migration out of the reservoir. These CO_2-rich fluids also transported hydrocarbons, which are observed in the same fluid inclusions (Figure 2d).

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References

Arthaud, F., Dazy, J. and Grillot, J.C., 1994. Distribution of Deep Carbon-Dioxide in Relation to the Structure and Tectonic Evolution of South-East France. Geodinamica Acta, 7(2): 86-102.
Razin, P. et al., 1996. Stratigraphic record of the structural evolution of the western extensional margin of the Subalpine Basin during the Triassic and Jurassic, Ardeche, France. Marine and Petroleum Geology, 13(6): 625-652.

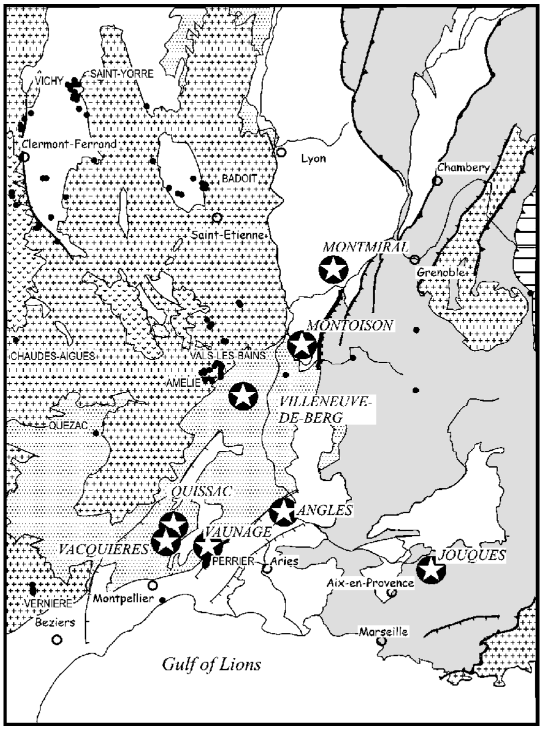

Figure 1: CO_2 accumulations within the Southeast Basin of France and CO_2-rich springs in the Massif Central.

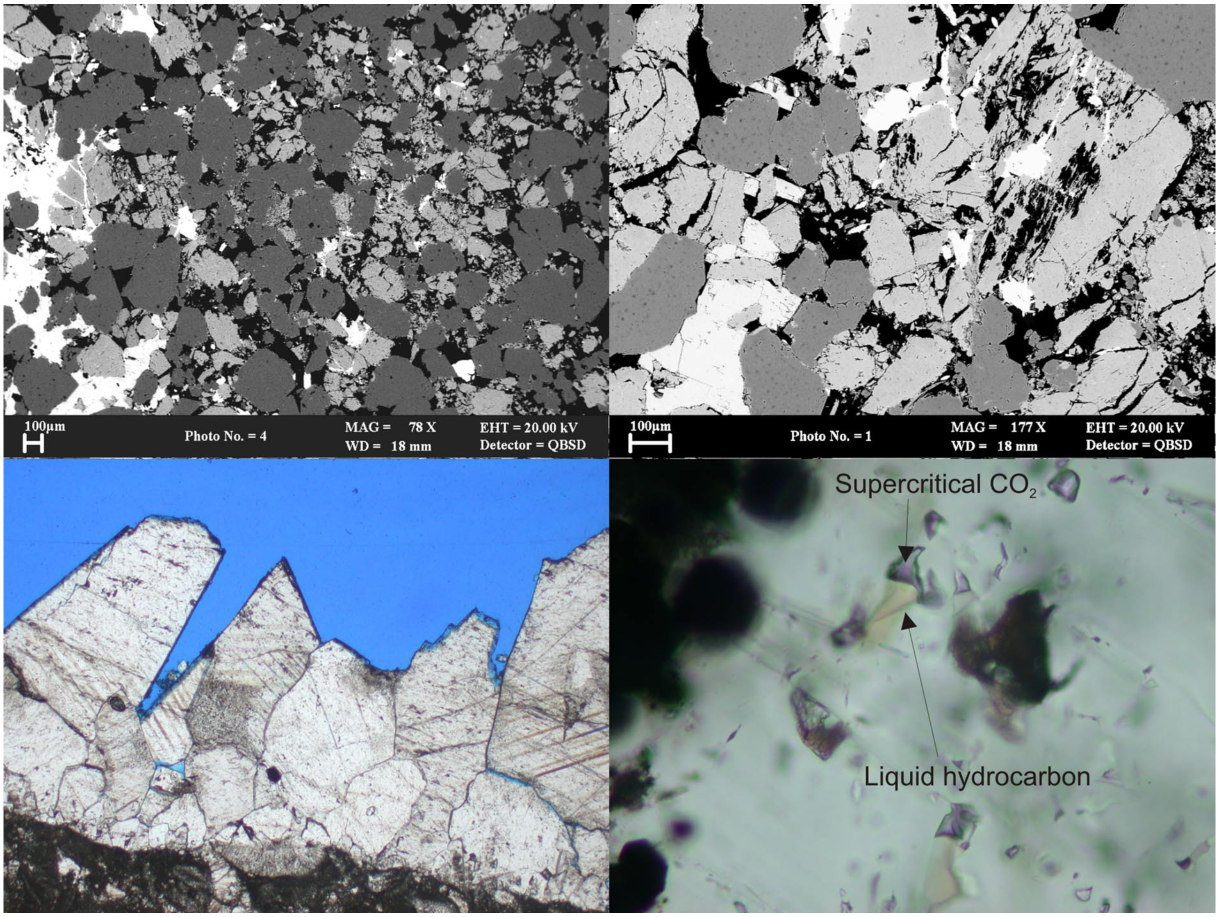

Figure 2a: Typical BSEM view of Sandstone in VMO2 (2431.3 m) with K-feldspar dissolution, secondary porosity development and mineralisation by barite.
Figure 2b: Detailed view of corroded K-feldspar with barite partially infilling secondary porosity.
Figure 2c: Typical euhedral late calcite mineralisation lining open fractures.
Figure 2d: A fluid inclusion, seen in the late calcite of 2c, that contains both supercritical CO_2 and hydrocarbons.