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# Geochemical assessment of the injection of $CO_2$ into Rousse depleted gas reservoir. Part I: Initial mineralogical and geochemical conditions in the Mano reservoir

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**Abstract**

Geochemical modeling of the $CO_2$ injection into the Rousse depleted gas reservoir (Lacq $CO_2$ injection pilot, France) requires an accurate knowledge of initial mineralogical and geochemical conditions in the formation.

Therefore, the primary objective of this work was to provide a detailed mineralogical and chemical composition of the Rousse reservoir (Mano dolomite), and accurate relative mineral proportions. This was achieved by use of a combination of techniques including in-house developed methodology for bulk rock quantitative mineralogy and complementary approaches such as optical microscopy, SEM-Quantax (chemical mapping) and Electron Miroprobe Analysis (mineral chemical composition).

Particular attention was paid the minute amounts of chlorite occurring in the reservoir, in order to obtain its exact chemical composition and textural habitus. The chlorite revealed to be Mg-rich and of a sudoite-like nature. As a consequence the initial geochemical model, which assumed the chlorite to be Fe-rich was corrected, so as to ensure more accurate reactive geochemical modeling.

A refined quantitative mineralogy and chemical composition of the Rousse reservoir (Mano dolomite), fulfilling thermodynamic equilibrium at initial conditions (150°C, 480bar), is provided.

## 1. Introduction

TOTAL is presently conducting the Lacq $CO_2$ injection pilot, which is the first French pilot to demonstrate the technical feasibility and reliability of an integrated $CO_2$ capture, transport, injection and storage scheme from a boiler at a $1/10^{th}$ scale compared to a real industrial project.

The reservoir formation selected for geological storage is the Late Jurassic Mano Dolomite. It is a depleted gas reservoir occurring at ca. 4.5km depth (4.2 km MSWL) in the field of Rousse in south-

western France and is referred to as the Rousse reservoir. Initial pressure was 480bar at discovery time and near 30bar at the end of the production period. $CO_2$ injection started in January 2010 in the RSE-1 well, the only well in the field to have penetrated the Rousse reservoir.

In 2008-2009 a preliminary geochemical modeling study was performed on the basis of limited mineralogical data for the Rousse reservoir [1]. The results indicated that $CO_2$ injection would have a minor impact on porosity and mineralogy, and highlighted as a possible reaction path according to which Fe-rich chlorite, if present, would dissolve to form siderite, thereby enabling $CO_2$ mineralization. In order to verify the likely-hood of such a scenario and quantify its impact on reservoir transformation, new petrographical and mineralogical characterization was conducted so as to refine the bulk quantitative mineralogical composition of the Rousse reservoir and establish the mineralogical and chemical composition of the chlorite occurring in the reservoir. Because chlorite is only present in trace amounts, the latter objective was particularly challenging.

## 2. Samples and analytical techniques

All samples investigated in this study come from well RSE-1 in which the Rousse reservoir (Mano dolomite) is 121m thick, with about 70m of core available. A total of 11 samples, ranging from 4577.25 to 4636.10m depth, were analyzed for mineralogy and petrography.

Bulk quantitative mineralogy was performed using an in-house developed methodology which provides accurate and robust mineralogical compositions. It is based on a fully integrated approach reconciling mineralogical, chemical and physical measurements obtained from X-Ray Diffraction (bulk and clay mineralogy), X-Ray Fluorescence (chemical composition), Picnometry (density), Cation Exchange Capacity (clay types), Insoluble Residue to HCl treatment (silicates), Loss On Ignition (water, organics, sulfides), Leico (insoluble organic matter). The methodology relies on iterative adjustments of mineral proportions (and chemical formula) until satisfactory matching of computed and measured values is obtained for a suite of 15 parameters ($Na_2O$, $MgO$, $SiO_2$, $Al_2O_3$, $K_2O$, $CaO$, $Fe_2O_3$, $TiO_2$, $BaO$, $MnO$ and $P_2O_6$, LOI, IR, , CEC). Quantification is valid when satisfactory match is achieved for all parameters and all samples treated as one dataset. Quality control is ensured by perfect matching of density values.

Refined characterization of clay minerals was achieved by performing XRD analyses of the <5µm and <1µm size separates, and applying standard chemical/heating treatments. Particular emphasis was placed on the characterization of the chlorite component, which chemical composition was obtained by use of SEM-Quantax (Scanning Electron Microscopy equipped with a Quantax XRF detector allowing spot chemical analysis and elemental mapping) and by Electron Microprobe Analysis (EMPA) in thin sections.

Mineral distribution and textural habitus were described by examination of petrographical thin sections by conventional optical microsopy and by SEM-Quantax chemical mapping.

## 3. Mineralogical and petrographical characteristics of the Rousse reservoir

### 3.1. Bulk mineralogy

Nine samples, covering a 60m depth interval, were analyzed for bulk mineralogy according the Total's procedure outlined above. The selected samples include the two main sedimentary facies recognized in the reservoir, i.e. dolomudstones and oolithic dolomites [1]. Results indicate the Rousse reservoir has a very consistent mineralogical composition (Table 1, Fig. 1).

Table 1.  Mineralogy of the Rousse reservoir (Mano dolomite)

| Mineral | range mass % | average mass % |
|---|---|---|
| Dolomite | 84-98 | 93.5 |
| Calcite | 0-4 | 0.5 |
| Quartz | 1-4 | 2.5 |
| Pyrite | 0-2 | 0.4 |
| Illite + I/S | 1-5 | 2.5 |
| Chlorite | 0-1 | 0.3 |
| Apatite | 0-1 | 0.2 |
| IOM | <<1 | 0.1 |

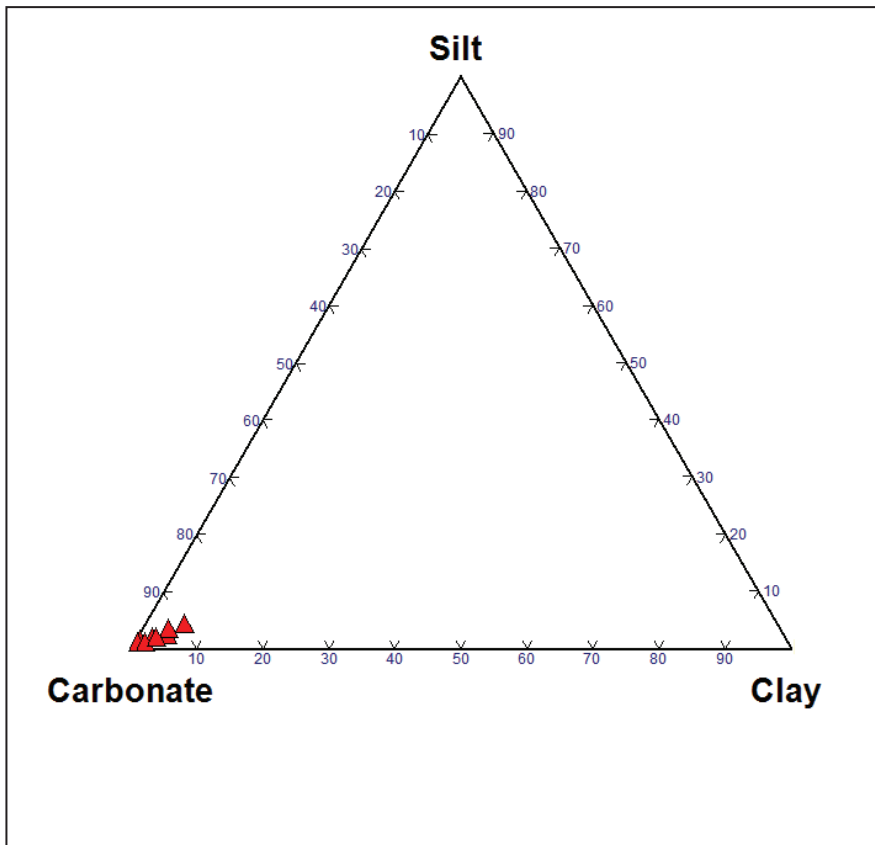IOM: Insoluble Organic Matter



Fig. 1.  Composition of the Rousse reservoir (Mano dolomite) in ternary coordinates

### 3.2. Petrography and mineral distribution

Examination of thin sections by optical microscopy and chemical mapping by SEM-Quantax permitted to characterize the textural habitus of the different minerals present in the reservoir. Main features are illustrated in Fig. 2.

The dolomite mainly occurs as a dolomicrosparitic or dolosparite continuous matrix constituting the bulk of the rock. Dolomite also occurs as sparitic saddle dolomite, slightly Fe-rich, in fractures and fissures crosscutting the reservoir. Dolomite-filled fractures are a common feature of the Rousse reservoir.

The calcite is exclusively found as filling thin microfractures and fissures, post dating saddle dolomite. This late generation of fractures is very heterogeneous in the reservoir, and often absent.

Quartz occurs as silt-size detrital grains disseminated in the dolomite matrix. Apatite which was not distinctly observed but certainly occurs as silt grains as well.

Pyrite occurs as framboidal aggregates or neoformed cubic crystals within the dolomite matrix, or as microfissures.

Illitic clays (illite and I/S) are found as microcristals disseminated in the dolomite matrix, mainly along joints between crystals or as local small-sized clay aggregates. Illitic clays are not observed in fractures.

Chlorite is essentially found along fracture walls at the interface between saddle dolomite cement and dolosparitic matrix. It forms an irregular discontinuous lining of chlorite crystals of authigenic origin, and post-dating the dolomite fill. It is also sporadically found as small aggregates in the dolomite matrix.

### 3.3. Chlorite chemical composition

Despite its low abundance, chlorite is a critical mineral phase to be taken into account in the geochemical modeling of $CO_2$ injection, because the following reaction can take place as a result of pH increase [1] :

$$\text{Chlorite-Fe} + CO_2 \implies \text{Siderite} + \text{Quartz} + \text{Kaolinite}$$

This reaction is of importance because it would lead to $CO_2$ sequestration as solid siderite.

The refined XRD analysis of the <1µm clay size fraction of Rousse reservoir samples suggested that chlorite occurring in the reservoir was mainly of a magnesian type. However, precise determination of its chemical composition was achieved by use of two different techniques:

1) SEM-Quantax spot analyses  (10 analyses)
2) Electron Microprobe Analysis (EMPA)   (24 analyses)

Both techniques were applied to the chlorite occurring as fracture lining in one sample of the Rousse reservoir. They yielded consistent chemical compositions, indicating the chlorite is exclusively of magnesian composition (Table 2), with the following average chemical formulae :

$$[ Si_{3.8} Al_{0.2} ] ( Al_{3.2} Mg_{1.3} ) O_{10} (OH)_8$$

The Rousse chlorite is a di-trioctahedral chlorite which composition is close to a sudoite. It shows however greater Si, lower Mg and greater octahedral vacancy than stoicchiometric sudoite.

The quantitative bulk mineralogy of the Rousse reservoir was recalculated using the above chemical composition for the sudoite-like chlorite. The impact on the calculated bulk abundance of chlorite in the Rousse reservoir is not significant.
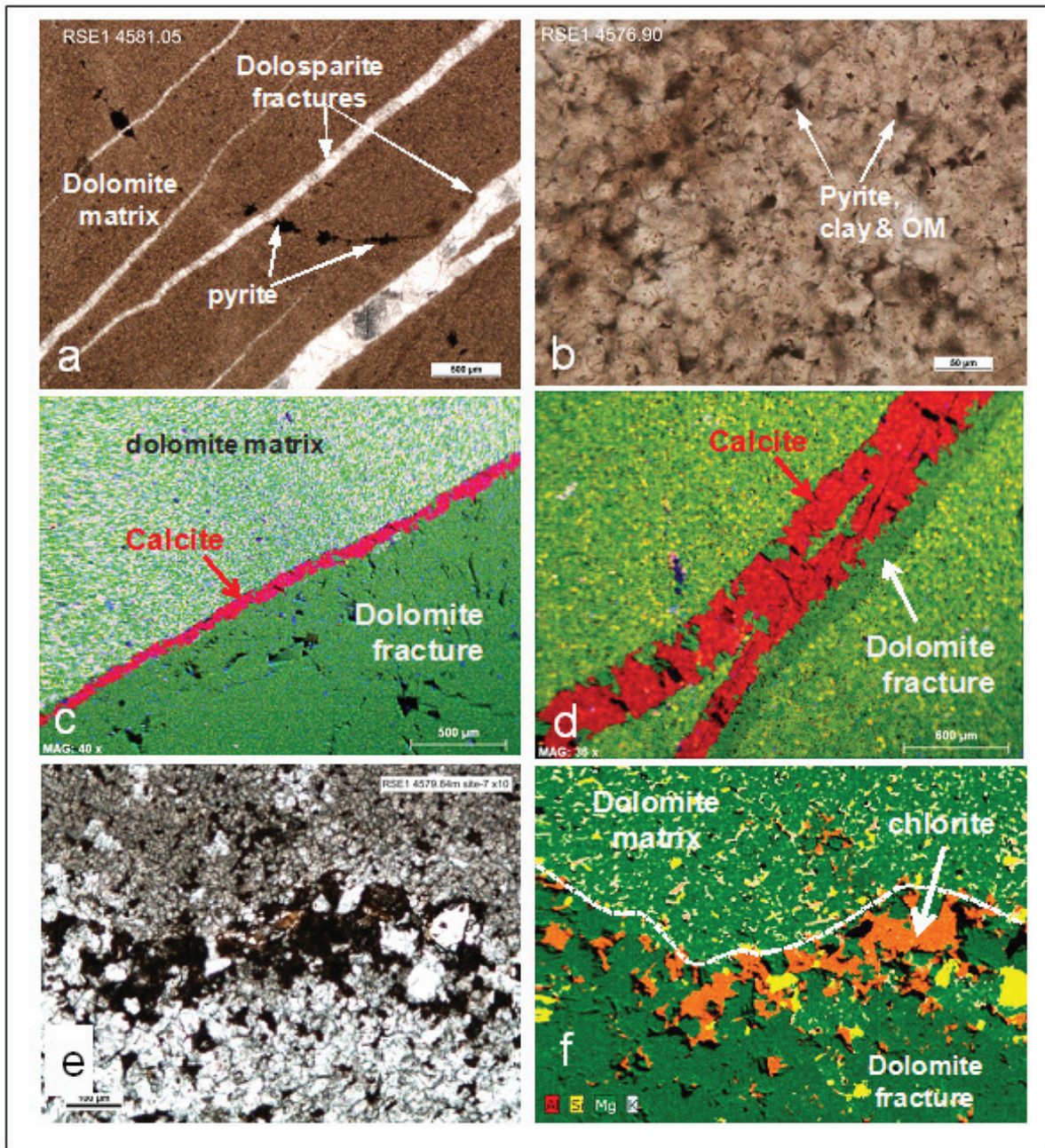
Fig. 2. Petrographic features and mineral distribution in the Rousse dolomite reservoir. (a) Typical dolomudstone crosscut by dolomite-filled fractures (plane light, optical microscope) (b) Detail of dolomite microspariric matrix (plane light, optical microscope), (c) Detail of dolomite fracture-fill and late calcite (SEM-Quantax mineral map), (d) Calcite fracture developed within a preexisting dolomite fracture (SEM-quantex mineral map), (e) and (f) Neoformed chlorite along fracture wall ((e) optical microscope microphotographs, (f) SEM chemical map).

Table 2. Chemical composition of the chlorite in the Rousse reservoir

| Chlorite formulae | EMPA (n=14) | SEM-Quantax (n=10) |
|:---:|:---:|:---:|
| Si | 3.7 | 3.8 |
| Al (IV) | 0.3 | 0.2 |
| (IV) | 4 | 4 |
| Al (VI) | 3.1 | 3.3 |
| Fe | - | - |
| Mg | 1.4 | 1.3 |
| Mn | - | - |
| Ti | - | - |
| (VI) | 4.5 | 4.6 |
| Vacancy VI | 1.5 | 1.4 |
| O | 10 | 10 |
| (OH) | 8 | 8 |

## 4. Initial thermodynamic equilibrium modeling

The new information derived from the refined characterization of the reservoir, in particular regarding the nature of the chlorite, is to used in the geochemical modeling of processes taking place during $CO_2$ injection. The results of the reactive geochemical modeling are presented in a detailed companion paper [2]. However the definition of the initial thermodynamic equilibrium model (reservoir and aqueous phase) at initial conditions (150°C, 480 bar) is reported below.

All thermodynamic runs were performed using the CHESS software, which uses a thermodynamic database derived and modified after the EQ3/6 database, and the B-dot activity model. Runs were performed following a procedure similar to that described in [1].

The mineral assemblage and their chemical formula used for thermodynamic modeling runs was first considered as follows:

- Dolomite-ordered: $CaMg(CO_3)_2$
- Calcite: $CaCO_3$
- Quartz: $SiO_2$
- Muscovite: $(Si_3Al) KAl_2 O_{10} (OH)_2$ (i.e. illite end-member)
- Montmorillonite-Na: $Si_4(Al_{1.67} Mg_{0.33} Na_{0.33}) O_{10} (OH)_2$ (i.e. smectite end-member in I/S)
- Sudoite-Rse: $(Si_3 Al_{0.2})(Al_{3.2} Mg_{1.3}) O_{10} (OH)_2$

Thermodynamics properties of the Sudoite-like chlorite in the Rousse reservoir (referred as sudoite-Rse from there on) identified in the reservoir were estimated from its measured chemical composition and appropriate correlations in the solid solution thermodynamic model for chlorite of [3]. Being authigenic and among the latest minerals formed in the Rousse reservoir, the observed sudoite-Rse chlorite is considered to be stable (or oversaturated) in reservoir conditions. Sensibility runs were performed using different values of logK. Results indicated that all minerals species are close to equilibrium only if the sudoite-Rse logK is set equal to 3.5, i..e a much higher value than that of 0.54 derived from Chess calculations at 150°C-480bar. In order to circumvent this problem, it was decided to use the reference sudoite implemented in Chess as an equivalent to the sudoite-Rse, as both chlorites have rather close

thermodynamic properties. In this case, all minerals species of interest revealed stable, i.e., in thermodynamic equilibrium with the aqueous phase (SI0), at all pH conditions between 4 and 7.5 following a minor adjustment of the logK value (10.5 instead of 11.9).

Based on the results above, the speciation of the reservoir pore water in equilibrium with the Rousse dolomite mineral assemblage (Dolomite-ord, calcite, quartz, muscovite, montmorillonite-Na, sudoite)  at initial conditions (150°C, 480bar) was modeled. An initial pH value of 4.9 was used in order to obtain a $Na^+$ concentration of ~1 molal (water salinity in reservoir is 1.2 molal NaCl).  $[CO_2]$ and $[H_2S]$ were set to values of 0.0826 and 0.0414 molal (mol/kg water).

Table 3 below provides the mineralogy and the mineral proportions considered to be representative of the Rousse reservoir system in initial conditions (150°C, 480bar), to be used as starting point for subsequent reactive geochemical modeling [2].

Table 3.  Initial mineralogy and mineral proportions in the Rousse reservoir to be used as reference for reactive geochemical modelling.

| Mineral | Formulae | %mass | M (g/mol) | %mol | %mass | mol/kg water | mol/m³ rock |
|---|---|---|---|---|---|---|---|
| Dolomite-ord | $CaMg(CO_3)_2$ | 93.6 | 184.40 | 89.77 | 93.69 | 1567.67 | 14109.94 |
| Calcite | $CaCO_3$ | 0.5 | 100.09 | 0.95 | 0.54 | 16.59 | 149.31 |
| Quartz | $SiO_2$ | 2.5 | 60.08 | 7.42 | 2.52 | 129.55 | 1165.95 |
| Pyrite | $FeS_2$ | 0.4 | 119.98 | 0.53 | 0.36 | 9.28 | 83.51 |
| Apatite | $Ca_5F(PO_4)_3$ | 0.2 | 504.30 | 0.08 | 0.23 | 1.40 | 12.60 |
| Sudoite | $(Al_3Mg_2)(Si_3Al)O_{10}(OH)_2$ | 0.3 | 536.84 | 0.05 | 0.14 | 0.83 | 7.47 |
| Muscovite | $(KAl_2)(Si_3Al)O_{10}(OH)_2$ | 0.8 | 398.31 | 0.35 | 0.80 | 6.19 | 55.75 |
| Montmorillonite-Na | $(Al_{1.67}Na_{0.33}Mg_{0.33})Si_4O_{10}(OH)_2$ | 1.7 | 367.02 | 0.83 | 1.71 | 14.41 | 129.71 |

## Acknowledgements

## References

[1] Thibeau S, Chiquet P, Mouronval G, Lescanne M. Geochemical modeling assessment of the injection of CO2 into Rousse depledted gas reservoir. *Energy Procedia 1 (2009) 3383-3390.*

[2] Chiquet P, Gunawan S, Thibeau S, Lescanne M, Hi-Billiot. Geochemical assessment of the injection of CO2 into Rousse depleted gas reservoir. Part II: geochemical impact of the CO2 injection. *Energy Procedia, this issue( 2012).*

[3] Holland TJB, Powell R. An enlarged and updated internally consistent thermodynamic dataset with uncertainties abd correlations: the system K2O-Na2O-CaO-MgO-MnO-FeO-Fe2O3-Al2O3-TiO2-SiO2-C-H2-O2.  *J. Metamorphic Geology 8 (1998) 89-124.*