

# From Injectivity to Integrity Studies of CO2 Geological Storage

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Dossier

$CO_2$ Storage in the Struggle against Climate Change
Le stockage du $CO_2$ au service de la lutte contre le changement climatique

# From Injectivity to Integrity Studies of $CO_2$ Geological Storage

## Chemical Alteration Effects on Carbonates Petrophysical and Geomechanical Properties

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**Résumé — Caractérisation de l'injectivité et de l'intégrité d'un stockage géologique de $CO_2$ : effets d'une altération chimique sur les propriétés pétrophysiques et géomécaniques des roches carbonatées** — La réussite technique et économique d'un projet de stockage géologique de $CO_2$ repose sur le maintien des propriétés d'injectivité et d'intégrité du site pendant sa durée de vie. Contrairement à l'injection d'un gaz d'hydrocarbure standard, l'injection de $CO_2$ implique des réactions géochimiques entre la saumure réactive mobile et les roches en place (réservoir et couverture) conduisant à des modifications de leurs propriétés pétrophysiques et géomécaniques. Cet article souligne les difficultés expérimentales soulevées par la faible perméabilité des échantillons représentatifs de la couverture ou tout au moins de zones de transition entre le réservoir et la couverture effective.

Les effets de l'acidification induite par l'injection de $CO_2$ ont été étudiés à l'aide d'une procédure expérimentale d'altération chimique, qui garantit un profil de dissolution homogène des échantillons de roche et évite en particulier tout développement de chenaux de dissolution (« wormholes ») qui conduirait inévitablement à des mesures erronées à l'échelle de l'échantillon. La porosité, la perméabilité et les propriétés géomécaniques d'échantillons de carbonates provenant de carrières ou de sites potentiels ont été mesurées dans leur état d'origine et à différents niveaux d'altération. Ce travail a été conduit au sein des projets ANR GéoCarbone-INJECTIVITE et GéoCarbone-INTEGRITE. Chacune des étapes expérimentales : altération chimique, mesure des propriétés pétrophysiques et caractérisation géomécanique, est traitée sous l'angle de l'injectivité et de l'intégrité. Les données expérimentales obtenues montrent de nettes tendances d'affaiblissement mécanique sous l'effet d'une altération chimique.

***Abstract* — *From Injectivity to Integrity Studies of $CO_2$ Geological Storage: Chemical Alteration Effects on Carbonates Petrophysical and Geomechanical Properties*** — *The technical and economical success of a $CO_2$ geological storage project requires the preservation of the site injectivity and integrity properties over its lifetime. Unlike conventional hydrocarbon gas injection, $CO_2$ injection implies geochemical reactions between the reactive brine and the in situ formations (reservoir and cap rock) leading to modifications of their petrophysical and geomechanical properties. This paper underlines the experimental difficulties raised by the low permeability of samples representative either of the cap rock itself or at least of transition zones between the reservoir and the effective cap rock.*

*Acidification effects induced by $CO_2$ injection have been studied using an experimental procedure of chemical alteration, which ensures a homogeneous dissolution pattern throughout the rock sample and especially avoids any wormholing process that would lead to erroneous measurements at the core scale. Porosity, permeability and geomechanical properties of outcrop and field carbonate samples of various permeability levels have been measured under their native state and different levels of alteration. The present work has been conducted within the framework of ANR GeoCarbone-INJECTIVITY and GeoCarbone-INTEGRITY projects. Each experimental step: chemical alteration, petrophysical measurements and geomechanical testing, is considered from the point of view of injectivity and integrity issues. The obtained experimental data show clear trends of chemically induced mechanical weakening.*

## NOMENCLATURE

### Latin letters

| | |
|---|---|
| $G$ | Shear modulus |
| $K_o$ | Drained bulk modulus |
| $p'$ | Terzaghi's effective mean stress |
| $p_c$ | Confining pressure |
| $p_p$ | Pore pressure |
| $q$ | Deviatoric stress |

### Greek letters

| | |
|---|---|
| $\varepsilon_a$ | Axial strain |
| $\varepsilon_r$ | Radial strain |
| $\varepsilon_d$ | Deviatoric strain |
| $\varepsilon_v$ | Volumetric strain |
| $\sigma_a$ | Axial stress |

### Acronyms

| | |
|---|---|
| HU | Hounsfield Unit |
| NMR | Nuclear Magnetic Resonance |
| PU | Porosity Unit |
| RAT | Retarded Acid Treatment |

## INTRODUCTION

$CO_2$ deep geological storage is extensively investigated as an efficient way to prevent $CO_2$ release into the atmosphere and reduce consecutive greenhouse effect. Whether considered in a deep aquifer or a waterflooded depleted oil reservoir, ensuring injectivity and integrity over the lifetime of such storage operations is essential for their technical and economical successes. When injected in the reservoir, $CO_2$ dissolves into the brine and forms a weak acid likely to react with the host rock and adjoining formations, including the cap rock. The associated dissolution/precipitation mechanisms induce changes in the rock properties, among which its petrophysical and geomechanical characteristics.

Considered injection depths involve bottomhole pressure and temperature causing $CO_2$ to exist in supercritical state. As injection goes on, the reservoir area around the injection well is expected to present different zones according to the saturation state. Close to the well, the pore fluid should be exclusively gaseous $CO_2$. As one moves away from the well, a mixture of supercritical $CO_2$ and acidified brine would then be gradually encountered. Even farther, the host rock should be saturated with an acidified aqueous $CO_2$ solution, before reaching a remote unaffected zone (André *et al*., 2007). Once present in the reservoir, $CO_2$ may enter the cap rock in gaseous state if the gas pressure exceeds the cap rock entry pressure or in dissolved state through diffusion processes.

This paper gathers experimental results obtained within the ANR GeoCarbone-INJECTIVITY and GeoCarbone-INTEGRITY projects (Lombard *et al*., 2007a; Fleury, 2007; Bemer, 2008). The aim was to study the effects of $CO_2$ injection on the poromechanical properties of reservoir and cap rocks from the Paris Basin, where the potential for setting up a $CO_2$ storage pilot site is extensively studied (Brosse *et al*., 2007). The present work was devoted to dissolution phenomena and did not considered desiccation effects possibly induced by gaseous $CO_2$. Only carbonate formations, more sensitive to acid dissolution and thus regarded as an unfavorable case, were studied as host rocks. Effective cap rocks in the Paris Basin mainly consist in Callovo-Oxfordian argillites. As well preserved cores from this formation were not available, the tests were conducted on field samples from a transition zone corresponding to a highly compact carbonate, which could act as a natural barrier to $CO_2$ progression.

In the near wellbore area, high flow rates and unbalanced geochemical reactions should lead to localized dissolution patterns such as wormholes growth (Bazin, 2001; Egermann *et al*., 2005). $CO_2$ effects are expected to be more homogeneous farther from the well (André *et al*., 2007). Since conducting hydromechanical tests requires samples which could be considered as representative elementary volumes, the experimental characterization of altered rock poromechanical properties should be restricted to far field issues.

At the laboratory scale, co-injecting supercritical $CO_2$ and brine, or directly injecting $CO_2$ saturated brine, leads to the growth of ramified extended channels at high flow rates (numerous pinholes evenly distributed over the injection face), and to more compact dissolution patterns at low flow

rates (limited number of large holes localized at the injection face), both resulting in non homogeneous samples and thus preventing their characterization through standard triaxial tests (Bazin, 2001; Egermann *et al*., 2005). IFP has developed a chemical alteration method which ensures a uniform dissolution pattern and especially avoids any wormholing process (Egermann *et al*., 2006). This alternative method implies acidification processes which do not actually involve $CO_2$. Further work will include an accurate comparison between the chemical effects induced by the used acid solution and $CO_2$ injection.

This paper first presents the studied carbonate rocks and their initial petrophysical properties. The alteration method is then thoroughly described with special emphasis on the time required to reach the chosen alteration level according to the sample permeability. The induced variations in petrophysical properties are given for each studied formation. Mechanical loading is likely to induce excess pore pressure generation for low permeability samples. Hence, a specific procedure, which aims at assessing the pore pressure variation within the sample, has been followed to carry out the geomechanical tests. The results obtained on intact samples are presented to illustrate the behavior of the samples in their native state. Data on altered samples and trends for the evolution of geomechanical properties induced by chemical alteration are then given. Triaxial test results notably show that altered samples have undergone a decrease in stiffness and shear strength. Finally, the magnitude of the measured geomechanical properties weakening between intact and altered reservoir and cap rock samples is compared to the variation which would be expected between two natural samples of the same rock type and with similar porosity difference.

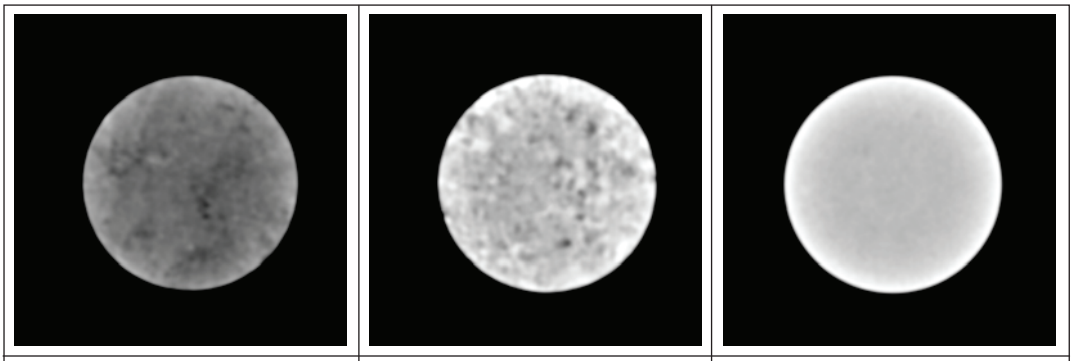
## 1 STUDIED CARBONATE FORMATIONS

Figure 1 shows CT-scanner images of samples from the studied carbonate formations. Comblanchian and Lavoux limestones correspond to potential host rocks for $CO_2$ injection, while transition zone limestone is regarded as a permeability barrier between the reservoir and the effective cap rock.

Comblanchian limestone comes from Charmottes field located in the Paris Basin and was supplied by Toreador oil company. Six samples were available for geomechanical testing (coring depth of 1820 meters), with a mean porosity of 14.7% ± 0.8% and a steady-state brine permeability ranging from 2 to 20 mD (see *Tab. 1*). Comblanchian limestone is composed of roughly 85% calcite, 5% dolomite and 10% quartz.

Lavoux limestone comes from a Dogger outcrop and is considered as an analog of the White Oolite formation of the Paris Basin. Several blocks were supplied. Their porosity ranges from 16 to 22% and their steady-state brine permeability from 150 to 250 mD. The samples were divided into two porosity classes: Class 1 (C1) samples have a mean porosity of 17.3% ± 0.9% (5 samples from block 1) and Class 2 (C2) samples a mean porosity of 20.6% ± 1.0% (5 initial samples from block 1, 6 samples from block 2 and 2 samples from block 3) (see *Tab. 1*). Lavoux limestone is almost exclusively made of calcite.

Transition zone samples also come from Charmottes field by courtesy of Toreador Oil Company. Five samples were available for geomechanical testing. As the coring depth is comprised between 2004 and 2011 meters, these samples are expected to encompass the vertical intrinsic dispersion of the formation. Porosities deduced from the difference between the



| Lavoux limestone<br>Sample C2 3<br>1450-2200 HU(1) | Comblanchian limestone<br>Sample 4-1 dV<br>1450-2950 HU(1) | Transition zone carbonate<br>Sample 109-1-1 dV<br>1450-2950 HU(1) |
|---|---|---|

1 X-ray attenuations are expressed in Hounsfield Units, which characterize the relative radiodensity of an object with respect to water. Hounsfield Units range from –1000 to 4000. On this scale, –1000 corresponds to air and 0 to water. Sandstones and limestones typically show attenuations around 1300-1800 HU and 1700-2700 HU respectively. The images are reconstructed 1-mm thick cross sections. The shade of gray of each 0.12-mm pixel represents the X-ray attenuation in the corresponding voxel, the darker pixels being associated to the lower densities.

Figure 1

CT-scanner images of studied carbonate formations.

TABLE 1

Petrophysical properties of the studied carbonate samples

| Formation | Sample | Origin(1) | Porosity(2) | Permeability |
|---|---|---|---|---|
| Comblanchian | 4-1 fV | 1820.58 m | 14.4% | 2.5 mD(3) |
| Comblanchian | 4-2 aV | 1820.35 m | 14.3% | 2.1 mD(3) |
| Comblanchian | 4-1 eV | 1820.58 m | 14.3% | |
| Comblanchian | 4-1 dV | 1820.69 m | 15.5% | 17.2 mD(3) |
| Comblanchian | 4-1 cV | 1820.69 m | 15.4% | 13.8 mD(3) |
| Comblanchian | 4-2 bV | 1820.35 m | 14.2% | 2.9 mD(3) |
| C1 Lavoux | 2 | Block 1 | 18.0% | |
| C1 Lavoux | 8 | Block 1 | 16.4% | |
| C1 Lavoux | 10 | Block 1 | 18.2% | |
| C1 Lavoux | 9 | Block 1 | 17.5% | 204.9 mD(3) |
| C1 Lavoux | 4 | Block 1 | 16.5% | 173.8 mD(3) |
| C2 Lavoux | 6 | Block 1 | 20.5% | |
| C2 Lavoux | 1 | Block 1 | 19.6% | |
| C2 Lavoux | 7 | Block 1 | 20.8% | |
| C2 Lavoux | 5 | Block 1 | 19.9% | 247.6 mD(3) |
| C2 Lavoux | 3 | Block 1 | 20.0% | 166.3 mD(3) |
| C2 Lavoux | 12 | Block 2 | 19.8% | |
| C2 Lavoux | 22 | Block 2 | 20.4% | |
| C2 Lavoux | 11 | Block 2 | 21.3% | |
| C2 Lavoux | 13 | Block 2 | 21.0% | |
| C2 Lavoux | 14 | Block 2 | 21.4% | |
| C2 Lavoux | 20 | Block 2 | 21.0% | |
| C2 Lavoux | A | Block 3 | 21.4% | 207.2 mD(3) |
| C2 Lavoux | E | Block 3 | 20.8% | 251.9 mD(3) |
| Transition zone | 109-1-1 dV | 2004.19 m | 3.1% | 0.1 μD(4) |
| Transition zone | 109-2-1 bV | 2006.56 m | 5.3% | 17.6 μD(4) |
| Transition zone | 109-2-1 dV | 2006.46 m | 5.3% | 1.1 μD(4) |
| Transition zone | 109-3-2 aV | 2010.42 m | 2.2% | 0.5 μD(4) |
| Transition zone | 109-3-2 bV | 2010.42 m | 2.2% | 0.4 μD(4) |

1 Coring depth for field samples and block number for outcrop samples;
2 Deduced from the sample dry and saturated weights;
3 Brine permeability (steady-state measurement);
4 Gas permeability (steady-state measurement).

sample brine saturated and dry weights range between 2.2% and 5.4% and permeabilities obtained through steady-state gas measurements are of the order of 1 μDarcy, except for the highest porosity sample which shows a steady-state gas permeability approaching 20 μDarcy (see *Tab. 1*). Unlike Comblanchian and Lavoux limestones, the transition zone limestone includes an argillaceous fraction of about 5%, the remaining part consisting in roughly 90% calcite and 5% pyrite and gypsum.

For standard reservoir rocks, porosity is easily deduced from the difference between the sample brine saturated and dry weights. The matter is entirely different when compact argillaceous rocks are considered. Besides significantly increased test durations, bound water, either trapped in micropores or clay particles, interferes with the definition and achievement of dry state. Nuclear Magnetic Resonance (NMR) measurement gives access to the whole amount of water present in a saturated sample. Bound water thus results in NMR porosity higher than the one deduced from weight measurements. Absolute differences between NMR and weight measurements porosity values given in Table 2 are less than 0.6% (PU) for Lavoux and Comblanchian limestones. The corresponding relative differences are within 3% and can thus be disregarded. For transition zone limestone, these two porosity values deviate from more than 1% (PU). This difference increases as the porosity level decreases (see *Fig. 2*), which leads to significant relative differences lying between 20% and 70%. The acronym PU, which stands for Porosity Unit and directly accounts for one percent pore volume, is used to distinguish absolute from relative porosity differences.

## 2 HOMOGENOUS ALTERATION METHOD

IFP homogeneous alteration method is based on the injection of a retarded acid solution, which is activated only under specific temperature conditions. The experimental device and associated processes have been extensively described by Egermann *et al.* (2006). The 40-mm diameter rock sample is set in a core holder (see *Fig. 3*) and submitted to several

TABLE 2

Comparison between weight measurements, NMR and CT-scanner initial porosity values

| Formation | Sample | Weight measurements porosity | NMR porosity | CT-scanner porosity |
|---|---|---|---|---|
| Comblanchian | 4-1 fV | 14.4% | 14.4% | 14.7% |
| Comblanchian | 4-2 aV | 14.3% | 14.7% | 14.6% |
| Comblanchian | 4-1 eV | 14.4% | | 14.7% |
| Comblanchian | 4-1 dV | 15.5% | 15.8% | 16.0% |
| Comblanchian | 4-1 cV | 15.4% | 15.4% | 15.8% |
| Comblanchian | 4-2 bV | 14.2% | 14.5% | 14.7% |
| C1 Lavoux | 2 | 18.0% | | 18.4% |
| C1 Lavoux | 8 | 16.4% | | 16.8% |
| C1 Lavoux | 10 | 18.2% | | 18.5% |
| C1 Lavoux | 9 | 17.5% | 17.1% | 18.0% |
| C1 Lavoux | 4 | 16.5% | 16.4% | 17.0% |
| C2 Lavoux | 6 | 20.5% | | 20.8% |
| C2 Lavoux | 1 | 19.6% | | 20.0% |
| C2 Lavoux | 7 | 20.8% | | 21.1% |
| C2 Lavoux | 5 | 19.9% | 19.5% | 20.2% |
| C2 Lavoux | 3 | 20.0% | 19.5% | 20.5% |
| C2 Lavoux | 12 | 19.8% | | 19.5% |
| C2 Lavoux | 22 | 20.4% | | 20.0% |
| C2 Lavoux | 11 | 21.3% | | 21.0% |
| C2 Lavoux | 13 | 21.0% | | 20.7% |
| C2 Lavoux | 14 | 21.4% | | 20.9% |
| C2 Lavoux | 20 | 21.0% | | 20.6% |
| C2 Lavoux | A | 21.4% | 21.2% | 21.7% |
| C2 Lavoux | E | 20.8% | 20.8% | 21.1% |
| Transition zone | 109-1-1 dV | 3.1% | 4.4% | 3.3% |
| Transition zone | 109-2-1 bV | 5.3% | 6.4% | 4.8% |
| Transition zone | 109-2-1 dV | 5.3% | 6.4% | 4.2% |
| Transition zone | 109-3-2 aV | 2.2% | 3.6% | 2.6% |
| Transition zone | 109-3-2 bV | 2.2% | 3.7% | 2.8% |

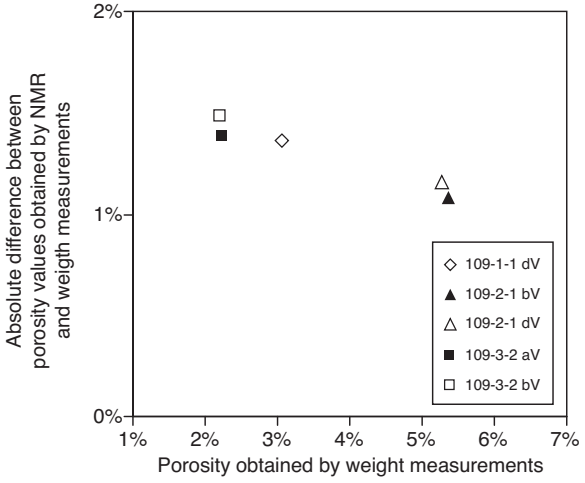



Figure 2

Absolute difference between porosity values obtained through NMR and weight measurements for transition zone samples.

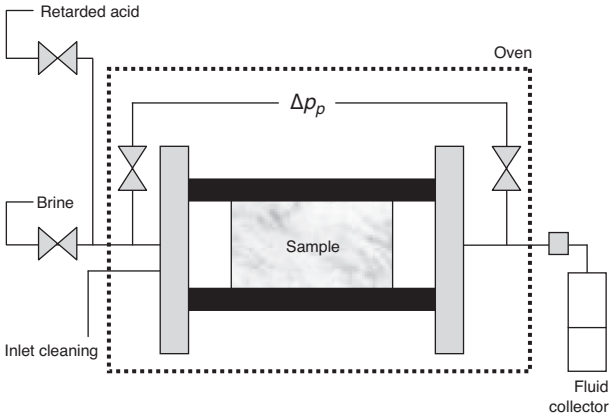



Figure 3

Experimental device for homogeneous alteration of the rock samples.

retarded acid treatments (RAT). Each alteration step includes the following stages:

– flushing of the sample with fresh retarded acid at ambient temperature (amount equivalent to about three times the sample porous volume);
– activation of the acid under temperature (60°C for at least one day);
– flushing of the sample with fresh brine at ambient temperature (amount equivalent to about three times the sample porous volume).

The number of successive RAT controls the final alteration level. Two different levels have been tested: the first one is obtained after three acid treatments and the second one after six acid treatments.

The sample petrophysical properties have been characterized before and after alteration. Porosity was obtained from brine saturated and dry weight measurements, NMR measurement and CT-scanner observation. Brine steady-state permeability was directly measured with the experimental device used for acid treatment. Note that the temperature at which the acid was activated corresponds to the heating temperature used to dry the samples for porosity measurement. As both intact and altered samples have seen this temperature, observed differences in behavior can not be attributed to thermal effects.

For standard reservoir rocks, a whole alteration step can be carried out in one day. For low permeability samples, the time required to substitute brine for acid and acid for brine becomes a major issue. To avoid too long-lasting tests, higher injection pressures have been used and fresh acid was directly injected after cooling at the end of the activation stage of the previous retarded acid treatment. On the downside, giving up the fresh brine flushing designed to properly end the alteration process led to more marked end effects (see *Fig. 4*). The damaged part has then to be cut away before carrying out the triaxial test. Considering the unfavorable case of lowest permeability sample 109-1-1 dV, 5 days were needed to complete the flushing by fresh acid and more than one month to achieve six successive acid treatments. Effective cap rocks are expected to show lesser permeability levels, which could induce a dramatic rise in test duration.



Figure 4

End effects induced by chemical alteration on transition zone samples.




Figure 5

Picture of intact and altered Lavoux limestone samples (I = Intact sample, SAT = sample submitted to a Standard Acid Treatment, RAT = sample submitted to a Retarded Acid Treatment).

## 3 VARIATION IN PETROPHYSICAL PROPERTIES INDUCED BY CHEMICAL ALTERATION

Direct observation of Lavoux samples in different states of alteration: intact, altered through standard acid injection and altered through retarded acid treatment, shows the definite improvement in external surface evenness provided by the retarded acid method (see *Fig. 5*). Except for end effects affecting the inlet face of transition zone samples, CT-scanner observation corroborates the homogeneity of the pore structure evolution (see *Fig. 6*).

Porosity values deduced from CT-scanner observation have been calculated from a correlation between measured radiation densities and data corresponding to pure calcium carbonate samples. Lavoux limestone being almost exclusively made of calcite, CT-scanner and weight measurements porosities are very close (see *Tab. 2*). Despite other minerals present in Comblanchian and transition zone formations, CT-scanner porosity proves to be consistent with the other measurements.

Table 3 gives the chemically induced increase in porosity for the whole set of altered samples. Initial porosity has systematically been deduced from weight measurements. The same applies for porosity variation of altered Comblanchian and Lavoux samples.

Due to end effects observed on transition zone samples, weight measurements and NMR methods were no more valid. Such methods provide a measure of the water content

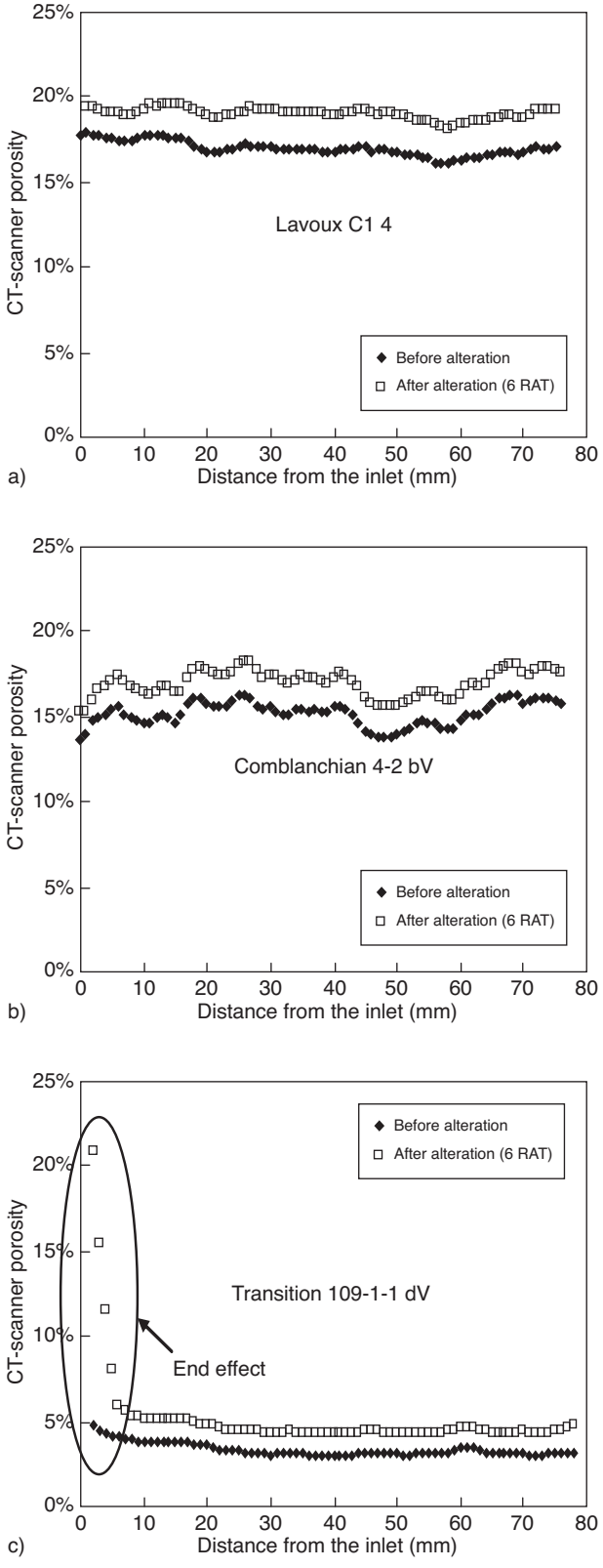



Figure 6

Example of CT-scanner porosity profiles before and after alteration (1-mm thick cross sections).

and calculate the porosity using a bulk volume determined from length and diameter measurements. Any hole created at the injection face is thus not taken into account, which amounts to underestimating the effective porosity value. As the increase in porosity was mainly caused by calcite dissolution, CT-scanner data obtained before and after alteration have been used to estimate the chemically induced porosity variation of the transition zone samples even if they were not pure calcite limestone. Only the data corresponding to the part of the sample unaffected by end effects have been considered to make this calculation. The altered porosity of transition zone samples has finally been taken as the sum of the initial porosity deduced from weight measurements and the porosity variation estimated through CT-scanner data.

For standard carbonate reservoir formations, previous work has shown that one retarded acid treatment leads to an additional porosity of approximately 0.3%-0.4% (PU) (Egermann *et al*., 2006). Three RAT should then result in about 1% (PU) additional porosity and six RAT in about 2% (PU) additional porosity. Comblanchian and Lavoux samples definitely fall into this trend (see *Tab. 3*). The two transition zone samples submitted to six RAT show a porosity increase lower than 2% (PU), the less porous sample being associated to the smaller increase. Further experimental work is in progress on a low permeability outcrop limestone to check these first results.

Figure 7 illustrates the intrinsic dispersion of samples initial porosity and compares altered porosity values with the overall intact porosity range of each studied formation. The number of applied RAT is indicated for each altered sample. Full lines mark the mean porosity and dotted lines the corresponding maximum deviation which remains below 1% (PU) for Comblanchian and Lavoux limestones. Caution will be required when considering results obtained on altered samples which show a porosity remaining in the overall intact porosity range of the corresponding formation. Transition zone samples coring depth spacing naturally results in a wider porosity range, which is only given for reference.

Permeability variations associated to observed porosity increases do not follow a clear trend (see *Tab. 4*):

– Comblanchian samples show both increase and decrease in permeability;
– Lavoux samples C1 9, C1 4, C2 5 and C2 3, show a decrease in permeability likely due to fine mobilization. As a matter of fact, Lavoux samples C2 A and C2 E, which were 20 mm shorter (60 mm long *versus* 80 mm for the others), have undergone a permeability increase;
– transition zone samples show a decrease in permeability.

$CO_2$ injection tests conducted on Lavoux samples have similarly shown both increase and decrease in permeability (Lombard *et al*., 2007b). Additional tests are needed to further investigate both fine mobilization issue and comprehensive effects of chemical alteration on permeability. This key

TABLE 3

Chemically induced increase in porosity

| Formation | Sample | Initial porosity | Number of RAT | Increase in porosity (PU) |
|---|---|---|---|---|
| Comblanchian | 4-1 dV | 15.5%(1) | 6 | 1.9%(1) |
| Comblanchian | 4-1 cV | 15.4%(1) | 6 | 1.9%(1) |
| Comblanchian | 4-2 bV | 14.2%(1) | 6 | 1.9%(1) |
| C1 Lavoux | 9 | 17.5%(1) | 4 | 1.5%(1) |
| C1 Lavoux | 4 | 16.5%(1) | 6 | 1.9%(1) |
| C2 Lavoux | 5 | 19.9%(1) | 3 | 1.0%(1) |
| C2 Lavoux | 3 | 20.0%(1) | 6 | 2.1%(1) |
| C2 Lavoux | A | 21.4%(1) | 3 | 1.1%(1) |
| C2 Lavoux | E | 20.8%(1) | 6 | 2.1%(1) |
| Transition zone | 109-1-1 dV | 3.1%(1) | 6 | 1.3%(2) |
| Transition zone | 109-2-1 bV | 5.3%(1) | 6 | 1.5%(2) |

1 Deduced from the sample dry and saturated weights;
2 Deduced from CT-scanner data variation.

TABLE 4

Steady-rate brine permeability before and after alteration

| Formation | Sample | Initial permeability | Number of RAT | Final permeability |
|---|---|---|---|---|
| Comblanchian | 4-1 dV | 17.2 mD | 6 | 16.6 mD |
| Comblanchian | 4-1 cV | 13.8 mD | 6 | 16.7 mD |
| Comblanchian | 4-2 bV | 2.9 mD | 6 | 2.8 mD |
| C1 Lavoux | 9 | 204.9 mD | 4 | 182.9 mD |
| C1 Lavoux | 4 | 173.8 mD | 6 | 154.7 mD |
| C2 Lavoux | 5 | 247.6 mD | 3 | 227.3 mD |
| C2 Lavoux | 3 | 166.3 mD | 6 | 137.8 mD |
| C2 Lavoux | A | 207.2 mD | 3 | 218.7 mD |
| C2 Lavoux | E | 251.9 mD | 6 | 304.0 mD |
| Transition zone | 109-1-1 dV | 0.3 µD | 6 | 0.1 µD |
| Transition zone | 109-2-1 bV | 11.8 µD | 6 | 3.4 µD |

petrophysical property might deeply affect the field injectivity index. Hence, its evolution under contact with a $CO_2$ saturated brine needs to be thoroughly understood.

## 4 GEOMECHANICAL CHARACTERIZATION

Geomechanical characterization of intact and altered carbonate formations has been conducted through standard triaxial tests. After drying, the cylindrical plug was equipped with three strain gauges for the axial strain measurement and three others for the radial strain measurement. The sample was then coated with an impermeable jacket and set in the triaxial device, which allowed the applying of a load in the axial direction, an all-around confining pressure and a fluid pressure at both ends (see *Fig. 8*). The jacket prevented the confining fluid from entering the sample and allowed independent control of confining and pore pressures.

The stress state in the rock sample was then axisymmetric and defined by applied axial stress $\sigma_a$, confining pressure $p_c$ and pore pressure $p_p$. As rock failure is governed by Terzaghi's effective stress (Vincké *et al.*, 1998; Boutéca and Guéguen, 1999), tests results have been studied in terms of effective mean stress $p'$ and deviatoric stress $q$:

$$p' = \frac{\sigma_a + 2p_c}{3} - p_p \quad \text{and} \quad q = \sigma_a - p_c \tag{1}$$

respectively associated with volumetric strain $\varepsilon_v$ and deviatoric strain $\varepsilon_d$:

$$\varepsilon_v = \varepsilon_a + 2\varepsilon_r \quad \text{and} \quad \varepsilon_d = \frac{2}{3}(\varepsilon_a - \varepsilon_r) \tag{2}$$

The sample was first saturated with an inert mineral oil under a small initial loading. After creating a high vacuum inside the sample, the saturating fluid has been injected under

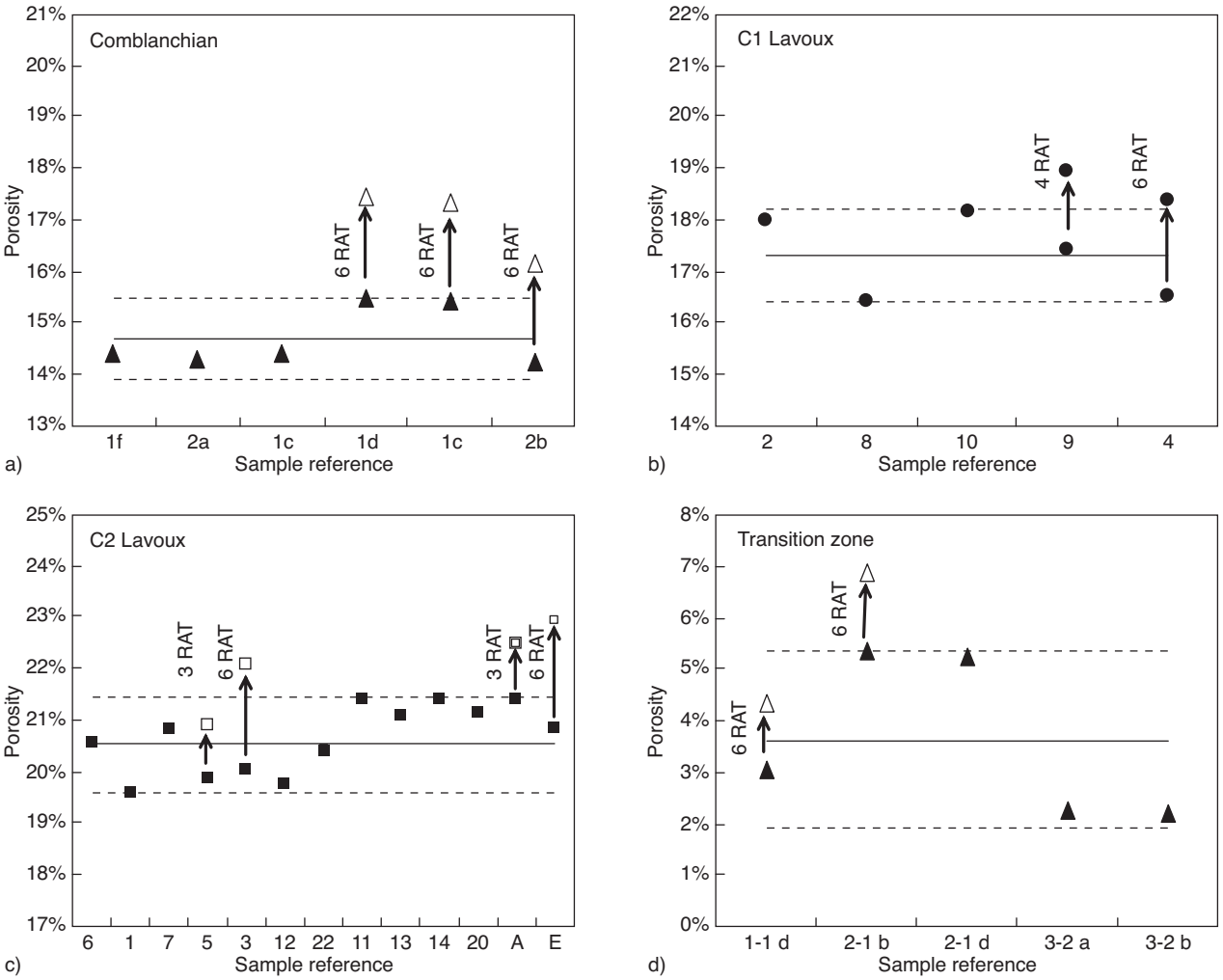



Figure 7

Sample porosity before and after alteration.

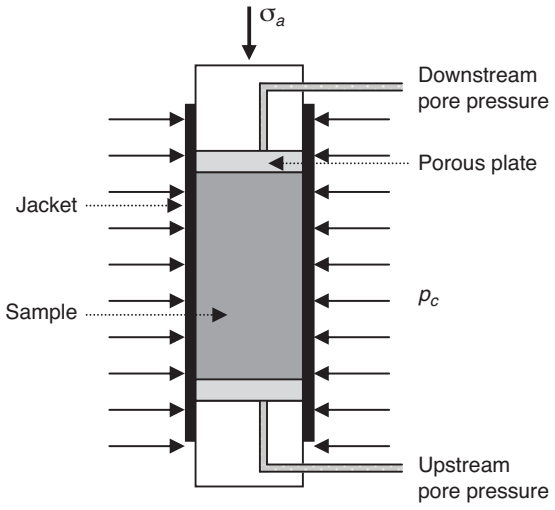



Figure 8

Principle of a triaxial test.

pressure at the upstream end, while the downstream end was kept under undrained conditions. When pore pressure equilibrium has been reached at the two faces of the sample, the downstream pressure was released several times to drive out any trapped air. Once the pore pressure was again uniform throughout the sample, an isotropic loading path (simultaneous increase of the axial stress and confining pressure at constant pore pressure) was followed until the chosen confining level was reached. The axial stress was finally increased up to the sample failure at a loading rate of 1 kN per minute, the confining and pore pressures being kept constant. According to Equation (1), the last part of the loading path should be associated with a straight line of slope 3 in *p'-q* plane. At least three tests conducted at different confining levels are required to estimate a brittle failure criterion of Drucker-Prager type (Fjær *et al*., 1992).

Such tests are conducted on a routine basis for standard reservoir rocks. However, the low permeability of transition

zone samples raised specific difficulties. First, the saturation phase lasted far longer and lower permeability samples have required a reversal of the injection direction to ensure the breakthrough of the pressure front. Direct saturation has notably been achieved within 5 days for sample 109-2-1 dV which showed a gas permeability of 1.1 μD, whereas still no pressure increase was observed at the downstream end of samples 109-3-2 aV (gas permeability of 0.5 μD) and 109-3-2 bV (gas permeability of 0.4 μD) after 8 days of injection. When pore pressure equilibrium was not reached after one week of injection, the upstream pressure was released and the downstream pressure set to the selected injection value. Following this flow reversal, the upstream pressure regained its previous value in less than one day. Several pressure releases were then carried out to improve the saturation level.

Second, the mechanical loading was likely to induce excess pore pressure generation within the sample. The assumption of homogeneous pressure field inherent to triaxial test interpretation could then be questioned. If the sample had been drained by both ends, upstream and downstream pressure transducers would have simply read the pressure set by the hydraulic pumps and no data on the pressure build-up within the sample would have been recorded. The tests have then been carried out under mixed drainage conditions: at one side, the pore pressure was set by the hydraulic pump, while the other side was kept in undrained conditions. The pressure recorded by the pressure transducer located at the undrained side acted then as an indicator of the pressure variation within the sample.

The key parameters selected to follow the effects of chemical alteration are the drained elastic moduli (drained bulk modulus $K_o$ and shear modulus $G$) and the failure point in $p'$-$q$ diagram for a given confining pressure. Drained elastic moduli have been measured during an unloading stage (decrease of the axial stress at constant confining and pore pressures). Linear poroelastic constitutive law yields (Coussy, 2004; Bemer *et al*., 2001):

$$K_o = \Delta p'/\Delta\varepsilon_v \quad \text{and} \quad 3G = \Delta q/\Delta\varepsilon_d \tag{3}$$

The failure point in $p'$-$q$ diagram corresponding to a given confining pressure has been obtained by substituting the axial stress at failure in Equation (1):

$$\left(p'\right)^F = \frac{\sigma_a^F + 2p_c}{3} - p_p \quad \text{and} \quad q^F = \sigma_a^F - p_c \tag{4}$$

With regard to transition zone samples, the effective mean stress used to assess both the drained bulk modulus and the failure point abscissa have been computed from three different pore pressure values:

- the mean pore pressure;
- the pore pressure set by the hydraulic pump;
- the pore pressure measured at the undrained side.

The two last data sets allowed the definition of error bars around $K_o$ and $(p')^F$ indicating the uncertainty in the measurements induced by the pore pressure field inhomogeneity.

Table 5 gives the followed test program, which has been defined according to the number of samples available for each formation. Additional tests have been conducted on intact C2 Lavoux samples to evaluate the rock failure properties intrinsic scattering and determine bounds for the confining pressure level corresponding to the transition between brittle and ductile failure. This transition pressure can be moderate for higher porosity samples. It is therefore essential to ensure that only confining pressure levels leading to brittle failure are considered while comparing samples intact and altered behavior.

TABLE 5

Test program defined in terms of effective confining pressure levels ($p_c' = p_c$-$p_p$) and number of retarded acid treatments

| Formation | Geomechanical tests on intact samples | Geomechanical tests on altered samples |
|---|---|---|
| Comblanchian (6 samples) | $p_c'$ = 5.2 MPa<br>$p_c'$ = 12.7 MPa<br>$p_c'$ = 20.3 MPa | 6 RAT and $p_c'$ = 5.2 MPa<br>6 RAT and $p_c'$ = 12.7 MPa<br>6 RAT and $p_c'$ = 20.3 MPa |
| C1 Lavoux (5 samples) | $p_c'$ = 0.6 MPa<br>$p_c'$ = 9.7 MPa<br>$p_c'$ = 14.7 MPa | 4 RAT and $p_c'$ = 12.7 MPa<br>6 RAT and $p_c'$ = 12.7 MPa |
| C2 Lavoux (13 samples) | $p_c'$ = 0.6 MPa<br>$p_c'$ = 5.1 MPa<br>$p_c'$ = 12.7 MPa<br>6 additional tests | 3 RAT and $p_c'$ = 12.7 MPa (2 samples)<br>6 RAT and $p_c'$ = 12.7 MPa (2 samples) |
| Transition zone (5 samples) | $p_c'$ = 5 MPa (1)<br>$p_c'$ = 12.5 MPa (1)<br>$p_c'$ = 20 MPa (1) | 6 RAT and $p_c'$ = 12.5 MPa (1) (2 samples) |

1 Effective confining pressure calculated from the applied confining and upstream pore pressures.

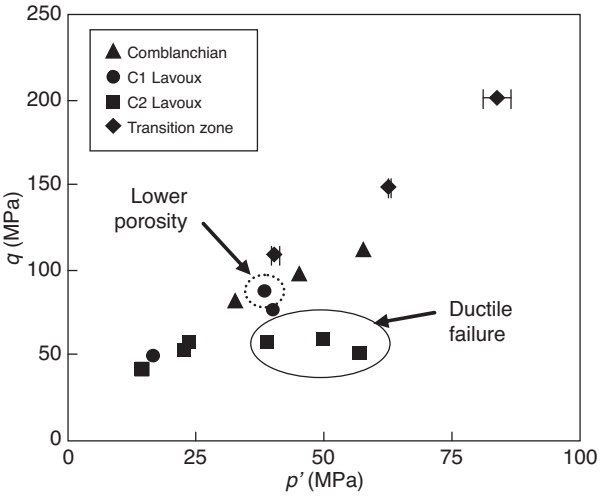



Figure 9

Failure points of intact samples.

Figure 9 gives the failure points in *p'-q* plane for the whole set of intact samples. Error bars on *p'* values plotted for transition zone samples indicate the variation range allowed by the difference between upstream and downstream pore pressures. The various formations show consistent failure behavior, samples of lesser porosity being globally stronger. Results obtained on C2 Lavoux samples denote a quite reproducible failure behavior. For these samples, brittle failure occurred for effective confining pressures less than or equal to 12.7 MPa, while ductile failure has been obtained for effective confining pressures above 20 MPa.

The reference effective confining pressures of 12.5 and 12.7 MPa taken to compare intact and altered behavior of transition zone and reservoir samples thus lies in the intact brittle failure domain of each formation. These values correspond to the effective horizontal stresses expected in the cap rock and the reservoir at the considered $CO_2$ injection depth in Saint-Martin de Bossenay field, which has been selected as a case study by ANR GeoCarbone-Picoref project (Brosse *et al*., 2007).

Full symbols in Figure 10 correspond to intact elastic moduli measured during axial unloading stages conducted at various confining pressures. Error bars added on drained bulk moduli for transition zone samples express the uncertainty associated with the pore pressure field inhomogoneity. Comblanchian and Lavoux limestones show a quite standard intrinsic scattering and elastic properties which can be considered independent of the applied confining pressure as is usual for carbonate rocks. Transition zone samples were expected to show both larger scattering due to gaps in coring depths and higher elastic moduli in accordance with their low porosity. The observed variation range is effectively wider, but the measured elastic moduli appear to be less or equal to values obtained for Comblanchian and Lavoux samples. This lower stiffness can be related to the argillaceous fraction present in transition zone samples.

## 5 VARIATION IN GEOMECHANICAL PROPERTIES INDUCED BY CHEMICAL ALTERATION

Figure 11 plots the followed stress paths and associated failure points in *p'-q* plane for intact and altered samples. Note that pore pressure variations taking place during triaxial tests on transition zone samples lead to non linear stress paths (thick lines showing the theoretical stress paths of slope 3).

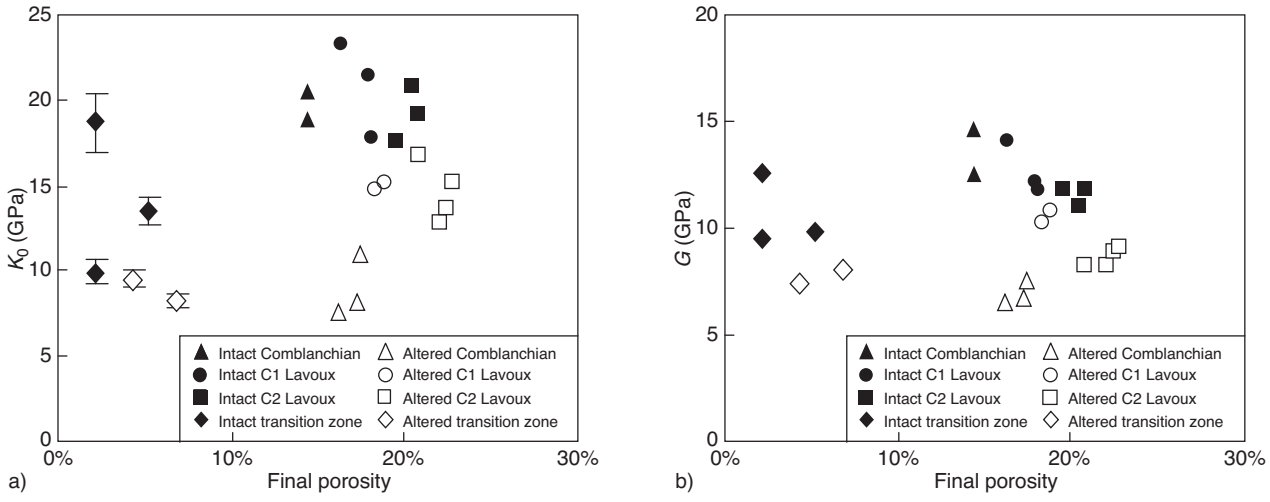



Figure 10

Drained elastic moduli of intact and altered samples.

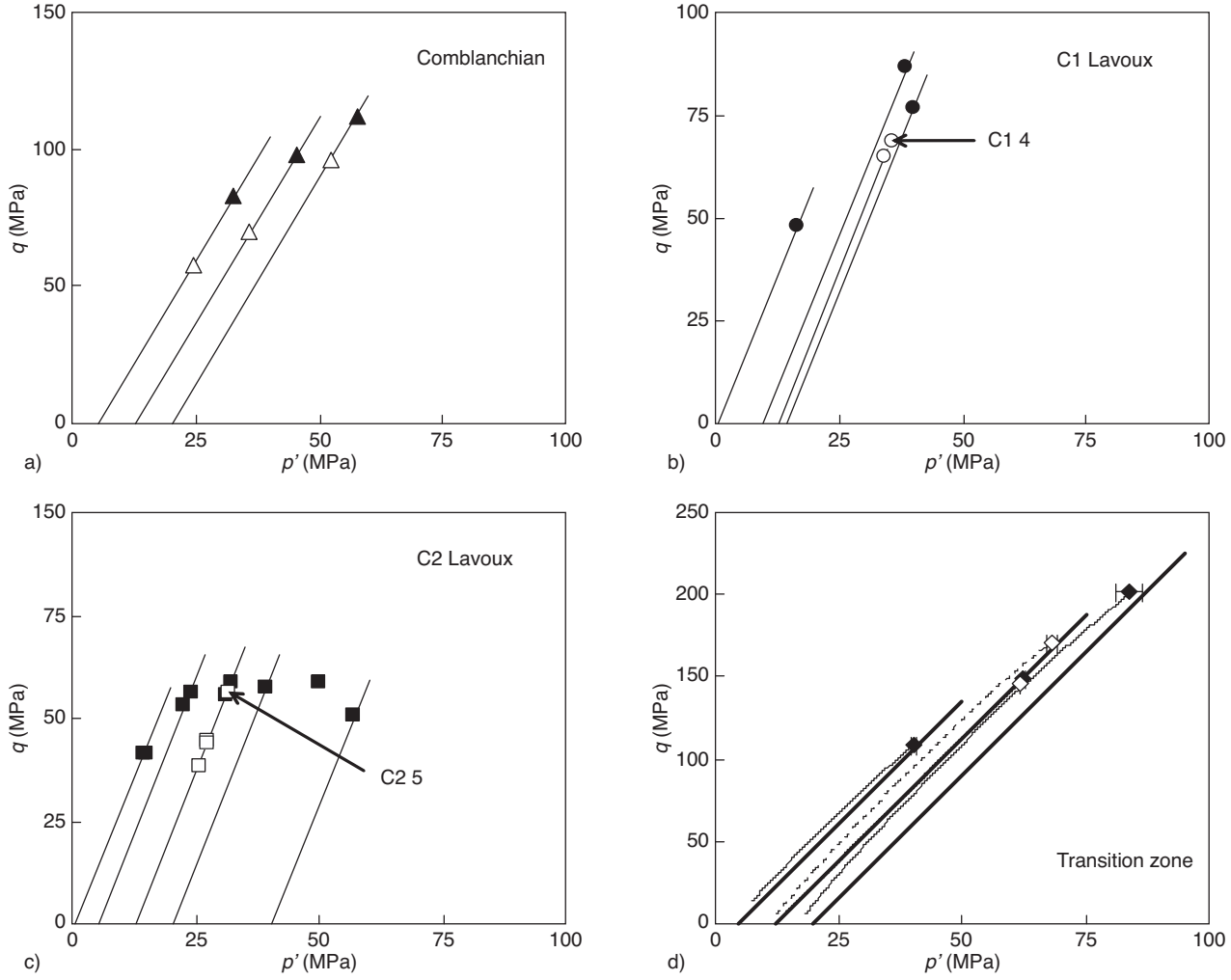



Figure 11

Failure points of intact and altered samples.

The two experimental points showing nearly no chemical effects on shear strength correspond to Lavoux C1 4 and C2 5 samples, whose porosities after alteration remain in the corresponding intact porosity ranges. Apart from these unrepresentative samples, chemical alteration proves to induce a clear decrease of reservoir formations failure strength. Data scattering associated with transition zone samples does not allow a chemically induced strength decrease to be identified. Figure 10 shows that altered samples, transition zone ones included, appear to have lesser average elastic moduli than intact samples. Additional data, in particular on low permeability carbonate rocks, are nonetheless required to extend these results.

These trends are in accordance with the altered samples enlarged porosity. The point is to determine whether the observed weakening in strength and/or stiffness exceeds the variation which would be expected between two natural samples of the same rock type and with similar porosity difference. Bemer *et al*. (2004) have proposed empirical variation laws linking carbonates elastic and failure properties to the sole porosity level. Despite naturally rather important associated errors, these formulae allow first order estimates to be easily obtained.

Figure 12 shows the failure points of intact and altered samples together with the brittle and ductile failure criteria predicted from each formation mean intact porosity (thin lines). Upper and lower thick lines illustrate the uncertainty associated with the empirical model for a given porosity value and thus delimit an acceptable failure area for intact samples. Despite the usually observed chemically induced strength decrease, the range of variation allowed by the empirical failure model is too large for the altered samples strength to fall beyond. Hence, advanced models taking into account characteristics of the studied formations other than the sole porosity level are required to represent chemical alteration effects.

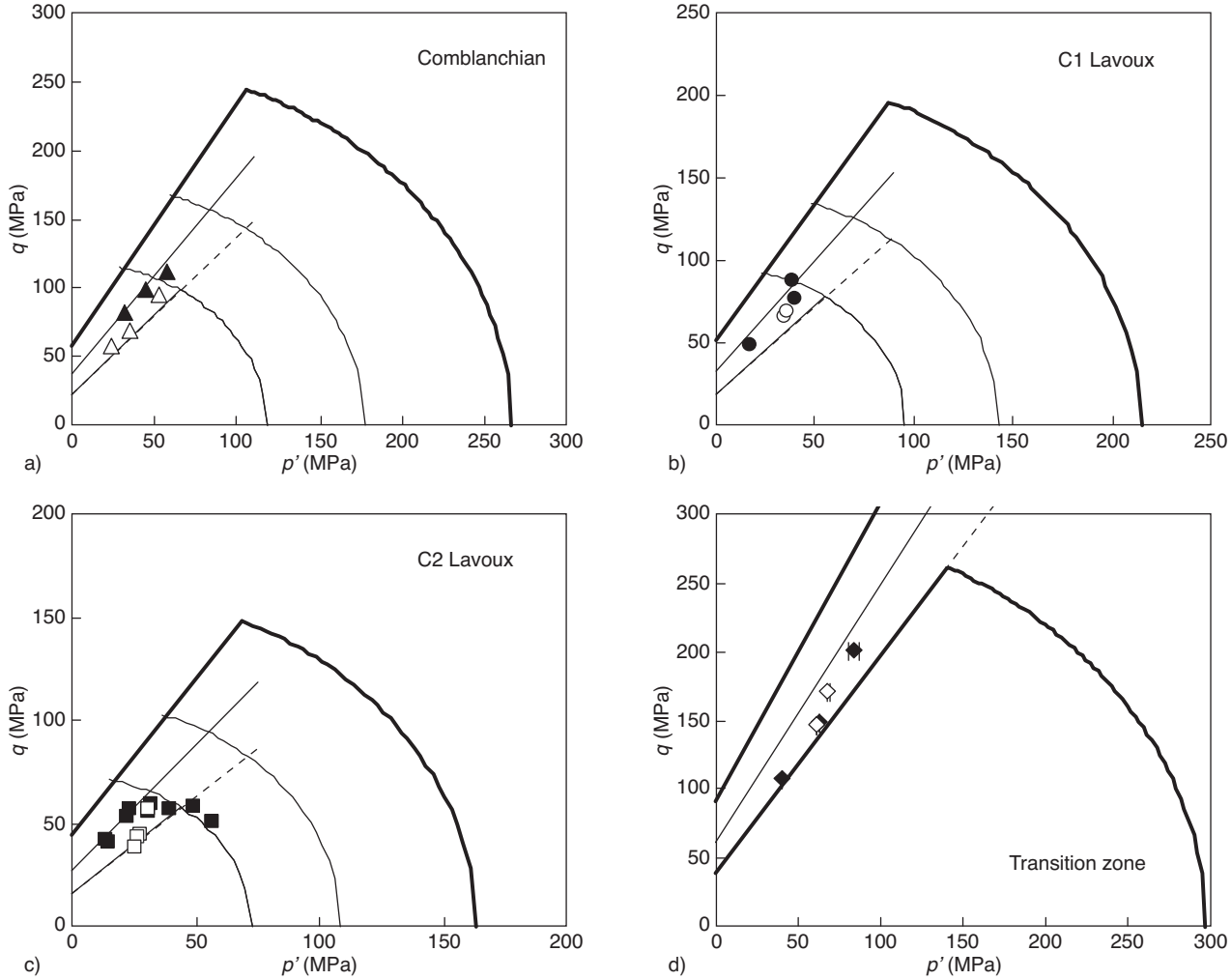



Figure 12

Altered samples failure points compared with empirical failure criteria associated with intact samples.

Figure 13 plots the drained elastic moduli measured on intact and altered Comblanchian and Lavoux samples together with independent literature data for various carbonates (Bemer *et al*., 2004). The continuous curves correspond to the predicted natural trends as a function of porosity and the dotted curves give the upper and lower bounds assessed from the available literature data. Data corresponding to transition zone samples are not indicated on this graph due to the softening effect of the argillaceous fraction which is not taken into account by the empirical model.

Elastic moduli of intact Lavoux samples rank among the model higher half. The decrease in stiffness induced by chemical alteration makes the altered Lavoux samples fall in the model lower half. They however remain within the allowed range. Comblanchian samples show both intact elastic moduli in the model lower half and more significant stiffness decrease under the effect of chemical alteration. Elastic moduli of altered Comblanchian samples thence fall distinctly out the allowed range: the irreversible porosity increase induced by chemical alteration thus appears to lower their stiffness farther than the natural trend. A first explanation of the higher sensitivity of Comblanchian limestone to chemical effects can be found in the differences of structure and mineralogy between the two studied carbonates: Comblanchian limestone being a wackestone and Lavoux limestone a grainstone.

## CONCLUSIONS AND PROSPECTS

This study provides a set of experimental data concerning the evolution of carbonates geomechanical properties under chemical alteration. The available results do not yet allow the definition of constitutive laws taking into account the chemomechanical coupling. Clear trends of chemically induced mechanical weakening have nonetheless been outlined for reservoir formations. Additional experimental data are needed

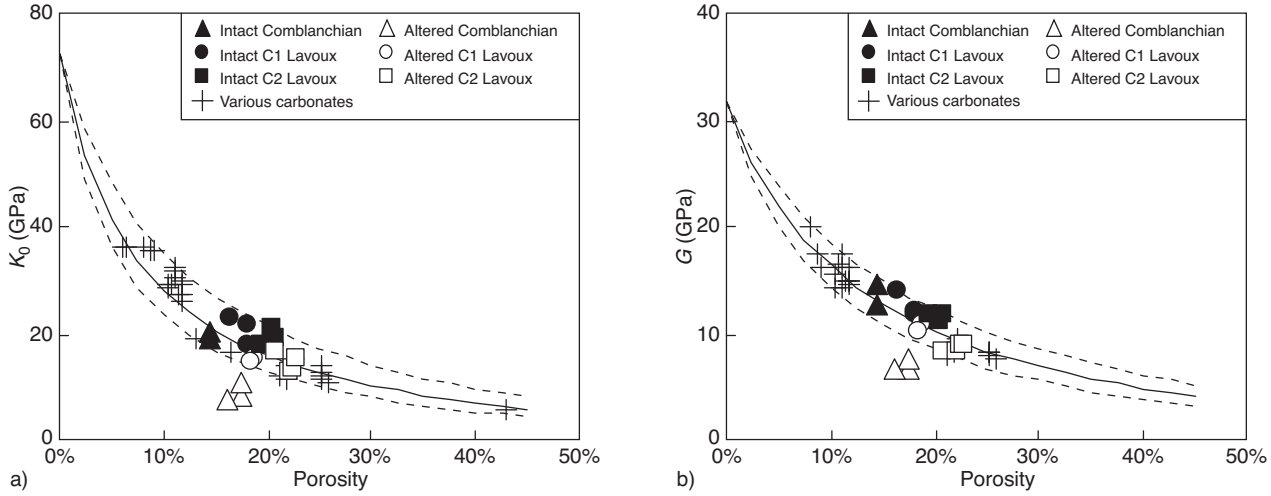



Figure 13

Natural trends for carbonates drained elastic moduli.

to further investigate the effect of chemical alteration on carbonates geomechanical properties, in particular for low permeability formations. This extended geomechanical test campaign should be conducted on carbonates with various structures and mineral contents to identify at the microscopic scale the modifications affecting the macroscopic properties. The scope of the study should then be extended to calcite-cemented sandstones and argillaceous cap rocks. Another key point for $CO_2$ geological storage studies will be to accurately compare the dissolution processes induced by $CO_2$ injection and retarded acid treatment. This specific issue is currently investigated at IFP.

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