

# **Application au cas des bassins sédimentaires**



# Chapitre 6 : Application au cas des bassins sédimentaires

Dans ce chapitre, nous allons nous intéresser à l'utilisation des données acquises expérimentalement pour estimer les surpressions dans les réservoirs profondément enfouis. En effet comme nous l'avons vu, cette thèse s'inclut dans un contexte d'exploration pétrolière. Parmi les phénomènes classiquement utilisés pour expliquer la présence de surpressions dans les bassins sédimentaires, on retrouve la libération d'eau par réaction minérale (Wangen (2001)) et dans le cadre de notre étude nous nous sommes focalisés sur la réaction de déshydratation des smectites en vue d'estimer la contribution de la libération d'eau sur les surpressions observées dans la nature.

Ce chapitre est articulé de la façon suivante : tout d'abord, on introduira la problématique des surpressions dans les bassins sédimentaires ainsi que les origines qui leur sont classiquement attribuées, puis l'impact de la déshydratation des smectites et de l'illitisation sur les surpressions. Enfin, on s'intéressera à l'approche employée dans cette thèse ainsi qu'à l'application à un cas d'étude réel dans le delta du Niger.

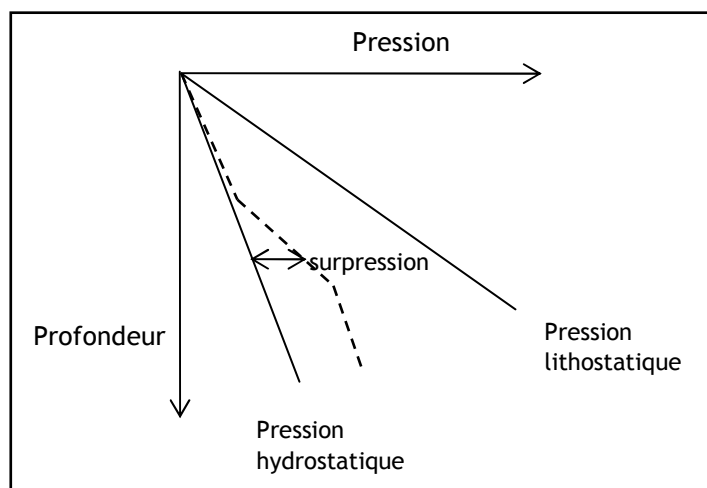
## I. Les surpressions dans les bassins sédimentaires

### I.1. Les surpressions

#### *I.1.1. Les régimes de pression dans les bassins*

La sédimentation est un phénomène géologique qui a lieu par exemple lorsqu'une rivière chargée en particules solides arrachées aux roches voient leur vitesse de transport diminuer, comme lorsqu'elles se jettent dans la mer. En effet, les solides se déposent alors, puis, au cours des temps géologiques, sont recouverts par de nouveaux apports et s'enfouissent. Sous le poids des nouveaux dépôts, les sédiments se compactent et peuvent donner lieu à des transformations chimiques sous l'effet de la température et de la pression.

Au moment du dépôt, les sédiments ne sont pas compactés et présentent une porosité et une perméabilité relativement élevées. La porosité est remplie de fluide et tant qu'il existe un chemin reliant la porosité au fond de la mer, la pression de pore est en équilibre hydrostatique. Lors de l'enfouissement, le poids des nouveaux dépôts compacte les sédiments déjà en place, entraînant une expulsion du fluide contenu dans la porosité et pouvant isoler les sédiments de la surface. Ainsi la pression de pore dévie du gradient hydrostatique, on parle de régime de pression anormale. Si cette nouvelle pression est supérieure à la pression hydrostatique, on parle de surpression. (Figure 61) (Mello *et al.* (1994)). Si la surpression est trop importante, elle peut atteindre la pression lithostatique, qui correspond au poids de la colonne de sédiments, et ainsi entraîner la fracturation de la roche.



**Figure 61 :** Profil de pression dans un puits dans lequel la pression suit un régime hydrostatique jusqu'à une profondeur donnée puis il y a apparition d'une surpression

### 1.1.2. L'origine des surpressions

Les surpressions apparaissent lorsque le fluide est expulsé de roches faiblement perméables et donc a du mal à s'écouler. Depuis de nombreuses années, la question de l'origine des surpressions est au centre des préoccupations des compagnies pétrolières. Wangen (2001) a recensé les principaux mécanismes susceptibles d'être à l'origine des surpressions. Le plus important est la sous-compaction, c'est-à-dire que le système se compacte mais que les fluides contenus dans la porosité ont du mal à s'échapper. Les autres mécanismes cités sont l'expansion thermique du fluide contenu dans l'espace poreux, la libération d'eau par réaction minérale, la génération d'hydrocarbures et la cimentation de l'espace poreux.

Dans son étude, Wangen quantifie les effets de chaque mécanisme. Il en déduit que la sous-compaction et la cimentation de l'espace poreux sont les mécanismes qui génèrent le plus de surpressions dans les réservoirs profondément enfouis. Cependant, si la perméabilité du milieu est suffisamment faible et si les variations de volume solide ne compensent pas totalement le volume de fluide expulsé, les autres mécanismes sont également susceptibles d'avoir une contribution non négligeable sur la génération de surpressions.

## **I.2. Estimation des surpressions liées aux réactions minérales**

Cette partie décrit succinctement d'une part les travaux précédents sur les estimations de la contribution des réactions d'illitisation et de déshydratation des smectites et d'autre part l'approche mise au point dans le cadre de cette thèse pour estimer les surpressions.

### ***1.2.1. Étude bibliographique : contribution de l'illitisation et de la déshydratation des smectites***

L'influence de l'eau libérée par réactions minérales, et en particulier l'illitisation des smectites, a été étudiée par de nombreuses équipes au cours des 50 dernières années. Les réactions de déshydratation au sens large du terme ont été identifiées comme étant des sources potentielles de surpressions dans les années 1960 (Powers (1967) ; Burst (1969)). L'illitisation a été fortement étudiée en raison du fait qu'une grande quantité d'eau est relâchée mais peu de travaux tiennent en compte du couplage de la compaction et de la déshydratation et l'influence sur la pression de pore et la porosité (Colton-Bratley (1987) ; Osborne et Swarbrick (1999)). Audet (1995) et Yang (2000) ont mis au point des modèles mécaniques pour la compaction des sédiments dont l'épaisseur des couches augmente au cours du temps. La réaction de déshydratation est thermiquement activée mais leurs modèles géochimiques de la réaction d'illitisation sont encore très simplifiés.

Les études modélisant la déshydratation des smectites négligeaient soit l'effet de la température (Powers (1967)), soit étaient basées sur des hypothèses thermodynamiques fausses telles que considérer que les variations de volumes de solide et d'eau quand on

augmente la température et la pression (Colton-Bratley (1987)). Les premiers travaux de thermodynamique ont été menés dans les années 1990 par Ransom et Helgeson (Ransom et Helgeson (1994a) ; Ransom et Helgeson (1994b) ; Ransom et Helgeson (1995)) mais à cause du manque de données expérimentales, leurs études sont basées sur des paramètres thermodynamiques estimés. Plus récemment, dans les années 2000, grâce à la compilation de données expérimentales et naturelles, les paramètres thermodynamiques ont pu être déterminés pour les smectites et les illites, afin d'enrichir des modèles existants (Parra *et al.* (2002) ; Vidal et Dubacq (2009) ; Dubacq *et al.* (2010)).

### ***1.2.2. La méthodologie suivie : couplage de données thermodynamiques et modélisation de bassin***

Afin d'estimer la contribution de la déshydratation des smectites sur les surpressions, nous avons choisi de coupler des résultats de thermodynamique avec des données de modélisation de bassin. Cette discipline, très prisée par les géologues, permet de rendre compte de l'histoire du bassin. Avant de décrire la méthodologie employée, une brève présentation de ce en quoi elle consiste sera faite.

#### **1.2.2.1. La modélisation de bassin**

La modélisation de bassin permet de rendre compte de l'histoire d'un bassin (dépôt des sédiments, évolution de leurs propriétés pétrophysiques, circulation des fluides...). Elle est donc utile pour la reconstruction de l'histoire thermique du bassin, l'évaluation de la maturation de la matière organique, l'évaluation de l'historique de pression et l'estimation des migrations d'hydrocarbures. Le logiciel utilisé au cours de cette thèse est Temis, développé à IFP-Énergies Nouvelles et commercialisé par Beicip-Franlab.

La construction d'un modèle de bassin s'effectue de la manière suivante :

- Tout d'abord il s'agit de construire le bloc 2D ou 3D à partir de données à l'actuel (épaisseur des couches, profondeurs bathymétriques actuelles, distribution de faciès et de matière organique), en assemblant des cartes géologiques avec une colonne chronostratigraphique. Il faut également renseigner le calculateur avec des données topographiques et structurales,
- Ensuite il faut définir un maillage du bloc permettant de représenter les principaux objets géologiques et de simuler les phénomènes les affectant au cours du temps. Ce maillage évolue en fonction du temps lors du dépôt des couches de sédiments,

- L'étape de restauration (ou "backstripping") consiste à reconstruire la géométrie du bloc dans le passé à partir des données actuelles en remontant dans le temps. Pour chaque étape de la colonne chronostratigraphique, les sédiments déposés sont enlevés ou ajoutés dans les zones d'érosion. Les sédiments restants sont ensuite décompactés selon les lois de compaction définies pour chaque lithologie.
- La dernière étape est la simulation directe permettant de reconstruire le bloc en tenant compte de la compaction, des régimes de pression des fluides et de leurs migrations et de l'histoire thermique. Il faut ainsi résoudre simultanément les équations de conservation de la masse, de compaction, de conservation de l'énergie, de maturation pour les hydrocarbures et les équations de Darcy généralisées pour un système triphasique.

#### 1.2.2.2. Couplage de thermodynamique et de modélisation de bassin

Le principe de l'approche est de combiner des calculs thermodynamiques avec des données extraites de la modélisation de bassin. En effet, nous avons traité la déshydratation des smectites comme une réaction thermodynamique, comme nous l'avons vu précédemment.

Dans cette thèse, nous avons précédemment décrit les smectites dans une gamme de compositions chimiques variées selon différentes solutions solides. Les paramètres de Margules calculés ont été utilisés pour compléter le modèle de Vidal et Dubacq (2009) et ainsi obtenir une description complète des variations des paramètres thermodynamiques des smectites quelle que soit la composition chimique, pour chaque état d'hydratation ainsi que la transition d'un état hydraté à un autre. Le logiciel utilisé pour réaliser ces calculs est Theriak-Domino (De Capitani et Brown (1987) ; De Capitani et Petrakakis (2010)). Ainsi on peut déterminer le long d'un chemin température/pression défini, les phases minérales stables dont les états d'hydratation des smectites stables ainsi que les bilans volumiques des minéraux et des fluides. Les données d'entrée pour ce calcul sont donc : le chemin température/pression, la base de données thermodynamiques et la composition chimique de la roche en terme de roche totale.

Les données de modélisation de bassin sont extraites de Temis (Beicip-Franlab) afin de calculer les surpressions générées par la déshydratation des smectites. Le chemin température/pression est extrait de l'historique d'enfouissement d'une cellule dans un modèle de bassin afin de tenter de représenter au mieux l'histoire du bassin.

Afin de pouvoir confronter les données obtenues par Theriak avec celles de Temis, il faut se placer dans des systèmes semblables. C'est pourquoi on ajuste la quantité d'eau initiale du système puis progressivement, à chaque étape du chemin température/pression

on retire un volume d'eau correspondant à la compaction. Ainsi on simule en chaque instant un système qui se compacte au cours du temps.

En se basant sur la loi de Darcy, selon laquelle le flux d'eau entre deux pas de temps géologiques est proportionnel au gradient de pression, on peut calculer la pression tenant compte de la déshydratation ( $OP_{ds}$ ) à partir de la pression donnée par Temis ( $OP_{Temis}$ ), qui n'en tient pas compte (Eq. 18).

$$OP_{ds} = \frac{\Delta V_{ds}}{\Delta V_c} \times OP_{Temis} \quad \text{Eq. 18}$$

où  $\Delta V_{ds}$  est la variation de volume effective, tenant compte à la fois de la diminution du volume solide lié au changement d'état d'hydratation de la smectite ( $\Delta V_s$ ) et à l'augmentation du volume d'eau ( $\Delta V_d$ ) dans l'espace poreux lors de la déshydratation ( $\Delta V_{ds} = \Delta V_d - \Delta V_s$ ) et  $\Delta V_c$  est le volume d'eau qui sort de la cellule lors de la compaction.



## **II. Article : La déshydratation des smectites dans les bassins sédimentaires compactants : une source additionnelle de surpressions**

Cette partie contient un article, soumis à Marine and Petroleum Geology, qui décrit la contribution de la déshydratation des smectites sur la génération de surpressions dans les bassins sédimentaires, mettant en application la méthodologie décrite précédemment sur un cas d'étude réel dans le delta du Niger. Une conclusion en français figure à la fin de l'article (p.204).

### **Résumé**

La prédiction des surpressions est un défi pour les compagnies pétrolières depuis des décennies. Les surpressions sont générées quand un fluide est relâché d'une roche peu perméable et que les sédiments ne peuvent se compacter normalement. Plusieurs mécanismes ont été mis en évidence pour expliquer la génération de surpressions et l'un d'entre eux est la génération d'eau lors de réactions minérales. Cette étude s'intéresse à la contribution de la déshydratation d'argiles gonflantes, appelées smectites, sur la génération de surpression dans les bassins sédimentaires compactants. Contrairement à l'illitisation, la déshydratation des smectites est une réaction rapide dans les conditions de laboratoire, elle peut donc être considérée comme instantanée à l'échelle des temps géologiques. De plus elle s'opère par paliers successifs: les couches d'eau sont relâchées les unes après les autres à des températures données. Ce travail combine des calculs thermodynamiques de stabilité des états hydratés et des bilans volumiques avec des données de modélisation de bassin extraites de Temis (Beicip-Franlab). Le modèle thermodynamique est basé sur les travaux de Vidal et Dubacq (2009) et les paramètres supplémentaires calculés au cours de cette thèse et tient compte des variations de volume des solides et des fluides. Le logiciel utilisé est Theriak-Domino. Cette méthodologie est tout d'abord testée sur un cas synthétique, puis sur un cas réel du delta du Niger, où de fortes surpressions ont pu être associées à la présence d'épaisses couches argileuses. Les surpressions calculées sont plus proches des données de puits que les précédentes estimations ne tenant pas compte de la déshydratation des smectites. La contribution de cette réaction est de l'ordre de 15 à 20 MPa, ce qui représente environ 40% de la surpression totale observée. La déshydratation des smectites semble donc avoir une contribution significative sur la génération de surpressions mais dans des environnements spéciaux, avec de forts taux de sédimentation et d'épaisses couches argileuses très peu perméables.

## **Smectite dehydration in compacting sedimentary basins: a source of additional overpressure**

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## **Abstract**

Overpressure prediction is a challenge for petroleum exploration since decades. Overpressure is met in sedimentary basins when the sedimentation rate is very high and is followed by an abnormal sediments compaction. Several mechanisms were put in evidence to explain the generation of overpressure. One of them is the impact of water released from mineral reactions. The presented study focuses on the contribution of swelling clays, namely smectites, to the overpressure generation in sedimentary basins. Unlike illitization, smectite dehydration can be considered as instantaneous at the geological time scale. This work combines thermodynamic calculations of smectite hydration states stability and solid and fluid volumes balance with basin modelling results extracted from Temis (Beicip-Franlab) to estimate the overpressures. The thermodynamic model takes into account the multi-step behaviour of smectite dehydration, water layers being released one after the other at discrete temperatures, and additional parameters, accounting for solid volumes variations. The calculations are done with Theriak-Domino software. Firstly, this methodology is illustrated on a synthetic case, then on a real case in Niger Delta, where high overpressures are observed at deep burial, corroborated with the presence of thick shale layers. A better agreement is observed with wells data considering smectite dehydration rather than accounting only for undercompaction as an active process generating overpressures. According to our calculations, in systems with high sedimentation rate and important undercompaction, the contribution of smectite dehydration is about 15 to 20 MPa, which represents about 10 to 40% of the total observed overpressure, varying the shale chemical composition and the geothermal gradient.

## **Keywords**

smectite dehydration, overpressure, compaction, clay diagenesis, solid solution, basin modelling

## 1. Introduction

With the rise of energy demand, major operators are expanding their search for new reserves, moving into deeper water and higher pressure and temperature environments. As a consequence, the offshore industry faces new challenges in finding and developing deepwater reserves.

When a well-bore is being drilled for oil exploration, drilling mud is used in the hole to maintain its integrity and safety. The used mud density depends on the pore fluid pressure in the rock, and drilling problems can occur in regions where overpressures are observed. Fluid pore pressure  $P$  is defined as the pressure within the fluid of the pore space of a sedimentary rock. This pressure can be higher than, equal to, or lower than the hydrostatic pressure, defined as  $P_h = \rho_f \cdot g \cdot z$ , where  $\rho_f$  is the fluid density,  $g$  the gravity acceleration, and  $z$  the depth. Pressure exceeding the hydrostatic pressure is equivalently termed abnormally high pore pressure, or overpressure (Mello *et al.*, 1994). Such overpressuring can substantially affect drilling rates and even causes serious problems during drilling. It is, therefore, critical to predict overpressuring before drilling and to identify its precursors during drilling (Thoomer *et al.*, 1961).

Quantitative basin modelling provides a method to test the consequences of geological models, that is why it is used to help the decision making about mud pressure for example. The development of overpressure in a geological compartment represents an out-of-equilibrium situation, due to the slow rate of fluid expulsion from this compartment. Several mechanisms are suggested for delaying fluid expulsion, such as mechanical compaction or a low vertical permeability, and overpressure build-up, such as aquathermal pressuring, hydrocarbon generation, cementation of the pore space or water released from mineral reactions (Osborne and Swarbrick, 1997 ; Yardley and Swarbrick, 2000). Wangen (2001) reviewed and compared quantitatively some of these mechanisms.

The present study focuses on water released from mineral reactions, in particular smectite dehydration (Powers, 1967; Burst, 1969), on changes in the amount of interlayer water associated with smectite under burial conditions and on the volume variations of smectites during dehydration. It combines the results of thermodynamic calculations based on Vidal and Dubacq (2009)'s work with new thermodynamic parameters (Meiller, 2013) using the software Theriak (De Capitani and Brown, 1987 ; De Capitani and Petrakakis, 2010) with data from basin modeling extracted from Temis (Beicip-Franlab), to estimate the overpressures. The methodology used during the study is described and the contribution of smectite dehydration to overpressure is first estimated for a synthetic case. The methodology is then applied to a case study from the Niger delta.

## 2. Background

Smectites belong to 2:1 phyllosilicates group: they are composed of one octahedral sheet surrounded by two tetrahedral sheets. Cationic substitutions and structural defects impart a net negative charge to the 2:1 layer, which is compensated by interlayer cations, such as  $\text{Na}^+$  or  $\text{Ca}^{2+}$ . These cations are highly hydratable and may accommodate water molecules in the interlayer space making the structure swells, so that smectites are called expandable. When temperature increases, smectites dehydrate and during this reaction, structural water bound within the sheet layers of smectite is released into the pore space, which may increase the pore pressure.

Although the smectite-to-illite transformation is one of the fundamental mechanisms of mineral reactions in clastic rock, few studies (Powers (1967), Colton-Bradley (1987), Osborn and Swarbrick (1999)) have taken into account the coupling of compaction with concurrent sediment dehydration, along with the associated effect on pore pressure and porosity. The simple gain or loss of interlayer water (hydration/dehydration) by smectite has often been confused with the smectite-to-illite transformation. Although release of interlayer water associated with smectite transformation occurs during smectite-to-illite transformation, the reaction mechanisms leading to the formation of illite are irreversible. Contrary to illitization, smectite hydration/dehydration is a reversible process, which only involves water exchange.

Audet (1995) and Yang (2000) presented a continuum mechanics model for the 1-D gravitational compaction of a sediment layer whose thickness increases with time. In this model, the sediment grains undergo a thermally activated dehydration reaction that releases water. The strength of Audet (1995) and Yang (2000)'s studies is related to the non-dimensional nature of the equations of their models, allowing to discuss the main features of the mineral reaction and its effect on pore pressure, although the smectite-illite reaction scheme suffers from large uncertainties. As underlined by these authors, a possible extension of their works is to include a more complicated real geochemistry, to be applicable in a more realistic geological environment.

The previous attempts of smectite hydration/dehydration modelling either neglected temperature effect (Powers, 1967), or were based on erroneous thermodynamic assumptions because the changes in entropies and molar volume of bulk and interlayer water with increasing pressure and temperature were considered negligible (Colton-Bradley, 1987). The first thermodynamic studies were lead by Ransom and Helgeson in the 1990s (Ransom and Helgeson, 1994a ; Ransom and Helgeson, 1994b ; Ransom and Helgeson,

1995), but they had to calculate the thermodynamic parameters with correlative methods because of the lack of experimental data. Later, experimental and natural data compilations lead to the determination of these thermodynamic parameters allowing the enrichment of thermodynamic models (Parra *et al*, 2002 ; Vidal and Dubacq, 2009 ; Dubacq *et al*, 2010) which take into account the transition between two hydration states and a part of smectites and illites chemical variability.

### 3. Geochemical model

In this study, smectite dehydration is considered on a thermodynamic point of view: at each temperature and pressure step, the mineralogy is calculated as the most stable and complete equilibrium, in order to determine which phases and in particular which hydration state are the more stable. The calculations are based on thermodynamic databases integrating most recent works on the topic. A review of earlier studies is presented in this part.

#### 3.1. Ransom and Helgeson (1994a, 1994b, 1995)

In the 1990s, Ransom and Helgeson (1994a, 1994b, 1995) established a thermodynamic model based on the description of smectite hydration as the possession or the lack of interlayer water. This non ideal solid solution model does not take into account interaction between cations in the structure. Moreover it is based on the hypothesis that there are only two hydration states: fully hydrated or totally dehydrated. The authors took into account the volume variation of water during hydration and dehydration and assumed that there are no other crystallographic changes in the smectite structure. The interlayer region in the silicate structure can be considered to be solvent, the water is the solute, and the solution is called solid-solution. Smectite dehydration can be described symbolically in terms of homologous hydrous (hs) and anhydrous (as) components writing the following overall reaction:



where n stands for the number of moles of water involved in the reaction.

The chemical and thermodynamic properties of interlayer water differ from those of pore water. Interlayer water can be considered as water bounded into a mineral forming a hydrated mineral. When the dehydration occurs, the interlayer water is released from the hydrated smectite to form H<sub>2</sub>O and a homologous anhydrous smectite. Thermodynamic parameters (S°, H°, V°, G°, Cp) for hydrated smectites are estimated according to the oxide

summation principle: thermodynamic properties for an unknown mineral are calculated from other known minerals, writing an analogous reaction involving the mineral with unknown parameters and minerals for which parameters are known.

In this way, molar volumes for smectites with any chemical compositions are estimated, at a dehydrated state  $V_{\text{lat}}^{\circ} + V_{\text{int}}^{\circ}$ , where  $V_{\text{lat}}^{\circ}$  and  $V_{\text{int}}^{\circ}$  denote the standard molar volume of the smectite lattice and dry interlayer respectively. To calculate the volume taking into account the amount of interlayer water Ransom and Helgeson (1994a) wrote the following equation:

$$V^{\circ} = V_{\text{lat}}^{\circ} + V_{\text{int}}^{\circ} + n_{\text{H}_2\text{O}(\text{il})} V_{\text{H}_2\text{O}(\text{il})}^{\circ} \quad \text{Eq. 20}$$

where  $n_{\text{H}_2\text{O}(\text{il})}$  (mol) and  $V_{\text{H}_2\text{O}(\text{il})}^{\circ}$  (cm<sup>3</sup>/mol) are respectively, the number of moles and standard molar volume of interlayer H<sub>2</sub>O. The number of moles of interlayer water is calculated for a totally hydrated state:

$$n_{\text{H}_2\text{O}(\text{il})} = \frac{\rho_{\text{il}} (V_{\text{il}}^{\circ} - V_{\text{cat}}^{\circ})}{M_w} = 4,5 \text{ mol} \quad \text{Eq. 21}$$

where  $\rho_{\text{il}} = 1.05 \text{ g/cm}^3$  stands for the interlayer water density (Hawkins and Egelstaff, 1980),  $V_{\text{il}}^{\circ}$  (cm<sup>3</sup>/mol) represents the molar volume the interlayer space calculated with the cell parameters,  $V_{\text{cat}}^{\circ}$  (cm<sup>3</sup>/mol) designates the volume occupied by the interlayer cations and  $M_w$  (g/mol) is the molecular weight of water.

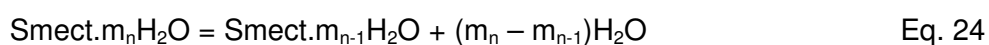
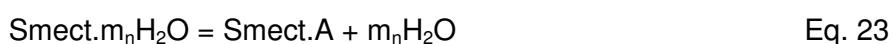
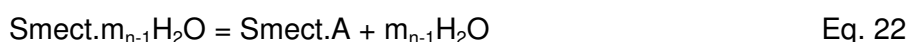
### 3.2. Vidal and Dubacq (2009)

In nature, smectite dehydration shows a multi-step behaviour: water molecules are intercalated as layers in the interlayer space and during burial, water layers are released one after the other at given temperatures. Classically, four hydration states are defined: 0W, 1W, 2W and 3W where the number represents the number of water layers in the interlayer space. The transition from one hydration state to another occurs at a given temperature. During burial history, a smectite will present several dehydration steps.

Vidal and Dubacq (2009) proposed a symmetric non ideal solid solution model for smectite dehydration, that reproduces the multi-step variation experimentally observed and takes into account the volume changes as a function of composition, pressure, temperature and nature of the interlayer cation. They described eight solid-solutions which involve smectite and mica end-members. The main limitation of their model is that they only take into account one

cationic substitution: the pyrophyllitic substitution i.e. the quantity of interlayer cation between two end-members: pyrophyllite  $\text{Si}_4\text{Al}_2\text{O}_{10}(\text{OH})_2$  and R-mica  $\text{Si}_3\text{Al}_3\text{RO}_{10}(\text{OH})_2$ .

This model is based on the same assumption for the solid solution description as Ransom and Helgeson. The volume variations and the water content are described through three equilibriums at any transition step:



where  $m_n$  and  $m_{n-1}$  are the number of moles of water at two successive hydration states, Smect.A is the totally dehydrated end member.

The non ideal part of this model is calculated using the following formalism (Mäder and Berman, 1992):

$$RT \ln \gamma_i = \sum_{i=1}^{nE-1} \sum_{j=i+1}^{nE} W_{i-j} \times X_j \times (1 - X_i) - \sum_{i=2}^{nE-1} \sum_{j=i+1}^{nE} W_{i-j} \times X_j \quad \text{Eq. 25}$$

where  $\gamma_i$  is the activity coefficient of the component  $i$ ,  $nE$  is the number of end-members in the considered solid-solution,  $X_i$  and  $X_j$  are the molar fractions of end-members  $i$  and  $j$ , and  $W_{i-j}$  are the Margules parameter corresponding to the interaction between end-members  $i$  and  $j$ .

This model can be used to estimate smectites thermodynamic parameters whatever is the hydration state or the chemical composition of the smectite, along one cationic substitution and to study the transition between two hydration states during burial.

### 3.3. This study

The volume balance of smectite dehydration has to take into account two variations: on one hand, the increase of water volume in the system due to the release from hydrated smectite and on the other hand the decrease of smectite volume due to the phase transition from a hydrated smectite to a less hydrated smectite.



In nature, smectites show a wide range of chemical compositions with different interlayer cations: Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> or K<sup>+</sup>. In order to consider the real behaviour of smectites in sedimentary basins, a model taking into account the global range of chemical compositions and the hydration states variations is necessary. Vidal and Dubacq (2009) assumed that the structure and organisation of the interlayer and the cation-water interactions are identical for all smectites with the same interlayer cation, interlayer charge and number of interlayer water molecules. This is a strong hypothesis because it does not account for some natural observations of smectites behaviour. It has been proven that for two smectites with identical interlayer charge, the one where the charge is located in the octahedral sites (montmorillonites) will more easily swell than the one where the charge is located in the tetrahedral sites (beidellites) (Foster, 1953 ; Foster, 1954 ; Harward and Brindley, 1965).

In the present study, smectite dehydration is studied in a wider range of chemical compositions in agreement with natural observations. Three substitutions were considered: the pyrophyllite substitution presented earlier, the illitic substitution between two end-members: R-Mg-celadonite (Si<sub>4</sub>AlMgRO<sub>10</sub>(OH)<sub>2</sub>) and pyrophyllite (PrI) and the Tschermak substitution between two end members: R-mica (Ms) and R-Mg-celadonite (cel), which are the three more common substitutions found in nature.

The present model is based on Vidal and Dubacq (2009)'s work that takes into account cationic interactions and describes in a more realistic way the multi-step variation during dehydration.

The solid-solution model is described with the following equation which takes into account the cationic substitutions occurring in interlayer and inside the layers. To better describe the interaction between cations in the system, four new Margules parameters for the volume (e.g. for Na-smectites : W<sub>Na-□</sub>, W<sub>□-Na</sub>, W<sub>Mg-Al</sub> and W<sub>Al-Mg</sub>, where □ stands for a cationic vacancy) have been estimated to consider a wider chemical range (Eq. 26).

$$V(x_{Na}, x_{Mg}) = (1 - x_{Na})V_{PrI}^{\circ} + (x_{Na} - x_{Mg})V_{Ms}^{\circ} + x_{Mg}V_{cel}^{\circ} + x_{Na}(1-x_{Na})W_{\square-Na} + x_{Na}(1-x_{Na})^2(W_{Na-\square} - W_{\square-Na}) + x_{Mg}(1-x_{Mg})W_{Al-Mg} + x_{Mg}(1-x_{Mg})^2(W_{Mg-Al} - W_{Al-Mg}) \quad \text{Eq. 26}$$

The same equation is used to calculate the thermodynamic parameters for Ca-smectites. These additional parameters are described in more details in another paper (Meiller et al., in prep.). They have been fitted on experimental volumes data on synthetic smectites estimated by Rietveld method (Rietveld, 1969). The Figure 62 summarizes what our model brings new in comparison to Vidal and Dubacq (2009).

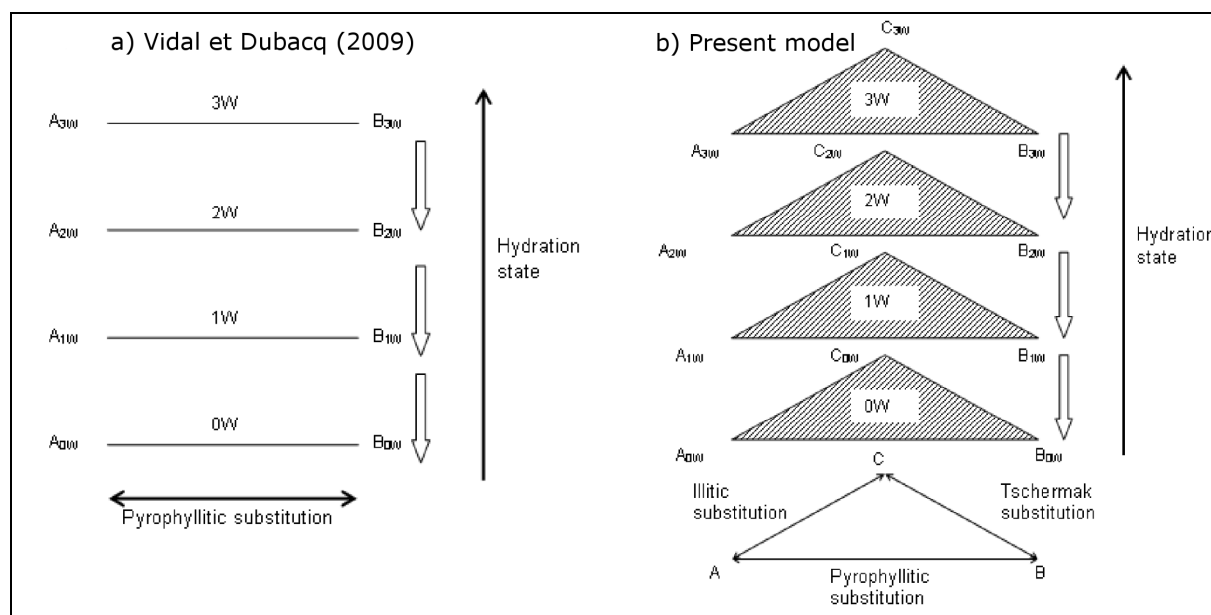


Figure 62: In order to consider the real behaviour of smectites in sedimentary basins, a model taking into account the global range of chemical compositions and the hydration states variations is necessary. a) Vidal and Dubacq (2009) take into account only one cationic substitution: the pyrophyllitic substitution between two end-members: pyrophyllite  $Si_4Al_2O_{10}(OH)_2$  and R-muscovite  $Si_3Al_3RO_{10}(OH)_2$  ( $R = Na^+$  or  $Ca^{2+}$ ) b) Our model describes three substitutions: the pyrophyllite substitution, the illitic substitution between two end-members: R-Mg-celadonite ( $Si_4AlMgRO_{10}(OH)_2$ ) and pyrophyllite (Pr1) and the Tschermak substitution between two end members: R-muscovite (Ms) and R-Mg-celadonite (cel)

The molar volumes values calculated according to the three available thermodynamic models (Ransom and Helgeson's model, Vidal and Dubacq's model, our model) are presented in Table 1 and compared with experimental data obtained with Rietveld method on synthetic samples, for a smectite with the structural formula:  $R_{\frac{0.3}{a}}^{a+}Al_2[Si_{3.7}Al_{0.3}]O_{10}(OH)_2$

where R is the interlayer cation and *a* its valence. Ransom and Helgeson's model allows calculating the dehydrated state and the fully hydrated state, but does not allow following the intermediate states of hydration. Vidal and Dubacq's model reproduces all the states of hydration, but does not match the volume change of the smectite related to the nature of the interlayer cation. Our model provides values for every hydration state regardless of the interlayer cation.

Table 1: Molar volume values according to the different models ( $\text{cm}^3/\text{mol}$ ) described earlier. Ransom and Helgeson: calculate the dehydrated state and the fully hydrated state. Vidal and Dubacq: reproduces all the states of hydration, but does not match the volume change of the smectite related to the nature of the interlayer cation. Our model: provides values for every hydration state whatever is the interlayer cation. The values for non available experimental data (1W and Ca 2W) are obtained with an extrapolation of our model with Dubacq et al (2010) method.

	Experimental values		This study		Vidal and Dubacq 2009	Ransom and Helgeson 1994	
	Na <sup>+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>	Na <sup>+</sup> and Ca <sup>2+</sup>	Na <sup>+</sup>	Ca <sup>2+</sup>
0W	133.0	140.4	133.2	143.3	138.5	121.2	155.7
1W	/	/	170.1	171.7	173	/	/
2W	212.4	/	209.4	206.2	207.8	/	/
3W	253.6	237.0	255.0	246.3	256	198.7	233.2

## 4. Numerical methodology

Our model describes the thermodynamic volume parameters of dioctahedral smectites with different interlayer cations at different hydration states. It allows calculating both water and mineral volumes variations as a function of hydration state.

Smectite hydration state depends chiefly on temperature and less so on pressure. At the scale of geological times and even at the laboratory time scale, smectite dehydration can be considered as instantaneous. Smectite hydration states can be considered at thermodynamic equilibrium. The software used to determine the stable phases with thermodynamic calculations at given conditions is Theriak-Domino (De Capitani and Brown, 1987; De Capitani and Petrakakis, 2010). Pressure and temperature are related to burial history, provided by basin modelling simulation. Then overpressures are estimated taking into account undercompaction and water released from smectite dehydration.

### 4.1. Theriak-Domino Suite

Theriak-Domino is a software collection (available for free download on <http://titan.minpet.unibas.ch/minpet/theriak/theruser.html>) that is able to calculate the stable mineral assemblage and equilibrium phase compositions for a given rock composition (solid and fluids) at specified pressure and temperature. The calculations are based on Gibbs free energy minimization, according to a thermodynamic database (De

Capitani and Brown, 1987 ; Berman, 1988). The general equation for the molar apparent Gibbs free energy of a phase ( $\Delta_a G$ ), at T and P is given by :

$$\Delta_a G = \Delta_f H^{T_0, P_0} + \int_{T_0}^T C_p dT - TS^{T_0, P_0} - T \int_{T_0}^T \frac{C_p(T)}{T} dT + \int_{P_0}^P V(T, P) dP \quad \text{Eq. 27}$$

where T is the temperature, P the pressure,  $T_0$  and  $P_0$  the standard state (25°C and 1bar, respectively),  $\Delta_f H^{T_0, P_0}$  is the molar enthalpy of formation at  $T_0$  and  $P_0$ ,  $S^{T_0, P_0}$  is the molar entropy at  $T_0$  and  $P_0$ ,  $C_p(T)$  is the molar heat capacity at  $P_0$  and  $V(T, P)$  is the molar volume function.

The database contains all thermodynamic properties ( $G^\circ$ ,  $H^\circ$ ,  $S^\circ$ ,  $V^\circ$ ,  $C_p$ ) for a set of end-members and a wide collection of solid solutions.

The used database is, for a wide range of minerals, based on data from Berman (1988). For smectites and illites, thermodynamic parameters were added from Parra *et al.* (2002), Vidal and Dubacq (2009) and Dubacq *et al.* (2010), and from our work on smectites and illites volume variations as a function of chemical composition (Meiller *et al.* in prep.). To perform a calculation, inputs are: the bulk composition of the rock and a T-P path. Theriak provides as output data, volume and number of moles of every solid phase and fluid phase, necessary to establish the volume balance in order to assess the overpressure.

#### 4.2. Temis

Basin models are useful for (1) the reconstruction of the thermal history of the basin, (2) the evaluation of the maturation of the organic matter, (3) the evaluation of the pressure history, and (4) an appreciation of hydrocarbon migration and reservoir filling.

A 2D or 3D case study is composed of four major steps which are: block building, gridding, backward simulation (restoration), and forward simulation. The 2D or 3D block is obtained by assembling a chronostratigraphic column with a set of maps. Each period of the column is correlated to one layer in the geometrical 3D block. For each of the layers, the set of maps are present-day thicknesses, facies distribution, kerogen distribution and Total Organic Carbon (TOC) distribution.

During backward restoration, the simulation begins at present day and for every period defined in the chronostratigraphic column, deposited sediments are removed and eroded sections are added to the block. Once sedimentation and erosion have been accounted for, the remaining sediments are decompacted or compacted in case of erosion by using porosity/depth relations for each lithology. This process, generally called backstripping allows

transformation of the real thickness maps into solid thickness maps which are later used for forward simulation.

During the last step, the forward simulation, the 2D or 3D fluid flow simulator solves simultaneously the mass conservation equations for solids and fluids, the compaction equation, the momentum conservation equation, the energy conservation equation, the maturation equations (three components: oil, gas, and coke) and the generalized Darcy equations for three phases flow. The physical concepts and their mathematical formulations are described in Schneider *et al.* (2000).

The multi-phase flow option has not been selected here. Within the monophasic Darcy fluid flow approach, the porosity of the matrix is only filled with water. The rock permeability as well as the characteristics of the water, mainly density and viscosity, influences the water flow. The water flow is related to the pressure gradient according to the Darcy law:

$$\vec{Q}_w = \phi \vec{V}_w = -\frac{k}{\mu} (\vec{\nabla}P - \rho_w \vec{g}) \quad \text{Eq. 28}$$

where  $\Phi$  is the porosity,  $\vec{V}_w$  is the pore velocity,  $k$  is the rock permeability, and  $\mu$  the water viscosity.

#### 4.3. Coupling for overpressure calculation

The approach of this study is that overpressure depends on the relation between the released water quantity and the available porous space. It is necessary to know the water volume released by dehydration, the solid volume variation and the porosity variation during burial. To calculate the overpressure due to smectite dehydration, the burial history of a cell (temperature, pressure, porosity) containing clays and which presents overpressures, due to undercompaction, is extracted from the basin modelling. Then, for each temperature and pressure step, the most stable assemblage is calculated and hydration state of smectites is determined.

The first step is to simulate with Theriak a system where all the initial porosity  $\phi_{Th}^i$  is full of water (all the water adjustment in Theriak are done by the variation of the number of moles of Hydrogen) and equals to the initial porosity used in Temis  $\phi_{Te}^i$ :

$$\phi_{Th}^i = \frac{V_{water}^i}{V_{solid}^i + V_{water}^i} = \phi_{Te}^i \quad \text{Eq. 29}$$

where  $\phi_{Th}^i$  is calculated with the volumes extracted from Theriak,  $V_{solid}^i$  and  $V_{water}^i$  designate respectively the initial solid volume and the initial water volume.

A difficulty is that Theriak does not take into account the expelled water by compaction. To simulate the water loss due to compaction calculated with Temis, water has to be removed in Theriak at each step. In order to simulate the compaction of the rock, the quantity of water present in the system in Theriak has to be modified manually, subtracting the water volume expelled during compaction, determined from Temis calculations. Thus, for each step the volume balance of water and solids present in the system is obtained and can be corroborated with the porosity data, that represents the available volume. By doing this, thermodynamic calculations can be performed with Theriak for a system having a water/rock ratio identical to the Temis cell. The Theriak outputs are the volumes of every solid and fluid phases, and allow to determine the effective volume variation of the system which impacts the pressure of the system. Since smectite dehydration corresponds to a water volume increase  $\Delta V_d$  in the porous space, and to a decrease of the mineral volume  $\Delta V_{sol}$ , the effective volume variation is:

$$\Delta V_{ds} = \Delta V_d - \Delta V_{sol} \quad \text{Eq. 30}$$

If the effective volume increases, the pressure of the system is expected to increase, unless the permeability of the rock is sufficiently high to drain it.

Therefore, to assess the pressure variation inferred to smectite dehydration, the effective volume has to be linked to the fluid flow in the basin. According to the Darcy's law (Eq. 28), the amount of water flowing through a rock between two geological events is proportional to the pressure gradient. The Temis forward simulation solves simultaneously the mass conservation equations for solids and fluids, the compaction equation, the momentum conservation equation, and assesses the pressure in every cells of the model associated to the water volume expelled by compaction. In other words, between two geological events, the Temis simulation provides the relation between the pressure and the volume of water leaving the cell. The pressure variations following the efficient volume, all other parameters being constant in the cell, can be calculated with the following equation:

$$OP_{ds} = \frac{\Delta V_{ds}}{\Delta V_c} \times OP_{Temis} \quad \text{Eq. 31}$$

where  $OP_{ds}$  stands for the total overpressure integrating the two mechanisms (compaction and smectite dehydration),  $OP_{Temis}$  is the overpressure calculated with Temis (taking into account solely the mechanical compaction without the contribution of smectite dehydration),  $\Delta V_c$  designates the water volume released by compaction and  $\Delta V_{ds}$  represents the effective volume (Eq. 30). The implicit hypothesis done in this calculation is that smectite dehydration does not modify the permeability of the sediment and the overpressure generated by dehydration does not significantly change the flow rate.

#### 4.4. Synthetic case

In order to illustrate the methodology previously exposed, a synthetic case is presented. It is a very simple geological structure made up of a 2D section filled by alternating layers of shale and sandstone.

For the synthetic case, a sedimentary rate of 100 m/My and a geothermal gradient of 40°C/km were considered. The burial history of the cell located at around 4000 m depth at present day is extracted from basin modelling (Table 2). The fluid flow calculations were performed for the default lithologies of Temis (shale, and sandstone respectively), with Kozeny-Carman permeability laws with specific surfaces equal to  $5 \cdot 10^7$  and  $4 \cdot 10^5$  m<sup>2</sup>/m<sup>3</sup>, respectively. The temperature increases with a normal trend due to the imposed geothermal gradient. The overpressure due to undercompaction is moderate (about 1.45 g/cm<sup>3</sup> equivalent mud weight). Even if the system is overpressured, the porosity of the sediments decreases until present day.

Table 2: Burial history of the studied cell

Data from basin modelling						
Age (My)	Temperature (°C)	Pressure (MPa)	Porosity	Depth (m)	OP <sub>Temis</sub> (MPa)	Mud weight
41	21.54	3.54	0.50	562.94	0.60	0.64
38	42.01	10.10	0.41	780.69	2.11	1.32
35	54.25	13.98	0.34	1079.22	2.97	1.32
32	68.14	17.89	0.27	1418.06	3.46	1.29
29	82.34	22.10	0.22	1764.41	4.17	1.28

<b>26</b>	<b>96.46</b>	<b>26.15</b>	<b>0.18</b>	<b>2108.81</b>	<b>4.74</b>	<b>1.26</b>
<b>23</b>	<b>112.44</b>	<b>31.65</b>	<b>0.17</b>	<b>2498.63</b>	<b>6.30</b>	<b>1.29</b>
20	125.13	36.01	0.15	2807.96	7.54	1.31
17	136.53	40.02	0.14	3086.08	8.74	1.32
14	147.24	43.91	0.13	3347.29	9.99	1.34
10.5	154.73	47.67	0.12	3530.03	11.90	1.38
7	163.67	51.79	0.11	3747.97	13.82	1.41
3.5	173.11	55.88	0.10	3978.37	15.58	1.43
0	182.86	60.17	0.10	4216.06	17.47	1.45

To perform calculations of mineral evolution, a sedimentary basin for which the cap rock mineralogy is composed of a mixing of clay minerals and silicates was considered. Considering a shale composed of about 33wt% of smectite, 25wt% of quartz, 40% of kaolinite and less than 1wt% of albite, a simple chemical system with only Si-Al-Mg-Na as cations in the minerals is then considered in Theriak. The mineralogical evolution of the shale along a P/T path experienced during burial is calculated according to the thermodynamic principle of Gibbs energy minimization with Theriak (Figure 63a). First the initial stable assemblage calculated by Theriak with the provided chemical composition reproduces the mineral assemblage of the shale described earlier. Along the P/T path, few mineralogical changes occur: smectite dehydration takes place between 96 and 112°C. In these conditions we observe only the first transition 3W → 2W.



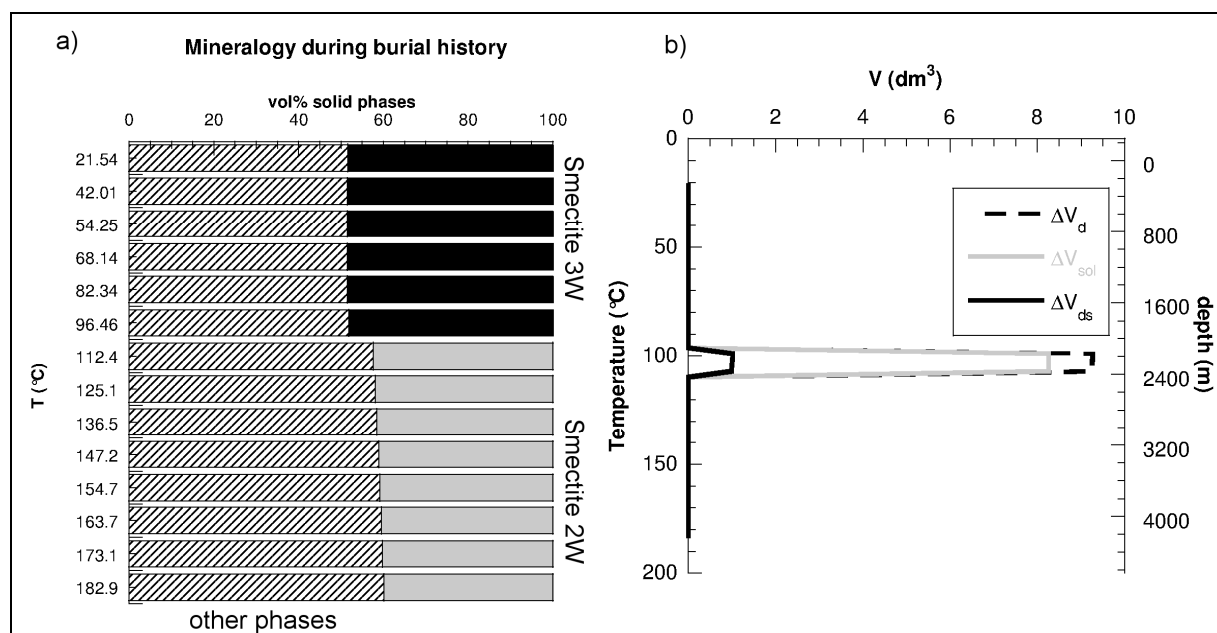


Figure 63: a) Mineralogical evolution of shale along a  $P/T$  path during burial according to Theriak calculations. The black area stands for smectite 3W, grey area for smectite 2W and the hatched area is for other phases, including quartz, kaolinite and albite ; b) Mineral and water volumes variations due to smectite dehydration for an initial deposit of  $1\text{m}^3$  of sediments ( $\Delta V_d$  being the volume water released by smectite dehydration,  $\Delta V_{\text{sol}}$  the decrease of mineral volume and  $\Delta V_{\text{ds}}$  the effective volume variation (Eq. 12)). Dehydration takes place at  $100\text{-}110^\circ\text{C}$  and we observe a positive effective volume variation ( $\Delta V_{\text{ds}}$ ), that testified the global volume increase that can lead to overpressure.

The considered cell is 320 m thick at present day. As described previously, smectite dehydration is an instantaneous phenomenon when a precise temperature is reached. The temperature calculated in Temis for each cell is however corresponding to the temperature at the centre of the cell. To simulate a progressive increase of temperature within the cell, the interval of time during which the dehydration will occur is divided into five intermediate steps, hereby allowing dehydration at different time throughout the thickness of the cell. The increasing in temperature and release of water is considered linear during the intermediate steps.

The calculated variations in mineral and water volumes due to smectite dehydration for an initial deposit of  $1\text{m}^3$  of sediments (Figure 63b) shows that the volume of water released by smectite dehydration ( $\Delta V_d$ ) is higher than the decrease of mineral volume due to the transition  $3W \rightarrow 2W$  ( $\Delta V_{\text{sol}}$ ), i.e. the effective volume  $\Delta V_{\text{ds}}$  is positive and the overpressure of the cell is expected to increase.

The pressure calculations taking into account smectite dehydration ( $P_{ds}$  according to Eq. 31) lead to higher values than the pressure calculated by basin modelling with only undercompaction as overpressure driving parameter ( $P_{Temis}$ ) (Figure 64).

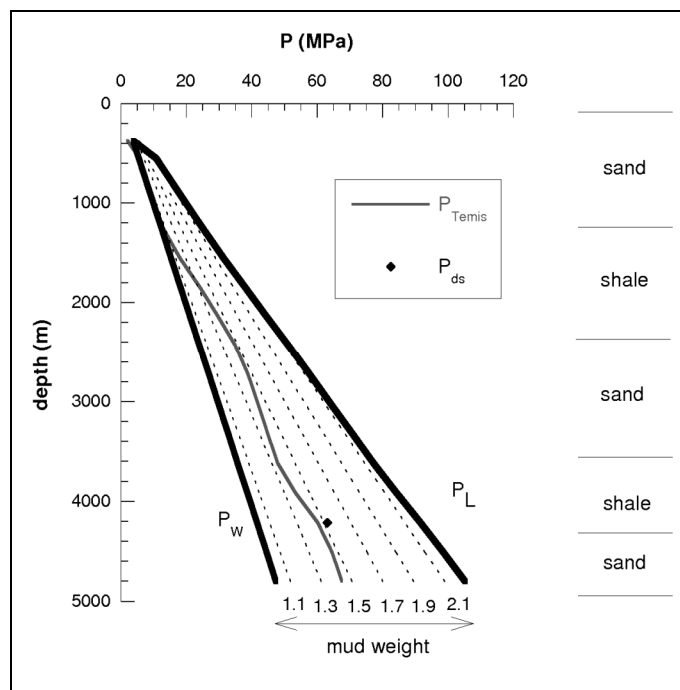


Figure 64: Pressure profile in the well at present day, for the synthetic case.  $P_w$  and  $P_L$  stands respectively for hydrostatic and lithostatic gradients, and  $P_{Temis}$  and  $P_{ds}$  stands respectively for the pressure calculated by basin modelling with only undercompaction as overpressure driving parameter and the pressure calculation taking into account smectite dehydration.

The calculated pressure taking into account the contribution of water release by smectite dehydration is around  $1.5 \text{ g/cm}^3$  equivalent mud weight at present day, which corresponds to a total overpressure of 21 MPa. The contribution of smectite dehydration is about 4 MPa, around 20% of the total overpressure.

## 5. Real case application

### 5.1. Geological context: Niger Delta

The Niger Delta is situated on the West Coast of Africa, at the triple junction between the South Atlantic, the Gulf of Guinea Margin and the Benue Trough (Figure 65). The zone of interest is located in the eastern part of the Delta.

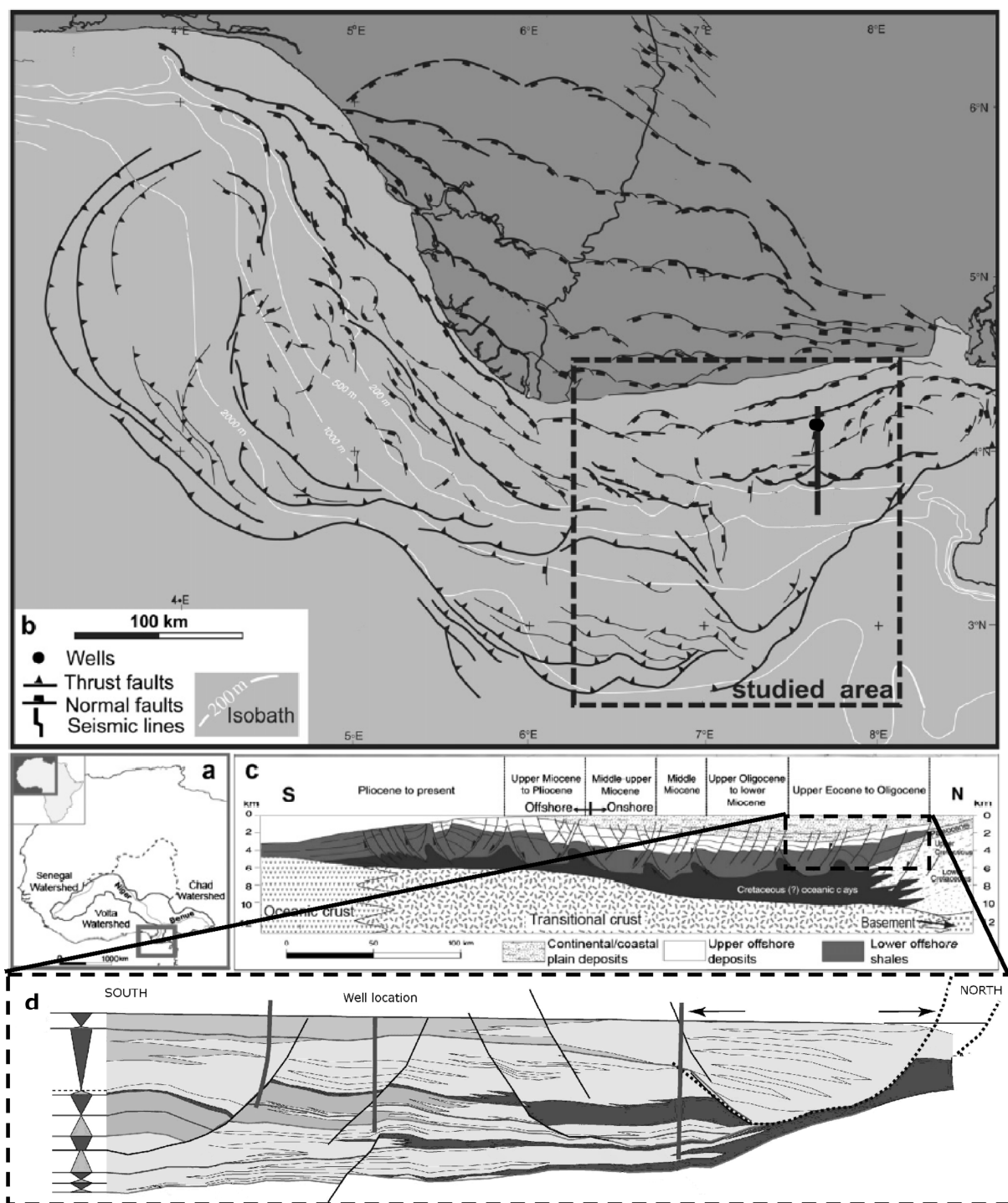


Figure 65:(a) location of the Niger Delta (b) structural map (c) synthetic cross section of the Niger Delta, from Jermannaud et al (2010) (d) Approximative well location, in the near offshore.

The geological history of the delta, its structure and stratigraphy have been controlled by the interplay between rates of sedimentation and subsidence. The Niger Delta is a prograding sequence of clastic sediments developed into a series of off-lap cycles (Jermannaud et al., 2010). Three main sedimentary environments can be identified: 1) organic-rich clay and poorly sorted sand 2) well-sorted sand 3) alternation of clay and well

sorted sand, from 50% clay/50% sand to 100% clay. The total thickness of these sequences since the early Miocene is estimated up to 12 km in the centre of the basin. The geometry of the sedimentary environments and the depositional profiles which can be found in the delta are beyond the scope of the present paper. The reader can consult for example Doust and Omatsola (1989) for the global outlines of the geology of the Delta, and Jermannaud *et al.* (2010) for a more detailed presentation of the stratigraphy of the sedimentary units, and a discussion of the factors controlling the stratigraphic architecture of the delta.

The pressure regime in the Niger Delta can be subdivided into two domains: the first domain is hydrostatic and a deeper second domain is overpressured, characterized by shale undercompaction. In the area studied here, the pore pressure build-up occurred in the deep series (Tortonian Age), mainly under the effect of rapid subsidence from early Tortonian to early Pliocene. Successive depocenters have been affected by gravity-driven deformations on regional detachments associated with over-pressured shales. This formed an upslope extensional domain of growth faults, either synthetic or antithetic of the general displacement (e.g. Doust and Omatsola, 1989) which can be seen on Figure 65d. However no explicit control of the fault on the pressure regime can be drawn. From middle Pliocene to the present day, the sedimentation rate decreased rapidly corresponding to a global progradation of the delta (Figure 65d.). Nevertheless, high pressures are still observed in the deep reservoirs today. Two assumptions can be put forward: (1) the overpressure due to undercompaction before early Pliocene have not yet return to equilibrium (hydrostatic regime) because of very efficient seals corresponding to thick shale deposits of Tortonian age, (2) other sources of overpressure are still active. This last assumption is strengthened by the observation of pressure values up to lithostatic pressure for several wells (Figure 69). It is well known that hydrocarbon (HC) column can increase the pressure in the reservoir due to the contrast of density between HC fluids and water, in the present paper, pressure values corrected for HC effect. The Niger delta forms an exceptional petroleum system, and it is quite obvious that HC generation participates to the present day pressures. But basin modelling simulations integrating HC generation will not be presented. The aquathermal pressuring effect can be ruled out, because the studied area does not present anomalous high temperatures, and the delta is relatively cold since the higher encountered reservoir temperatures are about 120 °C. The aim of the present paper is to determine if the smectite dehydration of Tortonian shale can participate actively to the pressure regime in the eastern part of the delta.

## 5.2. Overpressure estimation

The studied well is located at the east of the presented area (Figure 65b.). Two deep shale layers can be observed at present day separated with a sandstone layer. Mineralogical analyses are identical and the hypothesis that the sediments come from the same source is generally admitted. Therefore, basin modelling calculations are done considering only one type of shale.

Well profile pressure observations are showed in Figure 69. It can be seen that a first deviation to hydrostatic stress is observed at around 3000 m burial depth, this overpressure is about 15 MPa, and a second deviation is observed at around 4000 m burial depth, the overpressure is about 40 MPa. To assess the overpressure, basin modelling calculations are done taking into account the disequilibrium of compaction, i.e. the difference between the fluid expulsion velocity and the sedimentary rate. The permeability law of the shale deposit controls the magnitude of the overpressure for a given sedimentary rate. In agreement with mineralogical and sedimentary observations, the same permeability law is defined for both shale units. It appears that either upper shale pressure is adjusted and lower shale pressure is underestimated, or lower shale pressure is adjusted and upper shale pressure is overestimated. To fit the second overpressure step with only undercompaction mechanism the shale must have very low permeability at shallow depth. In other words, the system must be closed very early from a hydrological point of view, consequently the overpressure, close to lithostatic stress value, must be acquired very early and be preserved over all the geological history. This assumption does not seem realistic. The first step of overpressure may be explained by undercompaction and the second step needs an additional source of overpressure to be explained, for instance, water released from smectite dehydration.

To fit the present day overpressure in the shallow part of the well, we use a Kozeny-Carman relation for permeability with  $3 \cdot 10^8 \text{ m}^2/\text{m}^3$  as specific surface. The difference between the overpressure estimated with only undercompaction and observed data at 4000 m burial depth is about 25 MPa.

The cell of the second shale unit studied here is buried at about 4000 m depth at present day. To assess and discuss the contribution of smectite dehydration, four cases are presented in order to understand the sensitivity of two parameters: the temperature and the chemical composition of the shale. The temperature influence was studied varying the geothermal gradient : 30°C/km and 35°C/km, which are representative of the studied area. The chemical composition was studied with two mineralogical assemblages for the shale typical of this kind of geological environment: (1) a simple chemical system constituted of 30wt% of kaolinite, 30wt% of Na-smectite, 10wt% of quartz and less than 5wt% of albite, with only Si-Al-Mg-Na as cations ; (2) a more realistic chemical system constituted of 40wt% of

kaolinite, 20wt% of Na-smectite, 20wt% of Ca-smectite, 10wt% of quartz, 5wt% of albite and less than 3wt% of calcite, microcline and dolomite, with Si-Al-Mg-Na-Ca-K as cations. The second case presents two smectites with two different chemical compositions.

Thermodynamic calculations determine the stable mineralogy at each step of the cell history (Figure 66). It indicates that regardless of the geothermal gradient, Na-smectite dehydration takes place between 95 and 112°C and Ca-smectite dehydration between 122 and 128°C. In these conditions only the first transition  $3W \rightarrow 2W$  for both smectites is observed. For the Si-Al-Mg-Na-Ca-K system that contains two smectites, this transition is observed twice: one for each smectite.

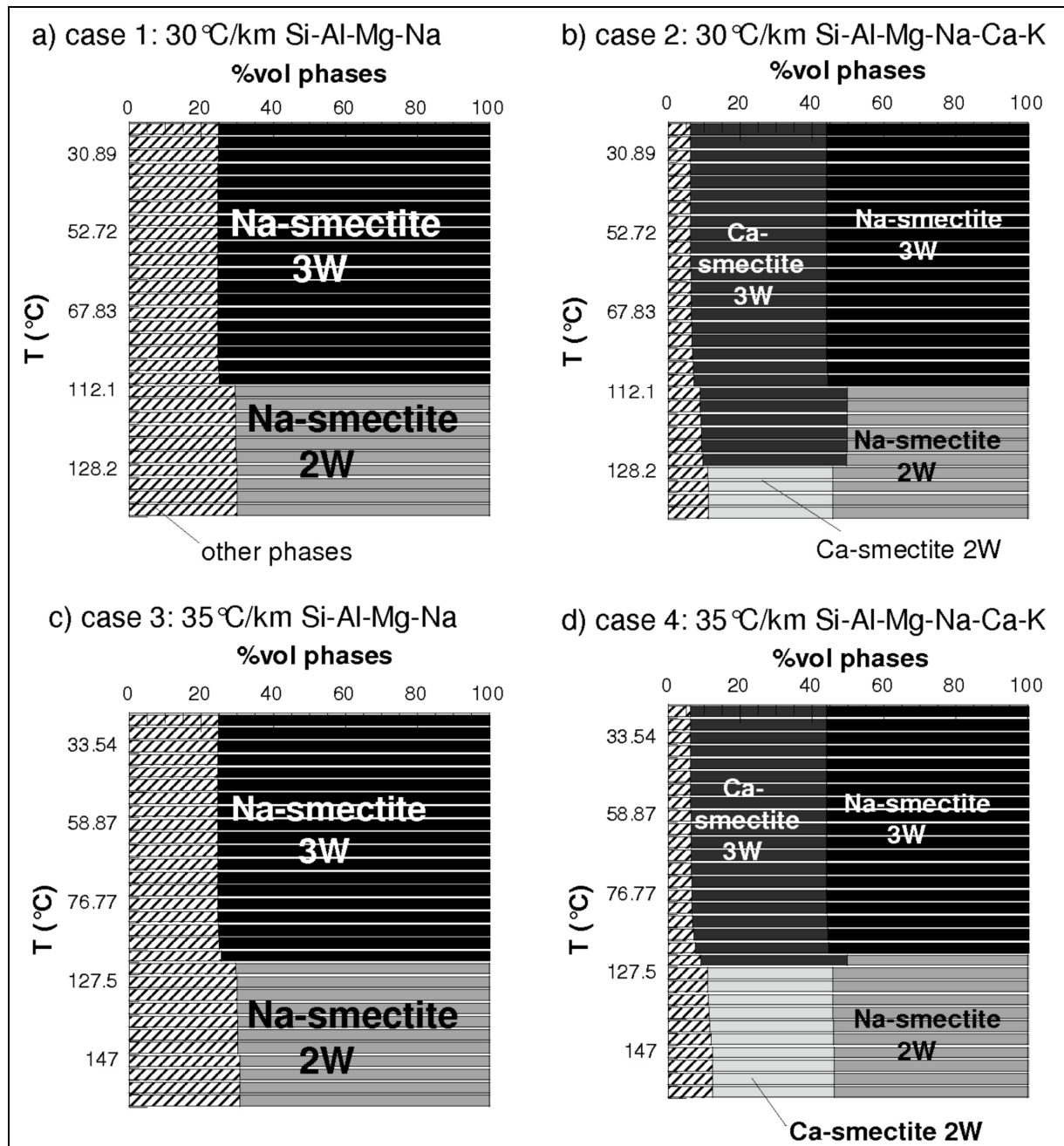


Figure 66: Mineralogy evolution during burial history, for different chemical compositions and geothermal gradients, a) case 1: 30°C/km, simple chemical system (Si-Al-Mg-Na), b) case 2: 30°C/km, more realistic chemical system (Si-Al-Mg-Na-Ca-K, allowing the presence of Na-, Ca-smectites and a potential illitization into K-illites) c) case 3: 35°C/km, simple chemical system, d) case 4: 35°C/km, more realistic chemical system

The thermodynamic calculations lead to the volumes data showed in Figure 67. The volume balance shows that the volume of water released from smectite dehydration ( $\Delta V_d$ ) is higher than the decrease of mineral volume due to the transition  $3W \rightarrow 2W$  ( $\Delta V_{sol}$ ). According to Eq. 30,  $\Delta V_{ds} > 0$ , overpressure increases in comparison with the calculations obtained by basin modelling which only takes into account undercompaction (Eq. 31).

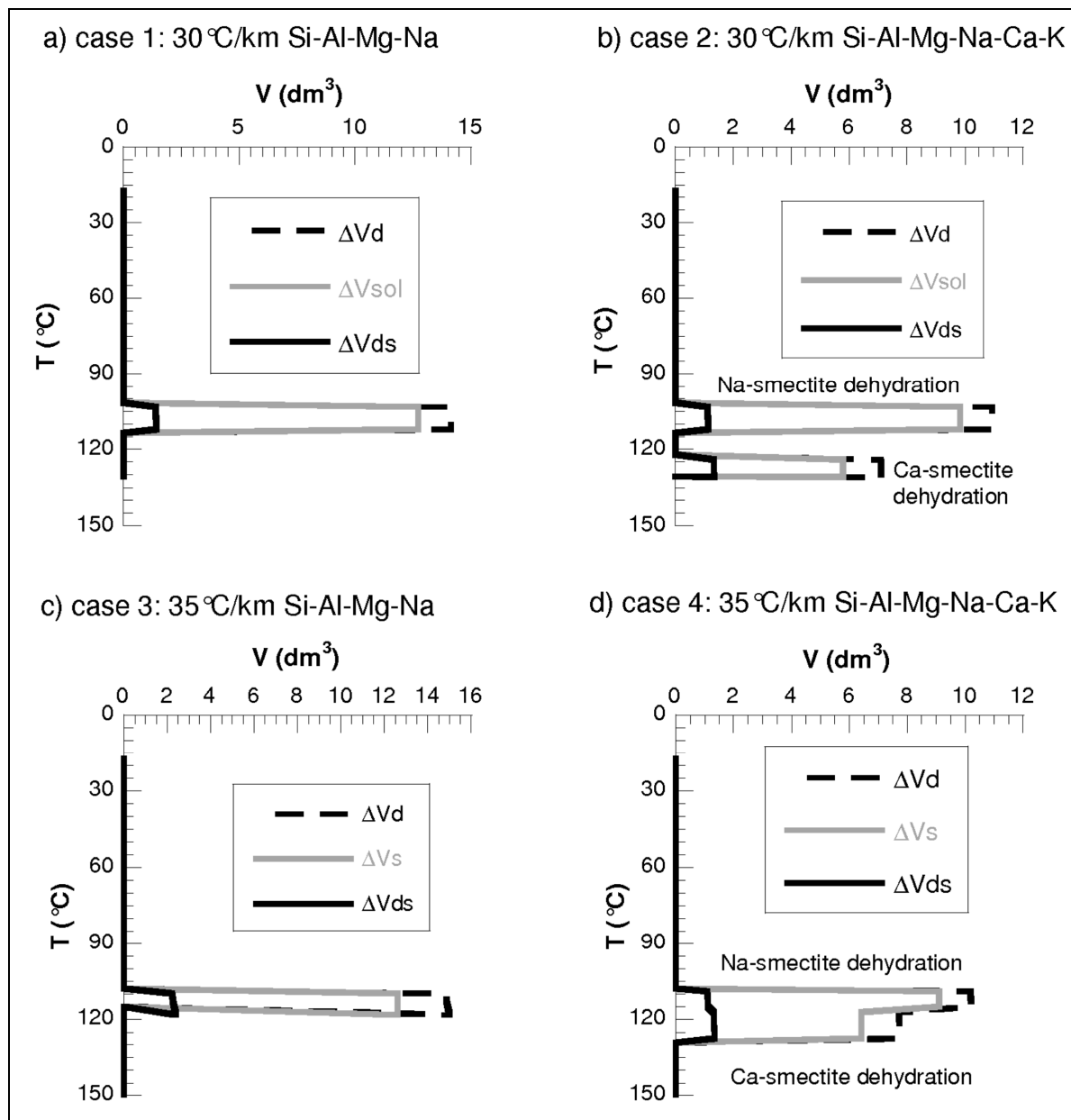


Figure 67: Mineral and water volumes variations due to smectite dehydration for an initial deposit of  $1\text{m}^3$  of sediments a) case 1:  $30^\circ\text{C}/\text{km}$ , simple chemical system, the porosity at the dehydration temperature is  $\Phi_{\text{Na}} = 21\%$  so that represents  $V_{\Phi_{\text{Na}}} = 210\text{ dm}^3$  for  $1\text{m}^3$  of sediments, b) case 2:  $30^\circ\text{C}/\text{km}$ , more realistic chemical system,  $\Phi_{\text{Na}} = 21\%$   $V_{\Phi_{\text{Na}}} = 210\text{ dm}^3$  and  $\Phi_{\text{Ca}} = 17\%$   $V_{\Phi_{\text{Ca}}} = 170\text{ dm}^3$ , c) case 3:  $35^\circ\text{C}/\text{km}$ , simple chemical system,  $\Phi_{\text{Na}} = 21\%$   $V_{\Phi_{\text{Na}}} = 210\text{ dm}^3$  d) case 4:  $35^\circ\text{C}/\text{km}$ , more realistic chemical system  $\Phi_{\text{Na}} = 21\%$   $V_{\Phi_{\text{Na}}} = 210\text{ dm}^3$  and  $\Phi_{\text{Ca}} = 20.5\%$   $V_{\Phi_{\text{Ca}}} = 205\text{ dm}^3$ . ( $\Delta V_d$ ,  $\Delta V_{\text{sol}}$  and  $\Delta V_{\text{ds}}$  stand respectively for the volume water released by smectite dehydration, the decrease of mineral volume and the effective volume variation (Eq. 12))

Figure 68 shows the pressure along a T-P path for the studied cell. The pressure calculations ( $P_{\text{ds}}$ ) leads to higher values than the pressure calculated with basin modelling ( $P_{\text{Temis}}$ ) with only undercompaction, close to the lithostatic gradient ( $P_L$ ) at present day. A jump of



pressure is observed for each dehydration step. The contribution to overpressure of smectite dehydration is about 40% of the total overpressure for the case 1 and 3, corresponding to the simple chemical system with two different geothermal gradients. For the cases 2 and 4 with two dehydration steps we observe a second step of pressure that is related to the release of water from the second smectite dehydration (Ca-smectite).

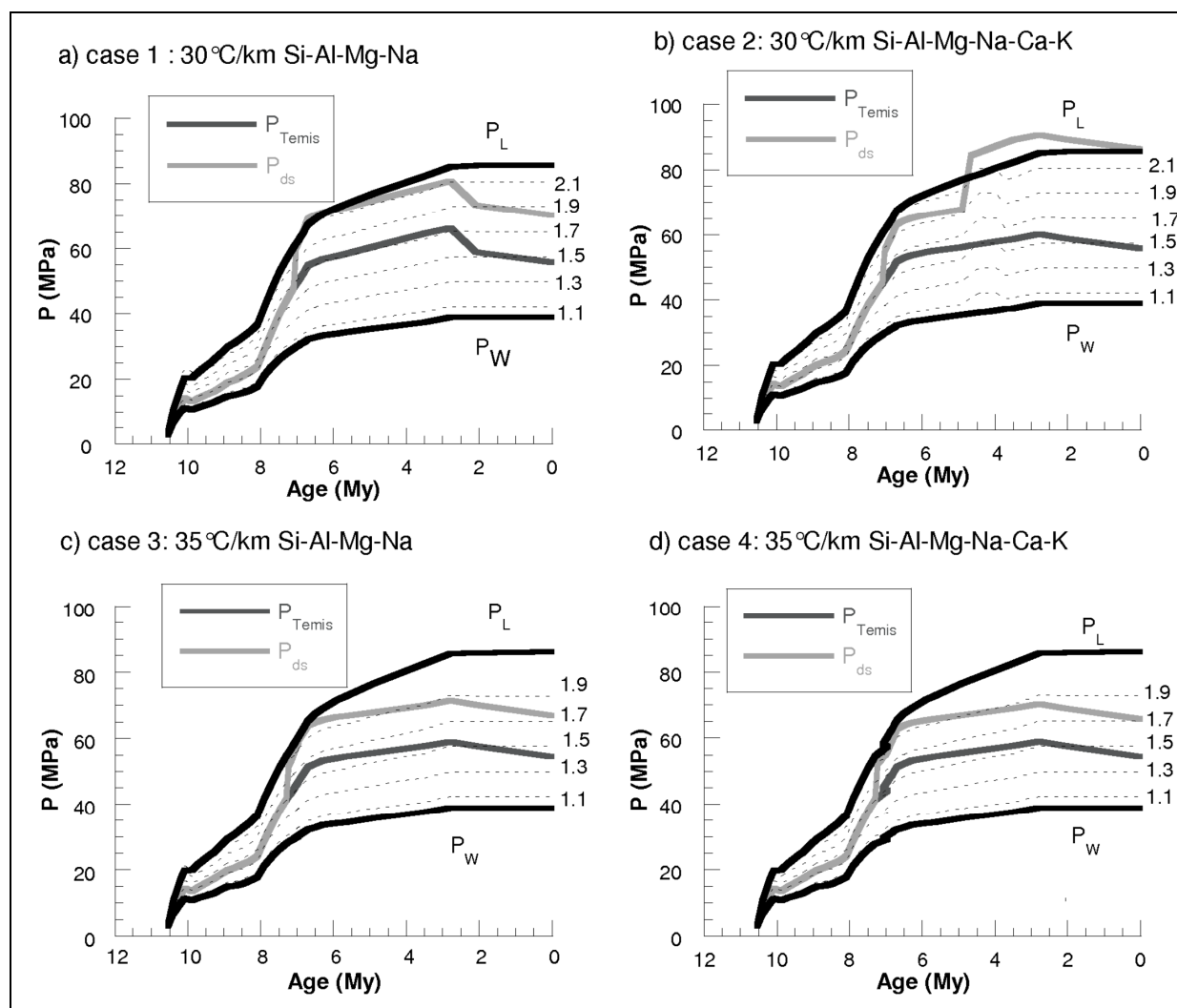


Figure 68: Pressure profile of the cell during burial history  $P_w$  = hydrostatic gradient and  $P_L$  = lithostatic gradient a) case 1: 30°C/km, simple chemical system (Si-Al-Mg-Na), b) case 2: 30°C/km, more realistic chemical system (Si-Al-Mg-Na-Ca-K), c) case 3: 35°C/km, simple chemical system, d) case 4: 35°C/km, more realistic chemical system

Figure 69 shows the profile pressure of the well at present day. Well pressure profile from Temis calculations ( $P_{Temis}$ ) is lower than the observed data ( $P_{well}$ ) of about 20 and 15 MPa respectively for the cases with a geothermal gradient equal to 30°C/km and 35°C/km at present day. The present day overpressure calculated with the contribution of smectite dehydration for the considered cell ( $P_{ds}$ ) is closer to observed data than the previous

estimations for the coldest geothermal gradient. Results for the case 2 show an overpressure higher than the lithostatic gradient, that normally leads to rock fracturing.

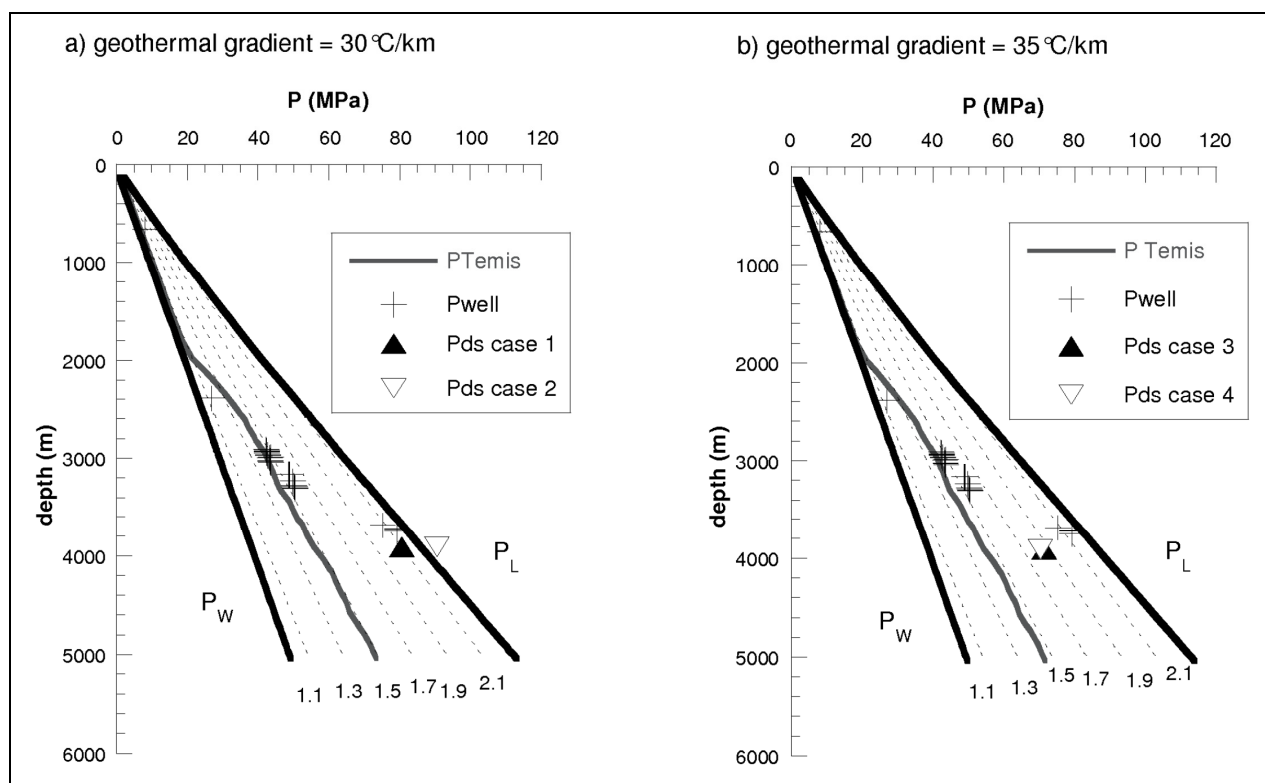


Figure 69: Pressure profile of the well for the two different geothermal gradients.  $P_w$  = hydrostatic gradient,  $P_L$  = lithostatic gradient,  $P_{Temis}$  = pressure calculated accounting only for undercompaction,  $P_{well}$  = observed data in the real well,  $P_{ds}$  = pressure calculated in this study, taking into account smectite dehydration. Cases 1 and 3 designate the simple mineralogical system (Si-Al-Mg-Na) whereas cases 2 and 4 designate the more realistic mineralogical system (Si-Al-Mg-Na-Ca-K).

## 6. Discussion

The calculations show that smectite dehydration can lead to a significant contribution to overpressure in the case of active deltaic environments. In cases where there are a fast sedimentary rate and thick shale layers with low permeability, the quantity of released water by dehydration seems enough to generate a significant overpressure. The main factor that controls the dehydration reaction is temperature. The nature of the interlayer cation in the smectite influences dehydration temperatures: Ca-smectites dehydrates at higher temperatures. For the considered temperature conditions, only the 3W-to-2W reaction has been observed for both Na- and Ca-smectites. It takes place respectively at around 100-110 °C and at around 120-125 °C. For higher temperatures, either in a deeper system or for a higher geothermal gradient, other dehydration steps are expected. The 2W-to-1W dehydration step for Na- and Ca-smectites takes place at around 180 °C and 280 °C

respectively. The 1W-to-0W dehydration step is expected to occur at around 230°C and 300°C respectively. The temperature range of dehydration is more sensitive to the chemistry for the 2W-to-1W and 1W-to-0W steps. Until 300°C, dehydration occurs about every 50°C (around 1500 m, in the case of a geothermal gradient of 30°C/km). Smectite dehydration as a water source is an active process over the entire sedimentary pile. At the exception of the 2W-to-1W Na-smectite transition which is expected to occur at 180°C, the other steps are beyond the classical temperature range of basin studies. However, basins can present older sedimentary units, deeper than the economic target, where the next dehydration steps can occur, and participate to the water budget. The permeability and porosity relationship usually employed in basin modelling cannot be easily extrapolated to these deeper and hotter conditions, but the two parameters are expected to decrease. The dehydration might therefore generate high overpressure in the deeper sedimentary layers. The main growth faults affecting the delta may take root in a low effective stress zone as well as décollement zones for compressive environments. Both phenomena may be related to smectite dehydration.

The permeability of the sediments is an important factor controlling the generation of overpressure for a given sedimentary rate. It can be put in evidence comparing the results of the real case with the two different geothermal gradients: the higher it is, the shallower the dehydration takes place, so when the sediments are less compacted. This is in agreement with the results showed earlier: with a higher geothermal gradient, the final overpressure is lower and the overpressure due to water released from Ca-smectite is higher because it takes place at greater depth than for Na-smectites, so when the permeability is lower.

The hypothesis made in this study is that despite the solid volume decreases due to dehydration, the permeability remains constant. When smectite dehydrates, the solid volume decreases and the water volume increases. The effective water volume released from smectite dehydration is about 15 to 20 times lower than the porous volume present in the sediments (Figure 67). In the case of geological environments with known undercompaction, like in the Niger Delta, released water cannot easily escape from impervious sedimentary layer. The system can be considered as closed. In that case, the permeability of the unit is not expected to be modified. However, in the case of geological environments where the water pressure regime is close to hydrostatic, the released water escapes from the shale. According to Figure 6, the mineral volume decreases and the sediment is expected to shrink, i.e. fast and strongly compacted. The shrunk sediment could become an efficient seal.

The release of water from smectite dehydration could also lead to a decrease of salinity of porous water since the released water is fresh. Hanor (1994) has observed that the top of the overpressure in deep shale layers in the Gulf Coast is associated with a strong decrease of

water salinity (Figure 3 in Hanor, 1994). This author suggested that this dilution can be explained by the illitization of smectites. Illitization is a chemical reaction that transforms smectite into illite. Among other phenomena, this reaction leads to a release of fresh water as well as dehydration of water initially located in the interlayer space of smectitic layers. Moreover, Vrolijk *et al.* (1991) show a dilution of pore water in the northern Barbados accretionary prism which can be related to illitization too.

Unfortunately no salinity information is available for the case study so smectite dehydration cannot be corroborated with any change of salinity of pore water.

Most of the results obtained from the presented calculations show overpressure close to the lithostatic gradient at present day and this is in agreement with observations in real wells. These systems seem to be close to fracturing. Moreover, the results do not take into account the contribution of hydrocarbon generation or migration, which should probably increase even more the estimated overpressure : a new volume balance between kerogens and oils should be taken into account.

Moreover, the compaction law of the shale layer could probably be adjusted accounting for the contribution of hydrocarbon generation and smectite dehydration. In the case where there is only undercompaction as an active process generating overpressure, the evolution of permeability is sudden, leading to very low permeability early in the burial history. Accounting for the contribution of hydrocarbon generation and smectite dehydration could lead to a smoother permeability law. It could also lead to cycles of fracturing and healing of the cap rock. This hypothesis could cause a modification of the oil reserves estimation.

## 7. Conclusions

The aim of this study was to estimate the contribution of smectite dehydration under burial conditions on the generation of overpressure in compacting sedimentary basins. Smectite dehydration is a reaction occurring rapidly at thermodynamic equilibrium and a thermodynamic model has been proposed by Vidal and Dubacq (2009). Thermodynamic volume parameters (Meiller (2013)) were added to the model to allow a better consideration of volume variation for a wider chemical range. The used methodology combines thermodynamic data with geological information provided by basin modelling integrating thermal, mechanical and hydrodynamic coupling. At each pressure and temperature step, corresponding to the burial history, the most thermodynamically stable assemblage is determined by calculation (i.e. for our purpose: to determine smectite hydration state) and the volume balance of the reaction is assessed.

This methodology has been applied to a real case from Niger Delta, where high sedimentary rate and thick shale layers can be found. At present day, the system presents high overpressures. In order to estimate the sensibility of our approach, two parameters have been studied: temperature and chemical composition of the shales. The calculations lead to the generation of overpressure in the four cases, between 15 to 20 MPa at present day and representing almost 40% of the observed overpressure in the well. Comparing the obtained results with the real case to those for a synthetic case, where the sedimentary rate was lower and the porosity and permeability higher, a conclusion is that the contribution of smectite dehydration to overpressure is significant in specific geological environment, where undercompaction already exists.

This work could be completed with a richer thermodynamic model, taking into account the behaviour of iron-bearing smectites, which are very commonly found in sedimentary environments. Moreover, smectitic layers can be also found in interstratified structures with illite, the non swelling clay. Estimating the contribution of volume variation of the swelling part of interstratified illite/smectite may allow a better consideration of the real mineralogy observed in sedimentary basins.

Studying the variations of permeability as a function of smectite dehydration and its potential influences on the fluid circulation in the basin would also be of interest. Moreover it could help to a better reserve assessment accounting for eventual hydrofracturing of cap-rock as a consequence of too much high overpressures caused by smectite dehydration.

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## Conclusion

Le but de cette étude était d'estimer la contribution de la déshydratation des smectites en conditions d'enfouissement sur la génération de surpressions dans les bassins sédimentaires. La méthodologie utilisée est la combinaison de résultats de thermodynamique issues du modèle de Vidal et Dubacq (2009) complété par les résultats de paramètres de Margules de volumes déterminés dans la première partie de cette thèse, avec des informations issues de la modélisation de bassin telles que des données thermiques, mécaniques et de couplage hydrodynamique. A chaque étape d'enfouissement d'une cellule, donc pour chaque couple température-pression, nous sommes capables de déterminer l'assemblage stable thermodynamiquement, c'est-à-dire l'état d'hydratation de la smectite, et d'effectuer le bilan volumique de la réaction.

Cette méthodologie a été appliquée à un cas du delta du Niger, où l'on rencontre de forts taux de sédimentation et d'épaisses couches argileuses, associées à de fortes surpressions aujourd'hui. Les deux paramètres étudiés ici sont la température, via le gradient géothermique, et la composition chimique de la couche argileuse. Les résultats obtenus mènent à la génération de surpressions, entre 15 et 20 MPa, dans les 4 cas présentés. Cette surpression représente environ 40% de la surpression totale observée dans le puits à l'actuel.

Le facteur principal contrôlant la surpression à un taux de sédimentation donné est la perméabilité. Pour un même volume d'eau libéré, la surpression générée est plus importante pour de faibles perméabilités. C'est pourquoi, les Ca-smectites entraînent de plus fortes surpressions que les Na-smectites : elles se déshydratent à plus haute température donc plus profondément, quand les sédiments sont plus compactés, avec une perméabilité plus faible. L'hypothèse faite dans l'étude est que la perméabilité du milieu n'est pas modifiée par la déshydratation des smectites. Quand la perméabilité est déjà très faible, comme dans le cas du delta du Niger, l'eau libérée aura du mal à s'évacuer et donc on s'attend à des modifications très faibles voire nulles de la perméabilité. Dans des cas où la perméabilité avant la réaction est plus élevée, lorsque le volume solide diminue à cause de la déshydratation, on peut s'attendre à observer une compaction très rapide et très forte des sédiments, entraînant une chute de la perméabilité et transformant la couche en couverture efficace. L'étude de la variation de perméabilité au cours de la réaction pourrait donc aider à prédire ce type de phénomène, ainsi que l'influence sur la circulation des fluides.

Un macro-marqueur de la réaction de déshydratation des smectites est la baisse de la salinité, puisque l'eau libérée est douce. En effet, il a déjà été observé que les dilutions de salinité sont reliées à des zones de surpressions. La déshydratation des smectites est un des facteurs principaux expliquant la baisse de salinité associée à l'augmentation de la

pression. Il serait donc intéressant d'étudier la variation de salinité dans le puits, malheureusement nous ne disposons pas des données de concentration en sel.

Afin de compléter notre approche, il serait intéressant de prendre en compte l'influence de la génération et de la migration des hydrocarbures, qui sont susceptibles d'augmenter encore plus la surpression. De plus, le modèle thermodynamique pourrait également être complété en ajoutant les paramètres pour des smectites contenant du fer, comme c'est le cas souvent dans la nature.