

Overpressure generation by smectite dehydration in sedimentary basins constrained by salinity dilution and stable isotopes

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- ¹ Overpressure generation by smectite dehydration in
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- and stable isotopes
- 4

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- 10 Graphical abstract



12 Abstract

The water released by smectite dehydration because of pressure and temperature increase during burial of claystone or clay-rich mudstone in sedimentary basins can generate overpressure and change the water salinity. Up until now, a clear distinction has been lacking between the water fraction produced by compaction and the water fraction produced by thermodynamic dehydration. Smectite dehydration is mentioned in the literature in pore pressure prediction or as a hypothesis for water freshening but direct evidence is missing.

Here, we bring this evidence by linking the δ^{18} O-H₂O water isotopic signature, salinity evolution and overpressure generation to the spatial and temporal fluid budget in a sedimentary pile involving smectite dehydration. Water samples indicating an increase in δ^{18} O-H₂O and a salinity decrease were sampled deep offshore in the Gulf of Guinea in sandstone lenses intercalated within shale layers. By using a numerical coupled approach, we were able to reproduce the fluid evolution by modelling smectite dehydration based on thermodynamic considerations during the burial of the sedimentary pile and the associated pressure and temperature evolution over geological ages.

26

27 Introduction

An understanding of fluid migration and trapping over the history of sedimentary basins is needed for the sustainable and cost-effective exploitation of geothermal and oil and gas subsurface resources as it ensures a more accurate evaluation of the resource and anticipation of its evolution. In deep geological settings considering the impact of clay-rich sediments on the fluid migration and pressure evolution remain a challenge. Migration of fluids and solutes is complexly impacted in deep claystones because of their low permeability, their membrane behaviour that can restrict the transport of waters and solutes and because of the water/rock interactions.

35 Smectite dehydration in sedimentary basins is sometimes cited as a process that can generate 36 abnormal pressure conditions (Audet, 1995; Bruce, 1984; Tanikawa et al., 2008; Tremosa et al., 2020) 37 or as a freshening mechanism. However, direct evidence of the influence of smectite dehydration on 38 fluid evolution at the scale of the basin or formation was still missing. Smectite dehydration consists 39 in the loss of interlayer water within smectite crystal that occurs with temperature and pressure 40 increase (Figure 1). The term 'smectite dehydration' also refers to the loss of water during the 41 smectite-to-illite transformation and attention was mainly paid to this latter process in sedimentary 42 basins. In both cases, when smectite dehydration of interlayer water occurs or when the smectite 43 structure evolves to an illite structure, the interlayer water is released to the shale porosity. The

smectite dehydration process must not be confused with the water produced by the compaction of
the clayey formations. In the latter process, interstitial water is drained by applying burial stress to
the formations.

47 Overpressures in sedimentary basins are hydrodynamic phenomena involving various coupled 48 geological processes over the basin history (Neuzil, 1995). When the different hydraulic, mechanical, 49 thermal and chemical couplings are considered, the interpretation of overpressure generation and 50 dissipation to obtain the present-day pressure profile provides good insights into the fluid migration and budget in the basin. At the basin scale, the expression of smectite dehydration can be recorded 51 52 by the pore pressure (Bruce, 1984; Tanikawa et al., 2008; Tremosa et al., 2020), but the 53 interpretation of the origin of the pore pressure profile generally remains uncertain (Bjørlykke et al., 54 2010) with smectite dehydration acting as an additional cause of overpressure (Audet, 1995; 55 Tremosa et al., 2020). Stable oxygen isotopic data are also commonly used to document the pore 56 fluid history in sedimentary basins (Hanor, 1994), taking into account the contribution of the different sources of water. Pore fluid enriched in ¹⁸O concomitantly to a decrease in salinity is often 57 58 interpreted as the consequence of smectite dehydration (Boschetti et al., 2016; Clayton et al., 1966; 59 Franks & Uchytil, 2016; Macpherson, 1992; Morton & Land, 1987; Nicot et al., 2018; Wilkinson et al., 60 1992). However, this interpretation of smectite dehydration influencing the δ^{18} O-H₂O isotopic signature and salinity is generally not based on a volume budget of water released by smectite 61 62 minerals and its mixing with porewater in the sedimentary pile. Moreover, the thermodynamics of 63 smectite dehydration are rarely checked (Colten-Bradley, 1987; Vidal & Dubacq, 2009). 64 Consequently, the effect of smectite dehydration remains a hypothesis that requires to be tested by 65 a coupled approach, combining burial, smectite dehydration and water freshening considerations.

66 Smectite dehydration is also documented in mud volcanoes (Dählmann & Lange, 2003; Hensen et al., 67 2007) and in subduction zones (Kastner et al., 1993), where correlations are observed between water 68 freshening and an increase in the δ^{18} O-H₂O isotopic signature, and are explained by smectite 69 dehydration. These studies generally relate water release to smectite-to-illite transformation, but a 70 few of them focus on the dehydration of interlayer smectite (Fitts & Brown, 1999; Hüpers & Kopf, 71 2012). In these studies, smectite dehydration was induced in laboratory experiments that considered 72 pressure and temperature conditions of convergent margins. In subduction zones and mud 73 volcanoes, smectite dehydration during illitisation has also been considered in the fluid budget of 74 numerical analyses to explain the observed water freshening with depth (Bekins et al., 1995; Brown 75 et al., 2001; Henry & Bourlange, 2004; Hüpers et al., 2019; Saffer & McKiernan, 2009; Vanneste et al., 76 2011). However, these studies only consider the temperature dependence of the smectite-to-illite 77 transformation, overlooking smectite dehydration.

In our study, we tested the effect of smectite dehydration on the δ^{18} O-H₂O isotopic signature, the 78 79 evolution of pore fluid salinity and overpressure generation in a sedimentary pile in the Gulf of 80 Guinea. The δ^{18} O-H₂O signature and the salinity are two records of smectite dehydration and of the volume of water that is consequently released in the sediments. Smectite dehydration is described 81 by considering a consistent thermodynamic model as a function of pressure and temperature 82 evolution during the burial of the sedimentary pile. The water budget then accounts for the release 83 84 of water by smectite dehydration depending on the geometry, pressure, temperature and properties 85 of the sedimentary pile and the timing of this water release.

86 Methods

87 Sampling and analyses

88 Field data were obtained from a well, drilled to explore the petroleum potential of the Gulf of Guinea. This well is located about 50 km from the coast, at a sea depth of about 2000 m. The drilling 89 90 penetrated through a sediment thickness of about 2700 m, from the seafloor. The main objective of 91 the well was to identify the Upper Cretaceous post-rift series and, in particular, the sandstone 92 reservoirs in turbidite systems. During the drilling operations and the following tests, a large set of 93 data was obtained regarding geology, lithology, mineralogy, pressure and temperature conditions and fluid composition in the reservoirs, amongst other information. The following data from the well 94 95 were used for hydrogeological interpretation and the modelling of the present study:

96 97

• The lithological and composite logs of the well at a scale of 1:500 were used to establish the lithological profile and the meshing.

- Biostratigraphic dating was available, based on foraminifera, nanoplankton and pollens
 identified on cuttings and cores. This dating was used together with the sediment thickness
 at the deposition to calculate the sedimentation rate.
- The formation pressure, corresponding to the fluid pressure, was measured in the well by 87 102 measurements using Schlumberger Modular Formation Dynamics Tester of which 28 gave 103 good quality results. The pressure was hydrostatic down to the Campanian deposit basis. A 104 moderate fluid overpressure was measured below, corresponding to an apparent density of 105 1250 to 1300 kg.m⁻³ in Turonian and Santonian levels ($\rho = \frac{P}{g \cdot z}$). The Turonian reservoirs 106 separated by shale layers are not hydraulically connected. In addition, the shale pressure was 107 measured to be close to the reservoir pressure.
- A temperature gradient of about 4.4 °C/100 m was measured between the seabed (4 °C) and
 the well foot during electrical logs.

 The mineralogy and petrography of samples presenting different facies and ages were determined through petrographic studies on 43 samples, by quantitative mineralogy analyses (bulk rock XRD-XRF, CEC, density, organic carbon and sulphur analyses and XRD clay fraction analyses) on 66 samples and by complementary mineralogical analyses on clay mineral phases (electron microprobe) on 3 samples.

- Five water samples were taken during MDT tests in the sandstone reservoir at depths between 2000 and 2600 m below the seafloor, allowing the determination of the chemical and isotopic (δ^{18} O and δ^{2} H-H₂O, 87 Sr/ 86 Sr, δ^{34} S and δ^{18} O-SO₄ and δ^{7} Li) composition of these waters.
- 119 Thermodynamic model for smectite dehydration

The chemical composition of pure smectite was determined for a shale sample of the Turonian age 120 121 from the well, by performing 150 electron microprobe analyses on the < 2 μ m clay fraction. Among them, the smectite compositions, expressed on a structural basis of O₁₀(OH)₂, were selected using 122 M⁺-4Si-R²⁺ diagrams (Meunier & Velde, 1989) (M⁺ = layer charge of ideal micas, 4Si = maximum Si 123 content of the tetrahedral sheet, R^{2+} = amount of bivalent cations in the octahedral position), 124 125 following which the compositions associated with mixtures of clay minerals and/or other silicate 126 minerals could be discarded. The following mean composition for smectite was obtained 127 $(Na_{0.085}K_{0.180}Ca_{0.037})(Si_{3.809}AI_{0.191})(AI_{1.720}Mg_{0.090}Fe^{2+}_{0.256})O_{10}(OH)_2$, with a molar mass of 379.51 g/mol. For 128 sake of simplicity in the application of the thermodynamic model in the burial model, the Na homoionized form of the smectite was considered. 129

The thermodynamic smectite dehydration model (Vidal & Dubacq, 2009) adapted for use in PHREEQC geochemical calculation code (Tremosa et al., 2020) considers binary solid solutions between hydrated smectite end-members with 1, 2 or 3 layers of water, which respectively contain 2, 4 and 7 moles of interlayer water per mole of smectite (on a structural basis O₁₀(OH)₂), and anhydrous smectite. The description of smectite dehydration then involves the three following binary solid solutions, where A refers to anhydrous, and 1w, 2w and 3w refer to 1, 2 and 3 layers of water, respectively:

- 137 Smect_Na.A Smect_Na.1w
- 138 Smect_Na.A Smect_Na.2w
- 139 Smect_Na.A Smect_Na.3w

141 The deployment of this smectite dehydration model required calculating the thermodynamic 142 properties (G, H, S, C_{p} , V) of the anhydrous end-member (Blanc et al., 2015) and of the hydrated 143 smectite end-members (Vidal & Dubacq, 2009) (Table 1) as well as the dependence of the smectite 144 equilibrium constant on temperature (Table 2). The interaction parameters of the non-ideal solid solution estimated for montmorillonites were used (Vidal & Dubacq, 2009). So, Margules parameters 145 of -10 kJ are considered for solid solutions between anhydrous smectite and the three hydrated 146 147 smectite end-members.

148 Preferential stability domains of the different hydrated smectite end-members were calculated 149 depending on the pressure and temperature conditions. The transition pressure and temperature 150 from a hydrated smectite end-member to a less hydrated smectite were then determined and used in the model coupling burial and dehydration. For a given smectite, three stability domains were then 151 152 defined corresponding to the pressure and temperature conditions where the solid solution with 3 153 layers of water, 2 layers of water and 1 layer of water are in play. The stability domains for Na smectite from the sedimentary pile are delimitated by the following functions: 154

155 - Transition Smect_Na.3w → Smect_Na.2w according (
$$P_{tr1}$$
, T_{tr1}) :
156 P_{tr1} = 102.53 T_{tr1} - 2843.9 (r² = 0.990)

 $P_{tr1} = 102.53 T_{tr1} - 2843.9 (r^2 = 0.990)$

157

- Transition Smect_Na.2w \rightarrow Smect_Na.1w according (P_{tr2}, T_{tr2}) : 158

159

 $P_{tr2} = 201.25 T_{tr2} - 20942$ (r² = 0.968)

160 , with P_{tr} expressed in bar and T_{tr} in °C.

161 Table 1 : Thermodynamic properties estimated for the smectite identified in the well and expressed as Na homoionized 162 smectite at 1.013 bar and 298.15 K. Clay mineral Cp(T) functions are expressed as $C_p(T) = A + B.10^3 T + C 10^5 T^2$, where A, B 163 and C are Maier-Kelley coefficients.

	<i>m</i> _n H₂O	∆G _f °	∆H _f °	δ <i>H_f°m</i> _n H₂O	S°	V°	<i>C_p</i> (25°C)	Α	В	С
	(mol/O ₁₀)	kJ/mol	kJ/mol	kJ/mol	J/mol/K	cm³/mol	J/mol/K	J/mol/K	J/mol/K ²	J/mol*°K
Smect_Na.A	0	-5277.00	-5641.05		293.60	134.32	314.25	329.41	235.20	-75.82
Smect_Na.1w	2	-5762.50	-6232.85	293.85	403.60	168.56	402.23	418.09	284.52	-89.50
Smect_Na.2w	4	-6239.71	-6816.35	291.75	513.60	202.81	490.21	506.76	333.84	-103.19
Smect_Na.3w	7	-6951.26	-7687.34	290.33	678.60	250.75	622.19	639.77	407.82	-123.72

165 Table 2 : Temperature dependence of the equilibrium constant (log10 K) for the dissolution of the identified Na smectite in 166 water, at 298.15 K and 1.013 bar. $log_{10}K = A_1 + A_2^*T + A_3/T + A_4^*log(T) + A_5/T^2$

	mրH₂O	log ₁₀ K	A1	A2	A3	A4	A5	Dissolution reaction
Smect_Na.A	0	4.78	-1.2871864E+03	-2.2190924E-01	6.9174286E+04	4.6807708E+02	-2.8539614E+06	$Na_{0.339}(Si_{3.809}AI_{0.191})(AI_{1.72}Mg_{0.09}Fe_{0.256})O_{10}(OH)_2 \\ \\ \cdot $
								$6.764H^{+} + 3.236H_2O = 1.911AI^{+++} + 0.256Fe^{++}$
								0.09Mg ⁺⁺ + 0.339Na ⁺ + 3.809H ₄ SiO ₄

Smect_Na.1w	2	2.82	-1.2400371E+03	-2.1299471E-01	6.5227041E+04	4.5146250E+02	-2.6249665E+06	$Na_{0.339}(Si_{3.809}Al_{0.191})(Al_{1.72}Mg_{0.09}Fe_{0.256})O_{10}(OH)_2:2H_2O + 6.764H^+ + 1.236H_2O = 1.911Al^{+++} + 0.256Fe^{++} + 1.916H_2O = 1.911Al^{+++} + 0.256Fe^{++} + 1.916H_2O = 1.911Al^{+++} + 0.916H_2O = 0.916H_$
								0.09Mg ⁺⁺ + 0.339Na ⁺ + 3.809H ₄ SiO ₄
Smect_Na.2w	4	2.30	-1.1928878E+03	-2.0408019E-01	6.1713440E+04	4.3484792E+02	-2.3959717E+06	$Na_{0.339}(Si_{3.809}AI_{0.191})(AI_{1.72}Mg_{0.09}Fe_{0.256})O_{10}(OH)_2:4H_2O$ +
								6.764H ⁺ = 1.911Al ⁺⁺⁺ + 0.256Fe ⁺⁺ + 0.09Mg ⁺⁺ +
								0.339Na ⁺ + 3.809H ₄ SiO ₄ + 0.764H ₂ O
Smect_Na.3w	7	2.28	-1.1246081E+03	-1.9110531E-01	5.6792159E+04	4.1082120E+02	-2.0593250E+06	$Na_{0.339}(Si_{3.809}AI_{0.191})(AI_{1.72}Mg_{0.09}Fe_{0.256})O_{10}(OH)_2:7H_2O +$
								6.764H ⁺ = 1.911Al ⁺⁺⁺ + 0.256Fe ⁺⁺ + 0.09Mg ⁺⁺ +
								0.339Na ⁺ + 3.809H4SiO4 + 3.764H ₂ O

168 Model coupling burial, dehydration and water freshening

The SURP code (Tremosa et al., 2020), a thermo-hydro-mechanical model coupled with chemical 169 170 reactivity, was used to calculate the pore pressure evolution during the burial of a sedimentary pile 171 under the combined effects of mechanical compaction, thermal expansion, water production by 172 mineralogical reactions and water flow. This model relies on the resolution of the continuity equation in a porous medium where the variation of fluid mass depends on the changes in fluid pressure, 173 mechanical stress and temperature over time. A source term is added to the water balance to 174 175 consider the coupling with production and consumption of water by mineralogical reactions. The 176 coupled flow equation can be expressed as follows:

177
$$Ss'\frac{\partial P}{\partial t} - Ss'\xi\frac{d\sigma_{zz}}{dt} - \rho_f g\Lambda'\frac{\partial T}{\partial t} = \nabla \left[g\frac{k\rho_f}{\mu_f}(\nabla P - \rho_f g\nabla z)\right] + \Gamma$$

where, $S_{s'}$ is the unidimensional specific storage coefficient (m⁻¹), *P* is the pore pressure (Pa), *t* is the time (s), ξ is the unidimensional loading coefficient (dimensionless), σ_{zz} is the total vertical stress (Pa), ρ_{f} is the fluid density (kg.m⁻³), *g* is the acceleration constant due to gravity (9.81 m.s⁻²), Λ' is the thermal response coefficient (°C⁻¹), *T* is the temperature (°C), ∇z is (0,0,1) if the *z* axis is orientated downward, μ_{f} is the fluid dynamic viscosity (Pa.s) and Γ is a source term corresponding to input or withdrawal of water in the porosity.

The chemical and isotopic evolutions of the water in the sandstone reservoirs were calculated by reproducing the mixing of sandstone water with water coming from the surrounding shale layers. For that, the water produced by smectite dehydration in the cells of the underlying and overlying shale layers was summed and mixed as fresh water in the water filling the sandstone layer. This mixing was performed during the PHREEQC operations of the SURP Python-PHREEQC coupling, using the keyword 'MIX' and considering the following mixing factor $F_{mix}^{dehydration}$:

190
$$F_{mix}^{dehydration} = \frac{\sum mass of dehydration water}{sandstone thickness \times \rho_f \times n}$$

191 where, *n* is the porosity.

192 This mixing factor allows the evolution of the isotopic signature to be calculated by mixing the 193 sandstone reservoir water which initially has a δ^{18} O-H₂O signature of 0 ‰, corresponding to connate 194 seawater, with water released by smectite dehydration with a δ^{18} O-H₂O signature of +20 ‰ (Savin & 195 Lee, 1988; Sheppard & Gilg, 1996). No isotopic fractionation was considered during dehydration 196 reactions.

197 The dilution of sandstone reservoir water due to a flow of fresh water, i.e. by ultrafiltration in the 198 shale or leakage, modifies the water salinity when the system becomes hydraulically closed. In this 199 way, a dilution factor was applied to the water filling the sandstone reservoirs when the intrinsic 200 permeability of the overlying shale layer was lower than 10⁻²⁰ m². As long as the system was 201 hydraulically open, it was assumed that the inflow of fresh water was equilibrated by advective 202 mixing and a decrease in salinity cannot be observed. The dilution factor applied in the sandstone 203 layer was adjusted to fit the observed salinity decrease.

204 The model mesh was built from the well log, and mineralogy and parameter profiles. The 2700 m 205 thick sedimentary pile was divided into 82 successive lithological layers. The thickness of these 206 lithological layers can vary between 2 m, for sandstone layers intercalated between shales, and 683 207 m, for shallow sediments not concerned by the mechanisms under study. A backstripping or 208 decompaction model (Sclater & Christie, 1980) was applied to calculate the thickness of each 209 lithological layer at the time of its deposit. The calculated thickness of the uncompacted sedimentary 210 pile is about 4400 m. Each lithological layer was then sliced into several meshes if the thickness of the uncompacted layer was greater than 10 m. The geometry of the sedimentary pile is therefore 211 212 described by 411 meshes of initial thickness varying between 2.2 and 19.4 m. Sedimentation rates (Table 3) were calculated from the uncompacted thickness of sediments and the biostratigraphic 213 214 dating for the well. The most significant sedimentation event occurred during the Santonian age, 215 with a sedimentation rate of 340 m/My.

217 Table 3: Sedimentation rates for forward modelling of IVOIRE-1X sediment deposition.

Geological age	Sedimentation rate	
		(m/My)
Since Miocene	15.97 My to present	60
Middle Eocene and	41.2 My to 15.97 My	0
Oligocene		
Paleocene and Middle	66 My to 41.2 My	20.4
Eocene		
Campanian and	83.6 My to 66 My	52.5
Maastrichtian		
Santonian	86.3 My to 83.6 My	340.1
Coniacian	89.8 My to 86.3 My	34.8
Turonian	93.9 My to 89.8 My	47.7
Cenomanian	100.5 to 93.9 My	39.4
Albian	113 to 100.5 My	40

218

Hydraulic and mechanical calculation parameters and initial content in smectite are reported in Table 4. In terms of hydraulic boundary conditions, hydrostatic conditions are considered in the layers of the sedimentary pile above the roof of the measured overpressure. A no-flow Neumann boundary condition is taken on the basis of the modelled sedimentary pile. This model considers a constant temperature gradient with depth (0.0446 °C/m) based on the present-day geothermal gradient, which is a simplification.

- 226 Table 4: Calculation parameters used in SURP modelling. 'sh', 'shsd' and 'sd' respectively correspond to the 'shale', 'shaly-
- 227 sandstone' and 'sandstone' facies encountered in the IVOIRE-1X sedimentary pile. n is porosity and e is the void ratio.

Intrinsic permeability <i>k</i> (m²)	'sh': $\boldsymbol{k} = \frac{\left(\frac{n}{(1-n)40 \times 2720}\right)^2}{3n^{-3}}$
	'shsd': $\mathbf{k} = \frac{\left(\frac{n}{(1-n) \cdot 40 \times 2680}\right)^2}{3 \cdot n^{-3}}$
	'sd' : $k = 9.87 \ 10^{-13} \times 0.03 n^3$
Biot coefficient α	$\alpha = 1 - (1 - n)^{3.8}$
(dimensionless)	
Poisson ratio v	v = 0.3
(dimensionless)	
Young modulus <i>E</i> (GPa)	$E = 25(1-n)^{10}$
Compaction index C _c	'sh' : $C_c = 0.7e + 0.44$
(dimensionless)	'shsd' : $C_c = 0.5e + 0.4$
	'sd' : $C_c = 0.15e + 0.35$
Mineralogy	'sh': Smectite_Na 30 %
	'shsd': Smectite_Na 15 %
	'sd': Smectite_Na 0 %

229

230 Geological context – Sand lenses draining water produced in shale

231 layers

Intercalations of sandstone lenses in thick shale layers of the Cenomanian, Turonian and Santonian ages were found in the transform margin context of the Gulf of Guinea (Antobreh et al., 2009; Mascle & Blarez, 1987). The exploration well is located offshore at a water depth of about 2000 m. The well is drilled through a sediment thickness of about 2700 m. Several sandstone lenses 3 to 20 m thick were intercalated between thicker shale layers 5 to 143 m thick in marine deposits corresponding to transgressive sequences during the first connections with the Tethysian domain, during the opening of the equatorial Atlantic Ocean. The sandstone corresponds to subarkose sandstones in the Folk

classification and present a porosity between 10 and 20 % for a permeability generally higher than 1 milliDarcy (10⁻¹⁵ m²). Shale layers consist in claystones composed of 30 to 45 % of clay minerals and mica, depending on the samples. Quartz and feldspars are the other main constituents. The smectite is montmorillonite showing octahedral substitutions. Permeability between 0.0005 and 0.1 milliDarcy were measured on the argillaceous sandstone facies but no measurements were made on samples richer in clay minerals of the claystone facies.

Figure 1 schematically presents the geometry of the sandstone lenses intercalated in thicker shale layers. The water released by the shales drains into the sandstone lenses where mixing with the initial porewater can occur. It is therefore thought that information on the fluid evolution can be deduced from water samples taken in the sandstone lenses at different depths.



Figure 1: Schematic representation of the sediment geometry crossed by the well in the sediments of the Santonian,
Coniacian and Turonian ages with sandstone lenses intercalated between thicker shale layers. Fluids expulsed from the shale
are drained and mixed in the sandstone lenses. Water in the clayrock is distributed between the water in the macroporosity,
expulsed by compaction, and the water in the interlayer space of smectite crystals, released during smectite dehydration.

254 Well data suggesting clay dehydration

249

255 Several chemical and isotopic parameters measured on the water sampled in different sandstone 256 lenses after the borehole drilling suggest that clay dehydration occurred in the shale layers (Figure 2, 257 Table 5). A salinity decrease is observed with increasing depth, where the total dissolved salt (TDS)

content decreases from 18 to 5 g/L between about 2000 m and 2600 m deep, below the seafloor. 258 259 Concomitantly to this salinity decrease, an increase in the δ^{18} O-H₂O isotopic signature is observed. The shallower water sample (sample 1 in Figure 2) has a δ^{18} O-H₂O signature of +0.6 ‰ vs SMOW 260 (Standard Mean Ocean Water), close to reference 0 $\% \delta^{18}$ O-H₂O for seawater. The δ^{18} O-H₂O 261 signature increases up to +7.1 % vs SMOW in the deeper water samples. This increase of the δ^{18} O-262 H_2O signature can be explained by a release of positive $\delta^{18}O$ during clay dehydration or alteration 263 264 (δ^{18} O of smectite ranges between +17 and +26 ‰ (Savin & Lee, 1988; Sheppard & Gilg, 1996)). Combined with the observed salinity decrease, the δ^{18} O-H₂O signature evolution suggests a two-step 265 266 evolution. First, the seawater trapped in the sediment is diluted without modifying its δ^{18} O-H₂O 267 isotopic signature. This dilution can be attributed to the water produced by the surrounding shale layers during compaction and possibly affected by ultrafiltration process (Kharaka & Berry, 1973). 268 269 Secondly, the salinity of sandstone lenses continues to decrease together with an increase of the 270 δ^{18} O-H₂O. The smectite dehydration produces pure water with an elevated δ^{18} O-H₂O signature causing the dilution and the rise of the δ^{18} O-H₂O signature. 271

The δD -H₂O isotopic signature evolution (Figure 2) first shows a decrease from -9.5 ‰ to -19.1 ‰ between the two shallower samples 1 and 2 and then an increase to -13.4 ‰ for the deeper sample. The causes of δD -H₂O evolution are more complex to identify because δD varies over a large range of isotopic signatures in smectite (δD from -95 ‰ to +33 ‰ in smectite (Capuano, 1992; Savin & Epstein, 1970)) and the induced variation can be overprinted by other factors, such as the interaction with alkane gases or the degradation of organic matter.

278 Insights on the water-rock interactions are given by the water chemistry evolution. In Figure 3, the 279 water composition is reported as ratio of reactive species content (Na, Ca, Mg and K) in relation to a 280 conservative species content (CI) to distinguish the reactive processes from transport and dilution 281 processes. The increase with depth of the Na/Cl, Ca/Cl, Mg/Cl and K/Cl content ratio indicates the 282 dissolution of primary mineral phases containing Na, Ca, Mg and K, such as feldspars, micas or clay 283 minerals, not followed by large precipitations of aluminosilicate phases. This identified trend in the 284 diagenesis in the sedimentary pile is confirmed by petrographic observations in samples that show only little precipitations of kaolinite as diagenetic formation of aluminosilicate phases. The main 285 286 authigenic minerals being observed are quartz and calcite. The fluid chemistry evolution does not 287 reflect smectite-to-illite transformation, with an observed increase with depth of the K content in 288 relation to the Cl content, while a decrease is expected if K is used for illite formation. In addition, the 289 only 3 mineralogical analyses performed on shale layers of the sedimentary pile do not show a 290 decrease in smectite content and an increase in illite content in the interstratified illite/smectite. It therefore appears that illitisation does not take place to a large extent and can be neglected in ouranalysis.

293 No or little cross-formation flow in the sedimentary pile between the different sand lenses is 294 suggested by the 87 Sr/ 86 Sr isotopic ratio and the δ^7 Li isotopic signature measured on the sampled 295 water (Figure 2). The ⁸⁷Sr/⁸⁶Sr isotopic ratio increases with depth, at values higher than the theoretical ⁸⁷Sr/⁸⁶Sr ratio of Cenomanian seawater. This increase of the ⁸⁷Sr/⁸⁶Sr is likely to be due to 296 297 the alteration of feldspar and clay minerals that release strontium richer in ⁸⁷Sr, whose alteration 298 increases with depth. The δ^7 Li isotopic signature in the water samples decreases with depth, from 299 +5.8 ‰ in the shallower water sample (sample 1) to +1.8 ‰ in the deepest sample. These δ^7 Li 300 signatures are lower than the signature of modern seawater (+31 ‰ vs L-SVEC) and their range is 301 compatible with an interaction with minerals of sedimentary rocks, such as clays. The decrease of the 302 δ^7 Li indicates the progress of the water/rock interaction with depth. The record of these progressive increase of $^{87}\text{Sr}/^{86}\text{Sr}$ and decrease of $\delta^7\text{Li}$ indicate the absence of connexion or a restricted connexion 303 304 between the different sampled sand lenses. The hydrogeological media around each sand reservoir is 305 thus closed, with little water flow and transport between the sand lenses and the surrounding shale 306 layers (Figure 1).



308

309 Figure 2: Data for water samples from the well showing: a) decreasing salinity with depth; b) δD as a function of the $\delta^{18}O$ 310 water isotope signature at different depths. The reference seawater signature and the global meteoric water line (GMWL) 311 are also shown; c) ⁸⁷Sr/⁸⁶Sr isotopic ratio increasing with depth and deviating from the ratio of the Cenomanian seawater; 312 and d) δ^7 Li isotopic signature decrease with depth. The circled numbers identify the five different water samples taken in the 313 well.



- **316** *Figure 3. Water chemistry data from the five water samples taken in the well in sand lenses (identified by circled numbers).*
- 317 The evolution of the concentration ratios (Na/Cl, Ca/Cl, Mg/Cl and K/Cl) helps identified the water/rock interactions within
- 318 the sedimentary pile.
- 319 Table 5: Data from water samples taken at different depth in the well: temperature, chemical composition and isotopic
- 320 signatures.

	Temperature	Salinity	δ^{18} O-H ₂ O	δD-H₂O	⁸⁷ Sr/ ⁸⁶ Sr	δ ⁷ Li (‰ vs	Na ⁺	K⁺	Ca++	Mg ⁺⁺	Cŀ
	(°C)	TDS (g/L)	(‰ vs	(‰ vs		LSVEC)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
			SMOW)	SMOW)							
Sample 1	93	18.27	+0.6	-9.5	0.7102	+5.8	5430	47	149	13	8177
Sample 2	104	8.89	+3.7	-19.1	0.7130	+3.9	2594	36	42	3.1	2461
Sample 3	107	6.61	+5.2	-16.4	0.7141	+5.0	1771	14	34	2.2	899
Sample 4	112	5.77	+6.2	-15.5	0.7153	+3.6	1522	19	24	2.1	717
Sample 5	117	5.02	+7.1	-13.4	0.7157	+1.8	1450	16	28	1.4	559

322

Model results – Reproducing the water isotope, salinity evolution and overpressure considering smectite dehydration during sedimentary pile burial

326 The water salinity and its isotopic composition in the sandstone lenses can be influenced by several 327 processes such as the expulsion of water during shale compaction, the release of water during 328 smectite dehydration and mixing of water from the sandstone and the shale. To individualise the 329 effect of smectite dehydration on the fluid evolution, it is necessary to consider these different 330 effects together and establish the water budget in the sedimentary pile. To this end, we calculated 331 the water production by smectite dehydration with a model reproducing the deposition of sediments, the compaction of these sediments, the temperature increase with burial and the water 332 333 flow and pressure evolution in the sedimentary pile (Tremosa et al., 2020).

334 Burial and smectite dehydration

Our 1D forward modelling of sediment burial is performed based on the present-day lithological log that identifies the thickness and lithology of the successive deposited lithological layers and on the dating of stratigraphic surfaces that allows varying sedimentation rates to be calculated over time. Sedimentation, compaction and pressure and temperature evolution in the sedimentary pile are then reproduced since the Albian (Figure 5). Burial simulation coherence is assessed by comparison with the present-day recorded thickness, porosity and temperatures profiles. 341 The calculated temperature and pressure evolutions over time allow the smectite dehydration model 342 to be applied (Tremosa et al., 2020; Vidal & Dubacq, 2009). This model describes smectite 343 dehydration as three possible binary solid solutions between hydrated and dehydrated smectite endmembers. The hydrated smectite can have 1, 2 or 3 layers of water in the smectite interlayer space, 344 depending on the calculated thermodynamic stability of each hydrated smectite for given 345 temperature and pressure conditions. With increasing temperature, smectite dehydrates according 346 347 to the most stable solid solution between hydrated and dehydrated smectite. However, at the 348 temperature transition between two stability domains of solid solutions, a consequent release of 349 water occurs because hydrated smectite loses one full layer of interlayer water. The thermodynamic 350 model is based on the standard state properties of hydrated and dehydrated smectite end-members 351 and integrates excess parameters for non-ideal solid solutions. Its results are in fair agreement with 352 the smectite dehydration experiments (Vidal & Dubacq, 2009). The release of water by smectite 353 dehydration is then simulated over the geological time across the investigated sedimentary pile 354 (Figure 4).





356 Figure 4: Evolution of the stable hydrated solid solution end-member in the smectite dehydration model as a function of 357 sediment burial from the Albian to the present day. The black lines correspond to the depth evolution over time of the 358 different stratigraphic surfaces and the grey area to the basement of the sedimentary pile, taken from the modelled domain.

359 Pressure profile

360 Pore pressure evolves in the sedimentary pile because of sediment compaction which induces a 361 porosity reduction and a compression of the water filling the pores, water expansion during 362 temperature increase, water release by smectite dehydration and advective water flow. An 363 overpressure of 150 to 170 bar is observed in the Turonian reservoirs at a depth of around 2500 m 364 below the seafloor. The model that considers smectite dehydration in addition to compaction and 365 temperature increase reproduces the present-day pressure profile (Figure 5). When smectite dehydration is omitted in the model, the pressure is about 40 bar lower, indicating that smectite 366 dehydration contributes to about 25 % of the recorded overpressure. The model indicates that the 367 368 overpressure is generated during the last burial episode that started 16 My ago. The transition of 369 smectite hydrated with two layers of water to one layer of water is crossed in the Cenomanian to 370 Santonian layers during this burial event (Figure 4), leading to a consequent release of water that 371 contributes to the pore pressure.



372

Figure 5: Measured and calculated pressure profiles at present day, with and without smectite dehydration in addition to
 compaction. Hydrostatic and overburden pressures are shown for comparison.

375 Chemical and isotopic evolution of fluids

The evolution of the chemical and isotopic composition of water in the sandstone lenses is calculated by mixing, in the sandstone levels, the water originated from the surrounding shale layers, in order to respect the water balance within the geometry and the evolution of the considered sedimentary pile. Dilution of the initial seawater in the sandstone lenses by compaction water flowing from the shale layers or produced by smectite dehydration is simulated when intrinsic permeability of overlying shale drops below 10⁻²⁰ m², by effect of compaction. This criterion on the permeability of the shale assumes that the hydrogeological media formed of a sandstone lens and its surrounding shale layers
becomes closed to external flow below this permeability. It corresponds to a burial depth of about
1900 m and to the depth of the overpressure roof in the present-day pressure profile.

The water isotopic signature remains unchanged during the dilution by compaction water because the water trapped in the porosity of both shale and sandstone sediments was seawater with a δ^{18} O-H₂O signature of 0 ‰. Besides, smectite dehydration releases water with a positive δ^{18} O-H₂O signature of +20 ‰ SMOW, in agreement with the δ^{18} O signature of smectite referenced in the literature (Savin & Lee, 1988; Sheppard & Gilg, 1996).

390 The model considering smectite dehydration during basin burial reproduces, in good agreement, the related evolution with a depth of δ^{18} O-H₂O signature and salinity of sampled water from sandstone 391 levels in the well (Figure 6). During the modelling of the burial, the salinity in the sandstone layer 392 393 corresponding to the deepest sampled sandstone lens first decreases due to seawater dilution 394 without changing its isotopic signature and then decreases together with an increase in the $\delta^{18}O$ signature of water. The model captures the effect of releasing water with positive $\delta^{\rm 18}O$ during 395 396 smectite dehydration. The mixing of this released water in the associated sandstone level follows the 397 measured $\delta^{18}O-H_2O$ signature to obtain a $\delta^{18}O-H_2O$ of +6.8 ‰ for the deepest sampled sandstone 398 lens. The transition of a hydrated smectite with 2 layers of water to 1 layer of water is modelled at a 399 depth between the first and the second sampled sandstone lenses, with the associated freshening calculated. It is worth noting that the δ^{18} O-H₂O signature and salinity evolution are obtained for the 400 401 corresponding shale and sandstone thickness, smectite content in shale and timing of smectite 402 dehydration.



403

404 Figure 6: δ¹⁸O-H₂O isotopic signature compared to the salinity (concentration of chlorine) of the sampled water in sandstone
 405 lenses of the well. The model accounting for smectite dehydration during basin burial reproduces the evolution of water
 406 samples observed with depth. The salinity decrease is also shown as a factor of seawater dilution. Circled numbers
 407 correspond to the water samples, as in Figure 2.

408 Discussion

409 First evidence of smectite dehydration at the scale of the sedimentary pile

410 The present results constitute the first consistent evidence of the influence of smectite dehydration on the fluid salinity and pressure in a sedimentary basin. The model coherence in reproducing the 411 412 δ^{18} O-H₂O isotopic signature, the salinity and the pressure profile supports this influence of smectite 413 dehydration. Up to now, the influence of smectite dehydration was advanced for the evolution of the 414 chemical composition and isotopic signature of the sediments porewater (Hanor, 1994) or for its contribution to the fluid overpressure (Tremosa et al., 2020), but both effects were not simulated 415 416 together. The burial of Cretaceous sediments was modelled in the Gulf of Guinea and the fluid pressure and smectite dehydration were simulated during this burial. Calculations showed that 417 smectite dehydration explains about a quarter of the present-day recorded overpressure, in addition 418 to disequilibrium compaction and temperature increase. Water freshening caused by ultrafiltration 419 420 flow and by smectite dehydration can reproduce the salinity evolution with depth in sandstone 421 lenses surrounded by thick shale layers. The salinity decrease is accompanied by an increase in the 422 δ^{18} O-H₂O signature that exactly matches the δ^{18} O-H₂O signature evolution modelled by the release of water by smectite dehydration during the burial of the sedimentary pile, where the water budgetduring smectite dehydration and its timing are respected.

425 Uncertainties on the isotopic signature of smectite interlayer water

A calculation hypothesis was made on the δ^{18} O signature of the water released during smectite 426 dehydration. Relatively few data are available on the δ^{18} O signature of smectite and these signatures 427 428 can present some contamination because of the difficulties in purifying smectite and clay minerals (Sheppard & Gilg, 1996). However, δ^{18} O signatures for smectite ranging between +17 and +26 ‰ 429 430 (Savin & Lee, 1988) seem reasonable. It is more difficult to estimate the δ^{18} O signature of smectite 431 interlayer water because the interlayer water can be lost during sample preparation or interstitial 432 water can remain sorbed on the clay mineral (Sheppard & Gilg, 1996). In the literature, it has been 433 claimed that the exchange between porewater and interlayer water is fast and that the δD and $\delta^{18}O$ 434 signatures of interlayer water do not provide geological information (Savin & Epstein, 1970). 435 However, this affirmation is in disagreement with studies on the interstitial water of mud volcanoes 436 that showed a clear influence of smectite dehydration on their water isotope signature (Dählmann & 437 Lange, 2003; Hensen et al., 2007) and rather suggest that the δ^{18} O signature of interlayer water is 438 close to the δ^{18} O signature of structural smectite. The distinction between structural and interlayer 439 δ^{18} O isotopic signatures hence remains to be investigated, by dedicated experiments in order to 440 distinguish between the production of pore and interlayer water in a smectite (Fernández et al., 441 2014) or from insights given by molecular dynamics simulations.

442 Discarding other sources of water isotopic signature variations

443 The influence on the δ^{18} O-H₂O isotopic signature evolution of other water-rock interaction 444 (carbonate precipitation and smectite illitisation) or transport (ultrafiltration) processes can be 445 discarded in the sedimentary system under consideration. The isotopic fractionation during the precipitation of carbonate minerals is known to modify the δ^{18} O-H₂O isotopic signature. In the 446 447 studied lithological column, petrographic observations indicate an early cementation of calcite, 448 during the early stage of burial and compaction, at temperature estimated at about 30°C. If the δ^{18} O-449 H₂O isotopic signature has been modified at that time because of calcite precipitation, it occurred in 450 a hydraulic open system, where water can be flushed. The simulation scenario considers the dilution and isotopic shift when the system becomes closed on a hydraulic point of view, namely, when the 451 intrinsic permeability of the overlying shale layer becomes lower than 10⁻²⁰ m², corresponding to a 452 453 burial depth of about 1900 m. Hence, the precipitation of early carbonates is not expected to change the calculated δ^{18} O-H₂O evolution since this precipitation occurred before. The isotopic fractionation 454 during the smectite-to-illite transformation can also lead to an increase of the δ^{18} O-H₂O isotopic 455

signature at increasing temperature (Suchecki & Land, 1983). The data on mineralogy and water 456 457 chemistry available from the well indicate an absence of noticeable illitisation. Consequently, the 458 recorded δ^{18} O-H₂O isotopic signature in the sand lenses is certainly not impacted by smectite 459 illitisation process. During ultrafiltration flow, a flow of water with solute transport partially impeded 460 because of the membrane behaviour of the shale, a moderate isotopic fractionation can occur 461 (Agrinier et al., 2021; Coplen & Hanshaw, 1973). However, the effect of this isotopic fractionation 462 during ultrafiltration is not clearly established, with contradictory studies reporting a depletion or an enrichment of the δ^{18} O-H₂O signature of the water flowing out of the shale (Agrinier et al., 2021). The 463 effect of ultrafiltration on δ^{18} O-H₂O isotopic signature is difficulty distinguished from the effect of 464 465 water-rock interactions. In the simulations executed in the present study, a flow of fresh water 466 expulsed from the shale layers that can correspond to ultrafiltration is mimicked by considering a 467 progressive dilution of the water in the sand lenses. Since the effect of ultrafiltration on the $\delta^{18}O-H_2O$ isotopic signature remains unclear and probably weak and because the simulation of ultrafiltration 468 469 process is complex, this possible effect has not been considered in this analysis.

470 Likely occurrence of smectite dehydration compared to illitisation

471 In studies on fluid evolution or overpressure generation by the water released by smectite, the 472 analysis is often restricted to smectite-to-illite transformation, but more rarely consider the 473 dehydration of interlayer smectite, notwithstanding that interlayer dehydration is 474 thermodynamically and kinetically easier than illitisation. However, even in high pressure 475 environments in which the total dehydration is predicted at a temperature of 300°C or higher, the 476 main dehydration steps (3 layers of water to 2 and 2 layers of water to 1) take place at temperatures 477 lower than 150°C (Vidal & Dubacq, 2009), concomitantly to smectite illitisation. The formation of 478 illite consumes potassium and, then, a depletion of potassium in the porewater indicates the 479 occurrence of a significant illitisation. In the present study, such a marker of illitisation was not 480 observed from the K/Na ratio and smectite-to-illite transformation was ruled out. At the contrary, 481 when the porewater composition shows a consumption of potassium (Vanneste et al., 2011), smectite illitisation is rationally to consider in the fluid budget analysis. 482

483 Implications on fluid budget in sedimentary basins

Our demonstration of the identification of smectite dehydration as the source of fluid modification in the studied sedimentary pile in the Gulf of Guinea highlights the importance of considering coupled approaches to understand the origin of fluids in sedimentary basins. Assessing the fluid budget in a sedimentary basin requires dedicated and integrated studies accounting for the temporal and spatial production of fluid and using a sound and calibrated model of fluid production. Notably, the water release during smectite dehydration was calculated using a predictive thermodynamic model
calibrated on experimental data. Thanks to this approach, it is possible to use the water's isotopic
evolution as a hydrogeological constraint in regional studies of fluid migration.

492

493 Conclusions

494 Smectite dehydration was advanced as a process that can influence the fluid pressure and the water 495 composition and isotopic signature in sedimentary basins, but a direct evidence has been lacking up 496 to now. In the sedimentary pile studied in the Gulf of Guinea, the dehydration of smectite interlayer 497 water influences the overpressure and the porewater composition and isotopic signature. This 498 influence was evidenced thanks to the simulation of the water production during the burial using a 499 modelling approach that couples hydraulic, mechanical, thermal, thermodynamic and isotopic 500 processes. In the model, smectite dehydration is described using a thermodynamic model and driven 501 by the temperature and pressure changes during the burial where the volume of water released 502 depends on the geometry of the sedimentary pile. This spatial and temporal fluid budget shows that 503 smectite dehydration contributes to about 25 % of the present-day overpressure of 150 to 170 bar, 504 together with classical purely hydro-mechanical processes. In addition to influence the overpressure, 505 smectite dehydration induces a dilution of porewater salinity and an increase of the $\delta^{18}O-H_2O$ 506 isotopic signature with increasing depth. Unique data from a deep well of more than 5000 m of total 507 depth, including 2000 m of water, were used in our analysis. The simulation of these hydraulic, chemical and isotopic markers are goods clues of the on-going geological process in the sedimentary 508 509 basin.

The influence of smectite dehydration is specific to each sedimentary system and evaluating the contribution of smectite dehydration requires performing a water budget involving smectite dehydration during the burial of the studied sedimentary pile. Our study is focused on the evaluation of fluid migration in sedimentary basins for the potential exploitation of energy fluids but it is also of interest to have a better understanding of the effect of smectite dehydration in other contexts. For example, our findings and the methodology undertaken here can be directly be applied in studies on the behaviour of fluids in subduction zones or in mud volcanoes.

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522 Author contributions

523 J.T. adapted a previous version of the SURP code, made the coupled modelling and interpreted the 524 results. H.G. calculated the thermodynamic parameters describing smectite dehydration. E.C.G. took 525 the water samples, ordered the isotopic and chemical analysis and emitted the hypothesis that the 526 isotopic and salinity data reflected smectite dehydration. J.T. wrote the early version of the 527 manuscript. E.C.G. and H.G. contributed to the writing of the manuscript. All authors participated to 528 conceptualize this study and commented on the final version of the manuscript

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