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## Modelling clay diagenesis using a combined crystalchemistry and thermochemistry approach: a case study on smectite illitization

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### Abstract

A general procedure that integrates laboratory mineral analysis and numerical tools is proposed to investigate the main diagenetic processes occurring in clayey and arenaceous sediments. The methodology relies on the use of experimental data from natural samples as input, on the use of numerical algorithms to estimate the thermodynamic parameters of site-specific dehydrated phyllosilicates, and produce an internally consistent thermodynamic database in a ready-to-use format for the Geochemist's Workbench, PHREEQC, and TOUGHREACT simulators. A set of non-isothermal 0D and 1D numerical models is set-up to explore the efficiency of smectite-illite transformation under variable geochemical conditions.

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## 1. Introduction

### Nomenclature

EDX	Energy Dispersive X-Ray
BRGM	Bureau de Recherches Géologiques et Minières
TDB	Thermodynamic Data Base
FESEM	Field Emission Scanning Electron Microscopy
GWB	Geochemist's WorkBench
I/S	Mixed layer illite/smectite
LogK	Logarithm of the thermodynamic constant of mineral formation
PEPITA	Parameter Estimation and Parameter Interpolation for Thermodynamic Analysis
PSM	Petroleum System Model
RTM	Reactive Transport Model
SSP	SUPCRT92 software package
XLS	MS Excel tool to estimate standard thermochemical parameters of phyllosilicate formation
XRD	X-Ray Diffraction
WDX	Wavelength Dispersive X-Ray

Diagenetic transformations occurring in layered sand and shale successions are complex processes depending on many parameters and coupled phenomena that should be taken into account when trying to formalize the web of reactions occurring in the sediments [1]. The main diagenetic process taking place in the clays is the smectite illitization that is considered to proceed more efficiently with the increase of depth (increase of pressure and temperature) and availability of potassium. This reaction greatly influences the chemical and physical evolution of the sediments, both clays and sandstones, and proceeds through the formation of I/S that are characterized by a progressive reduction of Si (as others cations as Fe, Ca), increase of Al and K and ordering in the structure [2, 3].

Numerical models may represent valid tests to check and verify the conceptual picture of such a diagenetic scheme although they may suffer the high crystalchemistry variability of the clay mineral phases and the lacking of the thermodynamic and kinetics parameters to describe their reactive behaviour. The kinetics parameters are usually not available and sensitivity is the generally accepted approach used to overcome these limitations. On the contrary, the thermochemical parameters can be estimated from the stoichiometry and the structure of the pure mineral phase through different methods [4].

The aim of the present activities is the compilation of a consistent thermodynamic database to describe and model the smectite illitization reaction in burial diagenesis environments. This reaction has a pivotal role in influencing the physico-chemical and mechanical properties of the sediments, mainly due to:

- mobilization and redistribution of the chemical elements (as K,Al,Si, Fe, Ca, Mg and H<sub>2</sub>O);
- changes in sediment porosity (silica precipitation);
- overpressure (water release).

## 2. Methodology

A procedure that combines (i) laboratory analysis of the clays, (ii) estimation of specific thermochemical parameters and (iii) geochemical numerical models is proposed to investigate the illitization of smectite in different geochemical contexts.

The numerical procedure (PEPITA) consists of the following steps (Fig. 1):

- smectite, illite and I/S from natural samples are firstly investigated in the laboratories for their structural characteristics and analyzed for their chemical composition;

- based on the stoichiometry of these mineral species, a number of selected thermodynamic and structural parameters (enthalpy, entropy, and free energy of formation, thermal capacity, molar volume, molar weight) are estimated relying on a XLS specifically developed at the BRGM;
- the output parameters are then used to feed the SSP to derive logK values to be incorporated in thermodynamic databases used by standard geochemical codes such as GWB [5], PHREEQC [6], TOUGHREACT [7];

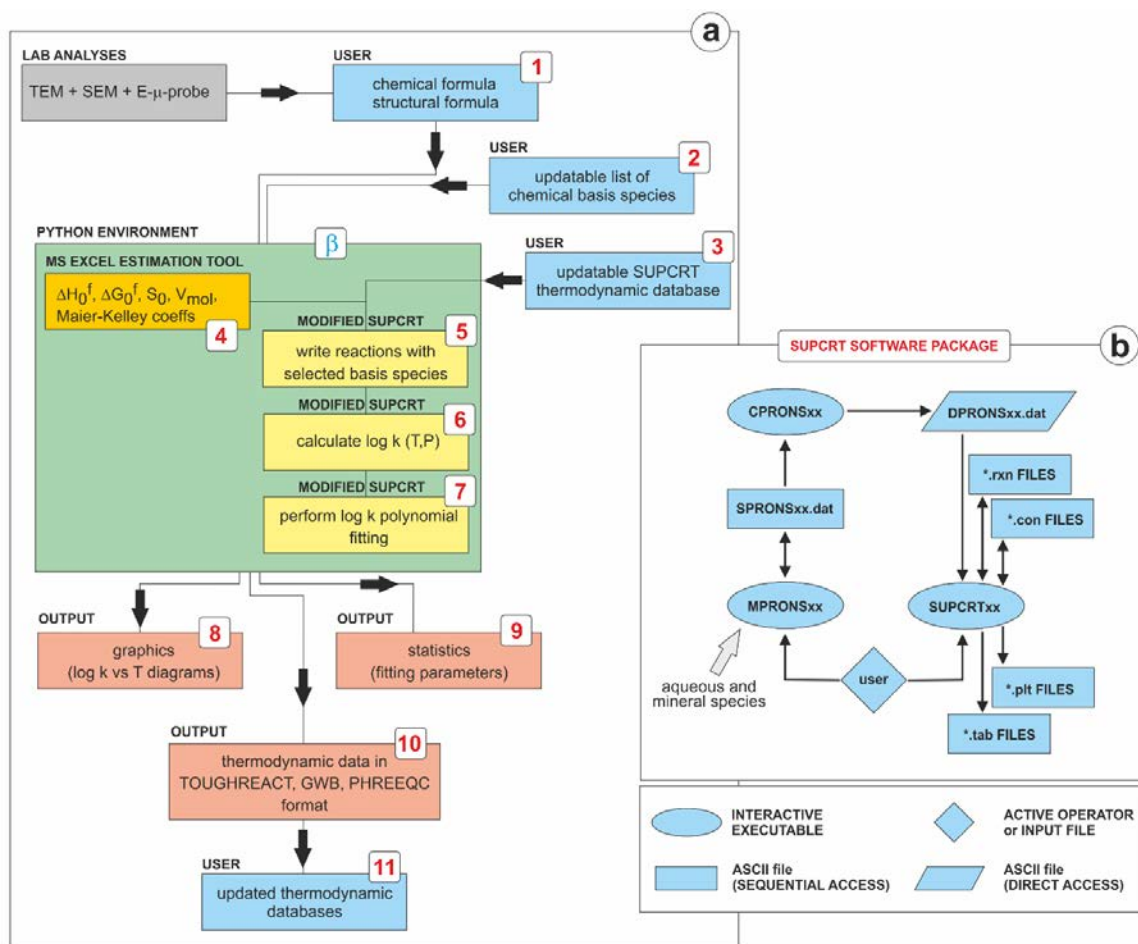


Fig. 1. (a) A suite of python modules (“wrapping environment”  $\beta$ , green shaded region) has been developed to automate the steps needed to augment the thermodynamic database. The procedure consists of the following steps: (1-3) collection and formatting of external information provided by the user; (4-7) integration of the MS XLS tool with a modified version of SSP to convert external information provided by the user into thermodynamic parameters; (8-10) creation of specific outputs for more convenient handling and inspection of computation results; (11) compilation of the thermodynamic database. (b) Details of the SUPCRT workflow.

The three main steps of the procedure are discussed in detail in the following paragraphs.

### 2.1. Laboratory analysis of the clays: analytical electron microscopy and stoichiometry determination

The difficulty of determining clay stoichiometry and particularly of smectite-illite is due to the small dimensions of crystallites (usually platelets), typically hundreds of nanometers long and tens of nanometer thick (Fig. 2a), stressing the spatial resolution limit of common micro-analytical techniques. Moreover, some elements are present at low level (0.1-0.3% wt), stressing their sensitivity limits as well. The methodology takes the advantage of the recent developments of the high resolution scanning electron microscopy such as FESEM.

The following samples were analyzed; Imt-1 illite (from Silver Hill, Montana), SWy-1 Na-Montmorillonite

(Wyoming), STx-1 Ca-Montmorillonite (Manning Formation, Texas) and six shale samples at different depth from Alliance TMS Unit #6H Well, Barnett formation (containing only, as clays, a I/S mixed layer as defined by XRD).

FESEM analyses were carried out by a JEOL 7600F instrument equipped with an Oxford SDD X-MAX EDX detector and an Oxford WAVE WDX detector. The Inca Energy software allows integrating EDX and WDX analyses. WDX analyses are longer (about 1-2 min for each detected element) and accurate while EDX is fast (2 min for all elements) but less sensitive.

The samples were grinded; the  $< 2\mu\text{m}$  fraction was separated (in order to enhance clay content) and then embedded in resin, lapped with SiC paper and covered by a conductive carbon layer (Fig. 2b).

After an optimization work, the selected conditions were: 15 kV with 13 nA at 50000–300000 magnification interval on single particles; average values were obtained, discarding values differing more than 20% from the median one. Mg, Si, Al, K, Fe elements are determined by WDX while Na, Ca, Ti by EDX; both accuracy and time consuming (and therefore the possibility of degradation under electron beam) factors were considered in the optimization phase.

Orthoclase, dolomite and garnet standards from Micro-Analysis Consultants Limited (MAC) were used for WDX. WDX analyses were performed on standard basis, while EDX analyses were performed without standards. In both cases the elements detected were normalized to 100; the results were, then, recalculated on oxide basis and normalized to 100 again.

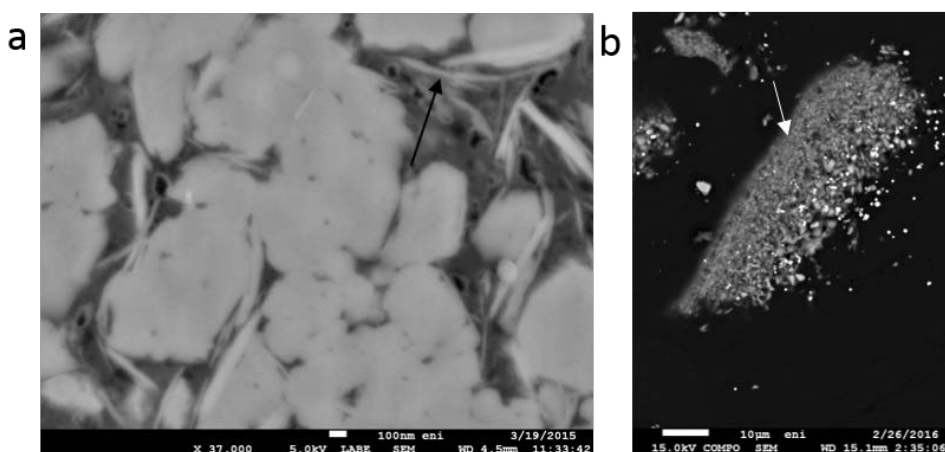


Fig. 2. FESEM-BSE images of natural shale samples: (a) ion-milled surface of bulk sample (b) cross section of  $< 2\mu\text{m}$  fraction. The arrows show an example of small illitic platelets.

In order to reconstruct the stoichiometry of a clay mineral the assumptions are that each mineral is electrically neutral and that the positive charges of the cations are balanced by an appropriate quantity of oxygen anions. The number of oxygen anions is different for each mineral phase (for the illite/montmorillonite mineral group it is eleven or its multiples, eight for chlorite group). The resulting mineral formula is then defined by assigning the cations to their crystallographic sites (tetrahedral, octahedral and interlayer) on the basis of their probable/common coordination numbers. Particularly, for the illite and smectite clays, taking into account the Tetrahedral-Octahedral-Tetrahedral structure, we assumed that:

- Si is in the tetrahedral site (coordinated by 4 oxygen atoms, IV) up to 4 atoms;
- if the number of Si is less than 4 (as in the illite phase) Al is allocated in the tetrahedral site to complete the occupancy;
- the remaining Al ( $\text{Al}_{\text{tot}} - \text{Al}_{\text{tetra}}$ ) is allocated in the octahedral site (coordinated by 6 oxygen atoms, VI) as Fe, Mg, Mn, Ti up to 2 atoms;
- Ca, K and Na are allocated in the interlayer up to 1 atom.

Unfortunately electron beam analyses do not differentiate among the valence states of iron and determines only the global content of iron (conventionally reported as FeO); we therefore assume that the fraction of  $\text{Fe}^{+3}$  is the one necessary to make the cation-site (octahedral) full and the mineral perfectly charge balanced.

In the Tab. 1 the stoichiometry of the analyzed standards and of the I/S mixed layer detected in the Alliance well are reported, together with the stoichiometry of smectite MX80 and illite IMT-2 as derived from the original Thermoddem database. These data are used in the numerical models as discussed later on. It is interesting to note that in the real case studied (Barnett shale – Alliance TMS Unit #6H Well), an illitization trend was detected: particularly the content of K (increasing with depth) and of Si (decreasing with depth, even if this behaviour is less clear) in good agreement with the increases of the illite component in the mixed layer I/S proved by the XRD analyses. Finally in the two Illite standards significant differences are highlighted in terms of Na and Fe content. This is the case also for the two smectitic terms. To use one or another term could be crucial in the results of the numerical models as will be established in the next paragraph.

Table 1: stoichiometry of the selected standards and samples analyzed in this study. Also, the stoichiometry of illite (IMT-2), Na smectite (MX80), MgNa-mnt, and Mg-ill present in the Thermoddem TDB are included because these are used in the discussed numerical models.

Samples	Phases	Interlayer			Octahedral site				Tetrahedral site	
		K	Na	Ca	Al <sup>VI</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>	Mg	Si	Al <sup>IV</sup>
Imt-1	Illite	0.889	0.012	0.027	1.393	0.395	.019	0.288	3.444	0.556
Imt-2*	Illite	0.762	0.440	0.000	1.427	0.084	.292	0.241	3.387	0.613
STx-1	Ca-montm	0.005	0.024	0.111	1.245	0.029	.011	0.329	4.000	-
SWy-1	Na-smectite	0.011	0.158	0.040	1.637	0.179	.006	0.296	3.878	0.123
MX80*	Na-smectite	0.024	0.409	0.009	1.598	0.035	.173	0.214	3.738	0.262
Alliance 1	I/S mixed layer	0.268	0.082	0.026	1.828	0.103	.036	0.156	3.487	0.513
Alliance 2	I/S mixed layer	0.350	0.134	0.027	1.735	0.179	.037	0.165	3.455	0.545
Alliance 3	I/S mixed layer	0.322	0.058	0.032	1.783	0.102	.036	0.130	3.631	0.369
Alliance 4	I/S mixed layer	0.420	0.130	0.059	1.719	0.095	.031	0.160	3.572	0.428
Alliance 5	I/S mixed layer	0.483	0.071	0.007	1.780	0.084	.024	0.116	3.619	0.381
Alliance 6	I/S mixed layer	0.557	0.048	0.027	1.723	0.169	.031	0.186	3.367	0.633
NaMg-mnt*	NaMg-montm	-	0.34	-	1.660	-	-	0.340	4.000	-
Mg-III*	Mg-illite	0.85	-	-	2.350	-	-	0.250	3.400	-

## 2.2. Estimation (and validation) of the thermochemical parameters

Thermochemical parameters for selected phyllosilicates have been obtained by means of multiple estimation methods [4]. Entropy and heat capacity have been calculated by considering the decomposition into polyhedral units, as theorized by Holland [8]. In this approach the thermodynamic properties are a linear combination of the mineral stoichiometric composition and of additional physical variables, such as the volume. The assumption is that the mineral structural formulas can be decomposed into a sum of coordination polyhedra identical to those presented by Chermak and Rimstidt [9].

The enthalpy of formation has been estimated with a modified version of the parametric method originally proposed by Vieillard [10, 11]. This approach considers mineral-specific anion-cation interactions within the crystal structure of each phyllosilicate. The enthalpy of formation of clay minerals is computed from the enthalpy of formation of the constituent oxides. The electronegativity of each cation in the crystalline structure of the mineral is assumed constant and independent from the deviations in the interatomic variations of the various sites [4]. The present version of the model also accounts for the energy of interaction between different cations occupying the same crystallographic site. The Gibbs free energy of phyllosilicates is finally calculated by combining the enthalpy of formation and the entropy values estimated with the procedures described above.

This procedure allowed for the calculation of the thermodynamic properties for a number of site-specific phyllosilicates. These values have been introduced into an augmented version of the Thermoddem database [12] by insuring the internal consistency of the computed logK values by use of the SUPCRT code [13].

The consistency of the estimated thermodynamic properties has been evaluated by drawing relevant activity diagrams (Fig. 3). The incorporation of site-specific minerals into logarithmic activity diagrams allowed for a more realistic description of the equilibria between aqueous solutions and mineral assemblages, as revealed by a different topography of the mineralogical stability field boundaries, compared to those associated with phyllosilicate hypothetical end-members (e.g. stoichiometric illites and smectites, [14]).

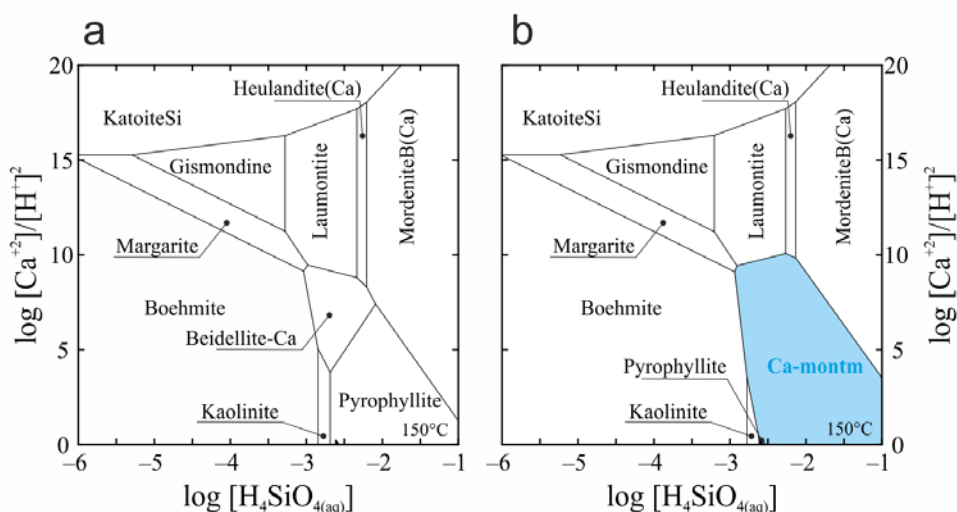


Fig. 3. Activity diagram for the  $SiO_2$ - $Al_2O_3$ - $CaO$ - $H_2O$  at 150 °C. (a) Diagram built after Blanc [4] with the Thermoddem database as compiled in 2015. (b) Diagram built with the augmented thermochemical database: the stability fields of the added Ca-montm (STx-1) is shaded in pale blue.

Once the thermodynamic parameters of the end-members (either ideal or experimentally determined) are computed and verified through the approach described above, the following step is to determine the I/S thermodynamic parameters. In particular, the input stoichiometry of intermediate I/S is estimated on the base of the assumed linear relationship of cogenetic mixed-layer minerals and associated smectitic and illitic end-members into the tri-linear  $M^{+}4Si-R^{2+}$  space ([14]; Figs 4a and 4c). Two cases are shown: in the first case (Fig. 4a) the two end members come from the original Thermoddem database, in the second (Fig. 4c) the smectitic member is an experimentally analyzed Ca-montmorillonite (STx-1). Each case has its own suite of I/S lying on the segment defined by the two respective poles.

The parameters obtained with this procedure are then verified by running exploratory non-isotherm (40-140 °C increasing linearly over 10 Myr) zero-dimensional simulations (Fig. 4b, 4d) in which a seawater preliminary equilibrated with an arenaceous sediment (composed by quartz, K-feldspar, calcite and smectite) reacts with a similar sediment containing also biotite that, by dissolution, acts as the driver of the smectite illitization.

The results of the 0D models indicate that a fluid phase of marine composition has the potential to promote the formation of I/S in arenaceous sediments, and that the efficiency of this process depends on the thermodynamic proxies considered in the calculations. For instance, here we show that measurable amounts of I/S are predicted to form when the smectitic and illitic end-members are represented by a Na-smectite of MX80 composition and a Fe-Mg illite of Imt-2 composition, respectively (Fig. 4b). On the contrary, I/S clays are not predicted to form when a Ca-montmorillonite of Stx-1 composition is considered in connection with Imt-2 illite (Fig. 4d). Numerical models also evidenced that the chemical composition of the circulating aqueous solutions is another first-order parameter affecting the efficiency of the smectite-illite transformation. This is an ill-defined parameter, largely variable under diagenetic conditions, that should be investigated by sensitivity analysis. To confine this analysis within reasonable boundaries, site-specific information (e.g. P,T conditions, mineral abundance, fluid inclusion salinity) are used to reduce the uncertainty associated with the computation of the chemical composition of the pore fluids at the time of the burial.

In this approach the chemistry of the minerals is projected only in the tri-linear  $M^{+}4Si-R^{2+}$  space. This is a simplified bi-dimensional representation that does not account for the entire chemical variability of the minerals. For instance the  $R^{2+}$  term lumps together all the divalent cations. Further activities are ongoing to overcome this approximation by considering other diagrams to capture the full complexity of the chemical composition of the mineral phases.

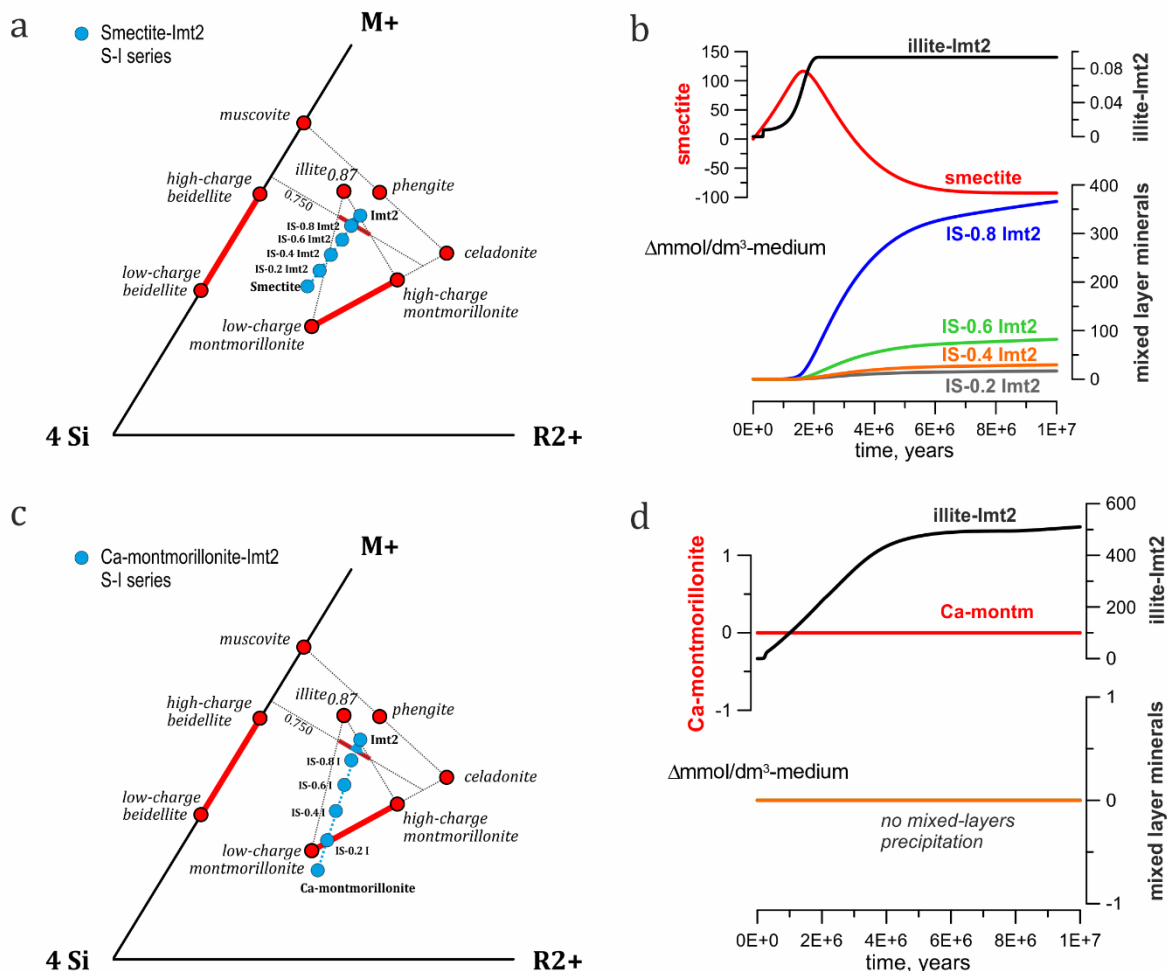


Fig. 4. (a, c) Meunier and Velde approach [14] for the estimation of the stoichiometry of co-genetic mixed-layer minerals associated to two different smectitic and illitic end-members of known composition; (b, d) example of zero-dimensional calculation to estimate the efficiency of smectite/illite transition under variable temperature and geochemical conditions. In (b) the smectite/illite transition occurs with a significant precipitation of the computed intermediates, while in (d) the mixed layers are less stable than the respective end-members and do not form.

### 2.3. Geochemical numerical models: 1D RTM of a compacting clay

The 0D models discussed above give a simplified description of specific processes since they do not consider the transport mechanisms of the species dissolved in the water phase. In order to consider the overall coupled reactions occurring in the arenaceous and clayey sediments, 1D RTMs are needed. The highly coupled physics of the phenomena make hard the setup of a model to reproduce the expected diagenetic events. Some simplifications are thus made to investigate the smectite – illite conversion in a dynamic non-isothermal ( $T = [70\text{-}120^\circ\text{C}]$ ) geochemical context. The thermochemical consistency is assured by using the upgraded TDB, but the smectitic and illitic end-members still have a simplified chemical composition. The I/S related to these poles are computed following the procedure described in the previous paragraph.

A custom version of TOUGHREACT that accounts for the effects of the uniaxial grid compaction is employed for performing the numerical simulations. The compaction is considered as a “geometric process” resulting from the reduction of porosity (the “voids” in the rocks) with a rate that is calibrated on the porosity evolution given by the PSM analysis. Despite the geometric nature of the compaction the resulting pressure gradients are correctly computed

since the mass balances equations are rigorously solved for each phase potentially present in the system (in our model a fully liquid saturation is supposed). The main characteristics of the model are reported in Fig. 5.

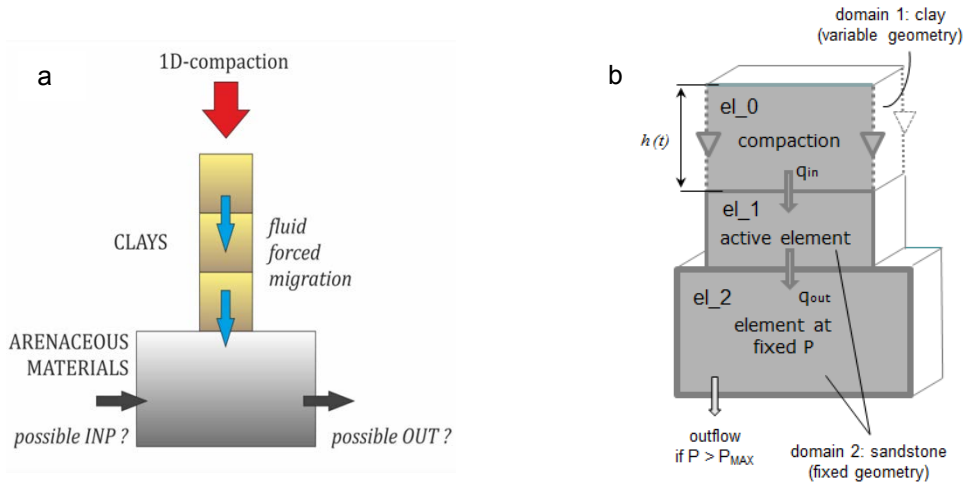


Fig.5. (a) Conceptual model and (b) numerical model. The simulation grid consists of a compacting clay (el\_0), and a sandstone (el\_1, el\_2).

The migration of the species dissolved in the aqueous phase is governed by advection according to the Darcy’s law and diffusion according to the Fick’s law (Tab. 2). Permeability ( $\kappa$ ) is set to  $1e-15 \text{ m}^2$ , viscosity ( $\mu$ ) and density ( $\rho$ ) are computed by the simulator according to the thermodynamic conditions and fluid composition,  $D_0 = 2.5E-9 \text{ m}^2/\text{s}$ ,  $E_a = -20.5 \text{ kJ/mol}$ ,  $T_0 = 298.15 \text{ K}$ , and  $R = 8.314 \text{ J/(K mol)}$ . In the formula,  $C$  is the concentration of the dissolved species,  $P$  the pressure, and  $\vec{g}$  is the vector of gravitational acceleration ( $g = 9.81 \text{ m/s}^2$ ).

Table 2. Transport mechanism considered in the model. The meaning and value of the parameters are given in the text.

Transport mechanism	Formal Expression
Darcy’s law (advective flow)	$\vec{F} = -\frac{\kappa}{\mu}\rho(\nabla P + \rho\vec{g})$
Fick’s law (diffusive flow)	$\vec{J}_D = D \cdot \nabla C, \quad D = D_0 \exp\left[\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right]$

The initial mineralogy and chemical composition of the pore water are given in Tab. 3.

Table 3. Mineral and chemical composition used in the numerical model.

Initial paragenesis	Initial Porewater
sandstone: quartz + K-feldspar, [A]	Seawater equilibrated with mineralogy [A]
clay: NaMg-mnt + Mg-III (+ calcite, quartz), [B]	Seawater equilibrated with mineralogy [B]

A sensitivity on smectite and illite kinetic parameters was preliminary performed starting from the parameters taken from Palandri and Karaka [15], and showed marginal effects on the overall behavior of the system on the timescale investigated.

The model evidences the smectite to illite conversion, mainly due to the availability of potassium from the water at the very beginning of the simulation and from the dissolution of K-feldspar in the sandstone at the later stages of the simulation and the precipitation of quartz (Fig. 6).

In more detail:

- Element 1 (clay): smectite converts into illite. The silica released by the reaction is expelled in the sandstone (el\_2)



- Element 2 (sandstone 1): the silica coming from clay (el\_0) is precipitated as quartz (porosity reduces due to quartz ppt) K-feldspar dissolve releasing potassium which diffuse in the clay (el\_0) promoting smectite to illite conversion
- Element 3 (sandstone 2): K-feldspar dissolve releasing potassium which diffuse in the clay (el\_1) promoting smectite to illite conversion

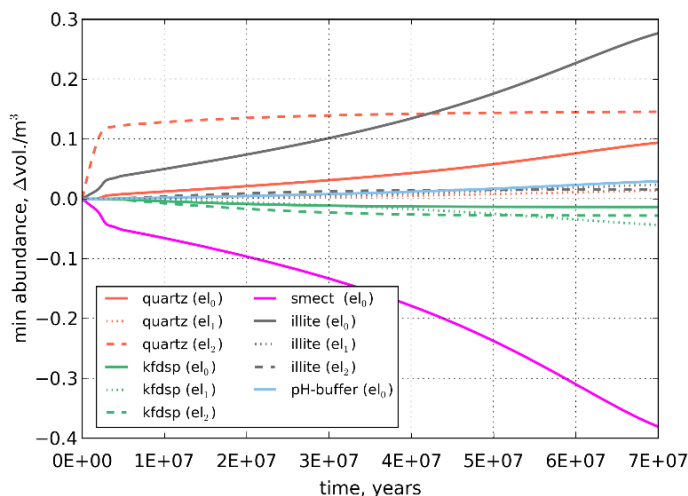


Fig. 6. Evolution of the mineral in the system, negative values mean dissolution, positive precipitation. Volume in fraction, e.g.: 0.1 = 10 %.

Some major observations can be drawn by the proposed numerical model:

- microcline saturation has a pivotal role: temperature and pH are the master variable controlling this parameter: high T and low pH might favour microcline dissolution and potassium availability for the smectite illitization, higher pH values might cause microcline oversaturation, and possibly inversed illite to smectite transformation, even at high temperature.
- the presence of the I/S is negligible and ephemeral (not reported in the graph for sake of clarity);
- the remarkable coupling of the physics considered in the system (thermal flows, advection, diffusion and mineral reactivity) make difficult to drive the model towards the main experimental observations: smectite illitization in the clay and quartz precipitation in the sandstone;
- the introduction of a diffusion coefficient that increases with temperature promotes a more efficient smectite-to-illite conversion at higher T;

Other considerations that came out in the course of our numerical analysis with 1D models are that:

- the reactive processes taking place during the simulation are highly sensitive to the choice of the smectite – illite couple since it constrain saturation indexes of the all other minerals present in the system;
- the chemical composition of equilibrium pore waters and the uncertainty in illite and smectite kinetic parameters do not play a major role.

### 3. Conclusions

A procedure that integrates experimental analysis and numerical thermochemical/geochemical tools is developed to improve the numerical description of the smectite illitization process. To this purpose a new thermodynamic database to be used in RTM was developed incorporating the parameters of mineral phases taken from natural samples.

The new estimated thermochemical parameters are tested and checked with activity diagrams and simple batch zero-dimensional models that showed that is possible to simulate the smectite illitization through the I/S mixed layer.

A 1D compaction model is proposed to test the effects of temperature, fluid flow rates and mineralogical composition on the illitization of smectite. The proposed model is able to reproduce the petrological observations, even though the smectite illitization proceeds without a significant presence of intermediate I/S.

A further step to improve the proposed methodology is to extend the use of chemographic approach for estimating the thermochemical parameters of I/S (Fig. 4) and to test the 1D model in geological situations where the presence of the I/S is more probable.

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