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# Smectite quantification in hydrothermally altered volcanic rocks

Léa Lévy<sup>1,2</sup>, Thraínn Fridriksson<sup>3</sup>, Nathaniel Findling<sup>4</sup>, Bruno  
Lanson<sup>4</sup>, Bernard Fraisse<sup>5</sup>, Nicolas Marino<sup>6</sup>, and Benoit Gibert<sup>6</sup>

<sup>1</sup>Laboratoire de Géologie, Ecole Normale Supérieure, Paris  
Sciences et Lettres, UMR8538, CNRS, Paris, France

<sup>2</sup>Nordic Volcanological Center, Institute of Earth Sciences,  
University of Iceland, 101 Reykjavík, Iceland

<sup>3</sup>ÍSOR - Iceland GeoSurvey, Reykjavík, Iceland

<sup>4</sup>Univ. Grenoble Alpes, Univ. Savoie Mont-Blanc, CNRS, IRD,  
IFSTTAR, ISTerre, F-38000 Grenoble, France

<sup>5</sup>Institut Charles Gerhardt Montpellier (ICGM), CNRS, Univ.  
Montpellier, 34090 Montpellier, France

<sup>6</sup>Géosciences Montpellier, University of Montpellier, France

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## **Abstract**

In volcanic environments, the presence of smectite may indicate re-  
cent hydrothermal circulations. Smectite is also responsible for enhanced  
rock electrical conductivity, as well as mechanical weakening. Therefore,

quantifying smectite is important in geothermal exploration. Smectite identification requires X-ray diffraction (XRD) but quantification based on XRD is time-consuming and not always accurate. In the present study, we investigate the use of an optimized unbuffered Cation Exchange Capacity (CEC) measurement, by back-titration of the Copper-triethylenetetramine(II) "Cu-trien" molecule, to quantify the smectite content of altered volcanic rock samples. We establish that a satisfying trade-off between the instrument uncertainty and an independant systematic error is theoretically reached for a fraction of reactants consumed of about 30% at the end of the exchange reaction. We suggest a modification to classical protocols to fall in that range. Finally, we show that optimized CEC measurements by Cu-trien are a direct measure of the smectite weight fraction in altered volcanic samples, with an average CEC of pure smectite of  $90 \pm 5$  meq/100g.

## 1 Introduction

One of the challenges of geothermal exploration at volcanoes is to detect the presence of active hydrothermal circulations in fractures. Geo-electrical and electromagnetic measurements are commonly used to this aim because electrical resistivity contrasts can delineate zones of intense hydrothermal activity (e.g. Árnason et al., 2000; Flóvenz et al., 2005; Flóvenz et al., 2012). Electrical resistivity of volcanic rocks is particularly sensitive to the presence of secondary "alteration" minerals, often witnesses of hydrothermal circulations in fractures, such as clay minerals. The distribution of clay minerals can provide estimates of the temperature distribution in volcanic or sedimentary systems where their formation is controlled by the geothermal gradient (Alt et al., 1986; Bourdelle et al., 2013; Kristmannsdóttir and Tómasson, 1978; Kristmannsdottir, 1979). In active hydrothermal systems, the formation of smectite is not only controlled

32 by the geothermal gradient, but also by the convective activity related to recent  
 33 fault opening and causing boiling as well as chemical disequilibrium (Beaufort et  
 34 al., 1995; Bril et al., 1996; Patrier et al., 1996). Compared to other clay minerals  
 35 (e.g. illite, chlorite, kaolinite), smectite is much more conductive (e.g. Kaufhold  
 36 et al., 2014; Kaufhold et al., 2015) and contributes significantly to the electrical  
 37 conductivity of rocks, through Electrical Double Layer mechanisms (Flóvenz et  
 38 al., 1985; Pezard, 1990; Revil and Glover, 1997; Waxman and Smits, 1968) and  
 39 interfoliar conduction (Henry, 1997; Lévy et al., 2018; Maraqah et al., 1990).  
 40 Smectite is also abundant in subduction zones (Hyndman et al., 1997) and in  
 41 some major faults (Chester et al., 2013) and may play a role in the mechanical  
 42 weakening of altered volcanic rocks (Heap et al., 2014; Kaufhold et al., 2012;  
 43 Meller, 2014).

44 In order to study in the laboratory the influence of smectite on electrical  
 45 conductivity and mechanical properties of volcanic rocks, the smectite content  
 46 needs to be quantified first. Smectite content in drill-cuttings can also provide  
 47 estimates of the porosity or permeability in a reservoir, by comparison with  
 48 in-situ borehole resistivity logs (Flóvenz et al., 2005; Pezard, 1990; Revil et al.,  
 49 1998; Rink and Schopper, 1974; Waxman and Smits, 1968).

50 The primary goal of our study is to provide geothermal industry with a  
 51 simple method to quantify smectite content in hydrothermally altered volcanic  
 52 rocks. Quantifying smectite in altered volcanic rocks is challenging because a  
 53 large number of minerals often coexist in the same rock formation. Quantifi-  
 54 cation of smectite by Rietveld-refinements of X-ray diffraction (XRD) patterns  
 55 (e.g. Taut et al., 1998) is hampered when smectite-containing mixed layers co-  
 56 exist with smectite. Moreover, high-quality XRD scans are required for these  
 57 quantifications, which can be time-consuming.

58 Due to its particular crystalline structure, smectite has a much larger Cation

59 Exchange Capacity (CEC) than other clay minerals (Bouchet et al., 2000). This  
60 CEC is mainly located in smectite interlayers (Dohrmann, 2006a; Lagaly, 1981;  
61 Vogt and Köster, 1978). Hower and Mowatt (1966) found a linear correlation  
62 between the CEC and the smectite fraction in a series of illite-smectite samples.  
63 Kauffhold and Dohrmann (2003) also observed that the CEC measured by back-  
64 titration of the Copper-triethylenetetramine(II) "Cu-trien" (Ammann et al.,  
65 2005; Bergaya, 1997; Meier and Kahr, 1999) was proportional to the smectite  
66 content in bentonites, qualitatively measured using the methylene blue method.

67 Altered volcanic rocks contain a larger variety of minerals than bentonite  
68 or illite-smectite series, with often a large fraction of zeolites. Some zeolites,  
69 such as clinoptilolite and heulandite, have a higher CEC than smectite, up  
70 to 300 meq/100g, thanks to their wide solid solution of extraframework cations  
71 (Fridriksson et al., 2004). However, the CEC of clinoptilolite drops to 5 meq/100g  
72 when measured by the Cu-trien method (Meier and Kahr, 1999), because the  
73 channels where extraframework cations are located cannot expand, unlike smec-  
74 tite interlayers, so that only small cations (smaller than Cu-trien) can enter  
75 clinoptilolite channels. Therefore, the Cu-trien molecule appears to be adequate  
76 to quantify the smectite content in altered volcanic rocks. Our study tests this  
77 possibility by comparing CEC measurements to smectite quantifications based  
78 on Rietveld-refinements of XRD patterns, for samples where smectite is the only  
79 swelling clay mineral.

80 Since altered volcanic rocks contain lower and more variable smectite content  
81 than bentonite or illite-smectite series, the solid/solution ratio needs to be op-  
82 timized for each sample, in order to minimize both the instrument uncertainty  
83 and systematic biases. The need for optimization of the reactants (exchange  
84 solution and sample) proportion was first addressed by Orsini and Remy (1976)  
85 for CEC measurements with the Cobalti-hexamine molecule, "Co-hex", on large

86 masses of soil samples. Orsini and Remy (1976) pointed out that the exchange  
 87 between Co-hex and soil samples could be considered as total only when the  
 88 initial quantity of Co-hex was at least three times superior to the CEC. Yet,  
 89 beyond eight times, the accuracy of the measurements would significantly de-  
 90 crease. Based on these observations, the authors recommended to carry out  
 91 experiments where the initial ratio between Co-hex and rock sample (expressed  
 92 in CEC units) represents 30% to 80% of the CEC, or equivalently where the  
 93 fraction of Co-hex consumed during the experiments ranges between 15% and  
 94 30%. Further development of the Co-hex back-titration method (Cieselski et al.,  
 95 1997; Ciesielski et al., 1997) allows extending the interval of Co-hex consumed  
 96 to 5%-35%. The need to optimize the solid/solution ratio by adjusting the ini-  
 97 tial mass of sample, for samples having a wide range of CEC values, is also  
 98 discussed for the Cu-trien method by Dohrmann and Kaufhold (2009) and by  
 99 Dohrmann (2006b) for the similar Ag-thiourea method.

100 Our study investigates the theoretical grounds for the observations of Dohrmann  
 101 and Kaufhold (2009) and the ranges suggested by Orsini and Remy (1976) and  
 102 Ciesielski et al. (1997) and presents a simple method for quantifying the smectite  
 103 content of altered volcanic rocks through optimized CEC measurements using  
 104 the Cu-trien exchange complex.

## 105 **2 Materials and Methods**

### 106 **2.1 Rock samples**

107 Thirty-eight samples from the Krafla high-temperature geothermal area are used  
 108 in this study. Core samples are collected from four cored boreholes (KH1, KH3,  
 109 KH5 and KH6) at varying depths. They represent a variety of lithologies and  
 110 secondary minerals (Table 1). Cylindrical plugs (2-3 cm long and 2.5 cm diame-

111 ter) are prepared from the original core samples for petrophysical measurements,  
112 presented by Lévy et al. (2018). From the lateral faces of the plugs, thin sec-  
113 tions and powders are prepared. Ten samples are used for optimization of CEC  
114 measurements, 24 samples for comparison between quantitative XRD analysis  
115 and CEC, 15 samples for chemical analysis by Electron Probe Micro Analy-  
116 sis (EPMA) and four samples for ICP analyses of exchangeable cations. Some  
117 samples are used for more than one type of analysis (Table 1).

Table 1: Description of the 38 samples used in this study (ID = sample name). The borehole (BH) and depth (in meters) from which the samples are extracted are indicated in Columns 2 and 3. The type of analysis for which the samples are used are indicated in Columns 4 to 6, where  $Opt_{CEC}$  corresponds to the optimization of CEC measurements. The CEC (in meq/100g) and the smectite weight per cent measured by XRD are given in Columns 7 and 8. The lithology (Litho) is given in Column 9; hyalo = hyaloclastite; v. lava = vesicular lava; d. lava = dense lava; ignimb. = ignimbrite. The presence of secondary minerals (if more than 1% as quantified by XRD quantification) is indicated in Columns 10 to 17. Sm = smectite; Chl = chlorite; Heu = heulandite (zeolite); Qtz = quartz; Clc = calcite; Pyr = pyrite; Tit = titanite; Oth. = other; Laum = laumontite (zeolite); Act = actinolite; Ep = epidote; Wai = wairakite; Ana = anatase; Jad = jadeite; Sid = siderite.

ID	BH	Depth	XRD	$Opt_{CEC}$	EPMA	CEC	Smec	XRD	Lithology	Sm	Chl	Heu	Qtz	Clc	Pyr	Tit	Oth.
L02	KH1	39.5	x			13.5	14%		breccia	x		x	x		x		
L04	KH1	42			x	17.6	17%		breccia	x		x	x		x	x	Ana
L05	KH1	45.3	x		x	6.1	5%		ignimb.	x		x	x				
L06	KH1	48.8	x	x		7.2	13%		breccia	x		x	x	x	x		
L09	KH1	60	x	x		25.9	26%		breccia	x		x	x	x	x		
L10	KH1	66	x			15.6	18%		v. lava	x		x	x				
L11	KH1	68.7	x			24.9	25%		d. lava	x		x	x			x	
L12	KH1	70	x		x	2.7	4%		d. lava	x		x	x	x			
L14	KH1	74.5	x			33.2	37%		hyalo	x		x	x	x	x		
L15	KH1	79.5	x			15.0	17%		d. lava	x		x	x				
L16	KH1	99	x			4.5	9%		d. lava	x		x	x	x		x	
L19	KH1	120.3	x			15.1	16%		d. lava	x		x	x	x	x	x	
L21	KH1	125.5	x			19.2	18%		d. lava	x		x	x			x	
L22	KH1	131.1	x			21.2	17%		v. lava	x		x	x	x		x	
L26	KH1	157.9	x		x	12.8	16%		v. lava	x		x	x				
L28	KH1	167.1	x		x	13.0	18%		d. lava	x		x	x		x	x	
L29	KH1	174.3	x		x	9.4	12%		v. lava	x		x	x	x		x	
L30	KH1	185.1	x		x	7.2	7%		dyke	x		x	x			x	
L31	KH1	188.5	x		x	20.0	21%		hyalo	x		x	x	x	x	x	
L119	KH3	60.4	x	x		45.7	49%		hyalo	x		x	x	x	x		
L40	KH5	190			x	10.9	-		v. lava	x	x		x	x			Laum
L58	KH5	429			x	3.5	-		dyke	x	x		x	x	x	x	Act
L126	KH6	295	x			53.4	67%		hyalo	x				x			Sid, Jad, Ana
L112	KH6	377.7		x		6.2	-		dyke	x	x		x	x			
L113	KH6	387		x		3.5	-		dyke	x	x		x	x			
L114	KH6	394.2		x		2.6	-		dyke	x	x		x	x			
L81	KH6	461.32	x		x	16.0	18%		d. lava	x			x				Horn
L82	KH6	486.5			x	5.8	-		d. lava	x	x		x	x	x	x	
L87	KH6	508.5			x	5.6	-		d. lava	x			x	x	x	x	
L91	KH6	537.2			x	8.4	-		hyalo	x			x	x	x		
L93	KH6	555			x	1.9	-		dyke	x	x		x			x	Ep
L99	KH6	587		x		34.0	-		hyalo	x	x	x					Wai, Act
L100	KH6	597.5				0.8	-		hyalo	x	x		x	x		x	Wai, Act
L80	KH6	448		x		4.8	-		d. lava	x	x		x				
L86	KH6	501		x		6.3	-		d. lava	x	x		x				
L89	KH6	515		x		5.0	-		d. lava	x	x		x				
L95	KH6	560	x			39.6	38%		hyalo	x			x	x		x	Wai, Act
L149	KH6	680	x			19.5	24%		breccia	x			x	x			



118 A first set of powders is used for the analysis of CEC uncertainty, carried out  
119 on 88 samples but presented here for 10 relevant samples. This set of powders  
120 is roughly grained to powder size, without any size control.

121 A second set of powders is used for XRD scans and associated mineral quan-  
122 tification by Rietveld-refinements. Powders from the first set are further ground  
123 for 10 minutes in ethanol, using an automatic grinder Retsch RM 200, dried and  
124 sieved before being prepared as randomly oriented mounts. For each sample,  
125 the exact same powder is used later on for independent CEC measurements that  
126 are later compared to XRD mineral quantification.

## 127 2.2 Mineral quantification by X-ray Diffraction

128 The powders are front-loaded onto the sample holder, using a razor blade to  
129 smooth out the surface, in order to minimize preferred orientation (PO) and  
130 shift of diffraction peaks (Bish and Reynolds, 1989). An example of PO issues  
131 when the sample is back-loaded is shown in Appendix A. The XRD scans are  
132 carried out over the range  $4-75^\circ 2\theta$  ( $4-65^\circ 2\theta$  for a few samples) with a Philips  
133 X’Pert Pro (radiation Cu-K $\alpha$ ; 45 kV; 30 mA; step size  $0.0167^\circ$ ; time per step 240  
134 s; X’Celerator Scientific high-speed detector; 240 mm goniometer radius). The  
135 XRD patterns are analyzed quantitatively with the Rietveld program BGMN  
136 and the Profex user-interface (Doebelin and Kleeberg, 2015; Taut et al., 1998).  
137 The following mineral phases are considered for the refinements: forsterite,  
138 labradorite, bytownite, orthoclase, albite, augite, diopside, kanoite, smectite-  
139 tri, zeolite (heulandite, clinoptilolite, philippsite, dachiardite, laumontite, anal-  
140 cime), pyrite, ilmenite, titanomagnetite, jadeite, siderite, hematite, maghemite,  
141 anatase, titanite, schorl, chlorite, calcite, quartz, wairakite, prehnite, epidote,  
142 actinolite, garnet, grossular. Two examples of refinements are shown, in Figure  
143 1 for a sample containing smectite as the only clay mineral and in Figure 2 for

144 a sample containing smectite, chlorite, and most likely chlorite-smectite.

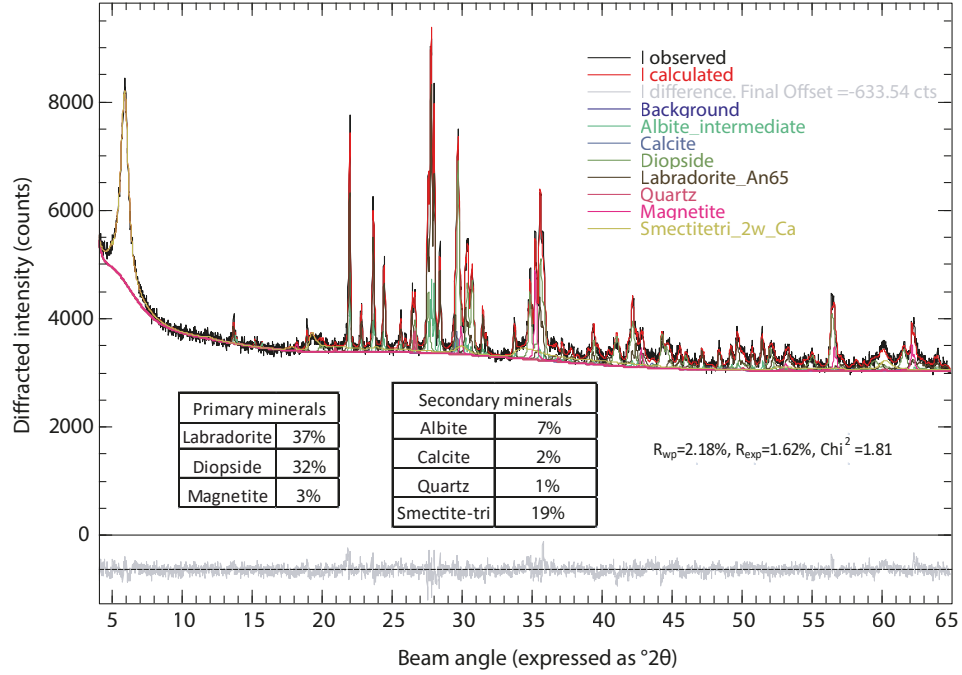


Figure 1: XRD quantitative analysis, using the BGMN software, for sample L15 containing smectite as the only clay mineral. The resulting mineral percentages and fit quality are indicated on the graph.

145 In samples containing a mixture of disordered clay phases (such as smectite  
 146 and smectite-containing mixed layers and/or disordered 1:1 minerals), smectite  
 147 content is difficult to quantify accurately by Rietveld-refinements, because of  
 148 the strong correlation between parameters, including background (e.g. Raven  
 149 and Self, 2017). XRD patterns of samples containing both smectite and chlorite  
 150 can be fitted (Figure 2) but the software adjusts both the chemical compo-  
 151 sition of chlorite and the relative quantity of chlorite and smectite to fit the  
 152 relative intensities of the  $d(001)$  peak at 14-15Å and the  $d(002)$  peak at 7.2Å.  
 153 This results in the non-uniqueness of the model parameters related to chlorite  
 154 chemistry and smectite and chlorite quantities. The chemistry of chlorite can be

155 constrained (especially the relative abundance of Fe and Mg), based on indepen-  
 156 dent chemical analyses, but this requires a large number of EPMA on polished  
 157 thin sections, to obtain a representative chemical composition of chlorite for  
 158 the sample, which is time-consuming and expensive. Moreover, assuming that  
 159 the chemistry of chlorite can be properly constrained, the combined presence  
 160 of smectite and chlorite often implies the presence of a chlorite-smectite phase.  
 161 This chlorite-smectite phase also contributes to the d(001) peak at 14-15Å and  
 162 its contribution can hardly be discriminated from that of pure smectite. As a  
 163 result, the fitted amount of "smectite" corresponds in reality to a quantity of  
 164 smectite + chlorite-smectite. Since only the quantity of smectite layers matters  
 165 for the comparison to the CEC, not the quantity "smectite+ chlorite-smectite",  
 166 this quantification is not appropriate. Therefore, only smectite quantifications  
 167 for samples containing no other clay phase are used in this study for further  
 168 comparison to CEC measurements.

169 Special studies are necessary to determine the exact type of smectite present  
 170 in each sample, especially regarding the type of interlayer cation ( $Ca^{2+}$  or  $Na^{+}$ ),  
 171 the number of water layers surrounding interlayer cations and the tri- or dioc-  
 172 tahedral character. The tri- or dioctahedral character mainly influences the  
 173 d(060) diffraction peaks, at high angles, which have a lower intensity and are  
 174 overlapping with other minerals such as quartz. These high-angle peaks only  
 175 negligibly affect (if at all) the refinement. On the other hand, low-angle peaks,  
 176 especially the d(001) around 14-15Å, which is influenced by the composition of  
 177 the interlayer space both in terms of cation and water layer, significantly affect  
 178 the refinement. Therefore, the patterns are fitted with two different types of  
 179 smectite phases: a phase corresponding to a "tri-octahedral smectite with in-  
 180 terfoliar spaces filled with Ca, accompanied by two water layers", and another  
 181 tri-octahedral smectite "saponite" with more flexible interlayer distance (see de-

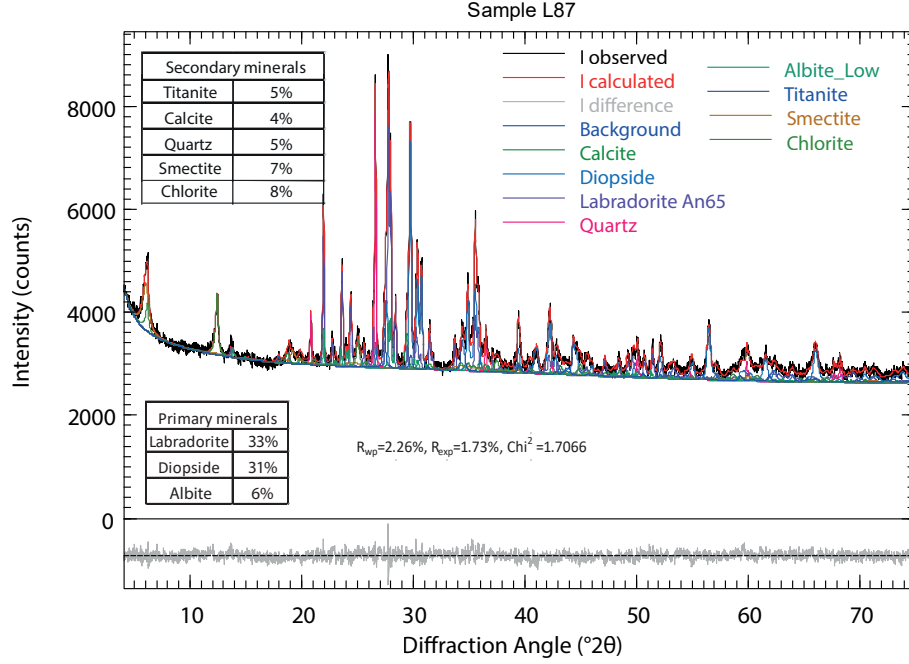


Figure 2: XRD quantitative analysis, using the BGMN software, for a sample containing smectite, chlorite and mixed layer chlorite-smectite.

tailed structure files in Appendix B). An uncertainty on the smectite content is calculated based on the discrepancy between the two fits. For the other minerals, the uncertainty is calculated based on the variance of the model parameters given by the software.

## 2.3 CEC determination

The CEC of altered volcanic rocks is measured by back-titration of the Copper-triethylenetetramine (Cu-trien) molecule, as in the original protocol designed by Meier and Kahr (1999) to measure the CEC of pure clay samples. This molecule is also used, for example, by Kaufhold and Dohrmann (2003) to measure the CEC of bentonites.

First, the sample is weighted in a beaker and then 50 ml of deionized water, measured with a volumetric flask, are added into the beaker. The few remaining

194 water drops in the volumetric flask, after adding water to the beaker, represent  
 195 an average of  $0.6 \pm 0.2$ . In order to reduce the uncertainty on the water volume,  
 196 we measure the exact mass of water added to the beaker and adjust it by  
 197 weight as close as possible to 50.00 g. Without this weight adjustment and  
 198 measurement, the volume of water added is  $49.4 \pm 0.2$  ml. The beaker containing  
 199 the water-rock mixture is then left in an ultrasonic bath for 5 minutes. Next,  
 200 10 ml of Cu-trien at about  $1.10^{-2}$  mol/L are added with a 5 ml pipette (two  
 201 steps). Details about the preparation and characterization of the exchange  
 202 Cu-trien solution at  $1.10^{-2}$  mol/L are given in Appendix C. The exchange is  
 203 considered complete after 5 minutes of magnetic stirring. Since most of the  
 204 exchange is expected to occur within interlayer spaces of swelling clay minerals  
 205 (smectite), 5 minutes are considered sufficient. A test, carried out on sample  
 206 L126, indicates that the difference in exchange yield after 5 and 60 minutes is  
 207 within the instrument uncertainty, and thus not significant (see more details in  
 208 Appendix C). If the CEC of higher charge clay minerals (e.g. vermiculite) were  
 209 investigated, longer contact times might be needed (Von Reichenbach, 1968).

210 After the exchange reaction is completed, solid and liquid are separated by  
 211 centrifugation. Finally, the absorbance of the supernatant solution is measured  
 212 by a spectrophotometer at 578 nm. The absorbance of the Cu-trien solution  
 213 before exchange, prepared independently by mixing 50 ml of deionized water and  
 214 10 ml of Cu-trien at  $1.10^{-2}$  mol/L, is also measured. The CEC (in meq/100g)  
 215 is then calculated with Equation 1.

$$CEC_{lab} = \frac{2(C_i - C_f)V}{m} \quad (1)$$

216 where  $V$  is the total volume of the solution (60 ml),  $m$  is the rock mass in  
 217 mg and  $C_i$  and  $C_f$  are the Cu-trien concentrations in the initial and final solu-  
 218 tions, respectively, in mol/L.  $C_i$  and  $C_f$  are calculated based on the absorbance

219 measurements and the calibration curve presented in Appendix C.

220 The rock mass suggested by Meier and Kahr (1999) is 200 mg but is a key  
221 parameter to be adjusted:  $m$  varies between 100 and 1000 mg in our experi-  
222 ments (see e.g. Dohrmann, 2006b; Dohrmann and Kaufhold, 2009). If the CEC  
223 can be approximately estimated, e.g. thanks to XRD measurements and rapid  
224 evaluation of the d(001) peak of smectite at 14-15Å, the mass of rock is chosen  
225 accordingly. If the d(001) is intense compared to other peaks and no d(002) at  
226 7.2Å is observed, meaning that there is little to no chlorite or chlorite-smectite,  
227 then 200 mg of rock sample are considered appropriate. If chlorite or chlorite-  
228 smectite are present in significant amount (e.g. if d(002) more intense than  
229 d(001)), 400 mg are used. If the d(001) peak is absent or small compared to the  
230 background, then 1000 mg are used. If no assumption on the smectite amount  
231 can be made priori to CEC measurement, then a first measurement with 200 mg  
232 is carried out. After the first CEC measurement, the mass of rock is adjusted  
233 accordingly to the result for the next measurement. At least two measurements  
234 with the same rock mass are carried out for each sample.

235 The protocol and equation presented here-above uses rock masses as dried at  
236 room temperature. The water content is determined independently by weighting  
237 a given mass of sample at room temperature and after drying in an oven at  
238 105°C. Water content measurements, as well as corresponding correction of  
239 CEC values, are presented in Appendix D.

## 240 **2.4 Analysis of exchangeable cations in smectite**

241 Chemical analyses of clay minerals are carried out on 15 polished thin sections  
242 at Géosciences Montpellier, using a CAMECA SX100 electron microprobe (22  
243 keV, 10 nA). The 15 samples used for these measurements are indicated in Table  
244 1.

Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) analyses are carried out at ÍSOR to characterize the main cations exchanged after reaction with Cu-trien. Magnesium, calcium and sodium concentrations are measured at the wavelengths 279.079, 373.690 and 589.592 nm, respectively. The exchangeable cations of four samples are investigated by this method: L119, L96, 31 and L99. Solutions are analysed at three steps of the reaction for each sample: after mixing rock and water, after ultra-sonic bath and after exchange with Cu-trien. This allows not taking into account cations coming from basic water-rock interaction (e.g. dissolution of glass or minerals).

### 3 Results and Discussion

#### 3.1 Estimation of the laboratory uncertainty

We calculate the total uncertainty on the CEC measurements,  $u_{tot}$ , by taking into account measurement dispersion,  $u_{disp}$ , and instrument resolution,  $u_{instr}$ . The general formula, based on the rule of error propagation by Taylor expansions, is presented in Equation 2 (e.g. Joint Committee for Guides in Metrology (JCGM), 2008; Ku, 1966).

$$\begin{aligned}
 u_{tot}(CEC) &= \sqrt{u_{instr}(CEC)^2 + u_{disp}(CEC)^2} \\
 u_{disp}(CEC) &= \sqrt{\frac{1}{n(n-1)} \sum_{i=1}^n (CEC_i - CEC_{avg})^2} \\
 \frac{u_{instr}(CEC)}{CEC} &= \sqrt{\left(\frac{u(V)}{V}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(C_i - C_f)}{C_i - C_f}\right)^2} \quad (2)
 \end{aligned}$$

where  $n$  is the number of measurements for each sample, usually two or three, and  $CEC_{avg}$  the average of the  $n$  measurements.  $u(V)$  and  $u(m)$  are the uncer-

263 tainties on volume and mass, respectively, and  $u(C_i - C_f)$  the uncertainty on  
 264 the difference between initial and final concentrations. We explain below how  
 265 these three terms are calculated.

266 The uncertainty on rock weighting is estimated to  $u(m) = 0.5$  mg, based on  
 267 the variations of the last digit of the scale.

The uncertainty on the total volume (60 ml) measurement is calculated by propagating the uncertainty of the three measured volumes (see Equation 3).

$$V = V_{wat} + 2V_{pip}$$

$$u(V) = \sqrt{u(V_{wat})^2 + 2u(V_{pip})^2} \quad (3)$$

268 where  $u(V_{wat})$  is the uncertainty on the 50 mL of water and  $u(V_{pip})$  is the  
 269 uncertainty on the 5 ml of Cu-trien (measured twice with a 5 ml micropipette  
 270 to obtain 10 ml).  $u(V_{pip})$  is estimated to 0.02 mL (by pipetting step).  $u(V_{wat})$   
 271 is reduced from 0.20 to 0.01 ml when the exact mass of water added to the rock  
 272 is measured. This results in a total volume uncertainty  $u(V) = 0.03$  ml, while it  
 273 amounts to  $u(V) = 0.20$  ml when the water is directly added from the volumetric  
 274 flask without further verification.

The calculation of the uncertainty on the concentration difference is presented in Equation 4.

$$A_i - A_f = L(C_i - C_f)$$

$$\left(\frac{u(C_i - C_f)}{C_i - C_f}\right)^2 = \left(\frac{u(A_i - A_f)}{A_i - A_f}\right)^2 + \left(\frac{u(L)}{L}\right)^2$$

$$= \frac{u(A_i)^2 + u(A_f)^2}{(A_i - A_f)^2} + \left(\frac{u(L)}{L}\right)^2 \quad (4)$$

275 where  $A_i$  and  $A_f$  are the initial and final absorbance, respectively, and  $u(A_i) =$   
 276  $u(A_f)$  their respective uncertainty.  $L$  is the slope of the calibration curve (ab-



sorbance versus concentration, see Appendix C) and  $u(L)$  is calculated using the error propagation rule presented above, with an expression of  $L$  based on the two extreme calibration points and their respective uncertainty (Joint Committee for Guides in Metrology (JCGM), 2008).

The uncertainty on the absorbance measured by the spectrophotometer is considered to be 0.001, based on the dispersion observed for repeated measurements of the same solution, as well as the spectrophotometer resolution provided by the manufacturer.

The total instrument relative uncertainty is given by Equation 5.

$$\frac{u_{instr}(CEC)}{CEC} = \sqrt{\frac{u(V_{flask})^2 + 2u(V_{pip})^2}{V^2} + \frac{u(m)^2}{m^2} + \frac{2u(A_i)^2}{(A_i - A_f)^2} + \frac{u(L)^2}{L^2}} \quad (5)$$

### 3.2 Increasing the rock mass decreases the laboratory uncertainty for low-CEC rocks

Based on Equation 5, we calculate, for six samples, the instrument uncertainty of CEC measurements using two different initial rock masses and the same initial Cu-trien solution. We show that the relative uncertainty decreases from up to 70% to less than 5% when increasing the rock mass from the 200 mg, as recommended for example by Meier and Kahr (1999), to 1000 mg (Figure 3). In the present case, increasing the rock mass from 200 to 1000 mg increases the fraction of Cu-trien consumed from less than 1% to about 13% (Sample L114 in Figure 3).

Figure 3 shows that the instrument uncertainty exponentially decreases with the fraction of Cu-trien consumed. This is consistent with Equation 5, where the denominator  $(A_i - A_f)^2$  controls the overall value of  $u(CEC)$  because  $\frac{u(V)}{V}$

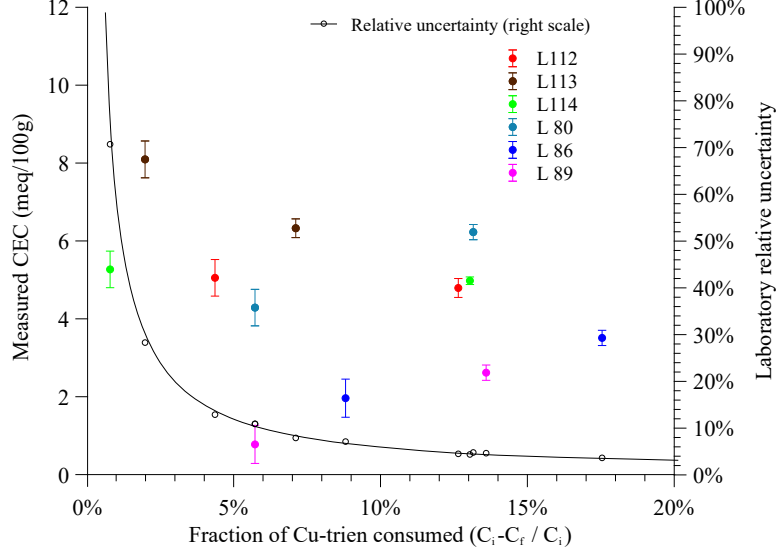


Figure 3: Measured CEC and relative laboratory (instrument) uncertainty as a function of the fraction of Cu-trien consumed. The circles with error bars correspond to the measured CEC (left axis) and the stars to the uncertainty, as calculated in Equation 5 (right axis). An increased fraction corresponds to an increased mass of rock initially present. Each color corresponds to one sample. The six samples used in this figure have a CEC lower than 5 meq/100g. Error bars (both positive and negative) are calculated as the product of the measured CEC by the relative uncertainty.

300 and  $\frac{u(m)}{m}$  are very small compared to the third term. This is particularly true  
 301 for samples with CEC lower than 5 meq/100g, i.e. with low smectite content.  
 302 This effect is due to the limited number of digits, which can be read on the  
 303 spectrophotometer (only three digits, with values always  $\leq 1$ ).

### 304 3.3 Increasing the rock mass decreases the yield of the 305 exchange reaction for high-CEC rocks

306 For high-CEC samples, we observe that the measured CEC can decrease by up  
 307 to 50% when the rock mass is increased, for fixed initial volume and concen-  
 308 tration of Cu-trien (Figure 4). Dohrmann and Kaufhold (2009) suggest that  
 309 an unsuitably small solution/solid ratio may result in a reduced selectivity of  
 310 the index cation (Cu-trien in their case) and thus in an incomplete exchange of

interlayer cations. A similar observation is mentioned in Cieselski et al. (1997) for CEC measured by the Co-hex index cation and attributed to a reduced yield of the exchange reaction when the fraction of Co-hex consumed exceeds a threshold.

Here, we investigate the mathematical expression of these empirical observations, in order to predict the yield of the exchange reaction between Cu-trien and the rock sample and determine an acceptable threshold of Cu-trien consumption at the end of the reaction. The yield of the exchange reaction is taken as the relative difference between the apparent measured CEC,  $CEC_{app} = CEC_{lab}$ , and the maximum CEC,  $CEC_0$ . We first write the theoretical relationship between  $CEC_{app}$  and  $CEC_0$ .

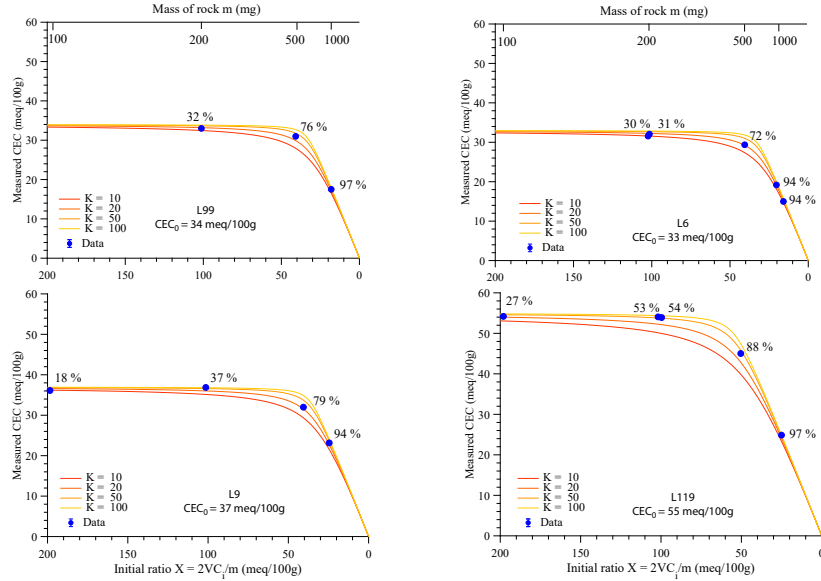
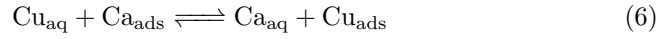


Figure 4: Measured CEC with different initial ratios of reactants (Cu-trien and rocks) for four samples (blue filled circles): L99, L9, L6 and L119. The initial concentration of Cu-trien is about constant ( $(1.6 \pm 0.1) \cdot 10^{-3}$  mol/L) but the mass of rock varies between 100 and 1000 mg (top x-axes). The fraction of Cu-trien consumed at the end of the reaction is marked aside each measurement. The laboratory (instrument) uncertainty is smaller than the symbols. The model predictions for four values of the thermodynamic constant  $K$  are also displayed as plain lines with a warm colorscale. The values of  $K$  are chosen on a trial-error basis, assuming  $K \geq 1$ . The value of  $CEC_0$  used for these predictions is marked together with the name of the sample, and corresponds to the measured CEC for the highest initial ratios. The values of  $CEC_0$  may differ from the values given in Table 1 because a different set of powder is used for these measurements than for the measurements related to the correlation with XRD refinements.

For simplification purposes, we consider only one bivalent exchange reaction,

323 between the Cu-trien(II) cations and  $Ca^{2+}$  cations filling the exchange sites  
 324 in the rock samples. According to chemical analyses of the smectite grains  
 325 carried out by EPMA, there is at least twice as much  $Ca^{2+}$  filling the interlayer  
 326 spaces than  $Na^+$ . There is an overall abundance of  $Mg^{2+}$  in the structural  
 327 formula of these saponites but EPMA does not allow differentiating  $Mg^{2+}$  in  
 328 the crystal lattice from  $Mg^{2+}$  in the interlayer space. The concentration of Mg,  
 329 Ca and Na, measured by ICP in the solutions after exchange with Cu-trien for  
 330 four samples, indicate that no Na has been exchanged and that exchanged-Ca  
 331 and exchanged-Mg represent 72-94% and 8-13% of the total cation exchange  
 332 capacity, respectively. These two types of result confirm that bivalent cations  
 333 represent the majority of interlayer cations and the exchange ratio with Cu-  
 334 trien(II) will be mostly 1:1 (Figure 5).

335 The chemical exchange reaction, considering a majority of  $Ca^{2+}$  in the initial  
 336 state, is written in Equation 6.



337 The thermodynamic constant  $K$  of this exchange reaction is defined in Equa-  
 338 tion 7.

$$K = \frac{X_{Cu,eq} a_{Ca,eq}}{X_{Ca,eq} a_{Cu,eq}} \quad (7)$$

339 where the subscript "eq" indicates that a chemical equilibrium is reached.  $X_{Cu,eq}$   
 340 and  $X_{Ca,eq}$  are the dimensionless chemical activities of cations Cu-trien(II) and  
 341  $Ca^{2+}$  filling sites in the rock at the end of the exchange reaction, respectively,  
 342 and  $a_{Cu,eq}$  and  $a_{Ca,eq}$  are the dimensionless chemical activities of cations Cu-  
 343 trien(II) and  $Ca^{2+}$  in the aqueous solution at the end of the exchange reaction,  
 344 respectively. Chemical activities are defined in Equation 8, where the subscript  
 345 "eq" is removed for clarity purposes, but we assume the thermodynamic equi-

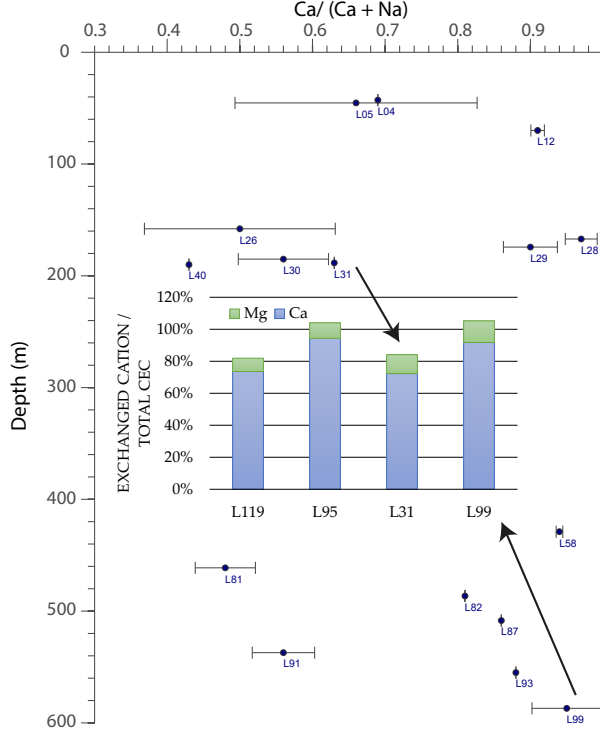


Figure 5: Number of exchangeable Ca-ions compared, to Na-ion and Mg-ion in the interlayer spaces of smectites. The relative number of exchangeable Ca versus Na is shown as a function of sampling depth. Sixteen samples, where chemical analyses by electron probe are carried out, are reported on this figure: L04 to L31 from KH1, L40-L58 from KH5 and L81-L99 from KH6. The error bar indicates the range of values found for the different smectite grains measured in each thin section. The histogram at the center shows the distribution of exchangeable Mg and Ca in four samples, as measured by ICP in the exchange solutions after reaction with Cu-trien. The sodium concentration in the solutions after exchange is not significantly higher than in the solutions before exchange (both before and after ultra-sonic bath) for any of the samples. Both types of measurements are available for two samples (L31 and L99).

346 librium is reached.

$$\begin{cases} a_{Cu} = [Cu]_{aq} \\ a_{Ca} = [Ca]_{aq} \\ X_{Cu} = \frac{meq(Cu)}{mCEC_0} \\ X_{Ca} = \frac{meq(Ca)}{mCEC_0} \end{cases} \quad (8)$$

347 where  $[Cu]_{aq}$  and  $[Ca]_{aq}$  are the chemical concentrations of cations (Cu-  
348 trien(II) and  $Ca^{2+}$ , respectively) in the aqueous solution, in mol/L, and  $meq(Cu)$

349 and  $meq(Ca)$  are the quantities of cations (Cu-trien(II) and  $Ca^{2+}$ , respectively)  
 350 filling sites in the rock, in millimol equivalent "meq". Each mmol of Cu-trien(II)  
 351 or  $Ca^{2+}$  corresponds to 2 meq, given the double positive charge carried by each  
 352 cation.  $a_{Cu}$  and  $a_{Ca}$  are normalized by an "infinite" theoretical concentration  
 353 of 1 mol/L. With  $CEC_0$  being the total CEC of the rock, in meq/g, and  $m$  the  
 354 mass of rock considered in the experiment, in g,  $mCEC_0$  is the total number  
 355 of exchange sites available in the rock, in meq. According to these definition,  
 356  $[Cu]_{aq}$ ,  $[Ca]_{aq}$ ,  $meq(Cu)$  and  $meq(Ca)$  are given in Equation 9.

$$\begin{cases} [Cu]_{aq} = C_f \\ [Ca]_{aq} = C_i - C_f \\ meq(Cu) = mCEC_{app} \\ meq(Ca) = m(CEC_0 - CEC_{app}) \end{cases} \quad (9)$$

357 Combining Equations 7, 8 and 9, the thermodynamic constant,  $K$ , can be  
 358 written as in Equation 10.

$$K = \frac{meq(Cu)}{meq(Ca)} \times \frac{C_i - C_f}{C_f} = \frac{CEC_{app}}{CEC_0 - CEC_{app}} \times \frac{C_i - C_f}{C_f} \quad (10)$$

Given that  $CEC_{app} = CEC_{lab}$  and following Equations 1, 9 and 10,  $meq(Cu)$   
 and  $meq(Ca)$  can also be written, as in Equation 11.

$$\begin{cases} meq(Cu) = 2V(C_i - C_f) \\ meq(Ca) = \frac{meq(Cu)(C_i - C_f)}{KC_f} = \frac{2V(C_i - C_f)^2}{KC_f} \end{cases} \quad (11)$$

Assuming that all exchange sites are filled with either Cu-trien(II) or  $Ca^{2+}$

at the end of the reaction, the total CEC,  $CEC_0$ , is described in Equation 12.

$$\begin{aligned}
CEC_0 m &= meq(Cu) + meq(Ca) \\
\iff CEC_0 &= \frac{2(C_i - C_f)V}{m} \left(1 + \frac{(C_i - C_f)}{KC_f}\right) \\
\iff KC_f CEC_0 &= CEC_{app}(KC_f + C_i - C_f) \\
&= CEC_{app}[(K - 1)C_f + C_i] \\
\iff C_f &= C_i \times \frac{CEC_{app}}{KCEC_0 + (1 - K)CEC_{app}} \quad (12)
\end{aligned}$$

By writing  $C_f$  as a function of  $C_i$ ,  $m$ ,  $V$  and  $CEC_{app}$  (Equation 1), Equation 12 gives Equation 13.

$$\begin{aligned}
C_i - \frac{mCEC_{app}}{2V} &= C_i \times \frac{CEC_{app}}{KCEC_0 + (1 - K)CEC_{app}} \\
\iff (KCEC_0 + (1 - K)CEC_{app}) \times (2VC_i - mCEC_{app}) & \\
&= 2VC_i CEC_{app} \quad (13)
\end{aligned}$$

Equation 13 can be re-written as a second-order equation of the variable  $Y = CEC_{app}$  (Equation 14).

$$\begin{aligned}
(1 - K)Y^2 + (KCEC_0 + \frac{2VKC_i}{m})Y - \frac{2VKC_iCEC_0}{m} &= 0 \\
\iff aY^2 + bY + c = 0 &\begin{cases} a = 1 - K < 0 \\ b = KCEC_0 + \frac{2VKC_i}{m} \\ c = -\frac{2VKC_iCEC_0}{m} \\ \Delta = b^2 - 4ac \end{cases} \quad (14)
\end{aligned}$$

with  $a < 0$  because  $K > 1$  (otherwise no exchange would occur). By solving the second-order equation (14) and keeping only the positive solution (which remains positive even if  $K < 1$ ), we obtain an explicit function for  $CEC_{app}$

(Equation 15).

$$\begin{aligned}
 Y = CEC_{app} &= \frac{-b + \sqrt{\Delta}}{2a} \\
 &= \frac{-(\alpha + X) + \sqrt{(\alpha + X)^2 + 2\alpha\beta X}}{\beta} \left\{ \begin{array}{l} X = 2V \frac{C_i}{m} \\ \alpha = CEC_0 \\ \beta = 2 \frac{1-K}{K} < 0 \end{array} \right. \quad (15)
 \end{aligned}$$

359 The function of  $X$  presented in Equation 15 increases monotoneously with  $X$   
 360 and reaches asymptotically the value of  $CEC_0$ . Since  $X$  is inversely proportional  
 361 to  $m$ , the sequence of equations presented here predicts that an increase of  
 362 rock mass (all other things being equal) will increase the difference between  
 363  $CEC_{app}$  and its asymptote  $CEC_0$ , which is equivalent to reducing the yield of  
 364 the exchange reaction.

365 This model based on simple assumptions predicts the observations of Dohrmann  
 366 and Kaufhold (2009) and Cieselski et al. (1997) that the sample mass is the de-  
 367 termining factor for optimum precision of the CEC and exchangeable cations,  
 368 if the same volume of solution is used. The function presented in Equation 15  
 369 can also predict our experimental observations on samples with large smectite  
 370 volume, provided that  $CEC_0$  is chosen accordingly (Figure 4). Values of  $K$  in  
 371 the range 10-100 are consistent with the observations but the value of  $K$  does  
 372 not affect much the predictions. Given the limited sensitivity of the model to  
 373 the value of  $K$ , we do not attempt here to evaluate precisely this constan. We  
 374 only suggest that the range 20-50 is appropriate to describe the reaction taking  
 375 place in the samples shown in Figure 4. In reality,  $K$  depends not only on the  
 376 exchanged cation but also on the type of minerals and of sites involved in the  
 377 exchange (Tertre, 2014; Reinoso-Maset et al., 2012; Durrant et al., 2018; Robin  
 378 et al., 2015; Robin et al., 2017).



### 379 3.4 Optimization of the CEC measurements

Equations 16 and 17 describe the "partial exchange" systematic error and "instrument" uncertainty, as a function of the fraction  $x = \frac{C_i - C_f}{C_i}$  of Cu-trien consumed after the reaction, based on Equations 12 and 5, respectively.

$$Err_{partial} = \frac{CEC_0 - CEC_{app}}{CEC_{app}} = \frac{(C_i - C_f)}{KC_f} = \frac{x}{K(1-x)} \quad (16)$$

$$\begin{aligned} \frac{u_{instr}(CEC)}{CEC} &= \sqrt{\frac{u(V_{flask})^2 + 2u(V_{pip})^2}{V^2} + \frac{u(m)^2}{m^2} + \frac{2u(A_i)^2}{(A_i - A_f)^2} + \frac{u(L)^2}{L^2}} \\ &= \sqrt{\frac{u(V_{flask})^2 + 2u(V_{pip})^2}{V^2} + \frac{u(m)^2}{m^2} + \frac{2u(A_i)^2}{x^2 A_i^2} + \frac{u(L)^2}{L^2}} \quad (17) \end{aligned}$$

380 Depending on the value of the thermodynamic constant,  $K$ , the optimal  
381 fraction of Cu-trien consumed to minimize both the instrument uncertainty  
382 and the partial exchange systematic error is somewhere between 30% and 80%  
383 (Figure 6), as suggested empirically for CEC measurements with Co-hex on soils  
384 by Orsini and Remy (1976). Since it is not possible to determine  $K$  with these  
385 simple measurements, we consider most resonable to aim at 30% consumption  
386 (most pessimistic value for  $K$ ) because the decrease of  $u_{instr}(CEC)$  beyond 30%  
387 is less important.

### 388 3.5 Quantification of smectite weight fraction in altered 389 volcanic rocks

390 A linear correlation is found between the smectite weight fraction and the CEC  
391 of altered volcanic rocks, where the only swelling clay mineral is smectite (Figure  
392 7). Due to the complexity of Rietveld refinements in whole rock samples when  
393 several types of clays are involved, only samples where a satisfying fit is obtained  
394 using only the clay phase "Smectite tri-octahedral with interlayers filled with Ca  
395 and 2 water layers" are reported in this figure. In samples where a peak at 7-

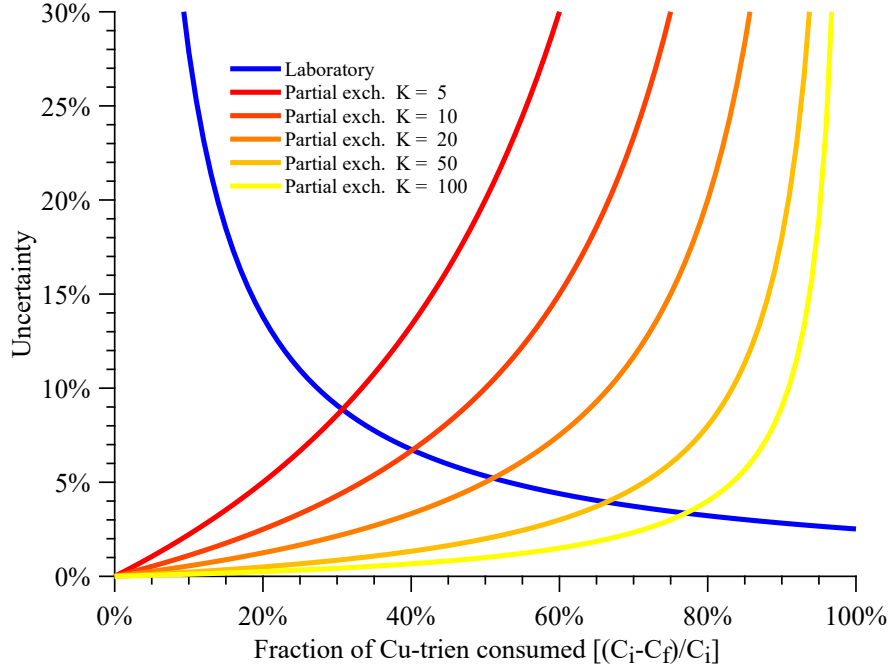


Figure 6: Laboratory uncertainty and "partial exchange" systematic error, as a function of the fraction of Cu-trien consumed.

396 7.5Å is observed (typical of chlorite and chlorite-smectite), the smectite quantity  
 397 derived from the fit is considered irrelevant for a quantitative comparison with  
 398 the CEC. An uncertainty on the quantification is calculated by fitting the same  
 399 diffraction patterns with a different smectite phase: "Saponite with interlayers  
 400 filled with undetermined cations and 2 water layers". The quantities derived  
 401 from the fit with the less constrained saponite are systematically lower. The  
 402 linear fit to the observations shown in Figure 7 has a slope  $CEC_{smec} = 90 \pm$   
 403  $5 \text{ meq/100g}$  and a regression coefficient  $R^2 = 0.945$ . The slope is consistent  
 404 with the known range of CEC for smectite, 80-120 meq/100g, caused by the  
 405 permanent negative charge of the crystal lattice, in the range 0.3-0.6 per half  
 406 unit cell  $Si_4O_{10}(OH)_2$ , that is compensated for hydrated interlayer cations (e.g.  
 407 Bouchet et al., 2000). A slope of  $CEC_{smec, 105^\circ C} = 94 \pm 5 \text{ meq/100g}$ , with a

408 regression coefficient of 0.952, is found when CEC values are corrected for the  
 409 water loss at 105°C (Appendix D).

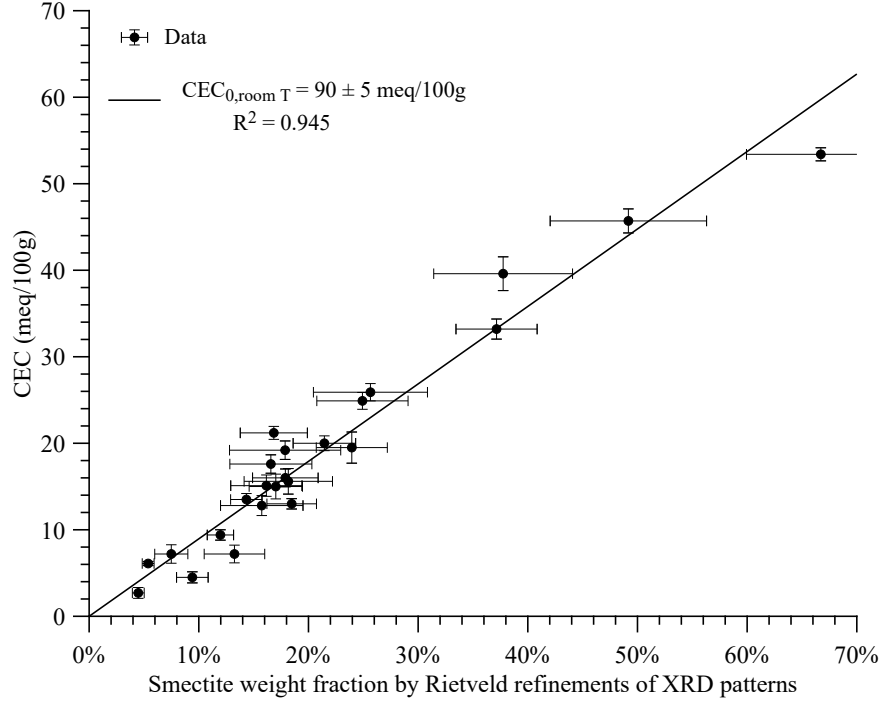


Figure 7: CEC measurements versus smectite quantification by Rietveld refinements of XRD patterns, for samples where smectite is the only swelling clay mineral. The slope and regression coefficient of the fitting line is given in the legend. CEC measurements and XRD scans are carried out on the exact same powders. The same figure, using CEC values corrected for taking the water content into account in each sample, is presented in Appendix D.

410 The contribution of other minerals to the measured CEC is also investigated,  
 411 in particular zeolites, illite and chlorite. Zeolites can be divided into two groups:  
 412 (i) "rigid" zeolites (e.g. laumontite, mesolite, analcime, natrolite and scolecite),  
 413 whose chemical formula is well-defined and in which extra-framework (other  
 414 than Al and Si) cations cannot be exchanged and only the water content can  
 415 vary and (ii) "flexible" zeolites (e.g. heulandite, chabazite and clinoptilolite),  
 416 which exhibit a wide and continuous range of extra-framework cation compo-  
 417 sitions. Although, CEC of heulandite and clinoptilolite can reach up to 300  
 418 meq/100 g (Fridriksson et al., 2004), CEC measurements by the method de-

419 veloped here result in CEC values in the range 0.5-1.5 meq/100g (Lévy et al.,  
420 2018). Therefore, the contribution of zeolites to the CEC measured by Cu-trien  
421 in altered volcanic samples is negligible.

422 The CEC of pure illite [Beavers Bend illite - Mankin and Dodd (1961)] is  
423 also measured using the same method (back-titration by Cu-trien), yielding  
424 4 meq/100g, which confirms the quasi-absence of non-mica layers in the illite  
425 sample (Mankin and Dodd, 1961) and the negligible CEC of pure illite compared  
426 to pure smectite (Hower and Mowatt, 1966). Moreover, the CEC of samples  
427 containing large amounts of chlorite, as well as in some cases wairakite and  
428 other "high-temperature" alteration minerals (epidote, actinolite), but no hint  
429 of smectite, is always lower than 0.5 meq/100g, when measured by this method  
430 (Lévy et al., 2018). We conclude that the linear trend presented in Figure 7 can  
431 be used to estimate the weight fraction of smectite in altered volcanic samples  
432 containing wide range of minerals. This weight fraction also includes smectite  
433 layers in mixed-layer chlorite-smectite or illite-smectite.

434 As mentioned in Section 2, the grain size of rock powders used for measure-  
435 ments presented in Figure 7 is strictly below 250  $\mu\text{m}$ . This is a requirement to  
436 transform the CEC measurement into absolute smectite weight fraction. The  
437 presence of larger grains (e.g. millimetric size) have less surface exposed during  
438 the exchange reaction, which might result in reduced smectite accessibility by  
439 the exchange solution and thus smaller measured CEC (Kaufhold et al., 2012).  
440 We do observe a discrepancy of 20% for a high-CEC sample, L99, between the  
441 CEC measured with the same initial and optimal conditions but ground to two  
442 different sizes. These two measurements were carried out by the Institut Na-  
443 tional de Recherche en Agronomie in Arras (France), which performs accredited  
444 measurements of CEC on soil: (i) using their standard size ( $\leq 2 \text{ mm}$ ) and (ii)  
445 using a smaller size ( $\leq 250 \mu\text{m}$ ) on our request.

446 Finally, heterogeneity of core samples from geothermal areas may cause sig-  
447 nificantly different CEC values depending on which lateral face of the cylindrical  
448 plug is used for the powder. Therefore, crushing and mixing together as much  
449 rock sample as possible (e.g. from the two lateral faces) is recommended.

## 450 4 Conclusions

451 In this study, we suggest a modified protocol to minimize the uncertainty of CEC  
452 measurements with the Cu-trien method and thus to quantify the smectite con-  
453 tent in altered volcanic rocks. We observe that using a fixed mass of sample for  
454 rocks covering a wide range of smectite content may cause a relative uncertainty  
455 of up to 70% for samples with low smectite content. We also show that XRD  
456 on randomly oriented powders is not sufficient for smectite quantification in  
457 samples containing other disordered clay minerals (including smectite-bearing  
458 mixed-layers) and/or chlorite. We establish that the fraction of Cu-trien con-  
459 sumed at the end of the reaction needs to be optimized in order to minimize  
460 the total uncertainty of the CEC measurement. Instrument uncertainty and  
461 systematic "partial exchange" error are anti-correlated with varying fraction of  
462 Cu-trien consumed. We suggest that a value of 30% for this fraction is optimal,  
463 as a rule. Finally, we show a linear correlation between the CEC, measured with  
464 an adequate Cu-trien consumption, and the smectite weight fraction determined  
465 by XRD, for 24 samples containing smectite as the only swelling clay mineral.  
466 Our study provides the geothermal industry with a simple method to quantify  
467 the smectite weight fraction (pure smectite or expandable layers in mixed-layer  
468 clays) of powders from all kinds of altered volcanic rocks. Different spectropho-  
469 tometric back-titration methods, using for example the Cobalti-hexamine (III)  
470 molecule, can be used in the same manner for smectite quantification, since a  
471 whole range of thermodynamic constants are considered for the cation exchange

472 reaction.

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492 etveld quantitative analysis are available as Supplementary Material.

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## **A Effect of preferred orientation on X-ray diffraction patterns: the case of heulandite**

The effect on XRD patterns of preferred orientation when samples are back-loaded onto sample holders, is illustrated in Figure A.1. The relative intensity of the heulandite peak at low angle (about  $10^\circ 2\theta$ ), compared to the other peaks, is much higher when sample is back-loaded. The residuals at the end of refinement (gray signal under each pattern) are also higher in this case.

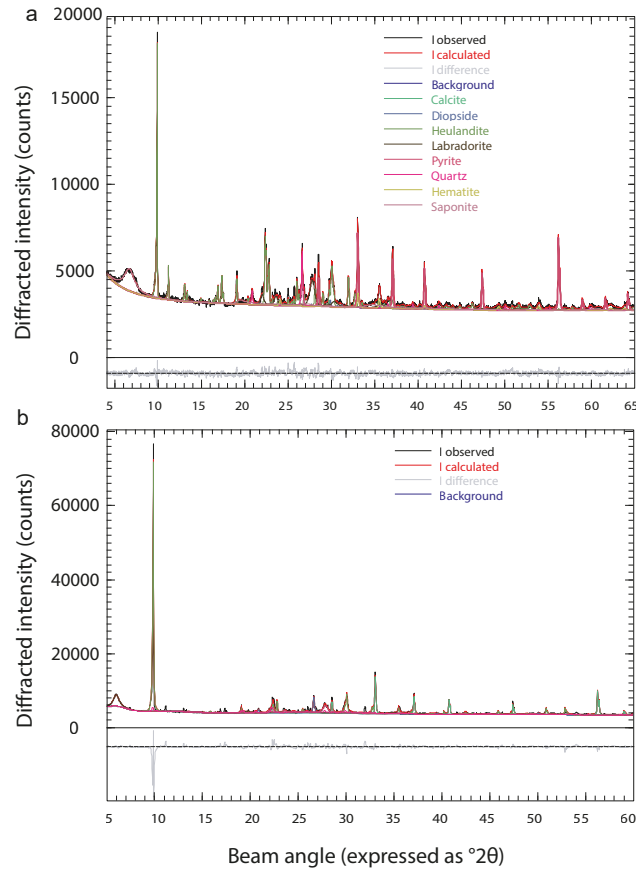


Figure A.1: Effect of preferred orientation on X-ray diffraction pattern for a sample (L02) containing a large amount of heulandite (zeolite). The upper pannel shows the diffraction pattern when the powder is carefully grained and front-loaded. The lower pannel shows the diffraction pattern for the exact same powder but back-loaded. The diffraction peak of heulandite at angle  $10^\circ 2\theta$  is four times higher in the lower panel and cannot be correctly fitted.

## 681 B Structure files for smectite and chlorite in BGMN 682 (Rietveld refinements)

### 683 B.1 Chlorite with Fe/Mg ratios constrained

```
684 PHASE=CHLORITE_Lea //
685 SpacegroupNo=12 HermannMauguin=C12/m1 //
686 PARAM=pa=0.6_0.5^0.8
```

```

687 PARAM=pb=0.6_0.5^0.8
688 PARAM=pc=0.6_0.5^0.8
689 PARAM=A=0.52558_0.51^0.55 PARAM=B=0.945_0.91^0.98
690 PARAM=C=1.42543_1.38^1.44
691 PARAM=BETA=95.587_94.5^98 //
692 RP=4 PARAM=B1=0_0^0.01 PARAM=k1=0_0^0.1 // PARAM=k2=0_0^0.00001 GEWICHT=SPHAR2
693 GOAL: chlorite2b=GEWICHT*ifthenelse( ifdef(d),exp(my*d*3/4),1)
694 E=(MG+2,FE+2(pa)) Wyckoff=a TDS=0.01
695 E=(MG+2,FE+2(pb)) Wyckoff=g y=0.6678 TDS=0.01
696 E=O-2 Wyckoff=i x=0.3150 z=0.9257 TDS=0.01
697 E=O-2 Wyckoff=j x=0.1890 y=0.1667 z=0.0774 TDS=0.01
698 E=(SI+4(0.6560),AL+3(0.3440)) Wyckoff=j x=0.2248 y=0.1669 z=0.1937 TDS=0.01
699 E=O-2 Wyckoff=i x=0.8030 z=0.7643 TDS=0.01
700 E=O-2 Wyckoff=j x=0.5110 y=0.2280 z=0.2363 TDS=0.01
701 E=O-2 Wyckoff=i x=0.8280 z=0.5711 TDS=0.01
702 E=O-2 Wyckoff=j x=0.1310 y=0.3463 z=0.4285 TDS=0.01
703 E=(MG+2,FE+2(pc)) Wyckoff=h y=0.8336 TDS=0.01
704 E=AL+3(0.9650) Wyckoff=d TDS=0.01
705 E=H Wyckoff=i x=0.2887 z=0.8552 TDS=0.02
706 E=H Wyckoff=i x=0.8377 z=0.6339 TDS=0.02
707 E=H Wyckoff=j x=0.1586 y=0.3359 z=0.3698 TDS=0.02
708 pMg=1- (pa+pb+pc)
709 GOAL=pMg

```

## 710 B.2 Saponite loosely constrained

```

711 PHASE=Saponite2wTest SpacegroupNo=5 HermannMauguin=C121
712 PARAM=A=0.53_0.525^0.535 B=A*sqrt(3) PARAM=c0=1.5_1.2^1.58

```

```

713 // old PARAM=c0=1.28_1.15^1.35
714 BETA=100.1
715 pi==2*acos(0)
716 RP=4
717 layer==10 // layer: factor for elongation in c direction
718 C=c0*layer // C: lattice parameter c for supercell
719 PARAM=b10=0.002_0^0.015 // isotropic broadening of hkl reflections
720 PARAM=b1l=0.08_0^0.15 // separate broadening of 00l reflections
721 B1=ifthenelse(and(eq(h,0),eq(k,0)),b10+b1l,b10)
722 // K20: strain broadening of hkl lines
723 PARAM=K20=0.000026_0.00001^0.0001
724 // K2l: strain broadening of 00l lines
725 // changer pour ressembler nontronite de 0.001 a 0.002
726 PARAM=K2l=0_0^0.002
727 breit2=1/sqr(C) // additional l-dependent broadening to avoid "ripples"
728 PARAM=GEWICHT=0.0_0 // refining the scale factor
729 // definition of the helper variable "Saponite..."
730 // for calculation of phase abundances
731 GOAL:Saponite2wTest=GEWICHT
732 // squared lorentzian (Gauss-like) broadening
733 B2=cat(R2=sqr(h/A)+sqr(k/B),Z2=max(sqr(sk)-R2,0),
734 orientierung2=Z2/sqr(sk),
735 ifthenelse(and(eq(h,0),eq(k,0)),K2l*sqr(sk),K20*sqr(sk)+breit2*orientierung2))
736 //
737 // scaling of classes (00l und hkl) and removal of redundant 00l reflections
738 GEWICHT[1]=GEWICHT*ifthenelse(and(eq(h,0),eq(k,0)),
739 ifthenelse(mod(l,layer),0,layer),1)

```



```

740 //
741 // == occupancies ==
742 //
743 // — interlayer —
744 PARAM=pINT=0.3_0.2^0.4
745 pOZ=pINT
746 //
747 // == rigid body of the interlayer complex ==
748 // cation , squared surrounded by 4 oxygen (water)
749 // definition of the positions in cartesian co-ordinates
750 //
751 dCAO=0.241 // distance cation - oxygen
752 //
753 set(ECA,0,0,0) // cation in the middle of the interlayer
754 // ajout de EOZ1 et EOZ2 comme dans nontronite15
755 set(EOZ1,0,0,dCAO) // O above
756 set(EOZ2,0,0,-dCAO) // O below
757 set(EOZ3,dCAO,0,0)
758 set(EOZ4,-dCAO,0,0)
759 set(EOZ5,0,dCAO,0)
760 set(EOZ6,0,-dCAO,0)
761 xx=0.69 // shifting parameter of the interlayer complex in x, fixed
762 yy=0.21 // shifting parameter of the interlayer complex in y, fixed
763 fi1=0 // the 3 Eulerian angles for rotation of the interlayer complex, fixed
764 fi2=0
765 fi3=-18
766 T(xx,yy,0.5*c0*sin(pi*BETA/180),fi1,fi2,fi3,ECA,EOZ1,EOZ2,EOZ3,EOZ4,EOZ5,EOZ6)

```

```

767 // shifting and rotation of the rigid body
768 //
769 // — isotropic temperature factors (nm^2), estimated —————
770 //
771 tdsint=0.01
772 tdsH2O=0.02
773 tdsoct=0.005
774 tdstet=0.003
775 tdso=0.007
776 //
777 // — positions —————
778 // trioctahedral coordinates from phlogopite ICSD 6259
779 // absolute positions in c-direction [nm]
780 // to avoid a stretching/shortening of the TOT layer by varying c0
781 //
782 zT=0.2708
783 zO11=0.112
784 zO12=0.104
785 zO2=0.328
786 //
787 E=MG+2 Wyckoff=a y=0.0 TDS=tdsoct // trans
788 E=MG+2 Wyckoff=a y=0.6673 TDS=tdsoct // cis
789 E=MG+2 Wyckoff=a y=0.3327 TDS=tdsoct // cis
790 E=(SI+4(0.93),AL+3(0.07)) Wyckoff=c x=0.9238 y=0.8335 z=zT/(layer*c0) TDS=tdstet
791 E=(SI+4(0.93),AL+3(0.07)) Wyckoff=c x=0.9238 y=0.1665 z=zT/(layer*c0) TDS=tdstet
792 E=O-1 Wyckoff=c x=0.979 y=0.0 z=zO2/(layer*c0) TDS=tdso
793 E=O-1 Wyckoff=c x=0.671 y=0.2315 z=zO2/(layer*c0) TDS=tdso

```

```

794 E=O-1 Wyckoff=c x=0.871 y=0.1668 z=zO11/(layer*c0) TDS=tdso
795 E=O-1 Wyckoff=c x=0.871 y=0.8332 z=zO11/(layer*c0) TDS=tdso
796 E=O-1 Wyckoff=c x=0.363 y=0.0 z=zO12/(layer*c0) TDS=tdso
797 E=O-1 Wyckoff=c x=0.6710 y=0.7685 z=zO2/(layer*c0) TDS=tdso
798 //
799 // list of interlayer positions
800 // change NA to CA et 1(pINT) to 2(pINT) + ajout de 2 ligne EOZ1 et EOZ2
801 E=CA+2(pINT) Wyckoff=c x=X(ECA) y=Y(ECA) z=Z(ECA) TDS=tdsint
802 E=O-2(pOZ) Wyckoff=c x=X(EOZ1) y=Y(EOZ1) z=Z(EOZ1) TDS=tdsH2O
803 E=O-2(pOZ) Wyckoff=c x=X(EOZ2) y=Y(EOZ2) z=Z(EOZ2) TDS=tdsH2O
804 E=O-2(pOZ) Wyckoff=c x=X(EOZ3) y=Y(EOZ3) z=Z(EOZ3) TDS=tdsH2O
805 E=O-2(pOZ) Wyckoff=c x=X(EOZ4) y=Y(EOZ4) z=Z(EOZ4) TDS=tdsH2O
806 E=O-2(pOZ) Wyckoff=c x=X(EOZ5) y=Y(EOZ5) z=Z(EOZ5) TDS=tdsH2O
807 E=O-2(pOZ) Wyckoff=c x=X(EOZ6) y=Y(EOZ6) z=Z(EOZ6) TDS=tdsH2O

```

### 808 **B.3 Tri-octahedral smectite, interlayer spaces filled with**

#### 809 **Ca and two water layers**

```

810 PHASE=Smectitetri_2w_Ca
811 SpacegroupNo=5 HermannMauguin=C121
812 PARAM=B=0.93_0.900^0.930 A=B/sqrt(3)-0.0015 PARAM=c0=1.50_1.42^1.6
813 BETA=100.2
814 pi==2*acos(0)
815 RP=4
816 layer==10 // layer: factor for elongation in c direction
817 C=c0*layer // C: lattice parameter c for supercell
818 PARAM=b10=0.002_0^0.015 // isotropic broadening of hkl reflections
819 PARAM=b11=0.03_0^0.1 // separate broadening of 00l reflections

```

```

820 B1=ifthenelse (and(eq(h,0),eq(k,0)),b10+b11,b10)
821 // K20: strain broadening of hkl lines
822 PARAM=K20=0.000026_0.00001^0.0001
823 // K2l: strain broadening of 00l lines
824 PARAM=K2l=0_0^0.001
825 breit2=1/sqr(C) // additional l-dependent broadening to avoid "ripples"
826 PARAM=GEWICHT=0_0 // refining the scale factor
827 // definition of the helper variable "smectite..."
828 // for calculation of phase abundances
829 GOAL:Smectitetri2wCa=GEWICHT*ifthenelse (ifdef(d),exp(my*d*3/4),1) //
830 // squared lorentzian (Gauss-like) broadening
831 B2=cat (R2=sqr (h/A)+sqr (k/B),Z2=max(sqr (sk)-R2,0),orientierung2=Z2/sqr (sk),
832 ifthenelse (and(eq(h,0),eq(k,0)),K2l*sqr (sk),K20*sqr (sk)+breit2*orientierung2))
833 //
834 // scaling of classes (00l und hkl) and removal of redundant 00l reflections
835 GEWICHT[1]=GEWICHT*ifthenelse (and(eq(h,0),eq(k,0)), ...
836 ...ifthenelse (mod(1,layer),0,layer),1)
837 //
838 // == occupancies =====
839 // — octahedra position ———
840 pMG=0.15_0.1^0.3 PARAM=pFE=0.06_0^0.3 pAL=(1-pMG-pFE)
841 PARAM=ptrans=1.0_0.0^1.0
842 // mixing parameter for cis- and trans-vacancy; 0 => trans-vacant
843 //
844 // — interlayer —————
845 PARAM=pCA=0.15_0.1^0.3
846 pOZ=pCA

```

```

847 //
848 // ===== rigid body of the interlayer complex =====
849 //      cation , octahedrally surrounded by 6 oxygen (water)
850 // definition of the positions in cartesian co-ordinates
851 //
852 dCAO=0.241          // distance cation - oxygen
853 //
854 set(ECA,0,0,0)      // cation in the middle of the interlayer
855 set(EOZ1,0,0,dCAO)  // O above
856 set(EOZ2,0,0,-dCAO) // O below
857 set(EOZ3,dCAO,0,0)
858 set(EOZ4,-dCAO,0,0)
859 set(EOZ5,0,dCAO,0)
860 set(EOZ6,0,-dCAO,0)
861 xx=0.7 // shifting parameter of the interlayer complex in x
862 yy=0.2 // shifting parameter of the interlayer complex in y
863 // the first two Eulerian angles for rotation of the interlayer complex ,
864 // fixed
865 fi1=45
866 fi2=180*acos(1/sqrt(3))/pi
867 // fi3 (3th eulerian angle) is a rotation around the cartesian z-axis
868 // which is perpendicular to the xy-plane
869 fi3=-20
870 T(xx,yy,0.5*c0*sin(pi*BETA/180),fi1,fi2,fi3,ECA,EOZ1,EOZ2,EOZ3,EOZ4,EOZ5,EOZ6)
871 // shifting and rotation of the rigid body
872 //
873 // — isotropic temperature factors (nm^2), estimated —————

```

```

874 //
875 tdsint=0.015
876 tdsH2O=0.025
877 tdsoct=0.01
878 tdstet=0.01
879 tdso=0.015
880 //
881 // ——— positions —————
882 // absolute positions in c-direction [nm]
883 // to avoid a stretching/shortening of the TOT layer by varying c0
884 //
885 zT=0.271350
886 zO11=0.10955
887 zO12=0.10553
888 zO2=0.33668
889 //
890 E=MG+2 Wyckoff=a y=0.0 TDS=tdsoct
891 E=MG+2 Wyckoff=a y=0.6673 TDS=tdsoct
892 E=MG+2 Wyckoff=a y=0.3327 TDS=tdsoct
893 E=(SI+4(0.93),AL+3(0.07)) Wyckoff=c x=0.9238 y=0.8335 z=zT/C TDS=tdstet
894 E=(SI+4(0.93),AL+3(0.07)) Wyckoff=c x=0.9238 y=0.1665 z=zT/C TDS=tdstet
895 E=O-1 Wyckoff=c x=0.979 y=0.0 z=zO2/C TDS=tdso
896 E=O-1 Wyckoff=c x=0.671 y=0.2315 z=zO2/C TDS=tdso
897 E=O-1 Wyckoff=c x=0.871 y=0.1668 z=zO11/C TDS=tdso
898 E=O-1 Wyckoff=c x=0.871 y=0.8332 z=zO11/C TDS=tdso
899 E=O-1 Wyckoff=c x=0.363 y=0.0 z=zO12/C TDS=tdso
900 E=O-1 Wyckoff=c x=0.6710 y=0.7685 z=zO2/C TDS=tdso

```

```

901 //
902 // list of interlayer positions
903 E=CA+2(pCA) Wyckoff=c x=X(ECA) y=Y(ECA) z=Z(ECA) TDS=tdsint
904 E=O-2(pOZ) Wyckoff=c x=X(EOZ1) y=Y(EOZ1) z=Z(EOZ1) TDS=tdsH2O
905 E=O-2(pOZ) Wyckoff=c x=X(EOZ2) y=Y(EOZ2) z=Z(EOZ2) TDS=tdsH2O
906 E=O-2(pOZ) Wyckoff=c x=X(EOZ3) y=Y(EOZ3) z=Z(EOZ3) TDS=tdsH2O
907 E=O-2(pOZ) Wyckoff=c x=X(EOZ4) y=Y(EOZ4) z=Z(EOZ4) TDS=tdsH2O
908 E=O-2(pOZ) Wyckoff=c x=X(EOZ5) y=Y(EOZ5) z=Z(EOZ5) TDS=tdsH2O
909 E=O-2(pOZ) Wyckoff=c x=X(EOZ6) y=Y(EOZ6) z=Z(EOZ6) TDS=tdsH2O

```

## 910 C More details about the CEC protocol and the 911 sources of uncertainty

### 912 C.1 Preparation of Cu-trien solutions and calibration of 913 the spectrophotometer

914 Exchange solutions are prepared by mixing copper sulphate  $CuSO_4$  and the  
915 organic compound tri-ethylene-tetramine "trien", in stoichiometric proportions,  
916 in a 1 L volumetric flask. The theoretical concentration of the stock solution is  
917 calculated following Equation 18.

$$C_{stock} = \frac{\min(\frac{m_{CuSO_4}}{M_{CuSO_4}}; \frac{m_{trien}}{M_{trien}})}{V_{tot}} \quad (18)$$

918 where  $m_{CuSO_4}$  and  $m_{trien}$  are the masses of  $CuSO_4$  and "trien", in g,  $M_{CuSO_4}$   
919 and  $M_{trien}$  are the molar masses of  $CuSO_4$  and "trien", in g/mol and  $V_{tot}$  is  
920 the total volume of the solution, in L. The masses of  $CuSO_4$  and "trien" are  
921 calculated to obtain a final concentration of 0.01 M Cu-trien (e.g.  $m_{CuSO_4} =$   
922 1.6114 g (anhydrous) and  $m_{trien} = 1.4941$  g).

923 The complex "Cu-trien" is formed by stoichiometric reaction between the  
924 two compounds, so that the quantity of Cu-trien formed (in mol) corresponds  
925 to the quantity of the compound initially present in lesser quantity, the "limiting  
926 reactant". According to Stanjek and Künkel (2016), one has to avoid using an  
927 excess of "trien" in the preparation, due to a possible complexation of trien  
928 with the interlayer cations of smectite (e.g. Ca, Mg) that would prevent a later  
929 exchange with Cu-trien. Since the "trien" compound (from Sigma-Aldrich) has  
930 a purity of  $\geq 97$  % (see also in Ammann, 2003; Stanjek and Künkel, 2016), and  
931 the masses are calculated as if trien were 100% pure,  $CuSO_4$  is theoretically in  
932 excess in our preparation.



Table C.1: Comparison of theoretical (conc. theo.) and ICP-measured Cu concentration (conc. ICP) in six Cu-trien solutions and two  $CuSO_4$  solutions. The first six rows correspond to Cu-trien solutions whose ICP-measured Cu concentration are used for the calibration curve in Figure C.1. The two last rows correspond to  $CuSO_4$  solutions, prepared with pentahydrated and anhydrous solids.

Solution	Conc. ICP mol/L	Conc. theo mol/L	Err
Cu-trien StdA	3.45E-04	3.59E-04	4%
Cu-trien StdB	1.04E-03	9.99E-04	-4%
Cu-trien StdD	1.63E-03	1.68E-03	3%
Cu-trien StdE	2.63E-03	2.53E-03	-4%
Cu-trien 1:6 a	1.58E-03	1.52E-03	3%
Cu-trien 1:6 b	1.50E-03	1.52E-03	-2%
CuSO4 (pentahyd.)	1.01E-02	1.00E-02	1%
CuSO4 (anhyd.)	9.73E-03	1.00E-02	-3%

Most of the exchange solutions are prepared with anhydrous  $CuSO_4$ . Since anhydrous  $CuSO_4$  is an hygroscopic compound and might have slightly rehydrated during storage, we measure the Cu concentration of both Cu-trien and  $CuSO_4$  solutions by ICP (calibrated with a standard for Copper at the wavelength 324.754 nm). We compare the measured concentrations to the theoretical solutions, calculated as if it were perfectly anhydrous (Table C.1). ICP results indicate that the theoretical Cu concentrations in the  $CuSO_4$  solutions, prepared with anhydrous and pentahydrated solid  $CuSO_4$ , are overestimated by 2.7% and underestimated by 0.8%, respectively. The relative difference in Cu concentration of 6 Cu-trien solutions, all prepared with anhydrous  $CuSO_4$ , carries between -4% and 4% (Table C.1). This indicates that no systematic error in the Cu concentration (due to possible rehydration and thus increase of the molar mass) shall be taken into account in the calculations.

Four independent Cu-trien stock solutions and respective dilutions are used for calibrating the spectrophotometer. This set of solutions includes the Cu-trien solutions whose Cu concentration is measured by ICP (Table C.1). It also includes two Cu-trien solutions directly prepared with the two  $CuSO_4$  solutions measured by ICP beforehand. In these cases, the mass of solution is weighted and a mass of "trien" corresponding to a stoichiometric ratio between Cu and

952 trien is mixed with deionized water and added to the copper sulphate solution  
 953 in a 1 L volumetric flask.

954 The corresponding calibration curve, presented in Figure C.1, shows that the  
 955 multiplicative factor  $L$  between absorbance and Cu-trien concentration ( $A =$   
 956  $L[Cu - trien]$ ) is determined with satisfying accuracy ( $L = 145.4 \pm 0.9$  L/mol).

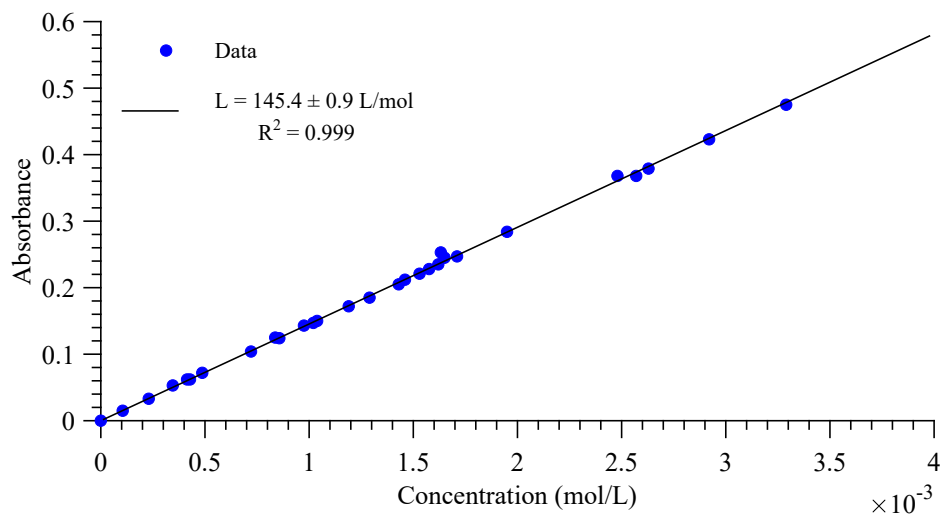


Figure C.1: Calibration curve (absorbance versus theoretical concentration) for the Cu-trien exchange solution. The fitted line is a linear function with an intercept forced to 0. The slope  $L$  of the linear fit and the regression coefficient are given on the figure. The absorbance is always measured at 578 nm.

## 957 C.2 Contact time with Cu-trien

958 A test is carried out on sample L126 to evaluate whether longer contact times  
 959 with Cu-trien might lead to increased exchange. The CEC measured after 5  
 960 and 60 minutes are  $53.4 \pm 0.7$  meq/100g and  $53.1 \pm 0.7$  meq/100g, respectively.  
 961 We consider the difference between these two numbers not significant, which  
 962 confirms that 5 minutes is a sufficient time for this type of samples.

## 963 D Water content and CEC correction

964 CEC measurements are carried out on rock samples dried at room tempera-  
965 ture. The CEC values presented in this study do not include a correction for  
966 the water content in the samples. In particular, the slope presented in Figure  
967 7 corresponds to the average CEC of smectite in samples dried at room tem-  
968 perature, i.e. containing up to 7% of bound water molecules. We present in  
969 Table D.1 measurements of the water content and corrected CEC values for all  
970 samples presented in this study. The water loss is quantified by drying a given  
971 mass of each sample at 105°C. Figure D.1 shows the correlation between CEC,  
972 as corrected for the water content, and smectite content. This slope results in  
973 a CEC of pure smectite slightly higher than when considering the uncorrected  
974 CEC values.

Table D.1: Water loss at 105°C and correction of the CEC values to take into account the water content.

ID	Water content wt. %	CEC (no correction) meq/100g (room T)	CEC corrected meq/100g (105 °C)
L02	3.1%	13.5	14.0
L04	2.4%	17.6	18.0
L05	1.0%	6.1	6.2
L06	2.6%	7.2	7.4
L09	6.0%	25.9	27.6
L10	3.9%	15.6	16.3
L11	2.1%	24.9	25.5
L12	1.3%	2.7	2.7
L14	3.6%	33.2	34.4
L15	1.8%	15.0	15.3
L16	1.6%	4.5	4.6
L19	2.0%	15.1	15.4
L21	2.9%	19.2	19.8
L22	2.4%	21.2	21.7
L26	0.9%	12.8	12.9
L28	2.7%	13.0	13.4
L29	1.5%	9.4	9.6
L30	1.3%	7.2	7.3
L31	2.4%	20.0	20.5
L119	7.2%	45.7	49.2
L40	0.5%	10.9	10.9
L58	0.4%	3.5	3.5
L112	1.5%	6.2	6.3
L113	1.0%	3.5	3.5
L114	0.7%	2.6	2.6
L81	1.0%	16.0	16.2
L82	0.3%	5.8	5.8
L87	0.6%	5.6	5.6
L91	0.5%	8.4	8.4
L93	0.6%	1.9	1.9
L99	4.1%	34.0	35.5
L100	4.8%	27.7	29.1
L80	1.2%	4.8	4.9
L86	1.1%	6.3	6.4
L89	1.2%	5.0	5.0
L95	5.1%	39.6	41.7
L126	7.4%	53.4	57.7
L149	3.6%	19.5	20.2

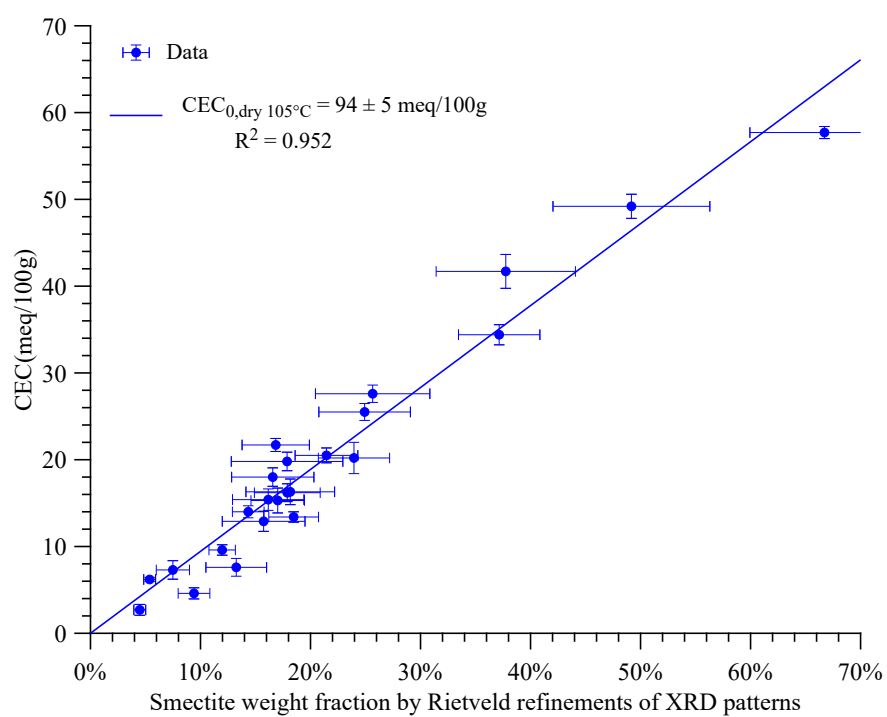


Figure D.1: Smectite content versus CEC, after correction of the CEC value for the water content, based on the water loss at 105°C. The slope and regression coefficient are indicated on the figure.