The effect of sulfate adsorption on the cation exchange capacity of high porosity chalks

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Understanding the process of sulfate adsorption onto the chalk surfaces is important as it has been associated with wettability change [1, 3] and it was also shown to impact the mechanical stability of high porosity chalks [2]. In this paper we determine the cation exchange capacity (CEC) from core floods with and without sulfate present in the pore fluids. We model the sulphate adsorption in terms of interaction with positive Ca sites at the calcite mineral surface [1]; resulting in a net negative surface charge. The cation exchange is believed to take place in the diffusive counter ion layer. Our experimental results remarkably show that CEC increases with almost a factor of 2 upon adsorption of sulfate and the retardation of Na+/K+ front as well increases significantly (see Table 1). The enhanced CEC due to sulfate adsorption could thus contribute to an improved understanding of the enhanced compaction as observed during rock mechanical tests.

Chalk	T	Sulfate ads.	With adsorbed SO4		Without adsorbed SO4	
			CEC	Retard. of Na+/K+	CEC (Exp.)	Retard. of Na+
	^{0}C	μmol/m^2	mEq/L	PV	mEq/L	PV
Liege	50	0.36	0.10	2.18	0.06	1.35
	90	0.80	0.11	2.05	0.05	1.28
	130	1.04	0.10	1.94	0.06	1.28
S.Klint	50	0.49	0.02	1.14	0.01	1.03
	90	0.81	0.02	1.12	0.01	1.04
	130	1.16	0.02	1.12	0.01	1.05

Table 1: Increasing trend in the CEC upon adsorption of sulfate.

[1] Hiorth *et al*. (2010) *TIPM* 10.1007/s11242-010-9543-6.
[2] Korsnes *et al*. (2008) *Journal Pet.Sci.Eng* **60**, 183–193.
[3] Strand *et al*. (2001) *Journal Pet. Sci.Eng* **52**, 187–197.

The structural determinants of silicon fractionation properties of silicate minerals: A first-principles density functional study

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Ab initio methods based on density functional theory have proven to be successful in reproducing the physical and chemical properties of complex systems. Within this framework, we have recently developed a methodology to predict equilibrium fractionation factors as a function of temperature (1). We use PBE functionals, combined with the use of pseudopotentials and planewave basis sets. Our previous work focused on the effect of the polymerization of the silicate network on Si-isotope fractionation (2), which had previously been predicted to be a determining factor. Our work does not confirm this assumption. To investigate the origin of this fractionation, we studied minerals with identical polymerization structures such as talc, pyrophyllite, muscovite, phlogopite or clinochlore. In the case of muscovite and phlogopite, the calculated quartz-mineral fractionations are in qualitative agreement with natural estimates. In this family of silicates, a strong correlation can be shown between the mineral-quartz fractionation of silicon and cationic content. Together with the simple shape of the fractionation laws, this permits to propose the following approximate law, valid for any temperature T (in K):

$$\ln\alpha(\text{phyllo.},\text{qtz},\text{Si},T)=a(T)*[\text{Mg(o)}]+b(T)*([\text{Al(o)}]+2*[\text{Al(t)}]),$$

where [Mg(o)], [Al(o)] and [Al(t)] represent the content of octahedric magnesium, aluminium and tetrahedric aluminium relative to 4 tetrahedral units, and $a(T)=-12.834x^2+14.39x^3$; $b(T)=-5.040x^2+4.20x^3$, with $x=10^2/T$

This relationship can apparently be extrapolated to fractionation properties of tectosilicates (quartz and albite) and inosilicates (enstatite) but fails to reproduce the properties of forsterite. To better understand the limits of this apparently general correlation, we plan to present calculations for several chain silicates (diopside, wollastonite, jadeite), and potentially nesosilicates (fayalite, zircon, garnet). We will also focus on the interpretation of this relationship in terms of cationic force field effects.

[1] Meheut et al. (2007) *GCA* **71**, 3170–3181. [2] Meheut et al. (2009) *Chem. Geol.* **258**, 28.