

## A reinvestigation of smectite illitization in experimental hydrothermal conditions: Results from X-ray diffraction and transmission electron microscopy—Reply

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### INTRODUCTION

Yates and Rosenberg (2011) have commented on our recent study of smectite illitization process based on alteration of pure montmorillonite in K-rich chloride medium (Ferrage et al. 2011), arguing that this latter is a duplication of the study of Whitney and Northrop (1988). They also claimed that our study suffers from misconception as compared to study of Yates and Rosenberg (1996, 1998, 2002) based on alteration of muscovite/illite+kaolinite/microcline+quartz/amorphous silica in 2 M KCl/HCl conditions. In the following, we respond to the most important points criticized by Yates and Rosenberg (2011).

### COUNTERPOINTS

**(1) Ferrage et al. (2011) study is a duplication of Whitney and Northrop (1988) study.** It seems that Yates and Rosenberg (2011) missed the main objective of our work. As stated in the background section of Ferrage et al. (2011), this objective was to follow the experimental plan of Whitney and Northrop (1988), which is a reference study in the field, and check for the possible coexistence of different illite-smectite mixed-layer minerals using XRD profile fitting tools that have been significantly improved over the last two decades. The most important result is that although the experimental conditions in Whitney and Northrop (1988) and Ferrage et al. (2011) studies are similar, the interpretation of the process of illitization was entirely revisited. Our results revealed that illitization is a step mechanism involving four phases with increasing illite content.

**(2) Influence of the starting material composition.** Yates and Rosenberg (2011) argued that the significance of our study is limited owing to the presence of “a fraction of semi-amorphous material of poorly defined structure and composition”. Residual amorphous silica precipitated during montmorillonite formation from volcanic glass is possibly present in our starting product. However, if any, the amount of amorphous silica in our sample is low. This is attested by the very low bumped background of XRD patterns and by the good fits obtained (profile modeling procedure cannot account for amorphous materials). Moreover, the increase of quartz reflection in all experimental samples pleads for the saturation of Si with respect to quartz in the fluid phase. Thus, potential additional source of Si resulting from the dissolution of amorphous silica is likely to impact the proportion of quartz in the altered samples but it is unlikely to have any effect on the illitization mechanism or on illite proportion in the clay mineral fraction.

Yates and Rosenberg (2011) also justified the use of a composite starting material to avoid the presence of collapsed layers. Recent studies have shown that K-saturated montmorillonite already contains 60% of collapsed layers at room relative humidity (Ferrage et al. 2005) and this proportion decreases down to 25% once the sample is ethylene-glycol (EG) solvated (Ferrage et al. 2011). Because these collapsed smectite layers are able to swell and to be re-exchanged in water, the smectite illitization mechanism was determined by Ferrage et al. (2011) after Ca-saturation of the samples. The choice of Ca-saturation, instead of Na-saturation done by Whitney and Northrop (1988), was motivated by the increased selectivity of the smectite interlayers in favor of Ca compared to Na. After Ca+EG saturation, the remaining collapsed layers in montmorillonite decreases to 1% (Ferrage et al. 2011). As a consequence, the collapsed layers in the experimental samples described by Ferrage et al. (2011) are true non-swelling and non-exchangeable K-saturated layers, which match perfectly with the definition of illite considered so far.

**(3) Nature of the experimental products.** Yates and Rosenberg (2011) questioned the attainment of equilibrium in our experiments owing to the lack of any attempt to reverse the reaction. There is no room for debate here: our experiments as those conducted by Whitney and Northrop (1988) are obviously out of equilibrium, which is the reason why no thermodynamic interpretation of the data was performed. At given temperature, the sequential appearance and disappearance of the mixed-layer minerals with less illite content as a function of time led us to call them metastable (transient) phases without further thermodynamic consideration. Yates and Rosenberg (1996) described the crystallization of K-deficient phases at 100 to 200 °C, but they did not observe them to break down into illite with time at fixed temperature ( $\leq 150$  °C) and fluid composition. This point led us to conclude that, in contrast to our experimental results, intermediate illite-smectite phases might be stable phases in Yates and Rosenberg (1996) experiments. In any case, the question of the stable or metastable nature of the intermediate phases observed during the illitization of smectite is still open. This point has been discussed by Aja (1997) in his comment of Yates and Rosenberg (1996) study, and the arguments will not be repeated here. In the same comment paper, Aja (1997) also cautioned against the use of the terminology S, IS, ISII, and I in the attempt made by Yates and Rosenberg (1996) to correlate the composition and crystal structure of these phases following fundamental particle concept. Aja (1997) underlined that this terminology refers to interlayer occupancies of intermediate

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phases and “*was not meant to carry any structural connotation*” including layer stacking ordering. Yates and Rosenberg (1998) further interpreted the intermediate phases as “*steps consisting of thermodynamically coherent sequences of fundamental particles*”. As expected by Aja (1997), XRD profile fitting results obtained by Ferrage et al. (2011) demonstrated the absence of such illite-smectite structural ordering, thus discarding the consideration of the fundamental particle concept to account for the crystal structures of intermediate phases.

**(4) Bias in the characterization of the experimental products.** Yates and Rosenberg (2011) argued that the TEM analyses used in our study were prone to bias. This technique was used to assess whether the different mixed-layer minerals determined from XRD modeling could result in contrasted particle morphologies and chemistries. About 20, 45, 20, and 28 analyses were performed on smectite flakes, aggregates, round, and polygonal morphologies, respectively, after Ca-saturations of altered samples. This re-saturation limits possible underestimation of interlayer cations due to boil-off effect as compared to when only K is present. In addition it also allows discriminating interlayer cations related to smectite interlayers from K associated to illite. There is no evidence of any analytical problem that could explain the observed scattered composition of the experimental products. Crystal edges on which Yates and Rosenberg (1998) performed chemical analyses represent obviously small and homogeneous systems, but these systems represent a very small proportion of the overall material as seen by their XRD patterns of reacted samples. In our experiments, more than 95% of the initial montmorillonite was dissolved at the highest temperature and reaction time conditions. Our chemical data appeared to be more scattered, but this chemical heterogeneity simply reflects the complexity of the sequential mechanism of illitization. It seems that the main concern of Yates and Rosenberg (2011) regarding our TEM analyses is that the composition of end-member illite would most likely have a lower potassium interlayer content than  $0.88 \text{ K/O}_{10}(\text{OH})_2$ , a value that Yates and Rosenberg (1997, 1988) consider with confidence for the end-member illite. There is still some room for discussion of this value, as discussed in the recent review of Srodon et al. (2009) on the different K-contents given in literature, ranging

from 0.5 to  $0.95 \text{ K/O}_{10}(\text{OH})_2$ .

In conclusion, we believe that Yates and Rosenberg (2011) comments and critics do not call into question the validity of Ferrage et al. (2011) results and conclusions. This is rather fortunate, as Ferrage et al. (2011) proposed an interpretation of smectite illitization process similar to that proposed by Yates and Rosenberg in their past publications (Yates and Rosenberg 1996, 1997, 1998). It should be however emphasized that our study and those of Yates and Rosenberg are far from providing a full understanding of the illitization process, which is partly illustrated by the impossibility to constrain kinetic data with this multiphase model (Ferrage et al. 2011).

#### REFERENCES CITED

- Aja, S.U. (1997) “Formation and stability of endmember illite: II. Solid equilibration experiments at 100 to 250°C and  $P_{\text{v, soln}}$ ”—Comment. *Geochimica et Cosmochimica Acta*, 61, 4450–4460.
- Ferrage, E., Lanson, B., Sakharov, B.A., and Drits, V.A. (2005) Investigation of smectite hydration properties by modeling of X-ray diffraction profiles. Part I. Montmorillonite hydration properties. *American Mineralogist*, 90, 1358–1374.
- Ferrage, E., Vidal, O., Mosser-Ruck, R., Cathelineau, M., and Cuadros, J. (2011) A reinvestigation of smectite illitization in experimental hydrothermal conditions: Results from X-ray diffraction and transmission electron microscopy. *American Mineralogist*, 96, 207–223.
- Srodon, J., Zeelmaekers, E., and Derkowski, A. (2009) The charge of component layers of illite-smectite in bentonites and the nature of end-member illite. *Clays and Clay Minerals*, 57, 649–671.
- Whitney, G. and Northrop, H.R. (1988) Experimental investigation of the smectite to illite reaction: Dual reaction mechanisms and oxygen-isotope systematics. *American Mineralogist*, 73, 77–90.
- Yates, D.M. and Rosenberg, P.E. (1996) Formation and stability of endmember illite: I. Solution equilibration experiments at 100–250°C and  $P_{\text{v, soln}}$ . *Geochimica et Cosmochimica Acta*, 60, 1873–1883.
- (1997) Formation and stability of endmember illite: II. Solid equilibration experiments at 100 to 250°C and  $P_{\text{v, soln}}$ . *Geochimica et Cosmochimica Acta*, 61, 3135–3144.
- (1998) Characterization of neoformed illite from hydrothermal experiments at 250 °C and  $P_{\text{v, soln}}$ : A HRTEM/ATEM study. *American Mineralogist*, 83, 1199–1208.
- (2011) A reinvestigation of smectite illitization in experimental hydrothermal conditions: Results from X-ray diffraction and transmission electron microscopy—Comment. *American Mineralogist*, 96, 1901–1902.

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