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

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INTRODUCTION

We were pleased to read that our multiphase illitization model (Yates and Rosenberg 1996, 1997, 1998) has been confirmed by further experimental studies (Ferrage et al. 2011). We agree that illitization is a dissolution-precipitation process following the Ostwald step rule in which metastable intermediate phases are transformed into end-member illite. Unfortunately, several misstatements and misconceptions about our previous studies are incorporated into the paper by Ferrage et al. (2011) and their experimental design is open to criticism.

GENERAL COMMENTS

(1) The multiphase model of Yates and Rosenberg (1996) is not based on the fundamental particle concept as claimed by Ferrage et al. (2011), but it is consistent with it and has been used to elucidate the model. However, in a previous paper we state that "it is not possible to rule out the Markovian model (Altaner and Bethke 1988; Altaner and Ylagan 1997) based on solution equilibration studies alone inasmuch as MacEwan crystallites of different ordering types may behave as thermodynamic phases" (Rosenberg et al. 1990).

(2) According to Ferrage et al. (2011), in our model smectite illitization occurs through the step-wise formation of thermodynamically stable mica-like phases. However, we actually conclude that solubility-controlling phases [0.28 K, 0.51 K, 0.69 $K/O_{10}(OH)_2$] represent metastable steps encountered in the formation of the stable phase, end-member illite. Furthermore, experiments in which muscovite reacted to form end-member illite, demonstrate the reversal of this reaction and thus, establish the stability of end-member illite (0.88 K) with respect to muscovite at temperatures from 100 to 250 °C (Yates and Rosenberg 1997, 1998).

(3) The paper by Ferrage et al. (2011) is largely a duplication of experimental investigations of the smectite to illite reaction in the temperature range 250–450 °C by Whitney and Northrop (1988) and Whitney and Velde (1993). The former authors also report collapsed layers while the latter devote considerable attention to particle morphology. Thus, the study by Ferrage et al. (2011) is, in essence, not an original contribution.

PROBLEMS WITH EXPERIMENTAL DESIGN

(1) No attempt was made to reverse reactions in the solution equilibration experiments of Ferrage et al. (2011). Thus, the attainment of equilibrium in these experiments is questionable. In our solution equilibration experiments, equilibrium was demonstrated by approach from three directions using solutions of different compositions and three solid phases (muscovite, illite, and kaolinite) as starting materials (Yates and Rosenberg 1996). Furthermore, the composition corresponding to end-member illite (0.88 K) was obtained not only by observing the step-wise reaction of solubility-controlling phases [0.28 K, 0.51 K, 0.69 $K/O_{10}(OH)_2$] to 0.88 $K/O_{10}(OH)_2$, but also by observing the reaction from muscovite (0.97 K) to this same end-member composition (Yates and Rosenberg 1997, 1998). Thus, we are confident that the interlayer composition of end-member illite is ~0.88 $K/O_{10}(OH)_2$. This conclusion is also supported by the studies of Meunier and Velde (1989) and Srodon et al. (1992), among others.

(2) As noted by Ferrage et al. (2011), the temperature range of their experiments (250–400 °C) is well above the range expected during smectite illitization in nature. The relatively high temperatures lead to an additional problem: competing reactions.

(a) Illitization by incorporation of K^+ into hydrous interlayer sites.

(b) Dehydration of interlayer H_2O leading to interlayer collapse.

Collapsed interlayers are not easily rehydrated. However, this problem can be largely avoided by starting with kaolinite rather than smectite and experimenting in a lower temperature range. The solubility-controlling phase in equilibrium with kaolinite at 100 and 150 °C (Yates and Rosenberg 1996) is much less susceptible to dehydration than is smectite at 250–400 °C (Koster van Groos and Guggenheim 1986). Furthermore, end-member illite is probably not stable above 350 °C (Rosenberg 2002), so it would be reasonable to expect the formation of muscovite, not illite, in the higher temperature experiments.

(3) Sample preparation procedures also limit the significance of their study. Experiments were carried out using the <1 μm size fraction of their smectite starting materials. Thus, their starting materials probably included a fraction of semi-amorphous material of poorly defined structure and composition. Yates and Rosenberg (1996, 1997) avoided this pitfall by using the 0.2–5.0 μm size fraction in their experiments.

Ferrage et al. (2011) suggest that the formation of illitic particles with increased K- and Al- and decreased Si-content provides the source of Si for the quartz that was observed in the products of their experiments. While this conclusion is reasonable, an additional source of Si could be the dissolution of the highly soluble semi-amorphous material contained in the finest

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size fraction (<0.2 µm) of their smectite starting materials.

(4) Description of the ATEM procedures used by Ferrage et al. is rather brief and fails to mention several details that are crucial to the interpretation of their data. For example, how many individual grains were analyzed for each sample? In the studies by Yates and Rosenberg (1997, 1998), 30–70 and 11–43 grains were analyzed in each sample, respectively. Also, the authors state that the data was "somewhat scattered" and that it was possible that some of the scatter is due to the analysis of several stacked grains at the same time. Was there any effort made to avoid this mistake? A selected area diffraction pattern collected from a suspect grain would clearly show whether it was a single grain or a stack of several grains. Finally, Ferrage et al. (2011) fail to demonstrate that the analytical conditions used minimized the problem of alkali boil-off during the analysis, as did Yates and Rosenberg (1998). Inasmuch as the authors do not specify whether the octahedral iron was in the 2^+ or 3^+ charge state, it is not possible to use charge balance to estimate any errors due to loss of alkali ions during the analyses.

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