

## COMMENT ON “THE ROLE OF $\text{H}_3\text{O}^+$ IN THE CRYSTAL STRUCTURE OF ILLITE” BY F. NIETO, M. MELINI, AND I. ABAD

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**Abstract**—The arguments of Nieto *et al.* (2010) in favor of the incorporation of  $\text{H}_3\text{O}^+$  rather than  $\text{H}_2\text{O}$  in interlayer positions of illite are disputable. Stoichiometric arguments suggest that the excess water in the Silver Hill illite is in the form of  $\text{H}_2\text{O}$ . Moreover, recent thermodynamic models assuming the incorporation of interlayer  $\text{H}_2\text{O}$  in illite provide reasonable estimates of temperature and water content using the AEM/TEM analyses of Nieto *et al.* (2010).

**Key Words**—Composition, Hydronium, Illite, Water.

### INTRODUCTION

Illite is a dioctahedral alkali-deficient mica with excess water incorporated in apparent interlayer vacancies (Hower and Mowatt, 1966; Loucks, 1991; Drits and McCarthy, 2007; Vidal and Dubacq, 2009; Dubacq *et al.*, 2010; Nieto *et al.*, 2010). These vacancies are cation-free crystallographic sites that appear due to charge-balance constraints of the pyrophyllitic substitution  $\text{K}^+ + \text{Al}^{3+} = \square + \text{Si}^{4+}$  (*e.g.* Abad *et al.*, 2006). Excess water in the interlayer is generally considered to be in the form of  $\text{H}_2\text{O}$  because a significant incorporation of  $\text{H}_3\text{O}^+$  would imply unrealistically low pH (Hower and Mowatt, 1966; Loucks, 1991; Jiang *et al.*, 1994). However, Nieto *et al.* (2010) suggest that the excess water in illite is in the form of  $\text{H}_3\text{O}^+$ . If this is true, a modification of the common assumptions made to calculate the structural formulae of alkali-deficient mica is necessary. A revision of the recent thermodynamic models of Vidal and Dubacq (2009) and Dubacq *et al.* (2010) would also be necessary, as the hydrated and dehydrated interlayer vacancies in illite are modeled using dehydrated and hydrated pyrophyllite end-members.

Although Nieto *et al.* (2010) performed a very careful and welcome study, we think that their arguments in favor of the incorporation of  $\text{H}_3\text{O}^+$  instead of  $\text{H}_2\text{O}$  in interlayer position are disputable. Thermogravimetric analyses (Drits and McCarty, 2007; Nieto *et al.*, 2010) or Fourier-transform infrared (FTIR) measurements (*e.g.* Dubacq *et al.*, 2010) indicate the presence of water in alkali-deficient mica, but do not allow us to distinguish  $\text{H}_3\text{O}^+$  from  $\text{H}_2\text{O}$ . Consequently, the arguments of Nieto *et al.* (2010) rely mainly on the calculation of structural formulae assuming the presence of either  $\text{H}_2\text{O}$  or  $\text{H}_3\text{O}^+$ :

(1) “The amount of interlayer water ( $\text{H}_2\text{O}(\text{i}) = 0.42$  a.p.f.u.) calculated from the chemical data of Silver Hill illites and the water content measured by Hower and Mowatt (1966) is higher than the available space in interlayer position ( $=0.3$  a.p.f.u.)” (a.p.f.u. = atoms or molecules per formula unit).

However, the amount of water measured by Hower and Mowatt (1966) ( $\text{H}_2\text{O} = 6.4\%$ ) is too great for the analysis selected by Nieto *et al.* (2010) as it leads to an oxide total  $>100$  wt.%. Ignoring  $\text{TiO}_2$  as in the study of Nieto *et al.* (2010), an oxide total of 100 wt.% is obtained for  $\text{H}_2\text{O} = 5.88\%$ , which corresponds to 0.305 a.p.f.u. ( $\text{H}_2\text{O}(\text{i})$ ) in the first column of Table 1, Case 1) and to the number of apparent interlayer vacancies. The same reasoning can be used for the structural formulae of illite reported by Nieto *et al.* (2010). With the value of  $\text{H}_2\text{O} = 5.88\%$  determined above,  $\text{H}_2\text{O}(\text{i}) = 0.28$  a.p.f.u. for the “average” composition listed in their table 2, which is again compatible with the value of 0.3 apparent interlayer vacancies. For the AEM/TEM analyses listed in table 1 of Nieto *et al.* (2010), the apparent vacancies range between 0.115 and 0.463. Assuming that they are occupied by molecular water,  $\text{H}_2\text{O}$  is found to range between 5 and 6.64 wt.%, with an average value of 5.8 wt.% (Table 1). The average value is in agreement with the value estimated above from the analysis by Hower and Mowatt (1966).

(2) “When assuming that the excess water corresponds to  $\text{H}_3\text{O}^+$  and eventually adjusting the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio, the calculated structural formulae have an octahedral occupancy (OC) of 2 and an interlayer occupancy (IC) of 1. It follows that the Si in excess of 3 a.p.f.u. and the amount of  $\text{Mg} + \text{Fe}^{2+}$  are explained by the Tschermak substitution alone.”

The total number of cations in the illite structural formula, calculated on the basis of 22 negative charges ( $\text{O}_{10}(\text{OH})_2$ ) and assuming that  $(\text{K}^+ + \text{Na}^+ + \text{H}_3\text{O}^+)_{\text{interlayer}}$

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Table 1. Structural formulae and maximum amount of H<sub>2</sub>O and H<sub>3</sub>O<sup>+</sup> wt.% calculated from the AEM/TEM analyses of Nieto *et al.* (2010) and the analysis from Hower and Mowatt (1966) (HM66). In Case 1, H<sub>2</sub>O was calculated assuming all apparent vacancies (= 1 - Na - K) being filled by molecular water, (XPrI + XPrIH) = (Si - 3 - XCel), XBT = (OC - 2), (XCel)<sub>Case 1</sub> = (Fe<sup>2+</sup> + Mg - 3XBt), (XMusc)<sub>Case 1</sub> = (Al<sup>VI</sup> + Fe<sup>3+</sup> - 2\*(XPrI + XPrIH) - XCel)/2. In Case 2, the structural formulae were recalculated on the basis of 22 negative charges, and H<sub>3</sub>O<sup>+</sup> (a.p.f.u.) was estimated in order to have (K + Na + H<sub>3</sub>O<sup>+</sup>) = 1, (XCel)<sub>Case 2</sub> = (Fe<sup>2+</sup> + Mg), (XMusc)<sub>Case 2</sub> = 1 - (XCel)<sub>Case 2</sub>.

	HM(66)	Imt-2/1	Imt-2/2	Imt-2/3	Imt-2/4	Imt-2/6	Imt-2/7	Imt-2/12	Imt-2/13	Imt-2/14	Imt-2/16	Imt-2/20	Imt-2/22	Imt-2/23	Imt-2/24	Imt-2/25	Imt-2/26	Imt-2/27	
Case 1: interlayer vacancies filled by H <sub>2</sub> O																			
H <sub>3</sub> O <sup>+</sup> wt.%	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	
H <sub>2</sub> O wt.%	5.89	6.00	5.51	5.89	6.15	5.99	6.63	5.53	6.39	5.61	5.53	5.86	6.55	5.00	6.66	5.04	5.32	5.29	
Si a.p.f.u.	3.66	3.44	3.41	3.38	3.43	3.44	3.63	3.34	3.45	3.33	3.44	3.40	3.63	3.28	3.68	3.43	3.35	3.42	
Al <sup>IV</sup>	0.34	0.56	0.59	0.62	0.57	0.56	0.37	0.66	0.55	0.67	0.56	0.60	0.37	0.72	0.32	0.57	0.65	0.58	
Al <sup>VI</sup>	1.38	1.48	1.48	1.51	1.58	1.65	1.51	1.57	1.51	1.54	1.45	1.55	1.63	1.54	1.65	1.43	1.49	1.48	
Fe <sup>2+</sup>	0.08	0.07	0.07	0.06	0.06	0.04	0.07	0.06	0.06	0.07	0.06	0.06	0.05	0.06	0.04	0.07	0.07	0.06	
Fe <sup>3+</sup>	0.27	0.21	0.23	0.19	0.17	0.12	0.21	0.17	0.20	0.21	0.19	0.20	0.14	0.18	0.13	0.21	0.23	0.20	
Mg	0.28	0.33	0.28	0.35	0.28	0.24	0.26	0.27	0.35	0.26	0.37	0.26	0.19	0.28	0.17	0.32	0.27	0.30	
K + Ca + Na	0.69	0.67	0.77	0.69	0.64	0.68	0.54	0.77	0.59	0.75	0.77	0.70	0.57	0.88	0.55	0.87	0.81	0.82	
H <sub>2</sub> O(i)	0.31	0.33	0.23	0.31	0.36	0.32	0.46	0.23	0.41	0.25	0.23	0.30	0.43	0.12	0.45	0.13	0.19	0.18	
OC	2.00	2.09	2.06	2.11	2.09	2.05	2.05	2.07	2.12	2.08	2.07	2.07	2.01	2.06	1.99	2.03	2.06	2.04	
XPrI+XPrIH	0.31	0.33	0.23	0.31	0.36	0.32	0.46	0.23	0.41	0.25	0.23	0.30	0.43	0.12	0.45	0.13	0.19	0.18	
XBt	0.00	0.09	0.06	0.11	0.09	0.05	0.05	0.07	0.12	0.08	0.07	0.07	0.01	0.06	0.00	0.03	0.06	0.04	
XCel	0.36	0.11	0.18	0.07	0.07	0.12	0.16	0.11	0.04	0.08	0.21	0.10	0.20	0.16	0.23	0.30	0.16	0.24	
XMusc	0.34	0.46	0.53	0.51	0.48	0.51	0.32	0.59	0.42	0.59	0.49	0.52	0.36	0.66	0.32	0.54	0.59	0.54	
Case 2: interlayer vacancies filled by H <sub>3</sub> O <sup>+</sup>																			
H <sub>3</sub> O <sup>+</sup> wt.%	1.52	1.64	1.12	1.51	1.76	1.57	2.24	1.12	1.99	1.21	1.12	1.46	2.11	0.58	2.21	0.63	0.92	0.87	
H <sub>2</sub> O wt.%	4.56	4.56	6.04	6.61	6.97	6.73	7.67	6.06	7.29	6.18	6.05	6.54	7.51	5.28	7.66	5.35	5.75	5.70	
Si a.p.f.u.	3.61	3.39	3.37	3.33	3.37	3.38	3.55	3.30	3.39	3.29	3.40	3.35	3.56	3.26	3.60	3.41	3.32	3.39	
Al <sup>IV</sup>	0.39	0.61	0.63	0.67	0.63	0.62	0.45	0.70	0.61	0.71	0.60	0.65	0.44	0.74	0.40	0.59	0.68	0.61	
Al <sup>VI</sup>	1.31	1.40	1.42	1.43	1.48	1.57	1.40	1.51	1.41	1.48	1.39	1.48	1.52	1.51	1.53	1.40	1.44	1.43	
Fe <sup>2+</sup>	0.08	0.07	0.07	0.06	0.05	0.04	0.07	0.05	0.06	0.07	0.06	0.06	0.04	0.06	0.04	0.07	0.07	0.06	
Fe <sup>3+</sup>	0.25	0.21	0.23	0.19	0.17	0.12	0.21	0.17	0.19	0.21	0.19	0.19	0.14	0.18	0.13	0.21	0.23	0.20	
Mg	0.27	0.33	0.28	0.34	0.28	0.24	0.25	0.27	0.34	0.26	0.37	0.26	0.19	0.28	0.17	0.32	0.27	0.30	
K + Ca + Na	0.67	0.66	0.76	0.68	0.63	0.67	0.53	0.76	0.58	0.74	0.76	0.69	0.56	0.88	0.54	0.87	0.80	0.82	
H <sub>3</sub> O <sup>+</sup>	0.32	0.34	0.24	0.32	0.37	0.33	0.47	0.24	0.42	0.26	0.24	0.31	0.44	0.12	0.46	0.13	0.20	0.18	
OC	1.91	2.00	1.99	2.03	1.99	1.96	1.92	2.01	2.01	2.01	2.01	1.99	1.89	2.02	1.87	1.99	2.01	1.99	
XCel	0.35	0.39	0.35	0.40	0.33	0.27	0.32	0.32	0.40	0.32	0.43	0.32	0.23	0.34	0.21	0.38	0.34	0.36	
XMusc	0.65	0.61	0.65	0.60	0.67	0.73	0.68	0.68	0.60	0.68	0.57	0.68	0.77	0.66	0.79	0.62	0.66	0.64	

= 1 a.p.f.u., is indeed less than if H<sub>2</sub>O is assumed to be incorporated in the interlayer position. As a result, both the Si content and the OC decrease and the extent of both di-trioctahedral and pyrophyllitic substitutions is reduced.

Unfortunately, Nieto *et al.* (2010) compared the structural formulae calculated assuming the incorporation of H<sub>2</sub>O or H<sub>3</sub>O<sup>+</sup> for the average illite composition only. The structural formulae of all the individual TEM/AEM analyses reported by Nieto *et al.* (2010) are listed in Table 1. In Case 2 (incorporation of H<sub>3</sub>O<sup>+</sup>), they have been calculated on a 22 negative charge basis, and H<sub>3</sub>O<sup>+</sup> was adjusted in order to obtain  $(K^+ + Na^+ + H_3O^+)_{interlayer} = 1$ . In contrast with the statement of Nieto *et al.* (2010), the OC is generally different from the ideal value of 2 a.p.f.u. (Table 1). It is often less than this value, which implies that the composition of illite cannot be explained by the Tschermak substitution alone (Ransom and Helgeson, 1993). This point is further illustrated in Figure 2, which shows that a linear combination of the celadonite ( $X_{Cel} = Mg + Fe^{2+}$ ) and muscovite ( $X_{Musc} = 1 - X_{Cel}$ ) end-members does not reproduce the Si content of the structural formulae. The scatter of the open symbols in Figure 1 shows that the octahedral ( $Fe^{2+} + Mg$ ) and tetrahedral Si contents cannot both be described by the Tschermak substitution alone between ( $K^+, H_3O^+$ )-celadonite and muscovite. Additional end-members are thus required. The OC obtained when assuming the incorporation of H<sub>2</sub>O (Case 1) are also different but generally >2. This is easily explained by the incorporation of a trioctahedral component in illite, as observed in phengite at high temperature or smectite at lower temperature. In this case, the molar fraction of pyrophyllite (PrI:  $Si_4(Al, Fe^{3+})_2O_{10}(OH)_2$ ), hydrated pyrophyllite (PrIH:  $Si_4(Al, Fe^{3+})_2O_{10}(OH)_2 \cdot H_2O$ ), biotite (Bt:  $(Si_3Al)(Mg, Fe^{2+})_3KO_{10}(OH)_2$ ), celadonite (Cel:  $Si_4(Al, Fe^{3+})(Mg, Fe^{2+})KO_{10}(OH)_2$ ), and muscovite (Musc:  $(Si_3Al)(Al, Fe^{3+})_2KO_{10}(OH)_2$ ) end-members

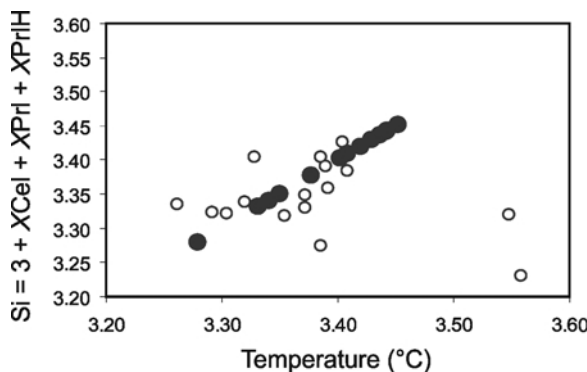


Figure 1. Si content calculated from the proportion of end-members in Cases 1 (incorporation of H<sub>2</sub>O, filled symbols) and 2 (incorporation of H<sub>3</sub>O<sup>+</sup>, open symbols) vs. Si content of the structural formulae. In Case 2, the molar fraction of Cel and Musc are calculated from the octahedral (Mg + Fe<sup>2+</sup>) content.

proposed by Dubacq *et al.* (2010) are listed in Table 1. The structural formulae are fully reproduced with these end-members, *e.g.* the Si content of the structural formulae (Figure 1, filled symbols).

Because of the stoichiometric reasons listed above, the excess water in the illite grains analysed by Nieto *et al.* (2010) is more likely, or at least possibly, in the form of molecular water rather than H<sub>3</sub>O<sup>+</sup>. The thermodynamic model of Dubacq *et al.* (2010) was used to estimate the amount of H<sub>2</sub>O(i) and the temperature of equilibrium among the Silver Hill illite, quartz, and water at 1 kbar (Figure 2). Although the illite compositions reported by Nieto *et al.* (2010) are highly variable, the calculated temperatures are quite similar and define conditions at ~210°C (Figure 2). Moreover, the predicted amount of interlayer water is very close in each case to the maximum value estimated from the stoichiometric criteria above. These results can be viewed as an additional and independent argument in favor of the incorporation of neutral water in the apparent vacancies of illite.

## CONCLUSION

(1) We agree with Nieto *et al.* (2010) that thermobarometric estimates cannot be made without consideration of excess water in illite, *i.e.* using the model of Vidal and Parra (2000) or Parra *et al.* (2002) derived for phengites. However, stoichiometric and thermodynamic arguments both suggest that the excess water in the Silver Hill illite is in the form of H<sub>2</sub>O rather than H<sub>3</sub>O<sup>+</sup>. An independent argument against a significant incorporation of H<sub>3</sub>O<sup>+</sup> is that it would imply unrealistically low pH, as already discussed by Hower and Mowatt (1966), Loucks (1991), and Jiang *et al.* (1994).

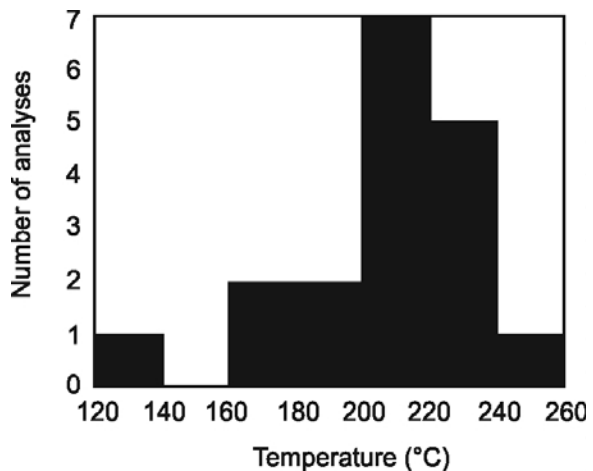


Figure 2. Frequency histogram showing temperatures of equilibrium for illite, quartz, and water, calculated using the model of Dubacq *et al.* (2010) for the compositions of the Silver Hill illite listed in Nieto *et al.* (2010).

(2) No evidence was found to support the assumption that octahedral occupancy in illite should exactly equal 2 or that the interlayers should sum exactly to unity.

(3) The thermobarometric model of Dubacq *et al.* (2010) gives reasonable estimates of equilibrium conditions and water content when assuming that H<sub>2</sub>O is incorporated in the interlayer position of illite. The thermodynamic model of Dubacq *et al.* (2010) is, therefore, in good agreement with the analytical results of Nieto *et al.* (2010).

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