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Kaolinite and halloysite –does octahedral Fe²⁺ introduce the extra water into halloysite?

Halloysite is a member of the kaolinite (kandite) group of minerals. The kaolinite structure is made up of a tetrahedral silica sheet and an octahedral alumina sheet, bonded together into an aluminosilicate layer. Kaolinite can be written as $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, while halloysite is ideally $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$, and usually has a high degree of disorder. The additional water molecules occur as partially confined interlayer water, which can be removed resulting in a reduction of the c-axis from approximately 1.0 nm to the kaolinite value of 0.7 nm.

A long-standing unanswered question is why does halloysite contain water, while kaolinite (and the closely related dickite and nacrite) do not [1]? Common theories have been that the incorporation of impurities (e.g., Al^{3+} for Si^{4+} in the tetrahedral sheet, Fe^{2+} or Fe^{3+} for Al^{3+} in the octahedral sheet, or other impurities in the octahedral sheet, which may be hydrated, etc) may create a charge imbalance which can encourage the incorporation of exchangeable cations. However, NMR measurements [2] have shown that there is no more tetrahedral Al in the Si layer than in kaolinites. Also, quasielastic neutron scattering analysis of interlayer water [3] has shown that halloysite has no exchangeable cations.

This leaves octahedral Fe^{2+} as the most likely remaining charge impurity. To determine the Fe^{2+} concentrations, we have taken Mössbauer measurements of three New Zealand halloysites: Opotiki, Te Akatea and Te Puke. The first two have appreciable Fe^{2+} concentrations of approximately 10% of the total Fe (respectively, ~1.7 and ~0.4 mmol Fe^{2+} /100g) which may provide measureable layer charge, while the Te Puke has a much smaller concentration (~1%) of a total Fe concentration of 14.06 mmol/100g [4] giving ~0.1 mmol Fe^{2+} /100 g. Unambiguous fitting of the spectra of these minerals is difficult because of the very broad lines, which reduces resolution. There is also the possibility of the presence of trace goethite and of slow paramagnetic relaxation in the structural Fe^{3+} . Progress in solving this riddle of halloysite will be detailed.

[1] Bailey, S.W. 1990 Proc. 9th Int. Clay Conf., Strasbourg, Vol II, Sciences Géologiques 86 89-98

[2] Newman, R.H. Childs, C.W. and Churchman, G.J. 1994 Clay Min. 29 305-312

[3] Bordallo, H.N. et al. J. Phys. Chem. C 2008 112 13982-13991

[4] Churchman, G.J. and Theng, B.K.G. 1984. Clay Min. 19 161-175

Primary author: Prof. CASHION, John (Monash University)

Co-authors: Prof. CHURCHMAN, Jock (University of Adelaide); Prof. ALDRIDGE, Laurie (Monash University); Prof. CADOGAN, Sean (UNSW Canberra at AFDA); Dr GATES, Will (Monash University)

Presenter: Prof. CASHION, John (Monash University)