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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 Al2Si2O5(OH)4, while halloysite is ideally Al2Si2O5(OH)4.2H2O, 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., Al3+ for Si4+ in the tetrahedral sheet, Fe2+ or Fe3+ for Al3+ 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 Fe2+ as the most likely remaining charge impurity. To determine the Fe2+ concentrations, we have taken Mössbauer measurements of three New Zealand halloysites: Opotiki, Te Akatea and Te Puke. The first two have appreciable Fe2+ concentrations of approximately 10% of the total Fe (respectively, ~1.7 and ~0.4 mmol Fe2+/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 Fe2+/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 Fe3+. 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

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