



## Kaolinite and Halloysite – Does Octahedral Fe<sup>2+</sup> Introduce the Extra Water into Halloysite?

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Mössbauer spectra of three New Zealand halloysites are consistent with all the iron being structural, that there are strong slow paramagnetic relaxation effects and that there are Fe<sup>2+</sup> fractions of 0.03 - 0.08. Comparison with previous work shows that there is a correlation between a high Fe<sup>2+</sup> concentration and the formation of halloysite in preference to kaolinite, although it is expected that other factors also play a significant part.

### 1. Introduction

The kaolin group of minerals, or kandites, are well known as the principal constituents of china clay for the manufacture of ceramics. Kaolinite is the most common member with a composition Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>, along with the polymorphs dickite and nacrite. The kaolinite structure is made up of a tetrahedral silica sheet and an octahedral alumina sheet, bonded together into an aluminosilicate layer. Halloysite is a hydrated form of kaolinite, ideally Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub>·2H<sub>2</sub>O, and usually has a high degree of disorder. The additional water molecules occur as partially confined interlayer water, which on removal results in an irreversible reduction of the c-axis from approximately 1.0 nm to the kaolinite value of 0.7 nm.

The unusual feature of halloysite is that it commonly occurs as tubes of diameter 10-30 nm and length 0.5-10 μm, but also as blocks and flaky plates. The tubes, in particular, are currently of interest as materials for composite strengthening, containing flame retardants and anti-corrosion chemicals, and since they are bio-compatible, for delivery of drugs and anti-microbials [1].

A long-standing unanswered question is why does halloysite contain water [2]? Common theories have been that the incorporation of impurities (e.g., Al<sup>3+</sup> for Si<sup>4+</sup> in the tetrahedral sheet, Fe<sup>2+</sup> or Fe<sup>3+</sup> for Al<sup>3+</sup> in the octahedral sheet, or other impurities in the octahedral sheet) may create a charge imbalance which can encourage the incorporation of exchangeable cations, either into the interlayer or on external surfaces. However, NMR measurements [3] have shown that there is no more tetrahedral Al in the Si layer than in kaolinites. Also, quasielastic neutron scattering analysis of interlayer water [4] confirms that halloysite has no exchangeable cations.

This leaves octahedral Fe<sup>2+</sup> as the most likely remaining charge impurity. To determine the Fe<sup>2+</sup> concentrations, we have taken <sup>57</sup>Fe Mössbauer measurements of three New Zealand halloysites: Opotiki (Bay of Plenty), Te Akatea (Waikato) and Te Puke (Bay of Plenty) at room temperature and 78 K.

### 2. Experimental

The collection of the samples has been described by Churchman and Theng [5]. Briefly, the raw samples were ultrasonically dispersed at pH 10 (NaOH) and the clay fraction separated by gravity sedimentation. The pH was lowered to pH 6 (HCl) to flocculate the separated



suspensions and then adding sufficient NaCl to bring the system to ~1 M. Excess salt was removed by centrifugation and washing with water or by dialysis. The total iron concentrations, given as wt% Fe<sub>2</sub>O<sub>3</sub>, were Opotiki (4.18%), Te Akatea (2.27%) and Te Puke (3.40%).

Note that small fractions of iron may be present as trace goethite, FeOOH, which would complicate the spectral fitting. It was also quite probable that there would be slow paramagnetic relaxation as first observed in minerals by Fysh et al. [6] in kaolinite and subsequently observed by Murad and Wagner in many kaolinite samples [7]. This occurs when the separation between magnetic ions is sufficiently large, typically ~1 nm, that the Fe<sup>3+</sup> spin system stays in the same J<sub>z</sub> state for a time comparable with the period of the nuclear Larmor precession frequency.

### 3. Results

The room temperature spectra of the samples were all similar. Fig. 1 shows the Opotiki spectrum consisting of a prominent ferric doublet (red), a much weaker ferrous doublet (green) and a broadened feature (light blue) which could have been due to slow paramagnetic relaxation, to superparamagnetism or to poorly crystalline goethite. Fig 2 has the spectrum of the Te Puke sample at 78 K showing the appearance of a broadened sextet with a very large hyperfine field of 53-55 T (dark blue), the two previous doublets and another central feature (light blue). The field for the broad sextet is larger than the hyperfine field for any of the iron oxides or oxyhydroxides, but fits well with the expected value for slow paramagnetic relaxation of 54.9 T [6] for the J<sub>z</sub> = |±5/2> levels, with a small reduction and broadening due to the minor unresolved contribution from the J<sub>z</sub> = |±3/2> level of 49.5 T [6]. The fitted parameters are given in Table 1 and we see that they are very similar to those of kaolinite, as already pointed out [7].

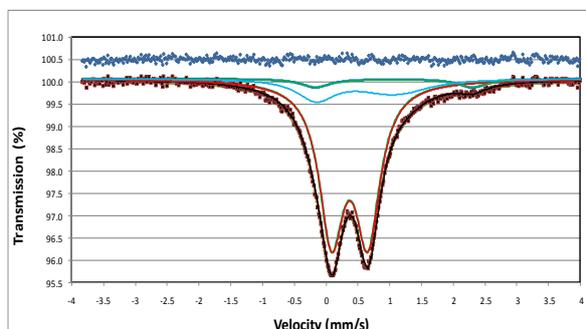


Fig. 1. Spectrum of Opotiki at room temperature.

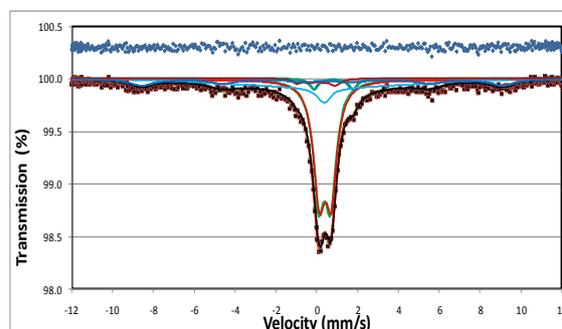


Fig. 2. Spectrum of Te Puke at 78 K.

The top blue dots represent the difference between the data and the fit in each spectrum.

With the interpretation of slow paramagnetic relaxation, we would expect that there would be a quasi-continuous distribution of Fe<sup>3+</sup> - Fe<sup>3+</sup> distances and this will lead to a distribution of relaxation frequencies. Thus the ions with the largest separation will contribute to the broadening in the room temperature spectrum. At 78 K, this group have split out into the full field, but the next group in the distribution now contributes to the smaller broadening (light blue) for which the shape is poorly defined.

For the small ferrous contributions, it was difficult to fit the left hand line because it overlaps with the dominant paramagnetic ferric contribution. Thus the positional parameters have a considerable uncertainty and have not been included in Table 1, but the areas are better defined with the best estimate for the ferrous contributions as a percentage of total iron being Opotiki: 3.5 ± 2%, Te Akatea: 8 ± 1% and Te Puke: 3 ± 1%.



#### 4, Discussion

We note first that no evidence for goethite was observed in the Mössbauer spectra of our samples and it would seem that all the iron is incorporated as structural iron replacing  $\text{Al}^{3+}$  in the octahedral sheet, regardless of in which subspectrum (Table 1) its contribution appeared. One of our samples, Te Puke, has been studied before [7], and no  $\text{Fe}^{2+}$  contribution was observed. Comparison of the two low temperature spectra shows that, although both samples originated from the same source, they are no longer quite identical with our spectrum having an enhanced shoulder at 2 mm/s in Fig. 2. This difference probably reflects differences in handling of the halloysite samples: in our case, care was taken to limit dehydration and accompanying oxidation.

Table 1. Parameters for Mössbauer spectra of halloysite samples.

Sample	Temp.	$\text{Fe}^{3+}$ doublet			Sextet		$\text{Fe}^{2+}$ doublet
		IS mm/s	QS mm/s	Area %	B T	Area %	Area %
Opotiki	RT	0.37(1)	0.57(1)	78.0			5.1
	78 K	0.47(1)	0.64(2)	73.9	53.1(3)	11.8	2.8
Te Akatea	RT	0.36(1)	0.57(1)	85.1			8.7
	78 K	0.41(1)	0.71(9)	55.0	53.3(18)	37.9	7.6
Te Puke	RT	0.36(1)	0.54(1)	70.0			2.2
	78 K	0.51(1)	0.59(2)	51.9	55.1(8)	15.0	3.8
Te Puke <sup>a</sup>	RT	0.347(2)	0.543(3)				-
	4 K	0.48(2)	0.53(3)		55		
Kaolinites <sup>b</sup>	RT	0.34	0.52				

<sup>a</sup> Ref [7]. <sup>b</sup> average values from ref [8]. Figures in parentheses are the error in the last digit. IS = isomer shift, QS = quadrupole splitting, B = magnetic hyperfine field.

The areas of the  $\text{Fe}^{2+}$  doublet given in Table 1 are well within the range of values observed in kaolinite [7,8]. However, in trying to determine the effect of ferrous ions on the crystallization, one should not be dealing with the ferrous fraction, but the total number of ferrous ions present. We have calculated this (Table 2) for the samples described in [7] (first 12 rows) and also our own samples (lower three rows). The first 10 samples are kaolinites and the last 5 are halloysites.

Ignoring the Te Puke sample from [7], we see that, although there is overlap between the values for the two minerals, all the halloysites have concentrations greater than 0.1%, while only three of the kaolinites are in this region. We must remember that the uncertainties in some of the values are quite appreciable, being larger for the samples with smaller  $\text{Fe}^{2+}$  fractions. For our samples, the uncertainty ranges from 12% to over 50%.

There will be other factors which affect the kaolinite-halloysite divide, so we should not expect a sharp distinction with  $\text{Fe}^{2+}$  concentration. Such factors will include the temperature, the pH, or more generally

Table 2. Calculated concentrations of  $\text{Fe}^{2+}$  from [7] and this work.

Sample	Conc %
Amazon	0.000
KGa-1	0.147
ST026	0.079
ST027	0.111
9a	0.076
#3	0.073
K160	0.029
Wolfka	0.038
201	0.083
Premier	0.146
Te Puke	0.000
BW208	0.250
Opotiki	0.146
Te Akatea	0.182
Te Puke	0.102



the Eh - pH conditions during crystallization, the particular rocks involved in the weathering (rhyolite, andesite, dacite, phonolite), other neighbouring rocks, and so on.

There is a patented method [9] for making halloysite purely from a mixture of Al(OH)<sub>3</sub> gel, silica sol and water, with Al:Si ratio of 0.5 to 1.2, water/silica molar ratio of 20-60, pH of 4-10 and a temperature of 230-270 °C. This is iron-free, but iron, or other desired additives for catalysis, etc, can be added. The presence of iron modifies the mismatch between the silica and alumina sheets and hence can modify the morphology, and the iron-free synthetic material consists principally of flakes and not tubes. The material has a larger surface area of 85-200 m<sup>2</sup>/g compared with typically 40-85 m<sup>2</sup>/g for natural samples, which makes for enhanced catalytic effects.

Satokawa *et al.* [10] showed that the pH variation from 0.2 to 7.0 affects the type and number of stacking faults in kaolinite and it seems reasonable to assume that the same will be true for halloysite, for which stacking faults seem to be a common part of the structure, although we cannot assert that it is essential. They concluded that the results implied that there were different kaolinization processes. The parent rocks for the three samples which we have studied were either rhyolite or andesite with the mechanism for producing halloysite being either weathering or hydrothermal action. Since both are higher in silica than required for halloysite, the low pH helps to dissolve the excess silica.

## 5 Conclusions

We conclude, from a limited set of samples, that an enhanced Fe<sup>2+</sup> concentration does correlate with the formation of halloysite, although the uncertainties in some of the data are considerable. In common with the conclusions of Satokawa *et al.* [9] on kaolinite, we suggest that there are also multiple routes to form halloysite. Although it is possible to form halloysite artificially under a range of conditions [9], we believe that there are natural conditions, yet to be elucidated, which enhance halloysite generation. The correlation, which we have shown, does not yet provide a mechanistic understanding of how this assists the incorporation of water into the structure.

## Acknowledgements

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