

# KAOLIN CLAY DEPOSITS ASSOCIATED WITH FOSSIL GEOTHERMAL SYSTEMS IN NEW ZEALAND

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## ABSTRACT

The occurrence of kaolinite in association with sinter caps in geothermal systems has been recognised for many years. Kaolins are used extensively in New Zealand in ceramics and as an industrial filler or coating pigment. During the 1960's and 1970's fossil geothermal systems in New Zealand were investigated to determine whether commercial kaolin deposits might exist beneath sinter caps.

Surface prospecting of late Tertiary acid volcanic rocks for evidence of siliceous sinter and kaolin clays was followed up by core drilling of promising areas and detailed laboratory evaluation.

This paper reports the results of investigations in the Northland and Coromandel regions of New Zealand in which two kaolin polymorphs, halloysite and kaolinite were identified. Commercially viable deposits formed by a combination of hydrothermal alteration and deep sub-tropical weathering were confirmed.

## INTRODUCTION

Silicification has long been recognised as an indicator of hydrothermal alteration. The association of kaolinite and siliceous sinter has been reported since the 1930's (Allen and Day (1934), Fenner (1936). At Wairakei in New Zealand Steiner (1953) recognised a surface zone of kaolinite, alunite and opal which had been formed by acid alteration of volcanic rocks due to interaction of groundwater with ascending geothermal fluids.

In New Zealand white kaolin clays are used extensively in ceramics and as a filler and coating pigment in the pulp and paper industry. In the late 1960's a detailed investigation was carried out of fossil geothermal systems in New Zealand to determine whether commercially viable kaolin deposits might be present beneath sinter caps.

Because of the requirement for white (low iron content) kaolins, attention was directed towards acid volcanic rocks in the Coromandel and Northland regions of New Zealand where extensive outcrops of late Tertiary rhyolites and dacites occur.

## THE POLYMORPHS OF KAOLIN

For the purpose of this paper, attention has been paid to the detailed structure of the kaolin polymorphs, halloysite and kaolinite. The morphology, degree of hydration and degree of crystallinity has an important bearing on the suitability of the kaolin for various industrial applications. The type of polymorph may also be used as a sensitive indicator of the conditions of formation.

The polymorphs of kaolin are:

### Typical Morphology

- \*halloysite 10Å - elongate
- \*halloysite 7Å - elongate
- kaolinite - hexagonal plates

\* Kaolin Terminology AIPEA Nomenclature (Brindley & Pedro 1975)

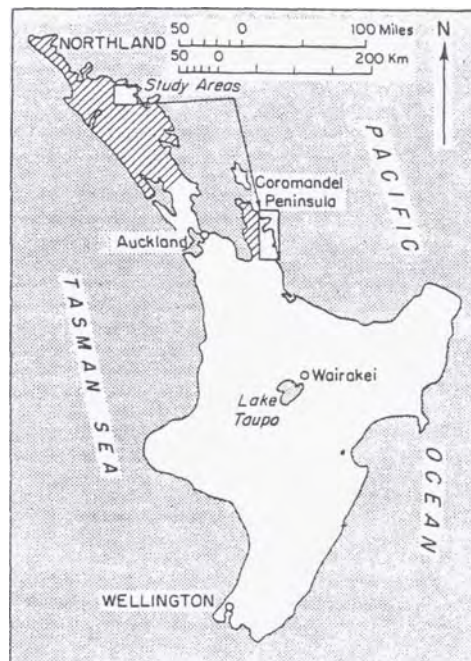


Figure 1: Locality Map - North Island of New Zealand

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The hexagonal platelets of kaolinite are highly favoured for use as a coating clay in paper manufacture because the platelets enhance such properties as viscosity, gloss and opacity. The elongate halloysite morphology is favoured in high quality ceramics because it contributes both strength and translucency to the ceramic body.

In regard to genesis, work by the N.Z. Soil Bureau has shown (Fieldes & Williamson (1955)) that the normal product of weathering in New Zealand is halloysite 10Å while kaolinite is present only as a product of hydrothermal alteration. In Mexico Keller et al (1971) reported halloysite 10Å in association with warm springs at 40°C. Hydrothermal bomb experiments by Churchman and Carr (1972) indicated that the upper limit of stability of halloysite 10Å was 80°C, above which it dehydrated irreversibly to halloysite 7Å. Separate experimental work by Eberl and Hower (1975) showed that at 150°C halloysite converted to kaolinite.

In the present study the presence of halloysite 10Å was considered to indicate weathering or low temperature alteration at less than 80°C. Halloysite 7Å is used as an indicator of temperatures above 80°C. Kaolinite in association with alunite and siliceous sinter is considered evidence for hydrothermal alteration.

#### STAGES IN THE INVESTIGATION

Surface prospecting identified numerous siliceous sinter deposits in Northland and Coromandel and also surface exposures of kaolin clays. Prospecting rights were obtained and core drilling carried out. Detailed laboratory investigation included:

1. Chemical Analysis
2. Particle Size Analysis
3. X-Ray Diffraction
4. Electron Microscopy
5. Oxygen Isotope Analysis

In this paper data are presented for two prospects (Locations see Figure 1).

1. Northland - Hydrothermal alteration and sub tropical weathering of a rhyolite dome.
2. Coromandel - Hydrothermal alteration on the flanks of a rhyolite dome.

#### NORTHLAND

##### Introduction

The Maungaparerua kaolin deposit is an altered rhyolite dome located approximately 230 km north of Auckland (Figure 1). The geological setting of Northland is basement greywacke rocks of Palaeozoic-Mesozoic age overlain by Mesozoic and Tertiary sediments. Volcanic activity during the Miocene was considered by Brothers (1974) to be associated with block faulting related to the development of a subduction zone at the boundary between the Australian and Pacific plates. This Miocene volcanic activity includes the Parahaki Volcanics to which the Maungaparerua rhyolite dome belongs.

The Maungaparerua rhyolite is bounded to the north, south and west by basalts of the Kerikeri Volcanics of Pliocene to Holocene age (Kear and Hay 1961) and to the east by Holocene alluvium.

The climate in the area is subtropical with a mean annual rainfall of 70-80 inches per year (300 cm) and a mean annual temperature of 17-18°C (64°F) (New Zealand Ministry of Works, 1964).

Paleobotanical evidence of Couper and McQueen (1954) and Couper and Harris (1966) has shown that the climate in the northern part of New Zealand has been subtropical since at least the Pliocene, meaning a very active weathering environment in the area of this study, for at least 15 million years.

The relief in the area is generally subdued of under 300 metres elevation with well rounded profiles on the rhyolite and surrounding basalt flows. In places however, marginal to the river system steep cliffs have been formed where areas of altered rhyolite have been eroded away.

##### Surface Prospecting

An initial survey of numerous rhyolite domes in Northland revealed numerous outcrops of siliceous sinter and white kaolin clays. The thickest mantle of alteration products appeared related to rhyolite domes surrounded by later emplaced basalt flows.

Three of these domes were examined in detail. Details of one of these domes, Maungaparerua are presented below. It is considered that the basalt flows have played a significant role in the genesis of these kaolin deposits.

1. Providing a heat source for hydrothermal alteration.
2. Enclosure of the domes by the basalts has raised the local groundwater level and protected the altered rhyolite from erosion.

##### Drilling Programme

A drilling programme was carried out over the Maungaparerua dome based on a 30 metre grid. Data are presented for two boreholes located as shown in Figure 2: Borehole M1 at the centre of the dome and Borehole N11/66 on the margin of the dome.

##### Chemical Data

Major and trace element analysis carried out on the drill cores by Inductively Coupled Plasma Arc Spectrometry (ICP) is reported in Table 1. In Borehole M1 an analysis of the parent rhyolite has been included. It is apparent that there is a progressive increase in the extent of alteration towards the surface from the drilled depth of 40 meters. This is reflected in the progressive decrease in the concentration of alkalis accompanying the alteration of the feldspar in the rhyolite. The increase in hydration with progressive alteration is due to the formation of the hydrated aluminosilicate kaolin minerals. The

Table 1: CHEMICAL DATA - MAUNGAPARERUA BOREHOLES

(a) Major Element Analysis												
Borehole Depth (m) Maungaparerua Ml	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	MgO	H <sub>2</sub> O+	Total
3-6	69.5	21.1	.58	.003	.025	.044	.172	.040	.004	.022	8.52	99.43
9-12	71.1	20.2	.29	.007	.065	.11	.163	.037	.005	.044	7.74	99.47
15-18	71.5	19.8	.35	.016	.248	.515	.159	.036	.003	.040	7.34	99.66
21-24	72.5	17.6	.43	.051	.72	1.20	.156	.037	.005	.026	5.99	98.29
27-30	73.3	17.3	.31	.026	1.02	1.36	.159	.036	.006	.011	5.57	98.79
33-36	73.6	15.7	.33	.17	2.16	3.17	.139	.033	.004	.035	3.39	98.40
39-42	74.3	15.4	.61	.17	2.50	3.67	.147	.067	.005	.030	2.82	99.11
Parent Rhyolite	75.7	12.9	1.34	.36	3.89	4.83	.120	.17	.009	.023	.96	98.96
Borehole N11/66												
3-6	65.8	23.64	.39	.005	.050	.018	.178	.050	.002	.005	9.77	100.0*
9-12	70.7	20.41	.26	.011	.022	.027	.248	.063	.004	.010	8.32	100.0*
15-18	69.7	21.35	.15	.005	.195	.010	.147	.153	.003	.004	8.28	100.0*
21-24	67.9	23.1	.10	.006	.017	.017	.129	.048	.002	.004	8.51	99.8
27-30	73.1	19.5	.35	.006	.039	.066	.175	.040	.002	.007	7.38	100.8
Feldspar Phenocrysts (Hand picked)	66.5	18.72	.14	.43	5.86	8.05	.015	.199	.005	.09	0.00	99.8
*Silica Determined by Difference												

(b) Trace Element Analysis												
Borehole and Depth (m) Maungaparerua Ml	Rb	Ba	Y	Th	V	Sr	Pb	Li				
3-6	2	6	7	43	6	0	14	80				
9-12	6	7	22	35	5	1	16	133				
15-18	11	22	21	36	4	3	13	117				
21-24	29	64	48	40	6	8	22	99				
27-30	44	75	36	35	5	7	32	103				
33-36	185	90	57	37	7	10	26	87				
39-42	255	92	78	37	10	9	45	82				
Parent Rhyolite	299	141	43	29	5	16	34	31				
Borehole N11/66												
3-6	5	52	17	41	12	1	9	13				
9-12	3	15	15	37	10	2	28	15				
15-18	2	11	20	41	10	4	56	19				
21-24	0	14	19	31	7	3	15	17				
27-30	0	10	27	37	10	3	15	14				
Feldspar Phenocrysts (Hand picked)	355	356	14	7	32	43	129	69				

Table 2: OXYGEN ISOTOPE ANALYSIS OF CLAYS

Maungaparerua Data					
Basalt/Rhyolite	Borehole Depth	Size Fraction	$\delta^{18}O$ (‰)		Major Clay Mineral
Contact Zone	N11/66	-1/2 $\mu$ m	14.8	14.8	Kaolinite
	21-24m	2-1/2 $\mu$ m	14.4	14.4	
Contact Alteration Zone	Sample A (0.6m below contact)	-1/2 $\mu$ m	21.1	21.1	Halloysite 7Å
		2-1/2 $\mu$ m	19.8	19.8	
Weathering Profile	Borehole M1 3-6 m	-1/2 $\mu$ m	22.2	22.3	Halloysite 10Å
		2-1/2 $\mu$ m	22.4	22.4	
Previously Published Data					
Weathering	Savin & Epstein (1972)		19 - 23		Kaolins from the weathering environment (Kaolinites and Dickite) (From Hydrothermal Areas)
Hydrothermal	Sheppard et.al. (1969)		6.4 - 14.9		
	Savin & Epstein (1972)		15 - 16		

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progressive increase in alumina and titania with increasing alteration reflects their relative immobility in the system, their increase being proportionate (on a mass balance basis) to the loss of alkalis and silica from the alteration of the feldspar.

Chemical analysis of trace elements Rb, Ba, Sr and Pb in borehole M1 also reflect the alteration of the feldspar (see selected feldspar phenocryst analysis in Table 1).

In contrast, the chemical data from borehole N11/66 shows no decrease in alteration with depth. Both alkalis and trace elements are very low. The variability in the alumina and silica values is possibly related to the mobility of silica in a geothermal environment.

#### Electron Microscopy and X-ray Diffraction

Samples from both of these boreholes were examined by scanning and transmission electron microscopy. The presence of elongates of halloysite were confirmed in the profile of borehole M1 while plates of kaolinite and some elongates were evident in borehole N11/66. X-ray diffraction analysis confirmed halloysite  $10\text{\AA}$  as the dominant clay mineral in borehole M1. X-ray diffraction of the clay mineral fraction from borehole N11/66 showed no evidence of any  $10\text{\AA}$  mineral, the dominant kaolin peak occurring at  $7.128$ .

The relative intensities of the  $7.1251$  and  $4.43\text{\AA}$  peaks indicated that kaolinite was the dominant kaolin polymorph present. However, electron microscopy revealed a mixture of plates and elongates, favouring an interpretation of a mixture of kaolinite and halloysite  $7\text{\AA}$ . The presence of both kaolinite and some elongates in borehole N11/66 indicates that halloysite  $7\text{\AA}$  is derived from the dehydration of halloysite  $10\text{\AA}$  at temperatures exceeding  $80^{\circ}\text{C}$  (Churchman and Carr 1972).

#### Data From Other Boreholes

Approximately 20 bores were drilled over the Maungaparerua Dome and cores were examined by similar analytical techniques (Harvey 1980). Bores drilled close to the centre of the dome showed decreasing alteration with depth and halloysite  $10\text{\AA}$  the dominant kaolin mineral. This is consistent with the data in borehole M1 (Figure 2).

Towards the margin of the dome, intermediate between boreholes N11/66 and M1, borehole N11/50 (Figure 2) showed evidence of some kaolinite down to a depth of 12 meters, below which the borehole contained halloysite  $10\text{\AA}$  and decreasing alteration with increasing depth.

#### Oxygen Isotope Analysis

Samples of the finer than 2 micron fractions of clays from boreholes M1 and N11/66 were analysed for oxygen isotope composition by the technique of Taylor and Epstein (1962). Data are presented in Table 2.

The data confirm a significant difference in the isotopic composition between the clays in the marginal-basalt contact area (N11/66) and those from the centre of the dome (M1). A third sample in the table was taken from a rhyolite-basalt contact zone elsewhere in the study area where halloysite  $7\text{\AA}$  was the dominant kaolin mineral. The data are in good agreement with published data of kaolins from the weathering environment (Savin and Epstein 1970) and hydrothermal clays from the Santa Rita Deposit, New Mexico (Sheppard et al 1969).

These workers showed that the oxygen (and hydrogen) ratios of clay minerals are dependent on the conditions of their formation and exchange. The fractionation factors ( $\alpha$ ) between compounds or phases containing oxygen is related to temperature ( $T$ ) by form  $\ln \alpha \propto \frac{1}{T^2}$  (Faure 1977).

The lower  $\delta^{18}\text{O}$  values from the hydrothermal zone therefore reflect higher temperatures of formation.

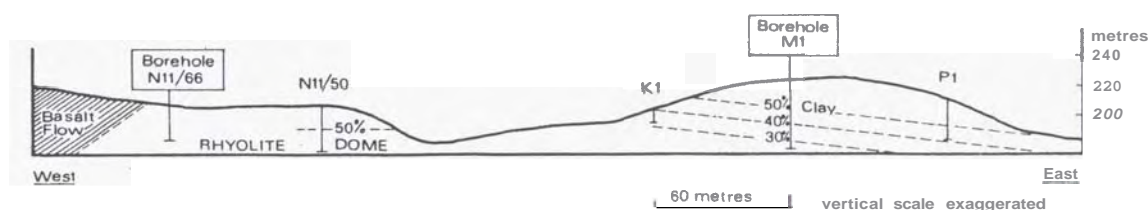


Figure 2: Cross-section across the part of the Maungaparerua Dome.

## Genesis

Interpretation of the genesis of the Maungaparerua deposit has been based on the chemical, mineralogical and oxygen isotope data. In borehole N11/66 at close to the contact between the basalt and the rhyolite hydrothermal alteration has resulted in:

1. The presence of surficial siliceous sinter
2. Intensive alteration to a depth of over 30 metres
3. The presence of halloysite  $^{18}O$  and kaolinite
4. Relatively low  $\delta^{18}O$  values in the clay mineral

In borehole M1 at the centre of the rhyolite dome subtropical weathering is the dominant agent of alteration as evidenced by:

1. Decreasing alteration with increasing depth
2. The presence of halloysite  $^{18}O$
3.  $\delta^{18}O$  values in the clay mineral comparable to kaolins from the weathering environment reported by Savin and Epstein (1970)

The emplacement of the basalt flow is believed to have provided a heat source for the hydrothermal alteration at the margin of the dome.

## COROMANDEL

### Introduction

A series of sinter caps in acid and intermediate Tertiary volcanic rocks were prospected on the east coast of the Coromandel Peninsula (Figure 1). Six prospect areas were drilled. In one prospect pyrophyllite, diasporite and kaolinite (Swindale and Hughes 1968) were associated with the sinter underlain by sulphides. In other prospects the association was confined to kaolinite plus alunite associated with the siliceous sinter, underlain by a zone of pyrites plus smectite (montmorillonite) clay (Harvey 1967). In all prospect areas the kaolinite was of restricted extent and associated with cristobalite and tridymite.

Data are presented of one prospect area at Hahei.

### Surface Prospecting

At Hahei, 5 km south of Whitianga on the east coast of the Coromandel Peninsula outcrops of siliceous sinter were prospected on the flanks of rhyolite domes of Pliocene age.

The surface indications of sinter and kaolinite were investigated by a core drilling programme and laboratory analysis.

### Drilling and Test Data

Drilling through the sinter cap into the alteration zone revealed an assemblage of

kaolinite, alunite, cristobalite, tridymite and minor quartz. At depth smectite and pyrites were encountered. A similar sequence with depth is reported by Steiner (1968) from Wairakei.

The alteration was restricted to a fractured zone or pipe (Figure 3) within low permeability spherulitic rhyolite rock. This fracture zone dipped towards the centre of the dome and possibly fracturing took place during contraction cooling at the time of emplacement of the dome. Healy (1964) reported a similar location of hot springs and hydrothermal activity on the margins of rhyolite domes in the Taupo Volcanic Zone of New Zealand.

X-ray diffraction and particle size analysis showed the clay fraction to be composed of a fine particle size well crystalline kaolinite. However, the limited tonnage and the presence of significant amounts of very fine cristobalite and tridymite (finer than 2 microns) placed severe limitations on the economic value of the deposit.

The alteration mineral assemblage of Hahei is considered to be evidence of hydrothermal alteration.

## OVERALL CONCLUSIONS

1. Prospecting of sinter caps associated with Pliocene volcanics in the Coromandel Peninsula revealed a mineral assemblage of kaolinite and alunite associated with the sinter. It is included that the kaolinite is the product of hydrothermal alteration. The restricted alteration in the Hahei (Coromandel) prospect is in part due to the low permeability of the spherulitic rhyolite host rock. The location of the sinter on the flanks of the domes and the dip angle of the alteration zone towards the centre of the dome is considered as evidence that hydrothermal alteration has taken place along cooling cracks developed on the dome margins during the dome-building phase of the volcanic activity.

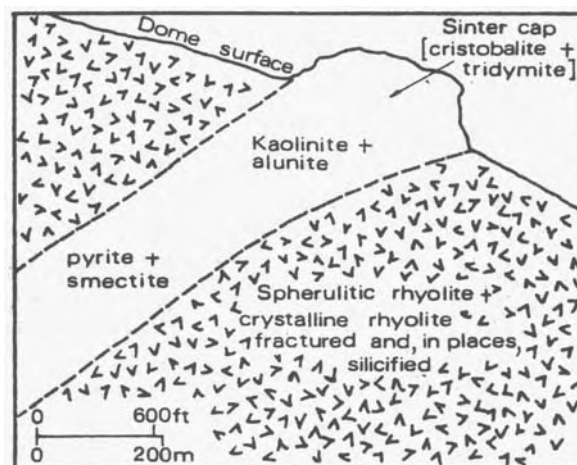


Figure 3: Cross-section through a sinter cap at Hahei Coromandel

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2. Investigation of altered Miocene rhyolite domes in Northland located commercial deposits of kaolin clays which had been formed by a combination of hydrothermal alteration and deep subtropical weathering.

The hydrothermal alteration is considered to be associated with the adjacent more recent basalt flows. The rhyolites may have been partly weathered at the time of emplacement of the basalt which permitted the development of a hydrothermal convection cell of heated meteoric water, within the permeable, partly weathered rhyolite. At Maungaparerua this convection cell was most active at the rhyolite-basalt contact zone in the vicinity of borehole N11/86.

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