

## CLAY MINERALS IN HYDROTHERMALLY ALTERED ROCKS AT WAIRAKEI, NEW ZEALAND\*

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**Abstract**—Geothermal fluid discharged by steam wells, which have been core drilled to depths as much as 4500 ft at Wairakei, New Zealand, has altered Pliocene to Pleistocene, silicic, mainly glassy volcanics and related aqueous tuffs and breccias. Measured temperatures (max. 265°C) indicate epithermal to mesothermal conditions in buried fault fissures, the locus of both the hydrothermal fluid and most intense alteration.

A supergene kaolinite alteration zone is distinguished from hypogene Ca-montmorillonite and combined micaceous and chloritic zones. The hypogene zones are usually wide and are temperature dependent and localized along fault fissures. Other common hypogene minerals are alkali feldspars, wairakite, epidote, quartz, calcite, laumontite, ptilolite, pyrite and pyrrhotite. Prehnite is rare.

The micaceous clay minerals include illite (about 10 Å) and a series of random mixed-layer illite-montmorillonites with  $d(001)$  values ranging from 10.28 to 12.45 Å. The amount of interstratified montmorillonite is related to temperature and fault fissures. Apart from rare mixed-layer swelling chlorite, the Fe-rich chloritic clay shows little or no variation in its composition. Both the micaceous clays and the chloritic clay result from alteration of earlier formed Ca-montmorillonite.

The stability of hydrothermal minerals is controlled by the temperature and chemical composition of the geothermal fluid ascending along the fault fissures. K-feldspar but not albite is deposited on fissure walls, but both alkali feldspars replace primary soda-lime plagioclase in the wall rock. The absence of albite on fissure walls is ascribed to low aqueous  $m\text{Na}^+/m\text{K}^+$  ratio. Primary quartz is not affected by the altering solution but hydrothermal quartz is deposited on fissure walls and in the wall rock.

### INTRODUCTION

THE WAIRAKEI thermal area, situated in the Taupo Volcanic Zone, lies almost in the middle of the North Island of New Zealand (Fig. 1). Exploratory core drilling for geothermal steam, to a maximum depth of 4500 ft, and petrological study of drill cores have revealed economically important information concerning hydrothermal rock alteration and the geothermal fluid†. The fluid discharged by the steam wells is a mixture of steam and hot water with a minor amount of gas. It is used for production of electric power, at present amounting to 140 MW. The measured temperatures, max. 265°C indicate epithermal to mesothermal conditions. No commercial ore deposits are associated with the hydrothermally altered rocks in the explored depth.

The Wairakei geochemical system now is comparatively well defined: because the mineralogical and chemical composition of fresh and

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†The term "geothermal fluid" is synonymous with "hydrothermal fluid" and "hydrothermal solutions".

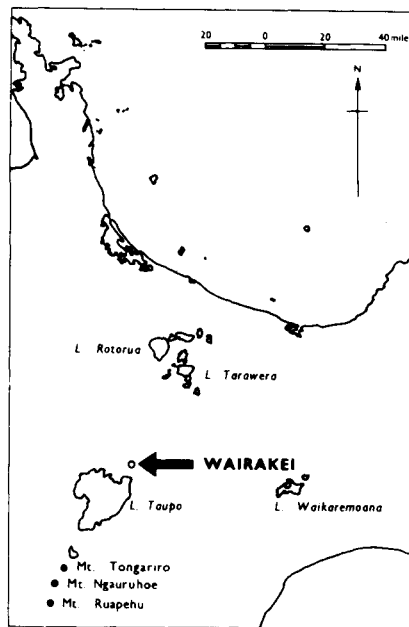


Fig. 1. Map showing a portion of North Island of New Zealand and the location of Wairakei.

altered rocks is known, the chemical composition of the geothermal fluid, tapped in the fault fissures, has been determined, the temperature of the fluid measured, and the prevailing water-vapour and lithostatic pressures, based on specific gravity determinations, have been calculated. These data provide the basis for studying the interaction between the rocks and the geothermal fluid. Moreover, the mineralogical and chemical composition of the fresh rocks is comparatively uniform, and so too is the chemistry of the geothermal fluid in the fissures. Therefore, the alteration products observed at various depths can be correlated readily with measured temperatures. This paper, however, is primarily concerned with hydrothermal clay minerals, and the chemical and physical conditions prevailing during their genesis.

#### PETROLOGY

##### *Stratigraphic sequence and original composition of the rocks*

The sequence of rocks penetrated by two drill-holes 71 and 225, is shown in Figs. 2 and 3. The rocks are mostly silicic volcanics and interbedded lake deposits of Pliocene to Pleistocene Age. The silicic volcanics comprise vitric and pumiceous tuffs, and ignimbrites. When unaltered, the volcanics contain phenocrysts of soda-lime plagioclase and commonly also quartz, sparse hypersthene and hornblende crystals and a little magnetite. Biotite is very rare, and primary K-feldspar is absent. The groundmass, often pumiceous, is glassy, devitrified or cryptocrystalline.

The lake sediments, derived from silicic volcanics, include pumice and rhyolite breccias, and sandy and silty tuffs. They usually contain a great portion of glassy material and varying amounts of detrital andesine and quartz, and occasionally ferromagnesian minerals.

In addition, andesite (Fig. 2) occurs locally at depth in the Wairakei area. Comparatively large phenocrysts of andesine, and relatively minute crystals of pyroxene and hornblende are common in fresh andesite. The hyalopilitic groundmass contains abundant minute granules of magnetite.

##### *Permeability, specific gravity and pressures*

Except for some minor silty, densely packed tuffs, both the silicic volcanics and the largely pumiceous lake sediments are relatively permeable, particularly when brecciated or fractured. In comparison, the andesite is a dense, little-fractured rock of low permeability. The average specific gravity, determined on 50 samples, representative of the penetrated rocks, is 2.06.

The variation of lithostatic and water-vapour pressures, and temperature with depth, is shown

in Figs. 2 and 3. For example, the lithostatic pressure prevailing at 4000 ft, as calculated from the average specific gravity, 2.06, amounts to about 240 bars. The water-vapour pressure at 265°C is approximately 49 bars.

##### *Fault fissures*

Slickensided, sheared and fissured cores have been recovered from numerous drillholes (Figs. 2 and 3). These cores and others with incrustations of hydrothermal K-feldspar, quartz and wairakite, and vugs lined with these minerals, as well as cavernous ground found by drilling in fissured zones indicate that fault fissures provide channels for the ascending geothermal fluid.

#### HYDROTHERMAL ROCK ALTERATION

The order of susceptibility for primary rock-forming minerals and volcanic glass to hydrothermal alteration with increasing temperature is volcanic glass, magnetite, hypersthene, hornblende, plagioclase, and biotite. Quartz remains unaffected by the solutions.

Hydrothermal alteration mineralogy is essentially uniform throughout the area explored. Hypogene alteration has converted primary soda-lime plagioclase into a variety of hydrothermal minerals including montmorillonite, micaceous clays, calcite, wairakite, albite, K-feldspar, quartz and epidote. The ferromagnesian minerals are altered to chlorite, micaceous clays, quartz, calcite, epidote, apatite, and pyrite; the groundmass to montmorillonite, micaceous clays, chloritic clay, calcite, wairakite, epidote, K-feldspar and quartz. Rock interstices may be filled with ptilolite, laumontite, wairakite, calcite and/or quartz. Pyrite and pyrrhotite are commonly disseminated, sometimes forming thin veinlets. Occasionally pyritization is associated with faults intersected by the drillholes at shallow depths, between about 600–700 ft. H<sub>2</sub>S sometimes escapes along these faults on the surface. Supergene alteration, developed only locally at and near the surface (Steiner, 1953) produces kaolinite, alunite and opal from primary plagioclase and ferromagnesian minerals, and groundmass.

#### ZONAL PATTERN

Zoning is a characteristic feature of hydrothermal rock alteration at Wairakei, and is shown both by the clay and non-argillaceous hydrothermal minerals. The zonal pattern shown in Figs. 2 and 3 is closely related to fault fissures and temperature, each zone being defined by the first and last appearance of its index minerals. Figures 2 and 3 distinguish whether a particular hydrothermal mineral is an alteration product of plagioclase or

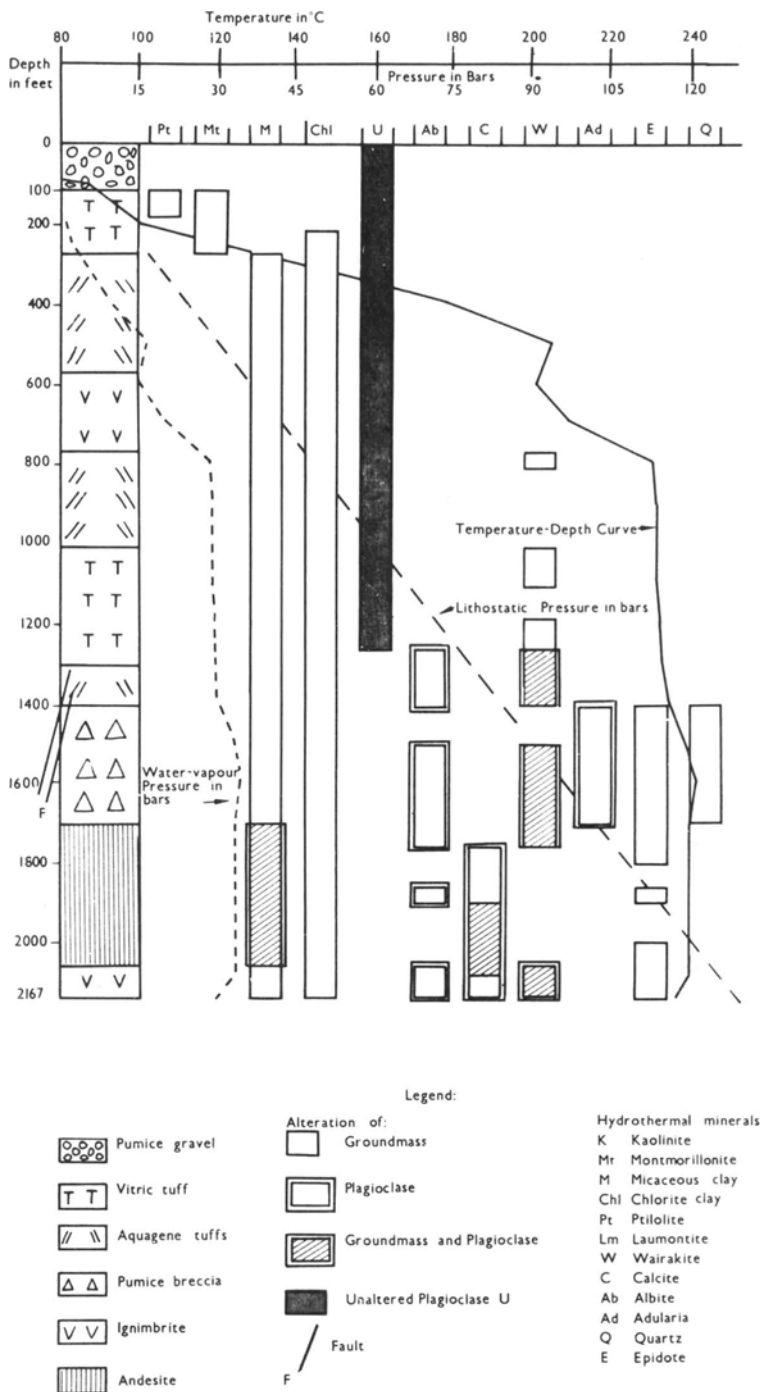


Fig. 2. Diagrammatic compilation of data obtained in Wairakei drillhole 71 showing stratigraphic sequence, faults, fresh rock, hydrothermal mineral distribution, temperature variations, and lithostatic and water-vapour pressures.

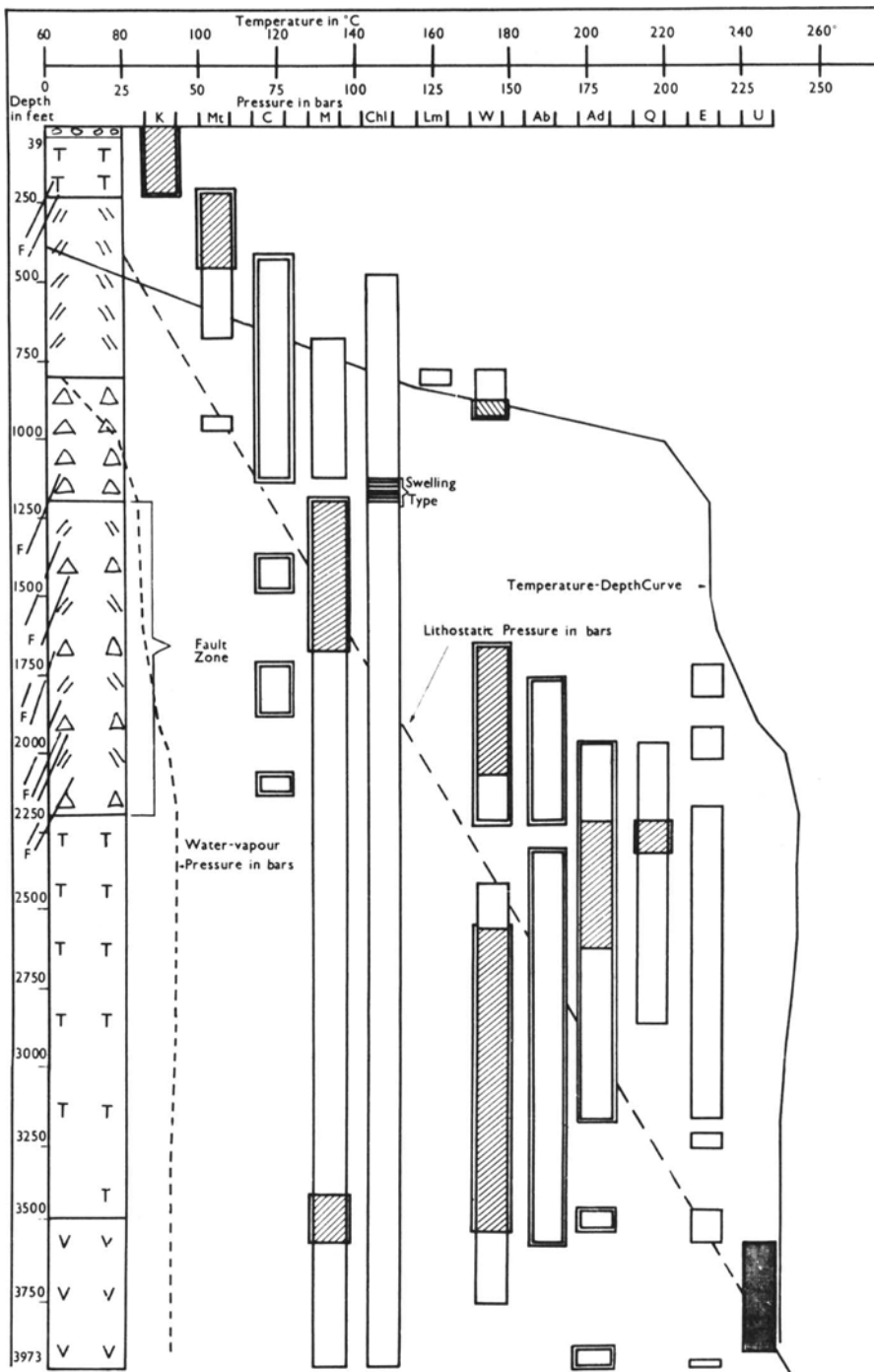


Fig. 3. Diagrammatic compilation of data obtained in Wairakei drillhole 225 showing stratigraphic sequence, faults, fresh rock, hydrothermal mineral distribution, temperature variations, and lithostatic and water-vapour pressures.

groundmass or both. Because of the scarcity of ferromagnesian minerals in the silicic rocks their alteration products are not important and, therefore, have been omitted in Figs. 2 and 3.

Micaceous clay minerals and chloritic clay are the most common clay minerals at Wairakei. With increasing temperature, the argillaceous zones comprise a near-surface kaolinite zone (K); followed by a montmorillonite zone (Mt); and a combined micaceous (M) and chloritic zone (Ch), extending over a wide temperature and pressure range. Thus, the clay minerals are ubiquitous alteration products, although commonly they occur in association with non-argillaceous hydrothermal minerals.

The non-argillaceous zones with increasing temperature are: (i) ptilolite (Pt) and laumontite (Lm); (ii) wairakite (W) and albite (Ab); and (iii) K-feldspar (Ad) zone. The montmorillonite zone commonly overlaps the ptilolite and laumontite zone, and the micaceous-chloritic zone is usually superimposed on the wairakite, albite and K-feldspar zones, which themselves also overlap. No kaolinite zone is present in drillhole 71 at and near the surface, where unaltered rock occurs.

In addition, the diagrams (Figs. 2 and 3) show the distribution of calcite (C) and epidote (E) and the zone of intense silicification (Q) as well as the vertical range through which the primary plagioclase remains unaltered (U). It can be seen that (a) the zone of intense silicification coincides approximately with the K-feldspar zone, and (b) epidote forms in about the same temperature range as albite. The absence of unaltered plagioclase at shallow depth in drillhole 225 contrasts with its presence at comparable depth in drillhole 71. The persistence of unaltered plagioclase in drillhole 71 to about 1275 ft seems to be due to the presence of a comparatively narrow fault fissure and to restricted flow of hot water at relatively lower levels in this drillhole as compared with the wide fissured zone at relatively shallow depth in drillhole 225. The presence of unaltered plagioclase at the bottom of drillhole 225 appears to be due to a slight temperature fall off below the fault fissure (Fig. 3).

Evidence from these and other Wairakei drill-holes suggests that the symmetrical arrangement of hydrothermal alteration products of plagioclase about the K-feldspar zone and the productive fissure, respectively, is a common feature, even at depth. For example, montmorillonite and laumontite occur at 4020 ft in a zone grading to almost unaltered rock at a distance of approximately 2500 ft below the productive fault fissure.

Pervasively wide alteration zones in altered pumiceous rocks seem to depend on the width and

openness of the fault fissures carrying geothermal fluid, as well as on the permeability of the wall rocks.

## CLAY MINERALS

### *Methods used for identification*

X-ray diffraction of air-dried and glycolated samples and petrographic examination were used for identification of the clay minerals. These techniques were occasionally supplemented by heat treatment and infrared absorption spectra. Usually, oriented aggregates on glass slides were prepared, though unoriented samples were sometimes used to obtain the 060 reflection. The X-ray data were obtained on a Philip X-ray diffractometer with  $\text{CuK}\alpha$  radiation and scanning speed  $1^\circ/\text{min}$ .

The identification of clay minerals was greatly facilitated by the fact that at Wairakei only two clay minerals occur together in most hydrothermally altered rocks. However, monomineralic samples were sometimes obtained. The presence of three clay minerals in altered rocks at Wairakei is rare. Because of the relatively small size of plagioclase phenocrysts, no attempt has been made to separate the clay formed by alteration of plagioclase from that produced by conversion of glass.

Chloritic clay has commonly been separated from material scraped out of altered pumiceous lapilli and pumice fragments for optical, X-ray diffraction and chemical studies. Sometimes, when the pumice was minute, it was necessary to powder the whole rock including ferromagnesian minerals. The separation was done by repeated sedimentation. No difference in optical properties and X-ray diffraction data has been noted between chloritic clays obtained by the two methods. Thus, little or no difference is apparent between chlorite produced by alteration of pumice and that produced by alteration of ferromagnesian minerals.

### *Kaolinite*

Only supergene kaolinite has been found. Occasionally, it occurs in crystals of vermicular habit with average  $N_x = 1.560 \pm 0.002$  and  $N_z = 1.568 \pm 0.002$ . Six air-dried samples from drillhole 225 between 120 and 225 ft gave three basal diffraction peaks with periodicity  $7.19 \text{ \AA}$ , their average values being  $7.19 \text{ \AA}$ ,  $3.59 \text{ \AA}$ , and  $2.38 \text{ \AA}$ . Heating of the sample from 215 to 225 ft to  $550^\circ\text{C}$  destroyed the diffraction pattern.

### *Ca-montmorillonite*

Montmorillonite usually occurs at shallow depth. Occasionally, however, it has also been found at greater depth, below fault fissures, where an inversion of temperature has been observed. Thus



montmorillonite is a low-temperature mineral. It is derived mainly from pumiceous volcanic glass and sometimes from plagioclase.

In hand specimen, pumice altered to montmorillonite is commonly dark olive-green. Under the microscope the colourless to dark green clay particles, appear to be oriented parallel to the elongated, drawn-out pumice vesicles. This is indicated by their aggregate extinction. In average  $N_x = 1.534 \pm 0.002$  and  $N_z = 1.568 \pm 0.002$ . The refractive index  $N_x$  changes in clove oil, first being lower and then higher than clove oil. If large enough, the montmorillonite flakes change relief on rotation, though in the opposite way to micaceous clays. The relief is higher when the length of the flakes is at right angles to the vibration direction of the lower nicol.

The 001 spacing of 16 air-dried samples ranges from 14.97 to 15.78 Å, and on treatment with ethylene glycol from 16.99 to 17.32 Å. The first order basal spacing at about 15 Å and its increase by approximately 2 Å indicates Ca-montmorillonite.

#### Micaceous clay minerals

*Illite and randomly interstratified illite-montmorillonite.* The term "illite" is here used in agreement with Bradley and Grim (in Brown, 1961, p. 225) for micaceous clay minerals showing little departure from 10 Å integral series. Thus, micaceous clay minerals with  $d(001)$  between 9.93 and 10.16 Å are in this study termed illites. The X-ray diffraction study has revealed that a series of micaceous clay minerals exists between illite,  $d(100)$  about 10 Å (Fig. 4, AA' and BB') on one end of the series and randomly interstratified illite-montmorillonite,  $d(001) = 12.45$  Å, on the other end of the series. Between these two end members

occurs a range of randomly interstratified illite-montmorillonites with  $d(001)$  between 10.28 and 11.94 Å (Fig. 4, CC'-GG').

Illite,  $D(001)$  about 10 Å, gives an integral series of basal spacings up to 004 (Fig. 4, AA' and BB'). It is not modified by ethylene glycol or by heating for 1 hr at 500°C. The peaks at 2.94 and 3.08 Å, obtained from unoriented samples, suggest the 1 M polymorph. On the other hand, the micaceous clays with  $d(001)$  ranging from 10.28 to 12.45 Å give a non-integral series of basal diffraction peaks, which are sensitive to treatment by ethylene glycol. In particular, the spacing of the first order basal peak invariably increases on glycolation, though the increase varies considerably. However, this increase in spacing indicates the presence of interstratified, expandable layers. Further, the 001 peak shifts on heating to a value between 9.93 and 10.16 Å. This suggests that mica layers are also present. Therefore, the micaceous clays with  $d(001) > 10.16$  Å are classified as randomly interstratified illite-montmorillonites. The 060 spacing of both illite and randomly interstratified illite-montmorillonites lies at 1.49-1.50 Å, indicating that the micaceous clay minerals are dioctahedral.

The  $d(001)$  values commonly obtained from air-dried and glycolated samples of illite, and mixed-layer illite-montmorillonites, are listed in Table 1. The corresponding amounts of interstratified montmorillonite layers are also given. The amount of expandable layers has been estimated using the curve of Weaver (1956, Fig. 2). Table 1 shows that the maximum amount of interstratified montmorillonite layers is greater than 40 per cent. A comparison with the theoretical curve for random mixtures of 10-17.7 Å computed by Brown and

Fig. 4. X-ray diffractograms of the most common clay minerals from various drillholes at Wairakei. Samples A to G are air-dried, and A' to G' are glycolated. CuK $\alpha$  radiation. Samples AA' and BB' are illites, I, (10.04 and 10.16 Å respectively); C-G and C'-G' are random mixed-layer illite-montmorillonites, I-M, with  $d(001)$  values from 10.28 to 11.94 Å; AA', BB', CC', DD', and GG' contain intermixed chloritic clay, Ch; HH' is a long spacing, random mixed-layer illite-montmorillonite; EE', FF', and HH' are monomineralic clays. Other phases present include quartz, Q, calcite, C, albite, Ab, and plagioclase, Pl.

Sample	Drillhole	Depth (ft)
A	226	2850-2855
B	225	1456-1461
C	221	3402-3405
D	226	1650-1653
E	225	855-858
F	71	1398-1400
G	71	450-455
H	225	1050-1055

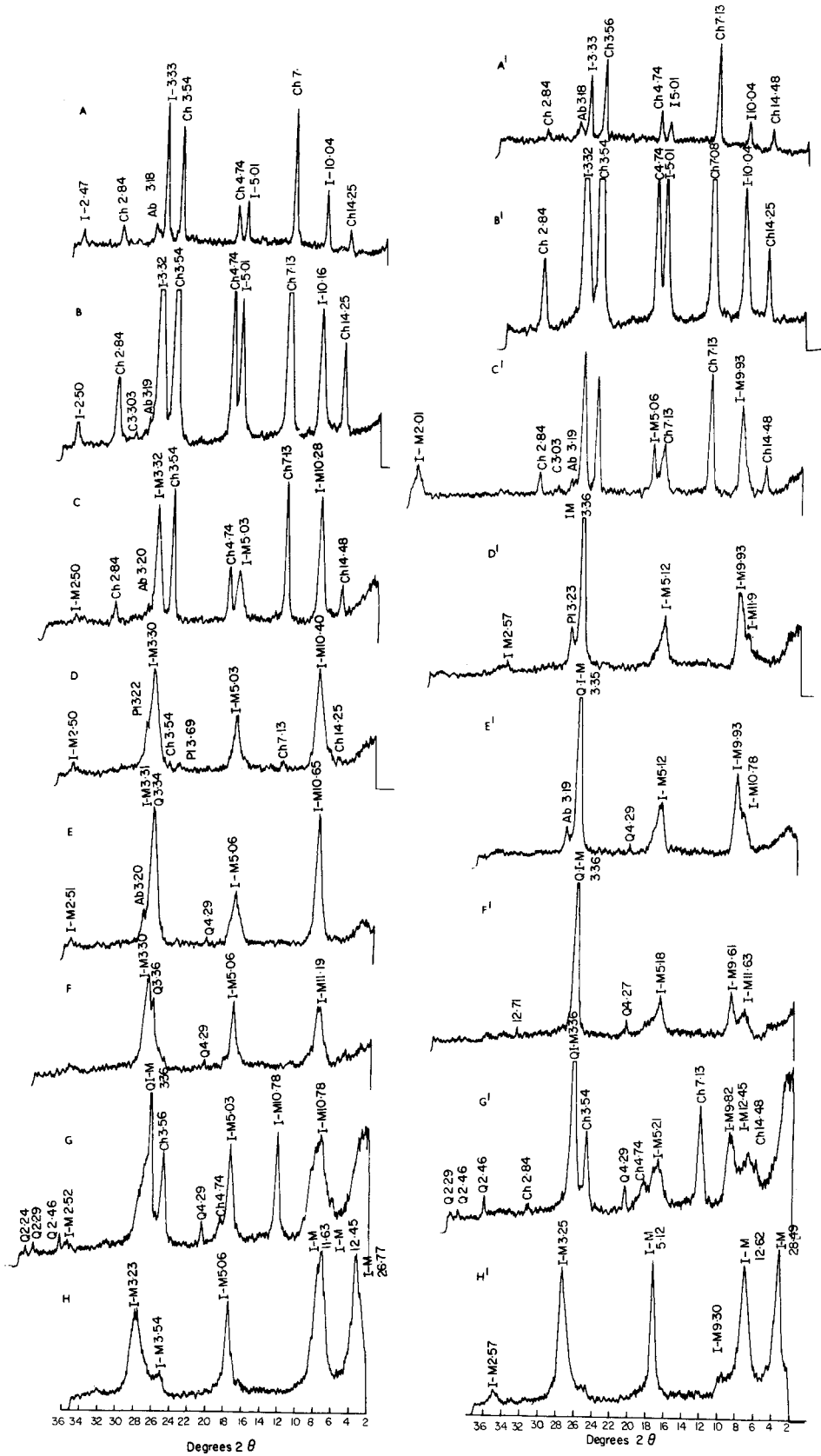


Table 1. Estimated proportions of interstratified montmorillonite in commonly observed micaceous clay minerals ranging from pure illite to randomly interstratified illite-montmorillonite with  $d(001) = 12.45 \text{ \AA}$

$d(001)$ (Å)		Amount of interstratified montmorillonite layers (%)
Air-dried	Glycolated	
12.45	14.97	> 40
11.78	13.60	< 35
11.63	13.39	> 30
11.33	13.19	> 30
11.05	12.98	30
11.19	12.77	< 30
10.91	11.94	25
10.78	11.33	> 20
10.52	11.19	20
10.40	10.91	< 20
10.40	10.65	> 15
10.28	10.16	< 10
10.16	10.16	0 or < 10
10.16	10.04	0 or < 10
10.16	9.93	0
10.04	10.04	0
9.93	9.93	0

MacEwan (1950) also suggests that the expandable layers do not exceed about 45 per cent. Diffractograms of eight typical air-dried and glycolated micaceous clay minerals whose  $d(001)$  varies from 10.04 to 12.45 Å are shown in Fig. 4.

The first order basal peaks of random mixed-layer illite-montmorillonites containing a marked amount of expandable layers are broad, asymmetric (Fig. 4, F-H), and thus differ conspicuously from the sharp 10 Å reflection of illite (Fig. 4, A). On glycolation, the (001) peak is either shifted towards the low angle side (Fig. 4, C') or splits into two peaks (Fig. 4, D'-G'), depending on the amount of interlayered montmorillonite. Sometimes, the 001, 002 and 003 peaks are doublets, suggesting the presence of two randomly interstratified illite-montmorillonites with somewhat different content of interlayered, expandable material. The existence of samples containing both montmorillonite and randomly interstratified illite-montmorillonite with a considerable amount of interlayered montmorillonite may be of genetic significance.

*Long spacing, random mixed-layer illite-montmorillonites.* Some mixed-layer illite-montmorillonites, particularly those occurring at no great distance below the montmorillonite zone, show a long spacing with  $d(001)$  varying between 25.24 Å and 26.77 Å when air-dried and between 27.60 Å and 29.44 Å on glycolation. These  $d(001)$  values indicate an interstratification of illite (10 Å) and Ca-montmorillonite (15 Å). The 001 reflections

of the long spacing, interstratified illite-montmorillonites give essentially a non-integral series but sometimes they exhibit a tendency to regularity. This can be seen on the monomineralic sample of the long spacing, mixed-layer illite-montmorillonite from drillhole 225 at 1050-1055 ft (Table 2). The long spacing, about 25 Å, together with the tendency to regularity indicates that the amount of interlayered montmorillonite approaches 50 per cent, probably not greatly exceeding 45 per cent.

Table 2. Observed and calculated spacing of 00l peaks of monomineralic, air-dried and glycolated interstratified illite-montmorillonite, which shows a marked tendency toward regularity. Drillhole 225, 1050-1055 ft

00l	Air-dried		Glycolated	
	$d(\text{Å})$			
	Obs.	Calc.	Obs.	Calc.
001	26.77	—	28.49	—
002	12.45	24.90	12.62	25.24
003	—	—	9.30	27.90
005	5.06	25.30	5.12	25.60
007	3.54	24.78	3.60	25.20
008	3.23	25.84	3.25	26.00
009	2.86	25.74	—	—
00,10	2.79	27.90	—	—
00,11	—	—	2.57	28.27

The long spacing of air-dried samples at 25.24-26.77 Å should not be confused with the broad, variable peak at about 30-33 Å, which Bradley, according to Weaver (1956) considers to be a statistical maximum. This maximum can sometimes be observed on random mixed-layer illite-montmorillonites, including those showing a long spacing at 25.24-26.77 Å. In contrast with the diffraction peak at 25.24-26.77 Å, the statistical maximum is not affected by glycolation.

*Spatial distribution and frequency of  $d(001)$  values.* As shown in Figs. 5 and 6 the  $d(001)$  value of micaceous clay minerals, ranging from illite (10 Å) to mixed-layer illite-montmorillonite (max. 12.45 Å) tends to decrease primarily with (i) increasing distance from the montmorillonite zone and (ii) increasing temperature towards the fault fissure. The spacing seems also to decrease with depth, but this is of only secondary importance. High  $d(001)$  values, indicating the presence of up to 45 per cent interlayered montmorillonite, commonly occur below the montmorillonite zone and are restricted mostly to the hanging wall of fault fissures (Figs. 5 and 6). Low  $d(001)$  values



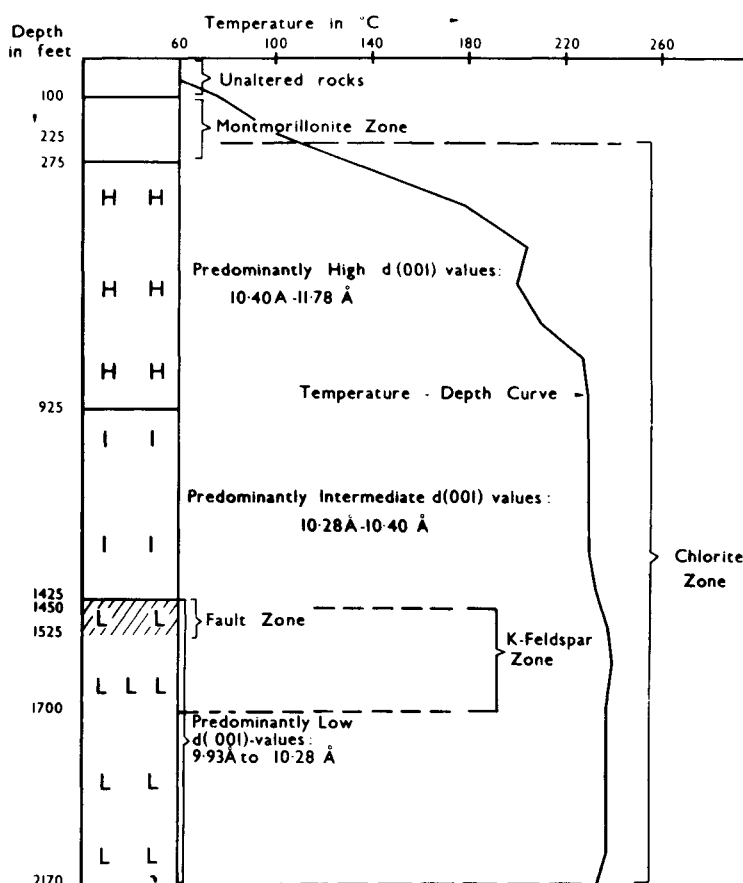


Fig. 5. Distribution of  $d(001)$  values of illite and random mixed-layer illite-montmorillonites in relation to the montmorillonite zone, fault fissure, and temperature. Wairakei drillhole 71. H, I, and L denote predominantly high, intermediate, and low  $d(001)$  values respectively.

predominate in fault fissures and in their footwall. Intermediate values (Fig. 5) occur in the vertical range between the low and high values, and are restricted to the hanging wall. In addition, the frequency of the  $d(001)$  values, as well as their distribution in relation to temperature, are given in Tables 3 and 4. The distribution of the  $d(001)$  values makes it possible to subdivide the micaceous zone into two or three subzones. It should be also noted that micaceous clay minerals, with low  $d(001)$  values and enriched in potassium, and K-feldspar are found together in and near fault fissures.

*Optical data.* The grain size of the micaceous clay minerals is commonly  $< 2 \mu$ , but occasionally they occur in comparatively large scales, forming spherulites and axiolites that can be examined optically. The maximum length of the scales is about  $18 \mu$ , and their maximum thickness does not

exceed  $2 \mu$ . The scales are length slow, and on rotation change relief like muscovite. The refractive indices of the micaceous clay minerals vary with the amount of interstratified montmorillonite. The variation of  $N_z$  can be seen in Table 5. Four coarsely grained micaceous clays with  $d(001) = 10.16 \text{ \AA}$  have in average  $N_x = 1.538 \pm 0.001$  and  $N_z = 1.573 \pm 0.002$ . The birefringence  $N_z - N_x = 0.035$ .

*Chemical data.* The chemical analysis of a mixed-layer illite-montmorillonite in Table 5a indicates a comparatively high content of  $K_2O$  (5.2 per cent), suggesting a micaceous clay, and the notable amount of  $CaO$  (1.8 per cent) points to the presence of interstratified Ca-montmorillonite. X-ray diffraction data indicate that the amount of interstratified montmorillonite layers exceeds 20 per cent.

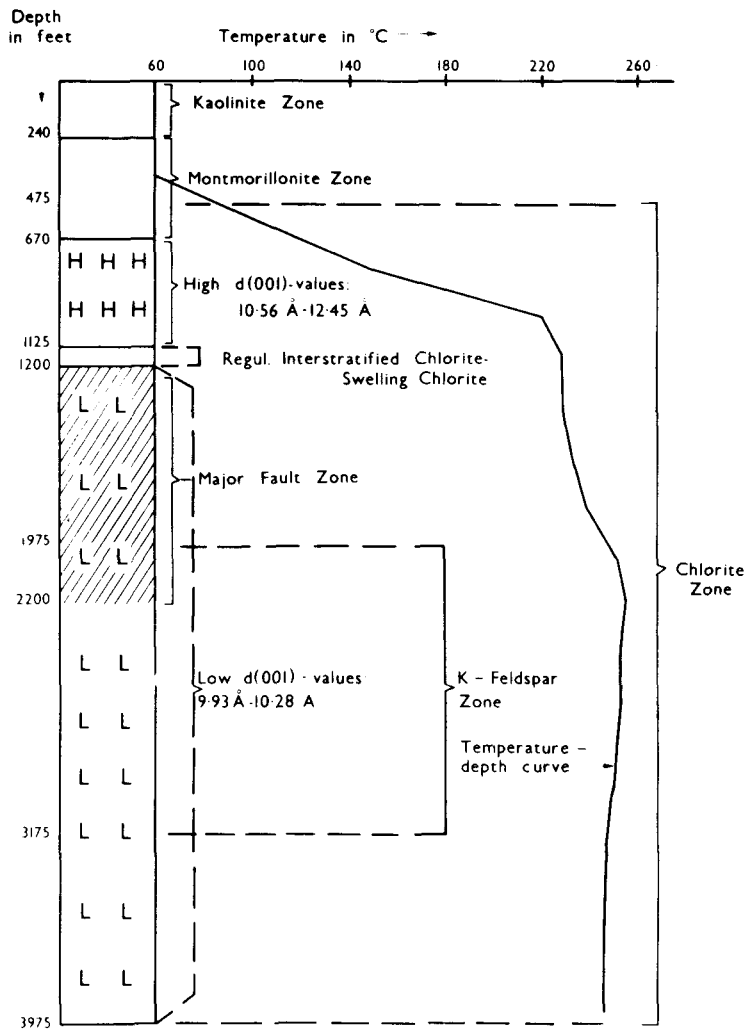


Fig. 6. Distribution of  $d(001)$  values of illite and random mixed-layer illite-montmorillonites in relation to the montmorillonite zone, fault fissure, and temperature. Wairakei drillhole 225. H and L denote high and low  $d(001)$  values respectively.

*Occurrence of hydrothermal mixed-layer illite-montmorillonites in other areas.* Mixed-layer illite-montmorillonite minerals appear to be common alteration products in hydrothermally altered silicate rocks. Apart from Wairakei, they have also been reported in hydrothermally altered cores recovered from drillholes in the thermal area at Steamboat Springs, Nevada (Sigvaldson and White, 1961, 1962 and Schoen and White 1965). Moreover, mixed-layer illite-montmorillonite minerals are common in many alteration zones surrounding hydrothermal ore deposits (Grim, 1953, p. 325; Tooker, 1955, 1963; Bundy,

1958; Sudo 1959, 1963; Bonorino 1959; Sudo, Hayashi and Shimoda, 1962; Harvey and Vitaliano, 1964).

In addition, Bundy (1958) also reported the presence of gradational sequences from montmorillonite through mixed-layer illite-montmorillonite to illite in hydrothermally altered igneous rocks from the Cochiti Mining District, New Mexico. But, he does not mention any limitation in the amount of interstratified montmorillonite. Sudo *et al.* (1962) described regularly and randomly interstratified hydrous micas from the Tsutsumi-zawa epithermal ore deposit in Japan. The ratio

Table 3. Distribution, frequency of occurrence of  $d(001)$  values, and temperature ranges of interstratified illite-montmorillonites in Wairakei drillhole 71

Depth (ft)	Total number of samples	$d(001)$ values			Temperature range (°C)
		Range (Å)	Frequency (%)	Predominantly	
300-900	10	10.40-11.48 10.04-10.16	70 30	High	130-230
950-1400	11	10.28-10.40 10.16 10.78 10.91-11.19	72.8 9.1 9.1 9.1	Intermediate	
1450-1955	11	10.16-10.28 10.40 10.52	72.8 18.2 9.1	Low	> 230

Table 4. Distribution, frequency of occurrence of  $d(001)$  values, and temperature ranges of interstratified illite-montmorillonites in Wairakei drillhole 225

Depth (ft)	Total number of samples	$d(001)$ values			Temperature range (°C)
		Range Å	Frequency (%)	Predominantly	
680-1100	7	10.56-12.45	100	High	120-230
1255-3900	33	10.16-10.28 9.93-10.04	75.7 24.2	Low	> 230

Table 5. Variation of the average refractive index  $N_z$  of micaceous clays with the basal spacing  $d(001)$ 

$d(001)$ Å	$N_z$
10.16-10.40	1.574 ± 0.001
10.52-10.91	1.570 ± 0.002
11.05-11.68	1.556 ± 0.002
12.10-12.45	1.548 ± 0.003

of the 10 Å and 15 Å layers in their randomly interstratified hydrous micas is about 70:30-80:20. Further, their regularly interstratified hydrous micas indicate that the amount of expandable layers does not exceed 50 per cent. Schoen and White (1965) have noted, similar to Wairakei, a limitation in interstratified montmorillonite layers to about 45 per cent in hydrothermally altered drill cores from Steamboat Springs, Nevada.

#### Chloritic clays

Two types of chloritic clays have been observed: iron-rich chlorite is a common alteration product whereas mixed-layer swelling chlorite has been found only in strongly sheared breccia in drillhole 225 at 1150-1155 ft.

*Fe-rich chlorite.* Pumiceous, silicic glass is the main source of iron-rich chloritic clay which occurs also, though in lesser amounts, as an alteration product of hypersthene and hornblende. Micaceous clay and finely grained quartz are commonly intergrown with the chlorite but the amount of the micaceous clay mineral usually predominates. Because of intimate intergrowth of chlorite and micaceous clay and quartz, complete separation was not achieved, as seen in Fig. 4 (AA'-DD' and GG').

*Optical data.* Under the microscope the Fe-rich chloritic clay is light to dark green; its grain size is usually less than 2 μ. Occasionally it occurs in minute scales forming spherulites. The scales, sometimes slightly pleochroic from yellow green

Table 5a. Chemical analyses of clay minerals

Oxides	Mixed-layer illite-montmorillonite (Drillhole 212, 1050 -1055 ft)	Chloritic clay (Drillhole 45 at 2338 ft) See also Table 7, Sample No. 1
	(%)	(%)
SiO <sub>2</sub>	50.9	37.7
Al <sub>2</sub> O <sub>3</sub>	30.2	21.0
Fe <sub>2</sub> O <sub>3</sub>	1.1	1.85
FeO	—*	19.6
MgO	0.05	5.8
CaO	1.8	0.9
Na <sub>2</sub> O	1.0	0.95
K <sub>2</sub> O	5.2	2.5
MnO	0.02	0.77
TiO <sub>2</sub>	0.64	0.06
Li <sub>2</sub> O	0.05	0.04
P <sub>2</sub> O <sub>5</sub>	0.16	0.17
H <sub>2</sub> O+	—	8.7
H <sub>2</sub> O—	—	0.2
Loss on ignition	8.8	—
Total	99.92	100.24

\*FeO not determined, sample too small.

to green, are up to 6  $\mu$  long and 2  $\mu$  wide. Because of the minute grain size, and intergrowth with micaceous clay, only  $N_z$  has usually been determined. The average  $N_z$  determined on eighteen samples is  $1.639 \pm 0.003$ . Two samples gave average  $N_x = 1.633 \pm 0.002$ , and  $N_z = 1.638 \pm 0.002$ . The birefringence  $N_z - N_x = 0.005$ .

*X-ray diffraction data.* The air-dried, Fe-rich chloritic clays obtained from altered pumiceous glass give an (00 $l$ ) series of reflections, usually five, which are an integral sequence of 14.21 Å. The spacings of the basal reflections are not affected by glycolation, and heating at 550°C modifies only slightly the intensities of the basal reflections. These clays have been, therefore, identified as chlorites. Their 060 reflection at 1.536 Å indicates a trioctahedral mineral.

With the exception of the 001 reflection, the spacings of the (00 $l$ ) reflections of the iron-rich chloritic clays vary little. The range, and average spacings of (00 $l$ ) reflections, and average intensities of 31 samples from various depths in drill hole 71 are listed in Table 6. The average first order spacing of 14.48 Å is somewhat higher than the value 14.21 Å, calculated from the lower order spacings. It is also higher than the values obtained by various workers (Brindley in Brown 1961, Fig. VI, 7, p. 270) and higher than the values of

Table 6. Range of 001 spacings and average intensity value for 31 chlorite samples from varying depths in drillhole 71

00 $l$	$d$ (Å)			Average intensity
	Range	Average	Calculated	
001	14.02-14.73	14.48	—	15
002	7.08-7.19	7.13	14.26	100
003	4.69-4.77	4.74	14.22	25
004	3.53-3.59	3.54	14.16	65
005	2.82-2.85	2.84	14.20	8
		<i>Mean</i>	14.21	

Albee (1962, Fig. 5, p. 867). The excessive value 14.48 Å appears to be due to instrumental error in the low angle region. To check the accuracy of the calculated mean value 14.21 Å, the spacing of the 005 reflection has been measured in relation to the spacing 2.458 Å of quartz, used as an internal standard. The value 2.84 Å so obtained confirms the accuracy of the 001 spacing at 14.21 Å.

The chloritic clays shown in Table 6 are Fe-rich. The even order diffraction peaks are strong (Fig. 4, AA'-CC' and GG'), a characteristic of iron chlorite (Brindley in Brown, 1961, p. 265). Since the strong  $d(002)$  and  $d(004)$  reflection of the chloritic clay (7.13 Å and 3.54 Å respectively) overlap the first order (7.16 Å) and the second order reflections of kaolinite (3.57 Å), the possibility of kaolinite being admixed with the chloritic clay has been specially examined. The absence of kaolinite is indicated by the invariable absence of the peak at 2.38 Å due to the 003 reflection of kaolinite. Further, the 060 reflection at 1.536 Å is characteristic of chlorites. No reflection at 1.49 Å indicating kaolinite, has been recorded. Finally, the absorption band at  $3698 \pm 2$  cm<sup>-1</sup> in the infrared absorption spectra, characteristic of kaolinite, is absent. This band appears even if a few weight per cent of kaolinite are present in the total amount of a mixture of clay minerals (Kodama and Oinuma, 1963). However, when considering the geochemical environment prevailing at the explored depth at Wairakei, it seems unlikely that chloritic clay and kaolinite would form contemporaneously.

*Chemical data.* The full chemical analysis of one Fe-rich chloritic clay from drillhole 45 at 2238 ft is given in Table 5a, and partial results of the same analysis are also shown in Table 7 (Sample No. 1). This sample has been obtained from an ignimbrite containing numerous pumiceous lenticules. The X-ray diffractogram of the analysed sample indicates the presence of small amounts of quartz and illite. These impurities account for

the comparatively high amounts of silica and potash, shown by the analysis. However, the chemical analysis confirms the results of the X-ray diffraction study, indicating that the chloritic clay derived from alteration of pumice, is an iron rich variety.

Prior to the separation of chloritic clay, a portion of the material scraped out of altered pumice lenticules (drillhole 45 at 2238 ft) was analysed for FeO (Sample No. 2, Table 7). After separating the clay fraction from a split sample of the whole rock, the remaining coarse fraction was also analysed for FeO (No. 3, Table 7). For comparison, the amounts FeO, Fe<sub>2</sub>O<sub>3</sub> and MgO obtained by

a complete analysis of the core from drillhole 223, at 4300–4303 ft, are also listed in Table 7 (Sample No. 4). This rock is an ignimbrite similar to and altered comparably to the ignimbrite from which the chloritic clay (Sample No. 1) was obtained. Finally, in Table 7 are given the amounts of FeO, Fe<sub>2</sub>O<sub>3</sub> and MgO found in another similar ignimbrite (drillhole 37, 3090 ft) in which however, only a small amount of chloritic clay is present (Sample No. 5).

*Mixed-layer swelling chlorite.* Long spacing, regular mixed-layer swelling chlorite has been noted only in the strongly sheared breccia at 1150–1155 ft in drillhole 225. Its X-ray diffraction data, obtained on examining monomineralic, air-dried and glycolated samples, as well as samples heated for 1 hr at 520°C, 600°C, 620°C and 750°C, are listed in Table 8.

The calculated mean spacing of  $d(001) = 29.42 \text{ \AA}$  suggests an alternation of 14.2 Å and 15.3 Å layers while the integral series of eleven orders is characteristic of highly regular alternation. The spacing at 1.537 Å, ascribed to the 060 reflection, indicates a trioctahedral mineral.

When treated with ethylene glycol the spacing of the (001) reflection increases to 31.04 Å (calculated mean). On subtracting 14.2 Å for chlorite, the value 16.8 Å thus obtained, fits the ethylene glycol-montmorillonite complex. Heating for 1 hr at 520°C and 600°C gradually contracts the  $d(001)$  spacing and the intensity of the (001) reflection, and at 620° and 750°C, no long spacing is recorded. The mean value calculated from two

Table 7. FeO, Fe<sub>2</sub>O<sub>3</sub> and MgO contents of Samples Nos. 1–5. Sample No. 1—Chloritic clay; No. 2—Chloritized pumice; No. 3—Chlorite-free fraction of the whole rock; No. 4—Strongly chloritized ignimbrite; No. 5—Weakly chloritized ignimbrite

Sample No.	FeO	Fe <sub>2</sub> O <sub>3</sub>	MgO
	(%)	(%)	(%)
1	19.60	1.85	5.8
2	7.85	—	—
3	0.48	—	—
4	2.60	0.80	1.50
5	1.40	0.60	0.40

Table 8. Observed and calculated (001) spacings for air-dried, glycolated and heat treated regular mixed-layer swelling chlorite, Wairakei drillhole 225, 1150–1155 ft

00l	Air-dried		Glycolated		Heated for 1 hr			
	Observed	Calculated	Observed	Calculated	520°C	600°C	620°C	750°C
	(Å)	(l)	(Å)	(Å)				
001	30.46	90	—	31.55	—	28.49	26.77	—
002	14.48	100	28.96	15.50	31.00	13.81	13.39	13.19 11.48
003	9.82	25	29.46	—	—	8.84	8.84	8.75
004	7.37	55	29.48	7.69	30.76	7.25	7.83	—
005	5.86	5	29.30	6.28	31.40	5.27	—	5.30
006	4.90	90	29.40	5.18	31.08	4.84	4.74	4.48
007	4.25	5	29.75	4.46	31.22	—	—	—
008	3.66	65	29.28	3.86	30.80	3.67	3.95	3.35 3.36
009	3.26	40	29.34	3.46	31.14	3.33	3.38	2.96
00,10	2.93	55	29.31	3.09	30.90	2.94	2.95	—
00,11	2.72	5	29.92	2.82	31.02	—	—	—
		Mean		Mean				Mean
		$d(001) = 29.42$		$d(001) = 31.04$				$d(001) = 24.92$

reflections obtained after heating at 750°C (Table 8) is 24.92 Å, equal approximately to 14.2 Å + 10.7 Å. The stability of the 14.2 Å layers suggests chlorite-type layers, and the spacing 10.7 Å points to a collapsing montmorillonite structure. A complete contraction of the montmorillonite structure seemingly requires prolonged heating above 620°C.

Infrared absorption spectra of the regular mixed-layer swelling chlorite have been compared with the data of Tuddenham and Lyon (1959) on chlorites and with the results of Oinuma and Hayashi (1965) who studied various interstratified clay minerals. The mixed-layer swelling chlorite shows a number of infrared absorption bands (3685, 3570, 3420, 1640, 1090, 825, 762, 675, 655, 530, 460 in  $\text{cm}^{-1}$ ) comparable with absorption bands of chlorites, as listed by Tuddenham and Lyon (1959), the absorption bands of montmorillonite, as given by Oinuma and Hayashi (1965) being superimposed on the chlorite bands. However, the infrared absorption analysis unequivocally indicates the presence of interlayered chlorite.

On the other hand, the refractive indices  $N_x = 1.536 \pm 0.002$  and  $N_z = 1.543 \pm 0.002$  conform more to montmorillonite than to chlorite, but the comparatively low birefringence 0.007 is suggestive of chlorite. From the X-ray data, including glycolation and heat treatment, infrared absorption analysis and optical data, it is inferred that the swelling chlorite is a long spacing, regular mixed-layer chlorite-montmorillonite.

#### GEOTHERMAL FLUID

The chemical composition of the geothermal fluid and its temperature are evidently important factors controlling hydrothermal alteration. The geothermal fluid discharged by the wells is a mixture containing 85 per cent water and 15 per cent steam by weight at 200 lb/sq. in. well head pressure. The typical chemical composition of hot water, without steam, tapped in a fissure by drillhole 27, is compared in Table 9 with that of hot water which travelled for some distance from a fissure through permeable rocks, and was tapped at relatively shallow depth (1503 ft) by drillhole 41 (Mahon and Glover, 1965). The average pH of the deep geothermal fluid at 260°C is 6.7 (Pers. com. Dr. A. J. Ellis).

As far as the stability of hydrothermal minerals is concerned, the most significant characteristics of the geothermal fluid are:

- (i) Temperatures up to 265°C.
- (ii) Comparatively high  $m\text{K}^+/m\text{H}^+$  and  $m\text{Na}^+/m\text{H}^+$  ratios, and low  $m\text{Na}^+/m\text{K}^+$  ratio.
- (iii) Saturation in silica with respect to quartz.
- (iv) Tendency to saturation with  $\text{CaCO}_3$ .

Table 9. Compositions of waters discharged from steam wells at Wairakei: drillhole 27 taps water in a fissure at about 2000 ft; drillhole 41 taps, at 1503 ft, water from permeable rock at some distance from a fissure

	Drillhole No. 27	Drillhole No. 41
pH	8.5	8.5
Li	13.2 ppm	12.4 ppm
Na	1200.0	1175.0
K	200.0	172.0
Rb	3.0	2.4
Cs	2.7	2.2
Ca	17.5	24.0
Mg	0.05	0.03
F	8.1	7.5
Cl	2156.0	2113.0
Br	5.9	5.8
I	0.6	0.3
$\text{SO}_4$	25.0	23.0
Total $\text{HBO}_2$	115.00	112.0
Total $\text{SiO}_2$	660.0	540.0
As	4.7	4.5
Total $\text{NH}_3$	0.15	0.15
Total $\text{CO}_2$	23.0	20.0
Total $\text{H}_2\text{S}$	2.0	3.0

Analyses are for waters separated at 98°C and atmospheric pressure (Mahon and Glover, 1965).

The most important differences between the waters in Table 9 are the losses of silica and  $\text{K}^+$  ions, and enrichment in  $\text{Ca}^{2+}$  ions away from fissures. This difference can be correlated with the formation of hydrothermal minerals in various alteration zones. Thus, potassium is fixed in K-feldspar, illite and mixed-layer illite-montmorillonites, and silica is lost by precipitation of quartz. The enrichment in calcium is ascribed essentially to replacement of plagioclase by K-feldspar and albite, and to progressive alteration of Ca-montmorillonite to mixed-layer illite-montmorillonites and illite. A very small amount of lithium was probably fixed in the micaceous clay minerals. No distinctive trend is shown by the  $\text{Na}^+$  ion distribution. In comparison with the calcium ion, and to a somewhat lesser degree with the potassium ion, the sodium ion is a relatively inert ion as far as its participation in the structure of hydrothermal minerals is concerned. Thus, sodium occurs only in albite whereas calcium is the chief ion in montmorillonite, laumontite, wairakite, calcite and epidote; and potassium appears in K-feldspar and a series of micaceous clay minerals.

Saturation of geothermal fluid in silica with respect to quartz is reflected in the stability of



primary quartz. Chemical analyses of altered rocks show that the amount of  $\text{SiO}_2$  has either remained constant or has increased. This suggests that the pore solutions are also saturated with respect to quartz and that at Wairakei hydrothermal quartz forms in equilibrium with the altering solutions.

#### GENESIS OF CLAY MINERALS

##### *Kaolinite*

The association of kaolinite with alunite and opal suggests that kaolinite has formed from sulphuric acid solutions, which result from oxidation of hydrogen sulphide and/or pyrite by oxygen dissolved in downward percolating meteoric water (Steiner, 1953; Steiner and Rafter, 1966). The temperature in the kaolinite zone in drillhole 225 does not exceed  $40^\circ\text{C}$ , though in another drill-hole temperatures up to  $58^\circ\text{C}$  were recorded.

The kaolinite zone, which is only locally developed, sometimes gives way at depth to unaltered rock. Where the kaolinite zone is absent the rocks at and near the surface remain unaltered. The presence of fresh rock below the kaolinite zone and the fact that  $\text{H}_2\text{S}$  escapes at the surface, near the area where kaolinite does form, suggests supergene origin of the kaolinite.

##### *Montmorillonite*

Hypogene origin of the montmorillonite is indicated by the following evidence: (i) the montmorillonite zone often occurs below unaltered rock, and the amount of montmorillonite in the rock increases with depth; (ii) the montmorillonite zone is spatially related to fault fissures; (iii) montmorillonite occurs also at depth, below fault fissures, in a zone transitional to unaltered rock.

Ca-montmorillonite seems to be derived directly from volcanic glass and plagioclase without a previous transitional phase. This is particularly well demonstrated when volcanic glass and plagioclase are partly altered to montmorillonite. As shown in Figs. 2 and 3, montmorillonite forms at comparatively low temperatures, up to  $120^\circ\text{C}$  and  $130^\circ\text{C}$  respectively, though generally not exceeding about  $160^\circ\text{C}$  (Steiner, 1953). The presence of montmorillonite below fault fissures can be correlated with an inversion of temperature.

##### *Illite and randomly interstratified illite-montmorillonites*

Illite and its predecessors, the mixed-layer illite-montmorillonites, form from two parent materials: most commonly, though indirectly, from volcanic glass, and less commonly but directly from plagioclase. They seem to form in a relatively wide temperature and pressure range.

*Formation from silicic glass.* The common

genetic sequence of alteration seems to be the conversion of volcanic glass to Ca-montmorillonite, followed by potassium fixation and the formation of interstratified illite-montmorillonite and finally illite. Evidence of this sequence comes from the following observations: (i) micaceous clay minerals invariably occur below the zone of Ca-montmorillonite (ii) mixed-layer illite-montmorillonites with high  $d(001)$  values, indicating the presence of considerable amounts of interstratified montmorillonite, occur characteristically immediately below this zone, and gradually give way to mixed-layer clays deficient in interlayered montmorillonite and finally to illite, as a fault fissure is approached; (iii) Ca-montmorillonite is sometimes associated with the mixed-layer illite-montmorillonites rich in interlayered montmorillonite. Moreover, volcanic glass partly altered to mixed-layer illite-montmorillonite or illite has not been noted.

This observed genetic relationship between illite and its main source material, *i.e.* volcanic glass, is indicated in Fig. 7. Each member of the series of micaceous clay minerals seems to be stable under conditions prevailing at its place of formation.

The association of illite and hydrothermal K-feldspar in the vicinity of fissures indicates that both derive their potassium from the geothermal fluid ascending through the fissures. In facilitating the flow of hydrothermal solutions, the permeability of fissures and wall rocks seems to be an additional factor controlling the character of the alteration mineral assemblage and, thereby, the  $d(001)$  values. Providing the permeability of the wall rocks is uniform, a linear concentration gradient would develop outward from the fault fissure. This seems

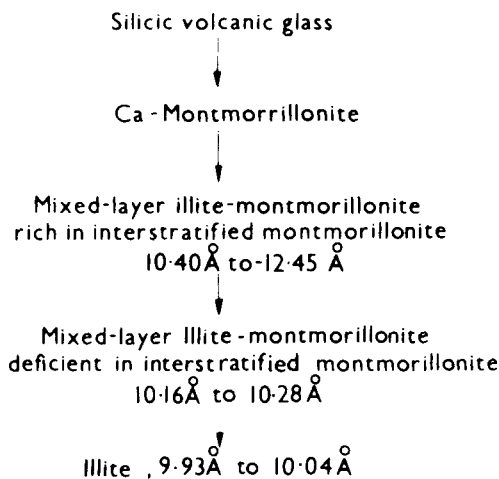


Fig. 7. Observed genetic sequence of hydrothermal alteration of silicic glass to illite.

to be nearly realised in drillhole 225 where the amount of non-expandable layers increases rather regularly towards the fissure (Table 4).

On the other hand, if the permeability varies somewhat, it causes an uneven concentration of  $K^+$  ions in the pore solution. Therefore, the resulting mixed-layer clays also vary in their content of montmorillonite layers, and the distribution of the  $d(001)$  values becomes somewhat irregular (Table 3).

The formation of illite and mixed-layer illite-montmorillonite clays from montmorillonite, and the limitation of interlayered montmorillonite to about 45 per cent, may be well explained by base exchange reaction and unmixing of interlayer cations (Glaeser and Méring, 1958). Accordingly, the  $Ca^{2+}$  ions in the Ca-montmorillonite would be exchanged for  $K^+$  ions in the altering solution. No structural changes will be noted until the ionic ratio  $K^+/Ca^{2+}$  of the interlayer cations reaches a critical value, which seemingly approaches unity. At this stage, the two kinds of ions would tend to unmix, and two types of layers, almost equal in numbers would result. Thus, the first mixed-layer illite-montmorillonite would consist of almost equal numbers of illite and montmorillonite layers, with illite layers (about 55 per cent) slightly predominating over montmorillonite layers (about 45 per cent). Subsequently, the base exchange reaction would gradually convert the remaining montmorillonite layers, and thus produce a series of mixed-layer illite-montmorillonites, their  $d(001)$  values ranging from about 12.45 to 10.28 Å, until finally pure illite (10 Å) is formed. The charge difference would be balanced by addition of  $H^+$  ions or, possibly hydronium ions.

The absence of interstratified illite-montmorillonites with a greater amount of interlayered montmorillonite than about 45 per cent suggests that such mixed-layer minerals are not stable under T-P-X conditions prevailing at Wairakei. Random interlayering of illite and montmorillonite occurs in all possible ratios in mixed-layer illite-montmorillonites from shales in the U.S.A. (Weaver, 1956). Byström (1954) described an interstratified illite-montmorillonite with 80 per cent of interlayered montmorillonite from Ordovician bentonite beds in Sweden.

Interstratification of illite and montmorillonite might suggest to some that illite formed first and subsequently has been transformed into mixed-layer illite-montmorillonites. This has been suggested by Shimoda and Sudo (1960) and Sudo *et al.* (1962) for hydrothermal interstratified mica-like minerals in Japan. It has been shown above, however, that the montmorillonite zone and the

micaceous subzones are related to temperature, and fissures carrying geothermal fluid, relatively rich in  $K^+$  ions and depositing K-feldspar. Under the temperature and chemical conditions prevailing at Wairakei, the transformation of illite into mixed-layer illite-montmorillonites would represent retrograde metamorphism, and this is considered to be improbable.

*Formation from plagioclase.* The alteration of plagioclase to micaceous clay minerals is much less common than the formation of micaceous clays from glass (Figs. 2 and 3). Optical study indicates that the micaceous clay mineral resulting from alteration of plagioclase does not differ from the micaceous clay derived from the co-existing glass. This study also indicates that plagioclase is sometimes partly altered directly to a micaceous clay mineral. No transitional phase has been noted in contrast with the alteration of pumice to micaceous clays.

*P-T conditions for micaceous clay formation.* The distribution of hydrothermal minerals and temperature data from drillholes give excellent evidence for pressure and temperature being controlling factors in the formation of alteration zones. The diagrams (Figs. 2,5 and 3,6) show that low temperatures, between about 130°C and 230°C in drillhole 71, and between 120°C and 230°C in drillhole 225, prevail at shallow levels where mixed-layer minerals with high  $d(001)$  values are forming. In contrast, micaceous clays with low  $d(001)$  values form at comparatively high temperatures, *i.e.* above about 230°C, measured at greater depth in and near fault fissures. Correspondingly, mixed-layer clays with abundant inter-stratified montmorillonite form at low lithostatic and water vapour pressures whereas comparatively high pressures are required for the formation of illite and mixed-layer clays deficient in montmorillonite. The temperature-pressure conditions at which micaceous clay minerals form at Wairakei are essentially similar to the T-P conditions at which Velde (1966) synthesized various mixed-layer illite-montmorillonites.

#### *Fe-rich chloritic clay*

Hydrothermal alteration of silicic glass to chlorite is a comparatively recent discovery, though such alteration of ferromagnesian minerals and plagioclase is well known. In contrast to the trioctahedral, iron-rich, chloritic clay resulting from alteration of silicic glass at Wairakei, the chlorite described by Mueller (1961, 1963) from the hydrothermally altered glassy groundmass of a quartz porphyry in the Black Forest, Germany, is aluminous and dioctahedral. It appears that the difference in the chlorites is essentially due to

different temperature and/or chemical composition of the altering solutions.

The iron-rich chloritic clay results from stepwise alteration of silicic glass which, when fresh, contains up to 1.40 per cent by weight FeO and up to 0.30 per cent by weight MgO. Moreover, the geothermal fluid contains only minute amounts of Fe, commonly varying between 0.03 and 0.17 p.p.m. (Koga, 1965), and Mg, usually ranging from 0.03 to 0.06 p.p.m. (Mahon, 1965).

The evidence as to whether chloritic clay forms directly from glass or is derived from a transitional mineral is not so definite as for the micaceous clay minerals. However, the following evidence appears to be significant: (i) Chloritic clay like the micaceous clay minerals occurs below the montmorillonite zone; (ii) chloritic clay is commonly associated and intergrown with micaceous clays over a wide range of temperatures and pressures. Thus, the chloritic and micaceous clays replacing silicic glass, may have a common origin, i.e. both clays are derived from earlier-formed montmorillonite. However, the mechanics of formation of chloritic clay from transitional montmorillonite would differ from those of micaceous clays. The chemical data in Table 7 suggest that the iron, and probably also the manganese, fixed originally in the glassy groundmass, is preferentially concentrated in the chloritic clay. A minute amount of iron, freed during the alteration of magnetite into pyrite or epidote may be also fixed in the chloritic clay. Further, minute amounts of Fe and Mg may be introduced also by prolonged interaction between the rocks, particularly the pumice, and the altering solution. Thus, the transformation of montmorillonite into micaceous clay minerals by fixation of  $K^+$  ions takes place at the same time as iron is preferentially concentrated in the chloritic clay, and the freed silica crystallizes as quartz. The widely spread association and intergrowth of chloritic and micaceous clay minerals which is also characteristic of low grade metamorphic rocks, suggests equilibrium conditions.

#### COMPARISON WITH EXPERIMENTAL RESULTS

The hydrothermal minerals at Wairakei, and specifically the occurrence of K-feldspar near fissures, compare very favourably with experimentally determined stabilities for these phases; however, some deviations exist. An important observation is that K-feldspar but not albite is deposited on fissure walls, and that K-feldspar replaces plagioclase in wall rocks adjacent to fissures. The stability fields of both alkali feldspars were determined experimentally by Hemley and Jones (1964). The ratios  $mK^+/mH^+$  ( $1.75 \times 10^4$ ) and  $mNa^+/mH^+$  ( $1.8 \times 10^5$ ) of the Wairakei

geothermal fluid and its maximum temperature, 265°C, are plotted on the diagrams of Hemley and Jones (1964) reproduced in Figs. 8 and 9. Both values  $1.75 \times 10^4$  and  $1.8 \times 10^5$  refer to the total discharge, i.e. water plus steam (pers. comm. Dr. A. J. Ellis). Thus, the points A and B (Figs. 8 and 9) should represent the stability conditions of K-feldspar and albite, respectively, in fault fissures at Wairakei. The occurrence of K-feldspar near fissures is in agreement with the location of the point A within the stability field of K-feldspar (Fig. 8). But it contrasts with considerably higher concentrations of  $Na^+$  ions than  $K^+$  ions in the geothermal fluid tapped in fissures (Table 9) and with the location of the point B within the stability field of albite (Fig. 9).

Lithostatic pressures prevailing at depths where fissures were intersected vary between 75 and 130 bars. These pressures are considerably lower than the experimental pressure of 1000 bars (Hemley and Jones, 1964). Because the geothermal fluid ascending through fissures is a watery phase, the effect of lower pressures on the boundary of the stability fields should be much less pronounced than under experimental conditions. It can be expected therefore, that the stability field of K-feldspar will be only slightly extended into the region of lower  $mK^+/mH^+$  ratios. However, the high aqueous silica activity characteristic of the geothermal fluid will stabilise K-feldspar at lower  $mK^+/mH^+$  values than those existing under stable equilibrium conditions (Hemley, 1959). Thus the position of point A (Fig. 8) suggests that K-feldspar is a stable phase.

Since the aqueous alkali cation/ $H^+$  ratios are comparatively high, the absence of albite on fissure walls appears to be due to a somewhat low aqueous  $mNa^+/mK^+$  ratio, about 10 (Hemley and Jones, 1964). The replacement of plagioclase concurrently by K-feldspar and albite further away from fissures, and replacement of plagioclase by albite only at still greater distance from fissures suggests that as the pore solution is progressively depleted in  $K^+$  ions, the aqueous  $mNa^+/mK^+$  ratio increases until it first reaches the equilibrium value required for the formation of both alkali feldspars. Finally, the ratio  $mNa^+/mK^+$  reaches a value at which only albite is the stable phase. Thus, the aqueous ratio  $mNa^+/mK^+$  appears to be an important factor controlling the stability relation between K-feldspar and albite at Wairakei.

It is significant that the values for the aqueous ratios  $mK^+/mH^+$  and  $mNa^+/mH^+$  are comparatively high, and that in either system,  $K_2O-Al_2O_3-SiO_2-H_2O$  and  $Na_2O-Al_2O_3-SiO_2-H_2O$ , the corresponding ratio falls well outside the stability field of kaolinite, requiring low alkali/ $H^+$

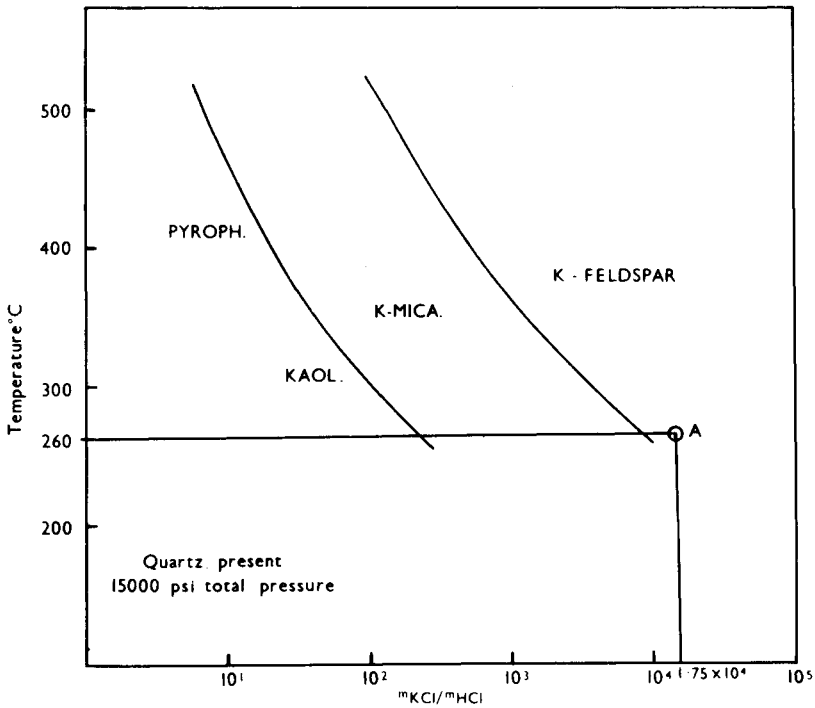


Fig. 8. The ratio of  $mK^+/mH^+$  and maximum temperature of Wairakei geothermal fluid plotted in the diagram of Hemley and Jones (1964, Fig. 1), showing the mineral stability fields in the  $K_2O-Al_2O_3-SiO_2-H_2O$  system.

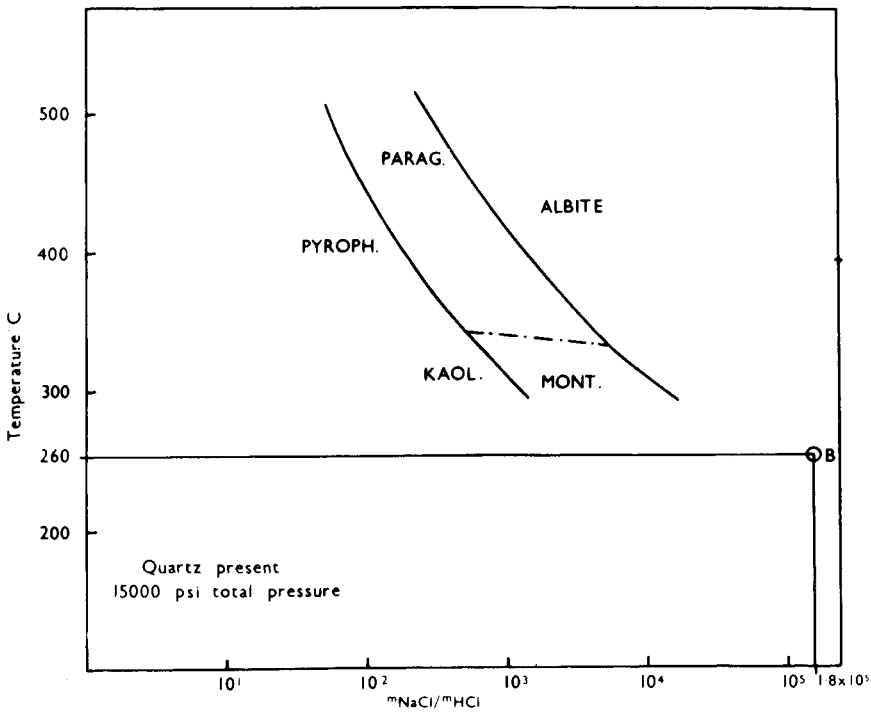


Fig. 9. The ratio of  $mNa^+/mH^+$  and maximum temperature of Wairakei geothermal fluid plotted in the diagram of Hemley and Jones, (1964, Fig. 2) showing the mineral stability fields in the  $Na_2O-Al_2O_3-SiO_2-H_2O$  system.

ratio. Thus, the high alkali/H<sup>+</sup> ratios of the geothermal fluid appear to ensure that hypogene kaolinite does not form at Wairakei.

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#### REFERENCES

- Albee, A. L. (1962) Relationship between mineral association, chemical composition and physical properties of the chlorite series: *Am. Mineralogist*, **47**, 851–870.
- Bonorino, F. G. (1959) Hydrothermal alteration in the Front Range mineral belt, Colorado: *Geol. Soc. Am. Bull.* **70**, 53–90.
- Bradley, W. F., and Grim, R. E. (1961) Mica clay minerals, in Brown: *The X-ray identification of clay minerals* Mineral. Soc., London, 208–241.
- Brindley, G. W. (1961) Chlorite minerals, in Brown: *The X-ray identification of clay minerals*. Mineral. Soc., London, 242–296.
- Brown, G., and MacEwan, D. M. C. (1950) The interpretation of X-ray diagrams of soil clays, Part II: *J. Soil Sci.* **1**, 239–253.
- Bundy, W. M. (1958) *Wall-rock alteration in the Cochiti Mining District, New Mexico*: State Bureau of Mines and Mineral Resources, New Mexico Inst. Min. and Techn., Bull. **59**, 71 pp.
- Byström, A. M. (1954) "Mixed-layer" minerals from the Ordovician bentonite beds at Kinnekulle, Sweden: *Nature* **173**, 783.
- Glaeser, R., and Méring, J. (1958) Le rôle de la valence des cations échangeables dans l'hectorite: *C. R. Acad. Sci., Paris* **246**, 1569–1572.
- Grim, R. E. (1953) *Clay Mineralogy*: McGraw-Hill New York, 384 pp.
- Harvey, R. D., and Vitaliano C. J., (1964) Wall-rock alteration in the Goldfield District, Nevada: *J. Geol.* **72**, 564–579.
- Hemley, J. J. (1959) Some mineralogical equilibria in the system K<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O: *Am. J. Sci.* **257**, 241–270.
- Hemley, J. J., and Jones, W. R. (1964) Chemical aspects of hydrothermal alteration with emphasis on hydrogen metasomatism: *Econ. Geol.* **59**, 538–569.
- Kodama, H., and Oinuma, K. (1963) Identification of kaolin minerals in the presence of chlorite by X-ray diffraction and infrared absorption spectra: *Clays and Clay Minerals* **11**, 236–249, [Pergamon Press, New York].
- Koga, A. (1965) Iron, aluminium and manganese concentrations in waters discharged from Wairakei drillholes. *Departmental report, Chemistry Division, D.S.I.R., Wellington, New Zealand, CD:118/16-AK2*.
- Mahon, W. A. J. (1965) Calcium and magnesium in the natural thermal waters of New Zealand: *New Zealand J. Sci.* **8**, 66–78.
- Mueller, G. (1961) Vorläufige Mitteilungen ueber ein neues dioctaedisches Phyllosilikat der Chlorit-Gruppe: *N. Jb. Miner. Mh.* **5**, 112–120.
- Mueller, G. (1963) Zur kenntnis dioctaedischer Vierschicht-Phyllosilikate (Sudoit-Reihe der Sudoit-Chlorit-Gruppe): *International Clay Conference*, Pergamon Press, New York, 121–130.
- Oinuma, K., and Hayashi, H. (1965) Infrared study of mixed-layer clay minerals: *Am. Mineralogist*, **50**, 1213–1227.
- Schoen, R., and White, D. E. (1965) Hydrothermal alteration in GS-3 and GS-4 drillholes, Main Terrace, Steamboat Springs, Nevada: *Econ. Geol.* **60**, 1411–1421.
- Shimoda, S., and Sudo, T. (1960) An interstratified mixture of mica clay minerals: *Am. Mineralogist*, **45**, 1069–1077.
- Sigvaldason, G., and White, D. E. (1961) Hydrothermal alteration of rocks in two drill holes at Steamboat Springs, Washoe County, Nevada: *U.S. Geol. Surv. Prof. Paper 424-D*, 116–122.
- Sigvaldason, G. and White, D. E. (1962) Hydrothermal alteration in drill holes GS-5 and GS-7 Steamboat Springs, Nevada: *U.S. Geol. Surv. Prof. Paper 450-D*, 113–117.
- Steiner, A. (1953) Hydrothermal rock alteration at Wairakei, New Zealand: *Econ. Geol.* **48**, 1–13.
- Steiner, A., and Rafter, T. A. (1966) Sulfur isotopes in pyrite, pyrrhotite, alunite and anhydrite from steam wells in the Taupo Volcanic Zone, New Zealand: *Econ. Geol.* **61**, 1115–1129.
- Sudo, T. (1959) *Mineralogical Study on Clays of Japan*: Maruzen Company, Tokyo 328 pp.
- Sudo, T. (1963) Interstratified minerals from Japan, their geological behaviours and origins: *International Clay Conference*, Pergamon Press, 113–120.
- Sudo, T., Hayashi, H., and Shimoda, S. (1962) Mineralogical problems of intermediate clay minerals: *Clays and Clay Minerals* **9**, 378–392. [Pergamon Press, New York].
- Tooker, E. W. (1956) Altered wall rocks along vein deposits in the Central City-Idaho Springs Region, Colorado: *Clays and Clay Minerals* **4**, 348–361. [Natl. Acad. Sci.–Natl. Res. Council pub. 456].
- Tooker, E. W. (1963) Altered wallrocks in the Central Part of the Front Range Mineral Belt Gilpin and



- Clear Creek Counties, Colorado: *U.S. Geol. Surv. Prof. Paper* 439, 102 pp.
- Tuddenham, W. M., and Lyon, R. J. P. (1959) Relation of infrared spectra and chemical analysis for some chlorites and related minerals: *Anal. Chemistry* 31, 377–380.
- Velde, B. (1966) Mixed-layer mineral associations in muscovite-celadonite and muscovite-chlorite joints: *Clays and Clay Minerals* 13, 29–32. [Pergamon Press, New York].
- Weaver, C. A. (1956) Distribution and identification of mixed layer clays in sedimentary rocks: *Am. Mineralogist*, 41, 202–221.

**Résumé**—Le fluide géothermique d'échappé par les puits de vapeur forés jusqu'à des profondeurs de 1500 m à Wairakei, en Nouvelle-Zélande, a modifié les roches volcaniques siliciques et en grande partie vitreuses du Pliocène à u Pleistocène, ainsi que les tufs et brèches aquos apparentés. Les températures mesurées (mz. 265°C) démontrent que les conditions sont entre épi- et mésothermiques dans les fissures de failles enfouies, lieu géométrique du fluide hydrothermique et de l'altération la plus intense.

On peut distinguer la zone d'altération de kaolin supergène des zones de Ca-montmorillonite hypogène ainsi que des zones micacé et chloritiques associées. Les zones hypogènes sont généralement larges et influencées par la température, et sont situées le long des fissures de failles. Les autres minéraux hypogènes courants sont les feldspaths alkalis, la wairakite, l'épidote, le quartz, la laumontite, la ptilotite, la pyrite et la pyrrhotite, mais la prehnite est rare.

Les minéraux d'argile micacé comprennent de l'illite (environ 10 Å) et une série d'illite-montmorillonites variées dans des couches mixtes aux valeurs  $d(001)$  comprises entre 10,28 Å et 12,45 Å. La quantité de montmorillonite interstratifiée est en rapport avec la température et les fissures de failles. A part les rares exemples de chlorite gonflante en couches mixtes, l'argile chloritique riche en fer montre peu ou pas de variations dans sa composition. Les argiles micacées aussi bien que les argiles chloritiques résultent de l'altération de Ca-montmorillonite formée antérieurement.

La stabilité des minéraux hydrothermiques est contrôlée par la température et par la composition chimique de fluide géothermique qui monte la long des fissures de failles. Il se fait des dépôts de feldspath-K mais non d'albite le long des parois des failles, mais les deux feldspaths alkalis remplacent la plagioclase soude-chaux primaire sur la roche pariétale. L'absence d'albite sur les parois de failles s'explique par le coefficient  $mNa^+/mK^+$  d'humidité peu élevé. La solution altérante n'a pas d'effet sur le quartz primaire, mais le quartz hydrothermique se dépose sur les parois de failles et sur la roche pariétale.

**Kurzreferat**—Die geothermische Flüssigkeit, die von den Dampfbohrlöchern abgegeben wird, welche in Wairaki, Neuseeland, bis zu Tiefen von 1500 m abgeteuft wurden, hat das Pliozän in Pleistozän, kieselsaures, hauptsächlich glasartiges Vulkangestein und ähnliche wässrige Tuffe und Breksien umgewandelt. Die gemessenen Temperaturen (265°C) weisen auf epithermische bis mesothermische Zustände in unterirdischen Verwerfungsbrüchen hin, wo die hydrothermische Flüssigkeit und die ausgeprägte Umwandlung zu finden ist.

Es wird eine supragene Kaolinit-Umwandlungszone von den hypogenen Ca-Montmorillonit- und kombinierten glimmerartigen und chloritischen Zonen unterschieden. Die hypogenen Zonen sind meist breit und temperaturabhängig und verlaufen an den Verwerfungsbrüchen entlang. Andere allgemein verbreitete hypogene Minerale sind Alkalifeldspate, Wairakit, Epidot, Quarz, Calcit, Schaumspat, Ptilotit, Pyrit und Magnetkies. Prehnit ist selten.

Die glimmerartigen Tongesteine enthalten Illit (etwa 10 Å) und eine Reihe von unregelmässigen Mischlagen von Illit-Montmorillonit mit  $d(001)$  Werten zwischen 10,28 Å und 12,45 Å. Die Menge des zwischengeschichteten Montmorillonits hängt von der Temperatur und den Verwerfungsbrüchen ab. Abgesehen von selten auftretendem Quellchlorit in den Zwischenschichten zeigt der eisenreiche chloritische Ton wenig oder keine Änderung in seiner Zusammensetzung. Die glimmerartigen Tone, sowie der chloritische Ton verdanken ihre Entstehung der Umwandlung von früher gebildetem Ca-Montmorillonit.

Die Beständigkeit hydrothermaler Minerale wird durch die Temperatur und die chemische Zusammensetzung der entlang der Verwerfungsbrüche aufsteigenden geothermischen Flüssigkeit bestimmt. K-Feldspat, aber kein Na-Feldspat, wird an den Bruchwänden abgelagert, doch ersetzen beide Alkalifeldspate die primären NaCa Feldspate im Wandgestein. Die Abwesenheit von Natronfeldspat an den Bruchwänden wird dem niedrigen wässrigen  $mNa^+/mK^+$  Verhältnis zugeschrieben. Der primäre Quarz wird durch die Umwandlungslösung nicht beeinflusst, aber es wird hydrothermischer Quarz an den Bruchwänden und im Wandgestein abgelagert.



**Резюме**—Геотермическая жидкость выпускается паровыми скважинами, которые были колонково пробурены до такой большой глубины, как 1371 м (4500 фут.) в Вейракей, в Новой Зеландии; она изменила плиоценовые осадки на плейстоценовые, кремниевые, главным образом вулканическое стекло и связанные с ними водные туфы и брекчии. Измеренные температуры (макс. 265°C) указывают на эпитеермальные до мезотермальных условия в сбросовых трещинах—в участке как гидротермической жидкости, так и наиболее интенсивного изменения.

Супергенная зона изменения каолинита отличается от гипогенной зоны кальциевого монтмориллонита и обобщенных слюдяных и хлоритовых зон. Гипогенные зоны обычно широкие, зависят от температуры и сосредоточены вдоль сбросовых трещин. Другие часто встречаемые гипогенные минералы—это щелочный полевоы шпат, вайракиит, эпидот, кварц, кальцит, ломонит, морденит, пирит и пирротин. Пренит встречается редко.

Слюдяные глинистые минералы включают иллит (прибл. 10 Å) и ряд иллитомонтмориллонитов с беспорядочно смешанными слоями и значениями  $b(001)$  от 10,28Å до 12,45Å. Количество переслаивающегося монтмориллонита зависит от температуры и от сбросовых трещин. Кроме редкого вспучивания хлорита со смешанным слоем, богатая железом хлоритная глина показывает мало изменений или вообще не имеет изменений в составе. Как слюдяные глины, так и хлоритная глина являются следствием изменения ранее образовавшегося кальциевого монтмориллонита.

Устойчивость гидротермических минералов регулируется температурой и химическим составом геотермической жидкости, восходящей вдоль сбросовых трещин. Калиевый шпат, но не альбит откладывается на стенках трещины, но оба щелочных шпата замещаются первичным натровым известковым плагиоклазом в боковой породе. Отсутствие альбита на стенках трещины приписывается низкому соотношению водного  $mNa^+/mK^+$ . Первичный кварц не подвергается воздействию изменяющего раствора, но гидротермический кварц отлагается на стенках трещины и в боковой породе.