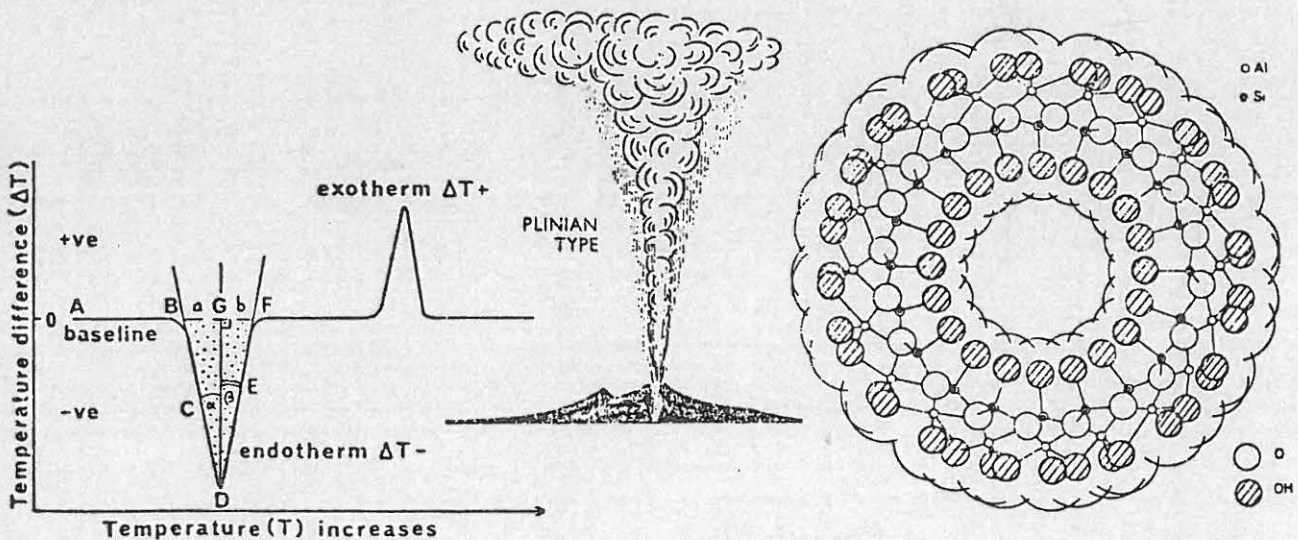


GUIDE TO THE NATURE AND METHODS OF ANALYSIS OF THE CLAY FRACTION OF TEPHRAS FROM THE SOUTH AUCKLAND REGION, NEW ZEALAND

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Preface to Second Printing

This manual was written in the early 1980s and some aspects are now out of date. Nevertheless, it is still considered to be a useful reference and so has been reprinted. Bibliographic citation should follow that given on the title page, i.e. Lowe and Nelson (1983) etc. Useful more recent articles on clay minerals in tephra deposits, or techniques of their analysis, include Wada (1985, 1987, 1989), Parfitt and Wilson (1985), Lowe (1986, in press), Parfitt (1986, 1990), Churchman (1986, 1990), Singer and Janitzky (1986), Blakemore et al. (1987), Whitton and Churchman (1987), Parfitt and Childs (1988), Parfitt and Kimble (1989), Dixon and Weed (1989), Mizota and van Reeuwijk (1989), Huang (1991), and Childs (1992). An earlier article, not originally cited in this manual but potentially helpful, is that of Claridge (1969), and a reference to Churchman et al. (1972) (added to p. 29) is listed below. An updated review of the clay mineralogy of tephra deposits and associated soils and paleosols in central and northern New Zealand was written by Lowe and Percival (1993).

Note that nanometres (nm) have replaced angstroms (Å) as the preferred unit of measurement in clay mineralogy.

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ABSTRACT

South Auckland tephras often contain a significant amount of clay-sized (<2 μ m) material derived principally from the in situ weathering of glassy and other components in the deposits. The clay fraction generally increases with age and is mainly dominated by allophane and/or halloysite, but can include also small quantities of other secondary constituents, such as imogolite, poorly ordered iron and aluminium oxides and hydroxides, silica polymorphs of cristobalite, tridymite or opaline silica, humus and humus complexes, and 14Å clay-vermiculite. This manual firstly reviews briefly the nomenclature and nature of these clay components and their general occurrence in South Auckland tephras. Concerning weathering sequences, it is emphasised that separate 'mineral' transformation pathways appear to exist for the various components according to their chemistry and to site weathering conditions, particularly as they affect the concentration of Si in solution and the availability of Al, and the opportunity for co-precipitation of these.

The main intention of the manual is to outline some of the more common laboratory procedures available for qualitatively and quantitatively analysing the composition of the tephric clays, many of which are difficult to determine because of their short range order or "amorphous" nature. Techniques described and assessed in terms of their rapidity and quantitiveness include X-ray diffractometry (XRD), infrared spectroscopy (IR), differential thermal analysis (DTA), transmission and scanning electron microscopy (TEM and SEM), sodium fluoride reactivity, chemical dissolution analyses, and surface area measurements. No one technique alone produces a definitive clay fraction analysis of tephric deposits.

The reference list includes more than 200 entries relevant to tephric clay studies in general, allowing for more specialist investigations where appropriate.

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INTRODUCTION

Tephra is a collective term for predominantly unconsolidated pyroclastic materials of both air-fall and flow origin (Schmid 1981; Self and Sparks 1981), although the term has previously been restricted to pyroclastic fall deposits only (Wright et al. 1980). This latter sense is generally retained for this article.

Tephtras, predominantly of Quaternary age and of mostly rhyolitic or andesitic composition, form widespread near-surface and surficial blanket deposits in the South Auckland region* of North Island, and consequently they are of paramount importance as soil-forming parent materials. They have originated mainly from peripheral volcanic centres on Coromandel Peninsula, from the Taranaki and Tongariro-Taupo-Rotorua districts, and from Mayor Island in the Bay of Plenty (Pullar and Birrell 1973a; Pullar et al. 1973; Howorth 1975; McCraw 1975; Vucetich and Howorth 1976; Hogg and McCraw 1983). Because of erosion, non-deposition, and other factors, the stratigraphic sequence of surficial tephra deposits varies widely from place to place. To date about 75 separate air-fall tephra formations have been named, ranging in age from a few hundred years to possibly a million years or more, and having a combined total thickness of as much as 10-12m (e.g., see references above and in Howorth et al. 1981, p. 131). Table 1 lists the tephtras that have been identified to date in the Hamilton-Raglan area, and includes their generalised thicknesses and ages. Individual tephtras may be separated by well defined paleosols (Gibbs 1980), although detailed laboratory analyses have indicated the composite nature of several of the otherwise apparently homogenous tephra deposits (e.g. Pullar and Birrell 1973b; Hodder and Wilson 1976; Hogg 1979; Lowe 1981; Hogg and McCraw 1983). In addition, subsurface drilling in the South Auckland lowlands shows that several pyroclastic flows (distal ignimbrites) reach into the region (e.g., Todd 1982), and future work will undoubtedly indicate also the presence of associated air-fall deposits at depth.

This manual outlines some laboratory procedures applicable to the mineralogical analysis of tephra deposits in the South Auckland region, with major emphasis on their clay fraction. A companion report exists describing X-ray diffraction (XRD) techniques of mineralogical analysis appropriate for many sedimentary deposits in South Auckland (Hume and Nelson 1982). The tephra deposits are treated

* This is generally taken to include the Pukekohe-Waikato-Bay of Plenty-Coromandel-King Country-Taupo areas.

Table 1. Names, sources, ages, and thicknesses of known tephra which have been deposited in the Hamilton-Raglan area. Unnamed tephra in addition to those listed also occur (Lowe, in prep.). Data mainly after Lowe (1981, 1981a, p. 70) and references therein.

Tephra Formation	Source (volcanic centre)	Approx. age years B.P.*	Max. thickness (cm)
Ngauruhoe Tephra	Tongariro	Historical	<1
Taupo Pumice	Taupo	1,800	5
Waimihia Formation	Taupo	3,400	1
Tuhua Tephra	Mayor Island	6,200	5
Mamaku Ash	Okataina	7,000	4
Rotoma Ash	Okataina	8,300	1
Opepe Tephra	Taupo	8,800	2
Andesitic Ash (Tsg19)	Egmont or Tongariro	9,000	2
Mangamate Tephra	Tongariro	10,000	4
Waiohau Ash	Okataina	11,500	3
Okupata Tephra	Tongariro	12,500	1
Rotorua Ash	Okataina	13,500	4
Rotoaira Lapilli	Tongariro	13,800	1
Rerewhakaaitu Ash	Okataina	14,700	3
Okareka Ash	Okataina	19,000	5
Kawakawa Tephra ¹	Taupo	20,000	15(?)
?Okaiia Tephra	Taupo	25,000	?
Tahuna Tephra ²	Okataina	39,000	15(?)
?Tihoi Tephra	Taupo	39,000	?
Rotoiti Breccia - Rotoehu Ash Mb. [†]	Okataina	42,000	30(?)
<hr/>			
Hamilton Ash (beds H1-H7)	Unknown (?central North Island)	~100,000-400,000 ³	500
<hr/>			
Kauroa Ash (many beds)	Unknown (?Coromandel & central North Island)	~200,000-1,000,000 ⁴	900

* Old half-life basis

† Mb. Member

? Uncertain

¹ Previously reported as Oruanui Ash

² Previously reported as (undifferentiated) Mangaoni Lapilli

³ Various estimates by McCraw (1975), Vucetich et al. (1978), and Henty et al. (1980), among others

⁴ Various estimates by Pullar and Birrell (1973a), McCraw (1975), Pain (1975), Davoren (1976), and Salter (1979), among others

Table 2. Relationship between tephra age and clay content of some predominantly rhyolitic tephra from the Waikato-Bay of Plenty regions. Data after Birrell and Pullar (1973), Hogg (1974), Davoren (1976), Salter (1979), Lowe (1981, and unpublished information).

Tephra	Approx. age years B.P.	Av. % clay (<2µm) in tephra	No. of samples analysed
Kaharoa Ash	700	6	1
Taupo Pumice	1,800	5	7
Waimihia Formation	3,400	5	2
Whakatane Ash	4,600	7	4
Mamaku Ash	7,000	8	8
Waiohau Ash	11,500	18	3
Rerewhakaaitu Ash	14,700	9	7
Okareka Ash and Te Rere Ash	19,000	15	7
Kawakawa Tephra	20,000	18	11
Tahuna Tephra and others	c.30,000	16	10
Rotoehu Ash	42,000	25	9
Hamilton Ash	~100,000	65	10
Kauroa Ash	~500,000	85	43

separately because of several special properties, including their glassy nature, their often considerable clay content, and their unique clay mineral compositions. For completeness, and to aid data interpretation, the manual is divided into two parts, the first describing the nature and nomenclature of the potentially complex array of tephra-derived clay mineral types, as well as commenting briefly on their genesis, and the second the various methods of sample preparation and analysis. A large number of references are included purposely for additional specialist reading and to provide follow-up details on either genesis or methodology. The reader interested solely in analytical procedures is referred directly to the introductory remarks of Part 2 (p. 22), as well as to Table 5 (p. 24), which aims to help guide the non-specialist clay mineralogist in the choice of analytical techniques which might best suit his or her intentions.

PART 1 : NATURE AND GENESIS OF TEPHRA-DERIVED CLAY MATERIALS

With increasing age the amount of clay-sized ($<2\mu\text{m}$) material in tephras generally increases dramatically as glassy and other components are broken down and transformed to clay minerals. For example, tephras less than about 2,000 to 3,000 years old have $<5\%$ clay, those from 3,000 to 10,000 years age have between 5 and 10% clay, those from 10,000 to 50,000 years age typically contain 15 to 30% clay, while those older than about 50,000 years contain $>60\%$ clay (Table 2). Environmental parameters such as depth of burial, climate, vegetation, and degree of leaching also influence the proportion of clay-sized material in a deposit, and, together with the primary composition of the deposit, determine the types of clay minerals within the clay fraction.

The clay fractions comprise mainly authigenic minerals with subordinate amounts of residual (primary) or accessory minerals. A notable feature of almost all tephra-derived clay fractions is the occurrence of short range order (often referred to as "non-crystalline", "poorly ordered", or "amorphous"; see Brindley 1977; Bailey 1980) clay minerals, in addition to well ordered or crystalline species. A key characteristic of the short range order materials is the dominant presence of active aluminium which occurs in various mineralogical forms (Wada 1980). Short range order minerals can also occur, usually in small amounts, in some soils (notably podzols) derived from non-tephric and non-vitric materials (e.g., Wada and Harward 1974; Milestone and

Wilson 1977; Tait et al. 1978; Ross 1978; Farmer et al. 1980; Wada 1980; Young et al. 1980; Farmer 1982). Studies on these minerals have helped elucidate the actual conditions and mechanisms of formation of their counterparts derived from tephric materials.

Types of clay components in South Auckland tephra materials

The most abundant secondary minerals occurring in the clay fractions of tephra are allophane and halloysite. Subordinate amounts of imogolite, poorly ordered iron and aluminium oxides and hydroxides (including gibbsite), secondary silica polymorphs of cristobalite, tridymite, and opaline silica, humus and humus complexes, 14Å clay-vermiculite, and very rare kaolinite have been additionally reported in central North Island and overseas tephra deposits. Other 2:1 and 2:1:1 layer lattice silicates and their intergrades occur in substantial amounts in some Japanese tephra-derived soils. Allophane-like constituents (defined by method of extraction) are also reported in the Japanese literature. Residual (primary) quartz, feldspar, cristobalite, and glass may also occur in tephra clay fractions. For most studies only a few of these minerals, excepting allophane and/or halloysite, are likely to be encountered in any one sample, and then in small amounts only. However, in specific and detailed "clays-oriented" studies some of the components other than allophane and halloysite may form a more critical part of the investigation. Consequently, explanatory background notes on each of the minerals listed above, and their general occurrence in South Auckland tephra, are summarised below.

For more detailed information some recent articles discussing the chemical compositions, chemical and physical structures, surface properties, and reactivities of these tephra-derived secondary minerals include Quantin (1974), Wada and Harward (1974), Gieseking (1975), Dixon and Weed (1977), Maeda et al. (1977), Brown et al. (1978), Sudo and Shimoda (1978), Schwertmann (1979), Theng (1980), Tuohy (1980), and Theng et al. (1982).

Allophane

Allophane is the name given to a series of naturally occurring hydrated aluminosilicate clays characterised by short range order and the predominance of Si-O-Al bonds. Their chemical composition varies but typically they show Al:Si molar ratios between 1.0 and 2.0 and H₂O(+):Al₂O₃ molar ratios between 2.0 and 4.5 (Wada 1977, 1980; Parfitt et al. 1980). This definition of allophane, despite its wideness, has been generally adopted by workers in Japan and U.S.A. (van Olphen 1971),

as well as in New Zealand (Rankin and Churchman 1981). Recent work has identified two main forms of allophane, one having an Al:Si molar ratio close to 1.0 and another with a ratio of ~ 2.0 . The latter form, which appears to predominate, has been termed 'proto-imogolite' allophane (Parfitt et al. 1980) and is discussed further below.

Allophane was originally described as being "amorphous" (to X-rays) and therefore having little or no structural organisation. However, high resolution electron microscopy has shown that all forms of allophane consist of irregular aggregates constructed of hollow, spherically shaped particles with diameters of 35 to 55Å (Fig. 1; Henmi and Wada 1976), and with surface areas of about 800m²/g (Parfitt and Henmi 1980) or more (Wada 1980). The wall thickness of individual spherules is between about 7 and 10Å and each contains about 8-10 pores (broken bond defects)

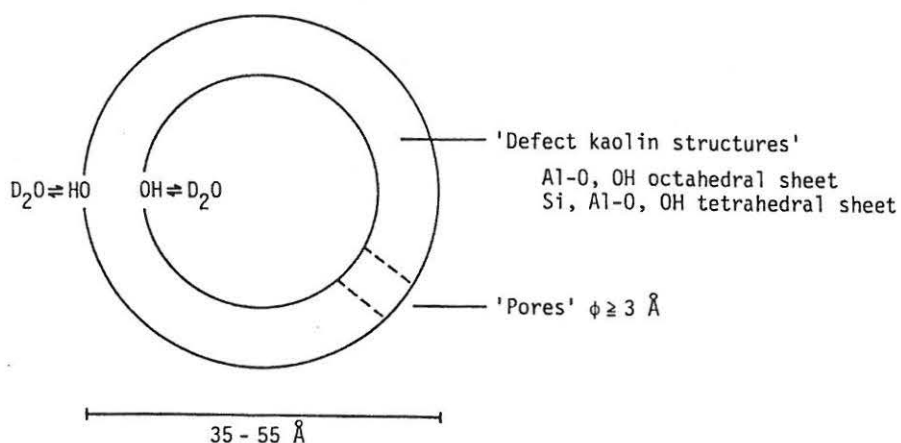


Fig. 1. A schematic representation of the spherical 'structural unit' of allophane (from Wada 1979, p. 538).

which allow the passage of water. Parfitt et al. (1980) suggested that the framework for the allophane structure is a gibbsitic Al octahedral sheet. The short range order or non-crystalline character of allophane derives from the local, non-repetitive nature of the spherical "structural unit" (Fig. 1; Okada et al. 1975; Wada and Wada 1977; Wada 1979).

Allophane is ubiquitous in tephras in the South Auckland region and in many cases is the dominant constituent of the clay fraction.

Imogolite

Imogolite is an hydrous aluminosilicate that was first described in a Japanese soil known as imogo, derived from glassy volcanic ash.

It is similar in many ways to allophane, but occurs as smooth and curved "filiform" threads, several microns long and 100 to 300Å in diameter (Wada 1980). The threads comprise finer tubular units with inner and external diameters of about 10 and 20Å respectively (Fig. 2), and an external surface area of about 1450m²/g (Theng et al. 1982).

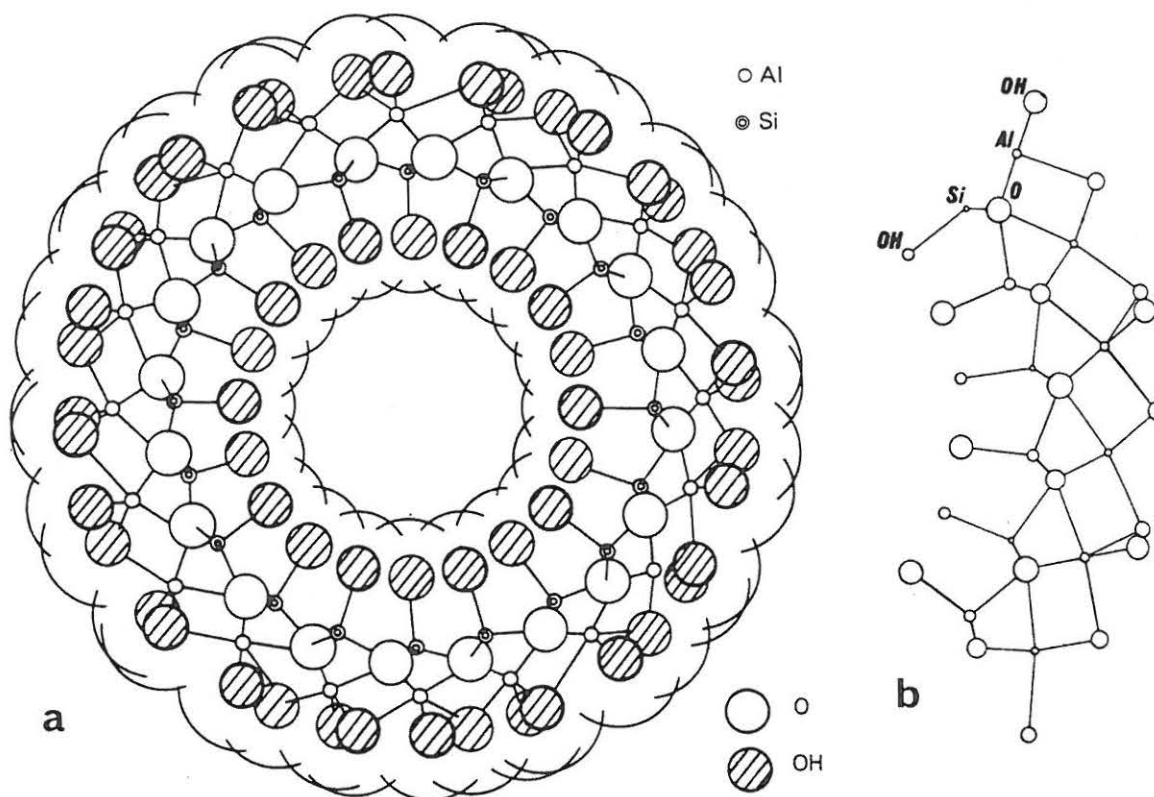


Fig. 2. (a) Cross-section of an imogolite tube viewed down the tube axis. The outside diameter is 21.4Å, the inside diameter 6.4Å. The external surface of the tube comprises a gibbsite-like structure but the internal surface has exposed Si-OH groups (SiO₃OH) with the Si in isolated tetrahedral sites (after Parfitt, 1980b, p. 169). (b) Curling of the gibbsite hydroxide sheet by contraction of one surface to accommodate the SiO₃OH tetrahedra (after Wada 1977, p. 618).

Cradwick et al. (1972) explained the tubular units as paracrystalline (i.e., 1-dimensional structural units somewhere between short and long range order; Wada 1977) cylindrical structures in which the OH groups of one side of a gibbsite sheet lose protons and bond to Si atoms, with the Si atoms out of the plane of the sheet. Because Si-O bonds are shorter than Al-O bonds, the unit is forced to contract to form a cylinder with a circumference of 10, 11 or 12 modified gibbsite unit cells (Fig. 2; Brown et al. 1978; Parfitt 1980b; Wada 1980). Compositionally, the SiO₂:Al₂O₃ range for imogolite appears to be slightly narrower than

for allophane, being 1.05 to 1.15 (Wada 1977).

Imogolite is usually present in only small amounts in New Zealand tephros (Yoshinaga et al. 1973; Parfitt et al. 1982) and has been reported in tephra material in the Waikato region (Jessen 1977).

'Proto-imogolite' allophane

This informal term refers to allophanes which have imogolite structures on the atomic scale but do not exhibit the tubular morphology of imogolite (Parfitt and Henmi 1980). Infrared spectroscopy yields an imogolite spectra, similar to that exhibited by synthetic 'proto-imogolite' gels, but electron micrographs indicate that the imogolite structural arrangement is distorted to give hollow spherules rather than tubes. 'Proto-imogolite' allophanes apparently have Al:Si ratios close to 2.0 and are the dominant type of naturally occurring allophane.

Samples of allophane with molar Al:Si ratios between 1.0 and 2.0 have been shown by Parfitt et al. (1980) to be mixtures of their allophane structure (Al:Si~1.0), and a proto-imogolite allophane structure (Al:Si~2.0), indicative of an allophane structural series (see also Wada 1979 ; Wada 1980, p. 90). Continued use of the term 'proto-imogolite' allophane is not generally favoured (Rankin and Churchman 1981) but appears to be well established in the literature. There is a trend, however, to qualify the allophane "type" simply by reporting its Al:Si ratio as a prefix or suffix.

'Proto-imogolite' allophane, initially characterised in New Zealand in samples from the Taranaki region, has been shown to be the dominant form of allophane (reported as allophane with Al:Si = 2.0) in the Waikato region (Parfitt et al. 1983).

Allophane-like constituents

These are defined as non-crystalline aluminosilicates, dissolved by citrate-dithionite and 2% Na₂CO₃ reagent (Wada 1977, 1980). As such, they are never directly observed and their infrared spectra are recorded only by a difference method, using samples before and after treatment. Parfitt et al. (1980) suggested that they may represent the Fe- or Al-rich part of the allophane wall or other defects, rather than representing a separate structure. Wada (1980) suggested that they are possibly polymeric hydroxy-aluminosilicate cations.

They are not generally reported in New Zealand tephros.

Halloysite

Halloysite is a kaolinite subgroup 1:1 layer silicate mineral. It occurs mainly as spherical, roughly concentrically-banded particles, or as tubes, scrolls, or curled flakes (Dixon 1977). Kirkman (1981) describes these morphologies as squat and elongate ellipsoids. Platy, tabular and disc-shaped halloysite has also been reported.

Halloysite can occur in two phases (Brown et al. 1978), one with two interlayer water molecules per formula unit (10Å spacing), and the other without (7Å spacing). The presence or absence of this interlayer water is one way of distinguishing hydrated halloysite from kaolinite (7Å).

The existence of these hydrated and dehydrated phases of halloysite has led to much confusion in the literature with respect to nomenclature. Brindley and Pedro (1975) have recommended that halloysite be referred to as either 10Å halloysite (equivalent to "hydrated halloysite" or "endellite") or 7Å halloysite (equivalent to "dehydrated halloysite" or "metahalloysite").

Halloysites have much larger unit particles than allophane (about 3000-6000Å cf. 50Å) and their properties and reactivities relate to this particle size as well as particle morphology, a relatively high degree of crystallinity, and a Si-O-Si outer surface in contrast with the Al-OH-Al surface of (Al:Si~2.0) allophanes (Theng et al. 1982).

In the South Auckland region halloysite is often the dominant clay mineral constituent in old or deeply buried tephras, such as the Hamilton Ash and Kauroa Ash beds (Table 1), and also occurs in varying amounts in other tephras older than about 10,000 years age and usually at depths of a metre or more below the modern land surface. It has been reported in Taupo Pumice and Mapara Tephra formations, aged 1,800 and 2,200 years respectively, buried beneath 2-2.5m of Taupo Pumice overburden (McIntosh 1979, 1980; see also genesis section below).

Secondary silica polymorphs

These include cristobalite, tridymite, and opaline silica (Table 3). Cristobalite and tridymite are crystalline and can be identified by their X-ray diffraction pattern, with characteristic d-spacings at 4.05Å and 4.08Å respectively (provided that the content of feldspar is low as it gives secondary peaks near these values; Wilding et al. 1977). Opaline silica occurs as laminar particles and is thought to be of pedogenic origin (Wada 1977, 1980; Shoji and Saigusa 1978; Henmi and Parfitt 1980). It appears to occur in the early stages of weathering

of tephtras in temperate climates, perhaps due to suppression of Al ion activity because of formation of Al-humus complexes (Henmi and Parfitt 1980).

Both cristobalite and tridymite can occur as primary or secondary minerals in tephtras (see references in Lowe 1981). Oxygen isotope ($^{18}O:^{16}O$) measurements may help determine the provenance and primary or secondary origin of these silica polymorphs, including quartz (e.g., Henderson et al. 1971, 1972; Jackson et al. 1977; Stewart et al. 1977). Significant amounts of secondary cristobalite occur in late Quaternary tephtras in the Waikato region (Hogg 1974; Lowe 1981). Here, the conditions of poor drainage, intense wetting and drying, and weathering always within the influence of the organic cycle have apparently promoted Si accumulation and Al-humus bonding, thereby limiting co-precipitation of Al and Si (Lowe 1981). Tridymite occurs in two beds in the Kauroa Ash Formation (Salter 1979) and possibly in the Rotongaio and Mapara tephtras (McIntosh 1979), but it is rarely reported in tephtra beds elsewhere (Yamada and Shoji 1977).

Humus and humus complexes

Potential reactions between humus and inorganic constituents are reviewed by Wada and Harward (1974) and Wada and Higashi (1976). Extraction and infrared spectroscopy analysis indicate that humus evolves from forms with a very low complexing ability for Al and Fe to forms that complex Al and Fe in the organic horizon (A_1) of soils; humus also interacts with allophane and imogolite in buried A_1 horizons (Wada 1980). The humus complexes are very stable, even when subjected to ultrasonic probe treatment and peroxidation (Fieldes 1957; Fieldes and Taylor 1961; Birrell and Fieldes 1968; Wada 1980). The complexes are best identified by selective chemical dissolution and difference infrared spectroscopy (Wada and Higashi 1976) or by differential thermal analysis (DTA) (Fieldes 1957; Jackson 1969; Satoh 1976; Schnitzer and Kodama 1977).

A deep (1m or so) accumulation of very dark to black humus is a striking feature of many Japanese, South American, and Mexican tephtra-derived soils which may have a C content of 5-10%, even up to 20% (Wada and Harward 1974; Shoji and Ono 1978). In Japan (where these soils were originally called "Ando" soils, giving the various soil classification terms such as Andosols, Andepts, and Andisols), these dark horizons are typically associated with a grass (especially pampas) vegetation (Wada and Harward 1974). Much smaller amounts of humus and humus complexes occur in New Zealand tephtras, and they have been studied less intensively

than have their Japanese counterparts. In fact, most studies have concentrated on removing the organic component by oxidation prior to clay analysis (see Part 2).

Poorly ordered iron and aluminium oxides and hydroxides

Iron and aluminium oxides and hydrous oxides, mostly with short range order, are common constituents of tephra clays and occur in several mineralogical forms as discrete particles or associated with surfaces of other minerals (Brown et al. 1978). Iron oxides are largely responsible for the red, orange, yellow, and brown colours in weathered tephras and soils and they also affect soil structure and fabric. With the exception of magnetite (or titanomagnetite) all are secondary weathering products and they tend to have variable properties due to differences in their environments of formation.

Terminology is frequently a problem. For example, ferrihydrite is now used to describe hydrous iron oxide phases previously called "amorphous ferric hydroxide" or "iron oxide gel". Other names are listed in Table 3.

Table 3. Names of naturally occurring hydroxides, oxyhydroxides and oxides of Fe, Al, Mn, Ti, and Si. After Brown et al. (1978, p. 135).

Iron		Aluminium		Manganese		Titanium		Silicon	
Goethite	$\alpha\text{-FeOOH}^*$	Diaspore	$\alpha\text{-AlOOH}$	Pyrolusite	MnO_2	Rutile	TiO_2	Quartz	SiO_2
Lepidocrocite	$\gamma\text{-FeOOH}$	Boehmite	$\gamma\text{-AlOOH}$	Birnessite		Brookite	TiO_2	Cristobalite	SiO_2
Akaganeite	$\beta\text{-FeOOH}$	Corundum	$\alpha\text{-Al}_2\text{O}_3$	Lithiophorite		Anatase	TiO_2	Tridymite	SiO_2
Hematite	$\alpha\text{-Fe}_2\text{O}_3$	Gibbsite	$\text{Al}(\text{OH})_3$	Hollandite				Opaline silica	SiO_2
Ilmenite	FeTiO_3	Nordstrandite	$\text{Al}(\text{OH})_3$	Todorokite					
Maghemite	$\gamma\text{-Fe}_2\text{O}_3$	Bayerite	$\text{Al}(\text{OH})_3$						
Magnetite	Fe_3O_4								
Ferrihydrite	$\text{Fe}_5\text{HO}_8 \cdot 4\text{H}_2\text{O}$								

* Greek letters are used to denote different polymorphs of the same chemical constitution. The γ -forms have structures based on cubic close packing of anions whereas the α -forms are based on hexagonally close-packed anions.

The most commonly used methods for detection of the oxides and hydroxides are XRD and DTA, although infrared and Mössbauer spectroscopy are increasingly being employed (e.g., Childs et al. 1979). Because of their short range order and often low abundances it is frequently necessary to concentrate the materials, for example by particle size separation of the very fine clay fractions or by dissolution of other minerals. X-ray patterns are usually weak or very weak; diagnostic characteristics of some iron oxide minerals are given in Table 4. A quick field test for free ferrous iron and ferric-organic complexes in soils has recently been developed by Childs (1981).

Table 4. Diagnostic characteristics of some iron oxide minerals. After Schwertmann and Taylor (1977, p. 147).

	Hematite	Maghemite	Magnetite	Goethite	Lepidocrocite	Ferrihydrite
X-ray spacings (Å)	2.70,3.68 2.52	2.52,2.95	2.53,2.97	4.18,2.69 2.45	6.26,3.29,2.47	2.50,2.20, 1.97,1.71, 1.50
DTA peaks (°C)	Nil	Exotherm 600-800	Nil ¹	Endotherm 280-400	Endotherm 300-350, exotherm 370-500	Endotherm 150, loss of adsorbed H ₂ O
IR spectroscopic peaks (cm ⁻¹)	345,470, 540	400,450, 570,590, 630	400,590	890,797	1026,1161,753	Nil ²
Usual crystal morphology	Hexagonal plates	Cubes	Cubes	Fibrous ³ or acicular	Laths, serrated elongated plates	Spherical
Colour (Munsell)	Bright red 5R-2.5YR	Reddish- brown	Black	Yellowish- brown 7.5YR-10YR	Orange 5YR-7.5YR	Reddish-brown 5YR-7.5YR

¹ Magnetite converts via maghemite or directly to hematite, depending on particle size

² Russell (1979) gives IR evidence of structural hydroxyl groups

³ Reported by Nakai and Yoshinaga (1980)

Other useful references for these minerals include Wada and Higashi (1976), Hsu (1977), Schwertmann and Taylor (1977), Brown et al. (1978), Schwertmann (1979), Nakai and Yoshinaga (1980), and Schwertmann et al. (1982).

In studies on tephra materials in the Waikato region, goethite and lepidocrocite have been identified in Horotiu and Te Kowhai soils derived from tephra and volcanogenic alluvium (McQueen 1975). Subordinate gibbsite occurs in both the Hamilton Ash (Taylor 1933; Tonkin 1970; Hogg 1974) and the Kauroa Ash (Salter 1979; Kirkman 1980a), and lepidocrocite occurs in two beds in Kauroa Ash (Kirkman 1980a). Gibbsite is reported to occur in the Egmont loam profile derived from late Quaternary andesitic tephras and "tephric loess" (Russell et al. 1981) but appears to be absent in andesitic tephras and paleosols in western Taranaki (Kirkman 1980b). Traces (<1%) have recently been reported for clays derived from mixed rhyolitic and andesitic late Quaternary tephras in the Waikato region by Lowe (1981) and Parfitt et al. (1983). Iron-manganese concretions occur frequently in tephra materials weathering under gleying or wetting and drying conditions in the Waikato region (McQueen 1975; Lowe 1981).

2:1 and 2:1:1 minerals

These include minerals such as vermiculite, smectite, illite, and chlorite (Hume and Nelson 1982). Their occurrence in tephras, sometimes in substantial amounts, has been almost exclusively reported from Japanese studies (e.g., Shoji and Saigusa 1977; Mizota 1978; Yamada et al. 1978; Shoji et al. 1981) but they have also been reported from studies in Colombia by Calhoun et al. (1972) and Cortes and Franzmeier (1972a, b), and elsewhere. Some Japanese workers suggest that the 2:1 clays, which are most common in dacitic and andesitic tephras, form from "amorphous" minerals, especially K-enriched volcanic glass, and possibly coevally with the formation of opaline silica or quartz under conditions characterised by excess silica and a low allophane content (Wada and Aomine 1973; Tokashiki and Wada 1975; Wada 1977; Kurashima et al. 1981; Shoji et al. 1981). Shoji et al. (1981) determined that in particular the mobilities of SiO₂, MgO, and K₂O were strongly related to the weathering of volcanic glass and the abundant formation of 2:1 minerals. Other explanations, all controversial, include: the transformation of mafic minerals (e.g., pyroxenes, amphiboles, and micas) by weathering; the incorporation of 'exotic' layer silicates into volcanic ash during eruption; the incorporation of layer silicates from underlying paleosols by mixing when the tephra

deposit is thin; and the addition of layer silicates as loess (Dudas and Harward 1975b; Mizota 1976; Wada 1980; Mizota and Takahashi 1982; plus Japanese studies referred to above).

In New Zealand, 2:1 minerals are rarely reported in tephra (Birrell and Pullar 1973; Kirkman 1975; McIntosh 1979) but are common in soils formed on loess derived predominantly from mica-bearing quartzo-feldspathic sedimentary rocks and alluvium, which also contain admixed accessions of tephra. Thus most New Zealand workers are suspicious of the pedogenic pathways suggested by the Japanese to account for the occurrence of 2:1 clays in tephra in Japan, and prefer a "loessic contamination" explanation (e.g., Stewart et al. 1977; Russell et al. 1981).

Lowe (1981) detected (by XRD) a 14\AA trioctahedral clay-vermiculite in clay fractions from a late Quaternary tephra composite in the Waikato region. He ascribed this to the weathering of biotite (derived from biotite-containing air-fall tephra) under special site conditions which favoured complete release of K (and Mg) from interlayers. A high concentration of Si and low concentration of Al is required (Buol et al. 1973) and the associated occurrence of authigenic cristobalite with the clay-vermiculite demonstrated that this condition was met (cf. Colhoun et al. 1972). That clay-vermiculite does not seem to occur in tephra of similar composition (i.e., biotite-rich) and origin is attributed to unsuitable site weathering conditions. Hogg (1979) identified sand-sized (macro-) vermiculite as a replacement product of biotite flakes in a paleosol developed on Rotoehu Ash in the Coromandel region, and a "vermiculite-intergrade" mineral in the H1 bed of Hamilton Ash (Hogg 1974). A smectite-vermiculite intergrade occurs in several beds in the Kauroa Ash Formation (Salter 1979), and traces of smectite have recently been identified in highly weathered, iron-rich, short range order clays derived from a strongly weathered distal ignimbrite in the Waikato region (D.J. Lowe, unpublished data).

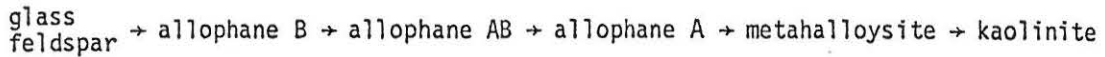
Residual primary minerals

Quartz and feldspar may occur in small amounts in clay fractions and, if present in sufficient quantities, are readily identified by XRD (Hume and Nelson 1982). Their occurrence in South Auckland tephra clay fractions is common.

Formation and transformation of clay minerals

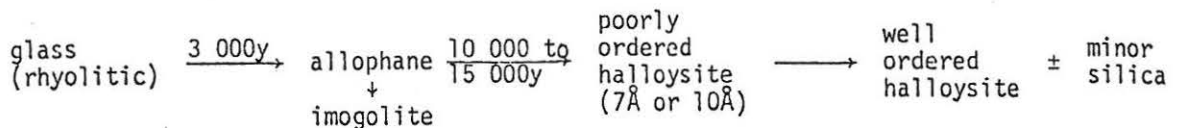
Weathering sequences

After the milestone paper of Fieldes and Swindale (1954), Fieldes (1955) published the following weathering sequence for tephra materials:



Since then, this sequence has been examined closely, particularly by New Zealand and Japanese workers, and modified. It has been suggested that allophane B = glass + opaline silica or cristobalite, allophane A = 'proto-imogolite' allophane or allophane, and allophane AB = a mixture of these components. Consequently, these allophane subdivisions (A, B, AB), and kaolinite, are probably best excluded from the sequence (Fieldes and Claridge 1975; Campbell et al. 1977; Nagasawa 1978a; Parfitt 1980a).

A widely adopted weathering sequence for rhyolitic tephra materials (e.g., Kirkman 1975, 1976, 1978, 1981, 1981a; Wada 1977; Sudo and Shimoda 1978) is:



From studies of the relative amounts of allophane and halloysite in rhyolitic tephra or associated paleosols, an age-related transition for allophane to halloysite has been estimated from about 10,000 to 15,000 y for New Zealand and 5,000 to 10,000 y in Japan in humid temperate conditions (Fig. 3). The relative abundance of 2:1 and 2:1:1 type clays, allophane-like constituents, gibbsite, and humus complexes in Fig. 3, which is derived from analyses of tephra in Japan, is in marked contrast to their absence or only sparse occurrence in New Zealand tephra.

That many of the volcanic glass- or feldspar-derived minerals, particularly allophane, imogolite, and halloysite, coexist in the same deposit, and also appear able to persist for long time periods (e.g., certain allophane-rich beds in the Hamilton Ash and Kauroa Ash Formations), implies that compositional and/or environmental effects (i.e., site weathering conditions) have possibly been underestimated in favour of the established time-based weathering sequence (Parfitt et al. 1982). Indeed, McIntosh (1979, 1980) reports the occurrence of significant amounts of authigenic halloysite in tephra in New Zealand

aged less than 2,500 y.

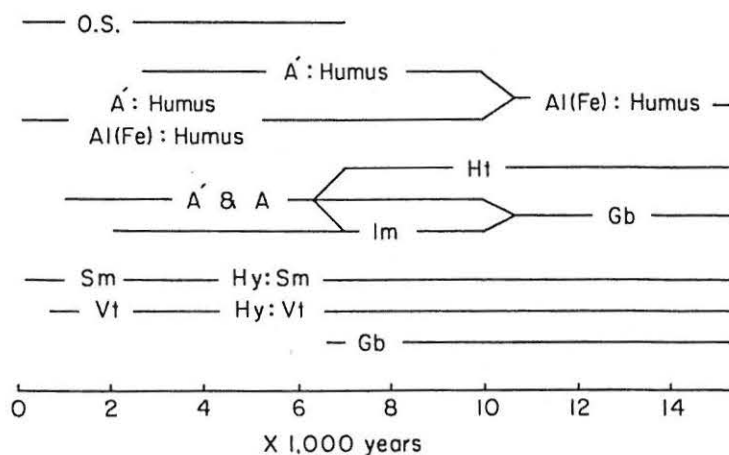
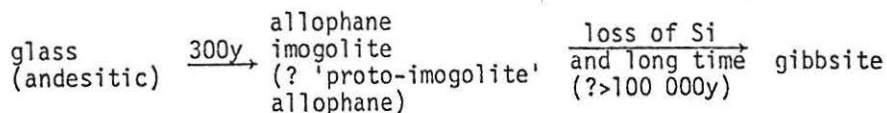


Fig. 3. Formation and transformation of clay minerals and their organic complexes in soils developed from tephras in humid, temperate climatic zones in Japan. A = allophane; A' = allophane-like constituents; Al(Fe) = sesquioxides; Ch = chlorite; Gb = gibbsite; Ht = halloysite; Im = imogolite; Sm = smectite; Hy-Sm = hydroxy interlayered smectite; O.S. = opaline silica; Vt = vermiculite; Hy-Vt = hydroxy interlayered vermiculite. Horizontal bars indicate approximate duration of the various constituents. From Wada (1977, p. 620).

Andesitic glass, with an intrinsically greater Al:Si ratio than rhyolitic glass, weathers much more rapidly and with marked loss of SiO₂ and mobile cations (Neall 1977; Kirkman and McHardy 1980). Kirkman and McHardy (1980) and Kirkman (1981a) concluded that the structure and chemical composition of allophane, and hence its behaviour and persistence, are governed chiefly by the chemical composition and bonding characteristics of the parent glass. This conclusion supports a previous study by Trichet (1969) involving laboratory leaching of glasses of differing compositions.

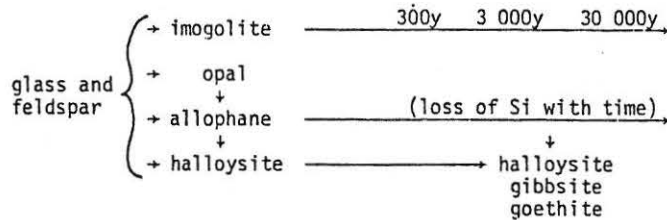
A weathering sequence for andesitic glass suggests that under humid temperate conditions allophane and possibly imogolite are stable for long time periods, and also predicts the ultimate formation of gibbsite (Kirkman 1978, 1980b, 1981, 1981a; Kirkman and McHardy 1980; Parfitt et al. 1982):



Gibbsite, however, generally occurs in minor amounts in weathered tephras in New Zealand (Fieldes and Taylor 1961; Hogg 1974; Salter 1979; Kirkman 1980a; Lowe 1981; Parfitt et al. 1983), presumably because of either unfavourable site conditions which essentially minimise desilication (Schwertmann 1979; Farmer et al. 1979; Kirkman 1980b) or possibly the presence of additional inhibitors such as iron oxide gels

(Kirkman and McHardy 1980). In contrast, significant amounts of gibbsite occur in clay fractions from tephras older than about 3,000-6,000y and weathering under humid, temperate conditions in Japan (Fig. 3; Mizota 1976). This, together with other evidence (e.g., Eswaran and de Coninck 1971; Macias Vazquez 1981), indicates that gibbsite formation is not restricted to a long period, nor is it necessarily dependent upon hot-humid (tropical) climatic conditions.

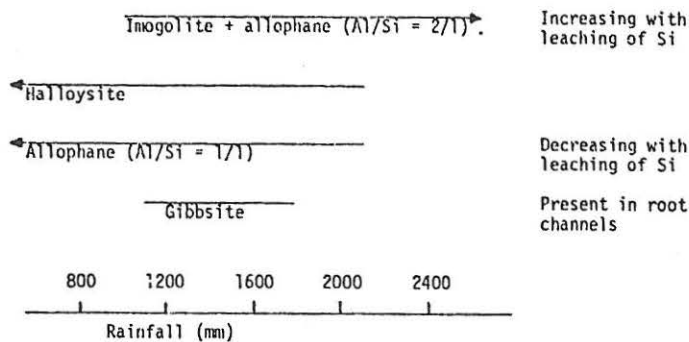
In a study of clay minerals formed in dacitic and andesitic tephra-derived soils under tropical conditions in Papua New Guinea, Parfitt (1975) suggested the following tentative weathering scheme:



He noted that the glass phase weathers rapidly and can form stable imogolite or allophane, as in Kirkman's scheme above. Halloysite may form directly from feldspars or from allophane, depending on the leaching and biotic conditions in the deposit. Gibbsite was found mainly in the older beds (30,000y) together with allophane, which tends to support the sequence postulated by Kirkman, but also occurred in much younger beds as shown above (see also Fig. 3).

The formation of gibbsite thus appears to rely on specific Si-deficient microenvironmental conditions, possibly together with an Al-rich primary mineral composition.

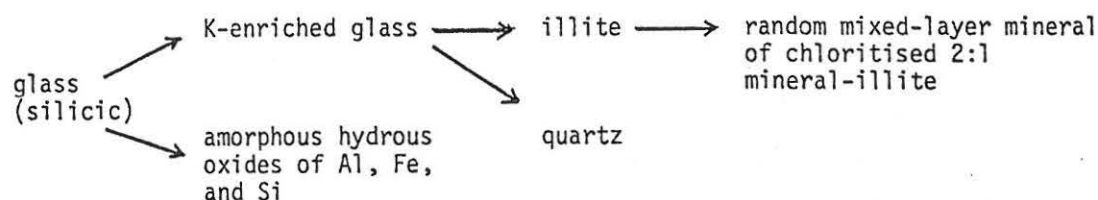
A weathering scheme which emphasises leaching (rainfall) and Si concentration more than time in clay mineral transformations for rhyolitic tephras aged between 2,000 and 100,000 years in New Zealand has been proposed by Parfitt et al. (1983) from studies in the Waikato region:



This work refines previous ideas on rainfall-clay mineral relationships postulated first by Taylor (1933) and later Ward (1967). It is

innovative in that it shows clearly the effects of environmental conditions, rather than time, on clay mineral genesis. Parallel studies by Lowe (1981) and Lowe and Gibbs (1981) in the region have emphasised the effect of seasonal distribution of rainfall (i.e., wetting and drying) in addition to the total amount of rainfall.

A markedly different weathering sequence has been determined by Shoji et al. (1981) from work in Japan on rhyolitic and dacitic tephra-derived topsoils weathering under humid temperate conditions. Their postulated sequence is:



They thus suggest that the dominant source of 2:1 type clay minerals frequently observed in Japanese tephra-derived soils is illite formed by alteration of volcanic glass in a solid-state reaction. That preferential retention of potassium occurs in the volcanic glass has been demonstrated by Yamada and Shoji (1982).

These workers also determined the facility of release of elements from the parent tephra materials as: $\text{CaO}, \text{Na}_2\text{O} > \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{MgO} > \text{SiO}_2, \text{K}_2\text{O}$, and a mobility sequence of the major elements during pedochemical weathering (Kurashima et al. 1981; Shoji et al. 1981) as: $\text{CaO}, \text{Na}_2\text{O} > \text{SiO}_2 > \text{MgO} > \text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3, \text{K}_2\text{O}$. These results differ from previous studies in the order of mobilities of SiO_2, MgO , and K_2O ; in particular, SiO_2 has the highest mobility of the three elements whereas normally it is shown to have the lowest (Kurashima et al. 1981). Overall, the mobility sequence indicates that loss by leaching is relatively large for CaO and Na_2O and small for SiO_2 , where $\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$, and K_2O accumulate relative to the chemical composition of fresh tephra.

An alternative viewpoint for the origin of the 2:1 type minerals in the Japanese soils is that they derive from continental aerosolic dusts carried by westerly winds. Evidence for this possibility comes from distinctive $^{18}\text{O}:^{16}\text{O}$ ratios of fine, silt-sized quartz particles isolated from various soils in Japan (Mizota 1982).

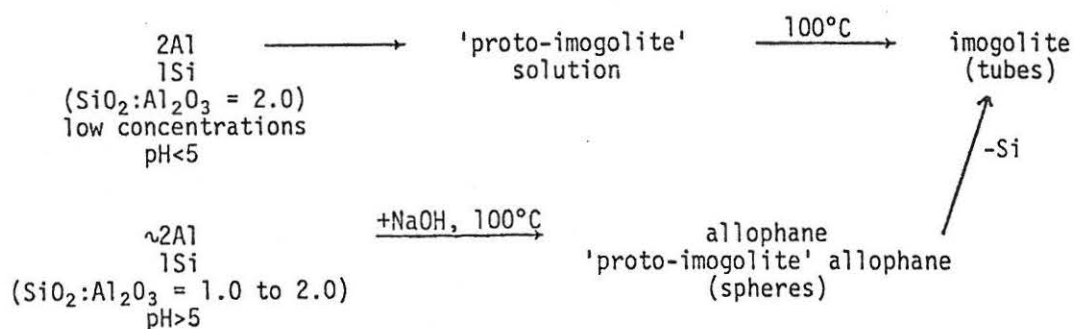
In conclusion, the framework of thinking in examining weathering sequences now tends to favour separate formation pathways for the various minerals according to their chemical composition and to site weathering conditions, particularly as they affect the concentration of Si in

solution and the availability of Al, and the opportunity for co-precipitation of these. Second, short range order minerals such as allophane, imogolite, and 'proto-imogolite' allophane are, in some cases, possibly transformation reaction end-points rather than short-lived transition products and are able to persist for long periods of time if conditions are favourable. Other clay minerals such as halloysite and gibbsite, often envisaged as time-dependent transformation products of precursory allophane and imogolite, are apparently able to form directly from the dissolution products of primary (or secondary) minerals depending mainly on whether the conditions favour resilication or desilication.

Genesis

The proposed mechanisms and conditions for formation of allophanic short range order minerals and halloysite from tephric deposits are detailed by Wada and Harward (1974), Wada (1977, 1978, 1980), Nagasawa (1978a), and Brown et al. (1978), among others. Recent work characterising New Zealand allophanes and halloysites is reported in Parfitt et al. (1980, 1982), Parfitt and Henmi (1980), Kirkman (1977, 1981), and Theng et al. (1982).

Studies involving synthesis of allophane and imogolite by Scottish and Japanese workers are reported in Wada (1980), and summarised as:



Allophane requires a neutral or alkaline pH to give maximum Al in 4-fold coordination, whereas imogolite requires an acid pH to maintain Al in 6-fold coordination in contact with monomeric silica (Brown et al. 1978). These differences in conditions for synthesis and the concomitant co-existence of allophane and imogolite are satisfied by observations on naturally-occurring counterparts. It appears that in tephra deposits allophane forms inside weathered glass or pumice fragments in which hydrolysis of the glass proceeds at a high Si concentration and pH. Imogolite forms outside, possibly by alteration of allophane exposed to external solutions of lower Si concentration and lower pH (<5), or by precipitation from such solutions (i.e., Al and Si form a soluble

complex (proto-imogolite) whose solutions are stable at pH less than 5; Farmer and Fraser 1979; Farmer et al. 1979).

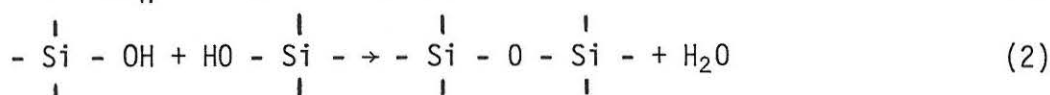
Gibbsite may also coexist closely with allophane and imogolite, it being associated with certain minerals in a rock fragment whilst the latter two minerals, as discussed above, occur actually within or adjacent to the glass or pumice fragment (Wada and Matsubara 1968; Brown et al. 1978). Gibbsite can apparently form at any stage of weathering given that an environment with <1 ppm SiO_2 in solution exists to prevent Al-silicate formation (Schwertmann 1979), as in highly leached tephra sequences.

The original proposal of Fieldes (1966) that halloysite essentially "crystallised" through increased cross-linkage of random aluminosilicate gels through (seasonal) dehydration is in large part misleading. It is now known that allophane and related minerals are not "random gels" and have short range order, and that halloysite may crystallise directly from dissolution products of glass or feldspar (i.e., without an intermediate or transition allophane phase). However, the apparent relationship between rainfall distribution and degree of leaching with the occurrence of a particular mineral type has been recently re-considered in transformation pathways by Parfitt et al. (1982). Allophane, allophane-like constituents, imogolite, and 'proto-imogolite' allophane generally occur where rainfall (i.e., leaching) is moderate or high (Wada and Harward 1974; Birrell et al. 1977; Wada 1980) and halloysite and allophane (Al:Si \sim 1.0) where rainfall is lower (Miehlich 1981; Benny et al. 1982; Parfitt et al. 1983). The principal effect of the rainfall distribution, hence degree of leaching, is in governing the relative proportions of the main chemical constituents, SiO_2 and Al_2O_3 , from which either allophane and imogolite or halloysite form. Parfitt et al. (1982) report that current evidence suggests that Al-rich allophane (with a 'proto-imogolite' structure) does not normally alter to halloysite as Si tetrahedra are considered to occur on the interior surface of the hollow allophane spherules as isolated SiO_3OH groups with apices directed away from outer gibbsitic units (Fig. 2; Farmer and Fraser 1979), the reverse of the kaolin structure. Thus alteration to halloysite would necessitate the allophane effectively turning "inside out" by passing through a solution phase with concomitant enrichment with polymerised silica.

Allophane and other short range order aluminosilicates may transform, via solution, to halloysite or gibbsite depending on whether the environment favours resilication (for halloysite) or desilication (for

gibbsite) (Parfitt 1975; Wada 1977; Saigusa et al. 1978; Mielich 1981). Under a high leaching regime, and low pH, SiO₂ and mobile cations are rapidly lost. Hence the formation of allophane (and possibly gibbsite), with an Al:Si ratio around 2 or more (i.e., SiO₂:Al₂O₃ = 1.0), is preferential to the formation of halloysite with an Al:Si ratio nearer 1 (SiO₂:Al₂O₃ = 2.0).

Clearly, as mentioned earlier, the Al:Si composition of the primary minerals will partly affect this resilication-desilication balance. The thickness of depositional overburden may also have an effect in that a thick sequence (>~2m) potentially provides a silica-rich environment for a buried tephra and hence favours the formation of halloysite (Wada 1977; Shoji and Saigusa 1977; Saigusa et al. 1978; Sudo and Shimoda 1978; McIntosh 1980). Similarly, poor drainage and hence minimal loss of soluble silica favours halloysite formation (Dudas and Harward 1975a). Lowe (1981) postulated that under poor drainage conditions and in an intense wetting and drying regime which promotes silica accumulation, secondary cristobalite, together with halloysite, forms in preference to allophane. There is some evidence that Al-humus complexing also favours the formation of secondary silica as cristobalite (Lowe 1981) or opaline silica (Wada and Higashi 1976; Shoji and Saigusa 1978) in that it inhibits co-precipitation of active Al and Si. The silica dissolves from glass (or from biogenic opal) and precipitates through seasonal concentration (by dehydration) coupled with Al-humus complexing. A possible method of crystal growth is by the uniting of tetrahedra and elimination of water (Jones and Segnit 1972, p. 419):



The role of living plants in determining monosilicic acid concentration, and biogenic opal formation, is discussed by Wilding and Drees (1971), Parfitt (1975), Wilding et al. (1977), Claridge and Weatherhead (1978), and Parfitt et al. (1983). Depending on conditions, uptake by plant cells of Si in solution to form biogenic opal and the drying and oxidising effect of plant roots may help formation of allophane (Al:Si~2.0) and gibbsite (as root pseudomorphs, for example; Hogg 1974). Alternatively, biogenic opal may be dissolved (under humid conditions) and either leached or precipitated with available Al to form allophane (Parfitt 1975), or the redissolved silica may form another polymorph such as cristobalite, as discussed above (equations 1 and 2; Lowe 1981).

The morphological forms of halloysite (i.e., as spheres or tubes, etc.) are possibly directly related to primary mineralogy; spherical halloysite may originate from glass, tubular halloysite from feldspar (e.g., studies by Parham 1969; Ngasawa and Miyazaki 1976; Violante and Violante 1977; Tazaki 1979; Kirkman and Pullar 1978; Kirkman 1981). Various mechanisms have been proposed to account for the different forms (e.g., see Dixon and McKee 1974; Kirkman 1977, 1981, 1981a; Sudo and Yotsumoto 1977; Kohyama et al. 1978; Wada et al. 1977; Salter 1979).

The occurrences and transformations of iron oxide minerals are summarised in Schwertmann and Taylor (1977) and Schwertmann (1979).

PART 2 : METHODS OF ANALYSIS OF CLAY FRACTIONS

Normally, no one technique is adequate alone to determine the clay mineralogy of tephric deposits, especially in quantitative studies of samples containing both crystalline and short range order materials. Hence several methods must be applied. The most useful method, at least initially, is X-ray diffraction (XRD). This has quantitative limitations in tephra studies because of their often high proportion of short range order (hence X-ray amorphous) clays, with widely varying chemical compositions.

Methods used in addition to XRD in tephra clay mineral studies include thermal analyses (differential (DTA) or thermogravimetric), electron microscopy (scanning (SEM) and transmission (TEM)), electron diffraction, infrared (IR) and Mössbauer spectroscopy, chemical analyses, dissolution analyses, sodium fluoride (NaF) reactivities, phosphate and chloride adsorption, X-ray fluorescence (XRF) spectroscopy, electric charge characterisation, gas chromatography, electron paramagnetic analysis, and surface area and porosity measurements. Several of these methods are highly specialised and are not discussed further in this report (see instead, e.g., Fripiat 1982). The methods described below are those most commonly used at the University of Waikato.

General sample preparation and selection of analytical methods

It is particularly important that whole tephra samples are not air dried prior to analysis. They should be maintained in field-moist condition until analysis is under way. This is especially important if particle-size determinations are being carried out in conjunction with the clay separation. Storage at 4°C in sealed plastic bags minimises irreversible alteration of the clay components.

Dry grinding procedures should be minimised because of various effects on the structure and properties of clay minerals. Henmi and Yoshinaga (1981) report that imogolite, for example, is very susceptible to alteration by prolonged grinding (more than a few minutes) which causes disruption of Si-O-Al bonds, polymerisation of the SiO₂ component released and loss of structural OH groups, and finally complete structural breakdown.

Sample preparation for most analytical methods usually involves suspension in distilled water, dispersion, and fractionation into <2 μ m and/or <1 μ m size fractions. Which of these (or other) size fractions is investigated depends partly on the nature of the project. In a general study in which the analysis of the clay fraction is but one part,

examination of the $<2\mu\text{m}$ fraction is normally sufficient. A more detailed study biased towards clay fraction composition in itself would usually necessitate examination of at least some selected $<1\mu\text{m}$ fractions for comparative purposes. Alternatively, analysis of the $<1\mu\text{m}$ clay fraction alone may be advisable as it tends to reflect mainly authigenic (secondary) minerals, whereas the $<2\mu\text{m}$ fraction often contains glass (residual) which is difficult to distinguish from allophane or other short range order minerals (e.g., see Kirkman 1975; McIntosh 1979). Hume and Nelson (1982) have emphasised the importance of size segregation of crystalline clay mineral species generally in sedimentary deposits from the South Auckland region.

Complete dispersion of tephric samples is often difficult to achieve, but the best method appears to be ultrasonication for 5-10 min. (see Lowe 1981, p. 372). Chemical treatment to alter the pH of the suspension is usually required, but should not be used if chemical dissolution studies on specific clay components are envisaged. Unless samples contain a very high proportion of organic matter, peroxidation with H_2O_2 , or deferration by dithionite (CBD) extraction, should not be routinely carried out because of degradation and dissolution of constituent clay materials (Lowe 1981). However, peroxidation or deferration may be necessary as an aid in dispersion, and for adequate analytical resolution (e.g., Hogg 1974; Salter 1979; Brewster 1980).

Fractionation can be achieved by sedimentation, filtration, or centrifuging. The easiest method is probably to decant, or extract by pipette, then filter the $<2\mu\text{m}$ or $<1\mu\text{m}$ fraction from the appropriate top part of a mud suspension in a 1l cylinder after routine particle size analysis (e.g., as in Folk 1968, and various Earth Sciences Department handouts on laboratory methods for sedimentology and soils courses; a centrifuging method appropriate for University of Waikato equipment is given in Lowe 1981, p. 134). Resultant clay-sized suspensions are then flocculated and saturated with either a Mg or K salt (such as MgCl_2). This is because most of the literature reports clay mineralogical analyses as either Mg- or K-saturated clay for diagnostic purposes (Rich and Barnhisel 1977). The saturated clay must be washed several times with distilled water, and either refiltrated or re-centrifuged, to remove excess salt.

The fate of the clay separate then depends on the analytical method being undertaken, which in turn relates chiefly to the nature of the materials under study and to the actual purpose of the study. For example, it depends on whether the study is general or specialised,

Table 5. General guide to selection of methods for analysing particular tephric clay materials based on the rate at which numbers of samples are able to be processed and whether results are qualitative or quantitative. The table is a subjective, preliminary guide for the non-specialist worker and applies to the general case only. Each of the methods outlined in Part 2 of this manual should be consulted, if even briefly, prior to beginning analysis. For the specialist, references containing further details of method and application are given under each method section. Examples of the use of the table are: A, 4 = the method is fast but usually gives only qualitative results; B, 1 = the method is moderately fast and accurate absolute amounts of the clay constituent under investigation can be determined; and C, 4 = the method is relatively time consuming and gives qualitative results only.

COMPONENTS	XRD	IR	DTA	SEM	TEM	NaF	CHEM. DISS. Δ	S. AREA
Allophane	-	A,2	B,2	C,4	D,4	A,3	C,1	C,3
Imogolite	-	A,2	B,2	C,2	D,2	A,3	C,1	C,3
'Proto-imogolite' allophane	-	A,2	B,2	C,4	D,4	A,3	C,1	C,3
Allophane-like constituents	-	A,4	-	-	-	-	C,4	-
Halloysite	A,3 [†]	A,2	B,2	C,4	D,4	-	C,3	C,3
Secondary silica polymorphs	A,4 [†]	A,4	-	-	-	-	C,4	-
Humus, humus complexes	-	-	B,3	-	-	-	C,2	-
Fe and Al oxides, hydroxides	B,4 ^{††}	A,4	B,3	-	D,4	-	C,3	-
2:1, 2:1:1 minerals	A,4 [†]	-	B,4	-	-	-	C,3	-
Residual primary minerals	A,3 [†]	A,4	-	-	-	-	-	-

Abbreviations for analytical techniques: XRD, X-ray diffraction; IR, Infrared; DTA, Differential thermal analysis; SEM and TEM, Scanning and Transmission electronmicroscope respectively; NaF, Sodium fluoride reactivity; CHEM. DISS., Chemical dissolution; S. AREA, Surface area measurements.

Capital letters refer to numbers of samples able to be processed: Many $\xrightarrow{\text{A}}$ $\xrightarrow{\text{B}}$ $\xrightarrow{\text{C}}$ $\xrightarrow{\text{D}}$ Few
 Numbers refer to degree of 'quantification' of results: Quantitative $\xrightarrow{1}$ $\xrightarrow{2}$ $\xrightarrow{3}$ $\xrightarrow{4}$ Qualitative only

- = not generally applicable or only in a 'negative' sense (e.g., low NaF reactivity implies a high proportion of layer silicate clays due to low Al-OH activity; similarly, XRD of allophane and imogolite gives a negative result, which in itself is often useful, but does not allow distinction between glass and allophane).

+ Degree of quantification depends partly on the proportion of short range order minerals present as these, through absorption of X-rays, tend to suppress the peaks of the crystalline minerals (Hume and Nelson 1982).

†† Method depends on degree of crystallinity of samples, and samples usually require extraordinary pretreatment.

Δ These methods, although reasonable routine, usually require comparison of materials before and after treatments using differential IR and XRD methods, hence are ranked C rather than B.

whether qualitative or quantitative results are required, the number of samples to be analysed, and the amount of time available for the investigation. A simple, subjective attempt to help guide the non-specialist novice clay mineralogist determining which methods to use is given in Table 5.

Some of the analytical methods available, such as XRD and IR, are relatively rapid and enable a large number of samples (50-100 or so), once prepared, to be run in a routine manner. XRD in particular, however, is largely qualitative or at best semi-quantitative for crystalline minerals (e.g., see Hume and Nelson 1982) and gives a negative result for short range order materials which are X-ray amorphous. Other methods, such as DTA and TEM, require more preparation and analytical time per sample and hence, in general, considerably fewer and carefully selected samples should be analysed. If a study is a specialised one on, say, clay mineral morphology, the EM methods are likely to be paramount but, because of the interpretative difficulties associated with these techniques, additional methods such as XRD or DTA are essential. Similarly, an investigation of the chemical structure of clays would certainly employ the IR method, while one involving soil genesis and mapping might be advised to measure NaF reactivity since this is one of the criteria used in some soil classification systems. However, it is re-emphasised that any one technique alone is unlikely to provide a definitive clay mineralogical analysis of tephric materials.

Where short range order clays are being examined and semi-quantitative results are required, DTA is appropriate for a limited number (say 20 or so) of selected samples; results necessitating greater "accuracy" should utilise chemical dissolution methods, possibly together with IR analysis.

Finally, it should be remembered that the interpretation and subsequent presentation of results normally takes at least 2-3 times longer than the time to simply prepare and analyse the samples. Clay mineralogical analysis and interpretation requires considerable judgment at every step of the way.

X-ray diffraction (XRD)

Preparation

A good review account of sample preparation is given in Rich and Barnhisel (1977). Oriented paste mounts of the Mg- or K-saturated clays are made using the smear-on-glass-slide (SOGS) method (Thiesen and Harward 1962; Gibbs 1971; Hume and Nelson 1982) which avoids size-

segregation (Schoen et al. 1972; Hume 1978). Dropper-on-glass-slide (DOGS) mounts containing allophanic materials often crack and peel from the slide upon drying. Some cracking of the SOGS paste may occur due to the short range order constituents (Cortes and Franzmeier 1972a) and/or high Fe content (Hume 1978), but it is usually negligible compared with that of DOGS mounts. The mounted specimens may be air dried (under cover to avoid dust contamination), usually for about 24h. Alternatively, slides may be dried slowly over distilled water (i.e., 100% r.h.) for 24 to 72h. The latter procedure has been adopted to prevent low temperature dehydration of 10Å halloysite (Nagasawa 1969, 1978b). This is important in some studies (Lowe 1981) as (a) it enables determination of the halloysite component in its actual 'field' hydration state; and (b) unequivocal distinction between halloysite and kaolinite species by XRD is difficult if all the halloysite is in the dehydrated (7Å) form. The dehydration process is irreversible in most circumstances (Grim 1968; Kirkman and Pullar 1978), hence rehydration of the 7Å halloysite to 10Å halloysite during this treatment is unlikely.

Sample mounts should be X-rayed immediately upon drying, since prolonged dehydration at ambient temperature reduces the size of the first order reflections (Lowe 1981). This effect was noted also by Nagasawa and Miyazaki (1976) and Kirkman and Pullar (1978) who overcame it by X-raying moist clay mounts.

Procedure and mineral identification

Specimens are scanned from 3° to 28°2θ at 2°2θ min⁻¹, using the instrument settings shown in Table 6. Clay minerals are identified

Table 6. Instrument settings for XRD analysis at University of Waikato using a Philips X-ray diffraction spectrometer system (CuKα radiation, λ = 1.5418Å). (See also Hume and Nelson 1982).

kV	30	High voltage	56%
mA	13	Window level	L-α
Time constant	4	Lower level	17%
Attenuation	2	Oscillator	High
Chart speed	20 mm. min ⁻¹	Divergence slit	1°
Scanning speed	2° 2θ min ⁻¹	Scatter slit	1 mm
Rate meter setting (RMS)	400 or 1000 cps		

by the position and movement of mainly their (001) reflections following heat and glycolation treatments (Table 7; see also Hume and Nelson 1982, fig. 8, and Brindley and Brown (1980) for more details).

Allophane, imogolite, and glass lack diffraction patterns, apart from occasional poorly defined background maxima commonly associated with X-ray amorphous materials (e.g., Campbell et al. 1977; Okada et al.

Table 7. Diagnostic XRD peak positions for identification of oriented tephra-derived Mg-clays and associated minerals. Compiled from various sources (after Lowe 1981, p. 178).

Mg-clay	Air-dried in humid atmosphere 24-72h. (100% r.h.)		Glycolated in ethylene glycol vapour 12h.	Heated 110°C 1h.	Heated 550°C 1h.
	d(001) in Å	c.2θ°			
Allophane (± imogolite)	X-ray amorphous ¹				
Halloysite (10Å)	9.8-10.2	8.8	Slight expansion to 10.6Å	Dehydrates to 7.0-7.3Å	Becomes X-ray amorphous
Halloysite (7Å) (or Kaolinite)	7.0-7.3	12.3	No change	No change; increases if 10Å halloysite present before heating	Becomes X-ray amorphous
Vermiculite ²	14.0-14.2	6.2	No change	Partial or complete dehydration from 14Å to 10Å (usually 11-12Å)	All to 10Å
Gibbsite ³	4.85 (002)	18.3	No change		
All of the above crystalline clays	(i) 3.5-3.6 (002, 003 or 004)	25.0	No change	No change [Peak increases if halloysite present]	Becomes X-ray amorphous
	[Larger peak if halloysite present] (ii) 4.4 (021)	19.9	No change	No change	Becomes X-ray amorphous
<u>Other Minerals⁴</u>					
Quartz	3.3 (101)	26.7			
Feldspars	3.18-3.2 (002, 202, 040)	27.5-28.4			
Cristobalite ⁵	4.05 (101)	21.9			
Tridymite	4.08 (101)	21.7			
Micas ⁶	10.0 (001)	8.8	No change	Persists at 10Å	Persists at 10Å

¹ Apart from broad background maxima (see text).

² Heat treatments may be inconclusive if micas-illites present (see 6 below).

³ Will not be detected unless >5% (or special pretreatments made).

⁴ Iron oxide minerals given in Table 4; for other minerals refer to Hume and Nelson (1982)

⁵ Positively identified only if primary feldspar peaks are low.

⁶ Identification can be uncertain as may have other 10Å minerals present in sample, both untreated (e.g., 10Å halloysite) and heat treated (e.g., clay-vermiculite). See also Brindley and Brown (1980) and Hume and Nelson (1982).

1975) (Fig. 4a). Crystalline mineral species in tephra clay fractions identified relatively easily by XRD reflections are 10Å and 7Å halloysite, clay-vermiculite, cristobalite, tridymite, and quartz. Less easily identified components are gibbsite and iron oxides, especially when present in low concentrations (see below). Mica may be difficult to positively identify if both 10Å halloysite and clay-vermiculite are present since the characteristic 10Å peak for mica may be over-shadowed by peaks from halloysite or vermiculite at various stages of treatment. The identification of cristobalite is usually straightforward because feldspars, which have a secondary peak at the same d-spacing as cristobalite (4.05Å), occur infrequently and in very low quantities in clay fractions.

A potential identification problem may arise where both 7Å halloysite and kaolinite are suspected to be present together (such as in reworked materials). The presence of kaolinite can usually be discounted where 7Å peaks invariably occur in combination with 10Å halloysite peaks with interstratification. The 7Å peak will increase in magnitude following heat treatment (110°C) due to loss of interlayer water from the 10Å halloysite. Furthermore, if the 7Å and 4.4Å peaks are broad and poorly defined, then an halloysitic nature is generally indicated (Churchman and Carr 1975; Brindley 1977; Lowe 1981). Churchman et al. (1982) have recently developed a rapid test for distinguishing 7Å halloysite from kaolinite based on the relative abilities of these minerals to intercalate polar organic compounds such as formamide and N-methylformamide. Formamide rapidly (<1 h.) and completely intercalates into dehydrated halloysite which consequently then gives a peak at 10Å, whereas the intercalation of formamide into kaolinite is very much slower (days) and incomplete.

Kaolinite has not been reported in South Auckland tephra materials except for the occurrence of b-axis disordered kaolinite (as relatively large "books") in several strongly weathered Kauroa Ash beds (Salter 1979).

The identification of iron (or aluminium) oxide minerals by XRD (Table 4) is often difficult because of their low concentrations, the diffuseness of patterns caused by small particle sizes and/or poor crystallinity, and the nature of the other minerals present. Schwertmann and Taylor (1977) recommend the use of CoK_{α} or FeK_{α} radiation in preference to CuK_{α} radiation to reduce background. A comparison of sample traces before and after extraction of the "free" iron oxides (e.g., by CBD method) is often helpful. A new method for identifying iron oxides by differential XRD is described by Schulze (1981) and this

should be consulted if a study is concentrating on the iron oxide minerals.

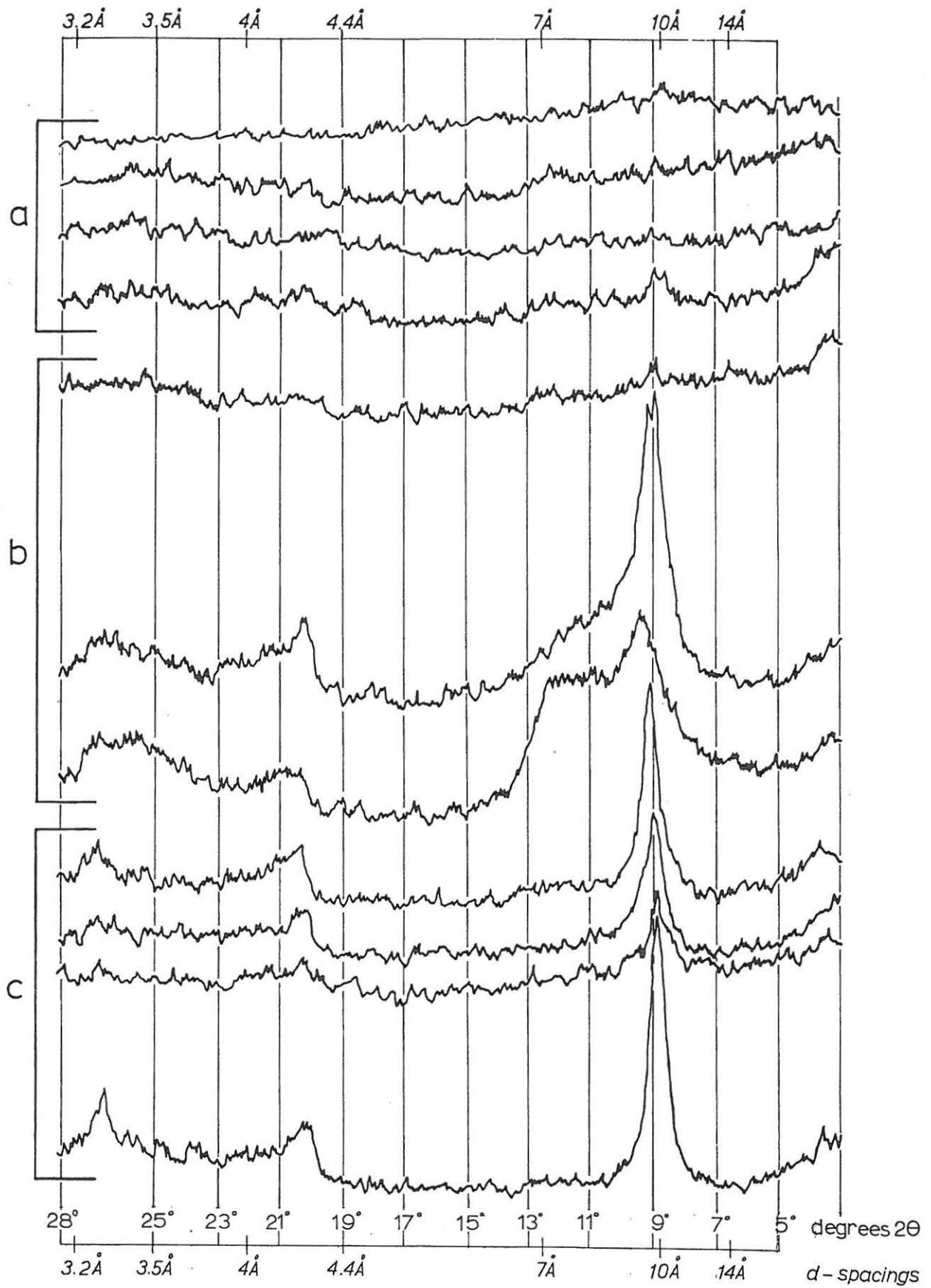
Application

Examples of XRD patterns of some Waikato tephra-derived clay fractions are given in Fig. 4. A series of examples is given to show the range of patterns which are liable to be encountered. More often than not, poorly defined peaks and high backgrounds rather than sharp and distinct or large peaks are typical. The dominant constituents in Fig. 4 are allophane (X-ray amorphous) and halloysite (peaks at 7Å and 10Å) with small quantities of clay vermiculite, cristobalite, and gibbsite in some samples.

Quantification of constituent mineral species is difficult because peak intensities and areas vary according to composition and other factors. However, an approximate estimate (at best $\pm 10\%$) of halloysite content from peak height (10Å plus 7Å) may be determined from Fig. 5. This graph was derived from comparison of semi-quantitative thermal analysis (DTA) data with XRD peak heights using late Quaternary tephra samples from the Waikato region and an halloysite standard. The amount of short range order material (which may include glass, imogolite, and poorly ordered iron oxides and humus complexes, as well as allophane) can be roughly estimated by difference. That is, the occurrence of only very small peaks of well ordered minerals such as halloysite implies that the sample is dominated by short range order material.

The degree of crystallinity of halloysite may be gauged partly from the sharpness of the 7Å and 10Å peaks. A broad or only moderately defined peak (e.g., Fig. 4d-i) indicates relatively poor crystallinity, but also may reflect the effect of partial dehydration of the halloysite. Peaks tend to become sharper and better defined, however, with increasing age or depth of burial of tephra materials (e.g., Fig. 4a-c,d-1) (Kirkman 1975; Lowe 1981).

The relative stability of interlayer water can be estimated from peak height-area relationships (e.g., Nagasawa and Miyazaki 1976; Wilke et al. 1978; Lowe 1981). The degree of interstratification has been related to climatic conditions by Lowe (1981) in that interstratification implies unstable interlayer water and seasonal dehydration. Churchman et al. (1972) state that these phases (7Å, 10Å) represent end members of a continuous series of hydration states in which the average interlayer water content encompasses all values between 0 and two molecules per unit cell. Dehydration (with shrinkage) occurs through an interstratification in which there is partial segregation of the two basic layer types.



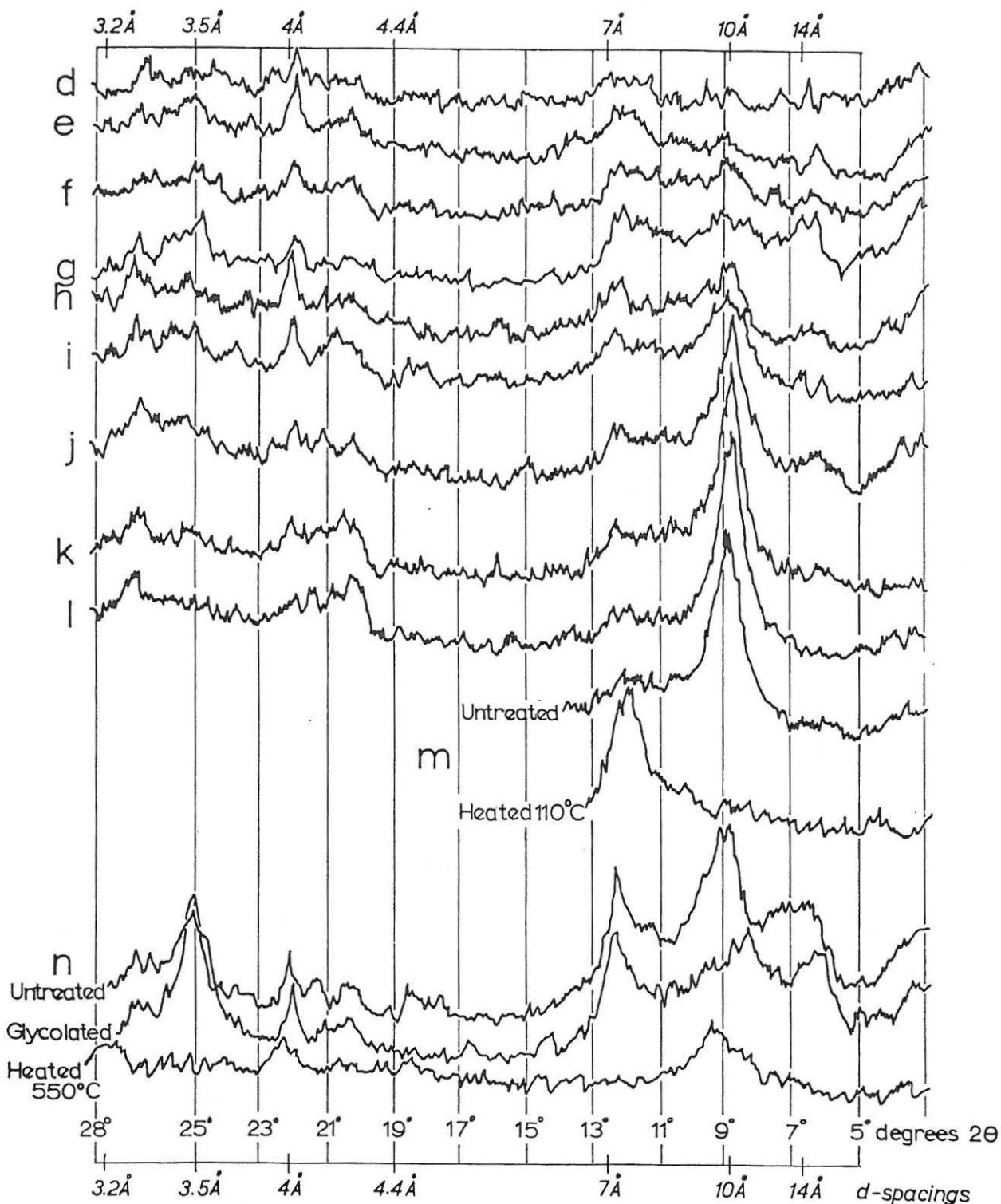


Fig. 4. XRD traces of some $<2\mu\text{m}$ Mg-clay fractions from tephras in the Hamilton Basin (see Table 1). a, tephras aged $<10,000$ years; b, Kawakawa Tephra (c. 20,000 years age) from different sites; c, tephras aged c.30,000-42,000 years age - bottom curve is Rotoehu Ash, others from Mangaone Lapilli; d-j, composite tephras of $\leq 42,000$ years age - samples arranged in order of increasing depth below surface; k-l, Hamilton Ash; m, composite tephra sample showing effect of low heat treatment - 10Å halloysite peak dehydrates to 7Å after 110°C heating for 1h.; n, composite tephra sample showing effects of glycolation and high heat treatment - glycolated trace shows slight expansion of 10Å halloysite peak, some interstratification between 7-10Å halloysite peaks, and no expansion of 14Å vermiculite peak; trace of sample heated to 550°C for 1h. shows disappearance of 7Å and 10Å halloysite peaks (become amorphous) and the dehydration of vermiculite at 14Å to heat-stable 9.8Å peak (refer also to Table 7). The diffractograms show that allophane (X-ray amorphous e.g., a traces) and halloysite (both 10Å and 7Å e.g., c, g-l) are the dominant constituents. Small amounts of clay-vermiculite (14Å e.g., d-g, n), α -cristobalite (4.05Å e.g., d-k, n), and possibly gibbsite (4.85Å e.g., lowest traces of a,b; and i,n) also occur. Interstratification between 7-10Å halloysite occurs in some samples (e.g., lowest trace of b, traces f-k). For further details see Lowe 1981, Ch. 6. From Lowe (1981, p. 180-181).

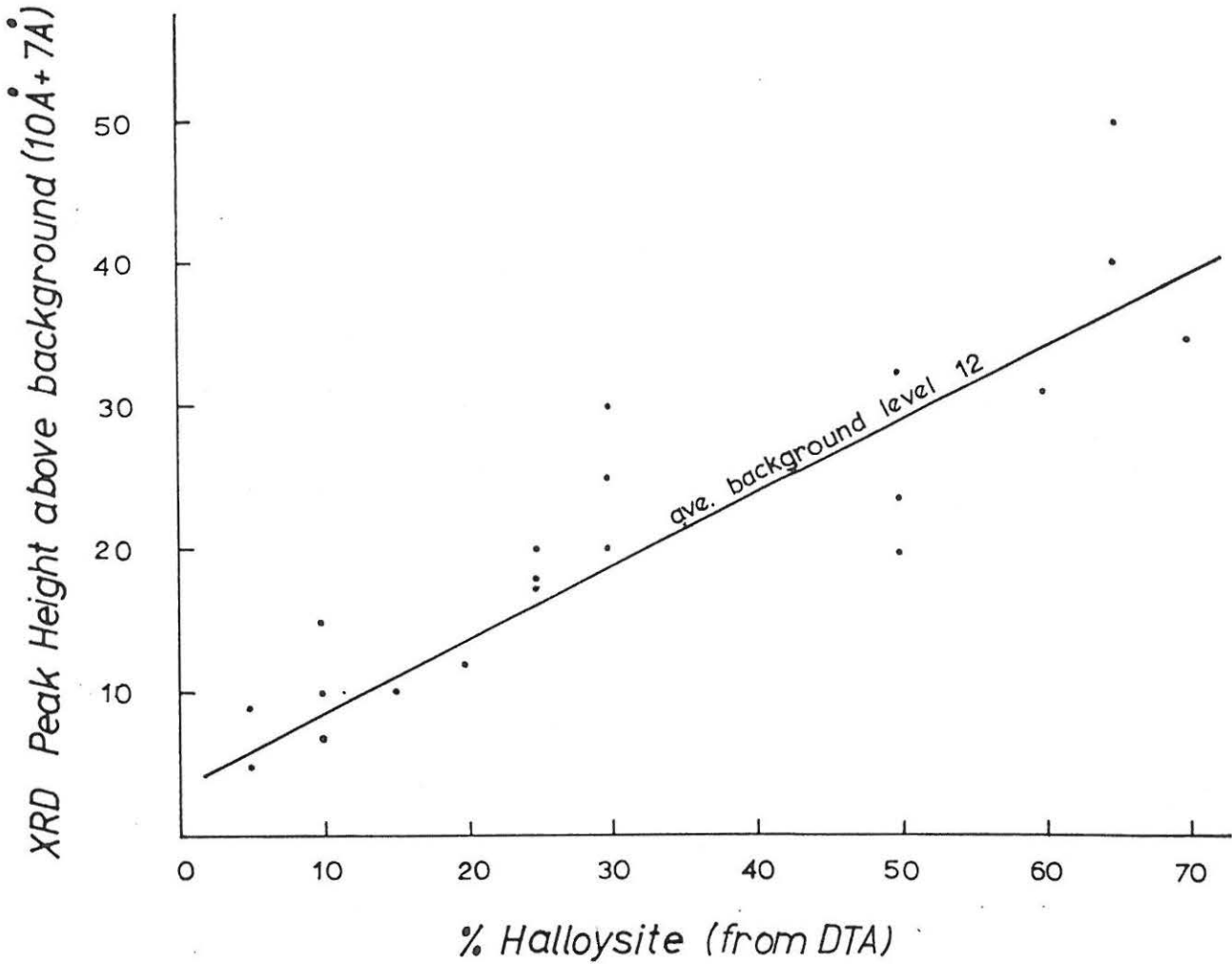


Fig. 5. Relationship between % halloysite as determined from DTA with XRD peak heights of 7Å + 10Å halloysite. XRD samples were untreated, oriented <2µm Mg-clay fractions run with instrument settings as in Table 6 (ratemeter setting 400cps). DTA analysis procedures were as given in DTA section below and Fig. 8. From Lowe (1981, p. 198).

Infrared spectroscopy (IR)

Infrared absorption involves passing a beam of infrared radiation (4000-200cm⁻¹) through a specimen and measuring the amount of absorption. Energy absorption will occur when the frequency of the incident radiation strikes a sample containing a bond between two atoms with a corresponding vibration frequency; radiation at other frequencies is not absorbed (Brown et al. 1978).

IR is equally applicable to gases, liquids, and glasses, as well as crystalline solids, and hence, together with chemical dissolution analyses, is becoming increasingly utilised as a major diagnostic

tool in studies of short range order clays from tephros. Quantitative determinations can be made, usually by comparing absorption or transmittance intensity with that of a suitable reference (e.g., Fieldes et al. 1972; Russell et al. 1981; Parfitt and Henmi 1982). An inherent limitation, however, is that the particulate nature of minerals and light scattering phenomena (known as the Christiansen effect) affect the relationship between the concentration of a given mineral component and the infrared radiation (see below; White 1977). A lack of "standard" reference minerals having the same structure, particle size distribution, composition, and spectral features as the component in the sample further limits the instances in which quantitative determinations can be accurately made. Nevertheless, reasonable agreement between chemical dissolution and IR methods has been achieved for estimates of allophane content in tephros (see Table 8, from Parfitt and Henmi 1982).

Some useful references on infrared studies include Fieldes et al. (1972), Farmer (1974), Giesekeing (1975), Farmer and Palmieri (1975), van der Marel and Beutelspacher (1976), Dixon and Weed (1977), Brown et al. (1978), Farmer et al. (1979a), Theng (1980), and Parfitt and Henmi (1980).

Preparation

One of the major problems encountered in the application of IR in earth sciences is the distortion of absorption due to the Christiansen effect. The mineral samples must have a particle size less than the wavelength of the IR radiation used. The usual wavelength range is from 2.5 to 50 μ m (i.e., frequency range of 4000 to 200 cm^{-1}), hence the <2 μ m clay fraction is suitable. Coarser fractions need to be reduced in size by careful grinding (see White 1977; Henmi and Yoshinaga 1981).

Several methods of sample preparation exist. At University of Waikato alkali halide discs (KBr) or oil mulls have been used. Disc preparation is as follows:

- (1) Grind the sample to a particle size that is less than the shortest wavelength likely to be examined. For the majority of spectrometers this is 2 microns.
- (2) Weigh approximately 200mg of spectrographically pure KBr (or KCl) and 1mg of sample. Mix the two intimately and transfer to a vacuum die for pressing. Mount inside a paper ring (which should not be destroyed later).
- (3) Raise the pressure on the die slightly and maintain while evacuating the die. When the die is totally evacuated, increase the pressure

on the die to approximately 8 to 9 tons. This pressure is not critical, but it is very important never to exceed the maximum pressure quoted by the die manufacturers as this may cause cracking of the polished surface or, worse, an explosion of the die wall. The KBr becomes liquid at these pressures and flows around the mineral fragments.

- (4) After maintaining the pressure for 3 to 5 min., release the vacuum and then the pressure. Using suitable spacers press out the completed disc. Ideally, this disc should be quite clear. If it is cloudy, either the KBr or the sample contained moisture, or the die was not sufficiently evacuated. The disc can be ground and pressed again if necessary.
- (5) The transparent disc thus obtained is brought into the path of the beam of the infrared spectral photometer. A tablet of pure KBr made by the same method is brought into the other path of the beam.

Procedure, mineral identification, and application

The University of Waikato has four infrared spectrometers, the least complex being a Perkin-Elmer Infracord which covers the 2.5 to 15 μ m (4000-650 cm^{-1}) range. The absorption of the specimen for the infrared spectrum is measured by linking the reference filter to a chart recorder pen and the prism to the chart drive. The prism is driven round slowly so that each wavelength in turn falls on to the detector. As the chart paper is linked to the prism the chart moves in synchronisation with the changing angle of the prism. The pen records the amount of attenuation required to bring the two beams into balance at each wavelength. The net result is a chart showing a measure of the absorption against wavelength.

Major absorption bands of allophane and imogolite occur in three regions: 2800 to 3800 cm^{-1} , 1400 to 1800 cm^{-1} , and 650 to 1200 cm^{-1} (Fig. 6; Wada 1977). The absorption bands in the first region are due to OH stretching vibrations (either structural OH groups or absorbed water). In the second region, an absorption band due to the HOH deformation vibration of absorbed water appears at 1630 to 1640 cm^{-1} . There may also appear absorption bands due to the vibrations related with COO (1700-1740 cm^{-1}) or COO⁻ (1580 and 1425 cm^{-1}) groups (due to humic materials or pretreatment decomposition products or anions, all of which are strongly retained by allophane and imogolite). The absorption bands in the third region are attributed mainly to Si(Al)O stretching vibrations and partly to SiOH and AlOH deformation vibrations (Wada 1977). The frequency of the Si(Al)O absorption maximum of allophane

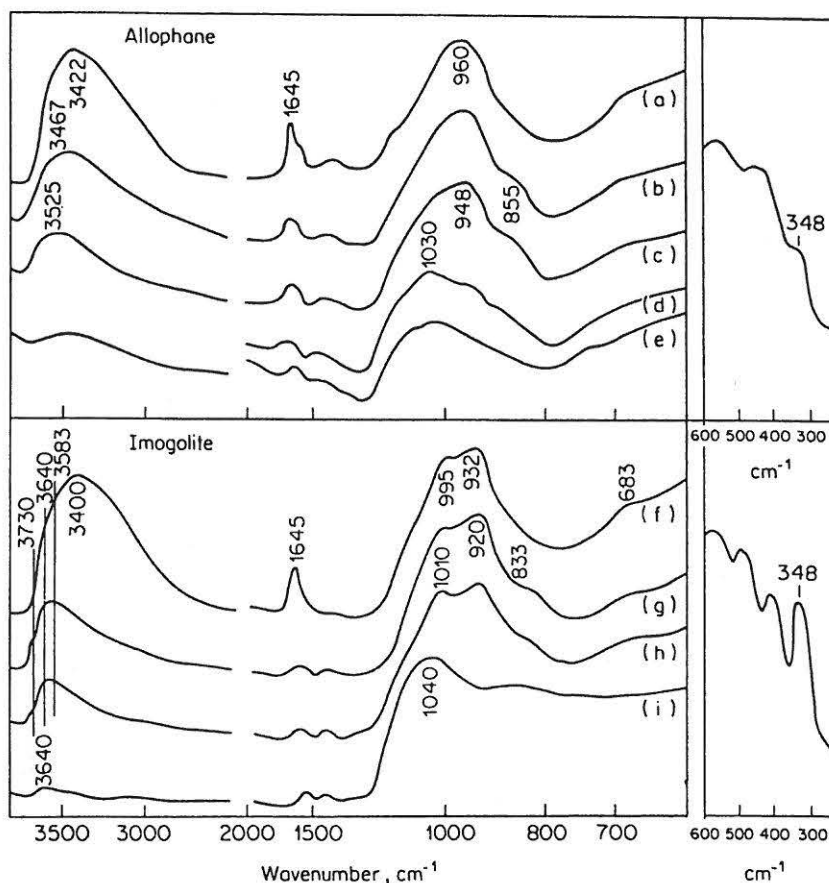


Fig. 6. Infrared spectra of allophane and imogolite showing their major absorption bands. The band at 348cm^{-1} is useful for recognising imogolite structures and has been used for quantitative analysis (see text and Table 8). The traces labelled (a)-(i) reflect differing analytical conditions in which temperature and evacuation pressures were varied. These conditions were: 20°C : a,f; 20°C , 10^{-2}mmHg : b,g; 150°C , 10^{-2}mmHg : c; 250°C , 10^{-2}mmHg : d; 350°C , 10^{-2}mmHg : e; 300°C , 10^{-2}mmHg : h; 475°C , 10^{-2}mmHg : i. The weak OH vibration at 3640cm^{-1} is due to a trace of micaceous impurity. Samples were prepared as films. From Brown et al. (1978, p. 157).

is between 940 and 1040cm^{-1} , the frequency increasing as the $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio increases (Wada 1980). The IR spectrum of imogolite shows two absorption maxima at 990 to 1010cm^{-1} and 925 to 935cm^{-1} , and a band at 348cm^{-1} is useful for recognising imogolite structures (Fig. 6; Brown et al. 1978; Wada 1980; Parfitt and Henmi 1980; Parfitt et al. 1980). This last absorbance at 348cm^{-1} has been used for estimating the amount of allophane ($\text{Al}:\text{Si}\sim 2.0$) or imogolite in a sample by comparing absorption intensity with that of a suitable reference material (Farmer et al. 1979; Russell et al. 1981; Parfitt and Henmi 1982) (Table 8). Pure air-dried allophane ($\text{Al}:\text{Si}\sim 2.0$) has a 348cm^{-1} absorbance of about 0.17 and air-dried imogolite has an absorbance of 0.27 (Parfitt and Henmi 1982).

Table 8. Comparison of analyses of clay fractions and % allophane estimated using chemical extraction methods and IR spectroscopy (from Parfitt and Henmi, 1982, p. 186). The % allophane (Al:Si=2.0) is estimated using the chemical composition of imogolite as a reference where 100% imogolite contains 27.2% Al and 14.1% Si. For example, the Egmont sample contains 19.1% oxalate-extracted Al (Al_o) which equals, from the proportion 19.1/27.2, about 70% allophane. Similarly, it contains 10.0% oxalate-extracted Si (Si_o) which also equates with 70% allophane from the proportion 10.0/14.1.

Sample	Oxalate extraction ^b			Pyrophosphate extraction ^b		Mole ratio $\frac{Al_o - Al_p}{Si_o}$	% Allophane (Al/Si=2/1)				
	C (%)	Al _o (%)	Si _o (%)	Fe _o (%)	Al _p (%)		Fe _p (%)	Al _o ^c	Al _{o-p} ^d	Si _o ^e	IR ^f
Ohaeawai	8.4	18.8	7.0	5.9	2.1	0.6	2.5	70	60	50	50
Papakauri	4.3	9.0	2.6	6.9	3.3	2.4	2.3	30	20	20	10
One Tree Point	5.3	24.2	11.2	0.2	2.5	0.2	2.0	90	80	80	85
Mairoa	7.5	23.0	11.2	5.3	4.5	0.7	1.7	85	70	80	85
Patua	9.7	20.9	8.6	2.7	4.6	1.1	2.0	75	60	60	70
Pumice	4.0	25.6	13.3	4.0	1.7	0.2	1.9	95	90	95	90
Egmont	4.5	19.1	10.0	4.1	0.8	0.2	1.9	70	65	70	70
Addison	— ^a	24.2	12.1	2.8	2.7	0.9	1.8	90	80	85	80
Flagstaff	— ^a	18.2	6.7	4.9	5.9	2.5	1.9	65	45	50	45
Te Anau	16.0	13.2	2.5	5.8	8.5	5.0	2.0	50	20	20	30

^a Insufficient sample. ^b Based on 150°C oven-dry clay. ^c Calculated from %Al_o. ^d Calculated from %Al_o-%Al_p. ^e Calculated from %Si_o. ^f Calculated from IR absorbance at 348 cm⁻¹.

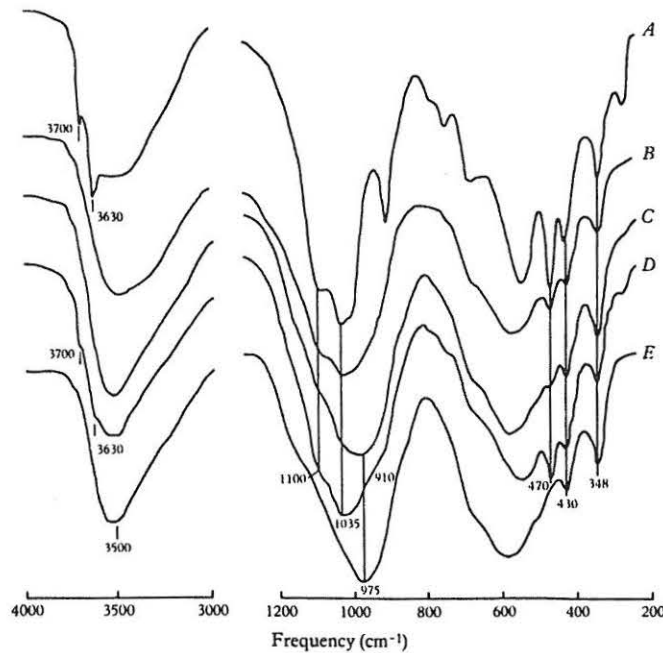


Fig. 7. Infrared spectra of halloysite and 'proto-imogolite' allophane from tephra-derived <2µm clay fractions. Sample A is largely halloysite only, sample E 'proto-imogolite' allophane only. The other samples (B-D) contain mixtures of both. The diagnostic bands for halloysite occur at 470, (530), 910, 1035, 3630, 3700cm⁻¹ whereas those of 'proto-imogolite' allophane occur at 348, 430, 570, 690, 990, and 3500cm⁻¹ (cf. Fig. 6 - note that the transmittance axis is inverted). These samples were prepared as KBr discs heated to 150°C, and derive from Waikato and Taranaki tephtras. After Russell et al. (1981, p. 188).

Examples of $<2\mu\text{m}$ clay samples containing mixtures of mainly halloysite and 'proto-imogolite' allophane (which has an imogolite IR spectrum) are given in Fig. 7. IR spectra of halloysite and other minerals which occur in tephra clays in New Zealand are shown in Hogg (1974), Kirkman (1975, 1980a,b), McQueen (1975), Kirkman and Pullar (1978), McIntosh (1980), Russell et al. (1981), Theng et al. (1982), and Parfitt et al. (1983).

Diagnostic IR peaks for some iron oxide minerals are listed in Table 4, and a table summarising the main absorption bands for some other minerals is given in White (1977, p. 857).

Differential thermal analysis (DTA)

DTA is a semiquantitative technique which is especially important in the study of short range order materials since it is applicable irrespective of the degree of crystallinity. The method determines the differences in temperature (T) between a sample and reference material as the two are heated at a controlled rate. When the sample undergoes a transformation, the heat effect causes a difference in temperature between the sample and reference materials. The difference in temperature (ΔT) is normally plotted against the temperature at which this difference occurs (Fig. 8).

Reviews of DTA and other related methods such as thermogravimetric analysis are contained in Mackenzie (1970), Mackenzie and Caillère (1975), and Tan and Hajek (1977).

Preparation

Aliquots of Mg-clay (or K-clay) $<2\mu\text{m}$ fractions separated for XRD analysis are air dried (this takes several days), lightly ground in a mortar (preferably agate if very accurate work is being undertaken) and equilibrated to constant humidity (56% r.h.) over saturated $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ for 7 to 14 days. Standards must also be equilibrated.

In many cases, samples need not be heated above about 700°C because: (a) exothermic peaks between 800 and 1000°C are markedly affected by pH (which varies according to dispersion and peroxidation treatments), particle size, and organic matter content (Campbell et al. 1968); and (b) high temperature peaks are qualitatively ambiguous i.e., they can be attributed to several crystalline clays in addition to short range order components (Hamblin and Greenland 1972; Fieldes and Claridge 1975). In addition, analytical time per sample is increased by an hour or more with the higher upper temperature limit, mainly because of the increased time required for the apparatus to cool.

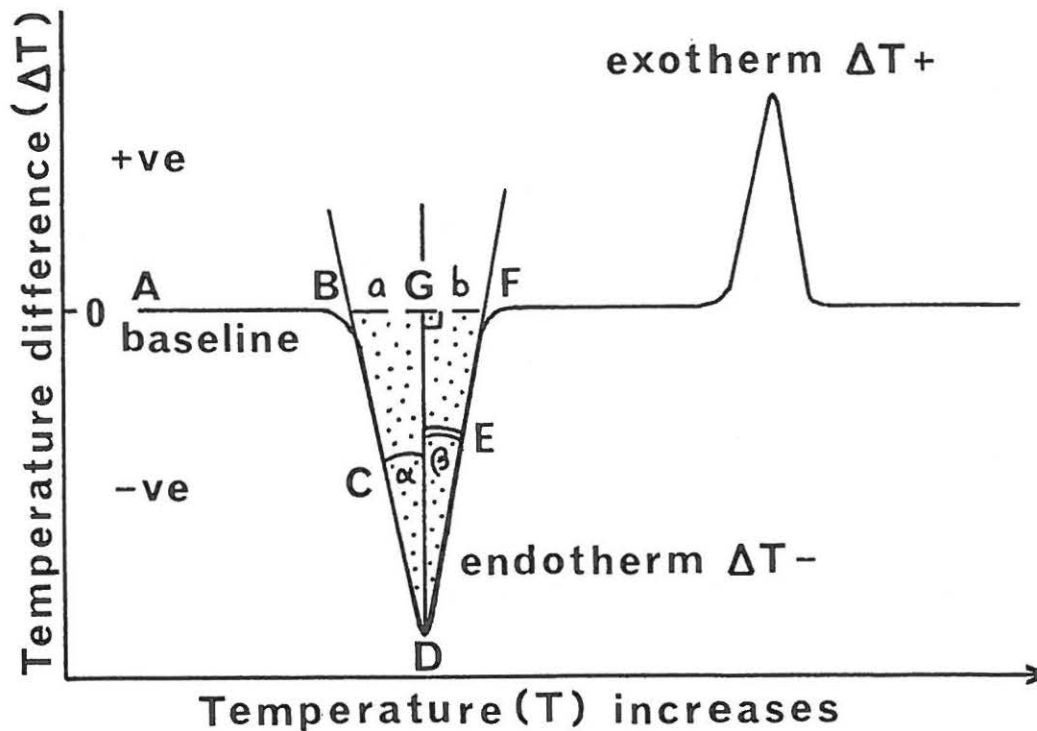


Fig. 8. Idealised DTA curve showing endothermic and exothermic peaks and the basis for determining peak area for quantification and slope ratio of the endo- or exotherm. The theory and nomenclature of the DTA method is as follows. Along the baseline AB, ΔT is 0 as no reaction occurs in the sample. At point B, roughly where an endothermic reaction begins, heat is absorbed by the sample which thus cools with respect to the reference (ΔT become -ve). ΔT increases until the rate of heat inflow into the sample equals the amount of heat absorbed by the reaction. This occurs, near the end of the reaction, at point D, after which the curve returns to the baseline at F. An exothermic reaction gives a peak in the opposite direction (i.e., ΔT is +ve).

Point D, peak temperature (although point B is actually more critical in terms of physical change to the specimen but is often difficult to position accurately); BF, peak width; DG, peak height (amplitude). The maximum rate of reaction occurs at about C, the end of the reaction at about E.

The degree of symmetry of the peak is given by the slope ratio, $\tan\alpha/\tan\beta (=a/b)$ (Bramao et al. 1952). The peak area (stippled) can be calculated from the relationship $(BF \times DG)/2$ (or by "counting squares" on the chart paper) and is usually denoted in $\text{cm}^2 \cdot \text{g}^{-1}$ of $<2\mu\text{m}$ clay or whole sample. For example, a 50mg sample of $<2\mu\text{m}$ clay giving a peak area of $10\text{cm}^2 = 0.5\text{cm}^2 \cdot \text{g}^{-1}$ $<2\mu\text{m}$ clay. Diagram after Tan and Hajek (1977, p. 867).

Because of the long time required to analyse a sample (2 to 3h.), samples should be selected with care. It is impractical in most cases to analyse more than about 10 to 20 samples for a project, taking into account the need to run duplicates as well.

Procedure and mineral identification

Analyses at University of Waikato are made with STONE DTA apparatus using the following instrumental settings:

Heating rate	10°C min ⁻¹
Thermocouple amplifier	300 μ V (150 x 2)
Chart speed	0.1 in min ⁻¹

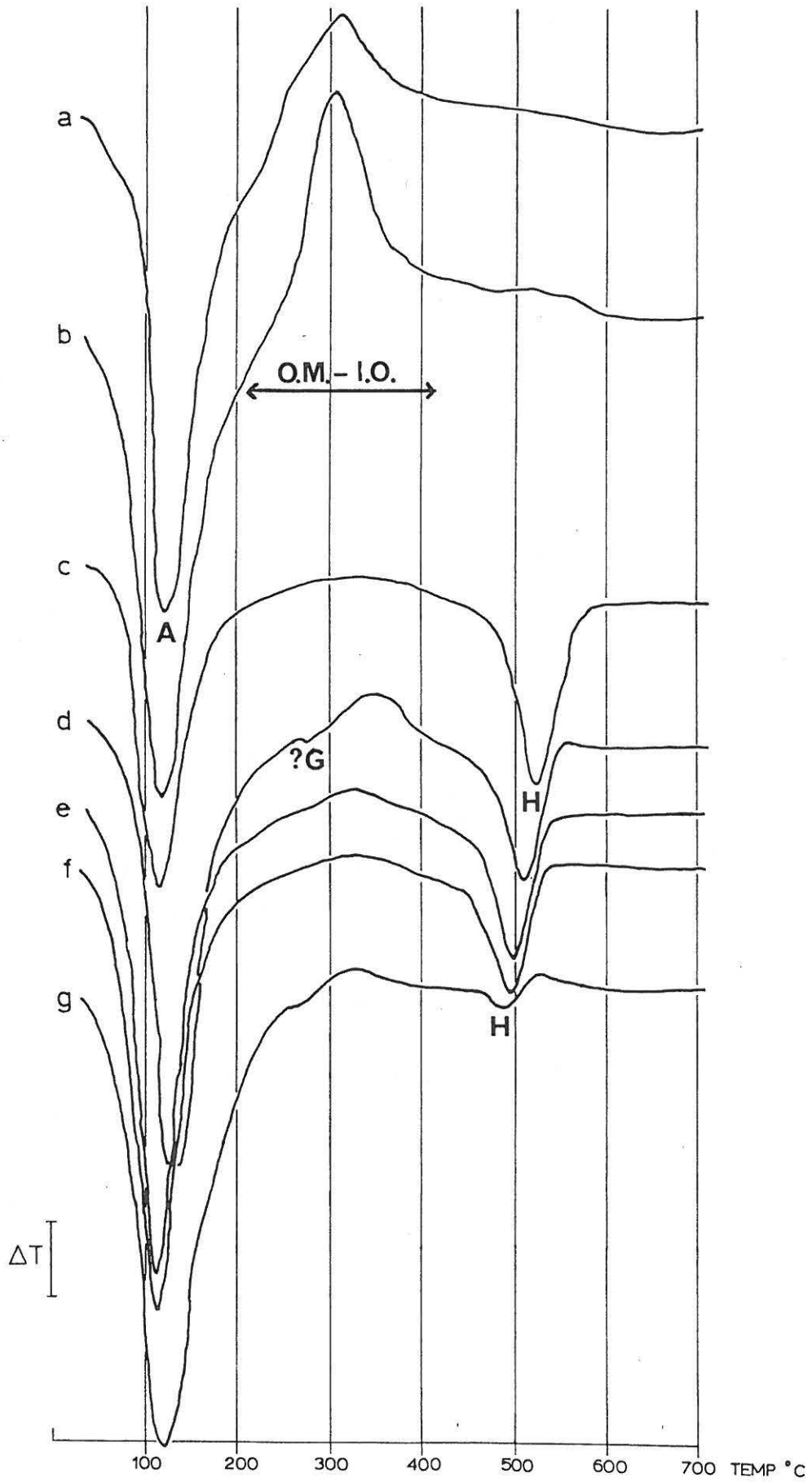
The thermocouple amplifier setting may be increased or decreased on an ad hoc basis.

Samples must be carefully and accurately weighed for quantitative analysis, and packed as uniformly as possible into the sample holder for each successive analysis to ensure valid intersample comparisons. 50 \pm 1mg samples are heated to about 1000°C using calcined (preheated) Al₂O₃ as the diluent (160mg) and reference (i.e., a 210 \pm 1mg sample of clay plus Al₂O₃ is packed into the sample holder; the reference cell contains pure Al₂O₃ and does not need to be replaced for each run). They may be heated in air, or in an oxygen or nitrogen atmosphere, which is advantageous for pyrolysis of organic matter.

Relative abundances of the chief constituents are determined from the endotherm peak areas, measured according to the criteria shown in Fig. 8 and as discussed in Mackenzie and Caillère (1975). Precise determination of the base line ($\Delta T = 0$) position may be difficult because of base line drift or displacement, or because of almost concurrent exothermic and endothermic peaks (e.g., Fig. 9h-k). In some cases, it is easiest to arbitrarily join the reaction peak shoulders (i.e., points B and F in Fig. 8) (see Tan and Hajek 1977, p. 876). Because of this potential problem, and for other reasons, experimental procedures must be maintained as constant as possible and replicate analyses carried out for quantitative work.

The most common constituents of New Zealand tephra clay materials, allophane and halloysite, are readily identified and quantified by DTA by comparing peak areas from prepared standards (available in Department of Earth Sciences) with those of unknown samples. Other minerals may be difficult to detect unless present in relatively large quantities or suitable pretreatments have been undertaken (Table 9).

Allophane (also imogolite) is identified by a low-temperature (110-120°C) dehydration endotherm (Fig. 9; Mitchell et al. 1964; Bracewell et al. 1970; van Olphen 1971; Fieldes and Claridge 1975), the area of which provides a measure of relative abundance. Water adsorbed on most clay-size materials, including organic matter, will contribute to this peak, as is evident from the sample comprising around 100% halloysite in thermogram n in Fig. 9. Consequently, the amount of allophane determined from the peak area is corrected by deducting a factor proportional to the amount of halloysite in the sample. The



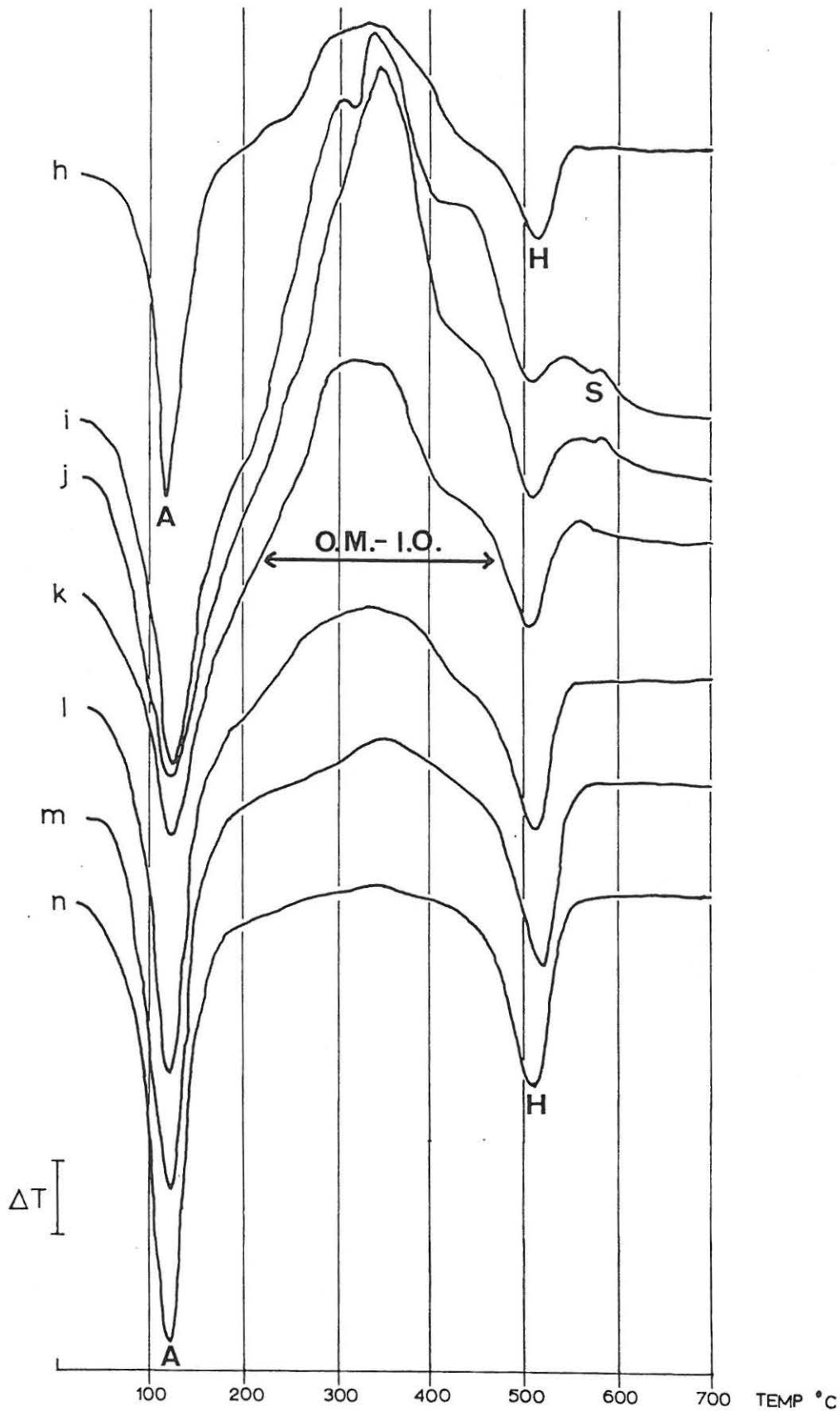


Fig. 9. DTA thermograms of some $< 2\mu\text{m}</math> Mg-clay fractions from tephras in the Hamilton Basin. a-b, tephras aged $< 10,000$ years; c, Kawakawa Tephra (c. 20,000 years); d-e, tephras aged c. 30,000 years; f-g, Rotoehu Ash (c. 42,000 years); h-l, composite tephras of $\leq 42,000$ years age arranged in order of increasing depth; m-n, Hamilton Ash. The thermograms illustrate that allophane (endothems A at 120°C) and halloysite (endothems H at 500°C) predominate in most samples. Organo-mineral complexes (O.M.), possibly together with some iron oxides (I.O.), are evident as strong exotherms in traces a, b, d, h-l. A trace of ?gibbsite (endothrm ?G at 280°C) may be present in trace e but the small peak may have been largely suppressed by the O.M.-I.O. exotherm. The small endotherms at 570°C in curves i and j probably represent silica (S) phase changes. Samples were prepared and analysed as outlined in the text. After Lowe (1981, p. 193-194).$

humidity equilibrium ensures that this remains relatively constant. Alternatively, the samples and standards may be glycolated, thereby replacing the adsorbed water, and allowing the allophane content to be estimated more directly (e.g., Sand and Bates 1953; Lowe 1981).

Imogolite (and gibbsite - see below) may display an endotherm at 390-420°C (Kanno et al. 1968; Yoshinaga et al. 1973; Dudas and Harward 1975a) due to dehydroxylation. The sample usually has to be selectively purified to show this, however, but the peak can be used for quantitative estimation.

Halloysite is indicated by weak to strong dehydroxylation endothermic peaks at about 500°C (Mackenzie 1970). Most late Quaternary tephra samples from the Waikato region show peak temperatures of 470-490°C (Fig. 9). These temperatures are consistent with those for halloysite formed from volcanic ash material elsewhere (e.g., Yoshinaga et al. 1973; Dudas and Harward 1975a; Kirkman 1975; Kirkman and Pullar 1978) and suggest a low degree of crystallinity, partially related to small particle size and possibly to the presence of amorphous material (Lowe 1981). Particle shape may also influence the peak temperature.

Bramao et al. (1952) suggested that halloysite and kaolinite are distinguishable on the basis of endotherm peak symmetry, measured as slope ratio (Fig. 8) : halloysite is usually more asymmetric than kaolinite because of a low temperature shoulder arising from weakly bound hydroxyls in the structure (Churchman and Carr 1975). While the technique seemed to apply to Kauroa Ash deposits (Salter 1979), the use of slope ratio to distinguish between halloysite and kaolinite is not universally applicable because of "overlap" of values in many instances (Nagasawa 1969; Mackenzie 1970; Lowe 1981). Thermograms of halloysite from Kauroa Ash show a mean slope ratio of 2.24 (Salter 1979), whereas those of halloysite from late Quaternary tephras examined by Lowe (1981) are <2, and often <1. These variations may be attributed to differing degrees of crystallinity, particle shape or size, or the effect of organo-mineral complexes in the clay fractions (Kirkman and Pullar 1978; Lowe 1981).

Gibbsite, if it occurs in sufficient quantity, is characterised by an endothermic peak around 300°C (280-330°C) (e.g., Fig. 9d; Hsu 1977). This peak overlaps with those of iron oxides which show endotherms (Table 4) in the range of 280 to 400°C (γ -FeOOH also shows exotherms from 370-500°C) (Schwertmann and Taylor 1977). In many cases, however, overlapping peaks may be resolved by chemical dissolution pre-treatments (Table 9; Mackenzie and Caillère 1975).

"Organo-mineral" or humus-complexes (probably involving Fe or Al oxides) are indicated by exotherms between 200 and 500°C, or higher (Jackson 1969; Satoh 1976); exotherms at about 330°C and 450°C arise from complex decarboxylation and oxidation respectively (Schnitzer and Kodama 1977). The humus complexes which occur in tephra materials are influenced by the organic cycle in the soil (Lowe 1981), and may have an important role in Al-humus formation and the limitation of Al and Si coprecipitation (Wada and Higashi 1976; Wada 1977; Lowe 1981). The humus complexes appear to be resistant to breakdown (Birrell and Fieldes 1968; Wada and Higashi 1976). This is illustrated in Fig. 9 in which sample h, which was peroxidised with H₂O₂, shows only moderate reduction in exotherms compared with equivalent sample i which was not peroxidised.

Quartz/crystalline silica $\alpha \rightleftharpoons \beta$ phase changes (Mackenzie 1970) may be identifiable in DTA curves (e.g., Fig. 9i,j).

Application

Some DTA curves of tephra materials are shown in Fig. 9. These thermograms illustrate a predominance of allophane (e.g., especially curves a,b) and halloysite (curves c-n) together with humus complexes and/or iron oxides (e.g., especially curves a,b,h-k) and possible traces of gibbsite (curves d,g). A variety of traces are shown to demonstrate the diversity, particularly of peak size and position, which can be expected from tephra samples.

Electron microscopy

There are two basic types of electron microscopes and microscopy : transmission (TEM) and scanning (SEM). Generally, larger particles or aggregates are studied by SEM, and dispersions of individual clay-size particles by TEM, which has better resolution (5Å cf. 200Å) (Gard 1971). Electron microscopy must be used in combination with other techniques such as XRD and thermal (DTA) or infrared (IR) analysis because many clay mineral species show several external shapes which are difficult to distinguish. For example, the apparent transition between allophane and halloysite frequently precludes micrographic identification of a given particle belonging to one or the other mineral species (Bates 1971). Another constraint is that sample sizes are, of necessity, very small and hence possibly "unrepresentative". Further, because the specimen is exposed to a high intensity electron beam it must be analysed in a high vacuum and will be in a dehydrated form, although special environmental cells to observe "natural" forms have been used (e.g., Parsons 1974; Kohyama et al. 1978). Special procedures

were operated by Jones and Uehara (1973) to detect "amorphous" coatings on mineral surfaces too thin to be resolved by most electron microscopes. A special problem in many analytical techniques which can be accentuated in TEM and SEM studies is the formation of artifacts by sample preparation methods. Accordingly, considerable care is necessary when interpreting EM images.

Projects involving clay mineralogical analysis should normally restrict electron microscope examination to a few carefully selected samples only. Both SEM (in the School of Science) and TEM (Meat Research Institute, Ruakura), the latter to a lesser extent, are available to workers at University of Waikato.

Transmission electron microscopy (TEM)

The TEM geometry is similar to that of the optical microscope. Electrons are emitted from a hot tungsten filament at the top of an evacuated column and are propelled down the column at a constant speed by a high electric potential between the filament and the anode. The electron beam is focused by an electromagnetic condenser lens on to the sample where diffraction and scattering occur. The resultant electron beams are focused from an initial image by the objective lens (McKee and Brown 1977).

The penetrating power of the electron beam is low and TEM samples must consist of either very thin films of material or very small particles supported on thin film substrates. The examination of opaque surfaces requires a SEM or the preparation of a TEM thin-film replica which duplicates the topography of the original surface. The replica is usually made by evaporating a thin film of metal and carbon directly onto the sample surface and then dissolving the sample while retaining the metal-carbon replica to be viewed by TEM (McKee and Brown 1977). Thus in TEM work the surfaces of clay particles are not directly observed.

Advantages of the TEM are the very high resolution and great depth of field. The TEM is now capable of showing that allophane consists of extremely small hollow spherules with an external diameter of 35 to 50Å and wall thicknesses similar to those of imogolite tubes (~10-20Å), the latter usually occurring as threads or bundles of parallel fibre pairs (Fig. 10; Henmi and Wada 1976; Jessen 1977; Wada and Wada 1977; Parfitt and Henmi 1980).

An important analytical capability of the TEM is the formation of an electron diffraction pattern from a crystalline sample (similar to

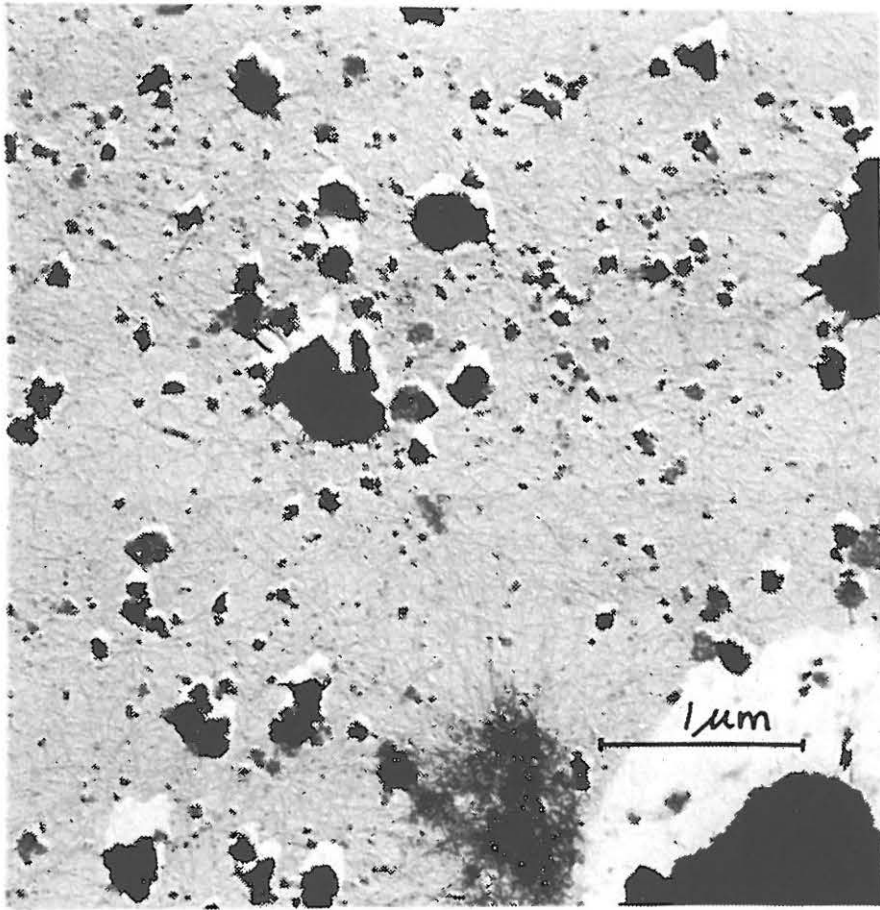


Fig. 10. High resolution electron micrograph of clay fraction containing imogolite threads and bundles and very fine allophane particles. The larger dark masses probably represent aggregates of allophane and in some cases felsic minerals. Sample is from Waihou silt loam, a freely drained soil derived from admixed tephra and tephric alluvium. Bar represents 1 μ m. From Jessen (1977, p. 116).

those obtained by XRD) which is useful for identifying particles or thin films below the detection limit of XRD (Gard 1971; Andrews et al. 1971; McKee and Brown 1977; Fripiat 1982).

Preparation

A good general review has been written by McKee and Brown (1977). At University of Waikato, Jessen (1977) used the following method of sample preparation: suspensions of $<1\mu\text{m}$ clay particles are diluted to 1% or less with distilled water, then spotted on to collodian films ("Formvar") which are supported by copper grids. Specimens are then shadowed by depositing a thin film of platinum at an angle of 45° to the specimen to enhance contrast and 3-dimensional effects.

Procedure, mineral identification, and application

Procedure is normally detailed in notes associated with the laboratory in which the TEM is operated. Mineral identification is based on comparison of images or micrographs with micrographs in the literature. TE micrographs of tephra materials from the South Auckland region are contained in theses of Hogg (1974), McQueen (1975), Davoren (1976), Fry (1977), and Jessen (1977), and in many papers, including Fieldes and Williamson (1955), New Zealand Soil Bureau (1968), Yoshinaga et al. (1973), Kirkman (1975; 1976; 1977; 1980a,b; 1981), Kirkman and Pullar (1978), McIntosh (1980), Henmi and Parfitt (1980), and Parfitt and Henmi (1980).

General reviews and applications are contained in Beutelspacher and van der Marel (1968), Bates (1971), Gard (1971), Giesecking (1975), Wenk (1976), Dixon and Weed (1977), Greenland and Hayes (1978), Whalley (1978), Sudo and Shimoda (1978), Theng (1980), Smart and Tovey (1981), and Sudo et al. (1981).

Scanning electron microscopy (SEM)

The SEM provides an enlarged, 3-dimensional view of the unmodified clay surface with high depth of focus. The SEM forms an image by scanning the surface of a sample with a finely focused electron beam (about $10^{-2}\mu\text{m}$ diameter) (McKee and Brown 1977). The high energy beam stimulates the emission of secondary electrons, back-scattered electrons, X-rays, and sometimes light photons from the sample surface. In the normal mode of scanning microscopy, the electrical signal derived from the collected secondary or back-scattered electrons is used to form a television-type image of the surface under examination. The X-rays emitted are characteristic of the elements present in the sample and can be collected and analysed (usually with a Li-drifted Si detector)

and counted with an energy dispersive multichannel analyser. Hence, in addition to particle size and morphological examination, the SEM is capable of determining the chemical identity and spacial distribution of the elements in the area under the electron beam. These data can be presented as spot mode spectral plots (Fig. 11) or as X-ray elemental maps (e.g., McKee and Brown 1977; Salter 1979). Another function is fabric study, whereby fracture planes in soil materials, for example, may be examined in 3-dimensions (e.g., Rogers 1978; Parker 1978; Ross and Walker 1982).

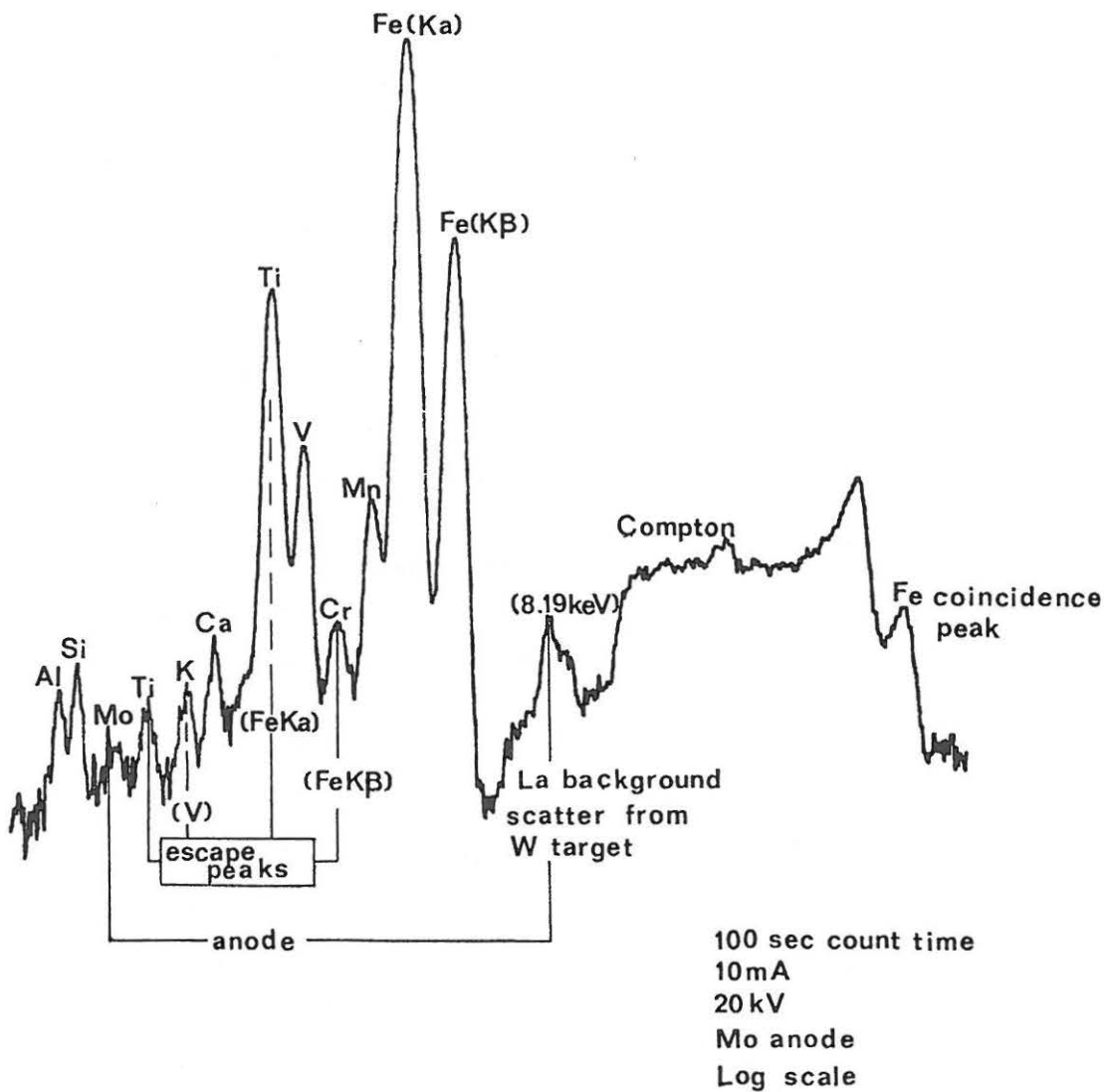


Fig. 11. Spectral plot of a titanomagnetite grain analysed by SEM with attached energy dispersive multichannel electronmicroprobe analyser. From Lowe (1981, p. 253).

Additional advantages of the SEM are its great depth of field and wide range of magnifications which allows correlation of optically visible features with features well beyond the resolution of optical systems (for example, sand and silt sized grains are very easy to study). Another advantage is the ease of sample preparation, and generally the lack of problems related with artifacts (McKee and Brown 1977).

Preparation

Prolonged storage of samples may result in the morphological alteration of some minerals (especially halloysite), hence preparation for analysis should be done as soon as possible after sample collection (Lowe 1981). The nature of the study will determine in part the preparation technique, but in most cases the sample must be separated, suspended and diluted, mounted and coated. (If soil fabric is being studied, the samples must be dehydrated to preserve the particle arrangement by critical point-drying or rapid freeze-drying (McKee and Brown 1977)). Prospective users should consult the SEM operator for advice on special preparation methods which may be required to suit their particular needs. A method used by Lowe (1981) for clays at University of Waikato is as follows:

- (1) 1 to 2cm³ of the <2 μ m Mg-clay suspension fractionated for XRD analysis is diluted with 50cm³ of distilled water and subjected to ultrasonic vibrations, in either a BRANSONIC 52 tank (20-30 min.) or with a DAWES SONOPROBE with microtip (3-6 min.), to ensure disaggregation. After a settling period of several hours most of the very fine colloidal material in suspension is decanted, and the coarser residual particles resuspended in \sim 10cm³ of specially double distilled water; the suspension is briefly (2-3 min.) re-ultrasonicated. Aliquots of 1 to 2cm³ are then successively diluted in \sim 10cm³ of water (3-4 times) until the ultimate suspension appears virtually clear.
- (2) Several drops of *tert.*-Butylamine [(CH₃)₃C.NH₂] are added to a similar amount of the dilute clay suspension as a peptiser (Beutelspacher and van der Marel 1968), mixed well, and a drop of the resultant suspension mounted on a polished brass SEM stub. Disposable Pasteur pipettes are used throughout to prevent carry-over contamination of samples.
- (3) The suspension is subsequently dried, initially under a heat lamp, then in an oven for 1 to 2 h. at 90°C. This alleviates low image quality observed during trial scans and attributed to evaporation

of hygroscopic water (Bohor and Hughes 1971) by the electron beam. The mounted specimen is almost invisible, appearing at most as a slight dullness on the stub surface.

- (4) Samples are coated for 2 min. with 200 to 500Å of gold-palladium in a diode sputtering system (POLARON E5000). The coating serves to prevent a build-up of electrons on the specimen surfaces by conducting away static electricity (Bohor and Hughes 1971).

If flocculation problems occur with the sample mounted on the stub, the specimen can alternatively be mounted on a fine-mesh metal grid (as for TEM) to aid dispersion of the constituent particles (McKee and Brown 1977; C.K. Beltz, pers. comm.).

Sample stubs must be stored in a dessicator.

Procedure and mineral identification

Samples are usually tilted to 45° and subjected to accelerating voltages between 10 and 25kV. The University of Waikato SEM is a JEOL JSM-35 model.

Problems potentially likely to be encountered include:

- (1) Charging effects (regions of the image appear excessively bright, often as lines or streaks on the micrograph in the direction of scan) - this occurs when all portions of the sample do not remain at the same electrical potential, and is usually alleviated by using lower scanning beam potentials and rapid scan rates (McKee and Brown 1977).
- (2) Sample contamination - contaminants have been known to originate from distilled water used in sample suspension and dilution (Lowe 1981), hence the need for an ultra-pure water source.
- (3) Poor image focus and astigmatism difficulties when magnification exceeds 15,000 times (Lowe 1981).
- (4) Inadequate resolution of some constituent clay species because of particle aggregation (mainly with allophanic materials) and with very fine particle sizes.

Application

The SEM has been applied in various studies at University of Waikato on tephra materials (e.g., Salter 1979; Phillips 1980; Lowe 1981). Most of the papers listed for TEM, plus Borst and Keller (1969), Askenasy et al. (1973), Dixon and McKee (1974), Espinoza et al. (1975), Keller (1978), Tazaki (1979), Smart and Tovey (1981), and Sudo et al. (1981), illustrate morphological features of tephra-derived clay minerals using the SEM. Allophane normally occurs as sponge-like, globular

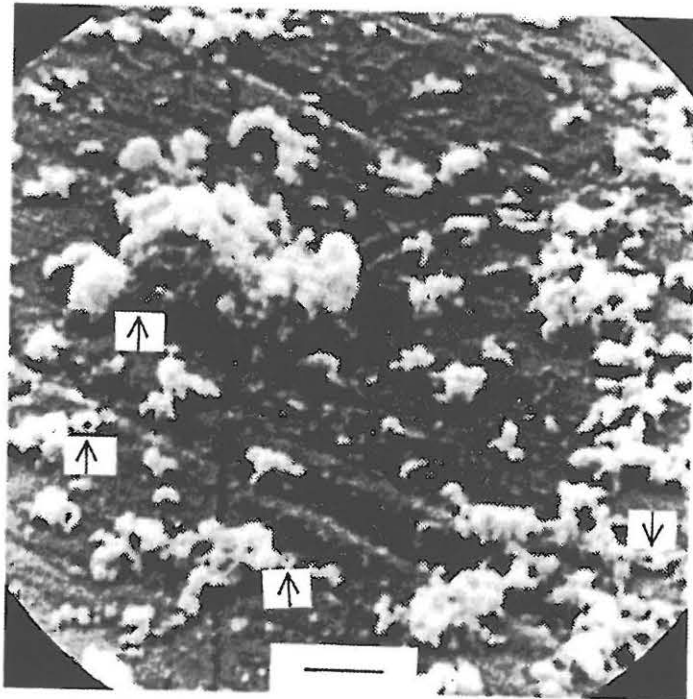


Fig. 12. Scanning electron micrograph showing sponge-like short range order material (arrowed) and fluffy aggregates and globules characteristic of allophane. Note that SEM resolution is unable to distinguish individual 'structural unit' allophane spheres which are only 35-50Å in diameter (see Figs 1 and 10). Sample is from Holocene tephra. Magnification 11,000X. Bar represents 0.9µm. Accelerating voltage 12kV. From Lowe (1981, p. 225).

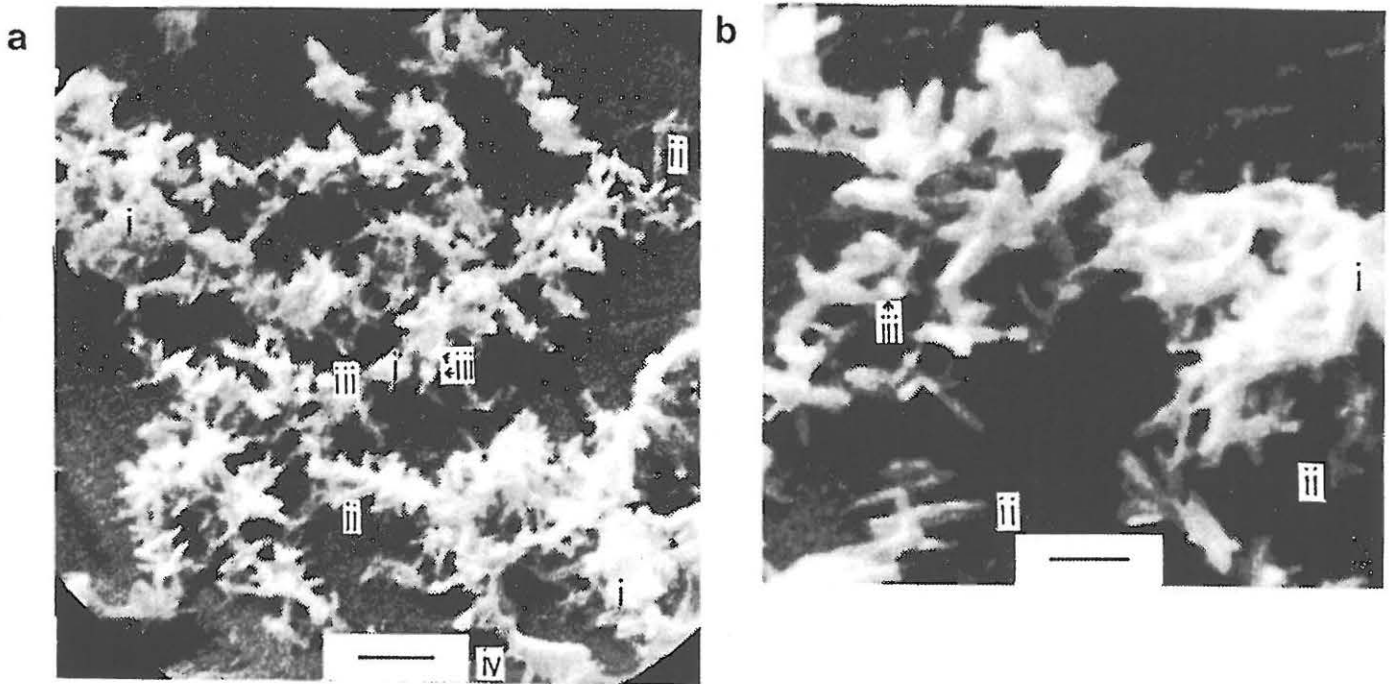


Fig. 13. Scanning electron micrographs showing interlaced halloysite tubes or laths which are frequently embedded in an "amorphous-gel" matrix (i). The tubes average 0.07µm x 0.3µm in size and occasionally appear split (ii), probably due to partial unrolling (to give "scrolls") or perhaps to interlayer separations between packets of layers along halloysite tube c-axes. The fine (0.1-0.15µm) semi-spheroidal particles (arrow iii) may represent allophane clusters, spheroidal halloysite or cross-sectional views of halloysite tubes. The gel-like platy material (iv) looks similar to the amorphous coatings in aluminosilicate systems described by Jones and Uehara (1973). Sample is from Hamilton Ash. (a) Magnification 12,000X. Bar represents 0.8µm. 23kV accelerating voltage. (b) 22,000X magnification. Bar represents 0.5µm. 23kV accelerating voltage. From Lowe (1981, p. 229).

aggregates (Fig. 12). Halloysite occurs in spherical, tubular (Fig. 13), and platy forms. Iron oxide minerals show a variety of forms (Table 4).

It must be stressed that the morphology of particles as shown by SEM (or TEM) is an aid to their identification, but not necessarily definitive. Similarly, relative abundances of species can seldom be accurately determined from SEM or TEM alone.

Sodium fluoride reactivity

Rapid (field) tests using NaF

Large OH^- release takes place when NaF is added to allophanic materials, and Fieldes and Perrott (1966) proposed this reaction as a rapid field test for allophane. The U.S. Soil Taxonomy system (Soil Survey Staff 1975) also utilises the test for classifying materials with an "exchange complex dominated by amorphous materials". Here the pH of a suspension containing 1g of soil in 50ml of 1N NaF is measured after 2 min.; a value of 9.4 or greater is taken as indicating an appreciable allophane content. Although these tests are not necessarily specific for allophane, as the reagent will react with any available Al associated with hydroxyls (Brydon and Day 1970; Wada 1977), their continuing use, in conjunction with other methods for determining allophane content, is generally supported (Rankin and Churchman 1981). The tests are used for distinguishing the B₂ horizons of podzols (which contain 'proto-imogolite' allophane) and other soils as well as in tephra-derived soils (Brydon and Day 1970; Loveland and Bullock 1975; Tait et al. 1978; Farmer 1982).

Laboratory tests using NaF

The kinetics of OH^- release are not yet clearly understood, but the reaction, summarised as $\text{M}(\text{OH})_{\gamma} + 6\text{F}^- \rightarrow \text{MF}_6^{3-} + \gamma\text{OH}^-$, occurs more slowly for crystalline material because of more stable structural hydroxyl groups (Kitagawa 1974), and hence has been used to differentiate well and poorly ordered inorganic materials by measurement of OH^- release at constant pH by titration under standardised conditions (Bracewell et al. 1970; Perrott et al. 1976a). Data in Brydon and Day (1970), Loveland and Bullock (1975) and Perrott et al. (1976a) demonstrate that Al-bonded OH^- (hydroxyaluminium) is more readily replaced by F^- than silica- or (free) ferric oxide-bonded OH^- . This trend is confirmed for synthetic aluminosilicate gels (Perrott et al. 1976b; Salter 1979), hence indicating that in general low $\text{Al}_2\text{O}_3:\text{SiO}_2$ ratios result in low reactivity values. As a corollary, Perrott et al. (1976b) suggested

using the reaction of fluoride to assess the Al:(Al + Si) mole fraction indirectly. Also, Shoji and Ono (1978) demonstrated close correlation between NaF(1:50) pH values and dithionate-citrate-soluble alumina constituents in Japanese tephra-derived soils.

Preparation

Samples of either whole soil or clay-size fractions (<2 μ m or <1 μ m) can be used. The method of preparation and analysis used at the University of Waikato is essentially that of Bracewell et al. (1970) and Perrott et al. (1976a) as modified by Salter (1979) and Lowe (1981).

The <2 μ m or <1 μ m clay fractions separated previously for XRD or DTA are air dried, lightly ground in a mortar, and equilibrated to constant humidity over saturated Mg (NO₃)₂.6H₂O prior to titration. If whole soil samples are used, they must be air dried and ground to <150 μ m, then equilibrated (the clay content should be known to enable the reactivity of the clay fraction to be calculated later).

Procedure and mineral identification

- (1) A 100 \pm 1mg soil or clay sample is introduced at zero time into 20ml 0.85M NaF solution maintained at 25 \pm 0.5°C, and stirred vigorously.
- (2) The OH⁻ released is titrated continuously with 0.1M HCl using a Radiometer Autoburette ABull and Titrator TTT60 for a 25 min. period, so that the pH is maintained constant at 6.8, as monitored by a PHM 64 Research pH meter. The titration is best set up in a constant temperature room.

The amount of OH⁻ released in 25 min., reported as mmol (meq) OH⁻/100g, is taken as the fluoride reactivity (FR) value. All samples should be analysed in duplicate or triplicate and the results averaged. Under these conditions the technique is very precise; relative deviations rarely exceed 3%, and are merely proportional to the magnitude of the fluoride reactivity values (Lowe 1981).

Conversion of the fluoride reactivity values into accurate percentages of short range order material is liable to inaccuracy because the constituents vary compositionally (e.g., Fieldes and Furkert 1966; van Olphen 1971; Henmi 1977), and the reaction with fluoride is compositionally dependant (Bracewell et al. 1970; Perrott et al. 1976a).

Application

Kirkman (1975) applied the technique to Holocene and late Pleistocene tephras in central North Island and showed that the fluoride reactivity

values reflect the gradation from allophane- to halloysite-dominated clay (<1 μ m) fractions. The Holocene tephras generally contained allophane, and hence highly reactive clay fractions (1000-2000 mmol OH⁻/100g clay), whereas the late Pleistocene tephras, with mainly (7Å) halloysite clay fractions, exhibited much lower reactivity values (100-600 mmol OH⁻/100g clay). Similar results are described by Klages (1978) for tephras in U.S.A..

Reactivities of <2 μ m clay fractions from late Quaternary tephras in the Waikato region (Lowe 1981) range from 185 to 1152 mmol OH⁻/100g and generally match those of Kirkman (1975) except that the very high values reported for his Holocene tephras do not occur. Comparison of the reactivity values with DTA estimates of allophane and halloysite content showed good correlation for sites under free-draining weathering conditions (Lowe 1981).

For the older halloysite-rich Kauroa Ash beds, Salter (1979) reports relatively low reactivity values (95-185 mmol OH⁻/100g), consistent with a low content of short range order aluminosilicate material. Some of the reactivity in this case was attributed to the fine particle size (see also Campbell et al. 1977) and hydrated status of the halloysite material.

Parfitt and Henmi (1980) used NaF reactivity, together with other tests, to show that imogolite is more ordered than allophane and has fewer defect sites and broken bonds where F can react with Al to break up the structure.

Comparison of the Fieldes and Perrott (1966) field test with the laboratory-determined reactivities shows excellent correlation (Lowe 1981). The field test is as reliable as, though less precise than, the laboratory procedure for determining the relative abundance of allophane (or rather the presence of active Al-OH groups) in whole soil samples under most site conditions.

Modified versions of the NaF reactivity field test are currently under trial in the Department of Soil Science, Lincoln College.

Chemical dissolution analyses

Short range order clay minerals have a large specific surface area and high chemical reactivity. These materials are thus more sensitive to chemical dissolution than crystalline clay minerals and dissolve differentially according to their elemental composition (Wada 1977). Thus, selective chemical dissolution can be used for determination of short range order clay constituents. The dissolution

of Al, Fe, and Si in various clay and humus constituents by treatment with different reagents is given in Table 9. This shows, for example, that allophane is dissolved by treatment with hot 0.5N NaOH or oxalate-oxalic acid (Tamm's solution) but not with dithionite-citrate or 2% Na₂CO₃ solution. However, because dissolution with one reagent only has some limitation in the specificity of the reaction, simultaneous characterisation of the dissolved material is recommended. This is

Table 9. Dissolution of Al, Fe, and Si in various clay constituents and organic complexes by treatment with different reagents. References detailing the extraction methods can be found in Wada (1977, p. 615; 1978, p. 152). After Wada (1978, p. 152).

Element in: Specified component and complex	Treatment with:				
	0.1 M Na ₄ P ₂ O ₇	Dithionite -citrate	2% Na ₂ CO ₃	0.15-0.2 M oxalate- oxalic acid (pH 3.0-3.5)	0.5 N NaOH
Al in:					
Organic complexes	good	good	good	good	good
Hydrous oxides					
Noncrystalline	poor	good	good	good	good
Crystalline	none	poor	poor	none	good
Fe in:					
Organic complexes	good	good	none	good	none
Hydrous oxides					
Noncrystalline	poor	good	none	good	none
Crystalline	none	good	none	none	none
Si in:					
Opaline silica	none	none	poor	none	good
Crystalline silica	none	none	none	none	poor
Al and Si in:					
Allophane-like	poor	good	good	good	good
Allophane	poor	poor	poor	good	good
Imogolite	poor	poor	poor	good-fair	good
Layer silicates	none	none	none	none	poor-fair

carried out typically by difference infrared spectroscopy (i.e., comparison of the IR spectra of the material before and after treatment), or from dissolution kinetics, whereby the steady-state portion of the dissolution-time curve is taken to indicate a limited attack on crystalline material (Wada 1977). Hodges and Zelazny (1980) report a procedure based on the loss in weight of a sample after it had been selectively dissolved by ammonium oxalate or sodium hydroxide as a measure of the non-crystalline material content of the sample. A differential XRD method involving selective dissolution treatment for identifying some iron oxide minerals is discussed by Schulze (1981) and Schwertmann et al. (1982).

Recent studies by Russell et al. (1981) and Parfitt and Henmi (1982) have demonstrated that for clays from predominantly andesitic tephras the acid-oxalate dissolution and infrared spectroscopy methods showed good agreement in determining allophane content where the Al:Si ratio of the extract is near 2.0 (Table 8, p.36). The methods compared

IR absorbance at 348cm^{-1} (characteristic of allophane and imogolite) with %Al and %Si extracted by acid-oxalate.

If the non-crystalline material content of samples is to be related to soil systems, Hodges and Zelazny (1980) recommend that whole samples be used for analyses, rather than only the $<2\mu\text{m}$ fractions. (See also method-related studies by Hetier et al. (1977) and Higashi and Shinagawa (1981)).

Useful references for dissolution methods and applications include Jackson (1969), Wada (1977), Dixon and Weed (1977), Brown et al. (1978), Theng (1980), Hodges and Zelazny (1980), and Parfitt et al. (1983), and papers cited therein.

Surface area measurements

Specific surface areas can be measured for allophanic clays using various adsorbates such as glycerol, ethylene glycol monoethylether, ethylene glycol, and water (Wada 1977), and low temperature nitrogen adsorption (Paterson 1977).

Specific surface area calculations for allophane range from 800 to $2210\text{m}^2/\text{g}$ using 43 and 50\AA as the inner and external diameters of the "spherule unit" respectively, and a density of 2.6 to $2.65\text{g}\cdot\text{cm}^{-3}$ (Espinoza et al. 1975; Wada 1980; Parfitt and Henmi 1980). Thus measurement of surface area can provide an estimate of allophane content.

Ethylene glycol and water adsorption methods used by Allbrook and Codlin (1981) to estimate allophane contents showed good correlation with determinations based on Tamm's acid-oxalate dissolution of Al, Si, and Fe, and OH^- release by titration to pH 6.8 after addition of NaF. Another study, by Claridge and Fieldes (1975), applied ethylene glycol retention measurements to particle morphology studies of allophane and halloysite.

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