

Mineral Commodity Report 20 - Clays

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Definition

Clay, as a rock term, describes a soft, loose, earthy material containing particles with an average grain size of less than 0.004 mm (4 μm) in the Wentworth grain size scale and less than 0.002 mm (2 μm) in most soil investigations. Clay is composed mostly of clay minerals, but may also contain quartz, feldspar, carbonates, ferruginous material, and other non-clay materials. All clays, apart from flint clay, can be made plastic when mixed with a small quantity of water. That is, they can be moulded into various shapes that harden when dried.

Clay minerals are essentially hydrous aluminium silicates with a sheet-like structure (phyllosilicates), in which magnesium or iron may substitute wholly or partly for aluminium, and with alkalis or alkaline earths as essential constituents resulting in variable chemical compositions. The most common clay minerals are kaolinite, halloysite, smectite, allophane, chlorite and illite.

History

Clay has been used in bricks and pottery for millennia. Sun-dried bricks were used from possibly over 10,000 years ago and kiln-fired bricks were used in the construction of a temple in the Euphrates region, considered to be more than 5000 years old. Sumerian and Babylonian builders constructed ziggurats, palaces, and city walls of sun-dried bricks and covered them with more durable kiln-baked bricks, often brilliantly glazed and arranged in decorative pictorial friezes.

The earliest form of pottery was earthenware (porous and coarse), which has been made for at least 9000 years. The earliest pottery yet discovered in the Middle East comes from Çatal Hüyük, in Anatolia (near modern Çumra, Turkey), and dates from 8500 years ago. Stoneware, a vitrified or glassy product, dates to the Shang dynasty in China around 3400 years ago. The oldest porcelain, a vitrified ware that rings when tapped and is usually translucent, originated in China during the T'ang dynasty (618-907 AD), but the porcelain best known in the West (where it is called chinaware) was not produced until the Yuan dynasty (1278-1368 AD). This "hard-paste" porcelain was made from petuntse, or china stone (a crushed kaolinised granite consisting of a mixture of kaolinite, sericite, feldspar and quartz), ground to powder and mixed with kaolin, and fired at a temperature of about 1450°C. Porcelain imported from China was considered a great luxury in Europe and attempts to imitate it led to the discovery in Florence during 1575 of "soft-paste" porcelain (or frit porcelain), a mixture of clay and ground glass fired at about 1200°C. The secret of hard-paste porcelain was discovered in about 1707 at the Meissen factory in Saxony

(Germany) by Johann Böttger and Ehrenfried von Tschirnaus. English bone china was first produced around 1800, when Josiah Spode added calcined bones to the hard-paste porcelain formula.

The use of clays (probably smectite) as soaps and absorbents was reported in Natural History by the Roman author Pliny the Elder (c. AD 77). The use of a kaolin-bearing surface on paper began in China about 400 AD when powdered kaolin was added to the pigment of paper coating.

In New Zealand, brickmaking and pottery were among the first established industries. Small brick works were established in many parts of New Zealand. There were 37 in 1867, but the total number expanded to 127 by 1880. Most of these works ceased production after WWII, when road transport improved. In addition to bricks and clay pipes, many of the brick works produced a limited range of domestic pottery and tableware, for example Amalgamated Brick and Pipe eventually had a "Specials Department" for pottery manufacture, which was later formed into a subsidiary company, Crown Lynn Potteries (1948-1989) (Bathurst, 1999). These companies were the original producers of the legendary railway cups. Other major pottery manufacturers were based in Christchurch, Milton and Temuka, of which the factory in Temuka is the only survivor. Studio pottery was established from the 1960s in Nelson (e.g. Crewenna and Waimea) and Coromandel (Driving Creek), and has developed into a large number of small operations, reviewed by Grzelewski (1999).

Origin of names

Attapulgit (palygorskite) is for Attapulgis, Georgia, USA. **Ball clay** is from the tradition of extracting clay by cuffing it into 1-cubic-foot blocks, which became rounded to form balls while rolling the clay to the cart. The resulting ball had a diameter of about 25 cm and weighed 13-22 kg. **Bentonite** is named after the Benton Shale Formation in Wyoming, USA, in which the first bentonite mine in 1897 was located. The Benton Shale drew its name from Fort Benton, Montana, USA. **Ceramic** is from the Greek *keramos* for potter's clay. **China clay** is a commercial term for kaolin, and was derived from its origin in China. **Clay** is derived from Latin and Old English words meaning "to stick". **Fuller's earth** originated from the practice of textile workers (or fullers) who cleaned raw wool by kneading it in a clay-water mixture that adsorbed oil, dirt, and other contaminants from the fibres. **Halloysite** was named after Baron Omalius d'Halloy (1707-1789), a Belgian geologist who first noted the mineral. **Hectorite** is named after Hector, California, USA. **Illite** is for the State of Illinois, USA. **Kaolinite** is named after **kaolin**, from the Chinese Kau-ling (or *Gaoling*), for a high ridge near the town of Jingdezhen in northwest Jiang Xi Province, China, where deposits of white kaolin were probably first worked over 2200 years ago. **Meerschau** is from the German for sea-froth, which it resembles, because its low density allows the mineral to float on water. **Montmorillonite** was named

in 1897 after Montmorillon, Vienne, France. **Natronite** for the locality in the Arrondissement of Norton, near the village of Saint Paradoux, France. **Palygorskite** is from Palygorskaja, Urals, Russia. **Porcelain** is from *porcellana*, used by Marco Polo to describe the pottery he saw in China. **Pyrophyllite** is from the Greek *pyr* meaning fire and *phyllite*, a rock or stone. **Saponite** is from the Latin *sapo* (-idos) = soap for its soaplike appearance. **Sepiolite** is from the Greek *sepion* = bone of the cuttle-fish, which is light and porous, similar to the clay mineral, and the Greek *lithos* for stone. **Vermiculite** is from the Latin word meaning “to breed worms,” alluding to the worm-like shape resulting from its expansion on heating.

Classification and properties

Clay structure

An important factor contributing to the properties of the different clay minerals is their molecular structure. Most clay minerals are based on two types of structure, the silica tetrahedral sheet and the alumina-magnesia octahedral sheet. Silica tetrahedral sheets are each about 4.7Å thick, consist of silica tetrahedra arranged in a plane and have a composition of $\text{Si}_4\text{O}_6(\text{OH})_4$. The sheets are bound together by aluminium and/or magnesium. Alumina-magnesia octahedral sheets are each about 5.05Å thick, consist of octahedra arranged in a plane, and have compositions of either $\text{Al}_2(\text{OH})_6$ (gibbsite) or $\text{Mg}_3(\text{OH})_6$ (brucite),

CRYSTALLINE
1:1 layer type
Equidimensional
Kaolinite group (kaolinite, dickite, nacrite)
Elongate
Kaolinite group (halloysite)
2:1 layer type
Expanding lattice
Equidimensional
Smectite group (e.g. smectite)
Vermiculite group
Elongate
Smectite group (e.g. nontronite, saponite)
Non-expanding lattice
Illite group
Pyrophyllite (talc) group
Chlorite group
2:1 chain-structure types
Palygorskite group (palygorskite, sepiolite)
AMORPHOUS
Allophane group

Table 1: Classification of some common clay and related phyllosilicate minerals.

depending on whether aluminium or magnesium are incorporated in the structure. The tetrahedral and octahedral structural units can be joined or stacked in several configurations of composite layers, producing various hydrated aluminosilicates that form layer-lattice minerals with a plate-like shape (e.g. kaolinite, smectite, illite and vermiculite) or chain-lattice minerals with an elongate shape (e.g. palygorskite and sepiolite). The layer-lattice structures are grouped as 1:1 layer structures containing one tetrahedral sheet linked with one octahedral sheet, and 2:1 layer structures with two tetrahedral sheets linked with one octahedral sheet. Less common clay minerals are either amorphous (non-crystalline; allophane) or have a structure based on double tetrahedral chains similar to that of amphibole minerals.

Clay minerals

Clay minerals may be classified into eight main groups on the basis of variations in structure and composition: (1) kaolinite, (2) smectite, (3) vermiculite, (4) illite, (5) pyrophyllite, (6) chlorite, (7) palygorskite, and (8) allophane (Table 1). Some clay minerals are intermediate between the clay mineral groups, formed by mixtures of the different clay structural layers, resulting in mixed-layer clay minerals such as interlayered illite-smectite and interlayered chlorite-kaolinite.

The clay minerals are very similar in physical properties (Table 2), and many can be distinguished only by X-ray diffraction, infrared spectroscopy, electron microscopy, or differential thermal analysis.

Kaolinite group includes the minerals kaolinite, halloysite, dickite and nacrite, which are all dioctahedral 1:1 layer silicates. Kaolinite is by far the most common mineral of the group. Halloysite is much less common, and dickite and nacrite are comparatively rare. All of these minerals have essentially the same composition, apart from a hydrated form of halloysite, which differs from the more common metahalloysite by having an extra two water molecules per unit cell. On heating to 100°C, hydrated halloysite dehydrates to metahalloysite irreversibly. Halloysite crystallises as elongated tubular or, in some cases, spheroidal shapes, whereas the other kaolinite group minerals form pseudo-hexagonal platelets or stacks of platelets. Kaolinite group minerals are the principle constituents of kaolin.

Smectite group clays have a 2:1 sheet structure and include the dioctahedral minerals smectite (also known as montmorillonite), beidellite and nontronite, and the trioctahedral minerals hectorite (Li-Mg-smectite) and saponite (Mg-smectite; also known as bowlingite and soapstone). These are expanding lattice clays that swell in water, are thixotropic and possess high cation-exchange capacities. Smectites are the principal constituents of bentonite and fuller’s earth.

Vermiculite is similar to smectite in structure and, in some cases, composition. When heated rapidly above 400°C, interlaminar water turns to steam and causes the mineral layers to exfoliate or separate into worm-like pieces. The increase in bulk volume is typically 8-20 times in commercial grades, but individual flakes can expand by as much as 30 times. Its specific gravity may be reduced to as low as 0.09.

Minerals	Colour	Transparency	Lustre	SG	H	Crystal symmetry	Habit	Size	Structure
Chlorite (Mg,Fe) ₆ AlSi ₃ O ₁₀ (OH) ₈	green	translucent	pearly	2.6-2.9	2-2.5	monoclinic	tabular or granular masses		
Halloysite Al ₄ Si ₆ O ₆ (OH) ₁₂	colourless, white; tinted yellowish, brownish, reddish, or bluish	transparent to translucent	pearly to dull	2-2.2	2-2.5	monoclinic	tabular, ultramicroscopic; compact-mealy masses	outside diameter 0.04-0.19μ	kaolinite layers (see below) separated by layers of oriented water molecules
Illite (K,H ₂ O)(Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ ((OH) ₂ ,H ₂ O)	white and various pale colours		dull	2.6-2.9	1-2	monoclinic (also orthorhombic?)	massive; extremely fine grained	0.1-0.3μ in diameter; 30Å thick	the same as smectite (see below) except that some of the Si is always replaced by Al
Kaolinite Al ₂ Si ₂ O ₅ (OH) ₄	colourless, white; tinted yellowish, brownish, reddish, bluish	transparent to translucent	pearly to dull earthy	2.6-2.63	2-2.5	triclinic	hexagonal platelets or scales; usually massive, compact, friable, or mealy	0.3-4.0μ wide; 0.025-2.0μ thick	single sheet of SiO ₂ tetrahedrons whose tips are oriented the same way and are joined to a single sheet of alumina octahedrons
Palygorskite (attapulgite) (Mg,Al) ₂ Si ₄ O ₁₀ (OH) ₄ H ₂ O	white, grey	translucent	dull	2.1	soft	monoclinic (and orthorhombic)	lath-shaped xls, elongated, in bundles	many μ long; 60-100Å wide	silica tetrahedrons in double chains linked through oxygens at their longitudinal edges; the tips of the tetrahedrons of successive chains point in opposite directions
Pyrophyllite Al ₂ Si ₄ O ₁₀ (OH) ₂	white		pearly	2.8	1-2	monoclinic	foliated or radiating masses		
Smectite (montmorillonite) (Na,Ca) _{0.33} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ .nH ₂ O	white, grey, yellowish, greenish, pink		dull	2-3	1-2	monoclinic	massive, very fine grained, claylike		sheet of alumina octahedrons sandwiched between two sheets of oriented SiO ₂ tetrahedrons whose tips point toward the alumina sheet
Sepiolite (meerschaum) Mg ₃ Si ₆ O ₁₅ (OH) ₂ .6H ₂ O	white, greyish, yellowish, or tinted bluish green or reddish	nearly opaque	dull	~2	2-2.5	orthorhombic	massive; fine fibrous; usually compact nodular, earthy or claylike	shorter and thicker than attapulgite	similar to attapulgite, except that three pyroxene chains are linked to form two amphibole chains
Vermiculite (Mg,Fe,Al) ₃ (A,Si) ₄ O ₁₀ (OH) ₂ .4H ₂ O	gold, brown, yellow-green, grey, blackish	transparent to translucent	vitreous to pearly	2.1-2.7	1-2	monoclinic	pseudohexagonal thin and thick laminae, scaly, massive aggregates		sheets of trioctahedral mica or talc separated by layers of water molecules

Table 2: Properties of some clay minerals (modified after Table 47 of Harben and Kuzvart, 1996).

Illite group clays have a dioctahedral 2:1 mica-like sheet structure, but differ from true mica by having more water and fewer inter-layer cations (mostly potassium), resulting in weak forces between layers and irregularity of stacking. Illite clays are intermediate in composition and structure between muscovite and smectite.

Palygorskite group (also known as palygorskite-sepiolite group; formerly hormite group) includes the minerals, palygorskite, also known as attapulgite, and sepiolite, also known as meerschaum. These minerals have a chain-like structure and form fibrous, lath- or needle-like crystals. The structure incorporates channels of approximately 6Å and features a high surface area (sepiolite has the highest surface area of all the clay minerals), porosity, surface charge and cation exchange capacities, resulting in excellent sorptive, colloidal and thixotropic (gelling) properties in water.

Amorphous clays are formless to X-ray diffraction because of their fine grain size or irregularity in the arrangement of their layers. Allophane is a hydrous aluminosilicate $(\text{SiO}_2)_{1-2}\text{Al}_2\text{O}_3(\text{H}_2\text{O})_{2.5-3.0}$ gel, formed from volcanic glass, but transforms to halloysite with time. It consists of hollow, irregular spherical particles with diameters of 35 to 50Å. The walls of the spheres are 7 to 10Å thick and contain openings that permit the passage of water molecules (Wada and Wada, 1977). The space within the walls is filled with water (10% by weight) which is strongly retained.

Clay rocks

Clay rocks are classified and named on the basis of their dominant constituent clay mineral (e.g. palygorskite, smectite, as listed above) or other names based on their use (as listed below).

Kaolin, also called China clay, is principally kaolinite, with lesser quantities of illite, smectite, quartz, feldspar, muscovite and other non-kaolinite minerals, and has a low total iron content. It is a soft white clay of variable but usually low plasticity and dry strength, that retains its white colour when fired.

Ball clay, flint clay and refractory clay (also known as **fire clay**) are varieties of kaolin. Ball clay has high plasticity and strength, but inferior whiteness compared with kaolin. Flint clay is a compact microcrystalline to crystalline clay that breaks with a pronounced conchoidal or “flinty” fracture, resists slaking, and has almost no plasticity. Refractory clay has a high temperature fusion point, typically above 1425°C. It is non-white burning. Generally the higher the level of alumina, the more refractory the clay. In some instances, this level can be enhanced to as much as 60% by the addition of bauxite minerals such as gibbsite, diasporite, or pure alumina. Chamotte is a refractory clay formed by calcining clay such as kaolin, flint clay or fireclay.

Bentonite is a clay consisting predominantly of smectite (montmorillonite) minerals. It is characterised by exchangeable Na^+ , Ca^{2+} or Mg^{2+} cations which greatly influence the properties of the clay (and therefore its commercial applications). There are two types of naturally occurring bentonite: a swelling bentonite which has a high sodium-to-calcium ratio (sodium bentonite or Wyoming bentonite) and is typically associated with marine sediments, and a non-swelling bentonite with a low sodium to calcium ratio (calcium bentonite) that is typically associated with

freshwater sediments. The swelling variety has the ability to absorb water and swell many times its original volume to form gel-like masses. Calcium bentonite can be converted to a sodium-type (termed sodium exchange bentonite) by treatment with soda ash to improve swelling capacity. It can also be used to produce acid-activated bentonite by treatment with inorganic acids to replace divalent calcium ions with monovalent hydrogen ions and to leach out ferric, ferrous, aluminium and magnesium ions, thus altering the crystal structure, and increasing the specific surface area and porosity.

Fuller’s earth is a group of clays that have a substantial ability to adsorb impurities or colouring bodies from fats, grease, or oils. In the United Kingdom, the term was introduced for clay in which the principal clay mineral is calcium smectite, but other minerals such as kaolinite, palygorskite and sepiolite may also be present and account for its variable chemical composition. In the USA, clays that are termed fuller’s earth are predominantly palygorskite or sepiolite. Fuller’s earth is fine-grained, found in a wide range of natural colours, from brown or green to yellow and white, and has a high water content. It crumbles into mud when mixed with water, so it has little natural plasticity.

Formation

Formation process

Clay minerals are formed by the processes of weathering, diagenesis and hydrothermal alteration (Table 3).

Weathering and soils

Soils and other residual clay deposits are formed by *in situ* weathering. Controlling factors include the nature of the parent rock, climate, topography, vegetation, and the time period during which these factors operated. Different environments, particularly different climatic and hydrologic regimes, may produce different clay minerals from the same parent rock type. Large kaolinite deposits formed by weathering are common around the world. Commercially exploited resources occur in the United States, Brazil, Guyana, Surinam, Ghana, Australia, and Europe.

Clays in sediments

Clay minerals occur widely in sedimentary rocks, particularly those with fine particle size such as mudstones and shales (argillaceous or clay-rich rocks). Illite and smectite, including mixed-layer clay minerals, kaolinite and chlorite are the principal clay mineral components of recent deep-sea sediments. Smectite and kaolinite are less abundant in pre-Devonian argillaceous sediments, which are composed largely of illite and chlorite. Kaolinite and illite are found in some coal measures. Most ball clays are Eocene to Lower Oligocene in age and formed in swampy sedimentary environments under subtropical to tropical conditions, assisted by post-depositional diagenesis and the presence of organic components. Palygorskite and sepiolite clay deposits are mostly associated with mid-Tertiary or younger shallow lagoonal sediments formed in sub-tropical to tropical environments.

Major commercially exploited sedimentary kaolin deposits are found in Georgia and South Carolina, USA, in the

Clay type	Major industrial applications	Genetic process	Typical parent rock or associated mineralogy	Examples	Age
Kaolin	Industrial fillers, coatings and pigment in paper, paint, plastics, rubber and related industries.	Residual weathering	Typically granites or acid volcanics	Belitung, Indonesia	Tertiary or Quaternary
	Modified to produce organo-clays for use in organic systems. Ceramic raw material.	Hydrothermal	Granites Acid volcanics	Cornwall, UK Northland, NZ	Late Tertiary
	Calcined kaolins with improved light scattering properties for use in paper and paint systems.	Sedimentary	Granites and gneisses	Georgia, USA	Cretaceous and Tertiary
	Halloysite: ceramics, industrial filler, cosmetics, framework for catalysts.			Rio Jari, Brazil	Pliocene
Smectite	Oil drilling, pelletising, foundry sand binder and filter aid.	Primary sedimentary or ash fall	Permeable volcaniclastics Basic or acid volcanics	Milos, Greece	Tertiary
	Containment barriers in landfills. Chemically modified for use in organic systems. Animal litter.			Wyoming, USA	Upper Cretaceous
Palygorskite-sepiolite	Oil drilling, bleaching oil, adsorbents, gellants, agricultural carrier.	Sedimentary	Source of smectite and a high concentration of magnesium	Georgia, USA	Mid Tertiary
Pyrophyllite	Refractories, ceramics, fibreglass.	Hydrothermal	Acid volcanics or intrusives in high-sulphidation hydrothermal systems	NSW, Australia Honshu, Japan	Devonian Late Cretaceous
Ball clay	Ceramics, pesticide carrier.	Sedimentary	In sedimentary basins or structural depressions adjacent to granites	Devon, UK	Tertiary

Table 3: Classification and major uses of industrial clays (modified after tables 1 and 2 of Harvey and Murray, 1997).

Amazon basin in eastern Brazil, and on the Cape York Peninsula in northeastern Australia.

Diagenesis

As temperature and pressure increase with the progression of diagenesis, clay minerals in sediments change to those stable under given conditions. Therefore, certain sensitive clay minerals may serve as indicators for various stages of diagenesis. Typical examples are the crystallinity of illite, the polytypes of illite and chlorite, and the conversion of smectite to illite.

With deeper and longer burial, ball clay becomes lithified to form fireclay. Fireclay is a sedimentary clay found in coal measures as “underclays”, situated immediately beneath a coal seam. Coal measures may consist of alternating sequences of coal and clay. Whereas ball clays are associated with lignite, fireclays are usually associated with higher rank coals, reflecting the greater lithification of their formation. Flint clay is typically sedimentary kaolin that has been subject to prolonged leaching and recrystallisation (e.g. most USA examples; Missouri, Kentucky) or metamorphism (e.g. some European flint clays).

Hydrothermal alteration

Clay minerals are formed as alteration products associated with geothermal areas and hot springs, and as aureoles around hydrothermal ore deposits. There is typically a zonal arrangement of the clay minerals around the source of the alteration as a result of decreasing temperature and changes in fluid composition along the fluid flow and reaction path. The zonal arrangement varies with the type of parent rock and the nature of the hydrothermal fluid. For example, in epithermal ore deposits, near-neutral hydrothermal fluids alter rocks to illite, chlorite, and smectite, whereas acid hydrothermal fluids result in the formation of kaolinite, dickite and pyrophyllite. Furthermore, there is typically a temperature dependent zonation of illite, interlayered illite/smectite and smectite with decreasing temperature in many epithermal/geothermal systems. Pyrophyllite is mainly found associated with hydrothermally altered volcanic rocks, particularly in Japan and Korea.

Bentonite deposits typically originate through the hydrothermal alteration and/or weathering of tuffaceous material rich in volcanic glass, particularly ash falls, which provide the open macro-structure (high-surface area) necessary for efficient devitrification. This includes the alteration of volcanic ash deposited in lacustrine environments, alteration by groundwater of deeply buried tuffs, the surface weathering of tuffs, and hydrothermal alteration, either at depth or in hot springs.

Uses

Commercially, the most important clays are kaolin (mainly kaolinite) and bentonite (smectite), with palygorskite, sepiolite, and vermiculite constituting small, more specialised markets (Table 3). Illite, the most abundant clay mineral in nature, is unimportant commercially as an individual mineral, but it is a prime constituent of common clay and shale.

Ceramics and bricks

Whiteware ceramics may be classified as: porcelain, including hard porcelain, soft porcelain, vitreous china (largely used for making tableware) and technical porcelain (such as electrical or insulator porcelain, and high alumina porcelain); stoneware (e.g. rustic tableware and art ware); and earthenware.

Kaolin is used extensively in the ceramics industry, because of its high fusion temperature and white burning characteristics. Kaolin intended for firing as a ceramic must have a high Al_2O_3 content as well as low content of fluxing (K_2O , Na_2O) and colouring (Fe_2O_3 , FeO , TiO_2) agents. In the manufacture of whiteware, the kaolin is usually mixed with approximately equal amounts of silica, feldspar and talc, and a somewhat smaller amount of ball clay to obtain the proper properties of plasticity, shrinkage and vitrification, for forming and firing the ware. Premium-grade halloysite may be utilised to add whiteness and translucency to porcelain and bone china, and for strength in technical ceramics and ceramic catalyst support bodies.

The composition of ceramic pipes is similar to whiteware, but contains more silica, fluxes and colouring agents. Potter's clay is less pure than pipe clay and sculptor's clay or modelling clay consists of a fine potter's clay, sometimes mixed with fine sand.

Bricks are made from an admixture of clay and sand with some ferruginous (iron-containing) matter. The main clay minerals used in brickmaking are kaolin and illite. Kaolin type clays are also used in the manufacture of refractory products such as firebricks and blocks, insulating bricks, refractory mortars and mixes, and monolithic and castable materials. Refractory clays have little or no lime, alkaline earth or iron (which act as fluxes), and are therefore infusible or highly refractory. Plastic clays, like kaolin and ball clay, are not so refractory as are the flinty, harder varieties, but are useful for bonding. Where flint clays are scarce, plastic kaolin may be calcined to form a hard, dense, refractory aggregate known as chamotte or refractory grog.

Fillers and coaters

The paper industry is by far the largest user of white kaolin, both as a filler and as a coating. In filling, the kaolin is mixed with the cellulose fibre and forms an integral part of the paper sheet to give it body, colour, opacity, and printability. In coating, the kaolin is plated along with an adhesive on the paper's surface to give gloss, colour, high opacity, and greater printability.

Palygorskite, sepiolite and acid treated smectite are used in the manufacture of NCR (no carbon required) paper, because of the colour they develop during reactions with certain colourless organic compounds.

Kaolin is used as a functional white filler in many other materials besides paper, both to reduce the cost and to add certain physical properties. In plastics it provides smooth surfaces, dimensional stability, and resistance to chemical attack; in rubber it adds strength, abrasion resistance, and rigidity; and in paint it provides high covering ability, as well as desirable flow and suspension properties. Kaolin is also used in a range of products that include cosmetics,

catalysts, inks, insecticides, food additives, and filter aids. Kaolin and pyrophyllite are used as fillers in fibreglass, providing a source of alumina.

Drilling mud

Bentonite is widely used in drilling muds. It is added to the drilling-water to increase the density of the circulation fluid and to provide thixotropic properties, so that when the drill string is stopped the drilling fluid converts to a gel, which supports the cuttings and drillhole walls. Bentonite also aids lubrication of the drilling bit and acts as an emulsifying agent in the drilling fluids. Palygorskite and sepiolite are also used in drilling muds, but they are inferior to bentonite in most applications except for palygorskite's resistance to flocculation under highly saline conditions and sepiolite's stability in high-temperature environments.

Sorbents

Bentonite, palygorskite and sepiolite have high adsorption (the ability to attract and hold ions or molecules of gas or liquid) and absorption (the ability to assimilate or incorporate material) properties. The original adsorbent was fuller's earth which was originally used to de-grease sheep wool and has been subsequently used to decolourise, deodorise, dehydrate, and/or neutralise various mineral, vegetable, and animal oils.

In a dry state, sorbents may be used as pet litter (more than 70% of sepiolite is used in pet litter in the USA, where the market exceeds 1 Mtpa), in materials used to clean oil spills, as an anti-caking agent, in pharmaceuticals, or as a carrier for fertilisers, pesticides, or hazardous chemicals (liquids can be transported as free-flowing solids). Sorptive clays may be used in animal feedstuffs, where they act as a binder or filler and promote growth by improving feed efficiency and preventing disease.

Another large market for sorbents is in the refining of liquids - mainly oils, but also sugar cane juice, beer and wine. Large amounts of naturally active calcium bentonite are used for this purpose, but acid-activated clay, which has superior absorption properties, is gradually replacing naturally active clay. Palygorskite also has a share of the bleaching and decolourising market, particularly in the USA, and a significant proportion of the sepiolite production from Turkey is used for the extraction of sulphur from light paraffin oils. Highly absorptive clays such as calcium smectite, palygorskite and sepiolite are used as clay liners in landfill sites and in synthetic membranes.

Allophane is used in New Zealand to remove phosphate from sewage affluent and can be used to adsorb organics (Benbow, 1990). It has applications in the cement industry and could be used in water purification.

Miscellaneous applications

Bentonite, and less commonly kaolinite, are surface coated with organic compounds such as amines, to make organoclays for use in nondrip paints, greases, printing inks, drilling muds and cosmetics. When added to liquid organic systems, organoclays alter the rheological characteristics including viscosity, solid suspension, and thixotropy.

Bentonite, kaolinite and halloysite are used in the manufacture of various catalysts and catalyst carriers, although

synthetic zeolites have now largely replaced this application for kaolinite and halloysite.

A major use of bentonite is as a binding agent in the production of iron ore pellets. About 5-10 kg of bentonite is used per tonne of pellets. Because of its good bonding characteristics, bentonite constitutes 4 to 6% of foundry moulding sands (calcium bentonite may be used in lower temperature foundry sands). Palygorskite is used to a minor extent in oil-bonded foundry sands; its binding characteristics are generally inferior to those of bentonite. Sodium bentonite is used to provide a bond in brake linings and as a plasticiser in refractory, abrasive and ceramic mixes.

Expanded vermiculite is used in lightweight concrete or plaster, and for thermal and acoustic insulation. Vermiculite is used in a wide range of growing media, composts and potting mixes, as a soil conditioner and a germination medium for seeds. Sepiolite has been used for making meerschaum tobacco pipes in Turkey, Hungary and Germany since the 1700s. It is highly prized for this application as it carves easily and, when smoked over a long time, it takes on a glass-like surface and deep plum-red colour. Kaolinite, smectite, hectorite, palygorskite and sepiolite are used in pharmaceuticals and cosmetics

Price

Prices for some selected clay minerals are listed in Table 4. New Zealand produces the world's most expensive clay, halloysite from Matauri Bay, which has sold at around US\$500-600 per tonne (Harvey, 1997).

World production and consumption

World-wide kaolin production capacity is more than 27 Mtpa from more than 50 countries. More than half of this total is relatively low-cost unprocessed "common clay" used in lightweight aggregate, cement, brick, civil engineering, sealing, and refractories. The remainder is the various forms of processed industrial grade kaolin, including ball clay and refractory clay.

Production of commercial grade ball clay is concentrated in the south-central United States (Tennessee, Kentucky and northern Mississippi; 1 Mt), the UK (Devon and Cornwall; 0.8 Mt), Germany (the Westerwald; 2 Mt) and the Czech Republic (Cheb basin), although many other countries produce plastic clays of lower quality including France (Provins and Charente), Portugal, Thailand, China (Pearl River Delta), and Ukraine. Refractory clays are produced in virtually every industrialised country, although there are four main areas of production, namely the USA, Europe, China and South Africa. Flint-clay production is restricted largely to the United States, France, South Africa, Australia, Hungary, Commonwealth of Independent States, and China.

The commercial development of high purity halloysite resources is restricted to New Zealand, Korea and Japan. Lower grade resources are exploited in Japan, USA and, to a smaller extent, the Czech Republic, France, the Philippines and Morocco.

About half of the world's bentonite production is from the USA mainly in Upper Cretaceous and Tertiary rocks. Major deposits of high-swelling or sodium bentonite occur in

Clay	Specifications	Unit	Price
Ball clay	Air-dried, shredded, bulk, FOB	1 tonne	£25-65
	Refined, noodled, bulk, FOB	1 tonne	£55-70
Bentonite	Wyoming, ex-works, rail cars, crude, bulk	2000 lb	US\$25-60
	Wyoming, ex-works, rail cars, foundry grade, bagged	2000 lb	US\$45-55
Fullers earth	Soda-ash treated, del, UK foundry grade, bagged	1 tonne	£98-115
Halloysite	New Zealand, processed ceramic grade, CIF into Japan	1 tonne	US\$500-600
Kaolin	Ex-Georgia plant, filler, bulk	2000 lb	US\$75-95
	Ex-Georgia plant, calcined, bulk	2000 lb	US\$320-375
Palygorskite	Georgia, powder, 40-100% - 325 mesh	2000 lb	US\$200-500
Pyrophyllite	Australian milled 300 mesh filler grade, min. 21 tonne container, FOB Sydney	1 tonne	US\$280
Vermiculite	Raw, ex-US plant, bulk	2000 lb	US\$130-200

FOB free on board

CIF cost including freight

Table 4: Prices of some selected clay materials (after Industrial Minerals, March 2000; Harvey, 1997).

Wyoming and Montana; low-swelling or calcium bentonite is found in Mississippi, Texas, California, Colorado, and Arizona. Bentonite is also produced in many other countries including Mexico, Canada (Alberta, Saskatchewan and Manitoba), Argentina, Brazil, Peru, Cyprus, the Czech Republic, France, Greece, Hungary, Italy (Sardinia), Poland, Romania, Spain, the UK, CIS (Ukraine, Azerbaijan, Kazakhstan Georgia, Turkmenistan, Uzbekistan), Germany, Yugoslavia, Algeria, Morocco, Mozambique, South Africa, Japan, Pakistan, Turkey and New Zealand.

World production of pyrophyllite is about 2.2 Mtpa, mostly from Japan (0.5 to 1.1 Mtpa) and South Korea (0.7 Mtpa).

World production of palygorskite and sepiolite clays is between 2.5 and 4 Mt, the exact production figure is uncertain because many of these clay deposits are classified as fullers earth. USA (Georgia and Florida) is the largest producer of palygorskite, although Senegal (Thies) has the most extensive resources. Other producers include Spain (Caceres and Cadiz), India (Gujarat), Turkey, Ukraine, Australia (Lake Nerramyne in WA), South Africa (Transvaal) and China. Sepiolite is produced in Spain (near Madrid; 750,000 t in 1998), USA (Lathrop Wells, Nevada; 40,000 tpa), China (Liling and Liuyang in Hunan province, and Pingxiang in Jiangxi province; 15,000 tpa), France, Turkey (Eskisehir and Balikesir regions), Korea and Tanzania.

Vermiculite is mined mostly in South Africa (211,000 t in 1997) and the USA (Montana and the Carolinas; 180,000 t), with smaller volumes produced in Brazil (23,000 t), Russia (20,000 t), Australia (16,600 t), Zimbabwe (14,800 t), Kenya and China.

Mining and processing

Clays are generally mined by highly selective open pit methods using hydraulic excavators, front-end loaders, or draglines. The clay is processed using either a dry (air flotation) or a wet process (water washing). The wet process produces a higher cost and higher quality product than the dry process.

The dry process involves crushing, drying, pulverising, and air flotation, to remove the grit particles (mostly quartz and feldspar). In the wet process, the first step is to remove the non-clay minerals, usually by extracting the grit from a clay slurry in drag boxes, classifiers, and/or hydrocyclones. The clay slurry is centrifuged and then thickened to about 30% solids in settling tanks. Further processing may involve ultraflotation and screening/filtering. In some cases flotation or high-intensity magnetic separation is used to remove iron and titanium impurities.

Bentonite may be further processed or treated. For example, swelling sodium bentonite, may be produced by treating calcium montmorillonite, the nonswelling bentonite, with soda ash. Acid-activated smectite is manufactured through the reaction of inorganic acids with smectite. The physical effects of acid activation include opening up the edges of the platelets, increasing pore diameters, and enlarging surface area. Also some bentonite and kaolinite are surface coated with organic compounds to make organoclays.

New Zealand occurrence

The locations of the New Zealand's clay deposits of economic importance are shown in Fig. 1. They can be grouped into residual clays formed by in-situ alteration of pre-existing rocks, mostly by weathering, and secondary clays formed by deposition of clay minerals through processes of sedimentation and hydrothermal alteration.

Weathering of basement rocks

Residual clays derived from weathering of gneiss and gneissic granite (Charleston Metamorphic Group) are mined at **Charleston**. The White Horse quarry and Bromielow Pit were worked for clay until 1986 by McSkimmings Industries, for the manufacture of sanitary ware at Benhar, South Otago. Bromielow pit is currently operated by Potters Clay (Nelson) Limited for pottery clay. The material contains about 30% white clay, with the remaining material mostly quartz and mica.

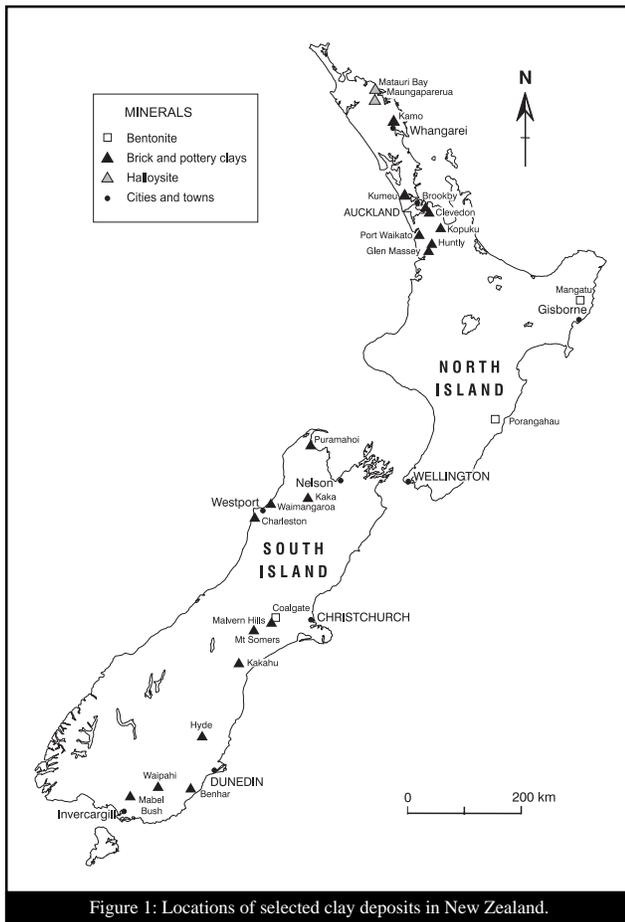


Figure 1: Locations of selected clay deposits in New Zealand.

Clay derived from weathered granite is worked at McGlashens Clay Pit on Rose Holdings' farm near Puramahoi, for Macs Mud Limited. Clays from weathered granite are also present at **Kawatiri** and **Baton** (Taylor, 1943), and clays from weathered schist are found at **Tuamarina** in Marlborough, and several locations in central Otago (see Fig. 20-5 of Fieldes et al., 1974).

Clays from weathering of Mesozoic greywacke suite rocks have been extracted at Port Waikato, Clevedon, Glen Massey, Te Kuiti, Ngaruawahia, Palmerston North and in the Wellington region (Fieldes et al., 1974).

The **Port Waikato** and **Clevedon** deposits in South Auckland are mined by CSR Building Materials (NZ) Limited (formerly Monier Brickmakers Ltd) for brick production in New Lynn, Auckland (Taylor, 1994). Port Waikato produces around 14,000 tpa of red burning argillite clay (illite, smectite and vermiculite) from weathered Jurassic argillite (Murihiku Supergroup). The clay is extremely hard and possesses good weather resistance properties. Clevedon clay pit, near Manukau City, produces 9,000 tpa of clay (halloysite with lesser kaolinite and illite) from weathered Jurassic argillite. The clay is used to improve the red body colour in the bricks. Clay from **Glen Massey (Waikato)** is derived from weathered greywacke. It is a grey-white and green-white, disordered kaolinite, containing about 40% quartz and minor iron, and is used mainly for mineral fillers. **Te Kuiti** clay is from weathered greywacke and has been used for brickmaking. **Ngaruawahia** clay is from deeply weathered siltstone and is used for pipe and tile manufacture (e.g. Verita Tiles Ltd). Clay from weathered greywacke (and loess) has been extracted from several locations in the

Wellington region. At **Plimmerton**, north of Wellington, clays were mined until 1987 from local pits and used in the production of bricks by Winstone Clay Products Limited. Similar deposits were worked at **Judgeford** and **Pauatahanui** (Paekakariki Hill Road) by Ceramic Pipes (Wellington) Limited (Grant-Taylor, 1968). Residual clay (dominantly halloysite) from weathering of greywacke (and loess) in the **Wellington** area has been used locally (e.g. Silverstream, Miramar, Khandallah, and Ngaio) for the manufacture of bricks, tiles and pipes.

Weathering of Tertiary and Early Quaternary sediments

At **Brigham's Creek**, Kumeu, CSR Building Materials (NZ) Limited extract about 12,000 tpa of clay (mainly halloysite) for use at their New Lynn brickmaking plant (Taylor, 1994). The clay is derived from weathering of Waitemata Group sediments and overlying volcanic ash. The halloysite can cause shrinkage and drying problems, which are controlled by the admixture of black ironsand from the Woodhill (Helensville) deposit. Pumiceous sand from the Waikato River may also be added, to promote fluxing.

Near **Te Kuiti**, clay from Te Kuiti Group and Mahoenui Formation has been worked for use as a cement additive. At **Taumarunui**, clay-rich, weathered, fine-grained Tertiary mudstone (papa) has been used to make bricks. At **Napier**, clay derived from weathering of Quaternary Kidnapper Group mudstone has been used by Te Mata Potteries and clay from Quaternary mudstone on Scinde Island was used by the Napier Brickyard (Kingma, 1971 p. 161).

Weathered sediments on the Nelson Penneplain are mined at Gates Road Pit, near Puramahoi, by Potters Clay (Nelson) Ltd. Production was 63 t of clay in 1998. At **Kaka**, in the Tadmor Valley near Nelson, kaolinitic clay deposits, apparently derived from weathering of transported granitic debris, are present within feldspathic lenses in the basal Glenhope Formation of the Tadmor Group (Pliocene) (Taylor, 1941; Wojtowicz, 1984). Clay production was from an underground mine, now closed. At **Wakapuaka**, Nelson Brick & Pipes Limited produced 8300 t of clay for bricks and pipes between 1968 and 1976. The pit is now closed. A pit at **Bishopdale** extracts clay from weathered and sheared Tertiary sedimentary rocks for brickmaking (Bishopdale Bricks Ltd).

Clays from Pleistocene lagoonal and swamp environments are mined at **Waimangaroa**, north of Westport (MacFarlan and Barry, 1991). A clay band, generally less than a metre thick, is worked in several pits on the low-lying coastal plain. In the **Greymouth** area, clay has been mined from mudstone of the Blue Bottom Group and used for making firebricks (Morgan, 1911; Gage, 1952). Morgan and Bartrum (1915) noted that the Kaiata Mudstone and Port Elizabeth beds are other potential sources, as is clay at McLeod Terrace near Ross noted by Morgan (1908).

Bentonite derived from weathering of volcanic ash

Bentonite deposited in a freshwater environment occurs in the Harper Hills near **Coalgate**, 65 km west of Christchurch and is mined and processed by OMYA New Zealand Limited. The Coalgate Bentonite is a member of the Miocene Harper Hills Volcanic Formation, which also

includes several basalt flows and beds of tuff and tuff breccia (Gregg, 1964). The bentonite rests directly on basalt and is overlain unconformably by Plio-Pleistocene sand, gravel and shellbeds, and by Pleistocene morainic gravels. Bentonite is present as a main bed up to 62 m thick, separated from a lower, 15 m thick carbonaceous bentonite bed by 3 to 4 m of quartz sand and gravel (Carlson and Rogers, 1974; Carlson et al., 1980). Ritchie et al. (1969) and Carlson and Rodgers (1974, 1975) consider that the bentonite was formed by weathering of glassy basaltic ash deposited in a lake.

Mineralogically the bentonite is a non-swelling (calcium-magnesium) ferri-ferrous-beidellite with minor ferri-ferrous smectite (Carlson and Rodgers, 1974), up to 20% kaolinite and illite and, typically, less than 3% quartz and feldspar (MacFarlan and Barry, 1991). It is processed by treatment with soda ash to produce the swelling type. Measured resources total around 11 Mt, but potential resources are much larger. The uses of Coalgate bentonite include: as a binder in foundry sand, for drilling muds, for sealing drillholes, for sealing dams and diaphragm walls in construction projects, as a bitumen emulsifier, in fibrous cement and as pellet binder in stock food.

Late Cretaceous to Eocene marine bentonitic beds occur along the east coast of both the North and South Islands (e.g. see Fig. 20-10 of Fieldes et al., 1974). The main localities are in the Gisborne, Hawkes Bay, Wairarapa, Marlborough and Canterbury districts (Ritchie, 1962; Ritchie et al., 1969), although occurrences are known from other locations such as Kaeo, Opuawhanga, Mount Parahaki and Motatau in Northland. Bentonite has been worked in the past at Mangatu, north of Gisborne and at Porangahau in southern Hawkes Bay.

The **Mangatu** deposit, north of Whatatutu, was briefly worked by the Dominion Bentonite Co. between 1948 and 1950. Swelling values of 95-89, with 4.5-8.3% CaCO_3 are reported (Ritchie, 1962). Further south, in the Gisborne area, the Eocene bentonite deposit at **Parahaka** Station is near-horizontal. It conformably overlies blue-grey siltstone, and is overlain unconformably by Miocene or Pliocene bedrock (MacPherson and Coventry, 1941; Ker, 1969). Gregg and Carlson (1971) have shown that the bentonite contains dominantly smectite clays (up to 70%) with lesser amounts of quartz (12-25%), calcite (2-4%), plagioclase (4-6%) and potash feldspar (2-4%). Swelling values (SV) of up to 73 were obtained by Gregg and Carlson (1971), although Ritchie (1962) obtained SV of 92-96 from the same area. High calcite values are generally localised, and associated with red bentonite. The deposit has been worked intermittently and resources of 4 Mt of extractable bentonite are indicated (Gregg and Carlson, 1971).

Bentonite at **Porangahau** was worked for many years and was used locally as a drilling mud. It is interbedded with sandstone and siltstone.

Elsewhere on the East Coast, Ritchie (1962) reported good swelling values from bentonite samples taken near Ruatoria (SV 93), Tuparoa (SV 95), near Ihungia (SV 97) and north of Whangara (Y17/654820; SV 97). Bentonitic mudstones occur in the Kopuawhara valley and on the Mahia Peninsula within an Eocene sedimentary sequence. Bentonite at Taiporutu Stream is calcareous and suitable for industrial uses, such as drilling muds (Ritchie, 1962).

In the South Island, thin bentonite beds were described from Kekerengu in Marlborough by MacPherson (1952) and in central Canterbury, sodium-rich bentonite occurs principally in Ashley Mudstone (Browne and Field, 1985). It is naturally swelling (SV 38-92) and thought to be derived by alteration from basaltic ash under marine conditions.

Allophane derived from weathering of volcanic ash

Allophane is the dominant clay mineral in Holocene volcanic ash (tephra) beds (e.g. Rotorua Ash), and is partly replaced by halloysite in Late Pleistocene tephra (Kirkham, 1975). Andesitic material promotes allophane stability over rhyolitic material because of its higher Al/Si ratio. The high fertility of volcanic soils in New Zealand owes much to the ability of allophane to adsorb plant nutrient anions such as phosphate.

Vermiculite formed by weathering

Vermiculite occurs as a weathering product of biotite in the Separation Point Granite of Nelson from Separation Point in the north to Baton Valley in the south, as well as in the Riwaka Valley (Grindley, 1971). Vermiculite forming coarse segregations in a granite pegmatite dike in the Motueka Valley, is also a weathering product. Small amounts of vermiculite have been noted in the Rameka Intrusives in Rameka Creek, northwest Nelson (Fieldes et al., 1974).

Sedimentary clays

Sedimentary clays are common in both marine and non-marine beds and have been used in the past for making bricks and pipes. For example, Figs 20-4 and 20-5 of Fieldes et al. (1974) lists claystones and mudstones at Whangarei, Dargaville, Auckland, Te Kuiti, Taumarunui, Waitara, Wairoa, Napier, Hastings, Wanganui and Greymouth, and loess at Christchurch, Timaru, Fairfield, and Gore. The parent materials include deeply weathered Mesozoic greywacke, from which were derived the loess and most of the younger sedimentary clay deposits of Cenozoic age. Most of the alluvial clays were washed into their present position by normal fluvial processes, but those near Wellington are thought to have been emplaced by superficial soil movement.

Clays formed in a fresh-water environment are widespread in Cretaceous and Tertiary coal measures, and are included in the following section. Thick Tertiary marine sedimentary sequences contain great thicknesses of claystones and mudstones (papa) that have occasionally been worked, mainly for bricks and tiles.

Loess has been worked for brickmaking in Canterbury, Otago and Southland, and, to a lesser extent, in the Wellington region. The deposits are up to 10 m thick and mainly derived from glacial debris of greywacke origin (Fieldes et al., 1974). On **Banks Peninsula**, loess was quarried for brick, pipe, and tile manufacture in Christchurch. Deposits of up to 15 m thick mantle the lower slopes of the Port Hills, but the clay is sandy and of low grade. Loess is still quarried on the peninsula, but used mainly as a stabilising additive for roading purposes. At **Allanton**, in south Otago, a loess deposit (approximately 20 Mt) has potential for use in brickmaking. In Southland,

clay-rich loess deposits have been worked at **Waikiwi**, **Gore** and **Pukerau** for use in the manufacture of drain tiles and bricks (Wood 1966).

Fireclays and other clays associated with coal measures

Clay deposits associated with coal measures originate as primary sedimentary deposits or as deposits of mudstone that have been acid leached to produce fire clays.

Clay from coal measures at **Kamo**, north of Whangarei, was used in the past by Kamo Green Refractories Limited to produce industrial refractory products such as crucibles and fire brick (MacFarlan and Barry, 1991). High-alumina clays from Waikato Coal Measures and white, leached chert from the Waipapa Group metasediments were also used.

Other Northland occurrences of fireclay include **Mt. Hikurangi**, **Mt. Parahaki** and **Hihivale Valley** (Whangarei). The composition of the clays approaches kaolin, the better grades containing at least 35% Al_2O_3 .

Potters clay occurs at **Kawakawa**, underlying a small outcrop of coal in the Waiomio Stream. Low iron and alkali contents make the clay suitable for the manufacture of fire bricks and high grade pottery.

Near the **Kopuku** coal mine at Maramarua, CSR Building Materials (NZ) Limited extracts 14,000 tpa of fireclay from a disused opencast coal mine, for use in their New Lynn brick factory (Taylor, 1994). The clay comes from mudstone lying above a coal seam in the Waikato Coal Measures. Four different clays are derived from this site, all of them possessing light burning colours, good strength characteristics and relatively high shrinkage characteristics. Clay from several other opencast mines has been used for brickmaking.

At **Huntly**, high-alumina clay from Waikato Coal Measures is used by Thermal Ceramics NZ Limited for refractory manufacture. The clay is extracted from below the coal seams in opencast mines near Huntly and used together with imported prepared refractory aggregates (MacFarlan and Barry, 1991).

In the **Rotowaro Coalfield**, Winstone Minerals (Huntly) Limited carried out an exploration drilling programme for fireclay during the early 1970s and demonstrated the presence of good quality, pale brownish fireclay. Further drilling is required to measure the quantity (Marston and Buck, 1972-1976).

At **Puramahoi**, northwest of Takaka, white fireclay seams, up to 1 m thick, are found in deeply weathered Early Tertiary Motupipi Coal Measures (MacFarlan and Barry, 1991). The deposit comprises a 0.6 m bed of white kaolin, which rests directly on deeply weathered Onahau Granite (Soong and Johnston, 1979). The deposit is currently mined by Potters Clay (Nelson) Limited. Similar clay has been worked nearby at **Tukurua** (MacFarlan and Barry, 1991).

In the **Buller Coalfield**, an 0.6 m thick clay bed, present locally between two thick coal seams, was worked in the Ironbridge mine at Denniston (Henderson, 1943). Clay has recently been produced from Brunner Coal Measures at Waimangaroa. In the **Greymouth Coalfield**, fireclays are present as “underclays” immediately beneath coal seams, and as thin, distinct beds which may be fossil soils, in the

Brunner Coal Measures and Dunollie Coal Measures. The floor clay of the main Brunner seam was worked in conjunction with the coal in several mines and was used for making firebricks and building bricks. More recently, coal seam underclay has been extracted at Eight Mile Pit. The clay is mostly kaolinite although some is siliceous. Muscovite is nearly always present in small quantities.

In the **Malvern Hills** (Glentunnel and Whitecliffs), west of Christchurch, clay is worked from the weathered Late Cretaceous coal measures of the Broken River Formation. Most of the usable clays occur directly below coal seams, and are high in impurities such as organic matter, fine sand, mica and iron oxide. Several pits have been worked. Prior to 1983, the clay was used for many years by McSkimmings Industries for brick, tile, and pipe manufacture at the Glentunnel pottery works. Clay from Glentunnel, Whitecliffs and Bush Gully, Sheffield, is now mined by W.D. Boyes & Son Ltd and used for making bricks by Canterbury Clay Bricks Limited of Darfield.

In the **Mt Somers** district, rhyolite of the Mt Somers Volcanics is overlain by coal measures of the Broken River Formation. Clay deposits are developed near the contact by the weathering and leaching of the rhyolite (Wellman et al., 1945; van der Lingen and Field, 1985; Oliver and Keane, 1989). The clay consists of 30 to 90% kaolinite and has been used for the manufacture of whiteware. Currently, W.D. Boyes & Son Ltd produce clay for use by N.Z. Insulators Limited.

Clay deposits in the vicinity of **Kakahu**, Geraldine, consist of kaolinite with a high quartz content and some iron and organic material. Wellman (1953) reported two main clay bands within the Broken River Formation: an 8 m thick lower band known as the “hard white fireclay” and a 6 m upper band known as the “cream ball clay”. The “hard white fireclay” is currently used by N.Z. Insulators Limited for the manufacture of refractory products and pottery through their pottery division, Temuka Potteries Ltd. In the past McSkimming Industries Limited used the “cream ball clay” as china clay for the manufacture of sanitary whiteware. Wellman (1953) noted that there is considerable vertical and horizontal variation in the quality of clay. Some sandy clay apparently has been used as refractory clay.

The Kakahu deposits were first worked in the 1860s, but it was only in 1916 that the forerunner of the present company – N.Z. Insulators Limited, incorporating Temuka Potteries – began producing tiles, bricks and porcelain electrical components. Temuka Potteries is today the only large-scale producer of table, oven and kitchenware in New Zealand.

Thompson (1989) summarised exploration work at **Chilsons' Ford**, about 6 km up the Tengawai River from Pleasant Point, South Canterbury, where sandy clay and clayey sandstone is present within the White Rock Coal Measures (Middle Miocene-Pliocene). Resources of ball clay were estimated as 4020 t measured and 1200 t inferred.

At Muddy Creek, **St Bathans**, clays are present beneath a coal seam in Eocene coal measures. Clay from St Bathans, analysed by New Zealand Geological Survey (in Walshe, 1980), consists of 40% quartz, 50% poorly crystalline kaolinite, 5-10% interstratified illite-montmorillonite, and traces of feldspar and organic matter. Resources have been estimated at about 3 Mt.

At **Hyde**, clay derived from coal measures has been mined for use in ceramics, pottery and mineral fillers. This clay is very fine-grained, mostly kaolinite, but with some smectite, quartz sand, organic material, and other accessory minerals (MacFarlan and Barry, 1991). Two pits operated by R.L. Tod & Company Limited produce clay for pottery and the ceramics industry, including N.Z. Insulators Limited.

At **Benhar**, coal measure clays have been used to produce white, heavy clay products (mainly sanitary ware). The clay is transported clay, derived from weathering of greywacke basement rocks (MacFarlan and Barry, 1991). Clay from the Gore Lignite Measures is mined near **Waipahi**, south Otago, for use as a mineral filler, and at **Mabel Bush**, Southland, for pottery (MacFarlan and Barry, 1991).

At **Ohai**, kaolin-rich clays are common in Late Cretaceous and Eocene coal measures, and in Eocene non-marine units elsewhere. Clay was worked at the Waimeamea Mine in the Beaumont Coal Measures during the 1950s for use in the Invercargill brickworks (Wood, 1969). Samples of clay from the Morley Coal Measures in the Black Diamond and Coaldale mines have been reported to be of promising quality for ceramic use, although the thickness of overburden and small resources limit potential for commercial development (Bowen, 1964). Clay has been mined from the Mako Coal Measures near Hedgehope (Rout, 1947) and from the Pomahaka Coalfield/Burning Plains area between Clinton and Clydevale (Bishop, 1965, 1986).

Hydrothermal alteration

Halloysitic and kaolinitic clays produced by hydrothermal alteration are found in Northland, Coromandel and the Taupo Volcanic Zone.

Halloysite clay, reputed to be “the world’s whitest clay”, is produced from deposits at Matauri Bay, Northland, by NZ China Clays Limited (Townsend, 1989; Harvey et al., 1990; Harvey and Murray, 1993; Luke, 1997). Two pits are worked on the Matauri Bay and Mahimahi rhyolite domes respectively, located 2 km apart (Figs 2 and 3). NZ China Clays Limited also has deposits at Shepherds Hill, 6.5 km to the west of Matauri Bay, and Maungaparerua, 8 km west of Kerikeri.

The clay is formed by hydrothermal alteration and subtropical weathering of Pliocene to Pleistocene rhyolite domes (Putahi Rhyolite) to material comprising approximately 50% clay and 50% quartz, cristobalite and minor feldspar. The clay is predominantly halloysite, but at Maungaparerua, Murray et al. (1977) also noted allophane and kaolinite. The degree of clay development is generally greatest at the surface, because of the effects of surficial weathering superimposed on the hydrothermal alteration. The presence of basalt flows partly overlying the domes may have been an important factor in the alteration process. Several other rhyolite domes are present in Northland, but most do not show extensive development of halloysitic clays (Bowen, 1974).

Matauri Bay clay deposit is derived from the alteration of a small (about 29 ha in area) rhyolite dome of low relief. It is completely surrounded and partly overlapped by thick (up to 60 m) flows of basalt. The raw clay is generally covered by 1 to 3 m of iron-stained material, which is removed together with soil and vegetation, before mining. The deposit is mined selectively by hydraulic excavators, and the material is transported by motor scrapers to stockpiles on concrete pads.



Figure 2: Matauri Bay clay pits, Northland. Matauri Bay pit and processing plant are in the left foreground and Mahimahi clay pit is in the left distance. Photo: New Zealand China Clays Ltd.



Figure 3: Matauri Bay clay pit, Northland. Photo: New Zealand China Clays Ltd.

alteration has been further altered by intense surficial weathering to produce relatively soft clay in an upper 8-30 m (averaging 15 m) thick zone, 600 to 700 m in diameter (Murray et al., 1977). On the western side of the dome, a zone of locally intense hydrothermal alteration in adjacent basalt consists of kaolinitic clays with siliceous sinters and disseminated metallic sulphides (Wodzicki and Weissberg, 1982; MacFarlan, 1992).

The high purity halloysite produced by NZ China Clays at Matauri Bay possesses exceptional whiteness and brightness, and an overall fine particle size. Unbleached brightness can attain 91-92% and iron oxides average 0.28%, with titania averaging 0.08%. The inherent brightness of the raw material, coupled with low iron and

titania levels, imparts commensurate whiteness and translucency to the finished product. A halloysite product is exported for the manufacture of high-quality ceramics, principally porcelain, but also fine bone china and technical ceramics. There are two main applications in the technical ceramics industry. The main market is in synthetic zeolite-based molecular sieves, whereas the other is in the manufacture of honeycomb catalyst supports. A coarser by-product is sold on the local market as filler clay. A silica sand by-product is used in the local building industry and for golf course bunkers.

Mahimahi deposit consists of a rhyolite dome similar to that at Matauri Bay, but emplaced through glauconitic sandstone (MacFarlan and Barry, 1991). Mining of the Mahimahi dome began during 1990, with clay processed at the Matauri Bay plant (Fig. 4).

Shepherds Hill rhyolite dome lies along the same east-west alignment as the Matauri Bay and Mahimahi deposits.

Maungaparerua is the largest of the Northland rhyolite domes (Bowen, 1969). It is semicircular in plan and 142ha in area. A hard siliceous clay formed by hydrothermal



Figure 4: Halloysite clay processing plant (centre) and Matauri Bay clay pit (bottom right), Northland. Photo: New Zealand China Clays Ltd.

	Exports		Imports	
	t	\$ (FOB)	t	\$ (CIF)
Kaolin	14,658	13,123,552	7,884	5,065,912
Bentonite	687	306,429	1400	700,256
Fuller's earth	5	10,431	2325	1,164,056
Fireclay	2	2,697	197	112,248
n.e.s.	5.9	10,318	1156	639,725
Chamotte	-	-	540	142,405
TOTAL	15,358	13,453,422	13,502	7,824,784

CIF cost including freight

FOB free on board

n.e.s. not elsewhere specified

Table 5: Exports and imports of clay in 1998 (data from Thompson and Christie, 1999).

The Northland halloysite deposits have been worked since 1969. About 80,000 tpa of raw clay is mined from the Matauri Bay and Mahimahi deposits with 50% of plant feed from each. Plant capacity is about 25,000 tpa of processed halloysite, with clay products being exported to more than 20 countries.

Sufficient resources exist at the Matauri Bay and nearby Mahimahi deposits to sustain production for over 30 years at current rates. Potential resources are present in other deposits at Shepherds Hill and at Maungaparerua.

In addition to the halloysite deposits of Matauri Bay and Maungaparerua, kaolin and halloysite deposits formed by alteration and weathering of volcanic rocks are widespread in Northland, but are generally of small extent. They include deposits of weathered and altered Pukekaroro Rhyodacite, Maungarei Dacite and Putahi Rhyolite. Kaolin deposits have been recorded from **Kaero** (Te Pene; Quennell, 1963, 1964), **Kauri** (Parekiore), **Whangarei Heads** (Parua Bay and Ocean Beach), **McLeods Bay** (Munroe Bay) and **Kaiwaka**. All are white clays of low plasticity and approach the clay minerals kaolin and halloysite in composition. Some are of excellent quality, having low iron and alkali ($\text{Na}_2\text{O} + \text{K}_2\text{O}$) content and have been used in the manufacture of china ware or porcelain ware, and in the case of Kauri pit, for the manufacture of refractory bricks (Kamo Green Refractories). Bowen (1966, 1974) has given resource estimates for some of these deposits, based on geological mapping and limited drilling. Thompson (1989) summarised the result of exploration at Ocean Beach and Kaiwaka. At **Mount Mitchell**, potters clay or potters earth has been recorded from a highly siliceous hot spring deposit.

In the Coromandel Peninsula, hydrothermal alteration of Minden Rhyolite domes in the **Cooks Beach**, **Hahei** and **Lees Road** areas has produced deposits of clay consisting dominantly of kaolinite, with lesser smectite, and minor cristobalite, tridymite, quartz, and alunite. Crown Lynn Potteries Limited drilled several of the deposits (Crown Lynn Potteries Ltd, 1965-66) and subsequently mined some areas for relatively small quantities of kaolin clay (e.g. at Hahei). 1820 t of clay were produced between 1968 and 1973, when an increasing iron content curtailed operations. At Cooks Beach, the clay contains minor pyrite and, at 2 microns, has 30% cristobalite present. Resources were

estimated as 190,000 m³ in 1965, but later estimates reduced the volume to 30,000 m³. At Lee's Road, west of Hahei, a kaolinite unit between silicified rhyolite and rhyolite breccia, is associated with cristobalite and minor gibbsite. The clay is plastic and has a very fine particle size. It has been used as a ball clay. The marginal zone is pyrite-rich and halloysite, derived from weathered rhyolite, is also present (Harvey, 1967).

Elsewhere in the Coromandel Peninsula, kaolinitic clay, derived from hydrothermal alteration of volcanic rocks, is present in the **Whangapoua Harbour** area between Owera and Otanguru streams (Skinner, 1976), at **Black Jack**, the **Tairua Valley**, **Pumpkin Hill**, **Thames Lookout Rocks** and **Waihi Monument**. Black Jack, Pumpkin Hill, Thames Lookout Rocks and Waihi Monument clay deposits were formed by alteration of andesite or dacite and are associated with siliceous deposits, at some locations previously termed sinters. The Black Jack deposit is mostly kaolinite although alunite is also present (Skinner, 1968; Parkinson, 1980). Pumpkin Hill is mostly kaolinite, with lesser pyrophyllite, diaspore and dickite (Swindale and Hughes, 1968). At Thames Lookout Rocks, dickite, kaolinite, pyrophyllite and natroalunite occur in an advanced argillic alteration cap above porphyry copper mineralisation (Merchant, 1986; Brathwaite et al., 1998). Waihi Monument is mostly kaolinite, but contains abundant pyrite (Skinner, 1975). Clays are also found in the hydrothermally altered rocks associated with the approximately 50 epithermal gold-silver deposits of the Coromandel Peninsula region summarised by Brathwaite et al. (1989). Kaolinite, smectite, illite and interlayered illite-smectite are the main clay minerals.

In the **Taupo Volcanic Zone**, clay occurs associated with hydrothermal alteration of Quaternary rhyolitic and dacitic rocks in the more than 17 active and several extinct geothermal fields. Kaolinite, smectite, interlayered clays and alunite, along with quartz, cristobalite and zeolites are the main alteration minerals found in the near surface parts of the deposits. The presence of alunite in many deposits imparts a high viscosity to the clays, precluding their use in paper coating (or ceramics) and making wet processing difficult (New Zealand China Clays unpublished internal report). Some coloured clays are used for producing souvenir bottles of clay with layered colours for the tourist industry.

Miscellaneous clay occurrences

Palygorskite has been reported in limestone caves near Te Kuiti (Lowry, 1964); at Waitoru Station, Waitomo district (Morgan, 1927; listed under Pilolite); near Mahoenui, Taranaki (Henderson, 1920); in fault gouge in greywacke, in Karori, Wellington City, (Soong and Perrin, 1983); in limestone in northwest Nelson (Soong, 1992); and in schist, and in faults and landslide gouge samples from Cromwell Gorge, Otago, (Soong and Bryant, 1987; Watters and Soong, 1991).

Railton and Watters (1990) listed three occurrences of **sepiolite**: laterite over serpentinite at North Cape (Thompson and Rogers, 1977); at Dun Mountain (Cox, 1883, p. 369); and in altered basalt near Port Chalmers, Otago (Allen, 1974, p. 213).

Production and resources

Clay for bricks and tiles

The total production of clay for bricks and tiles recorded in 1996 by Ministry of Economic Development (then Ministry of Commerce) was 27,159 t (Mining Inspection Group, 1997). The largest brick making operation is the plant operated by CSR Building Materials (NZ) Limited in New Lynn, Auckland (www.csr.co.nz). Clay for this operation is sourced from four clay pits: Brigham's Creek, Clevedon, Kopuku and Port Waikato (Taylor, 1994).

Smaller brick and tile works, which generally make a limited range of products using locally derived raw materials, include Heritage Tiles in Auckland, Clarks Potteries Limited in Auckland (clay field tiles), Handmade Brick Company Limited in Tauranga, Verita Tiles Limited in Ngaruawahia, Bishopdale Brick in Nelson, Canterbury Clay Bricks Limited in Darfield, the Brickworks in Dunedin, and Southtile Limited in Invercargill (paving and field tiles, and refractory bricks; www.southtile.co.nz).

Clays of suitable quality for brickmaking are found throughout the country. The quantity of clay present in most areas is poorly defined but almost certainly large, especially in weathered argillite and greywacke, and coal measure clay deposits. Some clay pits, particularly in the South Island, are small-scale operations working pockets of clay within larger areas of clay-bearing rocks.

Clay for ceramics and pottery

The total production of clay for pottery and ceramics recorded in 1996 by Ministry of Economic Development (then Ministry of Commerce) was 26,325 t (Mining Inspection Group, 1997). Matauri Bay (NZ China Clays Ltd) is the largest clay-mining operation in New Zealand, producing halloysite mainly for export. Smaller quantities of clay are mined elsewhere and used for the local ceramics industry, namely Pyrotek Products Limited in Auckland (advanced ceramic materials), Petra Ceramics Limited in Auckland (tableware), Studio Ceramics NZ Limited, Thermal Ceramics New Zealand Limited in Huntly (refractories and insulating products; www.thermal.co.nz), NZ Insulators Limited at Temuka (ceramic electrical insulators; www.nzinsulators.co.nz), Temuka Potteries at Temuka (tableware), Southtile Limited at Invercargill (refractory bricks) and a number of small-scale amateur and craft potters (Schofield, 1977; Grzelewski, 1999). The

main suppliers of potters clay are Nelson Potters Clays (Stoke, Nelson), Macs Mud Company (Brightwater, Nelson) and Southern Clays Limited (Dunedin). These companies each source clays from several clay pits in New Zealand and, in some instances, blend them with clays imported from overseas to produce a wide variety of clay products.

Bentonite

Bentonite is mined by OMYA New Zealand Limited near Coalgate. Annual production peaked at 19,722 t in 1970, and was 13,734 t in 1996 (Mining Inspection Group, 1997). Measured resources total around 11 Mt. At Stoddart's Farm, Porangahau, there is a resource of about 1 Mt of bentonite, but selective mining is necessary to produce to specification.

Industrial clay

Kaolin is used as a mineral filler in rubber, bitumen, adhesives, and several other industries. Premium grade halloysite clay was used in the raw mixture in experimental slip casting manufacture of O'-sialon-silicon carbide refractories for the aluminium industry (Barris et al., 1997).

The New Zealand paper industry currently imports paper coating and filler clays, but some investigations into the use of New Zealand clays have been made (MacFarlan and Barry, 1991). A study by Wells et al. (1985) concluded that Charleston kaolinite warranted further trials.

Exports

In 1998, 15,357 t of clay were exported to 29 countries (Table 5). The main recipient countries were Japan (3,458 t, \$3,514,272), Taiwan (2061 t, \$1,729,163), USA (1674 t, \$1,460,141) and Korea (1,447 t, \$1,261,101) for kaolin clays, and Australia (678 t, \$289,374) for bentonitic clay. Minor amounts of fuller's earth (2 t, \$10,431), fireclay (2 t, \$2,697) and other unspecified clay (5.9 t, \$10,313) were also exported.

Imports

In 1998, New Zealand imported 13,501 t of clay, mainly kaolin and fuller's earth from 16 countries (Table 5). USA supplied 5114.3 t (\$3,718,181) and Australia 2312.5 t (\$945,244) of kaolin clays. The main suppliers of bentonite were Australia (517.77 t, \$142,125), Indonesia (302.2 t, \$123,124), Italy (288.8 t, \$239,385) and USA (162.8 t, \$110,657). Fuller's earth was imported mainly from Australia (1,855 t, \$757,167), USA (395.8 t, \$359,924) and Malaysia (60 t, \$35,328). 192.5 t (\$63,415) of fireclay was imported from Australia, and 4.4 t (\$48,833) from USA. The main suppliers of other clays ("not elsewhere specified") were Australia (742.9 t, \$292,695) and USA (342.3 t, \$289,856). A very small amount (0.050 t, \$182) of refractory clay (andalusite, kyanite, sillimanite) was imported from India. 539.65 t of chamotte was imported from China (\$142,405).

Future trends

The use of kaolinite and halloysite in the technical or advanced ceramic sector is growing and has considerable potential for additional growth as new applications for ceramic components are developed to replace metal parts

(e.g. automotive glow plugs and turbocharger rotors). Other applications for advanced ceramics for which there is increasing demand include electronic and heat resistant components.

Finely ground carbonate and precipitated calcium carbonate (PCC) are substituted for kaolin in the paper-coating and paper-filler applications. Initially such pigments competed as a replacement for kaolin, but the present trend is towards the use of blends of kaolin and carbonate to maximise the benefits of both materials.

As the use of kaolin as a paper filler has declined the use of kaolin filler in the manufacture of fibre glass has increased, and may exceed the previous paper filler market in volume terms in the near future.

The use of calcium bentonite in foundry sands is expected to decrease slightly over the next few years, whereas there is increasing use of bentonite in ceramics, plastics, castings and pet litter. The world-wide oil drilling industry uses well-known Wyoming bentonite. The expansion of the New Zealand bentonite market is related to price and to the use of bentonite in non-oil well drilling applications, including foundry sands, binding agents, fillers, in land fill barriers and in the development of organic clays.

Demand for vermiculite is closely correlated with its price compared to potential substitutes such as perlite, rock wool, fibre glass and expanded shales, which can all be used in insulation products. Horticulture applications have seen growth in recent years but face competition from perlite, peat, bark and coconut fibre (coir). A potential growth market is the use of vermiculite as a substitute for asbestos in friction products. Pet litter applications of palygorskite, sepiolite and vermiculite face competition from paper-based, bio cat litter, diatomite and zeolite

Synthetic materials are replacing some clay applications. In the field of catalysts, the use of synthetic alumina and/or silica and synthetic zeolites have made inroads into the former use of bentonite, kaolin and halloysite. Of possible wider significance is the use of synthetic polymers in drilling muds which has significantly impacted the world usage of bentonite for this purpose.

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References

Allen, J.M. 1974: Port Chalmers Breccia and adjacent early flows of the Dunedin Volcanic Complex at Port Chalmers. *New Zealand journal of geology and geophysics* 17: 271-299.

Barris, G.C.; Brown, I.W.M.; Ekström, T.C.; White, G.V.; Cooper, M.T.; Hodren, G.M. 1997: Reaction bonded O'-sialon and O'-Sialon - silicon carbide. *Journal of the Australian Ceramic Society* 33(1/2): 15-22.

Bathurst, M. 1999: Pipes to pots – our ceramic past. *New Zealand geographic* 43: 88-91.

Benbow, J. 1990: New Zealand's minerals for domestic consumption. *Industrial Minerals* 273: 19-35.

Bishop, D.G. 1965: The geology of the Clinton district, South Otago. *Transactions of the Royal Society of New Zealand* 14: 205-230.

Bishop, D.G. 1986: Burning Plains clay deposit. New Zealand Geological Survey unpublished report, DDO file G45/309, Institute of Geological and Nuclear Sciences.

Bowen, F.E. 1964: Geology of Ohai coalfield. *New Zealand Geological Survey bulletin* 51.

Bowen, F.E. 1966: The Parahaki Volcanic Group and its associated clays. *New Zealand Geological Survey report* 6.

Bowen, F.E. 1969: Halloysitic clay at Maungaparerua, Northland (N11). *Industrial minerals and rocks* 1968: 44-55.

Bowen, F.E. 1974: The Parahaki Volcanic Group and its associated clays. *Department of Scientific and Industrial Research bulletin* 215.

Brathwaite, R.L.; Christie, A.B.; Skinner, D.N.B. 1989: The Hauraki Goldfield - regional setting, mineralisation and recent exploration. In: D. Kear ed. Mineral Deposits of New Zealand, *Australasian Institute of Mining and Metallurgy Monograph* 13: 45-56.

Brathwaite, R.L.; Simpson, M.P.; Skinner, D.N.B. 1998: Porphyry Cu-Au mineralisation, advanced argillic alteration and polymetallic sulfide-quartz-anhydrite veins at Ohio Creek, Thames, New Zealand. Proceedings of the 31st Annual Conference 1998, New Zealand Branch of the Australasian Institute of Mining and Metallurgy, pp. 41-59.

Browne, G.H.; Field, B.D. 1985: The lithostratigraphy of late Cretaceous to early Tertiary Pleistocene rocks of northern Canterbury, New Zealand. *New Zealand Geological Survey record* 6.

Carlson, J.R.; Rodgers, K.A. 1974: The Coalgate bentonite: a ferriferous-beidellite deposit from Canterbury, New Zealand. *Clay minerals* 10: 153-172.

Carlson, J.R.; Rodgers, K.A. 1975: The petrology and alteration of Tertiary basalts of the Coalgate area, northwest Canterbury. *Journal of the Royal Society of New Zealand* 5: 195-208.

Carlson, J.R.; Grant-Mackie, J.A.; Rodgers, K.A. 1980: Stratigraphy and sedimentology of the Coalgate area, Canterbury, New Zealand. *New Zealand journal of geology and geophysics* 23: 179-192.

Cox, S.H. 1883: Note on the mineralogy of New Zealand. *Transaction of the New Zealand Institute* 15: 361-409.

Crown Lynn Potteries Ltd. 1965-66: Drill logs - clay investigation at Hahei, Kuaotunu and Tairua. Unpublished

- open-file mining company report, Ministry of Economic Development M0226.
- Fieldes, M; McDowall, I.C.; Claridge, G.G.C.; Williams, G.J. 1974: Clays. Chapter 20 of Williams, G.J., Economic geology of New Zealand. *Australasian Institute of Mining and Metallurgy monograph 4*: 357-370. .
- Gage, M. 1952: Greymouth coalfield. *New Zealand Geological Survey bulletin 45*.
- Grant-Taylor, T.L. 1968: Plastic clays suitable for pipe manufacture in Wellington city. *New Zealand engineering 23*: 410-411.
- Gregg, D.R. 1964: Geological map of New Zealand 1:250,000, sheet 18, Hurunui. Wellington. Department of Scientific and Industrial Research.
- Gregg, R.C.; Carlson, J.R. 1971: Geological report on the bentonites of Parahaka Station, East Cape. Parehaka Research and Exploration Co. Ltd. Unpublished open-file mining company report, Ministry of Economic Development M2970.
- Grindley, G.W. 1971: Sheet S8 - Takaka. Geological Map of New Zealand 1:63,360. Wellington. Department of Scientific and Industrial Research.
- Grzelewski, D. 1999: A feeling for clay. *New Zealand geographic 43*: 74-103.
- Harben, P.W.; Kuzvart, M. 1996: Industrial minerals, a global geology. London. Industrial Minerals Information Ltd, Metal Bulletin PLC.
- Harvey, C.C. 1967: Rock alteration in the southeast Whitianga area. Unpublished M.Sc. thesis, University of Auckland.
- Harvey, C.C. 1997: Kaolinite & halloysite, ASEAN resources and trade. *Industrial Minerals May 1997*: 55-59.
- Harvey, C.C.; Murray, H.H. 1993: The geology, mineralogy, and exploitation of halloysite clays of Northland, New Zealand. In: Murray, H.H.; Bundy, W.M.; Harvey, C.C. eds, kaolin genesis and utilisation. Clay Minerals Society special publication 1: 233-248.
- Harvey, C.C.; Murray, H.H. 1997: Industrial clays in the 21st century: a perspective of exploration, technology and utilisation. *Applied clay science 11*: 285-310.
- Harvey, C.C.; Townsend, M.G.; Evans, R.B. 1990: The halloysite clays of Northland, New Zealand. Proceedings of the 24th annual conference 1990, New Zealand Branch of the Australasian Institute of Mining and Metallurgy, pp. 229-238.
- Henderson, J. 1920: A mineral new to New Zealand – pilolite. *New Zealand journal of science and technology 3*: 79-80.
- Henderson, J. 1943: Fireclay and ganister in New Zealand. *Department of Scientific and Industrial Research bulletin 88*.
- Ker, D.S. 1969: Bentonite on Parehaka Station, East Coast. Industrial minerals and rocks, 1968. *Department of Scientific and Industrial Research information series 63*: 67-75.
- Kirkham, J.H. 1975: Clay mineralogy of some tephra beds of Rotorua area, North Island, New Zealand. *Clay Minerals 10*: 437-449.
- Kingma, J.T. 1971: Geology of the Te Aute subdivision. *New Zealand Geological Survey bulletin 70*.
- Lowry, D.C. 1964: Palygorskite in a cave in New Zealand. *New Zealand journal of geology and geophysics 7*: 917
- Luke, K.A. 1997: Geology and extraction of the Northland halloysite deposits. 1997 New Zealand minerals and mining conference proceedings, Crown Minerals, Ministry of Commerce. Pp. 193-198.
- MacFarlan, D.A.B. 1992: Prospecting licence 31-2523 Maungapararua final technical report: Mintech (NZ) Ltd. Unpublished open-file mining company report, Ministry of Economic Development M3113.
- MacFarlan, D.A.B.; Barry, J. 1991: Mineral resources of New Zealand. *Energy and Resources Division, Ministry of Commerce, resource information report 11*.
- MacPherson, E.O. 1952: The stratigraphy and bentonitic shale deposits of Kekerangu and Blue Slip, Marlborough. *New Zealand journal of science and technology 33*: 258-286.
- MacPherson, E.O.; Coventry, R.G. 1941: Bentonite in southern Hawke's Bay. *New Zealand journal of science and technology 22*: 265-275.
- Marston, G.E.; Buck, M.D. 1972-1976: Drill results and geological reports, clay exploration in the Rotowharo area: Winstone Minerals (Huntly) Limited. Unpublished open-file mining company report, Ministry of Economic Development M615.
- Merchant, R.J. 1986: Mineralisation in the Thames district - Coromandel. In: Henley, R.W.; Hedenquist, J.W.; Roberts, P.J. eds, Guide to the active epithermal (geothermal) systems and precious metal deposits of New Zealand. *Monograph series on mineral deposits 26*: 147-163. Berlin, Gebruder & Borntraeger.
- Mining Inspection Group 1997: New Zealand annual mining review 1996. Resource Data and Publicity, Crown Minerals, Ministry of Commerce.
- Morgan, P.G. 1908: The geology of the Mikonui subdivision, north Westland. *New Zealand Geological Survey bulletin 6*.
- Morgan, P.G. 1911: The geology of the Greymouth subdivision, north Westland. *New Zealand Geological Survey bulletin 13*.
- Morgan, P.G. 1927: Minerals and mineral substances of New Zealand. *New Zealand Geological Survey bulletin 32*.
- Morgan, P.G.; Bartrum, J.A. 1915: Geology and mineral resources of the Buller-Mokihinui subdivision, Westport division. *New Zealand Geological Survey bulletin 17*.
- Murray, H.H.; Harvey, C.C.; Smith, J.M. 1977: Mineralogy and geology of the Maungapararua halloysite deposit in New Zealand. *Clays and clay minerals 25*: 1-5.
- Oliver, P.J.; Keane, H.W. 1989: Sheet K36 AC & part sheet K35 - Mt Somers. Geological map of New Zealand 1:50

000. Wellington. Department of Scientific and Industrial Research.
- Parkinson, P.C. 1980: Geology of the Mesozoic, Tertiary and Au-Ag mineralised rocks of Kuaotunu, Coromandel peninsula. Unpublished M.Sc. thesis lodged in the library, University of Auckland.
- Quennell, A.M. 1963: Report on Te Pene halloysite clay deposit, Kaeo, Northland: Clay Enterprise Ltd. Unpublished open file mining company report Ministry of Economic Development M17.
- Quennell, A.M. 1964: Report on drilling of Te Pene halloysite clay deposit, Kaeo, Northland: Clay Enterprise Ltd. Unpublished open file mining company report Ministry of Economic Development M20.
- Railton, G.T.; Watters, W.A. 1990: Minerals of New Zealand. *New Zealand Geological Survey bulletin* 104.
- Ritchie, J.A. 1962: Bentonite deposits in New Zealand: a review. *Dominion Laboratory report* 2053.
- Ritchie, J.A.; Gregg, D.R.; Ewart, A. 1969: Bentonites of Canterbury. *New Zealand journal of geology and geophysics* 12: 583-608.
- Rout, M.V. 1947: Geology of the Forest Hill survey district, Southland. *New Zealand journal of science and technology* 29B: 1-9.
- Schofield, J.C. 1977: Materials for the New Zealand potter. *Department of Scientific and Industrial Research information series* 118.
- Skinner, D.N.B. 1968: Alunite at Kuaotunu, Coromandel Peninsula. *New Zealand journal of geology and geophysics* 11: 1197-1199.
- Skinner, D.N.B. 1975: Pyrite mineralisation beneath the Waihi Monument Sinter Mounds (N53). In: Industrial minerals and rocks 1972. *Department of Scientific and Industrial Research information series* 108: 23-40.
- Skinner, D.N.B. 1976: Sheet N40 and part sheets N35, N36 & N39 - northern Coromandel. Geological map of New Zealand 1:63 360. Wellington, Department of Scientific and Industrial Research.
- Soong, R. 1992: Palygorskite occurrence in northwest Nelson, South Island, New Zealand. *New Zealand journal of geology and geophysics* 35: 325-330.
- Soong, R.; Bryant, J.M. 1987: An occurrence of palygorskite at Gibraltar Rock, Cromwell Gorge, South Island. *New Zealand Geological Survey record* 20: 69-71.
- Soong, R.; Johnston, M.R. 1979: Mineralogy of the Puramahoi kaolin deposits, Takaka, North-west Nelson. *New Zealand journal of geology and geophysics* 22: 575-583.
- Soong, R.; Perrin, N.D. 1983: An occurrence of palygorskite in a fault gouge, Karoroi, Wellington, New Zealand. *New Zealand journal of geology and geophysics* 26: 217.
- Swindale, L.D.; Hughes, I.R. 1968: Hydrothermal association of pyrophyllite, kaolinite, diasporite, dickite, and quartz in the Coromandel area, New Zealand. *New Zealand journal of geology and geophysics* 11: 1163-1183.
- Taylor, B.L. 1941: Feldspathic clay, Kaka, Nelson. *New Zealand journal of science and Technology* 23B: 33-43.
- Taylor, B.L. 1943: Decomposed granite, Baton, Nelson. *New Zealand journal of science and technology* 25B: 78-86.
- Taylor, C. 1994: Monier Brickmakers Limited. *New Zealand mining* 14: 29-31.
- Thompson, B.N. 1989: Non-metallic minerals. In: D. Kear, ed. Mineral Deposits of New Zealand, *Australasian Institute of Mining and Metallurgy monograph* 13: 15-23.
- Thompson, B.N.; Christie, A.B. 1999 New Zealand mineral exports and imports 1983/84, 1994 and 1998. *New Zealand mining* 26: 17-26.
- Thompson, R.C.; Rogers, K.A. 1977: Laterisation of the ultramafic - gabbro association at North cape, northernmost New Zealand. *Journal of the Royal Society of New Zealand* 7: 347-377.
- Townsend, M.G. 1989: Halloysite clay deposits in Northland. In: D. Kear ed., Mineral Deposits of New Zealand. *Australasian Institute of Mining and Metallurgy monograph* 13: 39-43.
- van der Lingen, G.J.; Field, B.D. 1985: Sedimentology and economic geology of the Mt Somers area. Excursion Guide. *Geological Society of New Zealand miscellaneous publication* 32B: 13-23.
- Wada, S.; Wada, K. 1977: Density and structure of allophane. *Clay Minerals* 12: 289-297.
- Walshe, K.C. 1980: Report on gold, ball clay and silica deposits, St Bathans, Otago (PL 31-296). Bronze Boulder Co. Ltd. Unpublished open-file mining company report, Ministry of Economic Development M1939.
- Watters, W.A.; Soong, R. 1991: Report on the mineralogy of fault and landslide gouge samples, Cromwell Gorge. DSIR Geology and Geophysics contract report 1991/36.
- Wellman, H.W. 1953: The geology of the Geraldine subdivision S102 sheet district. *New Zealand Geological Survey bulletin* 50.
- Wellman, H.W.; Dunn, L.R.L.; McDowall, I.C. 1945: Clays of the Mount Somers district. *New Zealand journal of science and technology* 26(B): 311-326.
- Wells, N.; Percival, H.J.; Churchman, G.J. 1985: *Potential of five New Zealand clays for coating paper*. *New Zealand journal of technology* 1: 109-114.
- Wodzicki, A.; Weissberg, B.G. 1982: The Maungaparerua sulphide deposit near Kerikeri, North Auckland. *New Zealand Geological Survey report* 105.
- Wojtowicz, T. 1984: The Kaka feldspathic clays, North-west Nelson. MSc thesis, University of Auckland.
- Wood, B.L. 1966: Sheet 24 - Invercargill. Geological map of New Zealand 1:250 000. Wellington, Department of Scientific and Industrial Research.
- Wood, B.L. 1969: Geology of the Tuatapere subdivision, western Southland. *New Zealand Geological Survey bulletin* 79.