

MOTUKOREAITE, A NEW MINERAL OCCURRING AS
BEACH-ROCK CEMENT AT
AUCKLAND, NEW ZEALAND.

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MOTUKOREAITE occurs as a white, clay-like cement in both beach-rock and volcanic tuffs on the flanks of a small, extinct, basaltic cone, Brown's Island (Motukorea), within Waitemata Harbour, Auckland, New Zealand (36°50'S, 174°55'E). The occurrence was originally recorded by Bartrum (1941) as "beach limestone" found at two places on the island's shores. Re-examination of these localities shows that motukoreaite is the major cementing substance (up to 23% of the rock) and calcium carbonate occurs in the beach-rocks solely as bioclasts. The larger of the two beach-rock localities is at the southernmost corner of the island where the main lava flow of the volcanic centre terminates. Beach-rock has formed in the intertidal zone on the partially eroded tip of the flow, covers a roughly rectangular area of 2500 m², and is some 0.2–0.3 m thick.

Petrography. The beach-rock consists of a grain-supported fabric of poorly sorted, well-rounded, alkali-olivine basalt pebbles and granules, subangular to subrounded fresh olivine sand and abraded sand- and gravel-sized bioclasts in a colourless to pale yellow-green aphanocrystalline matrix of motukoreaite. Additional detritals include a few grains of quartz, feldspar and sedimentary rock fragments derived from nearby Jurassic and Miocene sandstones. The shell fraction is dominated by abraded, occasionally torred, bivalve and gastropod fragments with rare benthonic foraminifera, echinoderm spines and plates, and serpulid material. The percent abundance of basaltic rock fragments, olivine and bioclasts in samples varies widely but generally conforms to the order: basalt > olivine > bioclasts. Intergranular pore space, which averages about 15% in samples, is generally fully, and less commonly partially, infilled by very low relief (r.i.v. = basen), isotropic, or near isotropic motukoreaite. This material commonly appears turbid as a result of included dust-like impurities and is slightly stained with limonite in the vicinity of basalt clasts. The bulk of the pore-filling motukoreaite appears structureless or has a weak platy fabric. However, about the margins of pores the motukoreaite not uncommonly occurs with a fibro-radiating habit in multiple crusts, each several μm thick, which coat the grains so as to conform to the shape of the pores. The drusy motukoreaite is most obvious wherever the central part of intergranular voids has not been subsequently occluded by massive textured motukoreaite.

Stereoscan examination of the surface of pieces of cement prised from the beach-rock showed a box-work of plate-like crystals with a hexagonal form in which the individuals measured about 3 x 3 x 0.02 μm (fig. 1).

In fig. 1, and on other stereoscan photographs, several of the plates show quite clearly the presence of a pyramid form; it is not a bipyramid, but probably a rhombohedron. Its angle to the basal plane is about 50–60°. This angle would be 54.00° for {101}, i.e. {101} of the single layer cell.



FIG. 1. Electron micrograph showing box-work of plate-like hexagonal crystals of motukoreaite forming cement in beach-rock. (a) x 10,000 (b) x 20,000.

Physical properties. Motukoreaite is a soft, dull, white mineral somewhat clay-like in general appearance. Crystalline masses are sectile with a hardness, on the Mohs scale, of 1–2. Using about 5 mg on a Berman balance (in toluene) the specific gravity was 1.48–1.53. The approximate refractive indices appear to be about 1.51 but determination was extremely difficult.

Chemistry. Two samples of the cement were analysed by A.J. Easton (British Museum, (Natural History)) and two, partially, by K.A. Rodgers (University of Auckland). These separates were prepared by magnetic methods, followed by hand-picking.

Efforts to remove traces of impurities, notably traces of limonite, calcite and some % quartz, using liquid separation and purification techniques invariably destroyed or altered the motukoreaite itself. For example, a slight effervescence occurs in cold, dilute hydrochloric acid and the mineral breaks down without going into solution. As such, the analyses were corrected with all SiO₂ being assigned to quartz, Fe₂O₃ to goethite and CaO to calcite. Halite was absent with Cl⁻ being less than 0.1%. Apart from these substances, homogeneity could not be conclusively proved. Scanning electron microscopy failed to show evidence of the quartz. Transmission electron microscopy showed traces of amorphous material but this may well have been carbon from the support film.

All samples proved to be reasonably consistent in both major and minor constituents. A spectrogram showed Mg and Al to be the dominant elements.

The average chemical analysis is given in Table I. Unit cell contents were derived both for a specific gravity of 1.53 and for a specific gravity of 1.43; the latter corresponds to a specific gravity of 1.48 corrected for 5.5% quartz, 0.8% goethite and 1.6% calcite, all taken as having specific gravity 2.65. Of several idealised formulae which may be proposed, NaMg₁₉Al₁₂(CO₃)₃6.5(SO₄)₄(OH)₅₄•28H₂O, with a calculated specific

gravity of 1.478, is preferred as being closest to the calculated unit cell contents.

TABLE I. An average chemical analysis and unit cell contents for

Weight percentages		Atoms per unit cell		Weight percentages	
		motukoreaite			
(1)	(2)	(3)	(4)	(1)	Determined
SiO ₂	5.55	Na+K	0.80	0.85	(2) Calculated for the idealised formula
Al ₂ O ₃	17.87	Mg+Mn+Zn	18.66	19.97	NaMg ₁₉ Al ₁₂ (CO ₃) ₃ 6.5(SO ₄) ₄ •
Fe ₂ O ₃	0.73	Al	11.15	11.93	(OH) ₅₄ •28H ₂ O
CaO	0.92	CO ₂	6.22	6.65	
MgO	22.98	25.49 SO ₄	3.97	4.25	
MnO	0.70	OH*	51.19	54.78	
ZnO	0.56	H ₂ O	27.20	29.09	
Na ₂ O	0.71	1.03	** to balance charges		Atoms per unit cell with
K ₂ O	0.10				g = 9.336 Å, c = 44.472 Å.
CO ₂	9.32	9.52			(3) for ρ 1.43 g cm ⁻³
SO ₃	10.00	10.65			(4) for ρ 1.53 g cm ⁻³
H ₂ O	19.62	32.96	Analyst	A.J. Easton, Department of Mineralogy, British Museum (Natural History).	
H ₂ O	10.35				
Total	99.41	100.00			

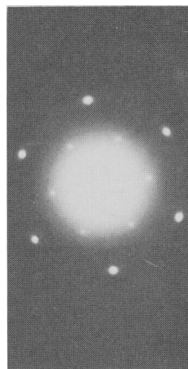


FIG. 2. Comminuted electron diffraction pattern showing hexagonal arrangement of diffraction maxima for a cell with a = 3.0 ± 0.1 Å.

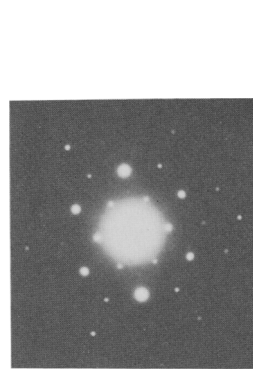


FIG. 3. Electron diffraction pattern showing additional superlattice reflections from a hexagonal cell with a = 5.2 Å.

Electron diffraction. A small quantity of the mineral was ground in absolute alcohol and dispersed on a carbon support film of a JEOL EM60 electron microscope specimen grid. Examination was made at 100 kV. The crystals take the form of euhedral plates showing a pronounced basal cleavage.

The commonest pattern shows a hexagonal arrangement of spots (fig. 2). The hexagonal unit cell has a repeat of 3.0 ± 0.1 Å. Many crystals, when first examined give patterns like fig. 3, which show additional reflections from a hexagonal cell with a = 5.2 Å (= √3 x 3.0 Å).

During examination in the electron beam the 5.2 Å superlattice reflections disappear within 1–2 minutes, leaving the 3.0 Å hexagonal cell. This latter pattern persists for about ten minutes but the intensity of the spots gradually falls. At the same time, three powder rings corresponding to MgO appear together with strong diffuse scattering which probably indicates the presence of amorphous material. One crystal gave not only the three MgO rings on decomposition but two additional rings which corresponded to magnesite with some preferred orientation. The damage in the electron beam is accompanied by the formation and the growth of pores and presumably involves the loss of H₂O.

The failure to observe reflections from the a = 9.336 Å unit cell derived from the X-ray data (see below) may also result from some decomposition or disordering process in the vacuum of the electron microscope or in the electron beam.

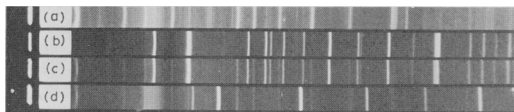


FIG. 4. X-ray powder patterns of beach-rock cement. Nonius-de Wolff focusing camera - 4.9670°/2θ/cm. (a) Cement alone - motukoreaite plus quartz and calcite impurities. (b) quartz alone. (c) cement plus admixed quartz. (d) cement plus admixed halite.

X-ray diffraction. No single crystals could be obtained. Powder photographs were taken in a Nonius-de Wolff quadruple focussing camera with a camera constant of 4.9670°/2θ/cm (fig. 4). The X-ray data obtained (Table II) agree closely with prominent, well defined diffractometer reflections which had been used to identify the mineral in various tuff beds and beach-rock deposits of the island. Reflections obtained at 4.24, 3.35, 1.81 Å could be attributed to about 3% quartz; reflections at 3.85 and 3.01 Å are explained as a trace of calcite. A number of other lines overlap weaker lines of quartz and calcite but are too strong to be wholly explained in this way.

The 11.32 Å line, with successive orders at 5.58 and 3.72 Å, shows preferred orientation effects typical of the basal spacing of a plate-like mineral. Data for the first ten accurately measured lines in Table II were transformed to values of sin²θ x 10³ in Table III and analysed by

TABLE II. X-ray powder data for motukoreite.

D_{Kα} radiation, Nonius-de Wolff focussing camera, 4.967° 2θ per cm. Indexed on a hexagonal cell, a 9.356Å, c 44.72Å

d	l _g	h _g	r-obs.	r-calc.	hkl	d	l _g	h _g	r-obs.	r-calc.	hkl	d	l _g	h _g
-	-	-	-	0.398	0001	-	-	-	-	-	-	-	-	-
-	-	-	-	0.796	0002	4.0	vwv	-	4.50†	-	4.445	2021	3.0†	w
-	-	-	-	1.194	0003	-	-	-	-	-	4.499	2022	-	wB
11.32	vwv	vwv	1.570*	1.592	0004	-	-	-	-	-	4.524	1126	-	w
-	-	-	-	1.991	0005	-	-	-	-	-	4.571	1.0, 1.10	2.998	-
-	-	-	-	2.203	1070	3.89 [§]	vw	-	4.649	-	4.588	2023	2.898	vw
7.61	mw	vw	2.339*	2.343	1071	-	-	-	-	-	4.711	2024	2.84	vwv
-	-	-	-	2.239	1072	-	-	-	-	-	4.752	1127	-	w
7.10	vw	vw	2.509*	2.507	1073	3.72	a	vwv	4.809*	-	4.807	0.0, 0.12	2.784	w
6.54	vwv	vw	2.723*	2.721	1074	-	-	-	-	-	4.864	2025	-	-
-	-	-	-	2.790	0007	-	-	-	-	-	4.934	1.0, 1.11	2.650†	mw
5.58	s	s	3.196*	2.973	1075	3.55	mw	7abs	5.045*	-	5.003	1128	2.578	s
-	-	-	-	3.192	0008	-	-	-	-	-	5.045	2026	-	-
-	-	-	-	3.256	1076	-	-	-	-	-	5.214	0.0, 0.13	2.386	s mw
-	-	-	-	3.562	1077	-	-	-	-	-	5.251	2027	-	-
-	-	-	-	3.594	0009	-	-	-	-	-	5.273	1129	2.34	vwv
-	-	-	-	3.828	1120	3.34	m	vwv	5.366	-	5.301	1.0, 1.12	2.34	vwv
-	-	-	-	3.849	1121	-	-	-	-	-	5.481	2028	2.268†¶	w
4.59	s	m	3.886*	3.886	1078	-	-	-	-	-	5.561	1.1, 2.10	2.235	w vw
-	-	-	-	3.911	1122	-	-	-	-	-	5.623	0.0, 0.14	2.158	s mw
-	-	-	-	3.997	0.0, 0.10	-	-	-	-	-	5.675	1.0, 1.13	2.128†	vwv
4.4	vwv	vw	4.04	4.013	1123	-	-	-	-	-	5.770	2029	2.029	w
-	-	-	-	4.151	1124	-	-	-	-	-	5.864	1.1, 2.11	2.029	vw
4.2†	m	w	4.215*	4.225	1079	-	-	-	-	-	5.883	2130	2.029	w
4.1	vwv	vw	4.35†	4.323	1125	-	-	-	-	-	5.897	2131	-	-
-	-	-	-	4.401	0.0, 0.11	3.03	vw	-	5.938*	-	5.939	2132	-	-
-	-	-	-	4.427	2020	-	-	-	-	-	-	-	-	-

All possible values of r-calc. are given for d greater than 3.0Å, r less than 6.0 cm. For r between 6.0 and 9.0 cm only values of r-calc. close to those of r-obs are shown. Above 9.0 cm the indexing is too ambiguous to make values of r-calc. worth giving.

- d: Interplanar spacings in Angstroms, derived from r-obs.
- l_g: Visually estimated relative line intensities for the focussing camera photograph.
- r: Visually estimated relative line intensities from a photograph taken with D_{Kα} radiation in an 11.46 cm diameter Debye-Scherrer camera, showing typical preferred orientation effects. The focussing camera is much better than the Debye-Scherrer camera in registering weak lines.
- r: Distance of the line from the image of the direct beam on the focussing camera photograph. Measured with a travelling microscope to 0.001 cm.
- †: 0.03 cm.
- ‡: Overlaps a quartz line but is much too strong to be due to quartz alone.
- §: Strong lines of calcite. Other calcite lines too weak to affect pattern.
- ||: Strong line of quartz, strong enough to account for the whole line intensity.
- ¶: Possibly strong lines of calcite.
- *: Lines used for least squares refinement of the powder data.

TABLE III. Values of sin²θ for low angle lines of motukoreite

Line	r-obs.	sin ² θ	l _g	hkl	Zone data values of sin ² θ × 10 ⁵
No	x 10 ⁵				h=0 h=1 h=2
1	1.570	462	vwv	002	1=0 obs. - - - calc. 0 908 3632
2	2.339	1024	mw	101	1=1 obs. - 1024 - calc. 119 1027 3751
3	2.509	1178	vw	?	1=2 obs. 462 1387 - calc. 476 1384 4108
4	2.723	1387	vwv	102	1=3 obs. - - 4706 calc. 1071 1979 4703
5	3.196	1907	s	004	1=4 obs. 1907 2811 - calc. 1904 2812 5536
6	3.886	2811	a	104	1=5 obs. - - - calc. 2975 3883
7	4.215	3301	m	?	1=6 obs. 4283 - - calc. 4284 5192
8	4.649	4006	vw	?	
9	4.809	4283	s	006	
10	5.045	4706	mw	203	

Lipson's method of differences (Henry, Lipson and Wooster, 1961) which quickly yielded the zone given in Table III, where the first line at 11.2Å is taken as (002) and the second line at 7.61Å is taken as (101). This zone accurately explains 7 of the first 10 lines in Table III while postulating only 9 absences, 5 of which could be explained as halvings of the c-axis. The value, 8.056Å, found for d(100) in the zone is nearly 3 times the value of d(1070) (2.70Å) for the simple brucite layer with a = 5.116Å, and roughly 3 times the value of d(1070) (4.5Å) for the 5.2Å super-lattice found on some electron diffraction patterns of motukoreite.

A graphical method failed to determine a unit cell of monoclinic symmetry or higher from this zone. However, a lengthy analysis of all possible hexagonal and rhombohedral unit cells derived from the results shown in Table III showed that the full pattern could be satisfactorily indexed for a four-layer hexagonal unit cell, taking the basal spacing as (004), and the full indexing is given in Table II. Cell dimensions were derived by least squares refinement of the line positions marked with an asterisk, using the weighting scheme of Hees (1951), and the final results are: a = 9.356Å, c = 44.72Å.

Speculations on a possible crystal structure. The 3.0Å cell dimension found by electron diffraction is similar to the c repeats of the pyroaurite-sjögrenite group and its congeners (3.14; Taylor, 1973) and a 5.2Å unit cell is also found in this group and related minerals. 3.0Å is approximately the c repeat distance in a close-packed oxygen sheet in a brucite layer and hence a 3.0Å sub-cell suggests that the structure is based on brucite layers and/or close-packed oxygen sheets, as are those of the pyroaurite group.

The X-ray g repeat is a multiple of the 3.116Å "brucite layer" repeat. This superlattice and the 3/2a lattice observed on some electron diffraction patterns probably result either from cation ordering in the brucite layers or ordering in the CO₃²⁻ and H₂O interlayer.

The basal spacing c* = 11.48Å differs from that of the pyroaurite-sjögrenite group (7.8Å). However, a comparison of the cell parameters suggests that the structure may amount to essentials to that of pyroaurite with an additional interlayer in the unit cell. The c repeat of such a structure would be expected to be greater than 10.9Å (7.8 + 3.1Å) owing to the weak van der Waals bonding between the interlayers and the repulsion between the oxygen atoms. Taylor (1973) has suggested that wermilite may have an extra layer of water molecules in the elementary

layer and the cell parameters of this mineral (a = 9.26 = 3 x 3.087Å; c = 22.52 = 2 x 11.26Å; Moore, 1971) are closely related to those of the Motukoreia mineral.

A double interlayer in motukoreite would accommodate the 30²⁻ groups which, being tetrahedra, could not easily fit into a single layer like the planar CO₃²⁻ groups. The Na⁺ ions, being too large to fit in the hydroxide layer, would also have to occupy positions in the interlayer, as would some Mg²⁺ and/or Al³⁺ since the number of these OH groups present exceeds that needed to form a "brucite-type" layer with the OH present.

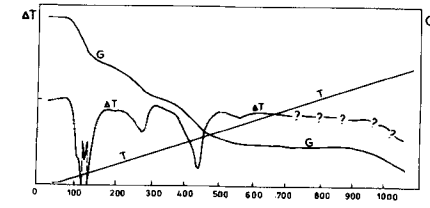


FIG. 5. Thermal decomposition curves (DTA and TGA) for motukoreite.

Thermogravimetry. A number of thermogravimetric runs have been made on motukoreite on both a Stanton Direct-reading Thermogravimetric Balance, coupled to a Stanton Differential Thermalanalytical Recorder, and on Shimadzu DT2B and DTG-2B instruments. With the Stanton apparatus 40-60 mg of sample was used with a heating rate of 7°C/min. With the Shimadzu, 200 mg and a heating rate of 10°C/min were employed. Otherwise, sample particle size (100-150 mesh) and reference material (ignited alumina) were the same. The Stanton equipment proved to have a lower sensitivity and the minima of all DTA endotherms recorded were at least 1°C lower than on the Shimadzu equipment, which was standardized with synthetic calcianite. Both TGA patterns were very similar.

The thermogravimetric analysis (Fig. 5) shows a large and continuous weight loss from 270°C to 1100°C with a total weight loss over this range in excess of 40%. Constant weight was not obtained even after prolonged heating at 1350°C and immediately cooling is commenced, a marked and frequently regular weight gain occurs.

Changes in the gradient of the TGA curve correspond, in the main, to a series of broad endotherms in the DTA pattern. Minima for these endotherms occur at 1280, 270, 440, 560 and 1080°C.

The 1280°C endotherm inflects between 75° and 180°C but the gradient of the weight loss curve lessens at 140°C. Up to this temperature, a weight loss of 10.5% occurs, which agrees closely with the 10.35% H₂O given in the analysis (Table I). This endotherm may represent the expulsion of adsorbed water and/or loosely bound water of crystallization.

The endotherm whose minimum lies at 270°C extends from 210° to 310°C and is similar to those found in basic magnesium carbonates, including pyroaurite, sjögrenite and hydrotaoite (Neskonen, 1970, p. 316).

The third endotherm inflects between 310° and 450°C, with a minimum at 445°C, and corresponds to a 10% weight loss over the temperature range 330-460°C. The gradient of the TGA curve lessens above 460°C until a steady state is reached at about 690°C with no further thermal changes until about 930°C. Much of the 4% weight loss in the temperature range 460-690°C is associated with the small endotherm between 510° and 600°C (minimum 560°C).

The final endotherm has its minimum at about 1050°C and a weight loss of at least 2% has been noted in this region.

The total weight loss to 700°C is close to 39% of the original sample, which matches the sum of H₂O, H₂O+ and CO₂ from the analysis (39.2%). In comparison with the 310-390°C endotherm of motukoreite, it may be noted that brucite displays a prominent dehydroxylation endothermic effect over the range 350-480°C (MacKenzie, 1970, pp. 245-248) and there are similar endotherms for pyroaurite and sibirgite (380-460°C), and hydrotalcite (450-520°C). AlOOH has endotherms at 240-585°C (diaspore) and 450-580°C (boehmite) (*ibid.* p. 280), which may correspond to the small 510-600°C endotherm of motukoreite. These endotherms seem to be characteristic of stages in the dehydration of "brucite-type" layers which all the structures of these minerals have in common, but the possibility that CO₂ loss may be involved in some cases cannot be eliminated.

The thermoanalytical behaviour of motukoreite is thus similar to that of the pyroaurite-sibirgite group and is generally consistent with the crystal structure proposed above.

Origin. As with the majority of volcanoes in the Auckland City field, activity at Motukorea was short-lived and on a small scale, consisting of minor phreatic, dominantly spatter and minor effusive phases. No evidence of solfataric or hydrothermal activity has been recorded. Eruption probably took place towards the end of the Otiran (= Wairu) glaciation less than 20000 years ago - certainly at a time of low sea level. However, at the moment no real evidence as to the origin of the motukoreite has been found, nor has the mineral been located elsewhere in the Auckland City area.

Name. It appears to be traditional, with new mineral species first recorded from New Zealand, to derive the name from the Maori name of the type locality, which in this case is Motukorea, meaning "Island of cormorants".

Type material is held at both the Department of Mineralogy, British Museum (Natural History) and the Department of Geology, University of Auckland.

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