

Motukoreaite—additional data and comparison with related minerals

G. W. BRINDLEY

126 Mineral Sciences Building, The Pennsylvania State University,
University Park, PA 16802

SUMMARY. Motukoreaite resembles hydrotalcite and has positively charged brucite-like layers separated by carbonate and sulphate anions and water molecules. Four phases are recognized. Phase I, the normal mineral with an 11.1 Å basal spacing, readily changes to a mixture of phase I and a partially dehydrated phase II. Phase III with a basal spacing 8.7 Å persists from 50–170 °C. Phase II is a pseudo-regular interstratification of phases I and III, with a spacing $11.1 + 8.7 = 19.8$ Å; second- and third-order reflections are observed. Phase IV with a 7.5 Å spacing is obtained by treating motukoreaite with sodium carbonate solution to replace SO_4 by CO_3 anions. Motukoreaite itself shows only slight tendency to transform to a 7.5 Å phase by heat-treatment alone. Comparison is made with the mineral carboydite, a NiAl sulphate carbonate hydrate. The possibility is considered that sulphate anions may substitute partially in the brucite-like layers to compensate for a deficiency of hydroxyl ions.

THE mineral motukoreaite, named and described by Rodgers *et al.* (1977), resembles hydrotalcite and other minerals of the pyroaurite group and consists of brucite-like Mg–Al hydroxide layers with sulphate–carbonate–water interlayers. A small sample of the beach rock containing this mineral was made available by Dr K. A. Rodgers from which enough motukoreaite was extracted for the tests described here.

Unit cell of motukoreaite. Rodgers *et al.* showed that X-ray powder patterns can be indexed with a hexagonal cell having $a = 9.336$ Å, $c = 44.72$ Å containing four structural layers each of thickness 11.18 Å. Electron diffraction data indicated a hexagonal sub-cell with $a' \approx 3.0$ Å or, when first examined, a hexagonal cell with $a'' = \sqrt{3}a'$. Taylor (1973) and others found similar a parameters for pyroaurite group minerals. The c parameters generally have values indicating two-layer and three-layer unit cells; the suggested four-layer unit cell is exceptional.

Bish (1977, 1978) showed that anion exchange occurs rather easily for several pyroaurite group minerals. When motukoreaite was treated with 1 M solution of sodium carbonate, a hydrotalcite-like product was obtained giving an X-ray powder

pattern corresponding to a structure with a hexagonal unit cell with parameters $a = 3.038$, $c = 22.68 = 3 \times 7.56$ Å (Table I). The indices are consistent with rhombohedral symmetry since $-h + k + l = 3n$. The layer spacing 7.56 Å is near the value normally found for hydrotalcite.

TABLE I. X-ray powder data for carbonate-exchanged motukoreaite

| <i>hkl</i> | <i>d</i> (obs) | <i>d</i> (calc) | <i>I</i> (obs) |
|------------|----------------|-----------------|----------------|
| 003 | 7.61 | 7.560 | 10 |
| 006 | 3.757 | 3.780 | 7 |
| 012 | 2.558 | 2.563 | 4 |
| 104 | 2.398 | 2.386 | 2 |
| 015 | 2.278 | 2.276 | 4 |
| 018 | 1.927 | 1.928 | 4 |
| 0,1,11 | 1.620 | 1.623 | 1 |
| 110 | 1.522 | 1.519 | 2 |

Calculated spacings based on a hexagonal cell with $a = 3.038$, $c = 22.68$ Å.

Table II shows the present X-ray diffractometer data for motukoreaite and the calculated spacings and indices based on a hexagonal cell with $a = 3.062$ Å, $c = 33.51 = 3 \times 11.17$ Å. The data were recorded with filtered Cu-K α radiation at $1^\circ(2\theta)/\text{min}$. Also listed are Debye-Scherrer camera data of Rodgers *et al.* with some additional reflections obtained with a Guinier camera; some very weak and very very weak Guinier-camera-recorded reflections are omitted. Apart from these exceedingly weak reflections, the two sets of data agree. In the present indexing most of the l indices are divisible by three, so that a single layer cell with $c = 11.17$ Å accounts for most of the reflections. A medium-strong reflection at $d = 4.58$ Å (4.59 Å, Rodgers *et al.*) can be indexed as 100 with a cell having $a' = \sqrt{3}a = 5.30$ Å, as Rodgers *et al.* also recognized. The rhombohedral condition is not

TABLE II. X-ray powder data for motukoreaite

| <i>d</i> (obs) | <i>d</i> (calc) | <i>hkl</i> | <i>I</i> (obs) | (Rodgers <i>et al.</i> 1977) | |
|----------------|------------------|-----------------|----------------|------------------------------|----------------------|
| | | | | <i>d</i> (obs) | <i>I_D</i> |
| 11.26 | 11.17 | 003 | 10 | 11.32 | vvs |
| 7.61 | — | — | 0.5 | 7.61 | vw |
| — | — | — | — | 6.54 | vw |
| 5.59 | 5.585 | 006 | 4 | 5.58 | s |
| 4.58 | * | * | 3 | 4.59 | m |
| 4.22? | — | — | 1? | 4.24 | w |
| 3.720 | 3.723 | 009 | 7 | 3.72 | vvs |
| 2.646 | 2.643 | 101 | 0.5 | 2.650 | mw(G) |
| 2.576 | 2.580 | 103 | 4 | 2.578 | s |
| 2.392 | 2.395 | 106 | 3 | 2.386 | mw |
| 2.272? | — | — | 0.3 | 2.268 | vw |
| — | — | — | — | 2.235 | vw |
| 2.160 | 2.160 | 109 | 2 | 2.158 | mw |
| 1.924 | 1.923 | 1,0,12 | 2.5 | 1.921 | ms |
| 1.710 | 1.708 | 1,0,15 | 3 | 1.709 | w |
| 1.565 | — | — | 1 | — | — |
| 1.529 | { 1.531 1.528 | { 110 1,0,18 | 1 | 1.528 | m(G) |
| 1.516 | 1.517 | 113 | 1 | 1.513 | m(G) |
| 1.476 | 1.476 | 116 | 0.5 | 1.477 | m(G) |

Hexagonal indices
 $a = 3.062$ $c = 33.51$ Å
 * 100 reflection, with $a' = \sqrt{3}a$

Intensities I_D
 from Debye-Scherrer camera except (G),
 Guinier camera data

satisfied by the indexing based on the three-layer cell.

The results suggest that the structure of motukoreaite approximates to a single-layer hexagonal cell, with $a = 3.062$, $c = 11.17$ Å, which may show superlattice reflections corresponding to $a' = \sqrt{3}a$. It is interesting to find that a three-layer hexagonal cell satisfying the rhombohedral condition is produced by the carbonate treatment; the results suggest that the CO_3^{2-} anions play a key role in ordering the layer structure.

Dehydration, rehydration of motukoreaite. The changes in the X-ray powder patterns when the mineral is treated at low temperatures (20–170 °C) and in various relative humidities are illustrated in fig. 1 which shows in slightly schematic form the diffraction patterns in the range $2\theta = 6$ –26°, Cu-K α radiation. Four phases, labelled I, II, III, IV are observed with basal spacings near 11.1, 9.8, 8.7, and 7.5 Å; the reflections from different spacings are distinguished by appropriate shading.

The pattern of the initial, almost pure motukoreaite, phase I, recorded with a randomly oriented powder, is shown in fig. 1a. Three basal

reflections from the 11.1 Å spacing are obtained and one non-basal reflection, marked *, with $d = 4.58$ Å. A small amount of phase IV, with $d \approx 7.5$ Å, also is observed. Fig. 1a, recorded shortly after the rock sample was received, was never again recorded in this almost pure state. The low-humidity atmosphere and the generally warm temperature of the laboratory probably caused a partial dehydration.

All subsequent patterns shown in fig. 1 were obtained with oriented samples on glass slides in order to emphasize the basal reflections. Pattern (b) was recorded on material kept in water at 70 °C prior to X-ray examination at about 100% relative humidity (RH). Pattern (c) was recorded at 75% RH. A new phase II appears, with spacings at about 9.8 and 6.0 Å, which is discussed later.

Patterns (d)–(i) were recorded after heating progressively from 50–175 °C, with 20 h duration at each temperature. Phases I and II both disappeared at 50 °C and phase III appeared with spacings 8.7 and 4.4 Å (fig. 1d). The profile of the 8.7 Å peak and the obvious doubling of the 4.4 Å peak indicate a mixture of two phases. The lower spacing component becomes less obvious as the temperature is raised. After heating at 170 °C, pattern (h) shows that the mineral is near to decomposition.

At each stage in this sequence, rehydration tests were made and it was always possible to return to a state similar to patterns (b) and (c) but rehydration became slower as the temperature was increased. Pattern (i) was obtained after exposing the 170 °C heated sample to 100% RH for 15 days.

Phase II, which appears in patterns (b), (c), and (i), is probably an ordered or partially ordered interstratification of phases I and III. The spacings 11.1 and 8.7 Å in an alternating sequence give an overall spacing of 19.8 Å with second and third orders at 9.9 and 6.6 Å, which can be compared with observed spacings at 9.8 and 6.0 Å. The agreement is not exact; the peak profiles are broad and still higher orders could not be obtained. The ordering of the layers must therefore be rather imperfect. Similar results, however, have been obtained with a hydrated sulphate form of hydrotalcite (Bish, 1977, 1978; Brindley and Kikkawa, 1979) which, after partial dehydration, gave ool reflections with $l = 2, 3, 4, 5$ from a regular interstratified sequence. Direct observation of the combined spacing near 20 Å, i.e. a first-order reflection, has not been obtained.

These results are in line with those of other investigations of pyroaurite- and hydrotalcite-like materials with interlayer sulphate anions. Phase I, with basal spacing near 11.1 Å, corresponds to a hydrated sulphate form and when this phase is dehydrated phase III is formed with a basal spacing near 8.7 Å. The difference corresponds to the space

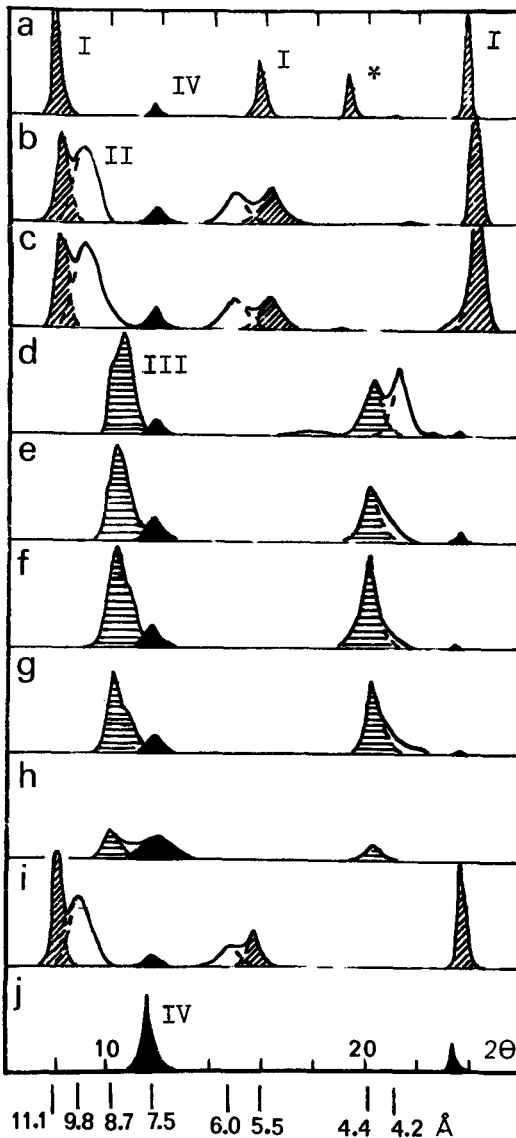


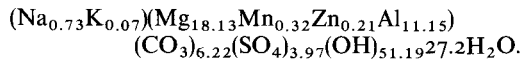
FIG. 1. Powder diffraction patterns of motukoreaite, $\text{Cu-K}\alpha$ radiation, $6-26^\circ$, 2θ . *a*. Random powder sample of original motukoreaite. *b-j*. Oriented powder samples on glass slides: *b*. After 1 day in water at 70°C ; sample dry in 100% RH. *c*. Sample 20 h in 75% RH. *d, e, f, g, h*. Sample successively at 50, 105, 125, 155, 170°C , for 20 h. *i*. After 20 h at 170°C , sample stored in 100% RH, 15 days. *j*. Motukoreaite, after treatment with sodium carbonate solution.

required for insertion of water molecules, not necessarily as a plane of water molecules but possibly as hydration of the sulphate anions. Nickel and Clarke (1976) discussed similar phases for the mineral carboydite (see later) and Bish (1977, 1978)

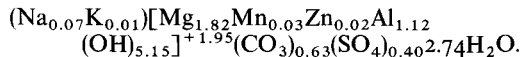
discussed sulphated forms of takovite and hydrocalcite; sulphated forms of hydrocalcite also have been studied by Brindley and Kikkawa (1979).

The apparent reluctance of phase III to pass into phase IV is understandable because the spacing of phase IV, about 7.5 \AA , is typical of the spacings of carbonate phases. A collapse of the 8.7 \AA spacing of the sulphate form to this spacing can be visualized only by a decomposition of the SO_4 anions, or by decomposition of the hydroxide layers so that the bulky SO_4 anions can be accommodated. Probably both processes are occurring as the mineral approaches the decomposition temperature around 170°C .

The formula of motukoreaite. Rodgers *et al.* gave the following formula:



They remarked that several idealized formulae are possible. The similarity of the mineral to hydrocalcite and other hydroxide layer structures suggests that normalizing the composition to three octahedral cations will facilitate such comparisons.¹ The formula then becomes:



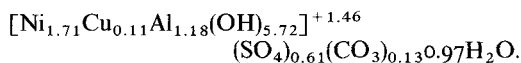
The layer charge of motukoreaite according to this formula is much higher than that of hydrocalcite and kindred minerals, partly because of the high proportion of trivalent ions and the deficit of hydroxyl ions. The ratio $R^{3+}/(\Sigma R^{2+} + R^{3+})$ lies mainly between about 0.20 and 0.33 for natural and synthetic hydrocalcites (Gastuche *et al.*, 1967; Brindley and Kikkawa, 1979); in the motukoreaite formula, this ratio is 0.37. The vacant hydroxyl positions might be filled with water molecules, which, however, would not affect the layer charge. Alternatively, as Nickel and Clarke (1976) suggested in relation to the mineral carboydite, sulphate anions might be incorporated in the hydroxide layers. One can visualize three oxygens of an SO_4^{2-} anion located in a plane of hydroxyl ions. The $0.40(\text{SO}_4)^{2-}$ anions in the motukoreaite formula almost ideally satisfy the charge requirements of the deficit of $0.85(\text{OH})^-$ ions, but also supply too many oxygens for the vacant $(\text{OH})^-$ positions. The main argument against incorporating $(\text{SO}_4)^{2-}$ anions in the hydroxyl layers is their easy replacement with $(\text{CO}_3)^{2-}$ ions, as Bish has discussed (1977, 1978).

A second aspect of the motukoreaite formula is that the total number of interlayer oxygens is 6.23

¹ $M_3(\text{OH})_6$ represents half the composition of a brucite-like layer within an 'ortho-hexagonal' cell with $a \approx 5.2$ and $b \approx 9.0 \text{ \AA}$.

or a somewhat smaller number if H₂O molecules or (SO₄)²⁻ anions are incorporated in the hydroxide layers. This number will fill two planes of oxygens between successive hydroxide layers when the total spacing is about 11 Å. Collapse of the layer structure to 8.7 Å is compatible with removal of interlayer water and a close packing of SO₄ groups between hydroxide layers, possibly with two oxygens of each group making contacts with each hydroxyl plane. Collapse of the layer structure to a 7.5 Å spacing is possible by replacing the SO₄ groups with CO₃ groups, as in fig. 1j, or by their incorporation in defective hydroxyl planes.

Motukoreaite compared with carrboydite. The mineral carrboydite, described by Nickel and Clarke (1976), has similarities to motukoreaite in that it is a hydroxide layer structure with sulphate and carbonate anions and also with the possibility of some sulphate anions being incorporated in the hydroxyl layers. The formula referred to three octahedral cations is as follows:



Compared with the motukoreaite formula, the hydroxyl ions approach more closely to 6.0, there are fewer interlayer water molecules, and the SO₄ anions exceed the CO₃ anions whereas the opposite occurs in motukoreaite. The number of interlayer oxygen ions per formula unit is 3.80 and these are easily accommodated in two oxygen planes between hydroxide layers.

The basal spacing of carrboydite is 10.34 Å with strong or medium-strong first-, second-, and third-order basal reflections similar to those in the motukoreaite pattern, fig. 1a; a spacing of 10.8 Å was observed with more gel-like material. Carrboydite collapses to a basal spacing of 8.6 Å at a temperature between 60 and 90 °C and decomposes between 150 and 200 °C; motukoreaite gives a basal spacing of 8.7 Å in the temperature

range 53–170 °C and is near decomposition at 170 °C. The similarity between the two minerals is very close apart from the main divalent cation being Ni in carrboydite and Mg in motukoreaite.

Bish (1977, 1978) considered that the easy exchange of SO₄ groups by CO₃ groups to give a hydrotalcite- or takovite-like structure points to a structure for carrboydite containing single hydroxide layers rather than double layers sharing octahedral faces as described by Nickel and Clarke. Similarly in motukoreaite, the hydroxide layers appear to be single layers. The possibility exists that SO₄ anions may partially compensate for an apparent deficiency of hydroxyl ions.

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