

AN AUTHIGENIC QUARTZ-CALCITE-RUTILE ASSEMBLAGE IN ORDOVICIAN LIMESTONES

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ABSTRACT

Optical examination and electron probe microanalysis show that intergrowth "clots" in basal Middle Ordovician limestones of the Kingston area are composed essentially of quartz, calcite, and rutile, pseudomorphic after sphene. It is proposed that the sphene was introduced as detrital material into the sediments, and that the breakdown to the equilibrium assemblage took place during diagenesis of the limestones. Because of the ubiquity of sphene in local Precambrian rocks, the presence of these distinctive intergrowths may be used as an indication of exposed Precambrian land masses during deposition of these sediments.

INTRODUCTION

In the vicinity of Kingston, Ontario, Precambrian rocks are progressively overlapped by rocks of lower Paleozoic age and are in turn overlain

by surficial deposits of Pleistocene age. The basal unit of the Paleozoic cover is the Cambrian Nepean Formation, a quartz sandstone and siltstone with local basal conglomerate. The remainder of the Paleozoic cover is of Middle Ordovician age and consists of shales with minor sandstones of the Shadow Lake Formation overlain by limestones of the Gull River Formation; see Liberty (1971). Locally, where both the Nepean and Shadow Lake Formations are absent over and on the flanks of Precambrian topographic highs, Gull River limestones directly onlap the Precambrian surface.

Although regionally the Paleozoic strata are essentially flat-lying, anomalously large dips up to 25° occur where Gull River limestones directly onlap Precambrian topographic highs. Recently, during an investigation (McIlreath 1971) of the extent to which initial inclination, compaction, and later uplift of the Precambrian basement are responsible for these anomalously high dips, authigenic rutile was identified.

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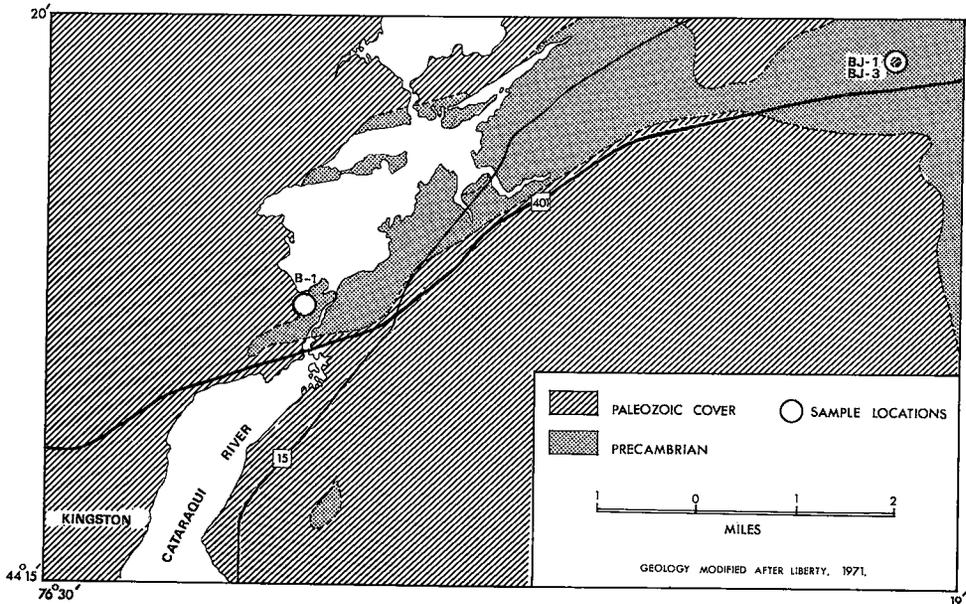


FIG. 1. Study area and location of samples.

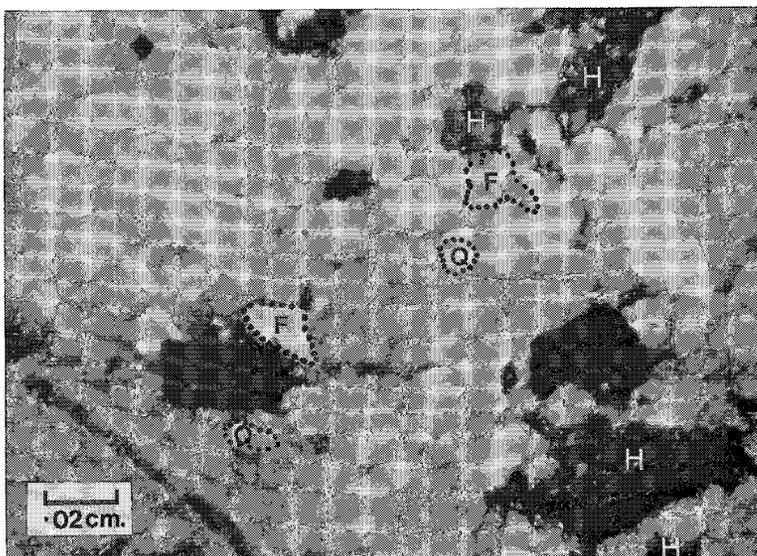


FIG. 2. The occurrence of intergrowth clots and other detrital material in Ordovician limestones. The groundmass is a felt of shell fragments in a calcitic matrix; the black regions are intergrowth clots. Other detrital fragments identified are quartz (Q) and feldspar (F). Plucking during specimen preparation has left holes (H) in the section. BJ-3, transmitted light, partly crossed nicols.

The rutile has a microcrystalline needle-like habit and occurs associated with calcite and quartz in very distinct, isolated, ivory white clusters or "clots" 0.125-0.500 mm wide. The rutile is authigenic as the nature of the delicate needle-like crystals within any given clot is inconsistent with a direct detrital origin. There is no evidence that the Paleozoic rocks have been metamorphosed.

In the Gull River Formation, the rutile-rich clots occur only in the "Rideau Facies". The Rideau Facies is a localized, shallow-water basal facies, locally developed where the Gull River limestones directly onlap the Precambrian surface. In the vicinity of Kingston, this facies is predominantly a green-weathering, calcareous lithic wacke which progressively grades upward into limestones. The wacke consists of locally derived, subangular, Precambrian rock fragments randomly oriented with variable concentrations of comminuted bioclastic fragments in a calcarenite-calcilutite matrix (see Fig. 2). In the Gull River Formation, the distribution of rutile-rich clots parallels that of the Precambrian detritus; both decrease laterally and vertically away from Precambrian topographic highs.

Methods of investigation

Three polished thin sections (from locations shown on Fig. 1) were made and examined optically. Regions containing intergrowth "clots" were marked and investigated with the electron probe microanalyzer. All microprobe work was carried out at 15 kv and 0.02 μ a specimen current, using a finely-focused electron beam (diameter about 1 micron).

Wavelength scans were made to identify the elements present in the intergrowths. X-ray scanning images were then photographed for each intergrowth for each element present. One or two spots in each of the phases identified in the x-ray scanning image photographs were analyzed semi-quantitatively (*i.e.* by background-corrected intensity ratios to known standards). Only semi-quantitative analyses were made because

- (a) all minerals present in the intergrowths could be unambiguously identified in this way;
- (b) fine grain size and poor polishing characteristics made any more quantitative treatment pointless.

Standards used for the analyses were synthetic $\text{Ca}_2\text{P}_2\text{O}_7$, natural quartz, titanium metal, and iron metal.

MINERALOGY

From the *x*-ray scanning image photographs, three phases could be identified as being consistently present in the intergrowths: one calcium-rich, one titanium-rich and one silicon-rich. The calcium-rich and titanium-rich phases were always intimately intergrown whereas the silicon-rich phase was confined to the borders of the intergrowth (Figs. 3-6). An iron-rich phase was occasionally seen in the vicinity of the intergrowth clots (Figs. 4, 5) and some iron was generally associated with the calcium-rich phase (Figs. 4 and 6).

Spot analyses of these phases indicated the following minerals to be invariably present: (a) calcite, slightly iron-bearing (*ca.* 0.2%). The calcite in the intergrowth clots may be distinguished from that in the groundmass carbonate rock by the presence of iron; (b) rutile (this polymorph is indicated by the needle-like crystal form); (c) quartz.

The iron-rich phase contains no sulphur and

roughly 60% iron; it is therefore identified as hematite or limonite.

GEOLOGICAL CONSIDERATIONS

Experimental work by Schuiling & Vink (1967) and calculations by Karpov (1966) indicate that the association, quartz-calcite-rutile, is stable only in low-temperature and/or high $P(\text{CO}_2)$ environments; even under low-grade metamorphic conditions, the reaction



is favoured.

Schuiling & Vink state that they searched in vain in metamorphic rocks for the assemblage quartz-calcite-rutile/anatase; this study shows that the assemblage exists in Ordovician limestones which have been subjected to conditions no more extreme than those prevailing during diagenesis, normally defined (*e.g.* Bayly 1968) as less than 100°C and 1000 bars.

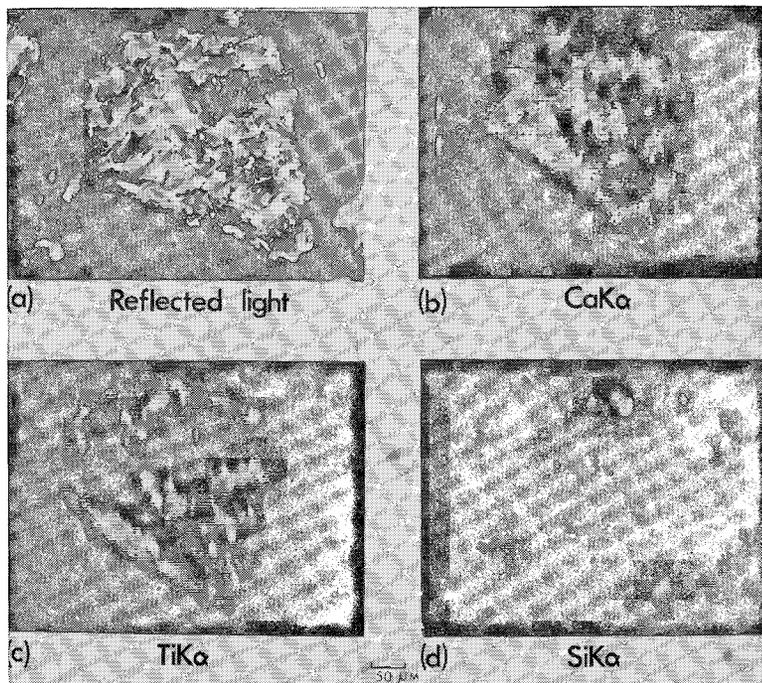


FIG. 3. Specimen B-1, intergrowth 3, showing the spatial relations of quartz, calcite, and rutile in the intergrowth region. (a) reflected light micrograph, showing the sphene-like form of the intergrowth and the relatively highly reflective rutile needles; (b), (c) and (d) *x*-ray scanning image photographs. Calcium- and titanium-rich phases (calcite and rutile) are intimately intergrown; the silicon-rich phase (quartz) is confined to the borders of the intergrowth clot, possibly reflecting the increased solubility (or colloid formation) of SiO_2 in the alkaline waters characteristic of carbonate formation and diagenesis.

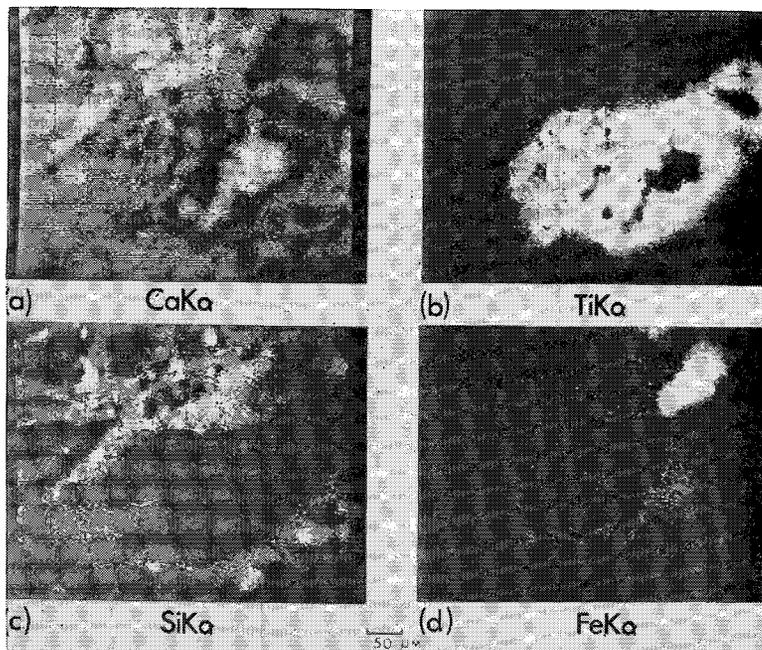
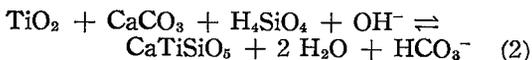


FIG. 4. Specimen BJ-1, intergrowth 1, x-ray scanning image photographs. Some intergrowth clots have an associated, but not intergrown, iron-rich phase (hematite or limonite). Note that the calcite within the intergrowth is Fe-bearing.

The consistent assemblage quartz-calcite-rutile, and the textural relations of the phases, indicate that they were formed in place by the breakdown of a detrital mineral. Both the bulk chemistry and the shapes of the intergrowth clots suggest that this detrital mineral was sphene. Indeed, quartz-calcite-anatase intergrowths, pseudomorphic after sphene, have been previously identified optically (Schei 1904).

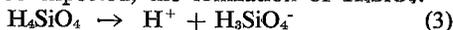
Equation (1) represents the stability of sphene in a CO_2 -solid state system. Given the aqueous environment present during sedimentation and diagenesis, it is more relevant to consider the stability of sphene relative to an aqueous CO_2 -rich solution. For example, one possible equation can be written:



The left side of this equation will be favoured by the low-temperature, high $P(\text{CO}_2)$ water-rich environment prevailing during diagenesis.

The pH of water in equilibrium with both air and CaCO_3 (*i.e.* the pH of a shallow water environment such as is postulated for the deposition of these sediments) is buffered at approximately 8 (Krauskopf 1967). At a pH of

8 or greater, the solubility of amorphous silica was found to increase rapidly due to the presence of the H_3SiO_4^- ion, in addition to H_4SiO_4 , in solution (Alexander *et al.* 1954). Thus, as might be expected, the ionization of H_4SiO_4 :



is favoured in alkaline environments. This reaction would also affect the equilibrium in equation (2), further stabilizing the left side of the equation.

The increased solubility of amorphous silica, and, by analogy, of quartz in alkaline water may explain the observed dispersion of quartz grains, presumably formed from the breakdown of sphene, outside the intergrowth clots.

A more common titanium-bearing mineral is ilmenite (*see, for example, Pettijohn 1957; Boswell 1933*); perhaps some of the rutile-rich intergrowths, in particular those with closely associated iron oxide or hydroxide grains (Figs. 3 and 4) may have formed by the breakdown of original ilmenite. Since iron-rich phases are not consistently present in the intergrowths, however, it is proposed that most of the authigenic rutile was formed by the breakdown of sphene rather than ilmenite.

This proposition is supported by the abun-

dance of sphene in the local Precambrian rocks, which also form the basement for these Ordovician sediments and are the source of most coarse clastic fragments. Sphene from one near-

by locality has been analysed; the analyses are given in Table 1. Note that this mineral is iron-bearing; it is a likely source of iron in the calcite of the intergrowths (see Figs. 4, 5, 6).

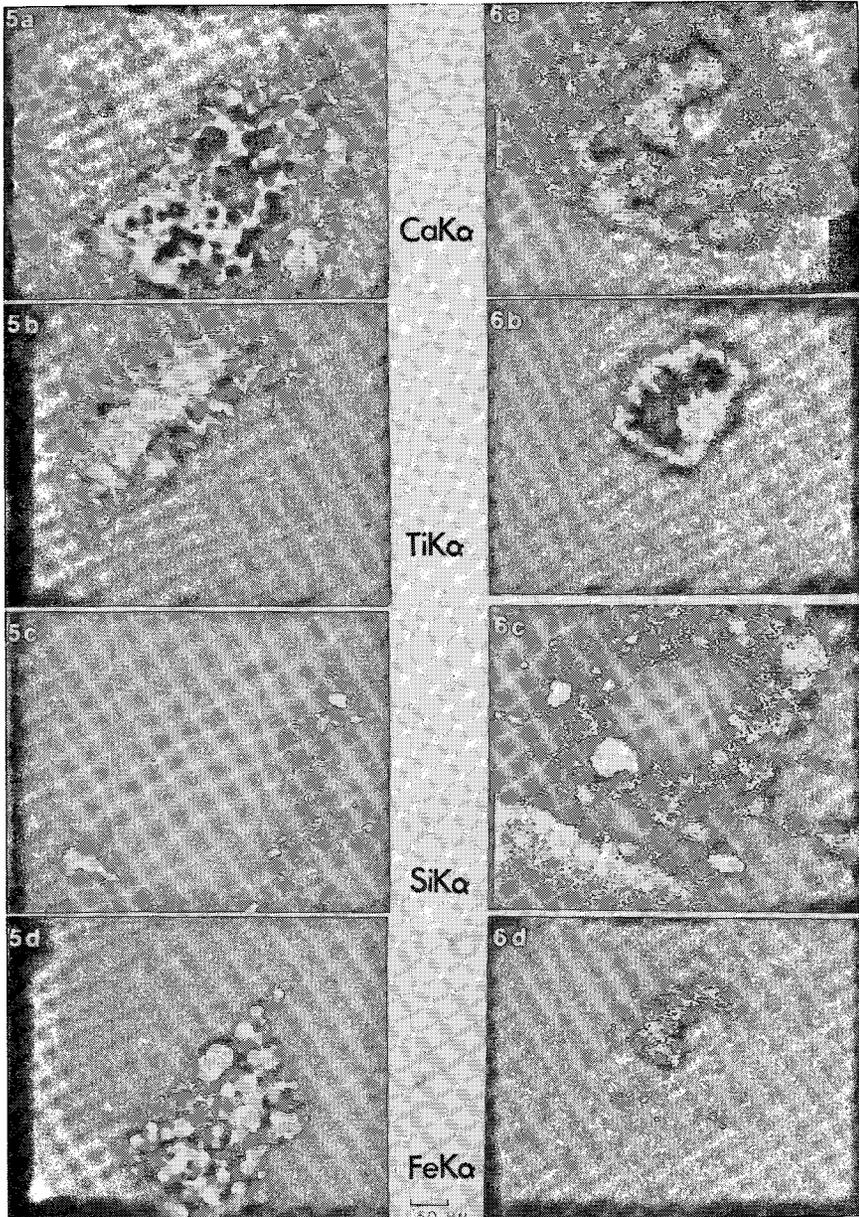


FIG. 5. Specimen BJ-3, intergrowth 5, x-ray scanning image photographs. Quartz-calcite-rutile intergrowth, with closely associated iron oxide or hydroxide. The extreme segregation of rutile and the iron-rich phase suggests that ilmenite is an unlikely source of titanium in these rocks.

FIG. 6. Specimen BJ-3, intergrowth 2, x-ray scanning image photographs. (d) was deliberately overexposed to illustrate the concentration of iron (0.2%) in the calcite of the intergrowth, in contrast to the surrounding iron-free calcite cement.

TABLE 1. ANALYSIS OF SPHENE FROM THE ALPORT QUARRY, VERONA, ONTARIO

| | Specimen CM-2-T | Specimen CM-3-T |
|--------------------------------|-----------------|-----------------|
| SiO ₂ | 30.66 | 30.47 |
| TiO ₂ | 39.40 | 39.38 |
| Al ₂ O ₃ | 2.01 | 1.88 |
| Fe as FeO | 0.98 | 0.92 |
| MnO | 0.00 | 0.00 |
| MgO | 0.50 | 0.62 |
| CaO | 28.35 | 27.42 |
| Na ₂ O | 0.10 | 0.25 |
| K ₂ O | 0.00 | 0.00 |
| Cr ₂ O ₃ | 0.00 | 0.00 |
| | 102.00 | 100.94 |

Electron probe microanalysis, 15 kv, 1.5 x 10⁻⁹ amp specimen current energy-dispersive detection system.

Mukherji & Winder (1970) identified detrital sphene in Black River limestones near Kingston; this indicates that the stable assemblage quartz-calcite-rutile is not *invariably* present. The breakdown of any mineral under such low-energy conditions is difficult. However our studies and those of Schuiling & Vink (1967), who were able to reverse reaction 1 at temperatures as low as 320°C within 14 days, indicate that such a breakdown of sphene can occur, at least occasionally.

Mukherji & Winder also list rutile and anatase as detrital minerals occurring in local Black River limestones. However, textural relations indicate that the TiO₂ mineral in the rocks we have studied is of authigenic origin.

The presence of distinctive and readily traceable detrital minerals (or their pseudomorphs) in sedimentary rocks may be used as a clue to the nearby topography during sedimentation; this principle has been used by Dietrich (1969) to estimate the period of erosion of the Platta nappe, southern Oberhalbstein, Switzerland, by studying the ophiolitic material occurring in conglomerates and sandstones of the eastern Switzerland molasse deposits between Lake Zug and Lake Constance. To be of use, the minerals and fragments must be clearly of detrital origin; some common minerals (feldspar, quartz) also form authigenically, and hence are less reliable topographic indicators.

If, as is postulated, the source of the sphene is the nearby Precambrian terrain, then the presence of sphene (or quartz-calcite-rutile) indicates the existence, during that period of deposition, of at least "islands" of Precambrian

rock in the Ordovician sea. Conversely, the disappearance of sphene or its pseudomorph, moving up through a stratigraphic section, is indicative of the removal of sphene-bearing Precambrian rocks as a source of detrital material. This line of evidence might prove useful in the debate on the age of the arching of the Frontenac axis.

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Manuscript received May 1974, amended June 1974.

SHORTER COMMUNICATIONS

PINCHITE, A NEW MERCURY OXYCHLORIDE FROM TERLINGUA, TEXAS

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INTRODUCTION

The mercury deposits near Terlingua, Brewster County, Texas, have been a long-standing source of interesting mineral specimens. In 1973 a small specimen from Terlingua was submitted to us by Mr. William W. Pinch of Rochester, New York, who had possessed the specimen for several years. Mr. Pinch, an experienced private collector, directed our attention to minute crystals which he believed to be a new mineral species, an opinion which our study readily confirmed. In recognition of Mr. Pinch's observations and his generous contributions to many of the major mineralogical museums of the world, we have named the mineral pinchite. The mineral and name have been approved by the Commission on New Minerals and Mineral Names of the I.M.A. Type specimens (milligrams) are preserved in the Royal Ontario Museum (No. M33258), in the private collection of Mr. Pinch, and in the Smithsonian Institution, Washington, D.C.

GENERAL APPEARANCE AND PHYSICAL PROPERTIES

Pinchite occurs as euhedral crystals up to 1 mm in size. Two habits have been observed and

are depicted in Figure 1. The forms present are: {001}, {010}, {100}, and {012}.

The mineral is black to dark brown and has a reddish brown streak. It is quite soft. No cleavage was observed.

Thin fragments of the mineral are transparent and show strong pleochroism from red to almost opaque black. No optical constants could be measured. The refractive indices are higher than 2.00 and the birefringence is very strong.

Pinchite is associated with montroydite (HgO) and terlinguaite (Hg₂OCl).

X-RAY AND CHEMICAL DATA

The first clue as to the identity of pinchite was the agreement of its single crystal data with those determined by Weiss *et al.* (1954) for synthetic HgCl₂•4HgO. The data for pinchite determined by the aprecision and Weissenberg methods in this study are: space group *Ibam*, *a* = 11.6, *b* = 6.07, and *c* = 11.7 Å. The data of Weiss *et al.* (1954) for synthetic HgCl₂•4HgO are: space group *Ibam*, *a* = 11.5, *b* = 6.0, and *c* = 11.7 Å.

A small amount of the synthetic HgCl₂•4HgO studied by Weiss *et al.* (1954) was kindly furnished to the writers by Dr. Gunter Nagorsen of the University of Munich. The x-ray powder diffraction data obtained for this material and for pinchite are presented in Table 1. The cell parameters of pinchite, refined from the x-ray powder data using the programme of Evans *et al.* (1963), are: *a* = 11.54, *b* = 6.08, and *c* = 11.64 Å.

An x-ray fluorescence scan of a few small crystals of pinchite detected only mercury. Through the kindness of Dr. R. G. V. Hancock, Department of Chemical Engineering, University of Toronto, a neutron activation analysis of pinchite was performed using synthetic pinchite and HgCl₂ as standards. The formula derived from the analysis (Table 2) agrees well with

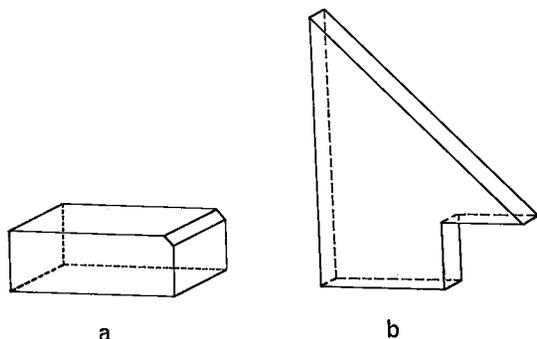


FIG. 1. Pinchite crystals showing (a) the more common habit and (b) the less common type.

TABLE 1. X-RAY POWDER DIFFRACTION DATA FOR SYNTHETIC $\text{HgCl}_2 \cdot 4\text{HgO}$ AND PINCHITE (Camera diameter 114.6 mm, $\text{CuK}\alpha$ rad.)

| synthetic $\text{HgCl}_2 \cdot 4\text{HgO}$ | | pinchite (ROM no. M33258) | | | hkl |
|---|-------------------|---------------------------|-------------------|--------------------|-------|
| λ | $d_{\text{obs.}}$ | λ | $d_{\text{obs.}}$ | $d_{\text{calc.}}$ | |
| 10 | 5.85 | 10 | 5.82 | 5.82 | 002 |
| 60 | 3.95 | 60 | 3.94 | 3.94 | 211 |
| 40 | 3.261 | 35 | 3.256 | 3.251 | 310 |
| 50 | 2.926 | 50 | 2.919 | 2.910 | 004 |
| 100 | 2.843 | 100 | 2.837 | { 2.846 | 213 |
| 80 | 2.694 | 80 | 2.695 | 2.696 | 022 |
| 5 | 2.595 | 5 | 2.597 | 2.598 | 204 |
| 3 | 2.547 | 2 | 2.549 | 2.543 | 411 |
| 20 | 2.176 | 20 | 2.169 | 2.168 | 314 |
| 10 | 2.098 | 5 | 2.094 | 2.093 | 420 |
| 10 | 2.053 | 10 | 2.044 | 2.049 | 404 |
| 10 | 1.974 | 10 | 1.968 | 1.969 | 422 |
| 15 | 1.929 | 12 | 1.923 | 1.923 | 600 |
| 10 | 1.825 | 10 | 1.822 | { 1.825 | 125 |
| 15 | 1.796 | 15 | 1.791 | 1.793 | 115 |
| 10 | 1.712 | 10 | 1.707 | 1.714 | 521 |
| 12 | 1.673 | 12 | 1.668 | { 1.666 | 330 |
| 15 | 1.641 | 15 | 1.636 | 1.636 | 332 |
| 10 | 1.610 | 10 | 1.610 | 1.610 | 325 |
| 15 | 1.570 | 15 | 1.568 | 1.566 | 316 |
| 10 | 1.527 | 15 | 1.524 | { 1.525 | 026 |
| 5 | 1.426 | 5 | 1.422 | 1.423 | 406 |
| 10 | 1.349 | 7 | 1.348 | 1.348 | 622 |
| 5 | 1.250 | 5 | 1.249 | 1.249 | 433 |
| 5 | 1.232 | 5 | 1.231 | { 1.232 | 530 |
| 15 | 1.137 | 15 | 1.135 | { 1.137 | 426 |
| | | | | 1.137 | 044 |
| | | | | 1.137 | 732 |
| | | | | 1.137 | 725 |
| | | | | 1.137 | 716 |
| | | | | 1.137 | 352 |
| | | | | 1.137 | 329 |

the theoretical formula of $\text{Hg}_5\text{O}_4\text{Cl}_2$. With $Z = 4$, the calculated density is 9.25 g/cm^3 (natural) and 9.37 g/cm^3 (synthetic). Weiss *et al.* (1954) obtained a density of 9.01 g/cm^3 by pycnometer. In the present study, ten small crystals measured with the Berman balance gave a density of 9.5 g/cm^3 .

TABLE 2. CHEMICAL ANALYSIS OF PINCHITE

| | theoretical wt % for $\text{HgCl}_2 \cdot 4\text{HgO}$ | pinchite | molecular proportions | atoms in unit cell |
|----------------|---|----------|--------------------------|-----------------------|
| HgO | 95.18 | 94.5 | 0.4363 | Hg 20.00 |
| Cl | 6.23 | 6.3 | 0.1777 | Cl 8.15 |
| Br | --- | 0.2 | 0.0025 | Br 0.11 |
| | { 101.41 | { 101.0 | --- | 0 15.99 |
| less O=(Cl+Br) | 1.41 | 1.4 | 0.0875 | |
| total | { 100.00 | { 99.6 | | |

Formula: $\text{Hg}_{20.00}\text{O}_{15.99}\text{Cl}_{8.15}\text{Br}_{0.11}$ or $4[\text{Hg}_{5.00}\text{O}_{4.00}\text{Cl}_{2.04}\text{Br}_{0.03}]$

ACKNOWLEDGEMENTS

The writers are pleased to acknowledge the assistance given them by Dr. R. G. V. Hancock for the neutron activation analysis and by Dr. Gunter Nagorsen for the sample of synthetic $\text{Hg}_5\text{O}_4\text{Cl}_2$. Particular thanks are due to Mr. W. W. Pinch who supplied the natural material and recognized it as a possible new species.

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Manuscript received May 1974.