WELOGANITE, A NEW STRONTIUM ZIRCONIUM CARBONATE FROM MONTREAL ISLAND, CANADA

ANN P. SABINA, J. L. JAMBOR AND A. G. PLANT

Geological Survey of Canada, Ottawa

ABSTRACT

Weloganite occurs in an alkalic sill which has intruded Ordovician limestone at St-Michel, Montreal Island, Quebec. Chemical analysis of the new mineral gave SrO 41.0,ZrO_2 19.4,CO_2 32.2,H_2O 6.6, sum 99.2, corresponding to $Sr_5Zr_2C_{9.3}H_{9.3}O_{32.2}$, ideally $Sr_5Zr_2C_9H_8O_{31}$.

Weloganite is trigonal, space group $P3_{1,2}$, hexagonal dimensions $a = 8.96, c = 18.06$ Å, $D_m = 3.22, D_c = 3.26$ for $Z = 2$. The strongest lines of the x-ray powder pattern are 2.81 Å (10), 4.35 (9), 2.59 (7), 2.227 (7), 2.009 (7). The mineral occurs predominantly as yellow crystals which are roughly hexagonal in outline and typically irregular in width.

INTRODUCTION

The new mineral weloganite was discovered during an investigation of mineral occurrences in the Montreal area in the summer of 1966. Weloganite occurs in an alkalic sill, 5 to 10 feet thick, which has intruded Trenton (Ordovician) limestone at St-Michel, Montreal Island, Quebec. The general geology has been described by Clark (1952) who regards the dykes and sills in the area as satellitic rocks genetically related to the plutonic alkalic intrusions forming the core of Mount Royal, one of the Monteregian Hills. The sill in which weloganite occurs is about four and a half miles north of Mount Royal and is well exposed in the limestone quarry operated by Francon (1966) Limitée. A report on the petrology of the sill will be given at a later date by L. Moyd of the National Museum of Canada.

Weloganite is named in honour of Sir William E. Logan, first director of the Geological Survey of Canada, 1842–1869, who laid the foundation of our knowledge of the geology of the area. T. Sterry Hunt in 1851 gave the name *loganite* to a mineral from Calumet Island, Ottawa River, Canada. However, in the Fifth Edition of Dana's System of Mineralogy (1868), the mineral was denied species stature and listed as an altered amphibole, near penninite in composition. Because loganite has not been considered as a valid species name for the past 100 years, both loganite and weloganite were considered as possible names for the new mineral from St-Michel. Of these, the name weloganite was approved by the Commission on New Minerals and Mineral Names, I.M.A.

CRYSTALLOGRAPHY

Although some weloganite is massive, much of the mineral occurs in vugs in the sill as poorly developed crystals elongate parallel to c. They are roughly hexagonal in outline, and the prism faces are always heavily striated and grooved parallel to the base because of pronounced oscillatory growth [001]. The crystals are thus characteristically very irregular in width. Termination of the crystals is roughly pyramidal and ranges from a blunt point formed by tapering of the prismatic faces to, in many cases, an abrupt flat pedion which is commonly wider than the main portion of the crystal. The pedion itself may be modified by two trigonal pyramids, but their presence is uncertain because of the complications arising from the oscillatory growth. Weloganite crystals range in size from more than 3 cm down to 2 mm parallel to the elongation, but smaller crystals have not been found.

Precession photographs of several fragments indicate that weloganite is trigonal, with diffraction symmetry $\bar{3}$. The hexagonal cell dimensions are $a = 8.96$, $c = 18.06$ Å. The measured d-spacings and visually estimated intensities of the x-ray powder pattern are given in Table 1. The only systematic absence observed on single crystal films is $000l$ with $l \neq 3n$. Thus, the space group of weloganite is $P3_1$ or $P3_2$ and the

TABLE 1. WELOGANITE: X-RAY POWDER DATA.
Camera diameter 114.6 mm, Cu $K\alpha$ radiation. Indexed with
hexagonal cell $a = 8.96$, $c = 18.06$ Å.

I_{est}	d_{meas}(Å)	d_{calc}(Å)	hkl	I_{est}	d_{meas}(Å)	d_{calc}(Å)	hkl
4	7.76	7.76	100	7	2.590	2.587	300
3	7.12	7.13	101	5	2.375	2.377	303
6	6.03	6.02	003	7	2.227	{2.236	117
$\frac{1}{2}$	4.75	4.76	103			{2.223	221
9	4.35	4.35	111	1	2.178	2.174	222
5	4.01	4.01	112	$\frac{1}{2}$	2.099	2.099	223
1	3.90	3.90	104	7	2.009	2.007	009
5	3.18	3.18	114	6	1.961	1962	306
4	3.01	3.01	006	<$\frac{1}{2}$	1.934	{1.937	217
$\frac{1}{2}$	2.93	2.93	210			{1.929	401
10	2.809	2.806	106	6	1.903	1.904	225
<$\frac{1}{2}$	2.635	2.637	213				

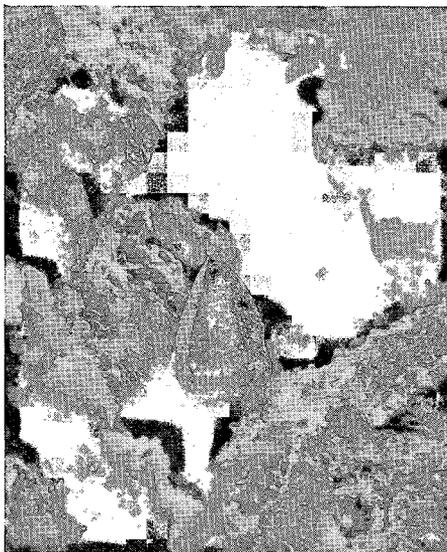| I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)	I_{est}	d_{meas}(Å)
<$\frac{1}{2}$	1.849	$\frac{1}{2}$	{1.424	2	1.199	1	0.9775
<$\frac{1}{2}$	1.778		{1.406	3	1.175	1	0.8935
3	1.687	1	1.354	$\frac{1}{2}$	1.120	1	0.8793
2	1.655	2	1.339	3b	1.089	$\frac{1}{2}$	0.8688
6	1.585	1	1.327	1	1.072	1	0.8040
4	1.535	3	1.294	2	1.024		
2	1.493	1	1.264	1	1.003		
1	1.450	4b	1.235	2	0.9885		

FIG. 1. Two crystals of weloganite joined together to form a single unit showing relatively well-developed pyramidal terminations. The basal twin plane is marked by the prominent re-entrant angle formed by lower pyramids which modify the basal pedion. ×2.

FIG. 2. Weloganite crystals showing pronounced oscillatory growth (bottom), basal cleavage (centre), and two crystals showing prominent pedial terminations (top left). × 1½.

mineral is one of the few known substances belonging to crystal class 3. The prismatic faces are two trigonal prisms $\{10\bar{1}0\}$, and $\{01\bar{1}0\}$, and the main pyramidal termination is a combination of the trigonal pyramids $\{10\bar{1}l\}$ and $\{01\bar{1}l\}$. One of the best examples of the subordinate pyramidal faces modifying the pedion is shown in Fig. 1.

PHYSICAL AND OPTICAL PROPERTIES

The colour of weloganite ranges from predominantly lemon-yellow to amber; thin fragments are colourless and transparent. Basal sections of many crystals are conspicuously zoned from white to various shades of yellow. The mineral has a vitreous lustre, white streak, conchoidal fracture, and perfect basal cleavage (Fig. 2). The hardness is $3\frac{1}{2}$. A specific gravity of 3.22 ± 0.03 was obtained by suspension of minute cleavage flakes in heavy liquids. Later, when more material became available, H. R. Steacy kindly measured 5 crystal fragments on a Berman Balance. These range in specific gravity from 3.16 to 3.22 with the average being 3.20.

Despite the trigonal symmetry, nearly all crushed grains of weloganite give an off-centred biaxial figure with $(-)$ $2V$ about $15°$, and $\alpha = 1.558$, $\beta = 1.646$, $\gamma = 1.648$, all ± 0.003. The refractive indices are somewhat variable, with $\alpha = 1.553$, and $\gamma = 1.654$ being the maximum range found. Likewise, in zoned basal sections $2V$ may vary, and in some cases the mineral appears uniaxial. Several grains showing pronounced zoning were checked for variations in Sr, Zr, Ba, and Ca across the zones using an electron probe, but no such variations were found.

CHEMISTRY

A composite sample of grains and crystals of weloganite hand-picked and cleaned under a binocular microscope was used for the chemical analysis. The identification of each fraction was checked by means of x-ray powder diffraction patterns. Strontium in the composite sample was determined by flame photometry whereas zirconium was determined with an electron probe using grains available in thin sections. For the microprobe work, zircon was used as a standard; corrections for atomic number and absorption effects were made with the appropriate data given in Adler (1966).

The chemical and microprobe results obtained for weloganite are given in Table 2. The mineral effervesces violently in cold dilute hydrochloric acid, but tests for sulphate and chlorine were negative. The analytical results recalculated to 100% yield $Sr_5Zr_2C_{9.3}H_{9.3}O_{32.2}$. In order to obtain comparable measured and calculated specific gravities, a slight excess of water in the analysis is assumed (Table 2), and the theoretical formula is taken as $Sr_5Zr_2C_9H_8O_{31}$. This gives a calculated specific gravity of 3.260 assuming 2 formula weights per unit cell. Weloganite is thus a most peculiar compound—not only is it a carbonate containing major amounts of zirconium, but it is also apparent that the zirconium must be bound in the mineral as a carbonated complex of some type. This is evident from the fact that a substantial excess of CO_3 is available even if all the strontium is combined to form $SrCO_3$ molecules in the structure.

TABLE 2. WELOGANITE: CHEMICAL ANALYSIS

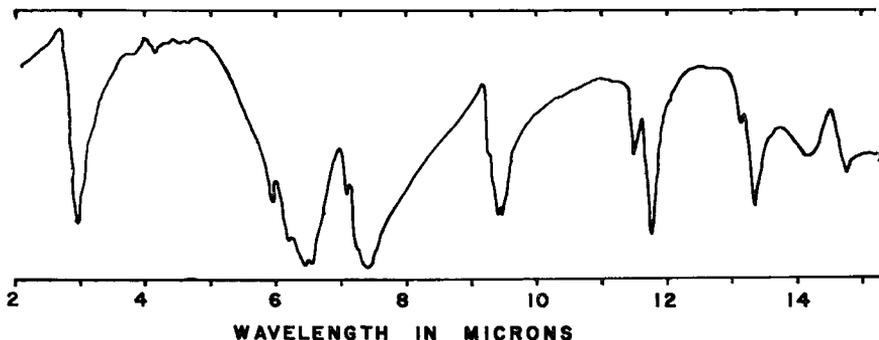|	Wt %	Recal. to 100%	Molecular ratio	Proportions	Theoretical contents $Sr_5Zr_2C_9H_8O_{31}$, wt%
SrO	41.0	41.33	0.3989	5.02	42.03
ZrO$_2$	19.4	19.57	0.1588	2.00	19.99
CO$_2$	32.2	32.46	0.7376	9.29	32.13
H$_2$O	6.6	6.64	0.3689	4.64	5.85
	99.2	100.00			100.00

WAVELENGTH IN MICRONS

FIG. 3. Infrared spectrum of weloganite.

The infrared spectrum of weloganite (Fig. 3) was obtained to establish whether part of the CO_3 might be present as the bicarbonate anion. Absorption bands characteristic of HCO_3 occur at about 10, 12, and 14 microns (Miller & Wilkins, 1952), and from an examination of nahcolite, $NaHCO_3$, and trona, $NaH(CO_3)_2{:}2H_2O$, Huang & Kerr (1960) found that additional bands caused by HCO_3 groups may occur near 5 and 7 microns. A further complication is that absorption bands appear in the 11 to 14 micron region even in hydrous carbonate minerals without HCO_3 (Adler & Kerr, 1963). These factors make the interpretation of the complex spectrum of weloganite rather difficult. The strong absorption band at 2.96μ is typical of OH absorption bands in basic carbonates and may be assigned to O–H stretching vibrations. The medium and strong absorption bands at 9.4–9.5μ and at 11.5–11.8μ are assigned to carbonate stretching and banding modes (v_1 and v_2 respectively). The strong absorbances in the 6–7.4μ region can also be partly attributed to CO_3 stretching vibrations (v_3). However, there are six resolved absorption bands between 5.95 and 7.4μ; some of these may be due to water or to hydrogen-bonded CO_3 groups. There is thus some support for the interpretation that weloganite is a hydrogen carbonate, but this is indirect at best in view of the absence of additional bands specifically attributable to HCO_3 groups. The common doubling of the CO_3 spectral bands suggests that there are two non-equivalent carbonate molecules in the structure; this is in harmony with the chemical evidence that carbonate is bound to both strontium and zirconium.

In their ideal proportions, the constituents of weloganite can be combined and rewritten in several ways, as for example, $5SrCO_3{\cdot}2Zr(CO_3)_2{\cdot}4H_2O$, or $5SrCO_3{\cdot}Zr_2O_3(OH)_2{\cdot}3H_2O$. The latter has some appeal because the compound $Zr_2O_3(OH)_2{\cdot}CO_2{\cdot}7H_2O$ is the commercial
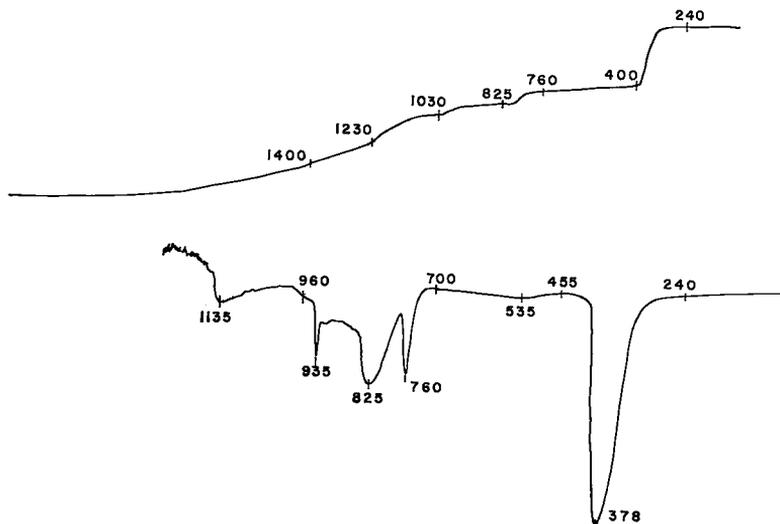
FIG. 4 Thermogravimetric (top) and differential thermal curves of weloganite. Temperatures are in °C

product known as carbonated hydrous zirconia. The formula Sr_5Zr_2-$(CO_3)_9 \cdot 4H_2O$ is perhaps most appropriate for weloganite because it is non-commital regarding the possible structural units.

THERMAL DECOMPOSITION

Differential thermal and thermogravimetric curves for weloganite are shown in Fig. 4. The heating rate for the D.T. curve was 12°C per minute, and for the T.G. curve, 385 ± 5°C per hour. Because of the unusual chemistry of weloganite, considerable effort was expended to establish the nature of the products and processes involved in the thermal decomposition of the mineral. The weight losses which accompany the breakdown are given in Table 3. It is apparent from Fig. 4 that the thermal decomposition of weloganite is a complex process. Partial chemical analyses of samples heated to various temperatures show that both CO_2 and H_2O are released in the first decomposition stage represented by the large endothermal break with its mid-point at 378°C. Only $SrCO_3$ was detected on powder patterns of the product, and no insoluble residue was found after treatment with dilute HCl. Zirconium may therefore be present as a soluble amorphous compound of uncertain composition.

The loss of an additional 2.3% of CO_2 is signalled by the shallow endothermal break with its mid-point at 535°C. The acid-insoluble portion of

TABLE 3. WEIGHT LOSSES RECORDED FOR THE THERMAL DECOMPOSITION
OF TWO SAMPLES OF WELOGANITE

	Temp. (C°)	Wt. loss, %	Cumulative %
1.	to 240	0.0	
	240–400	16.5	16.5
	400–700	3.3	19.8
	700–825	4.2	24.0
	825–1030	3.9	27.9
	1030–1230	8.4	36.3
	1230–1400	16.3	52.6
2.	to 455	17.05	17.05
	455–650	2.26	19.31
	650–740	0.70	20.01
	740–780*	1.34	21.35
	780–880	3.99	25.34

*Total weight loss on another fraction heated from room temperature
to 760°C was 20.1%.

the charge at 650°C is a crystalline zirconium compound whose x-ray diffraction pattern is not noticeably different from that of heated betafite. The strongest lines of the pattern in order of decreasing intensity are 2.99, 1.83, 1.56 and 2.59 Å. Both strontium and zirconium were detected in the residue by x-ray spectroscopy, with the former roughly estimated as being only about one tenth the amount of zirconium present. The compound may thus be a hydrous zirconium oxide of the betafite type which could be written as $Sr_{1-x}Zr_2(O,OH)_6(OH)$ in order to illustrate the type of compound being dealt with. Crystallinity of the material appears to improve with heating; at 650°C only diffuse x-ray powder patterns are obtained, but at 740°C the diffraction lines are relatively sharp.

The third endothermal break at 760°C marks the first appearance of strontium zirconate, $SrZrO_3$, and the disappearance of the Zr-betafite discussed above. The appearance of several endothermal breaks beyond this temperature may be an indication of high-temperature phase transitions in $SrZrO_3$ (Carlsson, 1967) but is also partly due to reactions in which additional $SrZrO_3$ is formed at the expense of $SrCO_3$. Although both compounds persist to at least 1135°C, the relatively large weight losses suggest that $SrCO_3$ decomposition is already in progress at this temperature.

The postulated reactions involved in the thermal decomposition of weloganite are summarized in Table 4. It should be noted that the crystalline phases do not necessarily account for the complete composition of the charges. Of particular interest, however, is the persistence of small amounts of water and large amounts of CO_2 to relatively high temperatures. All of the water and part of the CO_2 are almost certainly bound to

TABLE 4. THE THERMAL DECOMPOSITION OF WELOGANITE. Extraction temperature is the temperature to which weloganite was heated, stabilized (as evident on T.G. recorder), and then air quenched.

Extraction Temp. (°C)	Postulated composition of product at temp. cited	Losses	Wt. % CO_2 and H_2O in charge				Wt. % lost		Crystalline phases detected
			theoretical		analytical				
			CO_2	H_2O	CO_2	H_2O	meas	calc	
—	$5SrO \cdot 2ZrO_2 \cdot 9CO_2 \cdot 4H_2O$				32.2	6.6	—	—	weloganite
455	$5SrO \cdot 2ZrO_2 \cdot 6CO_2 \cdot \frac{1}{2}H_2O$	$3CO_2 \cdot 3\frac{1}{2}H_2O$	25.5	0.88	27.3	1.2	17.05	15.8	$SrCO_3$
650	$5SrO \cdot 2ZrO_2 \cdot 5\frac{1}{2}CO_2 \cdot \frac{1}{2}H_2O$	$\frac{1}{2}CO_2$	23.8	0.89	24.7		2.3	2.1	$SrCO_3 +$ "Zr betafite"
740	—				24.9	1.2	0.7		$SrCO_3 +$ "Zr betafite"
780	$5SrO \cdot 2ZrO_2 \cdot 5\frac{1}{2}CO_2$	$\frac{1}{2}H_2O$	24.1	0.0	23.8		1.3	0.9	$SrCO_3 + SrZrO_3$
860	$5SrO \cdot 2ZrO_2 \cdot 4\frac{1}{2}CO_2$	CO_2	20.6	0.0	20.3		4.0	4.4	$SrCO_3 + SrZrO_3$

zirconium, but their proportions are such that simple formulae are not readily apparent and the complex ones are not very convincing at this stage of our knowledge of zirconium chemistry. Although little is known about the chemistry of zirconium carbonate, the results obtained here for the most part conform with the empirical indications of Blumenthal (1958, p. 195) who states that "carbon dioxide is bound to zirconium atoms only if a hydroxyl or aquo group is also present."

ASSOCIATED MINERALS

Weloganite is most commonly associated with small colourless, euhedral crystals of calcite, quartz and dawsonite. Also a common associate is a white hydrous barium aluminium carbonate which generally occurs as botryoidal "warts" in cavities in the sill. This new carbonate and other as yet unidentified minerals will be described at a later date. Among the additional species so far identified with weloganite are plagioclase, siderite, dolomite, strontianite, barite, celestite, both black and colourless fluorite, cryolite, zircon, anatase, and a new barium analogue of dundasite. Marcasite, pyrite, galena, and sphalerite are also present. The sills at the nearby Miron limestone quarry contain vesuvianite, natrolite, analcite, calcite, dolomite, kaolinite, acmite, gypsum, fluorite, ilmenite, anatase, and burbankite, but no weloganite. An unidentified fine-grained white mineral which gives an x-ray pattern somewhat similar to that of gibbsite is relatively common at the Francon quarry and has also been detected in one specimen from the Miron quarry.

ACKNOWLEDGEMENTS

L. Moyd of the National Museum of Canada, and H. R. Steacy of the Geological Survey.

REFERENCES

ADLER, H. H., & KERR, P. F. (1963): Infrared spectra, symmetry and structure relations of some carbonate minerals, *Am. Mineral.*, **48**, 839–853.

ADLER, I. (1966): *X-ray emission spectroscopy in geology*, Elsevier, New York, 258 pp.

BLUMENTHAL, W. B. (1958): *The chemical behaviour of zirconium*, Van Nostrand Co., Toronto, 398 pp.

CARLSSON, L. (1967): High-temperature phase transitions in $SrZrO_3$, *Acta Cryst.*, **23**, 901–904.

HUANG, C. K., & KERR, P. F. (1960): Infrared study of the carbonate minerals, *Am. Mineral.*, **45**, 311–324.

MILLER, F. A., & WILKINS, C. H. (1952): Infrared spectra and characteristic frequencies of inorganic ions, *Anal. Chem.*, **24**, 1253–1294.