

## Murataite, a New Complex Oxide from El Paso County, Colorado<sup>1</sup>

JOHN W. ADAMS, THEODORE BOTINELLY, W. N. SHARP, AND KEITH ROBINSON

U.S. Geological Survey, Denver, Colorado 80225

### Abstract

Murataite, a new complex oxide with the general formula  $(\text{Na}, \text{Y}, \text{Er})_4(\text{Zn}, \text{Fe})_3(\text{Ti}, \text{Nb})_6\text{O}_{18}(\text{F}, \text{OH})_4$ , occurs in a pegmatite in the St. Peters Dome area, Colorado. The mineral is cubic, space group  $F432$ ,  $Fm3m$ , or  $Fm3$ ;  $a = 14.863(5)$  Å;  $Z = 8$ . Strongest lines of the X-ray pattern are: 8.51(3), 2.858(10), 2.468(6), 1.746(8), 1.489(8), and 1.432(5).

Megascopically the mineral is black and submetallic; in polished section it is gray in white light, darker in oil. The reflectance is  $13.6 \pm 0.14$  percent (air) at 546 nm wavelength. Murataite is translucent and brown in thin section, and is isotropic to very weakly anisotropic;  $n$  (est) = 2.13. Microhardness  $\text{HV}_{100} = 827$ . Density (meas) = 4.69 g/cm<sup>3</sup>; (calc) = 4.64 g/cm<sup>3</sup>.

Murataite is a very rare accessory in a pegmatite of complex mineralogy that is probably derived from the alkalic Mount Rosa Granite.

### Introduction

Fragments of a black, submetallic mineral found in debris from a small pegmatite in the St. Peters Dome area gave an X-ray powder diffraction pattern that could not be matched with that of any known mineral. Preliminary examination showed that the mineral contained an unusual assemblage of elements including zinc, niobium, and yttrium, which further supported the possibility that it was a new species.

Subsequent work showed the mineral to be a new complex oxide with the ideal formula  $(\text{Na}, \text{Y}, \text{Er})_4(\text{Zn}, \text{Fe})_3(\text{Ti}, \text{Nb})_6\text{O}_{18}(\text{F}, \text{OH})_4$ . The mineral is named murataite in honor of K. J. Murata, geochemist of the U.S. Geological Survey, in recognition of his pioneer work in the spectrochemical analysis and geochemistry of rare-earth elements in minerals. The mineral and name were approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

### Occurrence

The St. Peters Dome area where the murataite occurs is well known as a source of many rare minerals found in pegmatites related to the Pikes Peak Granite and the younger riebeckite-bearing Mount Rosa Granite (Gross and Heinrich, 1965, 1966).

The pegmatite that contains the murataite had been explored by a shallow pit now almost entirely filled with debris; consequently, the deposit is no longer exposed, and all the murataite and other minerals from the pegmatite were found in the debris in and near the pit. From the dump material it seems that the pegmatite consists mainly of quartz and microcline together with many accessory minerals including albite, riebeckite, astrophyllite, zircon, aegirine, rutile, thorite, pyrochlore, xenotime, genhelvite, murataite, and another unnamed complex oxide resembling murataite but of somewhat different composition and completely different X-ray powder pattern (mineral "Y"). The murataite is very sparse, but it is most commonly found as anhedral grains or poorly developed crystals that lie at the contact between astrophyllite and quartz (Fig. 1).

### Physical and Optical Properties

Murataite is black with submetallic luster. No cleavage was noted, but there is a conspicuous conchoidal fracture. In thin section the mineral is translucent, brown, and may show very weak anisotropism. The index of refraction is greater than 2.0 and is estimated from polished section to be near 2.13.

In polished section murataite is gray with low reflectance; in oil it is much darker. Reflection pleochroism is slight in air, but distinct in oil. Anisotropy is very weak in air; it is weak in oil and obscured by internal reflection. In air the internal reflection is

<sup>1</sup> Publication authorized by the Director, U.S. Geological Survey.

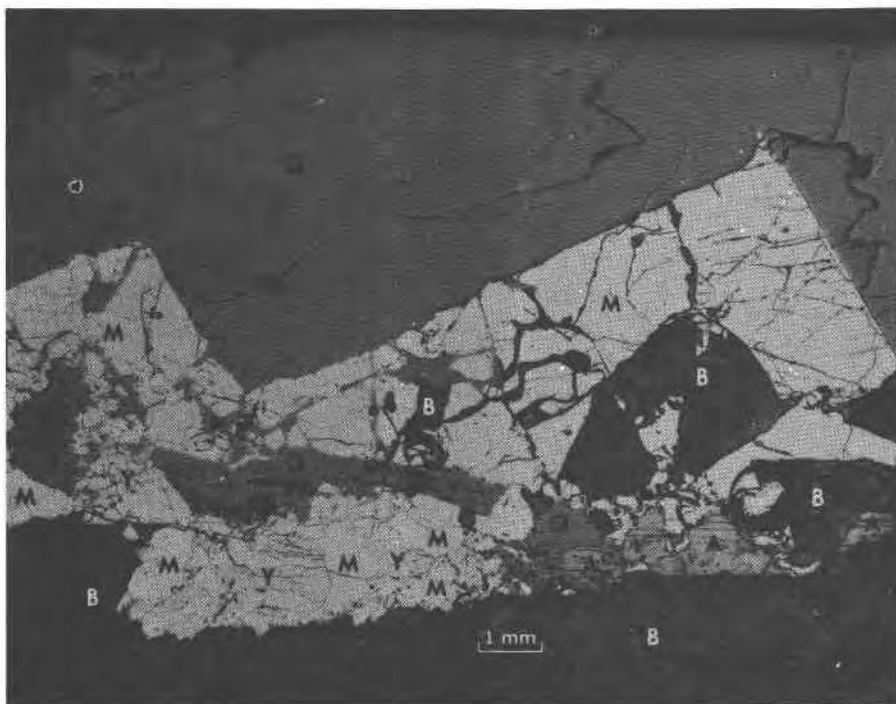


FIG. 1. Murataite (M) in polished section showing cubic form against quartz (Q). Other minerals are astrophyllite (A) and mineral Y (Y). Dark areas are mounting media (B). Reflected light.

faint orange; in oil it is conspicuous and pale orange to white. Reflectance at various wavelengths was measured by B. F. Leonard. Reflectance in oil at 589 nm was obtained by the coverglass method of Cambron in accordance with the precautions noted by Piller (1966). The reflectance values are given in Table 1.

The mean index of refraction,  $n$ , and the absorption coefficient,  $k$ , were calculated from  $R_{oil}$  and  $R_{air}$  by means of equations (2) and (3) of Gehlen and Piller (1964). At 589 nm,  $n = 2.13$  and  $k = 0$ . These calculated values are consistent with observations made in transmitted light that  $n$  is  $>2.0$  and that crushed fragments are translucent on thin edges.

Quantitative color data for murataite in air are: the brightness value  $Y$  is 13.3; the trichromatic coefficients are  $x = 0.303$  and  $y = 0.313$ ; the dominant wavelength  $\lambda_r = 486$  nm, and the excitation purity  $p_e = 0.028$ . The color data were calculated from the mean reflectances reported in Table 1 and referred to I.C.I. standard illuminant C (daylight). The data specify a nearly neutral surface of low brightness.

Murataite has a mean microindentation hardness

of  $HV_{100} = 827$  and a range of 782–870 as determined on 15 indentations made at 100-gram load. Indentations are straight-sided to slightly concave and slightly fractured. Microhardness determinations were made by B. F. Leonard with a Leitz Durimet hardness tester fitted with a Vickers diamond pyramid and green filter. Descent and indentation periods were 15 seconds each. The mean microhardness is equivalent to 6.0–6.5 on the Mohs hardness scale.

#### X-ray Data

Murataite is considered to be cubic, and the very weak anisotropism shown by some areas of the mineral is probably induced by strain. Cubic symmetry was determined using X-ray precession photographs by Mary E. Mrose of the U.S. Geological Survey. Consistent with this symmetry, the powder pattern data were successfully indexed (Table 2) and the unit cell refined by least-squares (Evans *et al.*, 1963) in the cubic system with  $Fm\bar{3}m$ ,  $F432$ , or  $Fm\bar{3}$  space group restrictions. This is in agreement with the initial  $F432$  space group assignment suggested by Mrose (written communication, 1971). The unit cell content was then calculated and a structural

TABLE 1. Reflectance Measurements\*

Wavelength, nm	R, %			
	470	546	589	630
	<u>Air</u>			
R <sub>O</sub>	--	13.7	13.1	12.7
R <sub>E</sub> <sup>†</sup>	--	13.3	12.7	12.3
R <sub>O-R<sub>E</sub></sub>	0.2	0.4	0.4	0.4
$\frac{2R_O + R_E}{3}$	--	13.6	13.0	12.6
$\bar{R}$	13.8 (1)	13.6 (1)	13.0 (2)	12.6 (1)
	<u>Oil</u>			
$\bar{R}$	--	--	2.8 (3)	--

*Reflectance measured with a Reichert photoelectric microphotometer. Mount press-leveled on plasticine. U.S. set of reflectance standards calibrated by National Physical Laboratory, Teddington, England; for α-silicon carbide (carborundum), R = 20.5, 20.1, 19.9, and 19.8% at 470, 546, 589, and 630 nm; for neutral glass, R = 4.42% at 589 nm. R<sub>air</sub> of mineral measured against carborundum only; R<sub>oil</sub> by Cambo method measured in air against both standards. ( ) values are standard deviation of eight sets of measurements of R<sub>air</sub>, two measurements of R<sub>oil</sub>.*

formula derived in conformity with the restrictions imposed by the inferred space groups.

The unit cell edge, as derived by the least-squares refinement of powder diffraction data, is 14.863 (5) Å. Cell volume is 3,283 (2) Å<sup>3</sup>, Z = 8.

The calculated density is 4.64 g/cm<sup>3</sup>. The measured density is 4.69 g/cm<sup>3</sup> obtained by the pycnometer method on 350 mg of the mineral.

### Analysis

Murataite was analyzed principally by X-ray fluorescence using hand-picked samples of the mineral which showed no impurities by X-ray diffraction. Accidental loss of the major part of our original sample that had been sent to Washington, D. C., for analysis delayed work on the mineral until more could be collected and isolated. All reported analyses were made in the Denver laboratories of the U.S. Geological Survey, with the exception of the total-water determination which was made in the Survey's Menlo Park, California, laboratory. The quantity of material available for analytical work was generally minimal.

The results of the analyses are given in Table 3, together with our interpretation of cell content. Several elements, such as Pb, Sn, Mn, and Ca, are not considered essential constituents and have been omitted from the proposed ideal formula of (Na,Y,Er)<sub>4</sub>(Zn,Fe)<sub>3</sub>(Ti,Nb)<sub>8</sub>O<sub>16</sub>(F,OH)<sub>4</sub>.

### Rare-Earth Distribution

Murataite contains a dominantly heavy rare-earth assemblage, with erbium the most abundant lan-

thanide. Cerium subgroup elements and terbium were below the limit of detection by emission spectroscopy and do not appear in the analysis. The distribution of the other lanthanides in atomic percent as calculated from the X-ray fluorescence analysis is: Gd 16.2, Dy 19.9, Ho 5.1, Er 27.4, Tm 3.1, Yb 25.5, and Lu 2.9.

### Mineral Y

In collecting murataite for study we noted that some black submetallic grains associated with astrophyllite and quartz were not murataite but another complex oxide mineral near murataite in composition. This mineral, differing significantly in physical and optical properties from murataite, may be an undescribed species and is presently under further study. We will refer to it as mineral Y. It is virtually opaque and is markedly anisotropic in polished section. The strongest lines in its X-ray powder diffraction pattern are: 3.40 (s), 2.93 (s), 2.87 (m), 2.27 (m), 2.16 (m), 1.82 (m), 1.62 (m), and 1.45 (s).

TABLE 2. X-Ray Powder Data for Murataite, El Paso County, Colorado

<u>h k l</u>	<u>d</u> <sub>obs.</sub>	<u>d</u> <sub>calc.</sub> <sup>*</sup>	<u>I</u>
111	8.51	8.56	3
200	7.38	7.42	1
220	5.25	5.24	1/2
311	4.46	4.47	1/2
222	4.29	4.28	1/2
400	3.708	3.708	1/2
331	3.414	3.403	1
420	3.314	3.317	1/2
422	3.028	3.028	1
511, 333	2.858	2.855	10
400	2.622	2.622	1/2
600, 442	2.468	2.472	6
533	2.265	2.262	1
444	2.141	2.141	2
711, 551	2.080	2.077	2
640	2.058	2.057	1
642	1.981	1.982	1/2
731, 553	1.933	1.931	1/2
733	1.811	1.812	1/2
660, 822	1.746	1.748	8
555, 751	1.713	1.713	1/2
842	1.620	1.618	1/2
931	1.557	1.555	1/2
844	1.516	1.514	1/2
755, 771, 933	1.489	1.491	8
773, 951	1.432	1.434	5
10.42	1.357	1.354	1
971, 11.31	1.294	1.296	1/2
973, 11.33	1.261	1.258	1/2
12.00, 884	1.238	1.236	1
11.51, 777	1.225	1.223	1/2
993, 11.71, 13.11	1.138	1.134	5
977, 11.73, 13.31	1.108	1.109	1/2
12.62	1.091	1.094	1/2

*Nickel-filtered CuKα radiation, λ = 1.5418 Å.*

*Intensities were visually estimated.*

*\*Calculated for cubic cell for which a = 14.836.*

TABLE 3. Analysis of Murataite<sup>a</sup>

	Weight percent		Formula units		Ideal formula units
Na <sub>2</sub> O	5.80	Na	17.23		
Y <sub>2</sub> O <sub>3</sub>	12.06	Y	9.85	} 15.97	} 32
Gd <sub>2</sub> O <sub>3</sub>	0.17	Gd	0.09		
Dy <sub>2</sub> O <sub>3</sub>	2.18	Dy	1.07		
Ho <sub>2</sub> O <sub>3</sub>	0.57	Ho	0.28		
Er <sub>2</sub> O <sub>3</sub>	3.09	Er	1.49		
Tm <sub>2</sub> O <sub>3</sub>	0.34	Tm	0.17		
Yb <sub>2</sub> O <sub>3</sub>	2.96	Yb	1.39		
Lu <sub>2</sub> O <sub>3</sub>	0.34	Lu	0.16		
CaO	0.90	Ca	1.47		
BaO	0.008 <sup>(b)</sup>				
PbO	0.11	Pb	0.04	} 23.84	} 24
SnO	0.17	Sn	0.12		
MnO	0.61	Mn	0.78		
ZnO	12.45	Zn	14.10		
FeO	4.37 <sup>(c)</sup>	Fe	5.60		
SiO <sub>2</sub>	0.64 <sup>(d)</sup>	Ti	3.20		
TiO <sub>2</sub>	37.87	Ti	41.06	} 48	} 48
Nb <sub>2</sub> O <sub>5</sub>	10.01	Nb	6.94		
F	6.55	O	143.3		144
H <sub>2</sub> O	0.55	F	31.79		32
	101.75				
Less for F	2.76				
	98.99				

Ideal formula (Na,Y,Er)<sub>4</sub>(Zn,Fe)<sub>3</sub>(Ti, Nb)<sub>6</sub>O<sub>18</sub>(F,OH)<sub>4</sub> Z = 8

(a) Rare earths, Zn, Ti, Nb, and Ca by fusion-X-ray fluorescence by J. S. Wahlberg; Na by flame-photometry by Wayne Mountjoy; F by volumetric method by W. D. Goss; Mn by electron microprobe by G. A. Desborough; Ba, Pb, and Si by semiquantitative spectrographic analysis by Harriet Netman; H<sub>2</sub>O by microcoulometric method by M. Cremer (Cremer et al., 1972).

(b) Rejected.

(c) All iron considered as FeO.

(d) Probable contamination; included as TiO<sub>2</sub>.

Extensive replacement of murataite by mineral Y is shown in thin sections, and it is possible that all mineral Y represents replaced murataite.

Because mineral Y has a greater magnetic susceptibility than murataite, the two minerals can be separated using a Frantz separator. With our equipment, a separation was made at 0.45 amperes, with a 15-degree side tilt and a 5-degree forward tilt.

### Origin of the Murataite

The pegmatites of the St. Peters Dome area have been considered by Gross and Heinrich (1966) to be of two types, one related to the Pikes Peak Granite and the other to the younger alkalic Mount Rosa Granite. These authors distinguish the two types chiefly on the basis of elemental and mineralogical differences. Although many mineral species are common to both types, a few—notably the sodic minerals aegirine, riebeckite, and astrophyllite—are characteristic of alkalic pegmatites or of rocks that have been subjected to alkalic metasomatism. These

three minerals are relatively abundant in the pegmatite where murataite occurs; therefore, we conclude that the deposit is related wholly or in part to the Mount Rosa event.

The pegmatite where murataite occurs seems very small. Indeed, most of it may be represented by the material now scattered around the prospect pit. From this debris the deposit apparently consisted mainly of quartz and microcline with minor platy albite and numerous accessory minerals of which zircon, riebeckite, and astrophyllite are the most common. Both riebeckite and astrophyllite show varying degrees of alteration and replacement. Some riebeckite has been replaced by aegirine; astrophyllite seems to be particularly unstable and alters readily to a greenish chloritic aggregate, or in some samples is completely replaced by a fine-grained mixture of quartz and anatase.

No attempt was made to study the total paragenetic sequence of this complex assemblage except for observing the relationship of murataite to the minerals with which it is directly associated. Even this was difficult because of the very few samples containing murataite that were suitable for thin- or polished-section preparation.

In almost all recovered specimens of murataite, the mineral is embedded partly in astrophyllite and partly in quartz. Any crystal faces shown by the murataite are in contact with quartz (Fig. 1). This relationship suggests that the murataite developed on free-growing astrophyllite crystals that were later enclosed by quartz. Some sections show that murataite has been locally fractured and replaced. Fractures are filled with mineral Y or with quartz and on an unusual botryoidal form of pyrochlore which rims the quartz veinlets and which seems to replace murataite. In one thin section, an area of murataite, dissected and partly replaced by mineral Y, is enclosed in xenotime (Fig. 2).

Murataite is probably an early mineral in the pegmatite, having formed contemporaneously with astrophyllite and riebeckite and just prior to quartz. Where astrophyllite was destroyed by later stage fluids, the murataite it enclosed was susceptible to attack and replacement. Replacement of murataite by mineral Y may have been extensive.

The high ZnO content (12.45 wt percent) of murataite is of interest inasmuch as zinc minerals are uncommon in pegmatites. In the St. Peters Dome area, however, sphalerite was reported by Gross and Heinrich (1966) as one of the minerals found in



FIG. 2. Dissected murataite (M) crystal enclosed in xenotime (X). Black areas (Y) are mineral Y. Assemblage cut by narrow veinlet of quartz and pyrochlore (P). Transmitted light.

the Mount Rosa-type pegmatites. Genthelvitte, another zinc mineral, has been found in several pegmatites in the area, including the one in which murataite occurs.

In addition, appreciable zinc was found in both riebeckite (1.5 percent) and astrophyllite (2.0 percent) from the murataite-bearing pegmatite. The zinc determinations on these minerals were made by the semiquantitative six-step spectrographic method by Harriet Neiman, U.S. Geological Survey.

The occurrence of the two zinc-bearing species, murataite and genthelvitte, and the presence of zinc in the structures of other silicates may reflect a sulfur deficiency that inhibited the formation of sphalerite, which is the most commonly found zinc mineral in pegmatites.

The occurrence of murataite is somewhat analogous to that of landauite (Portnov *et al.*, 1966), a titanate of zinc, iron, and manganese, reported from an alkalic pegmatite in the U.S.S.R.

#### Acknowledgments

The authors are indebted to Mary E. Mrose of the U.S. Geological Survey for the X-ray, single-crystal measurements; to Akira Kato of the National Science Museum, Tokyo, for helpful suggestions; and to B. F. Leonard of the U.S.

Geological Survey for much of the polished section information.

#### References

- CREMER, M., H. N. ELSHEIMER, AND E. E. ESCHER (1972) Microcoulometric measurement of water in minerals. *Anal. Chim. Acta*, **60**, 183–192.
- EVANS, H. T., JR., D. E. APPLEMAN, AND D. S. HANDWERKER (1963) The least squares refinement of crystal unit cells with powder diffraction data by an automatic computer indexing method (abstr.). *Amer. Crystallogr. Assoc., Annu. Meeting., Cambridge, Mass., Prog. Abstr.*, p. 42.
- GEHLEN, KURT V., AND HORST PILLER (1964) Zur Optik von Covellin. *Beitr. Mineral. Petrogr.* **10**, 94–110.
- GROSS, E. B., AND E. W. HEINRICH (1965) Petrology and mineralogy of the Mount Rosa area, El Paso and Teller Counties, Colorado. I. The granites. *Amer. Mineral.* **50**, 1273–1295.
- , AND ——— (1966) Petrology and mineralogy of the Mount Rosa area, El Paso and Teller Counties, Colorado. II. Pegmatites. *Amer. Mineral.* **51**, 299–323.
- PILLER, HORST (1966) Colour measurements in ore-microscopy. *Mineral. Deposita*, **1**, 175–192.
- PORTNOV, A. M., L. YE. NICOLAYEVA, AND T. I. STOLYAROVA (1966) A new titanium mineral, landauite. *Dokl. Acad. Nauk. SSSR*, **166**, 1420–1421 [trans. *Dokl., Earth Sci. Sec.* **166**, 143–145 (1966)].

Manuscript received, July 11, 1973; accepted for publication, August 23, 1973.