

Zigrasite, $\text{MgZr}(\text{PO}_4)_2(\text{H}_2\text{O})_4$, a new phosphate mineral from the Dunton Quarry, Newry, Oxford County, Maine, USA

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ABSTRACT

Zigrasite, ideally $\text{MgZr}(\text{PO}_4)_2(\text{H}_2\text{O})_4$, is a new secondary phosphate mineral from the giant 1972 gem tourmaline-bearing pocket at the Dunton Quarry, Newry, Oxford County, Maine, USA. It occurs as subhedral blocky grains sometimes exceeding 1 mm in maximum dimension and perched on tourmaline. These grains are complex aggregates of three distinct phases, zigrasite and two unnamed phases: the Ca analogue of zigrasite, $\text{CaZr}(\text{PO}_4)_2(\text{H}_2\text{O})_4$, and $\text{Zr}(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_4$. Zigrasite is associated with tourmaline, microcline, quartz, albite, beryl, amblygonite-montebasite, childrenite-eosphorite and apatite, and crystallized as one of the latest minerals during pocket formation. It is off-white to pale yellow or light tan, translucent with a white streak and a vitreous lustre, and shows light blue to pale yellow cathodoluminescence. Mohs hardness is 3 and the measured and calculated densities are 2.76(4) and 2.66 g/cm³. The mineral has imperfect cleavage in two directions, parallel to (010) and (001), shows no parting, is brittle and has a hackly fracture. In transmitted light, it is colourless and non-pleochroic, biaxial negative with α 1.597(1), β 1.622 (1), γ 1.635 (1), with $2V_{(\text{meas})} = 65.5(4)^\circ$ and $2V_{(\text{calc.})} = 71^\circ$. Zigrasite is triclinic, $P\bar{1}$, a 5.3049(2) Å, b 9.3372(4) Å, c 9.6282(5) Å, α 97.348(1)°, β 91.534(1)°, γ 90.512(4)°, V 472.79(5) Å³, $Z = 2$. The seven strongest lines in the X-ray powder diffraction pattern are as follows: d (Å), I , (hkl): 9.550, 100, (001); 4.108, 70, ($\bar{1}11$); 4.411, 50, (0 $\bar{2}1$); 4.008, 50, (111); 4.589, 40, (110); 3.177, 40, (112); 3.569, 30, (0 $\bar{2}2$), 2.660, 30, (200), (1 $\bar{3}1$), (130); 3.273, 20, ($\bar{1}12$). Chemical analysis by electron microprobe gave P₂O₅ 37.59, ZrO₂ 32.27, HfO₂ 0.34, FeO 0.20, MgO 10.37, ZnO 0.17, F 0.13, LOI 18.60, less O \equiv F 0.05 = total 99.62 wt.%. The resulting empirical formula is $(\text{Mg}_{0.97}\text{Fe}_{0.01}^{2+}\text{Zn}_{0.01})_{\Sigma=0.99}(\text{Zr}_{0.99}\text{Hf}_{0.01})_{\Sigma=1.00}\text{P}_{2.00}\text{O}_8(\text{H}_2\text{O})_4$ on the basis of 12 O atoms with H₂O = 4 per formula unit from crystal-structure analysis, and the end-member formula is $\text{MgZr}(\text{PO}_4)_2(\text{H}_2\text{O})_4$.

KEYWORDS: zigrasite, new mineral, phosphate, electron microprobe data, optical properties, X-ray powder-diffraction data, Newry, Maine, USA.

Introduction

MAHLMOODITE, $\text{Fe}^{2+}\text{Zr}(\text{PO}_4)_2(\text{H}_2\text{O})_4$, from the Union Carbide V ore deposit at Wilson Springs, Garland County, Arkansas, USA, was described by Milton *et al.* (1993) as small creamy-white spheres perched on sodic-pyroxene crystals in vugs. The crystals are variously described as platy

or fibrous, and "...too small to be mounted on a spindle stage..." (Milton *et al.*, 1993). The authors note the similarity of the X-ray powder-diffraction pattern to the unindexed powder-diffraction patterns of synthetic analogues of the form $M\text{Zr}(\text{PO}_4)_2(\text{H}_2\text{O})_4$ ($M = \text{Co}, \text{Ni}, \text{Cu}, \text{Zn}$) synthesized by Alluli *et al.* (1976). Clearfield and Troup (1973), Troup and Clearfield (1977) and Clearfield *et al.* (1984) showed that a sheet of corner-sharing octahedra and tetrahedra of the form $[\text{Zr}(\text{PO}_4)_2]^{2-}$ is a common structural element in a series of zirconium phosphates.

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Milton *et al.* (1993) recognized that this structural element is also present in mahlmoodyte, and this provided enough information for them to index their powder pattern and the powder patterns of Alluli *et al.* (1976). They reported mahlmoodyte as monoclinic with cell dimensions $a = 9.12(2)$ Å, $b = 5.42(1)$ Å, $c = 19.17(2)$ Å, $\beta = 94.8(1)^\circ$, $Z = 4$. Elton and Hooper (1995) found mahlmoodyte at Kerriack Cove, near Redruth, Cornwall, England. A small vein of sphalerite, pyrite, green chlorite and quartz, with minor galena and chalcopyrite, has small vugs that contain rare cream-brown spheres of mahlmoodyte.

While examining crystals of secondary minerals from a gem tourmaline-bearing pocket at the Dunton Quarry, Newry, Oxford County, Maine, USA, unknown small blocky crystals were found that resisted identification 'by eye'. Electron microprobe work suggested that the unknown phase is the Mg analogue of mahlmoodyte, despite the completely different habit and paragenesis. The mineral is named zigrasite after James Zigras (born June 12, 1981) of Paramus, New Jersey, USA, a prominent collector who discovered this mineral. Both the mineral and the name have been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2008-046). The holotype specimen of

zigrasite has been deposited in the mineral collection of the Royal Ontario Museum, 100 Queen's Park, Toronto, Ontario K1P 6P4, Canada; catalogue number M53323.

Occurrence

Zigrasite was found perched on a crystal of tourmaline from the giant 1972 pocket at the Dunton Quarry, Newry, Oxford County, Maine, USA. The Dunton Quarry is located in a complex rare-element granitic pegmatite that has produced large quantities of gem tourmaline as well as many rare phosphate species (McCrillis, 1975; King, 1975, 2000; King and Foord, 1994; Marshall and Francis, 2008). The pocket zone of the pegmatite is composed primarily of albite (var. cleavelandite), quartz and muscovite along with minor tourmaline (typically elbaite), cassiterite and columbite-tantalite (Marshall and Francis, 2008). A number of secondary phosphates including beryllonite, hydroxylherderite, moraesite, childrenite-eosphorite and members of the apatite group occur within the interstices of coarse blades of albite (var. cleavelandite) in the core margin of the pegmatite. However, with the exception of montebrazite and childrenite-eosphorite, phosphates are largely absent in the tourmaline-bearing pockets.

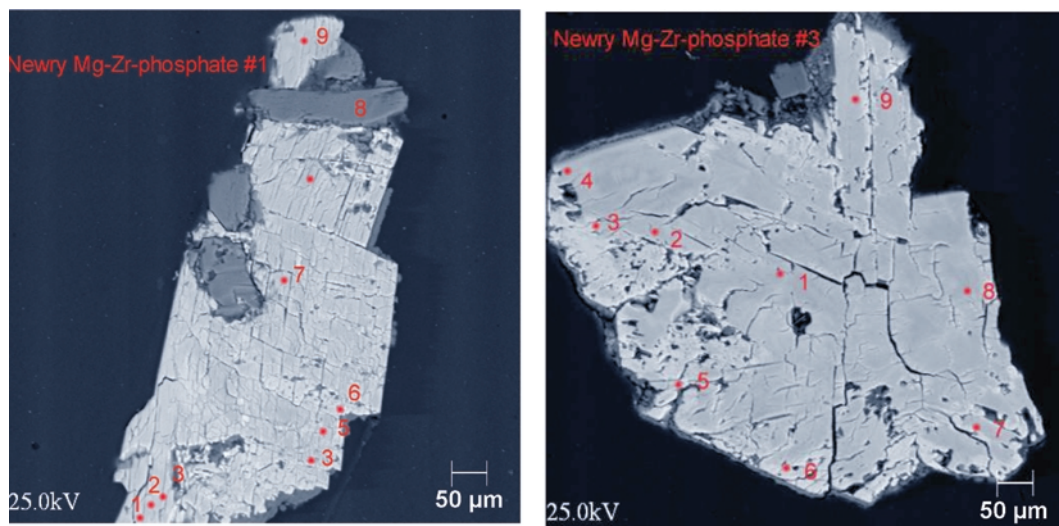


FIG. 1. BSE images of composite grains of zigrasite (pale grey), the Ca analogue of zigrasite (medium-grey) and unnamed $\text{Zr}(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_4$ (not visible here). The red circles indicate positions of compositional determinations by electron microprobe analysis.

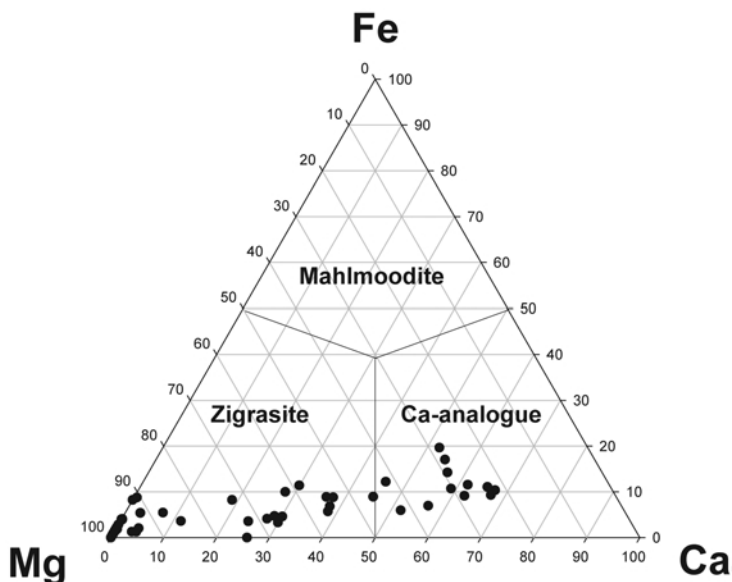


FIG. 2. Compositional variation in Zr phosphate grains from the giant 1972 pocket at Newry, Oxford County, Maine.

Zigrasite occurs as subhedral blocky grains sometimes exceeding 1 mm in maximum dimension in complex aggregates of three distinct phases, zigrasite and two unnamed phases, – the Ca-analogue of zigrasite, $\text{CaZr}(\text{PO}_4)_2(\text{H}_2\text{O})_4$ and $\text{Zr}(\text{PO}_3\text{OH})_2(\text{H}_2\text{O})_4$ (Fig. 1). The appearance of the grains in Fig. 1 and their compositional variation (Fig. 2) suggest that zigrasite and its Ca analogue are structurally coherent, and inspection of the structure in Fig. 3 indicates that Ca could replace Mg without major disruption of the connectivity. We were able to isolate fragments of zigrasite for structure work and the measurement of physical properties, but have been unable to do so for the other two phases. Zigrasite is associated with tourmaline, microcline, quartz, albite, beryl, amblygonite-montebasite, childrenite-eosphorite and apatite, and crystallized as one of the latest minerals during pocket formation.

There was late release of small amounts of Mg as seen in the outermost zones of tourmaline in the pegmatites of Oxford County, Maine, and Zr is abundant in this pegmatite as zircon. Zircon is very stable, and it is unlikely that the availability of Zr necessary for the crystallization of zigrasite resulted from corrosion of zircon. It seems likely that Zr was present as aqueous coordination complexes at the last stages of pegmatite formation, as was also probably the case in

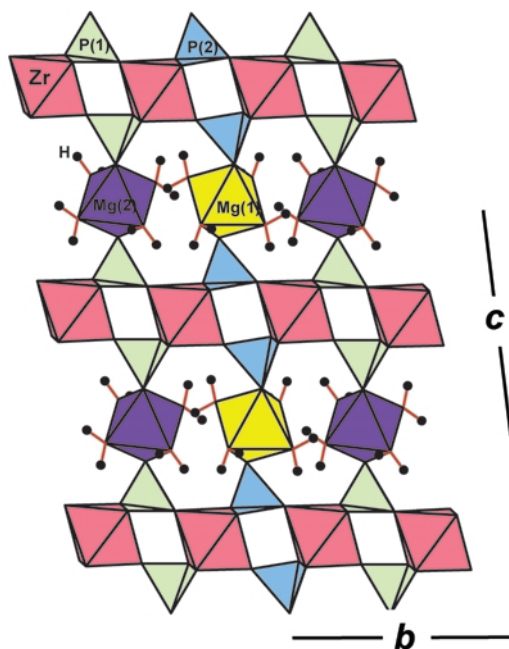


FIG. 3. The crystal structure of zigrasite projected onto (100). Symmetrically distinct (PO_4) tetrahedra are shown in green and light blue, symmetrically distinct $(\text{MgO}_2\{\text{H}_2\text{O}\}_4)$ octahedra are shown yellow and purple, (ZrO_6) octahedra are shown in red, H atoms are shown as small black spheres, and $\text{O}_{\text{donor}}\text{—H}$ bonds are shown as red lines.

Mount Mica where the pegmatite contains both zircon and the zirconium phosphate minerals kosnarite and mccrillisite (Brownfield *et al.*, 1993; Foord *et al.*, 1994).

Physical properties

Zigrasite is off-white to pale yellow or light tan, translucent with a white streak and a vitreous lustre, and shows light blue to pale yellow cathodoluminescence. Mohs hardness is 3 and the measured (Berman balance) and calculated densities are 2.76(4) and 2.66 g/cm³. Zigrasite has imperfect cleavage in two directions, parallel to (010) and (001), shows no parting, is brittle and has a hackly fracture. A spindle stage was used to orient a crystal for measurement of refractive indices and 2V by extinction curves (Bartelmehs *et al.*, 1992). The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by X-ray diffraction. In transmitted light, zigrasite is colourless and non-pleochroic, biaxial negative with indices of refraction α 1.597(1), β 1.622(1), γ 1.635(1) (measured with gel-filtered Na light, $\lambda = 589.9$ nm), with $2V_{(\text{meas.})} = 65.5(4)^\circ$ and $2V_{(\text{calc.})} = 71^\circ$. The orientations of the principal optical axes relative to the crystallographic axes are given in Table 1.

Chemical composition

Crystals were analysed with a Cameca SX100 electron microprobe operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a probe current of 10 nA, and a final beam diameter of 3 μm . The following standards and X-ray lines were used for analysis: synthetic kosnarite (P-K α ; Zr-L α), synthetic hafnon (Hf-L α), clinopyroxene (Mg-K α ; Fe-K α), fluoro-

riebeckite (F-K α) and synthetic Na-Zn-phosphate (Zn-K α), with peak count times of 20 s and background count times of 10 s. The average of six analyses is given in Table 2. Determination of the crystal structure of zigrasite (in prep.) shows it to contain $4 \times (\text{H}_2\text{O})$ groups per formula unit (p.f.u.), and the value given in Table 2 for LOI (loss on ignition) is close to that required for $4 \times (\text{H}_2\text{O})$ groups p.f.u. (19.08 wt.% H₂O). The empirical formula for zigrasite, calculated on the basis of 12 anions with $4 \times (\text{H}_2\text{O})$ groups p.f.u. is $(\text{Mg}_{0.97}\text{Fe}_{0.01}\text{Zn}_{0.01})_{\Sigma=0.99}(\text{Zr}_{0.99}\text{Hf}_{0.01})_{\Sigma=1.00}\text{P}_{2.00}\text{O}_8(\text{H}_2\text{O})_4$ and the end-member formula is $\text{MgZr}(\text{PO}_4)_2(\text{H}_2\text{O})_4$.

X-ray powder diffraction

The powder-diffraction pattern (Table 3) was recorded with Cu-K α X-radiation on a Debye-Scherrer camera with a diameter of 114.6 mm and a Gandolfi attachment. Refinement of the unit-cell parameters gave the following values: $a = 5.321(7)$ Å, $b = 9.360(10)$ Å, $c = 9.660(8)$ Å, $\alpha = 97.38(10)^\circ$, $\beta = 91.29(9)^\circ$, $\gamma = 90.58(9)^\circ$, $V = 477.0(5)$ Å³. Unit-cell dimensions were also determined on a Bruker single-crystal diffractometer using graphite-monochromated Mo-K α X-radiation and the resulting values ($a = 5.3049(2)$ Å, $b = 9.3372(4)$ Å, $c = 9.6282(5)$ Å, $\alpha = 97.348(1)^\circ$, $\beta = 91.534(1)^\circ$, $\gamma = 90.512(4)^\circ$) are in close agreement with those determined by powder diffraction.

Crystal structure

The crystal structure of zigrasite was determined by direct methods (to be published) and refined to an R_1 value of = 3.5%. The structure has one Zr

TABLE 1. The orientation of the optic axes, X, Y and Z, relative to the crystallographic axes a , b and c in zigrasite

	a	b	c
X	78.2°	94.0°	164.8°
Y	98.2°	9.6°	102.7°
Z	14.4°	81.3°	81.8°

TABLE 2. Chemical composition (wt.%) of zigrasite.

P ₂ O ₅	37.59
ZrO ₂	32.27
HfO ₂	0.34
FeO	0.20
MgO	10.37
ZnO	0.17
F	0.13
LOI (meas.)	18.60
Sub total	99.67
Less O \equiv F ₂	0.05
Total	99.62

TABLE 3. X-ray powder-diffraction data for zigrasite.

$I_{\text{obs.}}$	$d_{\text{meas.}}$ (Å)	$d_{\text{calc.}}$ (Å)	h	k	l
100	9.550	9.577	0	0	1
10	7.489	4.789	0	0	2
40	4.589	4.589	1	1	0
50	4.411	4.405	0	$\bar{2}$	1
70	4.108	4.107	$\bar{1}$	1	1
50	4.008	4.009	1	1	1
30	3.569	3.570	0	$\bar{2}$	2
20	3.273	3.263	$\bar{1}$	1	2
40	3.177	3.182	1	1	2
10	2.805	2.804	0	$\bar{2}$	3
10	2.688	2.690	$\bar{1}$	3	0
"	"	2.685	1	$\bar{1}$	3
30b	2.660	2.660	2	0	0
"	"	2.659	1	$\bar{3}$	1
"	"	2.659	1	3	0
10b	2.198	2.202	0	$\bar{4}$	2
"	"	2.200	$\bar{1}$	$\bar{1}$	4
10	2.052	2.054	$\bar{2}$	2	2
10b	2.006	2.005	2	2	2
"	"	2.001	0	4	3

$I_{\text{obs.}}$ values were estimated visually, an internal standard was not used.

site, coordinated by six O atoms, two P sites, each coordinated by four O atoms and two Mg sites, each coordinated by two O atoms and four (H₂O) groups. The (ZrO₆) octahedron shares corners with six (PO₄) tetrahedra, forming a [Zr(PO₄)₂] sheet parallel to (001). These sheets are stacked in the *c* direction and linked by [MgO₂(H₂O)₄] octahedra that share O atoms with the (PO₄) groups (Fig. 3). The structure is formally a heteropolyhedral framework structure, but the linkage is weaker in the *c* direction, accounting for the marked (001) cleavage.

Relation to other species

Zigrasite, MgZr(PO₄)₂(H₂O)₄, is isochemical with mahlmoodyite, Fe²⁺Zr(PO₄)₂(H₂O)₄. However, mahlmoodyite (Milton *et al.*, 1993; Elton and Hooper, 1995) is reported as monoclinic with a doubled unit cell (although the structure is unknown). Particular attention was paid to this issue in the experimental work on the crystal structure, but there was no trace of reflections indicating a doubled unit cell in the diffraction pattern of zigrasite.

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