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Kegginite, $Pb_3Ca_3[AsV_{12}O_{40}(VO)]{\cdot}20H_2O$, a new mineral with a novel ε-isomer of the Keggin anion

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ABSTRACT

Kegginite, $Pb_3Ca_3[AsV_{12}O_{40}(VO)]{\cdot}20H_2O$, is a new mineral species from the Packrat mine, near Gateway, Mesa County, Colorado, U.S.A. It is a secondary mineral found on asphaltum in a montroseite- and corvusite-bearing sandstone. Other secondary minerals found in close association with kegginite are ansermetite, gypsum, mesaite, and sherwoodite. Crystals of kegginite are orange-red simple hexagonal tablets. The streak is pinkish-orange, the luster is vitreous, the Mohs hardness is about 2, the tenacity is brittle, fracture is irregular, cleavage is good on {001}, and the calculated density is 2.69 g/cm^3. Kegginite is optically uniaxial (–) with pleochroism: *O* orange-red and *E* red-orange; $E < O$. Electron microprobe analyses yielded the empirical formula $Pb_{2.98}Ca_{2.39}Mg_{0.56}V_{13.05}As_{0.95}O_{61}H_{40.15}$. Kegginite is trigonal, $P\overline{3}$, with $a = 14.936(5)$, $c = 15.846(5)$ Å, $V = 3061(2)$ Å^3, and $Z = 2$. The crystal structure of kegginite ($R_1 = 0.064$ for 1356 $F_o > 4\sigma F$ reflections) contains a $[As^{5+}V^{5+}_{12}O_{40}(VO)]^{12-}$ polyoxometalate cluster, which is a mono-capped Keggin ε-isomer.

Keywords: Kegginite, new mineral species, polyoxometalate, Keggin anion ε-isomer, crystal structure, Packrat mine, Colorado

INTRODUCTION

With the ability to control experimental variables and chemistry, millions of synthetic compounds have been prepared in the laboratory, but, in contrast, in natural environments only ca. 5000 minerals have been characterized to date. Obviously, many compounds that have been synthesized have not been found in nature, and many of these have properties that make them useful in various chemical and industrial processes. One such group of compounds contains the well-known Keggin polyoxometalate anion, which has the general formula $[XM_{12}O_{40}]^{n-}$, where X is known as the heteroatom and M is known as the addenda atom; in the Keggin anion, a tetrahedrally coordinated X atom is surrounded by 12 octahedra centered on M ions (Keggin 1934). Numerous Keggin polyoxometalate phases have been synthesized (generally under acidic conditions), and various isomers and vacancy defect derivative structures are included in the Keggin family of compounds. Research on Keggin compounds comprises a very large body of literature because of the utility of Keggin compounds in catalytic reactions germane to industrial processes (Song and Tsunashima 2012).

Few Keggin compounds have been found in nature. The first Keggin-compound mineral was murataite, in which Keggin clusters are the fundamental building blocks of a framework (Ercit and Hawthorne 1995). Kampf et al. (2014) described ophirite, which contains a heteropolytungstate tri-lacunary Keggin anion; the tri-lacunary modifier signifies the three octahedral vacancies in the Keggin structure, yielding the $[Fe^{3+}W_9O_{34}]^{11-}$ tri-lacunary Keggin anion. The complex chemical environment in which ophirite occurs attests to the rarity of the conditions of mineral genesis under which Keggin structures might be found in nature; ophirite crystals occur where late acidic and oxidizing hydrothermal solutions, in the presence of pyrite and calcium-rich hornfels, reacted with dolomite and scheelite to produce the rare phase. Both murataite and ophirite contain the α-isomer of the Keggin anion. Kegginite, described herein, is the third mineral to be described that contains a Keggin anion, and is the first to contain the ε-isomer of the $[XM_{12}O_{40}]^{n-}$ Keggin polyoxometalate, in this case $[AsV_{12}O_{40}]^{15-}$.

The name kegginite is in recognition of the presence of the ε-isomer of the Keggin anion as the basis of the structural unit in the mineral. It also recognizes J.F. Keggin who first experimentally determined the structure of α-Keggin anions in 1934 (Keggin 1934). The new mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2015-114). Five co-type specimens of kegginite are deposited in the collections of the Natural History Museum of Los Angeles County, Los Angeles, California, U.S.A., catalog numbers 65636, 65637, 65638, 66474, and 66475.

OCCURRENCE

Kegginite was found in the main tunnel level of the Packrat mine, near Gateway, Mesa County, Colorado, U.S.A. (38°38′51.28″N 109°02′49.77″W). The Packrat mine is near the northern end of the Uravan Mineral Belt, in which uranium and

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vanadium minerals occur together in bedded or roll-front deposits in the sandstone of the Salt Wash member of the Jurassic Morrison Formation (Carter and Gualtieri 1965; Shawe 2011). The original claims on the Packrat no. 1 and no. 2 were filed in 1943, but mining apparently did not commence until the early 1950s. The mine remained in operation until 1990 and consists of several miles of drifts and numerous stopes. The mine site was reclaimed in 2002, but was reopened in 2007 for further exploration. It is currently inactive. The samples of the new mineral were collected by one of the authors (J.M.) on May 3, 2013, and September 20, 2016.

The mineral is very rare. It has been found very sparingly on only a few small specimens. Kegginite is a secondary mineral found on asphaltum in a montroseite- and corvusite-bearing sandstone. Other secondary minerals found in close association with kegginite are ansermetite, gypsum, mesaite (Kampf et al. 2016b), and sherwoodite. Other secondary minerals found in the mine include andersonite, calcite, dickthomssenite, gatewayite (Kampf et al. 2016a), hewettite, hummerite, lasalite, magnesiopascoite, martyite, morrisonite (Kampf et al. 2016a), munirite, navajoite, packratite (Kampf et al. 2016a), pascoite, pharmacolite, picropharmacolite, postite, rossite/metarossite, rösslerite, selenium, uranopilite, vanarsite (Kampf et al. 2016a), and potentially other new minerals, currently under study.

The new mineral forms from the oxidation of montroseite-corvusite assemblages in a moist environment. Mining operations have exposed unoxidized and oxidized phases. Under ambient temperatures and generally oxidizing near-surface conditions, meteoric water reacts with pyrite and an unknown As-bearing phase (perhaps arsenopyrite) to form aqueous solutions with relatively low pH (cf. Evans and Garrels 1958). The various secondary vanadate phases that form depend upon prevailing Eh-pH conditions and the presence of other cations (e.g., Na^+, Ca^{2+}, Mn^{2+}, Pb^{2+}). A detailed summary of the mineralogy, ore chemistry and conditions of mineral genesis are given in Shawe (2011), which summarizes more than half a century of work on the uranaium-vanadium deposits of the Colorado Plateau.

PHYSICAL AND OPTICAL PROPERTIES

Crystals of kegginite are orange-red hexagonal tablets exhibiting the forms {100} and {001}, up to about 0.2 mm in diameter (Figs. 1 and 2). The vitreous and transparent crystals have a pinkish-orange streak. Kegginite is non-fluorescent in long- and short-wave ultraviolet light. It has a Mohs hardness of about 2, brittle tenacity, irregular fracture, and good cleavage on {001}. There is insufficient material available for density measurement; the calculated density is 2.69 g/cm^3 based on the empirical formula using the single-crystal cell parameters. The mineral is insoluble in H_2O and soluble at room temperature in dilute HCl. Kegginite is optically uniaxial (–). The very small number of crystals, their small size, and their dark color made it impossible to obtain reliable measurements of the indices of refraction. The average index of refraction predicted by the Gladstone-Dale relationship is 1.721. The pleochroism is *O* orange-red and *E* red-orange; $E < O$.

CHEMICAL ANALYSIS

Five analyses of kegginite from a single crystal were performed at the University of Utah on a Cameca SX-50 electron microprobe with four wavelength-dispersive spectrometers operating with Probe for EPMA software. Analytical conditions were 15 keV accelerating voltage, 10 nA beam current and a beam diameter of 10 μm. Counting times were 20 s on peak and 20 s on background for each element. Raw X-ray intensities were corrected for matrix effects with a $\phi\rho(z)$ algorithm (Pouchou and Pichoir 1991).

No damage from the electron beam was observed. However, as is typical of highly hydrated phases with weakly held H_2O, kegginite partially dehydrates under vacuum either during carbon coating or in the microprobe chamber. This H_2O loss results in higher concentrations for the remaining constituents than are to be expected for the fully hydrated phase. Because insufficient material is available for a direct determination of H_2O, it has been calculated based upon the structure determination. Analytical data are given in Table 1.

The empirical formula of kegginite (based on 61 O apfu) is $Pb_{2.98}Ca_{2.39}Mg_{0.56}V_{13.05}As_{0.95}O_{61}H_{40.15}$. The simplified structural formula is $Pb_3Ca_3[(AsO_4)V_{12}O_{33}(VO_4)]\cdot 20H_2O$, which requires PbO 26.83, CaO 6.74, V_2O_5 47.38, As_2O_5 4.61, H_2O 14.44, total 100 wt%. The formula can be written as above to emphasize the vanadate and arsenate tetrahedra, or as $Pb_3Ca_3[AsV_{12}O_{40}(VO)]\cdot 20H_2O$ to emphasize the presence of the Keggin anion.

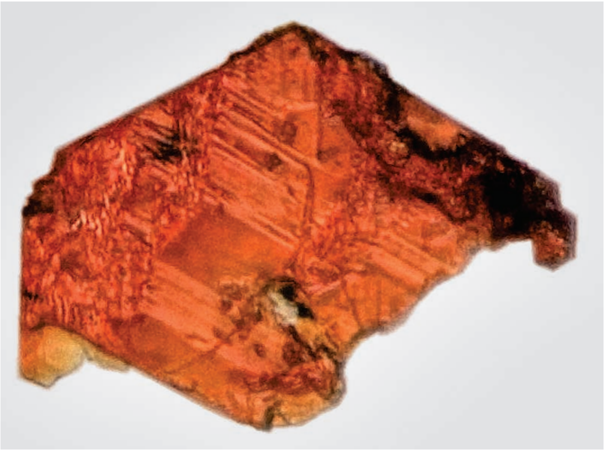

FIGURE 1. Kegginite crystal used in the structure study. FOV 0.2 mm across.

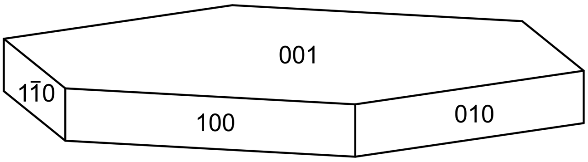

FIGURE 2. Crystal drawing of kegginite. Clinographic projection.

TABLE 1. Analytical results for kegginite

Constituent	Mean	Range	S.D.	Standard	Normalized
PbO	28.12	26.98–29.27	1.05	Pb metal	26.82
CaO	5.66	5.59–5.75	0.07	diopside	5.39
MgO	0.96	0.93–0.99	0.02	diopside	0.92
V_2O_5	50.20	49.01–51.30	0.89	V metal	47.87
As_2O_5	4.64	4.38–4.80	0.21	GaAs	4.42
H_2O^a	15.30				14.59
Total	104.88				100.01

[a] Based upon the crystal structure with V+As = 14 and O = 61 apfu.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

Powder and single-crystal X-ray diffraction data for kegginite were obtained on a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer using monochromatized Mo*K*α radiation. For the powder-diffraction study, a Gandolfi-like motion on the φ and ω axes was used to randomize the sample and observed *d*-values and intensities were derived by profile fitting using JADE 2010 software (Materials Data, Inc.). The powder data are presented in Table 2[1]. Unit-cell parameters refined from the powder data using whole pattern fitting are: $a = 14.950(2)$, $c = 15.882(3)$ Å, and $V = 3074.1(1.0)$ Å^3.

The Rigaku Crystal Clear software package was used for processing the structure data, including the application of numerical and empirical absorption corrections. The structure was solved by direct methods using SIR2011 (Burla et al. 2012). SHELXL-2013 (Sheldrick 2008) was used for the refinement of the structure. Kegginite crystals are small and diffract relatively weakly because of their high H_2O content; consequently, data were limited to $2\theta < 40°$. All As, V, and O sites in the structural unit refined to full occupancy, as did the Pb site in the interstitial unit. All of these sites exhibit high, but not unreasonable, displacement parameters. The other sites in the interstitial unit exhibit high displacement parameters and partial occupancies, suggesting considerable disorder. The Ca site is split into two sites (Ca1 and Ca2) 1.53 Å apart. The scattering powers of these sites were consistent with each site being half occupied by a combination of Ca and Mg: $Ca1 = Ca_{0.43}Mg_{0.07}$; $Ca2 = Ca_{0.38}Mg_{0.12}$. Not surprisingly, difference Fourier did not reveal the locations of the hydrogen atoms. Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, and selected bond distances and bond-valence sums in Table 5. The CIF file for kegginite is on deposit and available as listed below.[1]

DESCRIPTION OF THE STRUCTURE

The structure of kegginite (Figs. 3 and 4) consists of two distinct parts, a structural unit and an interstitial complex, as suggested by Schindler and Hawthorne (2001) for minerals with polymerized units of higher bond valence. The structural unit is a $[As^{5+}V^{5+}_{12}O_{40}(VO)]^{12-}$ heteropolyanion composed of 12 distorted VO_6 octahedra (distortion type 1+4+1, Schindler et al. 2000) surrounding a central AsO_4 (arsenate) tetrahedron and capped by a VO_4 (vanadate) tetrahedron, which shares three of its four vertices with VO_6 octahedra (Fig. 3). Without the capping tetrahedron, the heteropolyanion is the ε-isomer of the Keggin anion, $\varepsilon\text{-}[XM_{12}O_{40}]^{n-}$, which in this case has the formula $\varepsilon\text{-}[AsV_{12}O_{40}]^{15-}$. The ε-isomer of the Keggin anion has ideal tetrahedral symmetry and has the appearance of a tetrahedron with truncated corners and "cavities" in each of its four faces. The capping VO_4 tetrahedron is located over one of these cavities.

The interstitial unit has the formula $[Pb_3Ca_3 \cdot 20H_2O]^{12+}$, which exactly balances the charge on the structural unit and confirms the 5+ charges on all V and As in the structural unit (Table 5). The Pb site is located above each of the three remaining cavities in the mono-capped Keggin anion. Pb is in lopsided ninefold coordination, with 6 bonds, 3 short (2.28–2.33 Å) and 3 long (3.29–3.38 Å), to O atoms in one mono-capped Keggin anion and 3 other long bonds (2.82–3.00 Å) to an adjacent mono-capped Keggin anion. A tenth, much longer, Pb-O bond (3.62 Å) is to the partially occupied OW28a in the interstitial unit. The Pb-O bonds link the Keggin anions into a thick layer parallel to {001}. The two half-occupied Ca sites in the interstitial unit do not have regular coordinations. They are at reasonable distances for bonds to O sites in the Keggin anions and to H_2O sites in the interstitial unit and thereby serve to link the layers in the [001] direction (bond valences given in Table 5). However, the Ca sites surround the threefold axis and appear to be missing a coordinating O site on that axis. Some residual electron density in this region could represent highly disordered O sites, but none could be successfully refined.

TABLE 3. Data collection and structure refinement details for kegginite

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	Mo*K*α ($\lambda = 0.71075$ Å)/50 kV, 40 mA
Temperature	293(2) K
Structural formula	$Pb_3(Ca_{2.43}Mg_{0.57})_{\Sigma 3.00}[AsV_{12}O_{40}(VO)] \cdot 19.62H_2O$
Space group	$P\bar{3}$
Unit-cell dimensions	$a = 14.936(5)$ Å
	$c = 15.846(5)$ Å
V	3061(2) Å^3
Z	2
Density (for above formula)	2.690 g/cm^3
Absorption coefficient	10.958 mm^{-1}
$F(000)$	2315.3
Crystal size	110 × 90 × 10 µm
θ range	3.02–20.11°
Index ranges	$-14 \leq h \leq 12, -12 \leq k \leq 14, -15 \leq l \leq 15$
Refls collected/unique	8481/1889; $R_{int} = 0.112$
Reflections with $F_o > 4\sigma F$	1356
Completeness to $\theta = 20.11°$	97.5%
Max. and min. transmission	0.958 and 0.725
Refinement method	Full-matrix least-squares on F^2
Parameters/restraints	257/0
GoF	1.052
Final R indices [$F_o > 4\sigma F$]	$R_1 = 0.0640$, $wR_2 = 0.1498$
R indices (all data)	$R_1 = 0.0951$, $wR_2 = 0.1676$
Largest diff. peak/hole	+1.58/–1.27 e/A^3

Notes: $R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. GoF $= S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0.0862, b is 43.2287, and P is $[2F_c^2 + \text{Max}(F_o^2,0)]/3$.

Various capped Keggin anions have been synthesized and structurally characterized, but to our knowledge, a mono-capped Keggin ε-isomer equivalent to the $[As^{5+}V^{5+}_{12}O_{40}(VO)]^{12-}$ unit in kegginite has not been previously reported. Kegginite is not closely related to any other mineral. Other minerals that contain Keggin-related polyoxometalate clusters include ophirite, which has a trilacunary Keggin sandwich anion (Kampf et al. 2014), and murataite, in which Keggin clusters are the fundamental building blocks of a framework (Ercit and Hawthorne 1995). In both of these cases, the Keggin unit is the α isomer.

IMPLICATIONS

Many complex polyoxometalate anions have been synthesized, and they have been shown to have a remarkable array of technological and biochemical uses (cf. Cronin and Müller 2012; Song and Tsunashima 2012). The most widely known heteropoly anion is the Keggin anion, for which a very large body of literature exists because of its industrial utility. Capped

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[1] Deposit item AM-17-25834, CIF and Table 2. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (http://www.minsocam.org/MSA/AmMin/TOC/2017/Feb2017_data/Feb2017_data.html).

TABLE 4. Atom coordinates and displacement parameters (Å^2) for kegginite

	x/a	*y/b*	*z/c*	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pb	0.36763(8)	0.42910(8)	0.57446(7)	0.0374(5)	0.0352(8)	0.0320(8)	0.0463(8)	0.0025(5)	–0.0009(5)	0.0178(6)
Ca1[a]	0.5844(15)	0.3976(17)	0.8921(10)	0.103(6)	0.102(15)	0.18(2)	0.060(11)	0.026(11)	0.007(10)	0.097(15)
Ca2[a]	0.6989(15)	0.4760(17)	0.8796(11)	0.103(6)	0.100(16)	0.170(19)	0.065(12)	0.011(12)	0.009(10)	0.088(15)
As	0.3333	0.6667	0.6602(3)	0.0340(12)	0.0334(19)	0.0334(19)	0.035(3)	0.000	0.000	0.0167(9)
V1	0.3333	0.6667	0.8772(5)	0.054(2)	0.061(4)	0.061(4)	0.039(6)	0.000	0.000	0.0305(19)
V2	0.4682(3)	0.6884(3)	0.4627(3)	0.0319(12)	0.027(3)	0.031(3)	0.038(3)	0.001(2)	0.000(2)	0.015(2)
V3	0.5899(3)	0.6958(3)	0.6119(3)	0.0379(13)	0.037(3)	0.037(3)	0.038(3)	–0.004(2)	–0.008(2)	0.018(2)
V4	0.2383(4)	0.4258(4)	0.7773(3)	0.0463(14)	0.052(3)	0.051(3)	0.037(3)	0.011(2)	0.002(2)	0.027(3)
V5	0.0943(4)	0.5254(4)	0.7786(3)	0.0464(14)	0.045(3)	0.056(3)	0.043(3)	0.013(2)	0.016(2)	0.029(3)
O1	0.3333	0.6667	0.5551(18)	0.035(8)	0.018(10)	0.018(10)	0.07(2)	0.000	0.000	0.009(5)
O2	0.4487(12)	0.6819(12)	0.6959(10)	0.040(5)	0.039(11)	0.041(11)	0.044(12)	–0.007(9)	–0.011(9)	0.022(10)
O3	0.3333	0.6667	0.9806(17)	0.053(9)	0.067(15)	0.067(15)	0.026(19)	0.000	0.000	0.033(7)
O4	0.3492(13)	0.5615(12)	0.8432(10)	0.041(5)	0.049(12)	0.037(11)	0.038(12)	0.006(8)	0.008(9)	0.022(10)
O5	0.5468(11)	0.6968(12)	0.3877(10)	0.035(4)	0.025(10)	0.038(11)	0.043(11)	0.009(8)	0.019(8)	0.017(9)
O6	0.6914(12)	0.7057(13)	0.5686(10)	0.041(5)	0.026(10)	0.059(13)	0.044(11)	0.011(9)	-0.004(8)	0.026(10)
O7	0.2418(14)	0.3418(13)	0.8401(11)	0.053(5)	0.070(14)	0.049(12)	0.047(12)	0.013(10)	0.009(10)	0.034(11)
O8	0.0034(13)	0.5046(13)	0.8431(11)	0.053(5)	0.048(12)	0.048(12)	0.054(13)	0.011(9)	0.015(10)	0.018(10)
O9	0.4299(11)	0.7782(11)	0.4235(9)	0.029(4)	0.023(10)	0.030(10)	0.029(10)	0.001(8)	-0.005(7)	0.009(8)
O10	0.5598(11)	0.7826(12)	0.5463(9)	0.032(4)	0.016(9)	0.037(11)	0.034(11)	-0.011(8)	-0.011(7)	0.007(8)
O11	0.4871(11)	0.5956(12)	0.5413(9)	0.028(4)	0.029(10)	0.040(11)	0.032(10)	-0.001(8)	-0.003(7)	0.030(9)
O12	0.1533(12)	0.3502(12)	0.6935(10)	0.037(4)	0.039(11)	0.028(10)	0.035(11)	0.012(8)	0.001(8)	0.009(9)
O13	0.0315(12)	0.4373(13)	0.6947(10)	0.044(5)	0.041(12)	0.052(12)	0.027(11)	0.006(9)	0.003(8)	0.014(10)
O14	0.1427(13)	0.4513(12)	0.8316(11)	0.049(5)	0.043(12)	0.032(11)	0.062(13)	0.009(9)	0.017(9)	0.011(10)
O15	0.3614(11)	0.4643(13)	0.7171(10)	0.039(5)	0.027(10)	0.050(12)	0.032(11)	-0.003(8)	–0.009(8)	0.014(9)
OW1	0.631(2)	0.5270(19)	0.9945(14)	0.099(8)	0.14(2)	0.13(2)	0.058(16)	-0.004(14)	–0.008(14)	0.090(19)
OW2	0.6557(18)	0.477(2)	0.7401(13)	0.104(9)	0.093(18)	0.22(3)	0.044(14)	–0.033(16)	–0.010(12)	0.11(2)
OW3	0.8714(18)	0.591(2)	0.7953(19)	0.152(15)	0.065(17)	0.23(3)	0.17(3)	–0.15(3)	–0.030(17)	0.08(2)
OW4	0.431(3)	0.303(2)	0.9962(16)	0.149(12)	0.24(4)	0.14(3)	0.07(2)	0.007(17)	–0.03(2)	0.09(2)
OW5	0.0000	0.0000	0.766(4)	0.16(2)	0.14(3)	0.14(3)	0.20(6)	0.000	0.000	0.068(14)
OW6[a]	0.053(4)	–0.081(4)	0.675(3)	0.13(3)						
OW7a[a]	0.732(4)	0.668(4)	0.857(3)	0.11(3)						
OW7b[a]	0.763(7)	0.731(7)	0.771(7)	0.16(6)						
OW8a[a]	0.917(6)	0.766(6)	0.598(6)	0.15(5)						
OW8b[a]	0.918(5)	0.809(6)	0.527(6)	0.10(4)						

[a] Occupancies: Ca1 = $\mathrm{Ca}_{0.43}\mathrm{Mg}_{0.07}$; Ca2 = $\mathrm{Ca}_{0.38}\mathrm{Mg}_{0.12}$; OW6 = 0.55(7); OW7a = 0.53(7); OW7b = 0.36(8); OW8a = 0.44(9); OW8b = 0.33(8).

TABLE 5. Selected bond distances and bond valences for atoms in kegginite

	Distance	BVS		Distance	BVS
Pb-O11	2.282(15)	0.63	V2-O5	1.631(15)	1.59
Pb-O10	2.295(15)	0.61	V2-O9	1.811(15)	0.98
Pb-O15	2.333(16)	0.55	V2-O9	1.884(15)	0.80
Pb-O5	2.816(15)	0.15	V2-O10	1.920(15)	0.73
Pb-O6	2.863(17)	0.13	V2-O11	1.986(15)	0.61
Pb-O11	3.001(14)	0.09	V2-O1	2.378(18)	0.21
Mean/Sum	2.598	2.16	Mean/Sum	1.935	4.92
Ca1-OW1	2.35(3)	0.36	V3-O6	1.602(16)	1.72
Ca1-O8	2.58(2)	0.19	V3-O10	1.881(16)	0.81
Ca1-OW4	2.60(4)	0.18	V3-O11	1.885(15)	0.80
Ca1-OW2	2.66(3)	0.15	V3-O13	1.891(16)	0.79
Ca1-O3	2.77(3)	0.11	V3-O12	1.899(16)	0.77
Ca1-OW3	2.78(4)	0.11	V3-O2	2.413(17)	0.19
Mean/Sum	2.623	1.10	Mean/Sum	1.929	5.08
Ca2-OW2	2.31(3)	0.40	V4-O7	1.623(17)	1.63
Ca2-OW1	2.39(3)	0.32	V4-O12	1.793(16)	1.03
Ca2-OW3	2.64(4)	0.16	V4-O14	1.862(17)	0.85
Ca2-OW7A	2.68(6)	0.14	V4-O15	1.887(16)	0.80
Ca2-OW4	2.90(4)	0.08	V4-O4	2.141(17)	0.40
Ca2-O3	2.94(3)	0.07	V4-O2	2.307(16)	0.26
Mean/Sum	2.643	1.17	Mean/Sum	1.936	4.97
As-O1	1.66(3)	1.32	V5-O8	1.600(18)	1.73
As-O2(×3)	1.718(16)	1.14	V5-O13	1.773(17)	1.08
Mean/Sum	1.704	4.74	V5-O14	1.803(18)	1.00
			V5-O15	1.900(16)	0.77
V1-O3	1.64(3)	1.56	V5-O4	2.089(17)	0.46
V1-O4(×3)	1.785(16)	1.05	V5-O2	2.317(16)	0.25
Mean/Sum	1.749	4.71	Mean/Sum	1.914	5.29

Note: Bond valences are based on Brese and O'Keeffe (1991).

Keggin anions, in particular, have potential as building blocks for advanced materials or as components for molecular devices (cf. Bakri et al. 2012). Until recently, minerals that contain the Keggin anion were not known to occur, and kegginite is only the third discovered to date; it is the first mineral containing a Keggin ε-isomer and appears to be the first phase, either natural or synthetic, containing a mono-capped $[\mathrm{As}^{5+}\mathrm{V}^{5+}_{12}\mathrm{O}_{40}(\mathrm{VO})]^{12-}$ Keggin ε-isomer.

The environment of secondary mineral genesis at the Ophir Hill Consolidated mine in Tooele County, Utah, consisting of late acidic and oxidizing hydrothermal solutions and the presence of As, has recently yielded the tri-lacunary Keggin anion in ophirite, a tri-lacunary Keggin structure with three octahedral vacancies in the $[\mathrm{XM}_{12}\mathrm{O}_{40}]^{n-}$ Keggin anion. The occurrence of kegginite in a mine of the Uravan Mineral Belt, a different chemical environment from ophirite (although similarly acidic and oxidizing), extends the natural conditions under which Keggin anions can form, and suggests that other members of this class of compounds occur naturally.

It is worth noting that the decavanadate isopolyanion, $[\mathrm{V}^{5+}_{10}\mathrm{O}_{28}]^{6-}$, including its protonated and mixed-valence variants, is the most common polyanion found in the secondary mineral assemblages of the sandstone-hosted uranium-vanadium deposits of the Uravan Mineral Belt, as well as in similar deposits worldwide. The decavanadate anion is known to be quite stable in acidic and oxidizing aqueous solutions. The mineralization in the Packrat mine is unusual for having local enrichment in As, which is atypical of deposits in the Uravan Mineral Belt. This, coupled with intermediate oxidizing conditions, has resulted in the formation of four recently described minerals (vanarsite, packratite, morrisonite, and gatewayite; Kampf et al. 2016a) containing the novel mixed-valence $[\mathrm{As}^{3+}\mathrm{V}^{4+,5+}_{12}\mathrm{As}^{5+}_{6}\mathrm{O}_{51}]$ hetero-

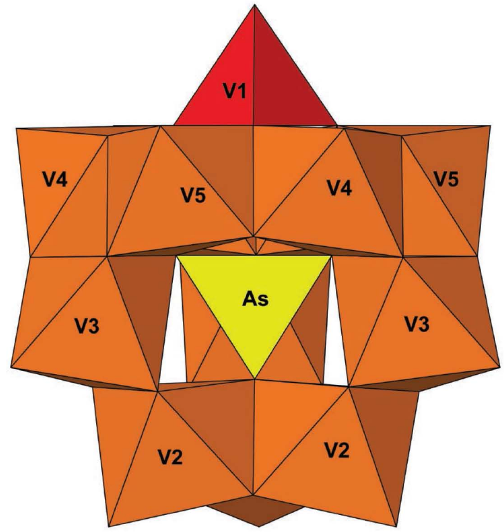

FIGURE 3. Mono-capped ε-isomer of the Keggin anion that is the $[As^{5+}V^{5+}_{12}O_{40}(VO)]^{12-}$ structural unit in kegginite.

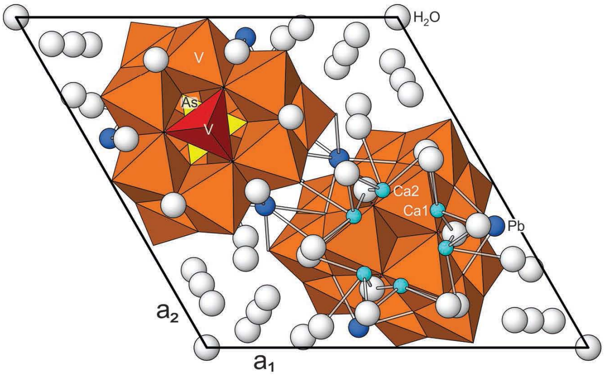

FIGURE 4. Structure of kegginite viewed down **c**.

polyanion. Kegginite formed in the same general assemblage, but apparently under more oxidizing conditions, as it contains the mono-capped $[As^{5+}V^{5+}_{12}O_{40}(VO)]^{12-}$ Keggin ε-isomer, in which all As and V is 5+. The presence of As in the system is crucial to the formation of these very rare polyanions, although it might be conjectured that a phosphate analog of kegginite could be formed if P^{5+} rather than As^{5+} is present.

The occurrence of kegginite further demonstrates that rare natural environments of mineral genesis can mimic laboratory conditions under which complex compounds can be created, and suggests that the limits of mineral structure complexity will be extended as these environments are explored. Furthermore, the fact that kegginite contains a mono-capped Keggin anion not previously synthesized demonstrates the importance of new mineral discoveries in providing insights into the development of potentially valuable technological materials.

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