

1 **Revision 1**

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3 **Kegginite, $\text{Pb}_3\text{Ca}_3[\text{AsV}_{12}\text{O}_{40}(\text{VO})]\cdot 20\text{H}_2\text{O}$, a new mineral with a novel ϵ -isomer of the**

4 **Keggin anion**

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13 **ABSTRACT**

14 Kegginite, $\text{Pb}_3\text{Ca}_3[\text{AsV}_{12}\text{O}_{40}(\text{VO})]\cdot 20\text{H}_2\text{O}$, is a new mineral species from the Packrat mine, near

15 Gateway, Mesa County, Colorado, U.S.A. It is a secondary mineral found on asphaltum in a

16 montroseite- and corvusite-bearing sandstone. Other secondary minerals found in close

17 association with kegginites are ansermetite, gypsum, mesaite, and sherwoodite. Crystals of

18 kegginites are orangish-red simple hexagonal tablets. The streak is pinkish-orange, the luster is

19 vitreous, the Mohs hardness is about 2, the tenacity is brittle, fracture is irregular, cleavage is

20 good on $\{001\}$, and the calculated density is $2.69 \text{ g}\cdot\text{cm}^{-3}$. Kegginite is optically uniaxial (–) with

21 pleochroism: *O* orange-red and *E* red-orange; $E < O$. Electron microprobe analyses yielded the

22 empirical formula $\text{Pb}_{2.98}\text{Ca}_{2.39}\text{Mg}_{0.56}\text{V}_{13.05}\text{As}_{0.95}\text{O}_{61}\text{H}_{40.15}$. Kegginite is trigonal, $P\bar{3}$, with *a*

23 $14.936(5)$, *c* $15.846(5) \text{ \AA}$, *V* $3061(2) \text{ \AA}^3$, and *Z* = 2. The crystal structure of kegginites ($R_1 = 0.064$

24 for $1356 F_o > 4\sigma F$ reflections) contains a $[\text{As}^{5+}\text{V}^{5+}_{12}\text{O}_{40}(\text{VO})]^{12-}$ polyoxometalate cluster, which

25 is a mono-capped Keggin ϵ -isomer.

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27 *Keywords:* kegginite; new mineral species; polyoxometalate; Keggin anion ϵ -isomer; crystal
28 structure; Packrat mine, Colorado.

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INTRODUCTION

31 With the ability to control experimental variables and chemistry, millions of synthetic
32 compounds have been prepared in the laboratory, but, in contrast, in natural environments only
33 *ca.* 5,000 minerals have been characterized to date. Obviously, many compounds that have been
34 synthesized have not been found in nature, and many of these have properties that make them
35 useful in various chemical and industrial processes. One such group of compounds contains the
36 well-known Keggin polyoxometalate anion, which has the general formula $[XM_{12}O_{40}]^{n-}$, where X
37 is known as the heteroatom and M is known as the addenda atom; in the Keggin anion, a
38 tetrahedrally coordinated X atom is surrounded by 12 octahedra centered on M ions (Keggin
39 1934). Numerous Keggin polyoxometalate phases have been synthesized (generally under acidic
40 conditions), and various isomers and vacancy defect derivative structures are included in the
41 Keggin family of compounds. Research on Keggin compounds comprises a very large body of
42 literature because of the utility of Keggin compounds in catalytic reactions germane to industrial
43 processes (Song and Tsunashima 2012).

44 Few Keggin compounds have been found in nature. The first Keggin-compound mineral
45 was murataite, in which Keggin clusters are the fundamental building blocks of a framework
46 (Ercit and Hawthorne, 1995). Kampf et al. (2014) described ophirite, which contains a
47 heteropolytungstate tri-lacunary Keggin anion; the tri-lacunary modifier signifies the three
48 octahedral vacancies in the Keggin structure, yielding the $[Fe^{3+}W_9O_{34}]^{11-}$ tri-lacunary Keggin

49 anion. The complex chemical environment in which ophirite occurs attests to the rarity of the
50 conditions of mineral genesis under which Keggin structures might be found in nature; ophirite
51 crystals occur where late acidic and oxidizing hydrothermal solutions, in the presence of pyrite
52 and calcium-rich hornfels, reacted with dolomite and scheelite to produce the rare phase. Both
53 murataite and ophirite contain the α -isomer of the Keggin anion. Kegginite, described herein, is
54 the third mineral to be described that contains a Keggin anion, and is the first to contain the ϵ -
55 isomer of the $[XM_{12}O_{40}]^{n-}$ Keggin polyoxometalate, in this case $[AsV_{12}O_{40}]^{15-}$.

56 The name kegginite is in recognition of the presence of the ϵ -isomer of the Keggin anion
57 as the basis of the structural unit in the mineral. It also recognizes J.F. Keggin who first
58 experimentally determined the structure of α -Keggin anions in 1934 (Keggin 1934). The new
59 mineral and name were approved by the Commission on New Minerals, Nomenclature and
60 Classification of the International Mineralogical Association (IMA 2015-114). Three cotype
61 specimens of kegginite are deposited in the collections of the Natural History Museum of Los
62 Angeles County, Los Angeles, California, USA, catalogue numbers 65636, 65637 and 65638.

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OCCURRENCE

65 Kegginite was found in the main tunnel level of the Packrat mine, near Gateway, Mesa
66 County, Colorado, USA (38°38'51.28"N 109°02'49.77"W). The Packrat mine is near the northern
67 end of the Uravan Mineral Belt, in which uranium and vanadium minerals occur together in
68 bedded or roll-front deposits in the sandstone of the Salt Wash member of the Jurassic Morrison
69 Formation (Carter and Gualtieri 1965; Shawe 2011). The original claims on the Packrat #1 and
70 #2 were filed in 1943, but mining apparently did not commence until the early 1950s. The mine
71 remained in operation until 1990 and consists of several miles of drifts and numerous stopes. The

72 mine site was reclaimed in 2002, but was reopened in 2007 for further exploration. It is currently
73 inactive. The samples of the new mineral were collected by one of the authors (JM) on May 3,
74 2013.

75 The mineral is very rare. It has been found very sparingly on only a few small specimens.
76 Kegginite is a secondary mineral found on asphaltum in a montroseite- and corvusite-bearing
77 sandstone. Other secondary minerals found in close association with kegginitite are ansermetite,
78 gypsum, mesaite (Kampf et al. 2016), and sherwoodite. Other secondary minerals found in the
79 mine include andersonite, calcite, dickthomssenite, gatewayite (Kampf et al. 2015), hewettite,
80 hummerite, lasalite, magnesiopascoite, martyite, morrisonite (Kampf et al. 2015), munirite,
81 navajoite, packratite (Kampf et al. 2015), pascoite, pharmacolite, picropharmacolite, postite,
82 rossite/metarossite, rösslerite, selenium, uranopilite, vanarsite (Kampf et al. 2015) and other
83 potentially new minerals, currently under study.

84 The new mineral forms from the oxidation of montroseite-corvusite assemblages in a
85 moist environment. Mining operations have exposed unoxidized and oxidized phases. Under
86 ambient temperatures and generally oxidizing near-surface conditions, meteoric water reacts with
87 pyrite and an unknown As-bearing phase (perhaps arsenopyrite) to form aqueous solutions with
88 relatively low pH (cf. Evans and Garrels 1958). The various secondary vanadate phases that form
89 depend upon prevailing Eh-pH conditions and the presence of other cations (*e.g.*, Na⁺, Ca²⁺,
90 Mn²⁺, Pb²⁺). A detailed summary of the mineralogy, ore chemistry and conditions of mineral
91 genesis are given in Shawe (2011), which summarizes more than half a century of work on the
92 uranium-vanadium deposits of the Colorado Plateau.

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PHYSICAL AND OPTICAL PROPERTIES

95 Crystals of kegginite are orangish-red hexagonal tablets exhibiting the forms {100} and
96 {001}, up to about 0.1 mm in diameter (Figs. 1 and 2). The vitreous and transparent crystals have
97 a pinkish-orange streak. Kegginite is non-fluorescent in long- and short-wave ultraviolet light. It
98 has a Mohs hardness of about 2, brittle tenacity, irregular fracture, and good cleavage on {001}.
99 There is insufficient material available for density measurement; the calculated density is 2.69
100 $\text{g}\cdot\text{cm}^{-3}$ based on the empirical formula using the single-crystal cell parameters. The mineral is
101 insoluble in H_2O and soluble at room-temperature in dilute HCl. Kegginite is optically uniaxial (–
102). The very small number of crystals, their small size and their dark color made it impossible to
103 obtain reliable measurements of the indices of refraction. The average index of refraction
104 predicted by the Gladstone-Dale relationship is 1.721. The pleochroism is *O* orange-red and *E*
105 red-orange; $E < O$.

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CHEMICAL ANALYSIS

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

114 No damage from the electron beam was observed. However, as is typical of highly
115 hydrated phases with weakly held H_2O , kegginite partially dehydrates under vacuum either
116 during carbon coating or in the microprobe chamber. This H_2O loss results in higher
117 concentrations for the remaining constituents than are to be expected for the fully hydrated phase.

118 Because insufficient material is available for a direct determination of H₂O, it has been calculated
119 based upon the structure determination. Analytical data are given in Table 1.

120 The empirical formula of kegginite (based on 61 O *apfu*) is
121 Pb_{2.98}Ca_{2.39}Mg_{0.56}V_{13.05}As_{0.95}O₆₁H_{40.15}. The simplified structural formula is
122 Pb₃Ca₃[(AsO₄)V₁₂O₃₃(VO₄)]·20H₂O, which requires PbO 26.83, CaO 6.74, V₂O₅ 47.38, As₂O₅
123 4.61, H₂O 14.44, total 100 wt%. The formula can be written as above to emphasize the vanadate
124 and arsenate tetrahedra, or as Pb₃Ca₃[AsV₁₂O₄₀(VO)]·20H₂O to emphasize the presence of the
125 Keggin anion.

126

127 X-RAY CRYSTALLOGRAPHY AND STRUCTURE DETERMINATION

128 Powder and single-crystal X-ray diffraction data for kegginite were obtained on a Rigaku
129 R-Axis Rapid II curved imaging plate microdiffractometer using monochromatized MoK α
130 radiation. The powder pattern obtained was a good fit for that calculated from the structure;
131 however, because of the very small amount of material available, the observed peaks were not
132 sufficiently above background to provide data of good quality. Consequently, we report the
133 powder data calculated from the structure in Table 2.

134 The Rigaku Crystal Clear software package was used for processing the structure data,
135 including the application of numerical and empirical absorption corrections. The structure was
136 solved by direct methods using SIR2011 (Burla et al. 2012). SHELXL-2013 (Sheldrick 2008)
137 was used for the refinement of the structure. Kegginite crystals are small and diffract relatively
138 weakly because of their high H₂O content; consequently, data were limited to $2\theta < 40^\circ$. All As, V
139 and O sites in the structural unit refined to full occupancy, as did the Pb site in the interstitial
140 unit. All of these sites exhibit rather high, but not unreasonable, displacement parameters. The

141 other sites in the interstitial unit exhibit high displacement parameters and partial occupancies,
142 suggesting considerable disorder. The Ca site is split into two sites (Ca1 and Ca2) 1.53 Å apart.
143 The scattering powers of these sites were consistent with each site being half occupied by a
144 combination of Ca and Mg: Ca1 = Ca_{0.43}Mg_{0.07}; Ca2 = Ca_{0.38}Mg_{0.12}. Not surprisingly, difference
145 Fourier did not reveal the locations of the hydrogen atoms. Data collection and refinement details
146 are given in Table 3, atom coordinates and displacement parameters in Table 4, and selected bond
147 distances and bond-valence sums in Table 5. The CIF file for kegginite is on deposit and
148 available as listed below.¹

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150

DESCRIPTION OF THE STRUCTURE

151 The structure of kegginite (Figs. 3 and 4) consists of two distinct parts, a structural unit
152 and an interstitial complex, as suggested by Schindler and Hawthorne (2001) for minerals with
153 polymerized units of higher bond valence. The structural unit is a [As⁵⁺V⁵⁺₁₂O₄₀(VO)]¹²⁻
154 heteropolyanion composed of twelve distorted VO₆ octahedra (distortion type 1+4+1, Schindler
155 et al. 2000) surrounding a central AsO₄ (arsenate) tetrahedron and capped by a VO₄ (vanadate)
156 tetrahedron, which shares three of its four vertices with VO₆ octahedra (Fig. 3). Without the
157 capping tetrahedron, the heteropolyanion is the ε-isomer of the Keggin anion, ε-[XM₁₂O₄₀]ⁿ⁻,
158 which in this case has the formula ε-[AsV₁₂O₄₀]¹⁵⁻. The ε-isomer of the Keggin anion has ideal
159 tetrahedral symmetry and has the appearance of a tetrahedron with truncated corners and

¹ Deposit items AM-17-xx1, AM-17-xx2 and AM-17-xx3 give anisotropic displacement parameters, observed and calculated structure factors, and CIF, respectively. Deposit items are available two ways: for paper copies contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the *American Mineralogist* Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

160 “cavities” in each of its 4 faces. The capping VO_4 tetrahedron is located over one of these
161 cavities.

162 The interstitial unit has the formula $[\text{Pb}_3\text{Ca}_3\cdot 20\text{H}_2\text{O}]^{12+}$, which exactly balances the charge
163 on the structural unit and confirms the 5+ charges on all V and As in the structural unit (Table 5).
164 The Pb site is located above each of the three remaining cavities in the mono-capped Keggin
165 anion. Pb is in lopsided 9 coordination, with six bonds, 3 short (2.28-2.33Å) and 3 long (3.29-
166 3.38Å), to O atoms in one mono-capped Keggin anion and 3 other long bonds (2.82-3.00Å) to an
167 adjacent mono-capped Keggin anion. A 10th much longer Pb-O bond (3.62Å) is to the partially
168 occupied OW28a in the interstitial unit. The Pb-O bonds link the Keggin anions into a thick layer
169 parallel to {001}. The two half-occupied Ca sites in the interstitial unit do not have regular
170 coordinations. They are at reasonable distances for bonds to O sites in the Keggin anions and to
171 H_2O sites in the interstitial unit and thereby serve to link the layers in the [001] direction (bond
172 valences given in Table 5). However, the Ca sites surround the 3-fold axis and appear to be
173 missing a coordinating O site on that axis. Some residual electron density in this region could
174 represent highly disordered O sites, but none could be successfully refined.

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

182

183

IMPLICATIONS

184 Many complex polyoxometalate anions have been synthesized, and they have been shown
185 to have a remarkable array of technological and biochemical uses (cf. Cronin and Müller 2012;
186 Song and Tsunashima 2012). The most widely known heteropoly anion is the Keggin anion, for
187 which a very large body of literature exists because of its industrial utility. Capped Keggin
188 anions, in particular, have potential as building blocks for advanced materials or as components
189 for molecular devices (cf. Bakri et al. 2012). Until recently, minerals that contain the Keggin
190 anion were not known to occur, and kegginite is only the third discovered to date; it is the first
191 mineral containing a Keggin ϵ -isomer and appears to be the first phase, either natural or
192 synthetic, containing a mono-capped $[\text{As}^{5+}\text{V}^{5+}_{12}\text{O}_{40}(\text{VO})]^{12-}$ Keggin ϵ -isomer.

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

201 It is worth noting that the decavanadate isopolyanion, $[\text{V}^{5+}_{10}\text{O}_{28}]^{6-}$, including its
202 protonated and mixed-valence variants, is the most common polyanion found in the secondary
203 mineral assemblages of the sandstone-hosted uranium-vanadium deposits of the Uravan Mineral
204 Belt, as well as in similar deposits worldwide. The decavanadate anion is known to be quite
205 stable in acidic and oxidizing aqueous solutions. The mineralization in the Packrat mine is

206 unusual for having local enrichment in As, which is atypical of deposits in the Uravan Mineral
207 Belt. This, coupled with intermediate oxidizing conditions, has resulted in the formation of four
208 recently described minerals (vanarsite, packratite, morrisonite, and gatewayite; Kampf et al.
209 2015) containing the novel mixed-valence $[\text{As}^{3+}\text{V}^{4+,5+}_{12}\text{As}^{5+}_6\text{O}_{51}]$ heteropolyanion. Kegginite
210 formed in the same general assemblage, but apparently under more oxidizing conditions, as it
211 contains the mono-capped $[\text{As}^{5+}\text{V}^{5+}_{12}\text{O}_{40}(\text{VO})]^{12-}$ Keggin ϵ -isomer, in which all As and V is 5+.
212 The presence of As in the system is crucial to the formation of these very rare polyanions,
213 although it might be conjectured that a phosphate analogue of kegginite could be formed if P^{5+}
214 rather than As^{5+} is present.

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

221

222

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276

277

FIGURE CAPTIONS

278

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

280

281 **FIGURE 2.** Crystal drawing of kegginite; clinographic projection.

282

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

285

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

287

288 **TABLE 1.** Analytical results for kegginite.

289

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 ₂ O ₅	50.20	49.01–51.30	0.89	V metal	47.87
As ₂ O ₅	4.64	4.38–4.80	0.21	GaAs	4.42
H ₂ O*	15.30				14.59
Total	104.88				100.01

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

290

291

292 **TABLE 2.** Calculated powder X-ray diffraction data (*d* in Å) for kegginite.

<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>	<i>I</i>	<i>d</i>	<i>hkl</i>
89	15.8460	0 0 1	9	3.0779	1 2-4	1	2.1661	2 3-5	2	1.7658	3 4 5
100	12.9350	1 0 0	5	2.9940	4 0 2	1	2.1562	2 2 6	2	1.7442	3 5-3
43	10.0204	1 0 1	10	2.9677	3 1 3	1	2.1361	6 0 1	2	1.7338	5 2 5
7	6.7554	1 1-1	18	2.9168	2 3 1	2	2.1268	3 1 6	3	1.7133	7 1 0
2	6.4675	2 0 0	2	2.8459	2 0 5	3	2.1078	4 1-5	2	1.7033	7 1-1
4	5.9879	0 2 1	2	2.8226	4 1 0	3	2.0803	2 4 4	1	1.6888	4 4 4
3	5.4344	1 1-2	7	2.7790	2 3-2	1	2.0713	2 5 0	2	1.6746	3 5-4
2	5.2820	0 0 3	7	2.7579	0 4 3	4	2.0538	3 4-2	1	1.6701	0 6 6
1	5.0102	0 2 2	8	2.6593	1 2 5	2	2.0040	1 5-4	1	1.6565	1 2 9
3	4.8890	2 1 0	1	2.6410	0 0 6	1	1.9960	6 0 3	2	1.6475	2 3-8
3	4.6717	1 2 1	1	2.5871	2 3-3	3	1.9726	3 4-3	1	1.6298	5 2 6
5	4.3124	1 1-3	2	2.5051	0 4 4	1	1.9575	1 6 1	1	1.5963	5 3 5
8	4.1606	1 2 2	2	2.4899	1 1 6	1	1.9356	4 2-5	1	1.5804	1 6 6
2	3.7872	0 3 2	1	2.4450	2 0 6	1	1.9283	5 2-3	1	1.5725	7 2-1
1	3.6345	2 2 1	1	2.4159	2 4 1	1	1.9144	3 1-7	1	1.5501	1 1 10
6	3.5879	1 2 3	1	2.3749	3 3 2	1	1.8936	6 0 4	1	1.5389	2 4-8
9	3.4990	3 1-1	1	2.3358	4 2 2	2	1.8736	3 4 4	1	1.5280	5 4 4
3	3.3777	2 2-2	2	2.3236	2 1 6	1	1.8545	4 0 7	1	1.5139	8 1 0
1	3.3401	3 0 3	1	2.2988	4 1 4	1	1.8481	0 5 6	2	1.5071	8 1 1
6	3.2681	3 1-2	1	2.2637	0 0 7	2	1.8354	3 5 1	1	1.4773	4 6-1
1	3.2337	4 0 0	1	2.2293	1 5 2	3	1.7996	3 5 2	1	1.4678	2 7 4
5	3.1684	4 0 1	1	2.2184	4 2-3	1	1.7825	0 6 5	1	1.4493	6 3-5

293

294

295 **TABLE 3.** Data collection and structure refinement details for kegginite.

296	Diffractometer	Rigaku R-Axis Rapid II
297	X-ray radiation / power	MoK α ($\lambda = 0.71075 \text{ \AA}$)/50 kV, 40 mA
298	Temperature	293(2) K
299	Structural Formula	Pb ₃ (Ca _{2.43} Mg _{0.57}) Σ 3.00[AsV ₁₂ O ₄₀ (VO)]·19.62H ₂ O
300	Space group	<i>P</i> -3
301	Unit cell dimensions	<i>a</i> = 14.936(5) \AA
302		<i>c</i> = 15.846(5) \AA
303	<i>V</i>	3061(2) \AA^3
304	<i>Z</i>	2
305	Density (for above formula)	2.690 g cm ⁻³
306	Absorption coefficient	10.958 mm ⁻¹
307	<i>F</i> (000)	2315.3
308	Crystal size	110 × 90 × 10 μm
309	θ range	3.02 to 20.11°
310	Index ranges	-14 ≤ <i>h</i> ≤ 12, -12 ≤ <i>k</i> ≤ 14, -15 ≤ <i>l</i> ≤ 15
311	Refls collected / unique	8481 / 1889; <i>R</i> _{int} = 0.112
312	Reflections with <i>F</i> _o > 4 σ <i>F</i>	1356
313	Completeness to $\theta = 20.11^\circ$	97.5%
314	Max. and min. transmission	0.958 and 0.725
315	Refinement method	Full-matrix least-squares on <i>F</i> ²
316	Parameters / restraints	257 / 0
317	GoF	1.052
318	Final <i>R</i> indices [<i>F</i> _o > 4 σ <i>F</i>]	<i>R</i> ₁ = 0.0640, <i>wR</i> ₂ = 0.1498
319	<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0951, <i>wR</i> ₂ = 0.1676
320	Largest diff. peak / hole	+1.58 / -1.27 e/ \AA^3
321	* <i>R</i> _{int} = $\Sigma F_o^2 - F_o^2(\text{mean}) /\Sigma[F_o^2]$. GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. <i>R</i> ₁ = $\Sigma F_o - F_c /\Sigma F_o $. <i>wR</i> ₂	
322	= $\{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where <i>a</i> is 0.0862, <i>b</i> is 43.2287	
323	and <i>P</i> is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.	
324		

325 **TABLE 4.** Atom coordinates and displacement parameters (\AA^2) for kegginite.

326		x/a	y/b	z/c	U_{eq}	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
327	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)
328	Ca1*	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)
329	Ca2*	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)
330	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)
331	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)
332	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)
333	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)
334	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)
335	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)
336	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)
337	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)
338	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)
339	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)
340	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)
341	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)
342	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)
343	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)
344	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)
345	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)
346	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)
347	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)
348	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)
349	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)
350	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)
351	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)
352	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)

353	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)
354	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)
355	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)
356	OW6*	0.053(4)	-0.081(4)	0.675(3)	0.13(3)						
357	OW7a*	0.732(4)	0.668(4)	0.857(3)	0.11(3)						
358	OW7b*	0.763(7)	0.731(7)	0.771(7)	0.16(6)						
359	OW8a*	0.917(6)	0.766(6)	0.598(6)	0.15(5)						
360	OW8b*	0.918(5)	0.809(6)	0.527(6)	0.10(4)						

361 * Occupancies: Ca1: Ca_{0.43}Mg_{0.07}; Ca2: Ca_{0.38}Mg_{0.12}; OW6: 0.55(7); OW7a: 0.53(7); OW7b: 0.36(8); OW8a: 0.44(9); OW8b: 0.33(8).

362

363

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

365	Pb-	Distance	BVS	V2-	Distance	BVS
366	O11	2.282(15)	0.63	O5	1.631(15)	1.59
367	O10	2.295(15)	0.61	O9	1.811(15)	0.98
368	O15	2.333(16)	0.55	O9	1.884(15)	0.80
369	O5	2.816(15)	0.15	O10	1.920(15)	0.73
370	O6	2.863(17)	0.13	O11	1.986(15)	0.61
371	O11	3.001(14)	0.09	O1	2.378(18)	0.21
372	Mean/Sum	2.598	2.16	Mean/Sum	1.935	4.92
373						
374	Ca1-	Distance	BVS	V3-	Distance	BVS
375	OW1	2.35(3)	0.36	O6	1.602(16)	1.72
376	O8	2.58(2)	0.19	O10	1.881(16)	0.81
377	OW4	2.60(4)	0.18	O11	1.885(15)	0.80
378	OW2	2.66(3)	0.15	O13	1.891(16)	0.79
379	O3	2.77(3)	0.11	O12	1.899(16)	0.77
380	OW3	2.78(4)	0.11	O2	2.413(17)	0.19
381	Mean/Sum	2.623	1.10	Mean/Sum	1.929	5.08
382						
383	Ca2-	Distance	BVS	V4-	Distance	BVS
384	OW2	2.31(3)	0.40	O7	1.623(17)	1.63
385	OW1	2.39(3)	0.32	O12	1.793(16)	1.03
386	OW3	2.64(4)	0.16	O14	1.862(17)	0.85
387	OW7A	2.68(6)	0.14	O15	1.887(16)	0.80
388	OW4	2.90(4)	0.08	O4	2.141(17)	0.40
389	O3	2.94(3)	0.07	O2	2.307(16)	0.26
390	Mean/Sum	2.643	1.17	Mean/Sum	1.936	4.97
391						
392	As-	Distance	BVS	V5-	Distance	BVS
393	O1	1.66(3)	1.32	O8	1.600(18)	1.73
394	O2(x3)	1.718(16)	1.14	O13	1.773(17)	1.08
395	Mean/Sum	1.704	4.74	O14	1.803(18)	1.00
396				O15	1.900(16)	0.77
397	V1-	Distance	BVS	O4	2.089(17)	0.46
398	O3	1.64(3)	1.56	O2	2.317(16)	0.25
399	O4(x3)	1.785(16)	1.05	Mean/Sum	1.914	5.29
400	Mean/Sum	1.749	4.71			
401	Bond valences are based on Brese and O'Keeffe (1991).					

Figure 1

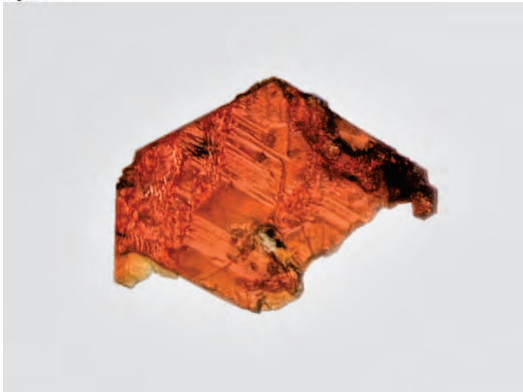


Figure 2

