Beckettite, $\text{Ca}_2\text{V}_6\text{Al}_6\text{O}_{20}$, a new mineral in a Type A refractory inclusion from Allende and clues to processes in the early solar system

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Abstract—Beckettite ($\text{Ca}_2\text{V}_6\text{Al}_6\text{O}_{20}$; IMA 2015-001) is a newly discovered refractory mineral, occurring as micrometer-sized grains intergrown with hibonite and perovskite, and surrounded by secondary grossular, anorthite, coulsonite, hercynite, and corundum. It occurs within highly altered areas in a V-rich, Type A Ca-Al-rich inclusion (CAI), A-WP1, from the Allende CV3 carbonaceous chondrite. The type beckettite has an empirical formula of $(\text{Ca}_{1.99}\text{Na}_{0.01})(\text{V}^{3+}_{3.47}\text{Al}_{1.40}\text{Ti}^{4+}_{0.57}\text{Mg}_{0.25}\text{Sc}_{0.08}\text{Fe}^{2+}_{0.04})(\text{Al}_{5.72}\text{Si}_{0.28})\text{O}_{20}$, with a triclinic structure in space group $P\bar{1}$ and cell parameters $a = 10.367 \text{ \AA}$, $b = 10.756 \text{ \AA}$, $c = 8.895 \text{ \AA}$, $\alpha = 106.0^\circ$, $\beta = 96.0^\circ$, $\gamma = 124.7^\circ$, $V = 739.7 \text{ \AA}^3$, and $Z = 2$, which leads to a calculated density of 3.67 g cm^{-3} . Beckettite's general formula is $\text{Ca}_2(\text{V}, \text{Al}, \text{Ti}, \text{Mg})_6\text{Al}_6\text{O}_{20}$ and the endmember formula is $\text{Ca}_2\text{V}_6\text{Al}_6\text{O}_{20}$. Beckettite is slightly ^{16}O -depleted ($\Delta^{17}\text{O} = -16 \pm 2\text{‰}$) compared to the coexisting hibonite and spinel $-24 \pm 2\text{‰}$. Beckettite is a primary high-temperature mineral resulting from igneous crystallization of an ^{16}O -rich V-rich CAI melt together with V-bearing hibonite, perovskite, burnettite, spinel, and paqueite. Subsequently, beckettite experienced an incomplete isotope exchange with an ^{16}O -poor aqueous fluid ($\Delta^{17}\text{O} = -3 \pm 2\text{‰}$) on the Allende parent asteroid.

INTRODUCTION

Calcium-aluminum-rich inclusions (CAIs) in carbonaceous chondrites are the oldest objects formed in the solar system and, therefore, preserve a history of its origin and early evolution. The constituent minerals in CAIs provide most of the information on their formation environments. Within this context, new minerals in CAIs are of particular interest because they either sampled special environments not encountered by most inclusions (e.g., Ma et al., 2011) or because they represent responses to aspects of an environment that was encountered by other phases but poorly recorded (e.g., Ma et al., 2014).

During a nanomineralogy investigation of the Allende CV3 (Vigarano type) carbonaceous chondrite, three new minerals, paqueite ($\text{Ca}_3\text{TiSi}_2[\text{Al}_2\text{Ti}]\text{O}_{14}$), burnettite ($\text{CaV}^{3+}\text{AlSiO}_6$), and beckettite ($\text{Ca}_2\text{V}^{3+}_6\text{Al}_6\text{O}_{20}$), were discovered in a V-rich, Type A CAI A-WP1 ($0.6 \times 1 \text{ mm}$

in size) in thin section USNM 7617. The CAI was previously studied by Paque (1985, 1989) and Paque et al. (1986, 1994, 2008). Beckettite is a new vanadium aluminate mineral of the warkite group within the sapphirine supergroup. This phase was previously described as an unknown phase in A-WP1 based on electron probe microanalysis (EPMA; Paque, 1985). In this paper, we describe beckettite and consider its origin and implications for the evolution of the V-rich CAI in the early solar system. Preliminary results of this work are given by Ma et al. (2016). Beckettite is one of 19 new minerals discovered in Allende since 2007 (Ma & Beckett, 2021).

MINERAL NAME AND TYPE MATERIAL

The new mineral beckettite (IMA 2015-001) has been approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (Ma et al., 2015). It is named

Fig. 1. Backscatter electron (BSE) images of the Type A CAI A-WP1 from Allende in USNM 7617. Beckettite is found in alteration regions of melilite outlined in (a); these are shown in detail in (b–d). The coulsonite+hercynite grains from (b) and (c) are shown in greater detail in Fig. 4. (Color figure can be viewed at wileyonlinelibrary.com.)

in honor of John R. Beckett (b. 1954), a cosmochemist at the California Institute of Technology, for his many contributions to research on CAIs in carbonaceous chondrites.

The holotype beckettite occurs in a polished section of Allende in the Type A CAI A-WP1, which is deposited under catalog # USNM 7617 in the Smithsonian Institution's National Museum of Natural History, Washington, DC, United States.

ANALYTICAL TECHNIQUES

EPMA, scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD) were used to characterize the chemical composition and structure of the new mineral and its associated phases. EPMA was conducted on a JEOL 8200 electron microprobe using

the Probe for EPMA program from Probe Software, Inc. operated at 10 kV and 5 or 10 nA, in order to minimize activation volumes. Anorthite ($\text{SiK}\alpha$, $\text{AlK}\alpha$, $\text{CaK}\alpha$), albite ($\text{NaK}\alpha$), fayalite ($\text{FeK}\alpha$), forsterite ($\text{MgK}\alpha$), TiO_2 ($\text{TiK}\alpha$), V_2O_5 ($\text{VK}\alpha$), and ScPO_4 ($\text{ScK}\alpha$) were used as standards and analyses were processed using the CITZAF correction procedure of Armstrong (1995). We also obtained backscatter electron images (BSE) and analyzed grains using an Oxford X-Max 80mm² SDD X-ray energy-dispersive spectrometer (EDS) mounted on a ZEISS 1550 VP field emission SEM with data processed using the XPP correction procedure of Pouchou and Pichoir (1991) and Oxford factory internal standards. EBSD was also conducted on the SEM using an HKL (now Oxford) EBSD system. Section USNM 7617 was vibro-polished and the SEM was operated at 20 kV and 4 nA for these measurements, with the

Table 1. EPMA data for type beckettite and associated primary phases in A-WP1.

Constituent wt%	Beckettite		Hibonite		Spinel		Perovskite	
	<i>n</i> = 5	SD	<i>n</i> = 15	SD	<i>n</i> = 3	SD	<i>n</i> = 5	SD
SiO ₂	2.02	0.03	0.15	0.21	0.17	0.06	0.38	0.33
TiO ₂	5.54	0.07	5.89	0.75	0.06	0.08	54.73	0.17
Ti ₂ O ₃	4.48							
Al ₂ O ₃	44.14	0.29	80.64	1.06	61.41	1.54	0.68	0.12
FeO	0.35	0.14	0.27	0.16	17.42	0.81	b.d.	
MgO	1.22	0.03	3.02	0.33	14.84	0.29	b.d.	
CaO	13.58	0.15	8.08	0.12	0.16	0.04	39.42	0.23
Na ₂ O	0.04	0.01	b.d.		0.06	0.02	b.d.	
V ₂ O ₃	31.60	0.10	1.86	0.21	4.27	1.75	4.79	0.16
Sc ₂ O ₃	0.70	0.03	0.15	0.03	b.d.		0.13	0.07
Total	99.19		100.10		98.38		100.13	
No. O atoms	20		19		4		4	
Si	0.28		0.02		0.00		0.01	
Ti ⁴⁺	0.57		0.50		0.00		0.93	
Ti ³⁺	0.52							
Al	7.12		10.78		1.92		0.02	
Fe	0.04		0.03		0.39			
Mg	0.25		0.51		0.59			
Ca	1.99		0.98		0.00		0.95	
Na	0.01				0.00			
V ³⁺	3.47		0.17		0.09		0.09	
Sc	0.08		0.01				0.00	
Cation sum	13.81		13.00		2.99		2.00	

n = number of analyses.

SD = one standard deviation of the mean based on all of the analyses.

b.d. = below detection limit, Na 0.03 wt%, Sc 0.03 wt%, Fe 0.06 wt%, Mg 0.02 wt%.

focused beam and a 70° tilt stage and in variable pressure mode (25 Pa of N₂ gas in the chamber). The EBSD system was calibrated using a single crystal silicon standard. Methods used for EBSD are described in detail by Ma and Rossman (2008, 2009). Micro-Raman analysis was carried out with a Renishaw inVia™ Qontor Raman microscope using a green laser (514 nm) averaging five scans at ~1.0 mW power on the sample.

Oxygen isotopic compositions of spinel, hibonite, and beckettite in the Allende CAI A-WP1 were analyzed with the University of Hawai'i Cameca ims-1280 secondary ion mass spectrometer (SIMS or ion microprobe). A primary Cs⁺ ion beam of ~25 pA focused to ~2 μm was used. Prior to oxygen isotopic measurements, the grains of interest were marked by electron beam using JEOL LV5900 SEM at the University of Hawai'i (for details, see Nagashima et al., 2015). The ion microprobe was operated at -10 keV with a 50 eV energy window. Three oxygen isotopes were measured simultaneously: ¹⁶O⁻ was measured on a Faraday cup, and ¹⁷O⁻ and ¹⁸O⁻ were measured on electron multipliers. The mass resolving power (*m*/*Δm*) for ¹⁶O⁻ and ¹⁸O⁻ was ~2000, and that for ¹⁷O⁻ was ~5500, sufficient to separate interfering ¹⁶OH⁻. A normal incidence electron flood gun was used for charge compensation. ¹⁶OH⁻ signal was monitored after

each measurement. Contribution of ¹⁶OH⁻ onto ¹⁷O⁻ was corrected based on a peak/tail ratio. The correction was typically <0.05%. Instrumental fractionation for all minerals measured was corrected using Burma spinel. Oxygen-isotope compositions are reported as δ¹⁷O and δ¹⁸O, deviations from Vienna Standard Mean Ocean Water (VSMOW; ¹⁷O/¹⁶O_{VSMOW} = 0.000380; ¹⁸O/¹⁶O_{VSMOW} = 0.002005; De Laeter et al., 2003) in parts per thousand: δ^{17,18}O_{SMOW} = ([^{17,18}O/¹⁶O_{sample}]/[^{17,18}O/¹⁶O_{VSMOW}] - 1) × 1000, and as deviation from the terrestrial fractionation line, Δ¹⁷O = δ¹⁷O - 0.52 × δ¹⁸O. Because no matrix-matched standards were used for beckettite and hibonite, only their Δ¹⁷O values should be considered. To verify the positions of the sputtered regions, the spots analyzed for oxygen isotopes were studied with secondary and BSE images using the ZEISS 1550 VP field emission SEM before and after SIMS measurements (Fig. S1 in supporting information).

RESULTS

Occurrence and Appearance

Ca-Al-rich inclusion A-WP1 consists of melilite, spinel, perovskite, grossmanite-davisite, hibonite, pakeite,

Fig. 2. (Left) EBSD patterns of two beckettite crystals in Fig. 1, and (right) the patterns indexed with the $P\bar{1}$ rhönite structure. (Color figure can be viewed at wileyonlinelibrary.com.)

Fig. 3. Raman spectrum of the type beckettite in Fig. 1d.

burnettite, beckettite, grossite, baghdadite, and refractory metal grains. Melilite is replaced to various degrees by secondary anorthite, grossular, nepheline, and sodalite; minor secondary phases include coulsonite, hercynite, and corundum. Beckettite occurs as irregular crystals, 4–8 μm in size, with hibonite and perovskite, in highly altered areas of A-WP1 containing secondary grossular, anorthite, coulsonite, hercynite, and corundum (Fig. 1).

Color, luster, streak, hardness, tenacity, cleavage, fracture, density, and optical properties of beckettite could not be determined experimentally because of the small grain size. The density, calculated from its crystal structure and the empirical formula, as described below, is 3.67 g cm^{-3} . Beckettite is not cathodoluminescent under the electron beam and we observed no crystal forms or twinning.

Composition and Crystal Structure

Chemical analyses of beckettite and associated phases were carried out using the JEOL 8200 electron microprobe as described above and analytical results are given in Table 1. Beckettite shows an empirical formula (based on 20 oxygen atoms per formula unit) of $(\text{Ca}_{1.99}\text{Na}_{0.01})(\text{V}^{3+}_{3.47}\text{Al}_{1.40}\text{Ti}^{4+}_{0.57}\text{Mg}_{0.25}\text{Sc}_{0.08}\text{Fe}^{2+}_{0.04}) (\text{Al}_{5.72}\text{Si}_{0.28})\text{O}_{20}$. The general formula is $\text{Ca}_2(\text{V}, \text{Al}, \text{Ti}, \text{Al}, \text{Mg})_6\text{Al}_6\text{O}_{20}$ and the endmember formula is $\text{Ca}_2\text{V}_6\text{Al}_6\text{O}_{20}$.

Beckettite grains are invariably found in the central portions of alteration regions composed of fine-grained secondary corundum + grossular(?), often in contact with primary V-rich hibonite (~1.86 wt% V_2O_3) and V-rich perovskite (~4.79 wt% V_2O_3) (Fig. 1). Spinel inclusions in melilite are relatively V-rich (~2 wt%), but

Fig. 4. BSE images showing (a) coulsonite and hercynite with hibanite and grossular, (b) coulsonite and hercynite with corundum. (Color figure can be viewed at wileyonlinelibrary.com.)

the most V-rich refractory phase in this CAI is burnettite (a new V-clinopyroxene with 9.35 wt% V_2O_3 and 6.89 wt% Sc_2O_3), occurring as one microcrystal in melilite (Ma & Beckett, 2016).

The EBSD patterns for type beckettite can be indexed only by the $P\bar{1}$ aenigmatite structure and give best fits using the Allende rhönite structure from Bonaccorsi et al. (1990) (Fig. 2), with a mean angular deviation of $0.38\text{--}0.46^\circ$. Beckettite has Space Group: $P\bar{1}$, showing $a = 10.367 \text{ \AA}$, $b = 10.756 \text{ \AA}$, $c = 8.895 \text{ \AA}$, $\alpha = 106.0^\circ$, $\beta = 96.0^\circ$, $\gamma = 124.7^\circ$, $V = 739.7 \text{ \AA}^3$, and $Z = 2$. X-ray powder diffraction data (Table S1, in $\text{\AA}$ for $CuK\alpha_1$, Bragg–Brentano geometry) were calculated from the cell parameters of Bonaccorsi et al. (1990) and the empirical formula from this work, using Powder Cell version 2.4. Raman spectrum of the type beckettite shows board bands at 145, 200, 440, 575, and 770 cm^{-1} (Fig. 3).

Associated Minerals

The inclusion also contains primary highly gehlenitic melilite (Ak_{6-15}), spinel, perovskite, paqueite, burnettite, grossmanite–davisite, hibanite, grossite, baghdadite, and refractory (platinum group element) metal grains. Baghdadite $\text{Ca}_3(\text{Zr,Ti})\text{Si}_2\text{O}_9$ in A-WP1 is the first meteoritic occurrence of this phase (Ma, 2018). Alteration minerals include grossular, anorthite, coulsonite, hercynite, corundum, nepheline, and sodalite (Paque, 1985; this study). Coulsonite identified here is the first confirmed meteoritic occurrence. Coulsonite $(\text{Fe}_{0.88}\text{Mg}_{0.12})(\text{V}_{1.18}\text{Al}_{0.82})\text{O}_4$ forms by exsolution from hercynite $(\text{Fe}_{0.61}\text{Mg}_{0.41})(\text{Al}_{1.84}\text{V}_{0.15})\text{O}_4$ surrounded by corundum + grossular (?) (Fig. 4).

Table 2. Oxygen isotopic compositions of spinel, hibanite, and beckettite in the Allende Type A CAI A-WP1.

Mineral	$\delta^{18}\text{O}$	2σ	$\delta^{17}\text{O}$	2σ	$\Delta^{17}\text{O}$	2σ
Spinel	−41.5	± 1.1	−46.2	± 2.4	−24.6	± 2.4
Beckettite	−26.2	± 1.1	−29.8	± 2.0	−16.1	± 2.0
Hibanite	−42.8	± 1.2	−46.4	± 2.3	−24.2	± 2.3

Oxygen Isotopic Compositions

Oxygen isotopic compositions of beckettite, hibanite, and spinel are given in Table 2 and shown in Fig. 5. Spinel and hibanite have close-to-solar oxygen isotopic compositions ($\Delta^{17}\text{O} = -24 \pm 2\frac{1}{2}$). Beckettite is slightly ^{16}O -depleted ($\Delta^{17}\text{O} = -16 \pm 2\frac{1}{2}$) relative to spinel and hibanite.

DISCUSSION

Beckettite, $\text{Ca}_2\text{V}_6\text{Al}_6\text{O}_{20}$, is not only a new mineral but, to our best knowledge, also a new material that has never been synthesized. It is a new member of the sapphirine supergroup and the V^{3+} -dominant analog of the recently described refractory minerals warkite ($\text{Ca}_2\text{Sc}_6\text{Al}_6\text{O}_{20}$; Ma et al., 2020) and addibischhoffite ($\text{Ca}_2\text{Al}_6\text{Al}_6\text{O}_{20}$; Ma et al., 2017). Both warkite and addibischhoffite are high-temperature primary minerals formed by gas–solid condensation and/or crystallization from CAI melts (Ma et al., 2017, 2020). The only known occurrence of addibischhoffite is in the CAI 1580-1-8 from the CH3.0 chondrite Acfer 214, where it coexists with hibanite, perovskite, kushiroite, Ti-kushiroite, spinel, and melilite; addibischhoffite and hibanite are similarly ^{16}O -rich

Fig. 5. Three-isotope oxygen diagram of the primary minerals (beckettite, hibonite, and spinel) in the Allende CAI A-WP1 (this study) and of the secondary minerals in the Allende coarse-grained igneous CAIs (data from Krot et al., 2021). The secondary minerals resulted from metasomatic alteration, mainly of the primary melilite and anorthite, by an aqueous fluid on the Allende parent asteroid; these have ^{16}O -poor compositions. Most secondary minerals plot along mass-dependent fractionation line with a slope of ~ 0.5 and $\Delta^{17}\text{O}$ of $\sim -3\frac{1}{2}$, which corresponds to $\Delta^{17}\text{O}$ of the Allende aqueous fluid. In contrast, hibonite and spinel in A-WP1 have close-to-solar ^{16}O -rich compositions ($\Delta^{17}\text{O} \sim -24\frac{1}{2}$) corresponding to that of the gaseous reservoir in the CAI-forming region. Beckettite is slightly ^{16}O -depleted ($\Delta^{17}\text{O} \sim -16\frac{1}{2}$) relative to hibonite and spinel, suggesting it experienced an incomplete oxygen-isotope exchange with the Allende aqueous fluid. CCAM = carbonaceous chondrite anhydrous mineral line (Clayton et al., 1977); PCM = primitive chondrule mineral line (Ushikubo et al., 2012); TF = terrestrial fractionation line. Oxygen isotopic compositions of the Allende aqueous fluid and of the Sun are from Krot et al. (2021) and McKeegan et al. (2011), respectively. (Color figure can be viewed at wileyonlinelibrary.com.)

($\Delta^{17}\text{O} \sim -24\frac{1}{2}$; Ma et al., 2017). Warkite was described in CAIs from several groups of carbonaceous chondrites: CH, CO, CM, and CV, where it coexists with perovskite or kankite, Sc-diopside and/or davisite, spinel, melilite, hibonite, eringaite, and grossite. In unmetamorphosed CM, CH, and CO chondrites (petrologic type 2–3.0), warkite has close-to-solar oxygen isotopic composition ($\Delta^{17}\text{O} \sim -24\frac{1}{2}$). In metamorphosed CO and CV chondrites (petrologic type >3.0), warkite is ^{16}O -depleted to various degrees ($\Delta^{17}\text{O}$ up to $-1\frac{1}{2}$), suggesting post-crystallization isotope exchange with an ^{16}O -depleted gaseous reservoir, either in the solar nebula or, most likely, during aqueous fluid–rock interaction on the CO and CV chondrite parent asteroids (Ma et al., 2020).

Beckettite is probably also a primary, high-temperature (igneous?) mineral formed contemporaneously with the crystallization of V-rich pyroxenes (burnettite, grossmanite–davisite), V-bearing hibonite, spinel, and perovskite. This interpretation is consistent with (i) the observed intergrowths of beckettite with perovskite and hibonite (Figs. 1b and 1c), (ii) relatively large grain sizes of beckettite compared to the surrounding fine-grained secondary grossular and corundum, and (iii) high titanium content in beckettite: titanium is generally not mobile during the relatively low-temperature ($\sim 300^\circ\text{C}$) metasomatic alteration experienced by Allende (Krot et al., 2021). We note, however, that secondary titanium-rich garnet (hutchinsonite, $\text{Ca}_3\text{Ti}_2[\text{SiAl}_2]\text{O}_{12}$) in association with grossular and wadalite/adrianite has been described in a coarse-grained igneous CAI from Allende (Ma & Krot, 2014). Therefore, the above mineralogical observations do not allow us to exclude a secondary (metasomatic) origin of beckettite, which is found exclusively in alteration regions of A-WP1, where melilite is replaced by corundum and grossular(?), for example,

If beckettite is a secondary mineral, it could have formed contemporaneously with other V-bearing secondary minerals—coulsonite and hercynite. In this case, the source of vanadium could have been burnettite, because other V-bearing primary minerals, hibonite, perovskite, and spinel, show no clear evidence for alteration (Figs. 1b and 1c). Schematically, this reaction can be expressed as:

The oxygen isotopic composition of beckettite allows us to clarify its origin. If beckettite resulted from the metasomatic alteration of primary minerals, its $\Delta^{17}\text{O}$ value should be close to $\Delta^{17}\text{O}$ for the Allende aqueous fluid. If beckettite co-crystallized with hibonite and spinel, all three minerals should have similar $\Delta^{17}\text{O}$, unless beckettite experienced a post-crystallization O-isotope exchange, for example, warkite in CAIs from CV chondrites (Ma et al., 2020). Spinel and hibonite in CV CAIs have typically ^{16}O -rich compositions and show no evidence for O-isotope exchange (Yurimoto et al., 2008).

Most secondary minerals replacing melilite and $\pm$ anorthite in the Allende CAIs have ^{16}O -poor compositions (Krot et al., 2021) and, on a three-isotope oxygen diagram, plot along a mass-dependent fractionation line with $\Delta^{17}\text{O}$ of $\sim -3 \pm 2\frac{1}{2}$ that corresponds to $\Delta^{17}\text{O}$ of the Allende aqueous fluid (Fig. 5). In contrast, hibonite, spinel, and beckettite in A-WPI are strongly ^{16}O -enriched compared to the secondary minerals (Fig. 5): Hibonite and spinel have close-to-solar $\Delta^{17}\text{O}$ ($\sim -24 \pm 2\frac{1}{2}$), whereas beckettite is only slightly ^{16}O -depleted ($\Delta^{17}\text{O} \sim -16 \pm 2\frac{1}{2}$). We infer that beckettite co-crystallized with hibonite and spinel originally from an ^{16}O -rich CAI melt, but subsequently experienced partial isotope exchange with the Allende aqueous fluid.

CONCLUDING REMARKS

The identification of new minerals, such as beckettite, provides us with further insight into the formation and evolution of CAIs, including their high-temperature crystallization in the solar nebula and secondary alteration processes on the chondrite parent bodies. It is only with an understanding of these processes that we can put together a history of the formation of chondritic components, their accretion into planetesimals, and subsequent thermal processing.

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SUPPORTING INFORMATION

Additional supporting information may be found in the online version of this article.

Fig S1. BSE image showing SIMS pits on beckettite, hibonite, and spinel in the Allende CAI *A-WPI*.

Table S1. Calculated X-ray powder diffraction data for beckettite ($I_{\text{rel}} > 1$).