KOKINOSITE, Na₂Ca₂(V₁₀O₂₈)•24H₂O, A NEW DECAVANADATE MINERAL SPECIES FROM THE ST. JUDE MINE, COLORADO: CRYSTAL STRUCTURE AND DESCRIPTIVE MINERALOGY

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Abstract

Kokinosite, Na₂Ca₂(V₁₀O₂₈)•24H₂O, is a new mineral species from the St. Jude mine, Slick Rock district, San Miguel County, Colorado, USA. Kokinosite typically occurs as tablets or blades up to 0.05 mm thick, with stepped faces, and 1 mm in maximum dimension. Crystals are yellow orange, although sometimes they are tinted orange brown; the streak of the phase is yellow. The luster of kokinosite is subadamantine, and the mineral is transparent; it does not fluoresce in short- or long-wave radiation. The Mohs hardness is ca. 1½. Kokinosite possesses a brittle tenacity, and displays one good cleavage on $\{01\overline{1}\}$. No parting was observed, and fracture is irregular. Density (calc.) = 2.353 g cm⁻³ on the basis of the empirical formula and the single-crystal cell data. Kokinosite is biaxial (-), with α 1.725(3), β 1.770(5), and γ 1.785(3). The 2V was measured as 56.6(3)° from extinction data, and $2V_{calc} = 58.7^{\circ}$. Dispersion is r < v, moderate. The optic orientation was incompletely determined, with X ^ a = 15°, $Y \approx \mathbf{b}$. The mineral is pleochroic: X, Z = orange yellow, Y = orange, and X = Z < Y. Electron probe microanalysis and the crystal structure solution gave the empirical formula (based on V = 10 and O = 52 apfu) $(Na_{1.88}K_{0.01})_{\Sigma_{1.89}}(Ca_{1.81}Sr_{0.12})_{\Sigma_{1.93}}(V_{10}O_{28})\bullet 24H_2O$. The simplified structural formula is Na₂Ca₂($V_{10}O_{28}$)•24H₂O. Kokinosite is triclinic, $P\overline{1}$, with a 8.74899(19), b 10.9746(3), c 12.8216(9)Å, α 114.492(8), β 105.093(7), γ 91.111(6)°, V 1070.25(11) Å³, and Z = 1. The strongest four lines in the diffraction pattern are [d in Å(I)(hkl)]: 9.88(100)(010, 011), 7.92(36)(101), 8.42(33)(100), and 6.01(31)(111, 110). The atomic arrangement of kokinosite was solved and refined to $R_1 = 0.0379$ for 3806 $F_0 > 4\sigma F$ reflections. The structural unit is a decavanadate polyanion, (V10O28)6-; charge balance in the structure is maintained by the [Na2Ca2(H2O)24]6+ interstitial unit that exists as Na(H2O)6 octahedra and Ca(H₂O)₈ polyhedra that link into chains by edge- and corner-sharing. The linkage between the structural unit and the interstitial unit occurs solely by hydrogen bonding. The new mineral is named in honor of Michael Kokinos (b. 1927) of Shingle Springs, California, a well-known mineral collector and member of the Micromounters' Hall of Fame.

Keywords: kokinosite, new mineral species, decavanadate, crystal structure, St. Jude mine, Gypsum Valley, San Miguel County, Colorado, USA

INTRODUCTION

The U and V (*Uravan*) deposits of Colorado and Utah have been a rich source of ore for the production of uranium, vanadium, and radium. Throughout the

Colorado Plateau Uravan Mineral Belt, uranium and vanadium minerals occur together in bedded or rollfront deposits in the sandstone of the Salt Wash member of the Jurassic Morrison Formation (Carter & Gualtieri 1965, Shawe 2011). The first production of uranium

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from the Colorado Plateau took place in the Slick Rock district, beginning around 1900; Shawe (2011) provides a comprehensive summary of the deposits of the Slick Rock district, and some of those details are recounted here.

Mining activity for uranium, vanadium, and radium in the Slick Rock district has been episodic, depending largely on the demand for the various ores. The last major period of mining occurred from 1949 to 1983, when uranium mining ended due to the large decline in the price of uranium ores. By the time mining activities ceased in the mid-1980s, 4,839,300 tons of uranium-vanadium ore had been produced in the Slick Rock district (Shawe 2011). With the resurgence of the price of uranium ore in 2007, several of the Slick Rock district mines reopened.

Collecting at the mines of the Slick Rock district by one of the authors (JM) has revealed numerous secondary vanadium minerals that result from oxidation of vanadium ore bodies that are exposed to near-surface conditions in the mining process. With the exception of martyite, $Zn_3(V_2O_7)(OH)_2 \bullet 2H_2O$ (Kampf & Steele 2008a), which contains the $(V_2O_7)^{4-}$ divanadate group, and dickthomssenite, $Mg(V_2O_6) \bullet 7H_2O$ (Hughes *et al.* 2001), and calciodelrioite, $Ca(VO_3)_2(H_2O)_4$ (Kampf *et al.* 2012a), which contain $(VO_3)^-$ vanadate chains, all of the recently described species contain the decavanadate anionic complex, $(V_{10}O_{28})^{6-}$, found in the pascoite family of minerals. All known minerals that contain the $(V_{10}O_{28})^{6-}$ decavanadate unit are listed in Table 1.

In addition to those minerals that contain the $(V_{10}O_{28})^{6-}$ decavanadate unit *sensu stricto*, the first minerals that contain protonated decavanadate groups have also been discovered in mines of the Colorado Plateau. The deposits have also yielded the first mineral

that contains a mixed-valence $(V_{10}O_{28})$ polyanion, the vanadylnonovanadate $\{(V^{4+}V^{5+}_{9})O_{28}\}$ group. The minerals that contain these variants of the decavanadate group and references thereto are also listed in Table 1.

Herein, we describe another new secondary mineral from the Uravan deposits. The new species was discovered in the St. Jude mine, Slick Rock district, San Miguel County, Colorado, USA. The mineral is named in honor of Michael (Mike) Kokinos (b. 1927) of Shingle Springs, California, U.S.A. Mike is a charter member of both the Southern California Micro-Mineralogists (SCMM) and the Northern California Mineralogical Association (NCMA), and is a member of the Micromounters' Hall of Fame; his collecting and his mentoring of others in the collecting community have led to the description of many new mineral species, and the naming of a new mineral in his honor is most appropriate.

The new mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2013–099). Six cotype specimens of kokinosite are deposited in the collections of the Natural History Museum of Los Angeles County, Los Angeles, California, USA, catalogue numbers 64004 (also a cotype for wernerbaurite), 64074, 64075, 64076, 64077, and 64078.

OCCURRENCE

Kokinosite was found in the St. Jude mine, Gypsum Valley, Slick Rock district, San Miguel County, Colorado, USA. The discovery site is a stope not far from the interconnected West Sunday and Sunday mines. All three mines are currently inactive and their entrances

A. {V ₁₀ O ₂₈ } ^{6–} Decavanadate	es
Na ₄ Mg(V ₁₀ O ₂₈) •24(H ₂ O)	Colombo et al. 2011
Na ₃ AI(V ₁₀ O ₂₈) •22(H ₂ O)	Rakovan et al. 2011
K ₂ Mg ₂ (V ₁₀ O ₂₈) •16H ₂ O	Hughes <i>et al.</i> 2002
Na ₂ Ca ₂ (V ₁₀ O ₂₈)•24H ₂ O	This work
Na ₂ Mg ₂ (V ₁₀ O ₂₈) •20H ₂ O	Hughes <i>et al</i> . 2008
MgCa ₂ (V ₁₀ O ₂₈) •16H ₂ O	Kampf & Steele 2008b
Ca ₃ (V ₁₀ O ₂₈) •17H ₂ O	Hughes <i>et al.</i> 2005
MgAl ₂ (V ₁₀ O ₂₈)(OH) ₂ •27H ₂ O	Kampf et al. 2012b
Na ₂ (H ₃ O) ₄ (V ₁₀ O ₂₈) •10H ₂ O	Kampf <i>et al</i> . 2013b
Ca ₂ (H ₃ O) ₂ (V ₁₀ O ₂₈) •16H ₂ O	Kampf et al. 2013b
B. {H _x V ₁₀ O ₂₈ } ^{(6-x)-} Protonated Deca	vanadates
Na ₄ (H ₂ V ₁₀ O ₂₈) •22H ₂ O	Kampf <i>et al</i> . 2011b
Na ₃ (H ₃ V ₁₀ O ₂₈) •15H ₂ O	Kampf <i>et al</i> . 2011a
Mixed-Valence {(V ⁴⁺ xV ⁵⁺ 10-x)O ₂₈ } ^{(6+x)-} V	anadylvanadate
Na ₃ Ca ₂ [(V ⁴⁺ V ⁵⁺ ₉)O ₂₈] •24H ₂ O	Kampf <i>et al</i> . 2013a
	A. $\{V_{10}O_{28}\}^{6-}$ Decavanadata Na ₄ Mg(V ₁₀ O ₂₈) •24(H ₂ O) Na ₃ Al(V ₁₀ O ₂₈) •22(H ₂ O) K ₂ Mg ₂ (V ₁₀ O ₂₈) •16H ₂ O Na ₂ Ca ₂ (V ₁₀ O ₂₈) •16H ₂ O Na ₂ Mg ₂ (V ₁₀ O ₂₈) •20H ₂ O MgCa ₂ (V ₁₀ O ₂₈) •16H ₂ O Ca ₃ (V ₁₀ O ₂₈) •17H ₂ O MgA ₂ (V ₁₀ O ₂₈) (OH) ² •27H ₂ O Na ₂ (H ₃ O) ₄ (V ₁₀ O ₂₈) •10H ₂ O Ca ₂ (H ₃ O) ₂ (V ₁₀ O ₂₈) •16H ₂ O B. {H _x V ₁₀ O ₂₈) •22H ₂ O Na ₃ (H ₃ V ₁₀ O ₂₈) •22H ₂ O Na ₃ (H ₃ V ₁₀ O ₂₈) •15H ₂ O Wixed-Valence {(V ⁴⁺ xV ⁵⁺ 10-x)O ₂₈) ^{(6+x)-} V Na ₃ Ca ₂ [(V ⁴⁺ V ⁵⁺ 9)O ₂₈] •24H ₂ O

TABLE 1. THE PASCOITE FAMILY OF MINERALS

are sealed. Kokinosite is rare; the mineral was found growing on a corvusite-montroseite-bearing sandstone block and is closely associated with gypsum, huemulite, metarossite, pascoite, rossite, and wernerbaurite (Kampf *et al.* 2013b). Other minerals found in the same area in the St. Jude mine include calciodelrioite (Kampf *et al.* 2012a), delrioite, hendersonite, hughesite (Rakovan *et al.* 2011), nashite (Kampf *et al.* 2013a), powellite, postite (Kampf *et al.* 2012b), and schindlerite (Kampf *et al.* 2013b). Other minerals found nearby in adjacent areas of the West Sunday mine are andersonite, gunterite (Kampf *et al.* 2011b), hewettite, munirite, natrozippeite, pyrite, rakovanite (Kampf *et al.* 2011a), sherwoodite, and tyuyamunite.

The 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 environments, water reacts with pyrite in the deposit to form aqueous solutions with relatively low pH. The various secondary vanadate phases that formed depend upon the Eh-pH and the presence of other cations (Na⁺, Ca²⁺, Mg²⁺, Al³⁺) (*e.g.*, Evans & Garrels 1958).

APPEARANCE AND PHYSICAL PROPERTIES

Kokinosite typically occurs as tablets or blades up to 0.05 mm thick, with stepped faces, and 1 mm maximum dimension (Figs. 1 and 2). Crystals sometimes form larger, irregularly stepped crystal masses up to several mm across. Kokinosite is yellow orange, although it is sometimes tinted orange-brown; the streak of the phase is yellow, typical of decavanadate-bearing minerals. The luster of kokinosite is subadamantine, and the mineral is transparent; it does not fluoresce in short- or long-wave



FIG. 1. Kokinosite crystals from the St. Jude mine. Field of view = 2 mm.

ultra-violet radiation. The Mohs hardness of kokinosite is *ca.* 1½. Kokinosite possesses a brittle tenacity, one good cleavage on {011}, and irregular fracture. The density of kokinosite could not be measured because the mineral dissolves in available aqueous density liquids and there is insufficient material for direct measurement. Density (calc.) = 2.35 g cm⁻³ on the basis of the empirical formula and 2.352 g cm⁻³ on the basis of the ideal formula, both using single-crystal unit cell data.

OPTICAL PROPERTIES

The optical properties of kokinosite were determined in white light. Kokinosite is biaxial (–), with α 1.725(3), β 1.770(5), and γ 1.785(3). The 2V was measured as 56.6(3)° from extinction data using EXCALIBR (Gunter *et al.* 2004), and 2V_{calc} = 58.7°. Dispersion is r < v, moderate. The optic orientation was incompletely determined, with X ^ **a** = 15°, $Y \approx$ **b**. The mineral is pleochroic: X, Z = orange-yellow, Y = orange, and X = Z < Y. Compatibility [1 – (K_p/K_c) = 0.003], as calculated from the empirical formula using the density derived from the single-crystal unit cell, is superior (Mandarino 1981).



FIG 2. Crystal drawing of kokinosite; clinographic projection in nonstandard orientation, *a* vertical.

THE COMPOSITION OF KOKINOSITE

Analyses of kokinosite (10 analyses from three crystals) were obtained at the University of Utah using a Cameca SX-50 electron microprobe with four wavelength dispersive spectrometers. Analytical conditions were 15 keV accelerating voltage, 10 nA beam current, and a beam diameter of 10 μ m. Counting times were 10 seconds for each element except Na, which was analyzed with five second count times. In the analytical routine, Na, Ca, and V were counted simultaneously, *i.e.*, first on their respective spectrometers. Raw X-ray intensities were corrected for matrix effects with a $\phi\rho(z)$ algorithm (Pouchou & Pichoir 1991).

There was no visible damage from the electron beam; however, as is typical of decavanadate phases (*i.e.*, postite, rakovanite, hughesite, gunterite, and lasalite), kokinosite partially dehydrates under the vacuum of 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 , the H_2O content was calculated based on stoichiometry. The analyzed constituents were then normalized to provide a total of 100% when combined with the calculated H_2O .

The results of the chemical analysis of kokinosite are contained in Table 2. The empirical formula of kokinosite (based on V = 10 and O = 52 *apfu*) is $(Na_{1.88}K_{0.01})$ $\Sigma_{1.89}(Ca_{1.81}Sr_{0.12})\Sigma_{1.93}(V_{10}O_{28})\cdot 24H_2O$. The simplified structural formula is $Na_2Ca_2(V_{10}O_{28})\cdot 24H_2O$, which requires Na_2O 4.09, CaO 7.40, V_2O_5 59.99, H_2O 28.52, total 100.00 wt.%.

CRYSTAL STRUCTURE: EXPERIMENTAL

Powder and single-crystal X-ray diffraction data for kokinosite were obtained with a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer using monochromatized MoK α radiation. The powder data presented in Table 3 are in good agreement with those calculated from the structure data. Observed *d* values and intensities were derived by profile fitting using JADE 2010 software (Materials Data Inc.).

The Rigaku Crystal Clear software package was used for processing of the structure data, including the application of an empirical multi-scan absorption correction using ABSCOR (Higashi 2001). The structure was solved by direct methods using SIR2004 (Burla et al. 2005). SHELXL-97 software (Sheldrick 2008) was used, with neutral atom scattering factors, for the refinement of the structure. O-H distances were restrained to be 0.90(2)Å, and H-H distances for each H₂O were restrained to be 1.45(3)Å. The U_{eq} for each H was set to 1.2× that of O to which it is bonded. Details of the sample, data collection, and structure refinement are provided in Table 4, final atom coordinates and equivalent isotropic temperature factors in Table 5, and selected bond distances are given in Table 6. Table 7 contains bond valences for selected bonds in kokinosite. A Table of structure factors, a CIF file, and a Table of anisotropic displacement parameters are available from the Depository of Unpublished Data on the MAC website [document Kokinosite CM52_15].

ATOMIC ARRANGEMENT OF KOKINOSITE

Minerals that contain the decavanadate group can be considered members of the pascoite family, pascoite (Ca₃V₁₀O₂₈•17H₂O) being the first-described decavanadate mineral (Hillebrand et al. 1914). All of the minerals of the pascoite family possess bipartite structures that contain a structural unit and an interstitial unit, as elucidated by Schindler & Hawthorne (2001). Those authors noted that the structural unit is an array of high-bond-valence polyhedra that is usually anionic in character, and in kokinosite that unit is the $(V_{10}O_{28})^{6-1}$ decavanadate polyanion. The structural units are linked by the interstitial unit, an array of large, low-valence cations, simple anions, and H₂O groups that is usually cationic in character. Interstitial units link the structural units with weak cation-anion and hydrogen bonds into a continuous structure; in kokinosite the interstitial unit has a composition of (Na₂Ca₂•24H₂O)⁶⁺.

-							
	Oxide	wt.%	Range	S.D.	Norm. wt.%	Formula	Probe Standard
	Na₂O K₂O	4.64	3.78–5.95 0.02–0.07	0.71	3.85 0.03	4.09	albite
	CaO	8.08	6.39–9.91	1.09	6.70	7.40	diopside
	SrO	1.01	0.52-2.54	0.70	0.84		Sr titanate (syn)
	V ₂ O ₅ *	72.43	70.66-74.08	1.29	60.06	59.99	Y vanadate (syn)
	H ₂ O*	-			28.52	28.52	
	Total	86.20			100.00	100.0	

TABLE 2. ANALYTICAL RESULTS FOR KOKINOSITE

^{*}Based upon crystal structure with V = 10 and O = 52 apfu.

In all the pascoite family minerals, the $(V_{10}O_{28})^{6-}$ decavanadate polyanion or its chemical variants (Table 1) form the structural unit of the mineral; the decavanadate polyanion, formed of ten distorted VO₆ octahedra, is depicted in Figure 3. The decavanadate unit is a polyoxometalate that has received considerable attention by the community of chemists and biologists over many decades (Aureliano 2011, Tracey *et al.* 2007).

The interstitial unit in kokinosite

In all decavanadate *sensu stricto* minerals [*i.e.*, those minerals containing the unprotonated $(V_{10}O_{28})^{6-}$ group with pentavalent vanadium], the 6⁻ charge of the structural unit is balanced by the 6⁺ charge of the interstitial unit. In Table 1-A, the compositions of the interstitial units are evident for all the decavanadate-bearing minerals.

I _{obs}	d _{obs}		$d_{\rm calc}$	I _{calc}	hkl	I _{obs}	d _{obs}		$d_{\rm calc}$	I _{calc}	hkl	l _{ot}	os	$d_{\rm obs}$		$d_{\rm calc}$	I _{calc}	hkl
30	11.24		11.1486	44	001				2.9234	1	130			0.050	ſ	2.0604	1	312
100	0.00	1	9.8817	49	010				2.9146	2	104	3	6	2.059	Ì	2.0556	2	204
100	9.00)	9.8081	51	011				2.8745	1	214					2.0491	1	141
33	8.42		8.3580	43	100				2.8707	4	131					2.0039	1	154
35	7.92		7.8987	36	101			1	2.8559	4	222				(1.9802	4	422
		(6.8930	5	110				2.8510	1	302	20	6	1.9613	í	1,9609	12	155
14	6.80	í	6 7 5 9 3	17	111				2 8411	2	031	3	1	1 9230	(1 9244	5	223
		`	6 1806	2	011	28	2 814	Į	2 8204	3	134		•	1.0200		1 8846	1	136
			6.1267	5	012		2.0		2.7950	2	312					1.8757	1	414
		(6.0266	15	111				2.7871	4	004	1.	1	1.8656		1.8709	7	423
31	6.01	{	5 9692	9	110				2 7654	3	311					1 8487	3	322
		(5 0035	1	101				2.7004	1	042	5		1 8170		1 9173	3	156
з	546		5.3033	7 2	101				2.7430	1	233		,	1.0170		1.0173	1	351
5	0.40	(4 9408	4	020				2 7183	2	200					1.7003	1	426
6	4.942	{	4 0041	2	020			/	2.6850	1	107				(1.6085	1	262
0	4 5 2 4	(4.5041	5	101				2.0000	1	041	7	,	1 6010	J	1.0905	2	202
0	4.551		4.0000	5 1	121	17	2.659	{	2.0094	4	041	,		1.0313		1.0940	4	537
			4.4072	1	201				2.0070	2	112				`	1.0009	1	276
		(4.3365	ו 2	201 112			ì	2.0431	2	231					1.0701	1	500
15	1 111	J	1 1//0	1	012	з	2 608	J	2.0044	1	201	6	:	1 6453		1.6/67	1	137
15	4.144		4 1177	4	012	5	2.000		2.0020	2	221	U U	,	1.0400		1.6301	1	127
2	4 032	`	4.0310	4	122			ì	2 5577	1	125				1	1.6001	2	262
2	4.002		4 0158	2	211				2 5518	1	321					1.6171	1	511
7	3.920		3.9046	6	212	8	2.540	ſ	2.5395	1	131	3	3	1.6176	ſ	1.6141	1	135
-			3.8246	1	123				2.5151	3	115					1.6126	1	235
4	3.695		3.6936	6	211			i	2.4684	3	321					1.5859	1	501
2	3.607		3.6037	1	032				2.4520	5	044				(1.5723	1	427
			3.4465	1	220	13	2.447	ſ	2.4423	8	313	3	3	1.5617	1	1.5621	1	362
8	3 378		3 3797	8	222				2 4370	1	104				ì	1 4741	1	362
0	0.010		3 3578	2	112				2 4 2 1 9	1	230	6	5	1.4722	{	1 4649	1	353
			3 3/00	3	221	з	2 300		2 3030	5	322				(1 4553	1	138
		1	3 2004	1	221	5	2.599	(2.3939	1	123				1	1.4365	1	126
			3 2030	1	030	2	2 237	J	2 2286	5	222					1.4353	1	601
12	3.285	{	3 2887	2	121	2	2.201		2 2148	2	145	8	3	1.4327	{	1 4341	1	438
			3 2694	2	033			ì	2 1971	4	045					1 4305	1	245
		`	3 2385	1	$\frac{000}{221}$				2 1895	4	213				`	1 4265	1	145
			3.2282	2	130	22	2 189	Į	2.1863	1	132	4	Ļ	1.4095		1.4104	1	530
			3.1718	3	133	~~~	2.100		2.1744	2	323				(1.3930	1	600
			3,1638	1	114				2.1675	3	314	5	5	1.3889	{	1.3859	1	373
		(3.1279	2	212			'	2.1573	1	231				ì	1.3781	1	605
٩	3 117	J	3 1225	1	124				2 1321	1	2/1	4	ŀ	1.3648	{	1 3565	1	177
9	5.117		2 1140	י ר	12 4 011			/	2.1021	1	402				(1.0000	1	101
		`	3.1140	∠ 2	∠11 013	e	2 000)	2.1000	1	$\frac{403}{245}$	6		1 2450)	1.3000	1	373
			3.0000	2	013	Ö	2.090		2.0009	1	233	6)	1.3450		1 3400	1	228
			5.0513	2	014			(2.0000	I	332				(1.3421	I	230

TABLE 3. POWDER X-RAY DIFFRACTION DATA FOR KOKINOSITE



TABLE 4. DATA COLLECTION AND STRUCTURE REFINEMENT DETAILS FOR KOKINOSITE

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	Mo <i>K</i> α (λ = 0.71075 Å)/50 kV, 40 mA
Temperature	298(2) K
Ideal Formula	Na ₂ Ca ₂ (V ₁₀ O ₂₈) •24H ₂ O
Space group	PĪ
Unit cell dimensions	a 8.74899(19) Å
	b 10.9746(3) Å
	c 12.8216(9) Å
	α 114.492(8)°
	β 105.093(7)°
	γ 91.111(6)°
V	1070.25(11) Å ³
Ζ	1
Density (for above formula)	2.352 g cm ⁻³
Absorption coefficient	2.479 mm ⁻¹
F(000)	756
Crystal size	120 x 80 x 30 μm
θ range	3.01 to 27.47°
Index ranges	$\overline{11} \le h \le 9, \ \overline{14} \le k \le 14, \ \overline{16} \le \ell \le 16$
Reflections collected/unique	20535/4885; R _{int} = 0.041
Reflections with $F_0 > 4\sigma F$	3806
Completeness to θ = 27.47°	99.6%
Refinement method	Full-matrix least-squares on F ²
Parameters refined	371
GoF	1.055
Final R indices $[F_0 > 4\sigma(F)]$	$R_1 = 0.0379, wR_2 = 0.0933$
R indices (all data)	$R_1 = 0.0529, wR_2 = 0.1009$
Largest diff. peak/hole	+1.15/–0.65 e A ⁻³

^{*} $R_{int} = \Sigma [F_0^2 - F_0^2(mean)]/\Sigma [F_0^2]$. GoF = $S = \{\Sigma [w(F_0^2 - F_c^2)^2]/(n-p)\}^{1/2}$. $R_1 = \Sigma [|F_0| - |F_c|]/\Sigma [F_0|$. $wR_2 = \{\Sigma [w(F_0^2 - F_c^2)^2]/\Sigma [w(F_0^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP]$ where a is 0.0503, b is 0.9223 and P is $[2F_c^2 + Max(F_0^2, 0)]/3$

Atom	x/a	y/b	z/c	U(eq)
V1	0.80250(6)	0.47931(5)	0.46000(4)	0.0191(1)
V2	0.99343(6)	0.24235(5)	0.47322(4)	0.0210(1)
V3	0.99148(6)	0.51228(5)	0.29221(4)	0.0222(1)
V4	0.82947(7)	0.72650(6)	0.69749(5)	0.0266(1)
V5	0.80443(7)	0.23481(5)	0.22879(5)	0.0264(1)
Na	0.5210(2)	0.1387(1)	0.6354(1)	0.0385(3)
Са	0.32122(9)	0.32248(7)	0.93686(6)	0.0312(2)
01	0.0075(2)	0.6077(2)	0.6031(2)	0.0187(4)
O2	0.8517(2)	0.6002(2)	0.3948(2)	0.0200(4)
O3	0.8527(2)	0.3721(2)	0.5470(2)	0.0205(4)
O4	0.6901(3)	0.5781(2)	0.5410(2)	0.0261(5)
O5	0.1481(3)	0.4111(2)	0.25020(19)	0.0270(5)
O6	0.1475(3)	0.1888(2)	0.39888(19)	0.0258(5)
07	0.6752(3)	0.3604(2)	0.33217(19)	0.0260(5)
O8	0.8277(3)	0.1560(2)	0.33586(19)	0.0260(5)
O9	0.8269(3)	0.3793(2)	0.18775(18)	0.0265(5)
O10	0.0175(3)	0.8267(2)	0.81227(19)	0.0291(5)
O11	0.9925(3)	0.1471(2)	0.5410(2)	0.0295(5)
012	0.6942(3)	0.7998(3)	0.7534(2)	0.0385(6)
O13	0.6594(3)	0.1333(2)	0.1177(2)	0.0405(6)
014	0.0128(3)	0.3894(2)	0.7732(2)	0.0327(5)
OW1	0.5575(4)	0.3016(4)	0.5709(3)	0.0622(10)
H1a	0.482(4)	0.343(5)	0.545(5)	0.075
H1b	0.482(4)	0.343(5)	0.545(5)	0.075
OW2	0.4723(4)	0.9660(3)	0.6947(3)	0.0577(8)
H2a	0.377(3)	0.908(4)	0.661(4)	0.069
H2b	0.550(4)	0.911(4)	0.695(4)	0.069
OW3	0.6999(3)	0.9971(3)	0.5364(2)	0.0386(6)
H3a	0.790(4)	1.038(4)	0.532(4)	0.046
H3b	0.745(4)	0.937(3)	0.562(4)	0.046
OW4	0.7456(3)	0.2575(3)	0.8106(3)	0.0445(7)
H4a	0.787(5)	0.201(4)	0.840(4)	0.053
H4b	0.819(4)	0.295(4)	0.795(4)	0.053
OW5	0.3774(3)	0.3281(3)	0.7602(2)	0.0322(5)
H5a	0.450(4)	0.394(3)	0.781(3)	0.039
H5b	0.300(3)	0.326(4)	0.699(3)	0.039
OW6	0.4855(6)	0.1541(4)	0.9129(3)	0.0908(15)
H6a	0.560(6)	0.151(6)	0.972(3)	0.109
H6b	0.480(7)	0.082(5)	0.840(3)	0.109
OW7	0.0909(4)	0.3804(4)	0.0099(3)	0.0698(11)
H7a	0.100(7)	0.293(3)	-0.012(4)	0.084
H7b	0.086(7)	0.407(5)	0.086(3)	0.084
OW8	0.1337(4)	0.1336(3)	0.7663(2)	0.0445(7)
H8a	0.137(5)	0.048(3)	0.743(4)	0.053
H8b	0.092(5)	0.145(4)	0.701(3)	0.053
OW9	0.3551(3)	0.5686(3)	0.9940(2)	0.0376(6)
H9a	0.310(5)	0.614(4)	1.052(3)	0.045
H9b	0.294(4)	0.579(4)	0.930(3)	0.045
OW10	0.4256(3)	0.4199(3)	0.1656(2)	0.0370(6)
H10a	0.513(3)	0.409(4)	0.210(3)	0.044
H10b	0.348(3)	0.423(4)	0.199(3)	0.044
OW11	0.2414(8)	0.1424(5)	0.0012(4)	0.069(2)
H11a	0.270(10)	0.057(5)	-0.033(6)	0.083
H11b	0.261(10)	0.156(7)	0.079(3)	0.083
OW12	0.8861(5)	0.0970(4)	0.9242(3)	0.0718(10)
H12a	0.930(6)	0.029(4)	0.885(4)	0.086
H12b	0.948(6)	0.174(3)	0.965(5)	0.086

TABLE 5. COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (\dot{A}^2) OF ATOMS IN KOKINOSITE

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.



FIG 4. Atomic arrangement of kokinosite viewed down [100]. Large white spheres are O atoms of isolated H₂O groups. Small white spheres are H atoms. The unit cell outline is shown by a dashed black line.

TABLE 6. SELECTED BOND DISTANCES AND ANGLES IN KOKINOSITE

V1–07	1.688(2)	Na–OW1	2.308(3)	Ca-OW6	2.331(4	1)
V1–04	1.692(2)	Na–OW2	2.384(3)	Ca–OW7	2.425(3	3)
V1–O3	1.917(2)	Na–OW3	2.399(3)	Ca–OW8	2.452(3	3)
V1–O2	1.931(2)	Na–OW4	2.405(3)	Ca–OW5	2.464(2	2)
V1–01	2.110(2)	Na–OW3	2.443(3)	Ca–OW9	2.476(3	3)
V1–01	2.148(2)	Na–OW5	2.617(3)	Ca-OW10	2.559(3	3)
<v1–o></v1–o>	1.914	<na–o></na–o>	2.426	Ca-OW11	2.583(5	5)
				Ca–OW9	2.814(3	3)
V2–011	1.614(2)			<ca–o></ca–o>	2.513	
V2-06	1.818(2)					
V2-08	1.826(2)		Hydr	ogen bonds		
V2-02	1.994(2)	D–H…A	D–H	H…A	DA	<dha< td=""></dha<>
V2-03	1.999(2)	OW1-H1AO	4 0.89(3)	2.05(3)	2.925(4)	171(5)
V2-01	2.235(2)	OW1-H1B-O	3 0.86(3)	1.96(3)	2.810(3)	178(5)
<v2–o></v2–o>	1.914	OW2-H2A-O	8 0.92(3)	1.93(3)	2.779(4)	153(4)
		OW2-H2B-O	12 0.91(3)	2.00(3)	2.859(4)	156(5)
V3–O14	1.614(2)	OW3–H3A…O	11 0.92(2)	2.07(3)	2.991(3)	174(4)
V3–O9	1.814(2)	OW3-H3B-O	6 0.91(2)	1.84(3)	2.750(3)	172(4)
V3–O5	1.829(2)	OW4–H4A […] O	W12 0.89(2)	1.95(3)	2.830(5)	173(4)
V3–O2	1.997(2)	OW4–H4B…O	14 0.86(3)	2.11(3)	2.970(4)	174(4)
V3–O3	2.005(2)	OW5–H5A···O	W10 0.86(2)	2.04(3)	2.881(4)	165(4)
V3–O1	2.235(2)	OW5-H5B···O	2 0.89(2)	1.97(3)	2.805(3)	157(3)
<v3–o></v3–o>	1.916	OW6–H6A […] O	13 0.88(3)	1.93(3)	2.773(4)	160(6)
		OW6–H6B···O	W2 0.93(3)	1.75(3)	2.672(6)	171(6)
V4–012	1.601(2)	OW7–H7A […] O	W11 0.89(3)	2.12(4)	2.921(7)	149(5)
V4–O10	1.846(2)	OW7-H7B-O	5 0.91(3)	2.02(3)	2.861(4)	155(4)
V4-06	1.873(2)	OW8–H8A···O	8 0.87(2)	2.10(3)	2.958(3)	168(4)
V4–05	1.885(2)	OW8–H8B […] O	11 0.88(2)	2.02(3)	2.897(3)	173(4)
V4–04	2.026(2)	OW9–H9A…O	W4 0.90(2)	1.94(3)	2.818(4)	167(4)
V4–01	2.311(2)	OW9–H9B···O	9 0.91(2)	1.84(3)	2.739(3)	173(4)
<v4–o></v4–o>	1.924	OW10-H10A-	·O7 0.87(2)	2.08(3)	2.922(3)	164(4)
		OW10-H10B.	·O5 0.88(2)	2.05(2)	2.921(3)	172(4)
V5–O13	1.603(2)	OW11–H11A	O13 0.92(3)	2.11(3)	3.033(6)	178(6)
V5–O10	1.826(2)	OW11–H11B	O12 0.92(3)	1.92(3)	2.834(5)	173(7)
V5–O8	1.876(2)	OW12-H12A	O10 0.87(3)	2.26(3)	3.105(4)	164(5)
V5–O9	1.887(2)	OW12-H12B	OW7 0.87(3)	2.34(3)	3.165(6)	160(5)
V5–07	2.064(2)					
V5–O1	2.300(2)					
<v5–o></v5–o>	1.926					

	V1	V2	V3	V4	V5	Na	Са	hydrogen bonds	Σ
O1	0.44	0.31	0.31	0.25	0.26				1.97
O2	0.39 0.71	0.60	0.59					+0.15	2.05
O3	0.73	0.59	0.58					+0.17	2.07
O4	1.35			0.55				+0.13	2.03
O5			0.93	0.80				+0.14 +0.14	2.01
O6		0.96		0.83				+0.19	1.98
07	1.36				0.49			+0.13	1.99
O8		0.94			0.82			+0.12 +0.15	2.03
O9			0.97		0.80			+0.19	1.96
O10				0.89	0.94			+0.09	1.92
O11		1.67						+0.11 +0.14	1.92
012				1.73				+0.14 +0.16	2.03
O13					1.72			+0.17 +0.10	1.99
O14			1.67					+0.12	1.79
OW1						0.22		-0.13 -0.17	-0.08
OW2						0.18		-0.15 -0.14 +0.21	0.10
OW3						0.18		-0.11 -0.19	0.03
OW4						0.16 0.17		-0.16 -0.12 +0.16	0.05
OW5						0.10	0.26	-0.14 -0.15	0.07
OW6							0.37	-0.17 -0.21	-0.01
OW7							0.29	-0.11 -0.14 +0.08	0.12
OW8							0.27	-0.12 -0.14	0.01
OW9							0.25	-0.16 -0.19	0.01
OW10							0.10 0.20	-0.13 -0.14 +0.14	0.07
OW11							0.19	-0.10 -0.16 +0.11	0.04
OW12								-0.09 -0.08 +0.16	-0.01
Σ	4.99	5.06	5.05	5.05	5.03	1.01	1.94		

TABLE 7. SELECTED BOND VALENCES AND BOND VALENCE SUMS (vu) IN KOKINOSITE

Na⁺–O bond strengths from constants of Wood & Palenik (1999); V⁵⁺–O, and Ca²⁺–O, and hydrogen bond strengths based on H···O bond lengths from constants of Brown & Altermatt (1985).

In kokinosite, the interstitial unit has a composition of Na₂Ca₂•24H₂O; the atomic arrangement is formed of the aforementioned (V₁₀O₂₈)^{6–} structural units that are linked by Na(H₂O)₆ octahedra and Ca(H₂O)₈ polyhedra that link into chains by edge- and corner-sharing (Fig. 4). Adjacent Na(H₂O)₆ octahedra share OW3– OW3 edges and adjacent Ca(H₂O)₈ polyhedra share OW9–OW9 edges, in each case forming edge-sharing dimers, and these adjacent Na- and Ca-centered dimers share OW5 corners. Indicating each polyhedron by its cation (Na or Ca), shared edges by "=" and shared corners by "–", the chain is thus (–Na=Na–Ca=Ca–)_∞. The interstitial unit also includes one isolated H₂O group.

Table 1-A lists the formulas of the pascoite-family minerals, which illustrates the composition of the interstitial unit in each phase. The contents of the interstitial units include Na, Mg, Ca, Al, H₂O, and hydronium ions; no interstitial O atom exists that is not fully hydrated. The interstitial cations occur in monomers, dimers, trimers, and infinite chains; in any given pascoite mineral more than one type of coordination can occur. Kokinosite is the only pascoite-family mineral in which all the interstitial cations are linked in infinite chains and no other interstitial polymer type is present; it may be that the similar size of the interstitial cations (Na, Ca) facilitates such polymerization in the interstitial group.

The linkage between the $(V_{10}O_{28})^{6-}$ structural units and the Na₂Ca₂•24H₂O interstitial unit is attained by hydrogen bonding alone; there are no bonds between the interstitial group cations (Na, Ca) and the O atoms of the decavanadate group. Table 7 lists the hydrogen bonds that link the interstitial unit and structural unit in kokinosite.

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