NASHITE, Na₃Ca₂[(V⁴⁺V⁵⁺9)O₂₈]•24H₂O, A NEW MINERAL SPECIES FROM THE YELLOW CAT MINING DISTRICT, UTAH AND THE SLICK ROCK MINING DISTRICT, COLORADO: CRYSTAL STRUCTURE AND DESCRIPTIVE MINERALOGY

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ABSTRACT

Nashite, Na₃Ca₂[(V⁴⁺V⁵⁺₉)O₂₈]•24H₂O, is a new mineral species from the Little Eva mine, Yellow Cat District, Grand County, Utah, and the St. Jude mine, Slick Rock district, San Miguel County, Colorado, USA. Nashite occurs as blades on a corvusitemontroseite-bearing sandstone block intimately associated with calcite, gypsum, huemulite, pascoite, rossite, and sherwoodite. Nashite is bluish-green, with a light bluish-green streak. The mineral is transparent, with a subadamantine luster. Nashite does not fluoresce in short- or long-wave ultraviolet radiation, and has a hardness ca. 2. Nashite has a brittle tenacity, irregular fracture, and one good cleavage on {010}. Density (calc.) = 2.350 g/cm³ based on the empirical formula and single-crystal cell data, and density (calc.) = 2.343 g/cm³ based on the ideal formula and single-crystal cell data. Nashite is biaxial (-), with α 1.737(3), β 1.762(6), and γ 1.775(3). $2V_{\text{meas}} = 70(2)^{\circ}$ and $2V_{\text{calc}} = 71^{\circ}$. Optic orientation is $Y = \mathbf{b}, X \approx \mathbf{a}$. The mineral is pleochroic, with X greenish blue, Y yellowish green, and Z yellow, with X > Y >> Z. Electron probe microanalysis and the crystal structure solution gave the empirical formula (based on O = 52): $(Na_{3.063}K_{0.007})_{\Sigma_{3.070}}(Ca_{1.984}Sr_{0.039})_{\Sigma_{2.019}}[(V^{4+}V^{5+}_{9})O_{28}] \cdot 24(H_{1.995}O)$. The simplified formula is $Na_3Ca_2[(V^{4+}V^{5+}_9)O_{28}] \bullet 24H_2O$. Nashite is monoclinic, $P2_1/n$, with a 10.0099(3), b 21.8472(7), c 11.1504(7) Å, and β 116.584(8)°. The strongest four lines in the diffraction pattern are [d in Å(I)(hkl)]: 9.044(100)(111, 101), 8.350(64)(110), 10.995(46)(020), and 2.9942(29)($\overline{3}31, \overline{3}32, \overline{3}03, 071, 310$). The atomic arrangement of nashite was solved and refined to $R_1 =$ 0.0293. The structural unit in nashite is a partially-reduced decavanadate group, with a composition of $[(V^{4+}V^{5+}_{9})O_{28}]^{7-}$; charge balance in the structure is maintained by the [Na₃Ca₂(OH₂)₂₂•2H₂O]⁷⁺ interstitial unit. The interstitial unit consists of chains of Na1 and Na2 octahedra and an irregular CaO2(OH2)6 polyhedron. The chains are linked to the structural unit by direct bonding to oxygen atoms of the $[(V^{4+}V^{5+}_9)O_{28}]^{7-}$ group and extensive hydrogen bonding between the H₂O molecules of the interstitial group and the oxygen atoms of the structural unit. The mineral is named for Dr. Barbara P. Nash (b. 1944), Professor of Geology and Geophysics at the University of Utah.

Keywords: nashite; new mineral species; decavanadate; crystal structure; Little Eva mine, Yellow Cat District, Grand County, Utah, USA, St. Jude mine, Slick Rock district, San Miguel County, Colorado, USA

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INTRODUCTION

The uranium and vanadium (Uravan) deposits of Colorado and Utah have been a rich source of ore in the production of these metals. Throughout the Colorado Plateau Uravan Mineral Belt, uranium and vanadium minerals occur together in bedded or roll-front deposits in the sandstone of the Salt Wash member of the Jurassic Morrison Formation (Carter & Gualtieri 1965, Shawe 2011). Recent collecting at these deposits by one of the authors (JM) has revealed numerous secondary vanadium minerals that result from oxidation of vanadium ore bodies under near-surface conditions. With the exception of martyite, $Zn_3(V_2O_7)$ (OH)₂•2H₂O (Kampf & Steele 2008a), which contains the divanadate group, [V₂O₇]⁴⁻, and dickthomssenite, $Mg(V_2O_6) \bullet 7H_2O$ (Hughes *et al.* 2001), which contains $[VO_3]$ - vanadate chains, all of the new species contain the decavanadate anionic complex, $[V_{10}O_{28}]^{6-}$, found in the pascoite family of minerals. The new minerals that contain $(V_{10}O_{28})^{6}$ sensu stricto include hughesite, Na₃Al(V₁₀O₂₈)•22H₂O (Rakovan et al. 2011), lasalite, Na₂Mg₂(V₁₀O₂₈)•20H₂O (Hughes et al. 2008), magnesiopascoite, Ca₂Mg(V₁₀O₂₈)•16H₂O (Kampf & Steele 2008b), and postite, Mg(H₂O)₆Al₂(OH)₂(H₂O)₈(V₁₀O₂₈)• 13H₂O (Kampf et al. 2012). In addition, the first minerals that contain protonated decavanadate groups have also been discovered, including rakovanite, $Na_{3}[H_{3}(V_{10}O_{28})] \cdot 15H_{2}O$ (Kampf *et al.* 2011a) and gunterite $Na_4(H_2O)_{16}[H_2(V_{10}O_{28})] \bullet 6H_2O$ (Kampf *et al.* 2011b). The recent collecting also yielded crystals of the decavanadate huemulite, $Na_4Mg(V_{10}O_{28}) \cdot 24H_2O$ (Gordillo et al. 1966), suitable for structure determination (Colombo et al. 2011). The only other previously known pascoite family mineral, hummerite, $K_2Mg_2(V_{10}O_{28}) \bullet 16H_2O$ (Hughes *et al.* 2002), also comes from the Uravan deposits. Sherwoodite, which contains a 14-vanadoaluminate complex anion of $[AIV_{14}O_{40}]^{n-}$ composition, also forms in the Colorado Plateau Uravan deposits (Evans & Konnert 1978).

Herein we describe another new secondary mineral from the Uravan deposits, the first with a $[(V^{4+}V^{5+})]$ O₂₈] vanadylnonavanadate polyanion. The new species was discovered in the St. Jude mine, Slick Rock district, San Miguel County, Colorado, USA. Better crystals suitable for structure determination and completion of the characterization were subsequently found in the Little Eva mine, Yellow Cat District, Grand County, Utah. The mineral is named for Dr. Barbara P. Nash (b. 1944), Professor of Geology and Geophysics at the University of Utah. Professor Nash is particularly known for her many contributions to the geochemistry and petrogenesis of volcanic systems. Dr. Nash has previously served as Associate Editor of the American Mineralogist, and has been the director of the Electron Microprobe Laboratory at the University of Utah since its inception in 1970. Recently, Dr. Nash has worked extensively on the chemical analysis of vanadium minerals from the Colorado Plateau, contributing to the descriptions of several new minerals (gunterite, hughesite, postite, and rakovanite). The new mineral and name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2011–105). The type specimens of nashite are deposited in the Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA. The holotype and one cotype from the Little Eva mine, Yellow Cat District, Grand County, Utah, USA, are assigned catalogue numbers 63583 and 63584, respectively; three cotypes from the St. Jude mine, Slick Rock District, San Miguel County, Colorado, USA, are assigned catalogue numbers 63585, 63586, and 63587.

OCCURRENCE

In the Little Eva mine, nashite was found on sandstone blocks. Crystals were found growing as blades on a corvusite-montroseite-bearing sandstone block intimately associated with calciodelrioite (Kampf *et al.* 2012), calcite, gypsum, huemulite, pascoite, rossite, and sherwoodite. Other minerals found nearby include andersonite, ansermetite, cobaltomenite, dickthomssenite, ferroselite, lasalite, martyite, melanovanadite, natrozippeite, schrockingerite, native selenium, tyuyamunnite, and uraninite. The mineral occurs in a similar assemblage at the St. Jude mine, Slick Rock district, San Miguel County, Colorado, USA. At both localities the mineral is rare.

The mineral forms from the oxidation of montroseitecorvusite assemblages in a moist environment. Mining operations have exposed unoxidized and oxidized phases; in addition to nashite, other mixed-valence V^{4+}/V^{5+} vanadium minerals are found in the association (sherwoodite, melanovanadite), which suggests that local oxidizing conditions can be controlled by the presence of organic matter and phases such as pyrite. Under ambient temperatures and generally oxidizing nearsurface 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 Eh-pH and the presence of other cations (Na⁺, Ca²⁺, Mg²⁺, Al³⁺) (*e.g.*, Evans & Garrels 1958).

APPEARANCE AND PHYSICAL PROPERTIES

Crystals of nashite are equant to tabular and commonly occur in stacked parallel intergrowths. Individual crystals are up to 0.3 mm in maximum dimension (Figs. 1, 2). Nashite is bluish-green, with a light bluish-green streak. The mineral is transparent, with a subadamantine luster. Nashite does not fluoresce in short- or long-wave ultraviolet radiation, and has a hardness of approximately 2.



FIG. 1. SEM image of nashite crystals from the Little Eva mine, Yellow Cat District, Grand County, Utah, USA.

Nashite has a brittle tenacity and one good cleavage on {010}. No parting was observed, and the mineral displays irregular fracture. The density of nashite could not be measured because the mineral dissolves in aqueous density liquids and there is insufficient material for direct measurement. Density (calc.) = 2.350 g/cm³ based on the empirical formula and single-crystal cell data, and density (calc.) = 2.343 g/cm³ based on the ideal formula and single-crystal cell data.

OPTICAL PROPERTIES

The optical properties of nashite were determined in white light. Nashite is biaxial (–), with α 1.737(3), β 1.762(6), and γ 1.775(3). The 2V was measured as 70(2)° from extinction data using EXCALIBRW (Gunter *et al.* 2004), and 2V_{calc} = 71°. Dispersion was not observed directly, but is probably strong based upon "anomalous" colors observed under crossed polars as crystals approach extinction position. The optic orientation is $Y = \mathbf{b}$, $X \approx \mathbf{a}$. The mineral is pleochroic: X greenish-blue, Y yellowish green, and Z yellow, with X > Y >> Z. Gladstone-Dale compatibility [1 – (K_p/K_c) = -0.020], as calculated from the empirical formula using the density derived from the single-crystal unit cell, is excellent.

THE COMPOSITION OF NASHITE

Analyses of nashite (32 analyses from eight crystals) from the Little Eva mine were performed 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. Sodium, Ca, and V were analyzed with their respective spectrometers before analyzing for other constituents. Magnesium was analyzed, but was below the limit of detection (0.03 wt.%). 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 hydrated decavanadate phases (*i.e.*, postite, rakovanite, hughesite, gunterite, and lasalite), nashite partially dehydrates under the vacuum of the microprobe chamber. This H₂O 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 H₂O, the H₂O content was calculated on the basis of the structure determination. The analyzed constituents were then normalized to provide a total of 100% when combined with the calculated H₂O.



FIG. 2. Crystal drawing of nashite (clinographic projection in standard orientation).

The crystal structure determination (see below) convincingly indicates that of the ten V atoms in the decavanadate group, the approximate equivalent of one V atom has a valence of 4+ and nine have a valence of 5+. Consequently, in the EMP analysis, we allocated VO₂ and V₂O₅ accordingly. The analytical data are presented in Table 1. On the basis of O = 52, the empirical formula is (Na_{3.063}K_{0.007})_{Σ 3.070}(Ca_{1.984}Sr_{0.039}) Σ _{2.019}[(V⁴⁺V⁵⁺9)O₂₈]•24(H_{1.995}O). The simplified formula is Na₃Ca₂[(V⁴⁺V⁵⁺9)O₂₈]•24H₂O, which provides ideal oxide wt.% values (Table 1) in excellent agreement with the analytical data.

CRYSTAL STRUCTURE: EXPERIMENTAL

Powder and single-crystal X-ray diffraction data for nashite were obtained with a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer using monochromatized MoK α radiation. The powder data presented in Table 2 are in good agreement with those calculated from the structure data. Observed *d* values and intensities were derived by profile fitting using JADE v. 9.3 software (Materials Data Inc.).

The Rigaku Crystal Clear software package was used for processing of the structure data, including the application of an empirical absorption correction. 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 refinement of the structure. Details of the sample, data collection, and structure refinement are provided in Table 3, final atom coordinates and equivalent isotropic temperature factors in Table 4, and selected bond distances and bond-valence values in Table 5. 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 Nashite CM51_27].

ATOMIC ARRANGEMENT OF NASHITE

Minerals that contain the decavanadate group can be considered members of the pascoite family, pascoite (Ca₃V₁₀O₂₈•17H₂O) being the first described decavanadate mineral. All of the minerals of the pascoite family possess bipartite structures that contain a *structural unit* and an *interstitial unit*, as elucidated by Hawthorne (1983). In all the pascoite family minerals, the $[V_{10}O_{28}]^{6-}$ decavanadate polyanion forms the structural unit of the mineral, and the structural units are linked by the interstitial unit, the cationic portion of the structure, with bonds of lower bond valence linking alkalis, alkaline earths, aluminum, and OH and H₂O groups to oxygen atoms of the structural unit (Hughes *et al.* 2008).

The structural unit in nashite

The structural unit in nashite is the $(V_{10}O_{28})$ polyanion, similar to that found in decavanadate-bearing minerals. The $(V_{10}O_{28})$ polyanion consists of ten distorted, edge-sharing octahedra. In the V2, V3, V4, and V5 octahedra in nashite, each octahedron contains one vanadyl bond, defined as a V⁵⁺–O bond less than 1.74 Å in length (Schindler *et al.* 2000). The V1 octahedron has two vanadyl bonds. In all cases, vanadyl bonds are *trans* to the longest V–O bond(s) of the octahedra, typical of the disposition of bonds in the octahedra of the decavanadate polyanion.

Prior to the recent mineral discoveries listed above that illustrate chemical and structural variations in the decavanadate group, the $[V_{10}O_{28}]^{6-}$ polyanion was the only form of the $[V_{10}O_{28}]$ group that had been found in minerals. The structures of rakovanite and gunterite with their triply and doubly protonated decavanadate groups, respectively, demonstrate that there are variants of the decavanadate group in natural materials previously known only in synthetic materials (Duraisamy *et al.* 2000).

Const.	wt.%	Range	S.D.	Norm. wt.%	Ideal wt.%	Probe Standard
Na ₂ O	6.99	5.84–8.13	0.61	6.15	6.04	albite
K ₂ O	0.02	0.00-0.07	0.02	0.02		sanidine
CaO	8.19	7.21-8.89	0.38	7.21	7.29	diopside
SrO	0.29	0.13-0.45	0.09	0.26		Sr titanate (syn)
V_2O_5	(66.98)	59.25-70.76	3.14			Y vanadate (syn)
VO ₂ *	6.11			5.38	5.39	
V ₂ O ₅ *	60.28			53.05	53.19	
H ₂ O	18.12†			27.94§	28.10	
Total	100.00			100.01	100.00	

TABLE 1. ANALYTICAL RESULTS FOR NASHITE

* Apportioned in accord with the structure

[†] By difference

§ Based upon crystal structure with V^{5+} = 9, V^{4+} = 1 and 52 O atoms.

TABLE 2. POWDER X-RAY DIFFRACTION DATA FOR NASHITE

I _{obs}	d _{obs} (Å)		$d_{\rm calc}({\rm \AA})$	I _{calc}	h k I	I _{obs}	d _{obs} (Å)		d _{calc} (Å)	I _{calc}	hkl	I _{obs}	$d_{\rm obs}({\rm \AA})$		$d_{\rm calc}({\rm \AA})$	I _{calc}	h k l
4 6	10.995(4)		10.9236	49	020			1	2.7708	1	202	11	7002/12)	ş	1.7910	1	0 12 1
100	9.044(3)	ş	9.0714	45	011	50	7574(15))	2.7670	2	204		.7903(12)	- 5	1.7882	1	336
100	9.044(3)	J	8.9408	55	<u>1</u> 01	52	./5/4(15))	2.7482	1	251	24	7501(0)	s	1.7537	1	246
64	8.350(3)		8.2833	68	110			(2.7457	1	253	31	.7521(8)	- 1	1.7392	. 1	094
7	7.445(11)		7.3646	5	021			(2.6588	2	123			(1.7049	1	256
15	6.962(5)		6.9188	15	121	152	.6521(6)	ł	2.6483	4	271	21	.7040(5)	- {	1.7014	1	353
2	5.926(10)		5.8810	3	031		. ,	l	2.6454	8	053		. ,	1	1.6981	1	382
		1	5.6464	3	131			(2.5638	1	134	31	.6649(4)		1.6635	4	613
	= =00(0))	5.5416	4	101	142	.5686(8)	ł	2.5601	5	270	21	.6473(7)		1.6455	1	366
17	5.526(3)	ſ	5.4618	2	040		. ,	l	2.5591	6	272			6	1.6171	1	392
		(5.3645	3	112	32	.505(2)		2.5025	4	4 02	41	.6147(5)	- 1	1.6158	1	$\overline{3}95$
		(4.9366	1	122			(2.4418	2	361			(1.5408	1	$\overline{2}$ 3 7
13	4.908(2)	ł	4.8786	6	211	92	.4374(8)	í	2.4304	5	024	31	.5411(6)	- 2	1.5390	1	3 10 2
		l	4.8608	1	012			i	2.3079	2	360		- (-)	1	1.5378	1	3 10 5
		(4 6625	2	140	32	313(3)	3	2 3063	2	363				1 5021	1	1 14 1
6	4.683(3)	1	4 6609	2	141			č	2 2648	1	371			- 1	1 4975	1	354
		,	4.0000	1	200	52	274(4)	3	2.2040	1	372			- 1	1 / 803	1	01/2
		١	4 4704	1	200			,	2.2040	- 1	054			- 1	1 /832	1	$\overline{2}$ 11 5
12	4.445(3)	Ś	4 4 1 0 0	1	131			1	2.1000	1	370	111	4841(10)	1	1 / 830	1	2110
		l	4.4100	1	131	132	.1605(13)	{	2.1500	2	373		.+0+1(10)	1	1 4700	1	207
		ć	4 1416	2	220			l	2 1523	2	115				1 4698	1	453
6	4.154(3)	3	1 137/	1	220			ċ	2 1230	2	124			- 1	1 /670	1	4 55
4	3 020(8)		3 0266	1	150	42	1133(17)	3	2.1200	3	3 9 1			- 1	1 4646	1	3 11 2
4	3.920(0)	6	3 7034	2	100				2.1010	1	131			,	1 4412	1	0 15 1
4	3.703(8)	3	2 6550	2	110	50	0746(17)	J	2.0743	1	104	21	1252(11))	1.4412	1	702
		2	3.0000	4	112	52)	2.0733	· · ·	135	21	.4303(14)		1.4200	1	703
15	2 5014(10)	ſ	3.3073	7	123)	2.0024	່ ວ າ	402				1.4231	1	7 1 4
15	3.5014(16))	3.4090	7	211	102	0210(5)	J	2.0201	ა ი	401			(1.4101	1	5 14 1
		2	2 2720	1	213	102	0210(5))	2.0191	2	403	71	4102(4))	1.4090	1	00Z
10	2 275(5)	J	2.2120	1	221	01	0650(6)	'	2.0134	4	005	/ 1	.4123(4)		1.4091	1	1 1 5 2
10	3.375(5))	2.3032	4	221	91	.9000(0)		1.9019	1	1 5 1			(1.4000	1	2 1 2 1
		č	2 2017	4	223			(1.9394	· I	025			2	1.4001	1	027
11	3.298(6)	3	2.2017	5	0 5 0	81	.9264(8)	{	1.9200	4	171	24	2772(7))	1.3900	1	4 10 2
-	0.404(0)	C	3.2001	5	052			1	1.9104	· 1	4/1	31	.3773(7)		1.3741	1	4 10 2
1	3.164(3)		3.1799	0 2	161			2	1.9100	1	4/3			Ì	1.3002	1	330 2116
			3.0431	د ا	101	21	.881(2)	3	1.0030	1	390			(1.3510	1	3110
		(2.9995	1	331		0=00/40	(1.8733	1	045	31	.3479(13)	- {	1.3513	1	345
20	2 0042(12)	J	2.9983	2	332	51	.8509(4)		1.8450	1	482			1	1.3429	1	444
29	2.9942(13)		2.9803	3	303			1	1.8259	1	292				1.3411	1	448
		l	2.9785	0	071				1.8248	1	294	04	2074(0)	5	1.3272	1	358
			2.9564	4	310	61	.8215(6)	{	1.018/	1	4/0	31	.3271(8)	1	1.3242	1	4 14 2
			2.94/0	3	1/0				1.01/2	1	4/4			(1.3227	1	0 10 6
			2.0152	2	323				1.0140	2	401						
12	2 8362/11	J	2.0094	2	043 152			'	1.0138	2	400						
13	2.0302(11)		2.0201	2	260												
		l	2.0240	2	200												
		'	2.0232	3	202												

Chemical formula	Na ₃ Ca ₂ [(V ⁴⁺ V ⁵⁺ ₉)O ₂₈]·24H ₂ O						
Formula weight	1009.77						
Temperature	293(2) K						
Wavelength	0.71075 Å						
Crystal size	0.050 x 0.090 x 0.110 mm						
Crystal system	monoclinic						
Space group	P21/n						
Unit cell dimensions	a = 10.0099(3) Å						
	b = 21.8472(7) Å						
	c = 11.1504(7) Å						
	$\beta = 116.584(8)^{\circ}$						
Volume	2180.67(17) Å ³						
Ζ	2						
Density (calculated)	2.307 g/cm ³						
Absorption coefficient	2.437 mm ⁻¹						
<i>F</i> (000)	1478						
Theta range for data collection	3.46 to 25.02°						
Index ranges	$-11 \le h \le 11, -26 \le k \le 26, -13 \le \ell \le 13$						
Reflections collected	17,847						
Independent reflections	3,849 [<i>R</i> _(int) = 0.0407]						
Max. and min. transmission	0.8878 and 0.7753						
Structure solution technique	direct methods						
Structure solution program	SHELXS-97 (Sheldrick 2008)						
Refinement method	Full-matrix least-squares on F ²						
Refinement program	SHELXL-97 (Sheldrick 2008)						
Function minimized	$\Sigma w(F_0^2 - F_c^2)^2$						
Data / restraints / parameters	3849 / 36 / 380						
Goodness-of-fit on F ²	1.092						
$\Delta \sigma_{max}$	0.043						
Final R indices	3144 data; $2\sigma(I)$ $R_1 = 0.0293$, $wR_2 =$	0.0679					
	all data $R_1 = 0.0404, wR_2 =$	0.0708					
Weighting scheme	w = $1/[\sigma^2(F_o^2) + (0.0295P)^2 + 2.2707P]$ whe $(F_o^2 + 2F_o^2)/3$	re <i>P</i> =					
Largest diff. peaks	0.368 and -0.434 eÅ ⁻³						

TABLE 3. CRYSTAL DATA, DATA COLLECTION, AND STRUCTURE REFINEMENT DETAILS FOR NASHITE

The minerals bearing the $[V_{10}O_{28}]^{6-}$ group are yellow-orange in color, typical of compounds that contain vanadium only in the pentavalent oxidation state. The blue-green color of nashite suggested the presence of both V^{4+} and V^{5+} in the crystal, yet paradoxically the structure solution demonstrated the presence of a $(V_{10}O_{28})$ group, previously recognized only with V^{5+} . In addition, with the putative $(V_{10}O_{28})^{6-}$ group, charge balance was not achieved. Calculation of bond-valence sums using parameters for pentavalent vanadium showed two V atoms (V4 and V5) with bond-valence sums differing from the pentavalent state by amounts atypical for such calculations in decavanadate groups, yielding 4.88 and 4.76 v.u., respectively (Table 5). Recalculation of those bond-valence sums using parameters appropriate for mixed-valence, V4+/ V⁵⁺ sites (Table 5) yielded bond-valence sums of 4.43 and 4.56 v.u. for V4 and V5, respectively. Thus, the $(V_{10}O_{28})$ group in nashite is a vanadylnonavanadate polyanion, with a mixed-valence vanadium composition of $[(V^{4+}V^{5+}_9)O_{28}]^{7-}$. Although mixed-valence V^{4+}/V^{5+} minerals are well-known (Evans & Hughes 1990), nashite is the first known mineral to incorporate a mixed-valence $(V_{10}O_{28})$ group in its atomic arrangement. In biological systems, a mixed-valance V^{4+}/V^{5+} $(V_{10}O_{28})$ compound has been synthesized; Ramasarma (2007) described a mixed-valence V^{4+}/V^{5+} blue decavanadate compound that, when oxidized with hydrogen peroxide, turns to a yellow-orange compound that contains the $[V_{10}O_{28}]^{6-}$ polyanion with only pentavalent vanadium. Ramasarma (2007) further noted that the reduced (4⁺) vanadium atoms in the decavanadate polyanion can undergo reversible redox changes.

Nashite displays the blue-green color typical of intervalence charge transfer (IVCT) in vanadium compounds. The two V octahedra that contain V⁴⁺ are V4 and V5, which are adjacent to each other at a distance of 3.094 Å. Between the two octahedra, bond-valence calculations yield 1.01 atoms of V⁴⁺ and 0.99 V⁵⁺ distributed between the two sites, thus attaining

	x/a	y/b	z/c	Ueq
V1	0.66529(6)	0 00082(2)	0 49774(5)	0.01536(13)
V2	0.40854(6)	0.90728(2)	0.32069(5)	0.01642(14)
V3	0.37017(6)	0.00120(2) 0.04485(2)	0.24803(5)	0.01721(14)
V4	0.61514(6)	0.13848(2)	0.42490(5)	0.01721(14) 0.01853(14)
V5	0.69161(6)	0.86274(3)	0.57045(5)	0.01877(14)
Ca	0.21384(7)	0.93734(3)	0.92824(7)	0.02013(16)
Na1	0.66412(16)	0.30409(7)	0.31612(15)	0.0358(4)
Na2*	0.0570(3)	0.80727(16)	0.6099(4)	0.0526(15)
01	0 7841(2)	0.94109(10)	0.5290(2)	0.0205(5)
02	0.7483(2)	0.06185(10)	0.4645(2)	0.0202(5)
03	0.5317(2)	0.98073(9)	0.3179(2)	0.0166(5)
04	0.7148(2)	0.02066(9)	0.6792(2)	0.0154(5)
05	0.4819(2)	0.06038(9)	0.4678(2)	0.0159(5)
06	0.3300(2)	0.89318(10)	0.1609(2)	0.0211(5)
07	0.3104(2)	0.85844(10)	0.3853(2)	0.0189(5)
08	0.5771(2)	0.86040(10)	0.3836(2)	0.0198(5)
09	0.2922(3)	0.02272(10)	0.0927(2)	0.0225(5)
010	0.2403(2)	0.09909(10)	0.2584(2)	0.0197(5)
011	0.5057(3)	0.10108(10)	0.2534(2)	0.0204(5)
012	0.7158(3)	0.18815(11)	0.3957(2)	0.0263(6)
013	0 4456(2)	0 18244(10)	0.0007(2)	0.0197(5)
014	0.8244(3)	0.81479(11)	0.5953(2)	0.0271(6)
OW1	0.0166(3)	0.89910(11)	0.9760(3)	0.0261(6)
H1A	0.031(4)	-0 1345(13)	0.026(3)	0.05
H1B	-0.064(3)	-0 1069(18)	-0.101(2)	0.05
OW2	0 4622(3)	0.90335(12)	0.9745(2)	0.0258(6)
H2A	0.473(4)	-0 1015(19)	-0.099(2)	0.05
H2B	0.534(4)	-0.0739(17)	0.032(3)	0.05
OW3	0.0200(3)	0.01659(12)	0.8453(3)	0.0318(6)
H3A	-0.071(3)	0.0131(18)	-0.217(3)	0.05
H3B	0.024(4)	0.0444(16)	-0.096(3)	0.05
OW4	0.0914(3)	0.91867(14)	0.6846(3)	0.0430(7)
H4A	0.142(3)	-0.0721(19)	-0.361(4)	0.05
H4B	-0.003(2)	-0.0716(19)	-0.360(4)	0.05
OW5	0.3190(3)	0.01924(12)	0.8373(2)	0.0306(6)
H5A	0.368(4)	0.0132(18)	-0.210(3)	0.05
H5B	0.247(3)	0.0456(16)	-0.206(4)	0.0
OW6	0.1987(3)	0.82121(14)	0.8753(4)	0.0544(9)
H6A	0.263(3)	-0.185(2)	-0.037(2)	0.05
H6B	0.118(3)	-0.1993(18)	-0.126(4)	0.05
OW7	0.9037(3)	0.30461(13)	0.3271(3)	0.0358(7)
H7A	0.907(4)	0.3194(18)	0.255(2)	0.05
H7B	0.955(4)	0.3289(16)	0.395(3)	0.05
OW8	0.4376(3)	0.30653(11)	0.3329(2)	0.0278(6)
H8A	0.362(3)	0.3206(16)	0.261(3)	0.05
H8B	0.424(4)	0.2686(10)	0.350(4)	0.05
OW9	0.5535(3)	0.25584(13)	0.1003(3)	0.0409(7)
H9A	0.467(3)	0.2395(17)	0.086(4)	0.05
H9B	0.614(3)	0.2298(15)	0.095(4)	0.05
OW10	0.7885(3)	0.30880(13)	0.5604(3)	0.0356(6)
H10A	0.839(4)	0.3363(15)	0.619(3)	0.05
H10B	0.723(4)	0.2911(17)	0.581(4)	0.05
OW11	0.5893(4)	0.39388(16)	0.1650(4)	0.0631(10)
H11A	0.533(4)	0.4030(19)	0.202(4)	0.05
H11B	0.593(5)	0.4178(17)	0.107(4)	0.05
OW12	0.9289(3)	0.76560(11)	0.8589(3)	0.0359(6)
H12A	0.888(4)	-0.2294(17)	0.771(2)	0.05
H12B	0.937(5)	-0.2732(10)	0.877(4)	0.05

TABLE 4. COORDINATES AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS $^{\$}$ (Ų) of atoms in Nashite

 $^{\S}U_{eq}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. * Occupancy of Na2 = 0.496(6).

V1 –	Distance	Bond V	alence	V2 –	Distance	Bond Va	alence		
O1	1.693(2)	1.35		O6	1.622(2)	1.63			
02	1.697(2)	1.33		07	1.805(2)	0.99			
O3	1.898(2	0.77		08	1.824(2)	0.94			
04	1.905(2)	0.76		04	2.001(2)	0.59			
05	2,148(2)	0.39		03	2.032(2)	0.54			
05'	2 151(2)	0.39		05	2 225(2)	0.32			
Mean, Sum:	1.915	4.99		Mean, Sum:	1.918	5.01			
V3 –	Distance	Bond V	alence	V4 –	Distance	Bond Va	alence*		
O9	1.623(2)	1.63		O12	1.610(2)	1.68	(1.64)		
O10	1.800(2)	1.01		O13	1.866(2)	0.84	(0.76)		
011	1.811(2)	0.98		07	1.905(2)	0.76	(0.68)		
04	2.012(2)	0.57		O11	1.911(2)	0.75	(0.67)		
O3	2.014(2)	0.57		02	2.061(2)	0.50	(0.45)		
05	2.217(2)	0.33		05	2.343(2)	0.23	(0.23)		
Mean, Sum:	1.913	5.09		Mean, Sum:	1.949	4.76	(4.43)		
							. ,		
V5 –	Distance	Bond V	alence*	Ca –	Distance	Bond Va	alence		
O14	1.616(2)	1.66	(1.61)	OW1	2.413(2)	0.31			
O13	1.824(2)	0.94	(0.86)	OW2	2.418(2)	0.30			
08	1.876(2)	0.82	(0.74)	OW3	2,452(2)	0.28			
O10	1.907(2)	0.75	(0.68)	OW4	2,463(3)	0.27			
01	2 094(2)	0.46	(0.42)	09	2 484(2)	0.26			
05	2 315(2)	0.10	(0.25)	0\\\/5	2 509(3)	0.20			
Moon Sum:	1.030	4 88	(0.20)	06	2.503(0)	0.24			
Mean, Sum.	1.959	4.00	(4.50)	00	2.513(2)	0.24			
				Moon Sum:	2.594(5)	0.20			
				Mean, oum.	2.401	2.10			
Na1 –	Distance	Bond V	alence	Na2 –	Distance	Bond Va	lence		
OW7	2.346(3)	0.22		O14	2.266(4)	0.26			
OW8	2.357(3)	0.21		012	2.305(4)	0.24			
OW9	2,397(3)	0.19		0\//9	2.379(5)	0.20			
OW10	2 438(3)	0.17		0\\\/7	2 525(5)	0.20			
OW10	2.400(0) 2.473(4)	0.16		0\\\/4	2.546(4)	0.14			
012	2.773(7)	0.10		0114	2.5+0(+)	0.10			
UIZ Maar Our	2.057(3)	0.10		Ovvo Maara Ourra	2.000(0)	0.10			
Mean, Sum:	2.445	1.07		Mean, Sum:	2.484	1.07			
	Bond Vale	ence Sums fo	or Oxvaen Ato	ms of Decavanadate	Group, Excluding H	Bonds			
O1: 1.81		O2:	1.83		O3: 1.88				
O4: 1.92		05:	1.91		O6: 1.87				
07:175		08.	1 76	O9: 1.89					
010.176		011	· 1 73		012.2.02				
013: 1.78		014	: 1.87		012. 2.02				
	5				and a First March	Danda			
01/11.0.21	Bond	a valence Su	Ims for Oxyge	n atoms of H ₂ O Mole	ecules, Excluding H	Bonas			
0101.0.31		0002	2. 0.30		0003. 0.28				
0004: 0.40		OW	5: 0.24		0006: 0.30				
OW7: 0.36		OWe	3: 0.21		OW9: 0.39				
OW10: 0.17		OW?	11: 0.16		OW12: 0.34	4			

Bond valences were calculated using the terms in Brese & O'Keeffe (1991). * The bond valences in parentheses for V4 and V5 were calculated using the parameters for mixed V⁴⁺/V⁵⁺ sites from Brown (1981).



FIG. 3. The atomic arrangement of nashite projected down [100], depicting the $[(V^{4+}V^{5+}_{9}) O_{28}]^{7-}$ structural unit and the $[Na_3Ca_2(OH_2)_{22} \bullet 2H_2O]^{7+}$ interstitial unit. The $[(V^{4+}V^{5+}_{9}) O_{28}]^{7-}$ polyanion is depicted in orange and the Ca atom is red; Na atoms are yellow. The unit cell is outlined in black, with the *b* axis horizontal.

charge-balance with the interstitial unit; the IVCT between the vanadium atoms in V4 and V5 are the cause of the blue-green color in nashite.

The interstitial unit in nashite and its linkage with the structural unit

The $[(V^{4+}V^{5+}_9)O_{28}]^{7-}$ structural unit is the anionic portion of the atomic arrangement, and in nashite its net charge of 7– is balanced by the *interstitial unit*, $[Na_3Ca_2(OH_2)_{22}\bullet 2H_2O]^{7+}$. The interstitial unit is formed of chains of $[Na_{31}(OH_2)_{14}]_{\infty}$, the vacancy a result of the half-occupied Na2 site [refined Na2 occupancy = 0.496(6)]. Like the oxide bronze mineral bannermanite (Hughes & Finger 1983), charge balance for the reduced vanadyl atom is attained by a half-occupancy of the Na2 site. Attached to the Na chains are the $[Ca(OH_2)_6O_2]$ polyhedra, sharing an OW4–OW6 edge with Na2. Figure 4 depicts the $[Na_3Ca_2(OH_2)_{22}]_{\infty}^{7+}$ chains. The interstitial unit contains two isolated H₂O molecules that complete the $[Na_3Ca_2(OH_2)_{22}\bullet 2H_2O]^{7+}$ composition.

The interstitial unit is linked to the structural unit by hydrogen bonding and bonding between the oxygen atoms of the vanadylnonavanadate polyanion and the interstitial cations. Oxygen atoms O6, O9, O12, and O14, exterior atoms of the structural unit, bond directly to the Na or Ca atoms of the interstitial unit. All oxygen atoms of the structural unit except O5, O6, O9, and O12 are linked through hydrogen bonding to the interstitial unit, as they are all less than 2.2 Å from H atoms of the interstitial unit.

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FIG. 4. The [Na₃Ca₂(OH₂)₂₂]⁷⁺ interstitial chain in nashite; Na = yellow, Na² = orange. Na² sites are half-occupied. The addition of two isolated H₂O molecules completes the interstitial unit of [Na₃Ca₂(OH₂)₂₂•2H₂O]⁷⁺.

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