

LASALITE, Na₂Mg₂[V₁₀O₂₈]•20H₂O, A NEW DECAVANADATE MINERAL SPECIES FROM THE VANADIUM QUEEN MINE, LA SAL DISTRICT, UTAH: DESCRIPTION, ATOMIC ARRANGEMENT, AND RELATIONSHIP TO THE PASCOITE GROUP OF MINERALS

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ABSTRACT

Lasalite, Na₂Mg₂[V₁₀O₂₈]•20H₂O, is a new mineral species from the Vanadium Queen mine, La Sal District, Utah, U.S.A.; the mineral is named after the mining district in which it was discovered. Lasalite occurs in efflorescences on the sandstone walls of the mine workings and in fractures in the sandstone. The mineral forms by oxidation of the primary vanadium oxide bronze phase (corvusite) by vadose water and reaction with dolomite and calcite cement of the host sandstone. Lasalite is yellow to yellow-orange with a yellow streak, and transparent with an adamantine luster. The Mohs hardness is 1; crystals are very brittle and shatter with the slightest pressure. No cleavage was observed. The density, measured with a Berman balance using an 8.4 mg sample, is 2.38(2) g/cm³, and the calculated density is 2.362 g/cm³, using the empirical formula. Lasalite crystallizes as blocky crystals elongate parallel to [010] to massive crusts of rounded crystals, up to 1–2 mm in diameter. On euhedral crystals, the forms present are {100}, {010}, {001}, { $\bar{1}11$ } and {111}. Twinning has not been observed. Lasalite dehydrates rapidly under the electron beam and is soluble in water. Therefore, the chemical analysis was performed by wet-chemistry methods, yielding (oxide, wt.%) Na₂O 4.06, MgO 5.42, CaO 1.75, K₂O 0.47, V₂O₅ 61.85, SO₃ 2.55, H₂O (difference) 23.88. The analyses yield the empirical formula (Na_{1.84}Ca_{0.44}K_{0.14})_{Σ2.42}Mg_{1.89}(V_{9.55}S_{0.45})_{Σ10.00}O_{28.55}•18.61H₂O (formula basis: V + S = 10 *apfu*); on the basis of the crystal structure, the ideal formula is Na₂Mg₂[V₁₀O₂₈]•20H₂O. The 2V_x for this optically negative biaxial mineral was determined at three wavelengths, 550 nm: 32(1)°, 589 nm: 43(1)°, and 650 nm: 53(1)°; lasalite thus exhibits strong *r* > *v* dispersion. The pleochroic formula is X light greenish yellow, Y light yellow, Z light brown. The indices of refraction are: α 1.743(5), β 1.773(5), γ 1.780(5) (at 589 nm). Lasalite is monoclinic, C2/c, with *a* 23.9019(7), *b* 10.9993(3), *c* 17.0504(5) Å, β 118.284(1)°. The structure was determined using direct methods and three-dimensional X-ray-diffraction data measured with a CCD detector and refined to *R* = 0.0289. The mineral is a member of the pascoite group of minerals, which have a structural unit containing the [V₁₀O₂₈]⁶⁻ decavanadate polyanion. In lasalite, the fully hydrated interstitial group has a composition of {Na₂Mg₂(H₂O)₂₀}⁶⁺. The interstitial unit is formed of Mg(OH₂)₆ octahedra and seven-coordinated Na atoms that occur in a [Na₂O₆(OH₂)₆] dimer. The Na-complex dimer of the interstitial unit links to the structural unit by hydrogen bonding and by sharing oxygen atoms with the decavanadate group, whereas the Mg(OH₂)₆ shares none of its oxygen with any other polyhedron, bonding to the structural unit only through hydrogen bonding.

Keywords: lasalite, crystal structure, pascoite group, decavanadate, vanadium, Vanadium Queen mine, La Sal District, Utah.

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SOMMAIRE

La lasalite, $\text{Na}_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}] \cdot 20\text{H}_2\text{O}$, est une nouvelle espèce minérale découverte à la mine Vanadium Queen, district de La Sal, Utah; le nom du minéral rappelle le camp minier où il a été trouvé. La lasalite se trouve en efflorescences sur les parois de grès de la mine et le long de fractures dans ce grès. Le minéral s'est formé par oxydation d'un bronze d'oxyde de vanadium primaire (la corvusite) par l'action de l'eau vadose et par réaction avec le ciment dolomitique et calcitique du grès encaissant. La lasalite est jaune à jaune-orange avec une rayure jaune; elle est transparente avec un éclat adamantin. La dureté de Mohs est 1; les cristaux sont très cassants et volent en éclats à la moindre pression. Aucun clivage n'est signalé. La densité, mesurée avec une balance de type Berman sur un échantillon de 8.4 mg, est 2.38(2) g/cm^3 , et la densité calculée à partir de la formule empirique est 2.362 g/cm^3 . La lasalite se présente en cristaux polyédriques allongés parallèles à [010] et en encroûtements massifs faits de cristaux arrondis atteignant 1–2 mm de diamètre. Les cristaux idiomorphes montrent les formes {100}, {010}, {001}, {111} et {111}. Nous n'avons pas décelé de macles. La lasalite se déshydrate rapidement sous le faisceau d'électrons, et elle est soluble dans l'eau. C'est pourquoi l'analyse chimique a été faite par voie humide, ce qui a donné (en % pondéraux d'oxydes): Na_2O 4.06, MgO 5.42, CaO 1.75, K_2O 0.47, V_2O_5 61.85, SO_3 2.55, H_2O (par différence) 23.88. Les analyses mènent à la formule empirique $(\text{Na}_{1.84}\text{Ca}_{0.44}\text{K}_{0.14})_{\Sigma 2.42}\text{Mg}_{1.89}(\text{V}_{9.55}\text{S}_{0.45})_{\Sigma 10.00}\text{O}_{28.55} \cdot 18.61\text{H}_2\text{O}$ (calculée sur une base de $\text{V} + \text{S} = 10$ apfu); en tenant compte de l'ébauche de la structure cristalline, la formule idéale est $\text{Na}_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}] \cdot 20\text{H}_2\text{O}$. Le $2V_x$ de ce minéral optiquement biaxe négatif a été déterminé à trois longueurs d'ondes, 550 nm: $32(1)^\circ$, 589 nm: $43(1)^\circ$, et 650 nm: $53(1)^\circ$; la lasalite fait donc preuve d'une forte dispersion, $r > v$. La formule pléochroïque est X jaune verdâtre pâle, Y jaune pâle, Z brun pâle. Les indices de réfraction sont: α 1.743(5), β 1.773(5), γ 1.780(5) (à 589 nm). La lasalite est monoclinique, $C2/c$, avec a 23.9019(7), b 10.9993(3), c 17.0504(5) Å, β 118.284(1)°. Nous en avons établi la structure par méthodes directes et par affinement de données de diffraction X tridimensionnelles mesurées avec un détecteur de type CCD, jusqu'à un résidu R de 0.0289. Il s'agit d'un membre du groupe de la pascoïte, minéraux qui contiennent le polyanion décavanadate $[\text{V}_{10}\text{O}_{28}]^{6-}$. Dans la lasalite, le groupe interstitiel pleinement hydraté possède la composition $\{\text{Na}_2\text{Mg}_2(\text{H}_2\text{O})_{20}\}^{6+}$. Cette unité interstitielle est formée d'octaèdres $\text{Mg}(\text{OH}_2)_6$ et d'un dimère contenant le Na à coordination sept, $[\text{Na}_2\text{O}_6(\text{OH}_2)_6]$. Ce complexe de Na forme des liaisons hydrogène avec l'unité structurale et partage aussi des atomes d'oxygène avec le groupe décavanadate, tandis que le $\text{Mg}(\text{OH}_2)_6$ ne partage aucun de ses atomes d'oxygène avec d'autres polyèdres; seules les liaisons hydrogènes assurent sa connexion avec l'unité structurale.

(Traduit par la Rédaction)

Mots-clés: lasalite, structure cristalline, groupe de la pascoïte, décavanadate, vanadium, mine Vanadium Queen, district de La Sal, Utah.

INTRODUCTION

Among the secondary minerals that form from the oxidation of vanadium orebodies in sedimentary rocks are the bright yellow to orange members of the pascoite group, which, in addition to pascoite, $\text{Ca}_3[\text{V}_{10}\text{O}_{28}] \cdot 17\text{H}_2\text{O}$ (Hughes *et al.* 2005), includes magnesiopascoite, $\text{Ca}_2\text{Mg}[\text{V}_{10}\text{O}_{28}] \cdot 16\text{H}_2\text{O}$ Kampf & Steele 2008), hummerite, $\text{K}_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}] \cdot 16\text{H}_2\text{O}$: Hughes *et al.* 2002), and perhaps huemulite ($\text{Na}_4\text{Mg}[\text{V}_{10}\text{O}_{24}] \cdot 24\text{H}_2\text{O}$ (Gordillo *et al.* 1966). Each of these minerals contains the decavanadate anionic complex, $[\text{V}_{10}\text{O}_{28}]^{6-}$, weakly bonded by alkali and alkaline-earth cations and H_2O molecules. Recent collecting at the Vanadium Queen mine (38°20'11" N, 109°04'58" E), 18 km east of La Sal, San Juan County, Utah, USA, produced an abundance of a mineral presumed by earlier workers to be pascoite. However, the X-ray powder-diffraction pattern does not match that of pascoite or any other known mineral. Data presented herein show that it is a new mineral, related to pascoite, magnesiopascoite, hummerite, and huemulite. The mineral and name, lasalite, in recognition of the type locality, have been approved as a new species by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA 2007–005). Cotype material has been deposited in the Smithsonian

Museum, Washington, D.C., USA (catalog number NMNH–174744). Subsequent to our description of the phase, we learned of the description of the synthetic phase equivalent to lasalite (Iida & Ozeki 2004). We comment on the similarity of the natural and synthetic phases below.

OCCURRENCE

Lasalite occurs in efflorescences on the sandstone walls of the mine workings and along fractures in the sandstone. The mineral forms by oxidation of the primary vanadium oxide bronze phase (corvusite) by vadose water and reaction with dolomite and calcite cement of the host sandstone. Evaporation leads to the formation of the efflorescent assemblage that contains lasalite, rossite, dickthomssenite, and hewettite. Uranium and vanadium minerals in the La Sal area, as elsewhere in the Colorado Plateau, occur together as bedded or roll-front deposits, impregnating sandstone of the Salt Wash Member of the Jurassic Morrison Formation (Carter & Gualtieri 1965). Primary ore minerals occur as reduced oxides of uranium and vanadium and silicates, formed near local concentrations of organic matter or other reducing agents. The Vanadium Queen claims were originally staked in 1931, but most mining occurred after 1954, when exploratory drilling by the

U.S. Geological Survey led to discoveries of major portions of the orebody.

The main ore minerals found at the Vanadium Queen mine are montroseite, corvusite, vanadium hydromica and uraninite, with the produced ore averaging 2.79% V₂O₅ and 0.35% U₃O₈. Oxidized ore consists largely of vanadium hydromica and tyuyamunite. Lasalite has been identified in samples of efflorescence from the nearby Firefly–Pigmy and Blue Cap mines, each tapping deposits in the same paleochannel as the Vanadium Queen orebody. Lasalite has also been identified in samples from other mines on the Colorado Plateau, for example the Yellow Cat district, Grand County, Utah, U.S.A.

APPEARANCE AND PHYSICAL PROPERTIES

The lasalite-rich efflorescent crusts are commonly 1 to 3 mm thick. The surfaces of the crusts may be rounded owing to dissolution, but may also glisten from exposed crystal faces. Some sandstone surfaces are coated with isolated single crystals 1 to 2 mm in length (Fig. 1).

Lasalite is transparent, yellow to yellow-orange with a yellow streak and an adamantine luster. Where lasalite forms a thin layer on dark sandstone, the apparent color is brown. In thicker layers, the yellow color is more apparent; even thicker crusts are yellow-orange. On prolonged exposure to conditions of low humidity, the crystals dehydrate to a yellow powder. The Mohs hardness is 1; the crystals are very brittle, and shatter with the slightest pressure. No cleavage was observed. Density, measured with a Berman balance using an 8.4 mg sample, is 2.38(2) g/cm³, and the calculated density is 2.362 g/cm³, calculated using the empirical formula.

Lasalite occurs as blocky prisms elongate parallel to [010] and as massive crusts of rounded crystals. On euhedral crystals, the forms present are {100}, {010}, {001}, {111} {111}, inferred by comparison with SHAPE[®]-generated drawings; no twinning was observed in lasalite. The deep orange color of lasalite easily distinguishes it from the very pale yellow to cream of the associated rossite (metarossite) and dickthomsonite. However, it is identical in all respects to pascoite and other members of that group, and can only be distinguished by X-ray diffraction or chemical methods.

THE COMPOSITION OF LASALITE

The high-quality crystal-structure determination of lasalite unequivocally yielded the ideal mineral formula Na₂Mg₂[V₁₀O₂₈]•20H₂O; indeed, even the hydrogen atoms were uniquely and easily located in the structure determination. However, microbeam methods of chemical analysis presented problems that resulted from volatilization of the mineral. Initial microbeam analyses

of the phase indicated that the major cations are V >> Mg ≈ Na, but the extreme softness of the mineral (Mohs hardness ≈ 1), its rapid dissolution in water, and the virtually instantaneous volatilization of the phase under an electron beam prohibited anything but a qualitative analysis by microbeam methods.

Two hand-picked samples of lasalite were prepared for wet-chemical analysis. The samples contained contaminants of matrix and other new minerals that have not yet been completely characterized. The lasalite crystals were dissolved in distilled water; concentrations of V, Mg, Ca, Na, S and K were determined on a Beckman Spectrascan V direct-current argon-plasma spectrometer by comparing the emission intensity at selected wavelengths against those of external standards made from 1000 µg/mL single-element ICP solutions purchased from Alfa Aesar; the concentration of H₂O was determined by difference. After a preliminary measurement, standard solutions were made that closely match the sample's composition in order to mitigate any possible matrix effects. The final results reported in Table 1 were obtained. Instrumental precision on the single analysis is estimated to be 5%. The mean analytical results represent the average of the wet-chemical analysis of a 82.97 mg sample of hand-picked material (see above) with two analyses at two dilutions and a 68.30 mg sample with one analysis (total of three analyses). The empirical formula of lasalite derived from these results (formula basis V + S = 10 *apfu*) is (Na_{1.84}Ca_{0.44}K_{0.14})_{Σ2.42}Mg_{1.89}(V_{9.55}S_{0.45})_{Σ10.00}O_{28.55}•18.61H₂O.

OPTICAL PROPERTIES

A spindle-stage-equipped microscope was used for the determination of the optical properties for lasalite. A single crystal was mounted on an X-ray goniometer head, and its orientation matrix was determined on both the light microscope and a single-crystal diffractometer; these data were then used to determine the optical orientation of the mineral, as discussed in Gunter & Twamley (2001), resulting in *b* = *Y*, and *c* : *Z* = 1°. The EXCALIBRW program (Gunter *et al.* 2004, 2005) was used not only to determine the orientation of the crystal and to measure its indices of refraction without appreciable error due to misorientation, but also to determine 2*V* for this optically negative biaxial mineral at three wavelengths, as follows: 550 nm: 32(1)°, 589 nm: 43(1)°, 650 nm: 53(1)°. These data show that lasalite exhibits strong *r* > *v* dispersion. The program EXCALIBRW also was used to obtain the pleochroic formula: *X* light greenish yellow, *Y* light yellow, *Z* light brown. Finally, the indices of refraction were determined by the methods discussed in Su *et al.* (1987) and found to be: α 1.743(5), β 1.773(5), γ 1.780(5) (at 589 nm).

The compatibility index, as discussed in Mandarino (1981), is a useful check on the physical properties of

a mineral (*i.e.*, density and mean index of refraction) and its chemical composition. In the case of lasalite, the compatibility index is -0.007 , showing excellent agreement. For lasalite, the index can be used to confirm the H_2O content, which proved difficult to determine. We found the H_2O content to be 23.88% by difference; if we recalculate the compatibility index with $\pm 5\%$ H_2O (*i.e.*, 18.88 and 28.88%), we arrive at values of -0.064 and 0.044 , respectively. Thus the compatibility index, in this case, serves to confirm the reported H_2O content.

CRYSTAL STRUCTURE: EXPERIMENTAL

A sample of lasalite was mounted on a Bruker Apex CCD diffractometer equipped with graphite-monochro-

mated $MoK\alpha$ radiation. Refined cell-parameters and other crystal data are listed in Table 2. Redundant data were collected for a sphere of reciprocal space, and absorption was corrected using semi-empirical methods as implemented in the programs SADABS (Bruker AXS, Inc. 2003). Data were integrated and corrected for Lorentz and polarization factors using the Bruker program SAINTPLUS (Bruker AXS, Inc. 2003).

The structure was solved using direct methods and difference-Fourier maps, as implemented in the Bruker SHELXTL v. 6.14 (Bruker AXS, Inc. 2000) package of programs; neutral-atom scattering factors and terms for anomalous dispersion were employed throughout the solution and refinement. Refinement was performed with anisotropic thermal parameters for all



FIG. 1. Lasalite crystals on sandstone surface (width of image 3.5 mm). Uppermost crystal shows the b face, and the prism is bounded by $\{100\}$ and $\{001\}$ pinacoids. Photo courtesy of Joe Marty.

TABLE 1. CHEMICAL COMPOSITION OF LASALITE

Constituent	wt.%	Range	Std. Dev.	<i>apfu</i> ($v + s = 10$)*
Na ₂ O	4.06	3.88 – 4.20	0.16	1.84
MgO	5.42	4.90 – 5.82	0.47	1.89
CaO	1.75	1.63 – 1.93	0.16	0.44
K ₂ O	0.47	0.41 – 0.51	0.05	0.14
V ₂ O ₅	61.87	59.00 – 64.02	2.59	9.55
SO ₃	2.55	2.34 – 2.91	0.32	0.45
H ₂ O	23.88	difference		18.61
Total	100.00			

* For all oxides except H₂O, *apfu* value is for the metal of the oxide species.

TABLE 2. LASALITE: CRYSTAL DATA AND RESULTS OF THE STRUCTURE REFINEMENT

Unit cell by least squares	space group: $C2/c$, 7077 reflections
Unit-cell parameters	a 23.9019(7), b 10.9993(3)
	c 17.0504(5) Å, β 118.284(1)°
Frame width, scan time, number of frames	0.20°, 15 s, 4500
Detector distance	5 cm
Effective transmission	0.9186 - 1.000
R_{int} (before and after SADABS absorption correction)	0.0252, 0.0192
Measured reflections, full sphere	44,151
Unique reflections, refined parameters	5758, 341
$R1$, $I > 4\sigma$	0.0289
Largest difference peaks	+0.45(8), -0.32(8) e ⁻ · Å ⁻³
Goodness-of-fit	1.139

non-hydrogen atoms, and the structure was refined on F²; the hydrogen atoms in lasalite were easily located with difference-Fourier maps. In Table 3, we list the atom parameters, and in Table 4, we present selected interatomic distances. Tables 5 and 6 contain anisotropic thermal parameters and observed and calculated structure-factors, respectively. Copies of Tables 5 and 6 are available from the Depository of Unpublished Data on the MAC web site [document Lasalite CM46_1365].

ATOMIC ARRANGEMENT OF LASALITE

As noted by Hughes *et al.* (2005) in their description of the atomic arrangement of pascoite, minerals

containing the (V₁₀O₂₈)⁶⁻ decavanadate polyanion commonly conform to the bipartite nature of mineral structures elucidated by Hawthorne (1983). In this definitive work on the atomic arrangements of minerals, Hawthorne recognized two distinct parts of complex mineral structures: (a) the *structural unit*, usually the anionic portion of the structure that contains bonds of higher bond-valence, and (b) the *interstitial complex*, typically the cationic part of the structure, with bonds of lower bond-valence between alkaline and alkaline-earth cations and (H₂O), (OH), and any Cl groups. Perhaps there is no mineral group more illustrative of this bipartite nature of mineral structures than the alkali and alkaline-earth vanadium oxide hydrates. Schindler *et al.* (2000) applied Hawthorne's (1983) observations to such vanadium minerals and elucidated the nature of the bonding between the two distinct parts of the structure. Below, we describe the anhydrous, polyanionic structural unit and the fully hydrated interstitial complex in lasalite; portions of the description are based on the discussion of the decavanadate-bearing mineral pascoite by Hughes *et al.* (2005).

As noted above, the synthetic analog of lasalite was described by Iida & Ozeki (2004). The structures of the natural and synthetic phases are identical, but the descriptions of the Na dimeric cations differ, as noted below.

The structural unit in lasalite

The [V₁₀O₂₈]⁶⁻ decavanadate polyanion in lasalite is depicted in Figure 2. The polyanion is formed of

TABLE 3. LASALITE: POSITIONS AND EQUIVALENT DISPLACEMENT PARAMETERS OF ATOMS, AND BOND-VALENCE SUMS FOR NON-HYDROGEN ATOMS

Atom	x	y	z	U _{eq}	BVS
Atoms of the (V₁₀O₂₈)⁶⁻ Structural Unit					
V1	0.011823(13)	0.08649(2)	0.852530(17)	0.01374(7)	5.05
V2	-0.072825(13)	-0.11481(3)	0.714987(18)	0.01598(7)	5.05
V3	0.071806(13)	0.29236(3)	0.783156(19)	0.01658(7)	5.05
V4	0.132628(14)	0.08738(3)	0.719361(19)	0.01731(7)	5.03
V5	0.155643(14)	0.09083(3)	0.911954(19)	0.01845(7)	5.04
O1	-0.04289(6)	0.08873(11)	0.88829(8)	0.0184(2)	1.88
O2	0.08380(6)	0.08685(11)	0.94487(8)	0.0185(2)	1.90
O3	-0.00967(6)	-0.08342(10)	0.67228(8)	0.0151(2)	1.89
O4	0.00969(5)	0.25823(10)	0.82766(7)	0.0153(2)	1.88
O5	-0.06272(5)	0.08728(10)	0.72167(7)	0.0145(2)	1.98
O6	-0.07332(6)	-0.26098(12)	0.71410(9)	0.0258(3)	1.69
O7	-0.13774(6)	-0.07787(11)	0.60724(8)	0.0196(2)	1.94
O8	-0.11641(6)	-0.07713(11)	0.77623(8)	0.0188(2)	1.77
O9	0.13689(6)	0.25559(11)	0.89341(8)	0.0199(2)	1.79
O10	0.11612(6)	0.25431(11)	0.72347(8)	0.0187(2)	1.73
O11	0.17222(6)	0.08862(13)	0.66527(9)	0.0258(3)	1.81
O12	0.19171(6)	0.08930(12)	0.83800(8)	0.0203(2)	1.83
O13	0.07163(7)	0.43782(13)	0.78232(9)	0.0271(3)	1.73
O14	0.21463(6)	0.08846(14)	1.01063(9)	0.0295(3)	1.71
Atoms of the (Na₂Mg₂(H₂O)₂₀)⁸⁺ Interstitial Complex					
Mg	0.11242(3)	0.59615(5)	0.59125(4)	0.01950(12)	2.22
Na	0.19432(6)	-0.17951(10)	1.03761(6)	0.0497(3)	0.83
O15	0.11247(8)	0.40968(13)	0.59659(10)	0.0280(3)	0.38
H15A	0.1126(15)	0.373(3)	0.634(2)	0.050	
H15B	0.0996(15)	0.372(3)	0.558(2)	0.050	
O16	0.04133(7)	0.40772(14)	0.96382(9)	0.0277(3)	0.40
H16A	0.0318(14)	0.363(3)	0.929(2)	0.050	
H16B	0.0213(15)	0.461(3)	0.941(2)	0.050	
O17	0.17730(7)	0.59206(14)	0.54119(10)	0.0267(3)	0.34
H17A	0.2095(15)	0.594(3)	0.572(2)	0.050	
H17B	0.1717(14)	0.633(3)	0.501(2)	0.050	
O18	0.17826(8)	0.59226(15)	0.72130(10)	0.0342(4)	0.41
H18A	0.1941(15)	0.643(3)	0.750(2)	0.050	
H18B	0.1952(15)	0.536(3)	0.744(2)	0.050	
O19	0.03719(8)	0.60329(15)	0.62597(11)	0.0299(3)	0.30
H19A	0.0456(15)	0.600(3)	0.675(2)	0.050	
H19B	0.0188(15)	0.657(3)	0.607(2)	0.050	
O20	0.11564(9)	0.21806(14)	1.09537(11)	0.0359(4)	0.39
H20A	0.1145(15)	0.185(3)	1.131(2)	0.050	
H20B	0.1039(14)	0.180(3)	1.054(2)	0.050	
O21	0.26202(9)	-0.29234(17)	1.16608(14)	0.0428(4)	0.22
H21A	0.2853(15)	-0.336(3)	1.168(2)	0.050	
H21B	0.2538(15)	-0.318(3)	1.204(2)	0.050	
O22	-0.05898(11)	-0.21698(16)	0.52068(12)	0.0446(5)	0.05
H22A	-0.0481(15)	-0.187(3)	0.490(2)	0.050	
H22B	-0.0469(14)	-0.181(3)	0.562(2)	0.050	
O23	0.18925(12)	-0.3592(2)	0.95033(15)	0.0604(6)	0.26
H23A	0.1861(14)	-0.429(3)	0.968(2)	0.050	
H23B	0.1629(16)	-0.357(3)	0.912(2)	0.050	
O24	0.23209(8)	0.62491(16)	0.29829(12)	0.0388(4)	0.00
H24A	0.2586(15)	0.627(3)	0.351(2)	0.050	
H24B	0.2067(15)	0.661(3)	0.295(2)	0.050	

TABLE 4. LASALITE: SELECTED BOND-LENGTHS (Å), BOND VALENCE OF EACH BOND (VALENCE UNITS) AND BOND-VALENCE SUMS

V1 – O1	1.6848(12)	(1.38)	V2 – O6	1.6079(14)	(1.69)
O2	1.6947(12)	(1.34)	O7	1.8018(13)	(1.00)
O3	1.9115(12)	(0.75)	O8	1.8380(13)	(0.91)
O4	1.9314(12)	(0.71)	O3	1.9924(12)	(0.60)
O5	2.0942(12)	(0.46)	O3	2.0273(12)	(0.54)
O5	2.1305(12)	(0.41)	O5	2.2329(12)	(0.31)
Mean:	1.908	(Σ 5.05)	Mean:	1.915	(Σ 5.05)
V3 – O13	1.6001(14)	(1.73)	V4 – O11	1.6042(13)	(1.71)
O9	1.8293(12)	(0.93)	O12	1.8383(13)	(0.91)
O10	1.8315(12)	(0.93)	O8	1.8595(13)	(0.86)
O4	1.9972(12)	(0.59)	O10	1.8863(13)	(0.80)
O4	2.0044(12)	(0.58)	O1	2.0588(13)	(0.50)
O5	2.2639(12)	(0.29)	O5	2.3228(12)	(0.25)
Mean:	1.921	(Σ 5.05)	Mean:	1.928	(Σ 5.03)
V5 – O14	1.6035(13)	(1.71)	Mg – O18	2.0220(16)	(0.41)
O12	1.8340(13)	(0.92)	O16	2.0275(15)	(0.40)
O9	1.8576(13)	(0.86)	O20	2.0450(15)	(0.39)
O7	1.8976(13)	(0.77)	O15	2.0530(15)	(0.38)
O2	2.0442(13)	(0.52)	O17	2.0952(15)	(0.34)
O5	2.3086(12)	(0.26)	O19	2.1445(17)	(0.30)
Mean:	1.924	(Σ 5.04)	Mean:	2.965	(Σ 2.22)
Na – O21	2.3660(21)	(0.22)			
O23	2.4421(28)	(0.18)			
O7	2.4521(15)	(0.17)			
O11	2.6656(17)	(0.10)			
O23	2.7251(30)	(0.08)			
O22	2.9282(26)	(0.05)			
O14	3.0571(25)	(0.03)			
Mean:	2.662	(Σ 0.83)			

ten distorted, edge-sharing octahedra, and is found in numerous synthetic vanadate compounds, listed in Hughes *et al.* (2005).

Schindler *et al.* (2000) defined the vanadyl bond as a V^{5+} -O bond of less than 1.74 Å in length. Each of the vanadium octahedra in lasalite contains one vanadyl bond except the V1 octahedron, which contains two vanadyl bonds. In the V2, V3, V4, and V5 octahedra, the vanadyl bond is *trans* to the long V-O bond, and the remaining four equatorial bonds are approximately equal; this disposition of bonds is typical of the decavanadate group in other compounds (Hughes *et al.* 2005).

Oxygen atoms of the decavanadate polyanion bond to Na and H atoms of the interstitial complex to link the structural unit and the interstitial unit. Atoms O7, O11, and O14, which are "exterior" atoms of the decavanadate polyanion (Fig. 2), bond to Na atoms of the interstitial complex, whereas other oxygen atoms of the decavanadate polyanion bond to the interstitial complex through hydrogen bonding.

As noted by Hughes *et al.* (2002), one oxygen atom of the decavanadate group is of particular interest. Oxygen atom O5 in the interior of the decavanadate group (Fig. 2) bonds to six vanadium atoms, a particularly unusual coordination for oxygen, and even more unusual where coordinated to a pentavalent cation. In each octahedron, the bond to O5 is the longest in the polyhedron, and thus the V-O5 bond valence is the

lowest in each polyhedron. The bond valence for O5, 1.96 valence units (*vu*), demonstrates that despite the unusual coordination for O5, the efficacy of the valence-matching principle is maintained.

The interstitial unit in lasalite

Figure 3 depicts the disposition of the structural units in the unit cell of lasalite. The anhydrous decavanadate structural units are linked by the interstitial unit in lasalite. The interstitial unit in lasalite is the hydrated portion of the atomic arrangement, and has a composition of $\{Na_2Mg_2(H_2O)_{20}\}^{6+}$. All oxygen atoms of the interstitial unit (O15-O24) are parts of H_2O molecules, and thus the interstitial unit is fully hydrated; atoms O24 bonds to the remainder of the structure only through hydrogen bonding.

The interstitial unit is formed of $Mg(OH)_6$ octahedra and seven-coordinated Na that occur in a $[Na_2O_6(OH)_6]$ dimer (Fig. 4). The Na dimer is similar to that described by Iida & Ozeki (2004), although we expand the radius of the Na bonds to include a seventh bond to each sodium atom as compared to their six bonds. The Na-complex dimer of the interstitial unit links to the decavanadate structural unit by hydrogen bonding and by sharing oxygen atoms O7, O11, and O14, whereas the $Mg(OH)_6$ shares none of its H_2O oxygen with any other polyhedron, bonding to the structural unit only through hydrogen bonding.

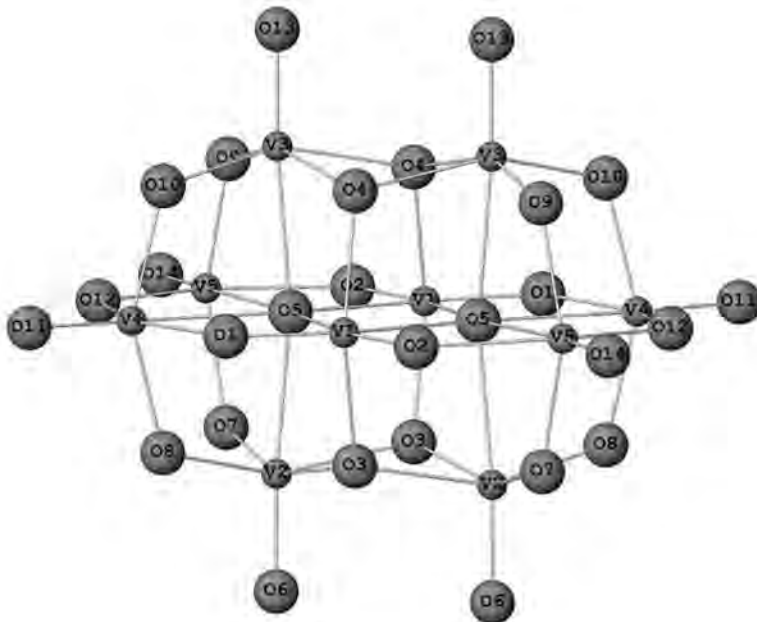


FIG. 2. The $[V_{10}O_{28}]^{6-}$ decavanadate group in lasalite.

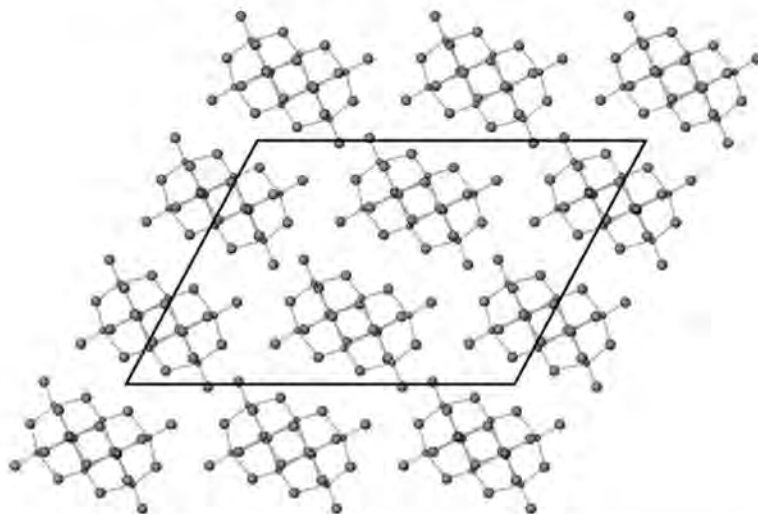


FIG. 3. The disposition of structural units in the unit cell of lasalite projected on (010).

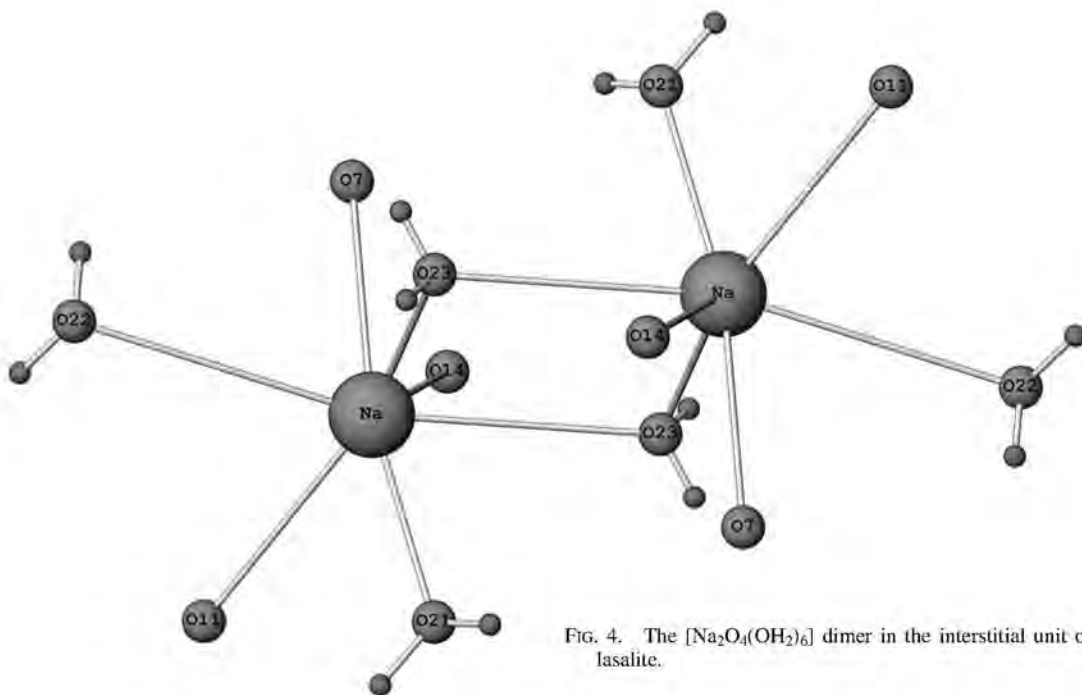


FIG. 4. The $[\text{Na}_2\text{O}_4(\text{OH})_2]_6$ dimer in the interstitial unit of lasalite.

Lasalite as a member of the pascoite group

The pascoite group of minerals is formed of pascoite, $\text{Ca}_3[\text{V}_{10}\text{O}_{28}] \cdot 17\text{H}_2\text{O}$, magnesiopascoite, $\text{Ca}_2\text{Mg}[\text{V}_{10}\text{O}_{28}] \cdot 16\text{H}_2\text{O}$, hummerite, $\text{KMg}[\text{V}_5\text{O}_{14}] \cdot 8\text{H}_2\text{O}$, perhaps

huemulite $\text{Na}_4\text{Mg}[\text{V}_{10}\text{O}_{28}] \cdot 24\text{H}_2\text{O}$ (structure not known), and now lasalite, $\text{Na}_2\text{Mg}_2[\text{V}_{10}\text{O}_{28}] \cdot 20\text{H}_2\text{O}$. Each of the known structures in the group has the $[\text{V}_{10}\text{O}_{28}]^{6-}$ decavanadate polyanion as the structural unit, virtually indistinguishable among the structures.

The structures differ, however, in the way in which the residual negative charge is balanced by the interstitial group.

In each of the pascoite-group structures, the anhydrous structural units are linked by fully hydrated interstitial groups. The pascoite-group minerals differ according to the cations that satisfy the residual 6⁻ charge of the decavanadate group and the amount of H₂O in the interstitial unit; pascoite Ca₃•17H₂O, hummerite: K₂Mg₂•16H₂O, lasalite: Na₂Mg₂•20H₂O, and huemulite: Na₄Mg•24H₂O. In each structure, the alkali and alkaline earth cations present in the local environment are accommodated in distinct interstitial groups to link the common [V₁₀O₂₈]⁶⁻ decavanadate polyanion.

ACKNOWLEDGMENTS

The staff members of the Instrumentation Laboratory at Miami University are recognized for their continuing maintenance of the X-Ray Diffraction Laboratory. This work was supported, in part, by NSF grant EAR-0003201 to JMH and JR. We thank Joe Marty for his assistance in collecting minerals at the Vanadium Queen mine and for his image of lasalite crystals. Reviewers Madison C. Barkley and Mark Van Baalen are gratefully acknowledged for their constructive comments. We sincerely thank Editor-in-Chief Robert F. Martin for his editorial handling of this manuscript and his dedicated efforts on behalf of the mineralogical community.

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Received October 26, 2007, revised manuscript accepted October 11, 2008.