

Virgilite: a new lithium aluminum silicate mineral from the Macusani glass, Peru

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Abstract

Virgilite is hexagonal, $P6_222$ or $P6_422$; $a = 5.132$, $c = 5.454\text{\AA}$; $\bar{n} = 1.520$, uniaxial (-). Cell content of the crystals studied is $\text{Li}_{0.61}(\text{Si}_{2.37}\text{Al}_{0.60}\text{Fe}_{0.02}\text{P}_{0.01})\text{O}_6$. Virgilite is found in volcanic glass of unusual composition from Macusani, Peru. It is the only naturally-occurring representative of the solid-solution series between β -quartz (Qz) and $\text{LiAlSi}_2\text{O}_6$ (Sp) with a stuffed β -quartz structure. The composition of our material corresponds to $\text{Sp}_{61}\text{Qz}_{39}$.

Introduction

The clear pale-green glass found as stream cobbles near Macusani, Peru (latitude 14°S , longitude $70^\circ 30'\text{W}$) has been a geological curiosity for over half a century (Linck, 1926; Preuss, 1935; Heide, 1936; Martin and de Sitter-Koomans, 1955; Barnes *et al.*, 1970). Its peculiarities are unusual clarity, high alumina content, and the presence of euhedral microphenocrysts of andalusite and smaller needles of sillimanite (Linck, 1926; French and Meyer, 1970). We report here the identification of a new mineral which occurs as a rare to common phase in the Macusani glass. The mineral has a stuffed β -quartz structure and is the only known naturally-occurring member of the β -quartz solid-solution series between $\text{LiAlSi}_2\text{O}_6$ and SiO_2 . The name *virgilite* is proposed for the $\text{LiAlSi}_2\text{O}_6$ end-member. In accordance with customary mineralogical practice, this name should be restricted to members of the solid-solution series with more than 50 mole percent $\text{LiAlSi}_2\text{O}_6$.

The name *virgilite* is given in honor of Professor Virgil E. Barnes of the Bureau of Economic Geology, University of Texas, Austin, Texas. It recognizes his pioneering work in the study of tektites, impactites, and other natural glasses, as well as his collection and investigation of the Macusani material which was used in our study. The mineral and name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Holotype material is deposited at the

National Museum of Natural History, Smithsonian Institution, Washington, D. C. under Meteorite Collection number NMNH 2143-17.

Morphology and occurrence

Virgilite occurs as colorless euhedral crystals up to $50\ \mu\text{m}$ across (Fig. 1), usually prominent hexagonal bipyramids modified by a hexagonal prism. Such euhedral crystals are rare in the 30 samples which we examined; but irregular rosette-shaped fibrous overgrowths of virgilite are commonly observed on the crystals of quartz (Figs. 2, 3), K-feldspar, biotite, and spinel in the glass. The virgilite crystals usually occur in parallel bands resembling flow structure, suggesting that virgilite is a primary phase which crystallized while the glass was molten. Three of the specimens we examined contain up to 10 percent by volume of euhedral virgilite; one sample contains oval partly-resorbed virgilite crystals.

Macusani glass has a granitic composition with an unusually high content of Al, F, Li and B. Chemical analyses (Martin and de Sitter-Koomans, 1955; Elliot and Moss, 1965; Barnes *et al.*, 1970) give (in weight percent): SiO_2 70-73, Al_2O_3 16-17, FeO 1-2, MgO 0.1-0.2, CaO 1-2, Na_2O 3-4, K_2O 3-6. Elliot and Moss (1965) report in addition B_2O_3 0.4, Li_2O 0.8, and F 1.4. Less than 1 weight percent H_2O has been found in the analyzed samples (Barnes *et al.*, 1970). Preliminary analyses made during the course of our study show some apparent discrepancies with these

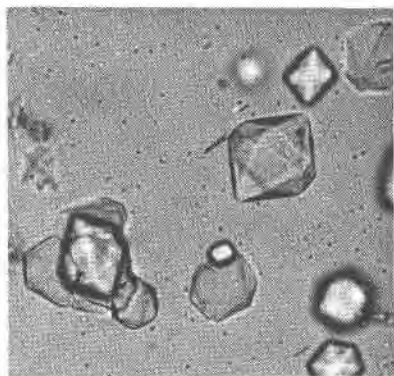


Fig. 1. Euhedral virgilite crystal (40 μ m diameter) surrounded by glass containing several other virgilite crystals. Plane polarized light.

published figures. Additional work is in progress to resolve the differences.

Although the Macusani glass was once considered to be a variety of tektite (Linck, 1926), subsequent studies strongly indicate a volcanic origin (Martin and de Sitter-Koomans, 1955; French and Meyer, 1970). The glass has not yet been observed in outcrop, but at the type locality it is associated with outcrops of an andalusite-bearing volcanic ash flow with a chemical composition virtually identical to that of the glass. The age of this volcanic rock has been determined to be about 4 million years (Barnes *et al.*, 1970).

Chemistry

Virgilite crystals and rosette-shaped overgrowths of virgilite on other minerals were analyzed on an

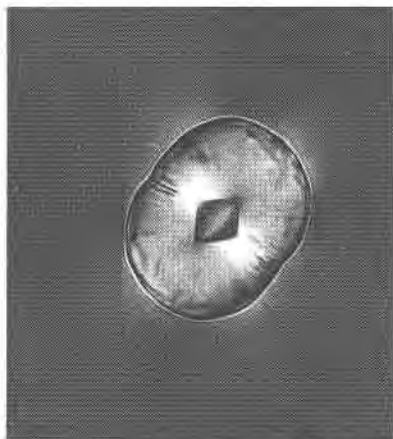


Fig. 2. Rosette-shaped fibrous overgrowth of virgilite on euhedral quartz. Pseudo-euhedral boundaries, as shown here, frequently occur at the glass-rosette interface. These boundaries are systematically related to the orientation of the quartz nucleus. The long axis of the rosette is 120 μ m. Partly crossed polarizers.

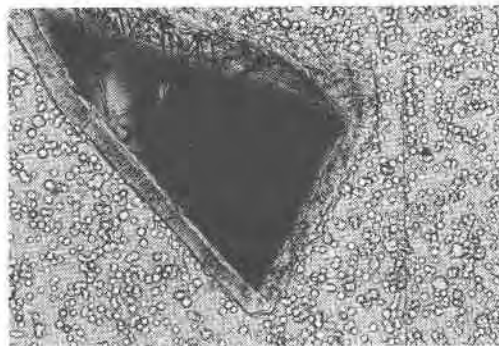


Fig. 3. Black-appearing anhedral quartz fragment overgrown by fibrous virgilite in Macusani glass filled with small euhedral virgilite crystals. This association of euhedral and fibrous virgilite is rare. The quartz fragment is 400 μ m long. Partly crossed polarizers.

ARL SEMQ electron microprobe, with 15kV accelerating voltage and 0.02 μ A sample current. Data were corrected by the method of Bence and Albee (1968). Microprobe standards used are: VG-568 (rhyolite glass; J. Norberg, Smithsonian Institution, personal communication) for Si, Fe, Na, and K; VG-2 (basaltic glass; Jarosewich, 1975) for Al; VG-A99 (basaltic glass; T. L. Wright, U.S. Geological Survey, personal communication) for Mg, Ca, and Ti; Corning-D glass for P; Mn-ilmenite for Mn; scapolite for Cl; and apatite for F.

Virgilite crystals within a single glass specimen show a very narrow composition range and are probably identical within analytical error (Table 1). Only FeO shows significant variation between virgilite from different samples. Li₂O in virgilite was determined to be 5 \pm 0.5 weight percent using a laser spectrograph (French and Meyer, 1970).

Fibrous virgilite rosettes, overgrowing other mineral grains, are identical in composition to euhedral virgilites in the same specimen. In many samples virgilite is present only as rosettes; their composition ranges are very similar to those of the euhedral crystals, with FeO showing the largest variation.

Crystallography

Single crystals of virgilite in host glass were investigated on the Buerger precession camera. Because of the small size of these crystals, unfiltered Mo radiation and exposures of up to 400 hours were necessary. The results show virgilite to have a β -quartz-type structure with space group $P6_222$ or $P6_422$ (hexagonal) and approximate cell dimensions $a = 5.13(2)$, $c = 5.44(2)$ Å. There is no evidence for doubling of a or c .

Powder diffraction data (Table 2) were obtained by the Gandolfi technique from glass fragments containing several small crystals. The internal standard was NBS Standard Reference Material 640 silicon powder, $a = 5.43088(4)\text{\AA}$. Intensities were visually estimated with calibrated intensity strips. The corrected powder diffraction data were indexed and refined with the iterative computer technique of Appleman and Evans (1973), to yield the final cell parameters $a = 5.132(1)$, $c = 5.454(1)\text{\AA}$; cell volume $V = 124.41(2)\text{\AA}^3$.

Optical and physical properties

The small size and physical incorporation of the virgilite crystals in the host glass make it impractical to separate them for optical measurements. *In situ* measurements in the glass show that virgilite is uniaxial (-) with an average index of refraction $\bar{n} \approx 1.520$ and birefringence 0.005–0.006. The Gladstone-Dale relationship gives a calculated mean refractive

Table 1. Chemical analyses of virgilite

Sample 2143-17		Sample 2143-3		
	wt%	Range	wt%	Range
SiO ₂	77.29	77.06–77.52	76.63	76.33–76.88
Al ₂ O ₃	16.57	16.40–16.75	16.14	15.99–16.39
FeO	0.64	0.59–0.68	1.50	1.40–1.65
Li ₂ O*	4.93		5.	
P ₂ O ₅	0.57	0.54–0.60	0.58	0.53–0.62
TiO ₂	tr		tr	
MgO	tr		tr	
MnO	tr		tr	
CaO	tr		tr	
Na ₂ O	tr		tr	
K ₂ O	tr		tr	
F	tr		tr	
Cl	0.0		0.0	
Total	100.0		99.85	

	Atoms/6	Oxygens
Si	2.37	2.37
Al	0.60	0.54
Fe	0.02	0.04
Li	0.61	0.62
P	0.01	0.01

Tetrahedral cations	
(Si, Al, P, Fe)	
3.00	3.01
(+) charges	
12.00	12.0

*Determined by laser spectrograph on 2143-3 (French and Meyer, 1970); obtained by difference on 2143-17.

Table 2. Virgilite X-ray powder diffraction data

h k l	d(calc.)	d(obs)	I/I ₀	h k l	d(calc.)	d(obs.)	I/I ₀
1 0 0	4.445	4.442	13	2 0 4	1.1621		
1 0 1	3.445	3.441	100	2 2 2	1.1610		
1 1 0	2.566	2.567	6	3 0 3	1.1484		
1 0 2	2.324	2.328	2	3 1 2	1.1233	1.1231	2
1 1 1	2.322			4 0 0	1.1112		
2 0 0	2.222	2.224	6	4 0 1	1.0888		
2 0 1	2.058	2.059	4	1 0 5	1.0592		
1 1 2	1.869	1.870	25	2 1 4	1.0586	1.0584	3
0 0 3	1.818			2 2 3	1.0483		
2 0 2	1.723	1.723	2	4 0 2	1.0290		
1 0 3	1.683			3 1 3	1.0203		
2 1 0	1.680			3 2 0	1.0197		
2 1 1	1.606	1.605	9	1 1 5	1.0038		
1 1 3	1.483	1.482	2	3 0 4	1.0032		
3 0 0	1.482			3 2 1	1.0023	1.0024	2
2 1 2	1.430	1.429	6	2 0 5	0.9791		
3 0 1	1.430			(24 calculated lines omitted)			
2 0 3	1.407	1.408	9	3 1 5	0.8169	0.8168	2
1 0 4	1.3034			3 2 4	0.8166		
3 0 2	1.3018	1.3017	4	3 3 2	0.8162		
2 2 0	1.2831	1.2833	3	4 2 2	0.8028		
2 2 1	1.2490			2 1 6	0.7994		
2 1 3	1.2338	1.2336	2	5 0 3	0.7986		
3 1 0	1.2328			5 1 0	0.7983		
1 1 4	1.2040	1.2031	6	4 1 4	0.7903	0.7903	2
3 1 1	1.2024			5 1 1	0.7898		

Gandolfi camera, 114.59 mm diameter, Cu/Ni radiation, Si standard. P6₂ 422; a = 5.132, c = 5.454A.

index $\bar{n} = 1.523$, based on the measured chemical composition (Table 1), the calculated density, and the constants of Mandarino (1976).

It has not been possible to measure the density of virgilite. A density of 2.46 g cm⁻³ is calculated from the refined cell dimensions (Table 2) and the cell contents: Li_{0.61}(Si_{2.37}Al_{0.60}Fe_{0.02}P_{0.01})O₆ (Table 1). Microhardness measurements (E. P. Henderson, Smithsonian Institution, personal communication) are 681 Vickers Hardness Number minimum, 722 VHN maximum. For comparison, quartz parallel with the *a* axis is 981 VHN, perpendicular to *c* 1130 VHN.

Synthesis, structure and stability

Virgilite is identical to an intermediate member of the “β-quartz₈₈” synthesized by Munoz (1969) along the join LiAlSi₂O₆ (“spodumene”)–SiO₂ (quartz). Munoz’ data indicate that continuous solid solution exists above 10 kbar between the compositions Sp₁₀₀Qz₀ and Sp₀Qz₁₀₀, all with a β-quartz (or stuffed β-quartz) structure. The composition of the natural virgilite from Macusani is approximately Sp₆₁Qz₃₉. The cell dimensions of this material agree almost exactly with those obtained by Munoz from synthetic material of composition Sp₆₀Qz₄₀.

Synthetic end-member virgilite with composition Sp₁₀₀ was designated “β-quartz₈₈ (LiAlSi₂O₆)” by Munoz (1969). Li and Peacor (1968) call this phase “LiAlSi₂O₆ III”. A crystal-structure refinement was performed on LiAlSi₂O₆ III by Li (1969). He found

that the compound had a stuffed β -quartz structure with a completely disordered (Al,Si) distribution in the single tetrahedral site. Li is also in tetrahedral coordination, with the Li tetrahedron sharing edges with the (Si,Al) tetrahedron. The single Li atom in the unit cell is disordered over an equipoint with multiplicity 3, so that statistically each Li site contains only 1/3 of a Li atom. By contrast, β -eucryptite ($\text{LiAlSi}_2\text{O}_6$) has a stuffed β -quartz structure with 2 types of superstructure reflections, indicating a doubling of both the a and c axes. These are due to ordering both of (Al,Si) and of Li (Pillars and Peacor, 1973).

Both our natural virgilite and the material synthesized by Munoz (1969) were checked carefully by single-crystal techniques and no evidence for any superstructure reflections was observed. This procedure was necessary because, as pointed out by Munoz, the powder diffraction patterns of β -eucryptite_{ss} and β -quartz_{ss} are essentially identical. Thus there is no question that virgilite has the stuffed disordered β -quartz structure described by Li (1969) for $\text{LiAlSi}_2\text{O}_6$ III.

Virgilite has not been identified in a series of so-called "stuffed β -quartz" glass-ceramics manufactured by Corning Glass (Beall *et al.*, 1967), even though the compositions of some of these products are virtually identical to that of the Macusani glass. Beall *et al.* report the formation of β -spodumene solid solutions and cristobalite in specimens of glass-ceramic crystallized at 700 to 900°C at 1 atmosphere. The small size of the crystals makes identification difficult, and virgilite could also be present in these synthetic materials.

Discussion

Virgilite in the Macusani glass represents the first natural occurrence of a mineral with a β -quartz structure in the $\text{LiAlSi}_2\text{O}_6$ - SiO_2 solid-solution series. It is noteworthy that the mineral occurs in peraluminous glass, coexisting with both andalusite and sillimanite. The P - T conditions of formation of virgilite are not yet known. Although Munoz (1969) suggested that " β -quartz_{ss}" similar to virgilite would probably be expected to form in nature only at pressures above 10 kbar, it seems unlikely that virgilite in the volcanic Macusani glass formed in this range. One possible explanation is that sluggish reaction rates in the system Li_2O - Al_2O_3 - SiO_2 necessitate high P and T to promote reaction in laboratory experiments with pure materials. In the natural Macusani glass, however, reaction rates may have been increased by the

presence of Fe, alkalis, volatiles, *etc.*, thus promoting the formation of virgilite at lower pressures within its stability field.

An equally probable explanation is that the virgilite crystallized as a metastable phase, well outside of its stability field. Favorable initial structure in the glass might promote this type of crystallization. The natural occurrence of virgilite does not help greatly in establishing the stability field of the phases in the Li_2O - Al_2O_3 - SiO_2 system.

Origin

The origin of the Macusani glass itself is a problem that deserves further study. The glass shows many chemical similarities to more common granitic pegmatites, and its composition is virtually identical to a minimum-melting composition in the granite system at $P(\text{H}_2\text{O}) = 3$ -4 kbar (Luth *et al.*, 1964). Available field data are consistent with the idea that both the glass and the associated ash-flow deposits resulted from the explosive eruption of a volatile-rich peraluminous granitic melt. It is possible that the original melt was formed by the deep melting of aluminous sediments, thus producing a melt with Li and Al concentrations high enough to stabilize a lithium aluminosilicate phase, virgilite, on the liquidus.

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