GEM-QUALITY YELLOW-GREEN HAÜYNE FROM OLDOINYO LENGAI VOLCANO, NORTHERN TANZANIA

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Yellow-green to green-yellow gem-quality haüyne was found for the first time in an alkaline plutonic rock from the active Oldoinyo Lengai volcano in northern Tanzania. The mineral has optical and physical properties that are typical for sodalite-group minerals. Infrared and Raman spectroscopy showed that in addition to the $(SO_4)^{2-}$ group, the haüyne also contains $(NO_3)^-$, $(CO_3)^{2-}$, and water in its structure. SEM-EDS and EDXRF analyses confirmed the presence of Na, Ca, Al, and Si as major cations, with minor amounts of K.

Oldoinyo Lengai volcano, located in the Gregory Rift, northern Tanzania, is the only active carbonatite volcano in the world (Dawson, 1962; Keller and Krafft, 1990; Mitchell and Dawson, 2007). It is a typical stratovolcano and 2,952 m high (figure 1). It consists of unusual silica-undersaturated volcanic rocks including nephelinite and phonolite, as well as natrocarbonatites. The rocks occur as ash, lapilli, tuff, and agglomerates interlayered with lava flows. The agglomerates contain blocks of unusual feldspathoid-rich plutonic rocks such as urtite and ijolite.

While visiting Oldoinyo Lengai volcano in 2003, researchers from Freiburg University in Germany found a block of plutonic rock ~0.35 m in longest dimension, which proved to have a composition intermediate between ijolite and urtite. The block was coarse-grained and pegmatitic, consisting primarily of nepheline and diopside with subordinate amounts of magnetite, apatite, and perovskite. It also contained large (up to 7 cm) anhedral gem-quality pale greenish yellow crystals that were subsequently identified as haüyne (figure 2), ideal formula $Na_6Ca_2(Al_6Si_6O_{24})(SO_4)_2$. However, published data on haüyne show that it is characterized by variable contents of Ca and Na, typically contains some K, and in addition to $(SO_4)^{2-}$ also contains Cl and S^{2-} (e.g., Deer et al., 2004). Thus, a more general formula of haüyne can be written as $(Na,Ca,K)_{4-8}(Al_6Si_6O_{24})(SO_4,S,Cl)_{1-2}$.

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Materials and Methods. Haüyne samples measuring 10–15 mm were extracted from the Oldoinyo Lengai block and cut into three faceted stones ~1.5 ct each (e.g., figure 3). The faceted gem shapes, all brilliant cut, were round, antique square cushion, and triangle. Gemological properties were determined on all three of the faceted stones (RI with a refractometer, hydrostatic SG, and UV fluorescence) and on some anhedral grains (RI with the immersion method) at St. Petersburg State University, Russia, using standard equipment. Hardness was determined on a rough fragment using a Mohs hardness mineral set.

Chemical composition was determined on rough fragments at the Natural History Museum in London by: (1) scanning electron microscopy–energy dispersive spectroscopy (SEM-EDS), and (2) combustion analysis (gas analysis after the sample is combusted to break it down into components) for C, H, and N. In addition, energy-dispersive X-ray fluorescence (EDXRF) analysis of a powdered sample was performed at Freiburg University. One faceted stone was also investigated by variable pressure SEM-EDS (no sample coating required). Powder X-ray diffraction analysis, single-crystal structure determination, and IR spectroscopy of the rough samples were performed at St. Petersburg State University. Raman spectroscopy of both rough and cut specimens was undertaken at the School of Earth Sciences and Geography, Kingston University, London.

Results and Discussion. The mineral was identified as haüyne on the basis of its X-ray diffraction pattern (unit-cell parameter a = 9.040 ± 0.001 Å), and its optical and physical properties, which are similar to those reported for haüyne and other sodalite-group minerals (e.g., Deer et al., 2004; Ballirano and Maras, 2005). However, the RI values were lower, and SG values were higher, than those reported

Figure 1. At 2,952 m high, Oldoinyo Lengai volcano in northern Tanzania is the only active carbonatite volcano in the world. Photo by E. O. Zaitseva.

for gem-quality blue haüyne by Kiefert and Hänni (2000). Nevertheless, the identification as haüyne was confirmed by data from the single-crystal structure determination.

The yellow-green color of our samples is quite different from that of the well-known gem-quality blue haüyne from Eifel, Germany (Kiefert and Hänni, 2000) and Dattaw, Myanmar (Grobon and Hainschwang, 2006). Other color variants of haüyne are white and shades of gray, green, yellow, and red (Roberts et al., 1990). The gemological properties of the Oldoinyo Lengai material are shown in table 1.

The infrared spectra of the Oldoinyo Lengai haüyne in the 1300–350 cm^{-1} region were similar to spectra for haüyne and SO_4-bearing sodalite from other localities (e.g., Ballirano and Maras, 2005). In addition, the IR spectra for

Figure 2. A large haüyne crystal (up to 7 cm) is embedded in this rock, which is composed of ijolite-urtite. Photo by A. N. Zaitsev.

Figure 3. This silver ring is set with a 1.53 ct round brilliant-cut haüyne that was faceted for this study. Photo by A. A. Antonov.

TABLE 1. Properties of haüyne from Oldoinyo Lengai, Tanzania.[a]

Color	Yellow-green/green-yellow
Munsell color system	YG/GY 3/1
RI (gem refractometer)	1.488 ± 0.002
RI (immersion method)	1.490 ± 0.002
SG (hydrostatic)	2.60
Hardness (Mohs)	≈5.5
UV fluorescence	
Long-wave	Light orange
Short-wave	Inert

[a] *Properties determined on the 1.53 ct stone in figure 3, as well as on anhedral grains (RI by the immersion method) and a rough sample (Mohs hardness).*

the Oldoinyo Lengai samples contained single peaks at 1364 cm^{-1} [$(NO_3)^{2-}$ groups], 1499 and 1412 cm^{-1} [$(CO_3)^{2-}$ groups], and 1692 cm^{-1}, as well as a broad band at 3600–3400 cm^{-1}; the latter two bands correspond to water molecules (Buhl and Löns, 1996; Ballirano and Maras, 2005).

Raman spectroscopy showed that the haüyne from Oldoinyo Lengai contains $(SO_4)^{2-}$ groups, as indicated by the presence of peaks at 990–980 and 449–446 cm^{-1}. No peaks were observed at ~1089 and 543 cm^{-1}, which are related to the S^{3-} group, as seen in the Raman spectra of blue haüyne from Eifel (e.g., Kiefert and Hänni, 2000; Di Muro et al., 2004).

SEM-EDS, EDXRF, and combustion analyses confirmed the very unusual composition of some of the anions in the haüyne. The analyses showed significant amounts of sulfur (6.6–7.1 wt.% SO_3); minor nitrogen (1.1–1.3 wt.% N_2O_5), water (0.9–1.0 wt.% H_2O), chlorine (0.6–0.7 wt.% Cl), and carbon (0.4–0.5 wt.% CO_2); and traces of phosphorous (0.1 wt.% P_2O_5). In addition to the major cations in haüyne (Na, Ca, Al, and Si), we found minor amounts of K (1.6–1.8 wt.% K_2O), and traces of Fe (0.2–0.3 wt.% Fe_2O_3) and Mg (0.1 wt.% MgO). The analytical results are given in table 2, from which we calculated an average empirical formula of: $(Na_{6.75}Ca_{0.87}K_{0.37})_{\Sigma 7.99}(Al_{5.97}Fe^{3+}_{0.03}Si_{6.00}O_{24})[(SO_4)_{0.89}(OH)_{0.54}(NO_3)_{0.23}Cl_{0.20}(CO_3)_{0.12}]_{\Sigma 1.98}$. To our knowledge, this is the first naturally occurring nitrogen-bearing mineral from the sodalite group.

Conclusions. Gem-quality haüyne has been found at the active Oldoinyo Lengai volcano. This haüyne has a very unusual yellow-green color and a complex chemical composition (including the presence of N and C). The future production of the haüyne is uncertain, but with growing numbers of visitors to this part of Tanzania, it is likely that more samples of this gem mineral may be found.

TABLE 2. Chemical composition of haüyne from Oldoinyo Lengai.[a]

Oxide (wt.%)	SEM-EDS		EDXRF	Combustion analysis	
	Average (10)	Range		Average (3)	Range
SiO_2	34.24	33.89–34.34	34.01	na	
TiO_2	bdl		0.02	na	
Al_2O_3	28.95	28.68–29.37	28.91	na	
Fe_2O_3	0.23	0.20–0.29	0.30	na	
MnO	bdl		bdl	na	
MgO	bdl		0.09	na	
CaO	4.62	4.58–4.65	4.47	na	
Na_2O	19.88	19.67–19.91	19.00	na	
K_2O	1.66	1.57–1.79	1.57	na	
SO_3	6.78	6.63–7.05	na	na	
P_2O_5	bdl		0.13	na	
CO_2	na		na	0.49	0.45–0.54
N_2O_5	na		na	1.20	1.08–1.34
H_2O	na		na	0.92	0.85–0.99
Cl	0.68	0.63–0.72	na		
$-O=Cl_2$	0.15				
Total	96.89		88.50	2.61	

[a] *Notes: Carbon, nitrogen, and hydrogen were analyzed as elements and recalculated into oxides. Calculation of the empirical formula was performed using SEM-EDS and combustion analyses and considering all Fe as Fe_2O_3. Abbreviations: bdl = below detection limit; na = not analyzed.*

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