Hazenite, KNaMg$_2$(PO$_4$)$_2$·14H$_2$O, a new biologically related phosphate mineral, from Mono Lake, California, U.S.A.

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**ABSTRACT**

A new biologically related, struvite-type phosphate mineral, hazenite, ideally KNaMg$_2$(PO$_4$)$_2$·14H$_2$O, has been found in and/or on completely dried-out or decomposed cyanobacteria on porous calcium-carbonate (mainly calcite and aragonite) substrates in Mono Lake, California. The mineral occurs as radiating clusters of prismatic crystals and is colorless, transparent with white streak and vitreous luster. It is brittle, with the Mohs hardness of 2–2.5; cleavage is good on {001} and no twinning was observed. The measured and calculated densities are 1.91(3) and 1.88(2) g/cm$^3$, respectively. Hazenite is biaxial (+), with $n_a = 1.494(1)$, $n_p = 1.498(1)$, $n_g = 1.503(1)$, $2V_{\text{meas}} = 41(2)^\circ$, $2V_{\text{calc}} = 42^\circ$, $X = b$, $Y = c$, $Z = a$, and does not fluoresce under long- or short-wave ultraviolet rays. The dispersion is strong with $r < v$. It is soluble in water. The electron microprobe analysis yielded an empirical formula of K$_{0.97}$(Na$_{0.09}$Ca$_{0.02}$)Mg$_{0.01}$(P$_{0.79}$S$_{0.04}$)O$_{13.90}$H$_{2}$O. Hazenite is orthorhombic with space group $Pmn\beta$ and unit-cell parameters $a = 6.9349(4)$ Å, $b = 25.174(2)$ Å, $c = 11.2195(8)$ Å, and $V = 1958.7(3)$ Å$^3$. There are many structural similarities between hazenite and struvite, as also revealed by their Raman spectra. The hazenite structure contains six symmetrically independent non-hydrogen cation sites, two for Mg$^{2+}$ (Mg1 and Mg2), two for P$^{5+}$ (P1 and P2), one for Na$^+$, and one for K$^+$. It can be viewed as three types of layers stacking along the $b$-axis, in a repeating sequence of ABCBABCB…, where layer A consists of Mg1(H$_2$O)$_6$ octahedra and NaO$_6$ trigonal prisms, layer B of P1O$_6$ and P2O$_6$ tetrahedra, and layer C of Mg2(H$_2$O)$_6$ octahedra and very irregular KO$_6$ polyhedra. These layers are linked together by hydrogen bonds, plus the K-O bonds between layers B and C (K-O5-P2). Interestingly, the combination of layers B and C in hazenite exhibits a configuration analogous to the struvite-(K) structure. Hazenite is believed to form in high pH environments through the involvement of cyanobacterial activities. To our knowledge, hazenite is the first struvite-type compound that contains two structurally distinct monovalent cations (K and Na), pointing to an exclusive role of biological activity in the mineralization process.

**Keywords:** Hazenite, struvite-type materials, phosphates, biomineral, crystal structure, X-ray diffraction, Raman spectra

**INTRODUCTION**

A new biologically related, struvite-type phosphate mineral, hazenite, KNaMg$_2$(PO$_4$)$_2$·14H$_2$O, has been found on the shoreline of Mono Lake, California. Mono Lake, located in the hydrologically closed Mono basin, eastern California, U.S.A., is known for its outstanding biological and geochemical features (Wiens et al. 1993 and references therein). This terminal lake currently consists of a hypersaline (84–92 g/L), alkaline (pH = 9.8) Na$^+$(CO$_3$)$_2$Cl-SO$_4$ brine, resulting from evaporative concentration of inflow water, rock weathering, and mineral precipitation (e.g., Garrels and Mackenzie 1967; Li et al. 1997; Oremland et al. 2004). The lake is endorheic and the basin’s volcanic setting includes numerous hydrothermal springs that contribute to its unique water chemistry (Bischoff et al. 1991; Council and Bennett 1993; Budinoff and Hollibaugh 2007). High concentrations of boron (34 mmol/L) and minor amounts of K, Mg, and Ca are found in the lake (e.g., Bischoff et al. 1991). Dissolved organic carbon concentration is ~6.7 mmol/L (Melack 1983), and phosphate is as high as 1.0 mmol/L (Mono Basin Ecosystem Study Committee 1987). The food web of Mono Lake is relatively simple, consisting of bacteria, phytoplankton, brine flies Ephe-dra hians, the brine shrimp Artemia monica, and migrating and nesting birds (Jørgensen et al. 2008 and references therein). Soda lakes, such as Mono Lake, are good analogs of putative ancient Martian and Archean terrestrial aquatic biomes and represent environmental extremes in terms of their high pH and salinities. They can also be sensitive indicators of local climate changes and provide records of paleoclimate (Stine 1994; Jellison et al. 1996; Benson et al. 1998; Hollibaugh et al. 2001). Nevertheless, Mono Lake is subject to recurrent periods of meromixis (persistent chemical stratification) as a consequence of natural and anthropogenic alterations of freshwater flow into the lake, with the most recent episodes persisting from 1995 until 2003, and from 2005 until 2007 (Budinoff and Hollibaugh 2007).

Several unusual biologically related phosphate miner-