A new biogenic, struvite-related phosphate, the ammonium-analog of hazenite, 
(NH$_4$)NaMg$_2$(PO$_4$)$_2$·14H$_2$O

HEXIONG YANG$^{1,*}$, LIVIA MARTINELLI$^{2,3}$, FLAVIA TASSO$^3$, ANNA ROSA SPROCATI$^3$, FLAVIA PINZARI$^{2,4}$, ZHENXIAN LIU$^5$, ROBERT T. DOWNS$^1$ AND HENRY J. SUN$^6$

$^1$Department of Geosciences, University of Arizona, 1040 E. 4th Street, Tucson, Arizona 85721, U.S.A.
$^2$Istituto Centrale per il Restauro e la Conservazione del Patrimonio Archivistico e Librario, Rome, Italy
$^3$Unità Tecnica Caratterizzazione, Prevenzione e Risanamento Ambientale, ENEA-CASACCIA, Rome, Italy
$^4$Consiglio per la Ricerca e la sperimentazione in Agricoltura Centro di ricerca per lo studio delle relazioni tra pianta e suolo, Via della Navicella 2-4, 00184 Rome, Italy
$^5$Geophysical Laboratory, Carnegie Institution of Washington, Washington, D.C. 20015, U.S.A.
$^6$Desert Research Institute, 755 Flamingo Road, Las Vegas, Nevada 89119, U.S.A.

**ABSTRACT**

A new biogenic, struvite-related phosphate, the ammonium analog of hazenite (AAH), ideally (NH$_4$)$_2$NaMg$_2$(PO$_4$)$_2$·14H$_2$O, has been found in cultures containing the bacterial strain *Virgibacillus* sp. NOT1 (GenBank Accession Number: JX417495.1) isolated from an XVII Century document made of parchment. The chemical composition of AAH, determined from the combination of electron microprobe and X-ray structural analyses, is [(NH$_4$)$_3$K$_{23}$]NaMg$_2$(PO$_4$)$_2$·14H$_2$O. Single-crystal X-ray diffraction shows that AAH is orthorhombic with space group *Pnma* and unit-cell parameters $a = 6.9661(6)$, $b = 25.236(3)$, $c = 11.292(1)$ Å, and $V = 1985.0(3)$ Å$^3$. Compared with hazenite, the substitution of NH$_4$ for K$^+$ results in a noticeable increase of the average $A$-$O$ ($A = NH_4^+$ for AAH and Na$^+$ for K$^+$) bond length and the unit-cell volume for AAH, as also observed for struvite vs. struvite-K. Both infrared and Raman spectra of AAH resemble those of hazenite, as well as struvite. Our study reveals that AAH forms only in cultures with Na-bearing solutions and pH below 10.0. No AAH or hazenite was found in experiments with K-bearing solutions, suggesting the necessity of a Na-bearing solution for AAH formation.

**Keywords:** Ammonium phosphate, hazenite, struvite-type materials, biomimetic, crystal structure, X-ray diffraction, infrared and Raman spectra

**INTRODUCTION**

Phosphate formation through microbial activities is one of the most common mechanisms for the biological transformation of inorganic phosphates (Gibson 1974; Kamnev et al. 1999; Desmidt et al. 2013). Among all biogenic phosphates, struvite, (NH$_4$)$_2$MgPO$_4$·6H$_2$O, is the most widespread in various environments, such as bat guano, decomposing foods, infection (e.g., urinary tract) stones in humans, water treatment facilities, and in a range of bacterial cultures (Sánchez-Román et al. 2007; Weil 2008; Desmidt et al. 2013 and references therein). The specific roles that microorganisms play in struvite formation are not well understood. It has been speculated that bacterial cell surfaces may serve as nucleation sites and biological activities provide a steady supply of phosphate and ammonia as the crystals grow (e.g., Ben Omar et al. 1994, 1995, 1998; Chen et al. 2010).

Several compounds are isotypic with, or structurally analogous to, struvite (Dickens and Brown 1972; Weil 2008; Yang et al. 2011). A general chemical formula for struvite-type materials can be expressed as $A$M$^{2+}$(X$_O$)$_{n}$·nH$_2$O, where $n = 6$–8, $X = P$ or As; $A = NH_4$, K, Rb, Cs, and TI; and $M = Mg$, Fe, Co, Ni, Zn, and Mn. A common structural feature of struvite-type compounds is that all $M$ cations are octahedrally coordinated by six H$_2$O molecules and no H$_2$O molecule is shared between $M$(H$_2$O) octahedra. The X$_O$ tetrahedra and $M$(H$_2$O)$_6$ octahedra are interlinked through hydrogen bonding. The struvite-type structure was once thought unable to accommodate $A$ cations smaller than K$^+$ (Banks et al. 1975). Nevertheless, Mathew et al. (1982) synthesized a Na-analog of struvite, NaMg(PO$_4$)$_2$·7H$_2$O, in which the small Na$^+$ (relative to K$^+$) is compensated by an additional H$_2$O molecule. More intriguingly, Yang and Sun (2004) and Yang et al. (2011) described the new biomiminal hazenite, K$_2$NaMg$_2$(PO$_4$)$_2$·14H$_2$O, which possesses many structural features similar to those for both struvite-(K), KMg(PO$_4$)$_2$·6H$_2$O (Mathew and Schroeder 1979; Graeser et al. 2008) and synthetic Na$_2$Mg(PO$_4$)$_2$·7H$_2$O (Mathew et al. 1982). Hazenite represents the first struvite-type phosphate that contains both K and Na as the $A$ ions. In this paper, we report a new biologically formed phosphate, an ammonium analog of hazenite, ideally (NH$_4$)$_2$NaMg$_2$(PO$_4$)$_2$·14H$_2$O.

**EXPERIMENTAL METHODS**

**Formation of the ammonium analog of hazenite (AAH)**

The AAH crystals used in this study were formed in cultures containing the bacterial strain *Virgibacillus* sp. NOT1 (GenBank Accession Number: JX417495.1), which was isolated from an XVII Century document made of parchment and identified through 16S rDNA sequencing. The growth medium was prepared in Blood Agar Base N.2 (Oxoid, Code: CM0271) with the following components: Proteose...