

## **Valleyite: A new magnetic mineral with the sodalite-type structure**

**SEUNGYEOL LEE<sup>1</sup>, HUIFANG XU<sup>2,\*</sup>,†, HONGWU XU<sup>3</sup>, RYAN JACOBS<sup>4</sup>, AND DANE MORGAN<sup>4</sup>**

<sup>1</sup>NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin–Madison, Madison, Wisconsin 53706, U.S.A. Orcid 0000-0002-0175-1389

<sup>2</sup>NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin–Madison, Madison, Wisconsin 53706, U.S.A. Orcid 0000-0002-7464-0057

<sup>3</sup>Earth and Environmental Sciences Division, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, U.S.A.

<sup>4</sup>Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, U.S.A. Orcid 0000-0003-2229-6730

### **ABSTRACT**

Valleyite,  $\text{Ca}_4(\text{Fe},\text{Al})_6\text{O}_{13}$ , is a new sodalite-type mineral discovered in late Pleistocene basaltic scoria from the Menan Volcanic Complex near Rexburg, Idaho, U.S.A. It is an oxidation product of basaltic glass during the early stage of the scoria formation and is associated with hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), luogufengite ( $\varepsilon\text{-Fe}_2\text{O}_3$ ), and quartz on the surface of vesicles. The measured crystal size of valleyite ranges from ~250 to ~500 nm. The empirical chemical formula of valleyite is  $(\text{Ca}_{3.61}\text{Mg}_{0.39})(\text{Fe}_{3.97}\text{Al}_{1.91}\text{Ti}_{0.09})\text{O}_{13}$ . The mineral has a space group of  $I\bar{4}3m$ . The (Fe,Al)-O bond distance and unit-cell edge are slightly larger than those reported for synthetic  $\text{Ca}_4\text{Al}_6\text{O}_{13}$ , presumably due to the presence of the larger  $\text{Fe}^{3+}$  cations, compared with  $\text{Al}^{3+}$ , in the structure. Density functional theory calculations predict that valleyite may be a metastable phase at low temperatures. Measured Curie temperatures for valleyite and luogufengite are 645 and 519 K, respectively. Their magnetization hysteresis loop indicates the magnetic exchange coupling between valleyite (soft magnet) and luogufengite (hard magnet) that aids in the understanding of magnetic properties and paleo-magnetism of basaltic rocks. This new mineral, valleyite, with the sodalite-type cage structure is potentially a functional magnetic material.

**Keywords:** Valleyite, sodalite-type structure, luogufengite, hematite, scoria, magnetic property, synchrotron X-ray diffraction, transmission electron microscopy; Isotopes, Minerals, and Petrology; Honoring John Valley