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

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ABSTRACT

Valleyite, Ca₄(Fe,Al)₆O₁₃, 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 (α-Fe₂O₃), maghemite (γ-Fe₂O₃), luogufengite (ε-Fe₂O₃), 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 (Ca₄Mg₀.₃₉)(Fe₀.₇₇Al₀.₂₉Ti₀.₀₉)O₁₃. The mineral has a space group of I₄₁/m. The (Fe₄Al)-O bond distance and unit-cell edge are slightly larger than those reported for synthetic Ca₄Al₆O₁₃, presumably due to the presence of the larger Fe⁺³ cations, compared with Al³⁺, 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

INTRODUCTION

The new nano-mineral, valleyite, was discovered in late Pleistocene (~10 000 yr) basaltic scoria from the Menan Volcanic Complex near Rexburg, Idaho, U.S.A. The Menan Volcanic Complex consists of broad, flat volcanoes, formed by low-viscosity eruptions, with tholeiitic basalts dominating the surface exposures (Hackett and Morgan 1988; Russell and Brisbin 1990; Hughes et al. 1999). The formation of scoria was related to the interaction of external water with the late-stage (late Pleistocene) eruption in the center of the Menan complex (Hackett and Morgan 1988; Hughes et al. 1999). In general, the scoria with a brown and dark color contains more valleyite nano-grains than the red scoria.

In this study, the crystal structure, chemical composition, and magnetic properties of valleyite are presented. The mineral name has been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA 2017-026) (Xu et al. 2017a). The newly discovered mineral species of Ca₄(Fe,Al)₆O₁₃ is named after John W. Valley (born in 1948) of the University of Wisconsin–Madison. Valley was the President of the Mineralogical Society of America (MSA) during 2005–2006. His groundbreaking contributions to mineralogy, petrology, and geochemistry have led to a deeper understanding of Earth’s crustal evolution from early Earth to the Anthropocene. Valleyite is deposited in the collection of the Geology Museum of the Department of Geoscience, University of Wisconsin-Madison, with specimen numbers UWGM 2352 and UWGM2353. Second locality of valleyite associated with essenite was recently identified in paralava (fused sedimentary rock) near Gillette, Wyoming.

SAMPLES AND METHODS

The samples were carefully scratched off from the vesicles’ surfaces of the collected basaltic scoria (Supplemental Fig. S1). These samples were placed in a 10 M NaOH solution at 80 °C for two days to remove the silicate glass by following previous procedures (Xu et al. 2017b; Lee and Xu 2018). After washing the sample powders with distilled water several times, valleyite was enriched using a magnetic bar to reduce the portion of non-magnetic minerals. The valleyite sample was further enriched by an iron needle to pick up the remnant magnetized crystals. These magnetic enrichment steps were repeated 5–7 times.

For comparison, a synthetic valleyite sample was prepared through thermal decomposition of a clay mineral, nontronite, from Quincy, Washington, as described in Lee and Xu (2016). Crushed nontronite powders were loaded into an alumina boat, which was then placed in a furnace to be heated at 850 °C for two days in air. After heating, the sample was quenched in cold water. Isolation of the ferric