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Discovery of New Minerals of Luogufengite and Valleyite Using Synchrotron X-ray Diffraction and Transmission Electron Microscopy

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The new nanominerals of luogufengite (IMA 2016-005) and valleyite (IMA 2017-026) were discovered in late Pleistocene basaltic scoria from the Menan Volcanic Complex near Rexburg, Idaho, USA [1,2]. Both new minerals are oxidation products of basaltic glass during the scoria formation and coexist with hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), and quartz. To obtain sufficient amounts of these nanophases for detailed characterization, the samples were scratched off from the vesicles' surfaces. These powders were placed in a 10M NaOH solution at 80 °C for 2 days to remove the silicate glass. After washing the samples with distilled water several times, luogufengite and valleyite were enriched using a magnetic bar to reduce the portion of non-magnetic minerals. The sample was further enriched by an iron needle to pick up the remnant magnetized crystals. Synchrotron X-ray powder diffraction (XRD) and transmission electron microscope (TEM) were used to determine their crystal structures and chemical compositions.

Luogufengite (ε-Fe_2O_3) is a dark brown nanomineral, which is an intermediate polymorph between maghemite and hematite [3]. The grain size of luogufengite ranges from ~20 nm to ~150 nm. Its empirical formula is $Fe_{1.71}Al_{0.24}Mg_{0.02}Ti_{0.03}O_3$. The crystals display (110) twins with twin boundaries of (110), (100), and (130) due to their pseudo-hexagonal symmetry (Figure 1A-1C). Valleyite [$Ca_4(Fe,Al)_6O_{13}$] is a sodalite-structure mineral. The crystal size of valleyite ranges from ~250 to ~500 nm (Figure 1D-1F), and its empirical chemical formula of valleyite is $(Ca_{3.61}Mg_{0.39})$ $(Fe_{3.97}Al_{1.91}Ti_{0.09})O_{13}$. The synchrotron XRD pattern of a treated scoria sample reveals the occurrence of luogufengite and valleyite (Figure 2A). The diffraction peaks from valleyite are sharper than those from nanophase luogufengite that have a smaller average size (40 nm) (Figure 2A). Measured Curie temperatures for valleyite and luogufengite are 645 and 519 K, respectively (Figure 2B). Their magnetization hysteresis loops indicate the magnetic exchange coupling between valleyite (soft magnet) and luogufengite (hard magnet) (Figure 2C). The new nanominerals may be important magnetic phases for paleomagnetism of volcanic rocks due to their magnetic coercivity. The unique magnetic property may explain the observed unusually high-remanent magnetization in some igneous and metamorphic rocks, lodestones (natural magnet), and even Martian surfaces [4].

This study demonstrates that a combination of advanced synchrotron XRD with high-resolution TEM is a powerful approach to identify nano-minerals in geological systems and to determine their nanocrystalline structures. Especially, the high brilliance and high coherence of synchrotron X-rays enable the clear separation of weak and broad XRD peaks of nanocrystalline phases (Figure 2B), which cannot be resolved or detected by conventional XRD. Also, direct imaging and analysis by HRTEM combined with SAED and X-ray EDS spectra allow determination of the structures and chemistry of minerals at the nanoscale. We expect that this integrated approach will be employed in finding new nano-minerals in the future.

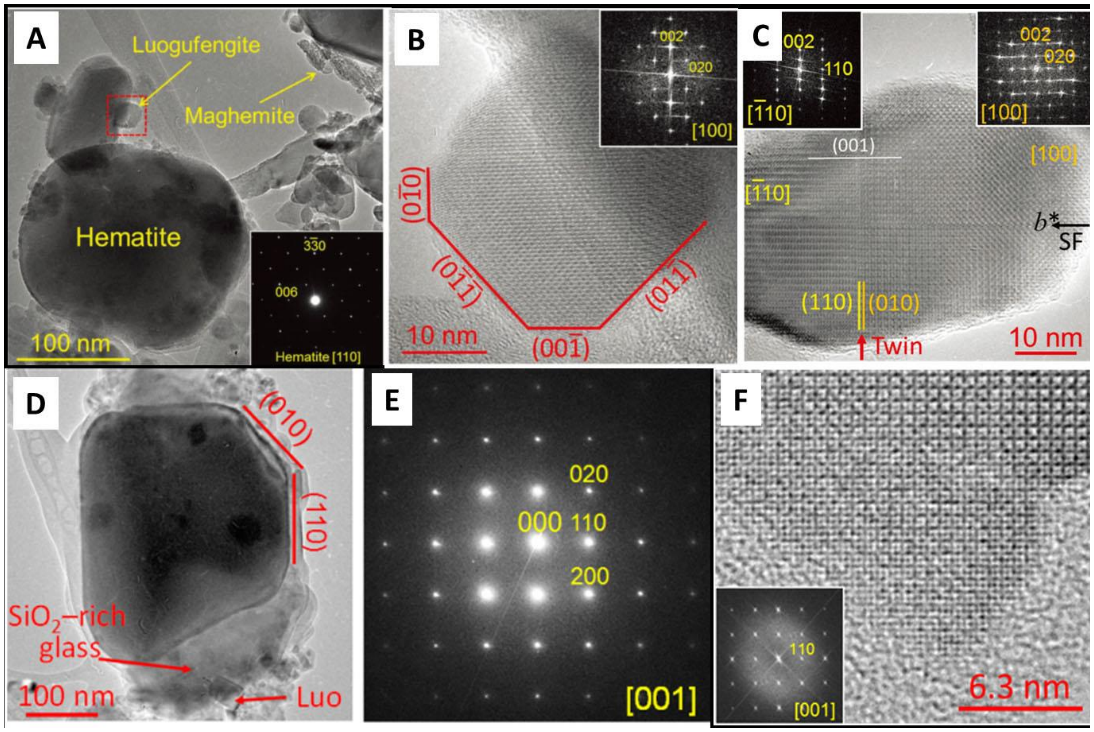

Figure 1. Bright-field TEM images, SAED, and High-resolution TEM, FFT patterns of (A-C) luogufengite and (D-F) valleyite.

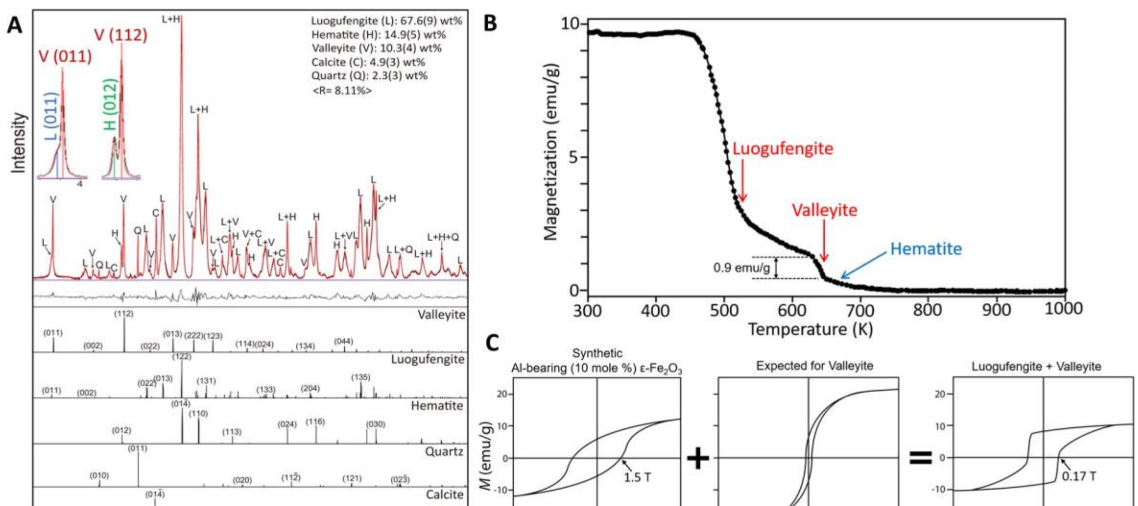

Figure 2. (A) Synchrotron X-ray diffraction pattern of a treated sample (B) Temperature dependence of magnetization of the luogufengite and valleyite. (C) Hysteresis loops of synthetic Al-bearing ε-Fe2O3, expected valleyite, and natural luogufengite/valleyite sample.

References

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