

DISCOVERY OF METEORITIC LOVERINGITE, $\text{Ca}(\text{Ti,Fe,Cr,Mg})_{21}\text{O}_{38}$, IN AN ALLENDE CHONDRULE: LATE-STAGE CRYSTALLIZATION IN A MELT DROPLET. Chi Ma^{1,2}, John R. Beckett¹, Harold C. Connolly, Jr.^{3,4,5}, and George R. Rossman¹; ¹Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena CA 91125, ²chi@gps.caltech.edu; ³Department of Physical Sciences, Kingsborough College of the City University of New York, Brooklyn NY 100235; ⁴Department of Earth and Planetary Sciences, AMNH, New York, NY 10024; ⁵Lunar and Planetary Laboratory, University of Arizona, Tucson AZ 85721.

Introduction: During our nanomineralogy investigation of the Allende CV3 meteorite, we identified loveringite, $\text{Ca}(\text{Ti,Fe,Cr,Mg})_{21}\text{O}_{38}$, along with zirconolite and ilmenite in a barred olivine chondrule ALL-C1. We used electron probe microanalysis (EPMA), high-resolution scanning electron microscope (SEM), energy dispersive X-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD) to characterize its composition and structure. In terrestrial rocks, loveringite occurs as a late-crystallizing phase in layered intrusions, ophiolites, and peridotites and their metamorphosed equivalents [e.g., 1-3]. Here, we describe the first confirmed occurrence of meteoritic loveringite and consider the origin of this and associated phases within the chondrule.

Appearance, Chemistry and Crystallography: Chondrule ALL-C1 is composed of a central region of barred olivine crystals (Fo_{85}) surrounded by a rim of euhedral to subhedral olivine of similar composition. Minor anorthite $\text{Ca}_{0.95}\text{Na}_{0.07}(\text{Al}_{1.88}\text{Fe}_{0.03}\text{Mg}_{0.01})\text{Si}_{2.06}\text{O}_8$, augite $(\text{Ca}_{0.74}\text{Mg}_{0.26})(\text{Mg}_{0.68}\text{Fe}_{0.17}\text{Ti}_{0.11}\text{Cr}_{0.04}\text{Mn}_{0.01})(\text{Si}_{1.78}\text{Al}_{0.21})\text{O}_6$ and clinoenstatite $(\text{Mg}_{1.41}\text{Fe}_{0.26}\text{Ca}_{0.18}\text{Al}_{0.07}\text{Cr}_{0.04})(\text{Si}_{1.96}\text{Al}_{0.04})\text{O}_6$ occur along olivine grain boundaries and between olivine bars (Fig. 1). Hercynite, magnesiochromite, loveringite, zirconolite, apatite, and troilite are accessory phases. The alteration products hedenbergite, andradite, and nepheline are present mostly within the central barred olivine region, especially along fractures.

Loveringite occurs in ALL-C1 as irregular crystals, 3-8 μm across within interstices between olivine crystals in contact with ilmenite, or zirconolite, or chromite, with anorthite and clinoenstatite nearby (Figs. 1-3). The phase has a mean chemical composition of (wt%) TiO_2 71.59, FeO 13.38, Cr_2O_3 6.29, CaO 3.63, MgO 1.70, MnO 0.70, Al_2O_3 0.47, ZrO_2 0.15, sum 97.91. Y was not detected by EPMA (<0.23 wt%); Preliminary measurements using EDS imply low REE contents <0.4 - 0.6 wt%. The empirical formula based on 38 oxygens is $\text{Ca}_{1.10}(\text{Ti}_{15.23}\text{Fe}_{3.17}\text{Cr}_{1.41}\text{Mg}_{0.72}\text{Mn}_{0.17}\text{Al}_{0.16}\text{Zr}_{0.02})\text{O}_{38}$, yielding a simplified formula of $\text{Ca}(\text{Ti,Fe,Cr,Mg})_{21}\text{O}_{38}$. One loveringite grain has a Zr-rich region (2.51 wt% ZrO_2) with a formula of $\text{Ca}_{1.11}(\text{Ti}_{14.50}\text{Fe}_{2.94}\text{Cr}_{1.91}\text{Mg}_{0.77}\text{Zr}_{0.35}\text{Al}_{0.30}\text{Mn}_{0.12}\text{Nb}_{0.02})\text{O}_{38}$. Relative to terrestrial loveringites, the meteoritic material is generally Mn-rich and Al-poor. The compositions of loveringite from chondrule ALL-C1 are

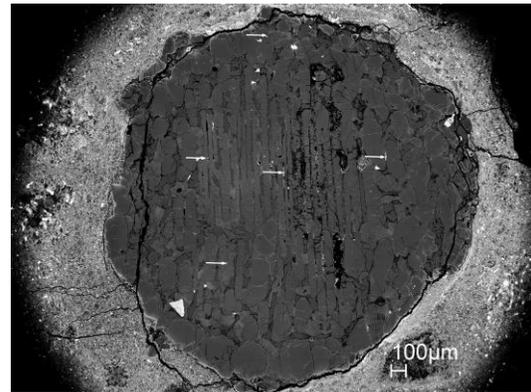


Fig. 1. Backscatter electron (BSE) image showing an overview of the loveringite containing Allende chondrule ALL-C1. Loveringites marked by arrows.

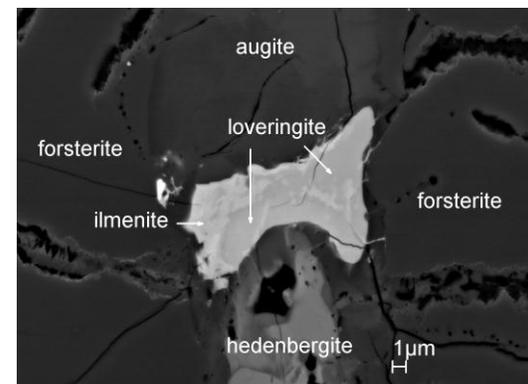


Fig. 2. BSE image showing loveringite with ilmenite, augite, plagioclase, hedenbergite, and enstatite.

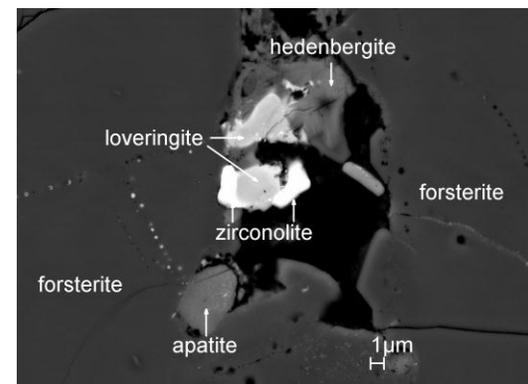


Fig. 3. BSE image showing loveringite with adjacent zirconolite, and nearby apatite.

readily distinguished from their terrestrial counterparts in Fig. 4.

Loveringite is generally viewed as a rare phase in terrestrial rocks although it is likely more common than the available reports would indicate because the grains tend to be quite small and the chemistry can often be interpreted in terms of an $R^{2+}R^{4+}_3O_7$ - $R^{3+}_2R^{4+}_2O_7$ solid solution. Indeed, a Ti-rich oxide previously observed in an Allende Ca-, Al-rich inclusion by Haggerty [5] and described in terms of an X_4O_7 formula unit may well be a loveringite.

Identification of loveringite in terrestrial rocks is usually based on chemistry because crystals in the loveringite-davidite clan are generally metamict due to radiation damage, making it necessary to heat the crystals to obtain definitive structural information. Allende loveringite, however, produces high quality EBSD patterns with no artificial thermal processing. The EBSD patterns can only be indexed using the $AM_{21}O_{38}$ crichtonite-group structure and the composition (>0.5 cations of Ca per formula unit) then indicates that the phase is a loveringite. Based on the structure and cell parameters of synthetic loveringite [4], the Allende crystal is trigonal, $R\bar{3}$, with $a = 10.42 \text{ \AA}$, $c = 20.94 \text{ \AA}$, $Z = 3$, and a density of 4.21 g/cm^3 .

Occurrence and Associated Minerals: Loveringite in chondrule ALL-C1 occurs as an interstitial phase between olivine crystals, both in the barred region and within the surrounding rim of subequant olivine grains. In addition to olivine, loveringite is observed in contact with one or more of ilmenite, chromite (as an inclusion), zirconolite, and clinoenstatite. Anorthite, augite, and Cl-bearing apatite are often within 10-15 μm of loveringite but were not observed in direct contact.

Zirconolite in chondrule ALL-C1 has a formula of $(Ca_{0.45}Fe_{0.19}Mg_{0.14}Y_{0.14}Nd_{0.05}U_{0.01})Zr(Ti_{1.73}Zr_{0.11}Al_{0.09}Cr_{0.07})O_7$ (note the presence of significant concentrations of REE and U) but shows no EBSD pattern due to radiation damage to the crystal structure. This contrasts sharply with the loveringite crystals, which display well defined EBSD patterns and, therefore, must have very low U and Th contents. Zirconolite and apatite are likely the primary hosts of the REE and actinides in chondrule ALL-C1. Ilmenite is Mg-rich with a formula of $(Fe_{0.66}Mg_{0.17}Ca_{0.03}Mn_{0.02})(Ti_{1.03}Cr_{0.04})O_3$. Chromite $(Fe_{0.73}Mg_{0.28})(Cr_{1.04}Al_{0.95})O_4$, magnesiocromite $(Mg_{0.52}Fe_{0.46}Mn_{0.01})(Cr_{1.08}Al_{0.85}Ti_{0.06})O_4$, and hercynite $(Fe_{0.58}Mg_{0.44})(Al_{1.16}Cr_{0.82})O_4$, are spinel-type phases, occurring as irregular to euhedral crystals, 3 – 100 μm in size.

Origin and Significance: Texturally, loveringite is consistent with being a late-stage crystallization product of a cooling chondrule melt, as are zirconolite, ilmenite, chromite and apatite. If partition coefficients

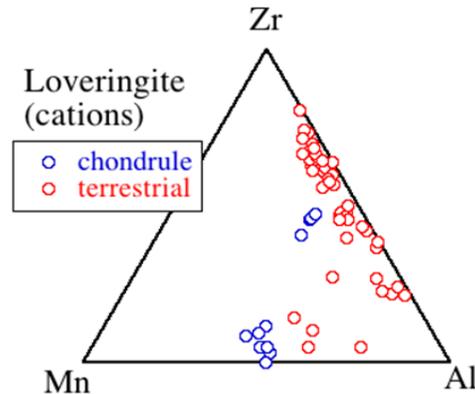


Fig. 4. Relative amounts of cations of Al, Zr, and Mn in loveringite from Allende chondrule ALL-C1 (this study) and for a compilation of analyses from the literature for terrestrial occurrences. Data from [5] are not shown because Zr was not analyzed. Compositions of terrestrial loveringites that are the most similar to those of the chondrule phases are from [2].

based on a Ti-, REE-enriched andesitic melt [6] are relevant, Y and the light REE are compatible in loveringite. Thus, low actinide and REE contents of loveringite in chondrule ALL-C1, would suggest that loveringite crystallized after REE and actinides had been largely scavenged by other nearby phases (e.g., zirconolite and apatite), although additional analysis will be required to quantify this effect. An alternative is that the loveringite is a metasomatic product of the alteration of ilmenite or, perhaps pseudobrookite, Ti-rich, REE/actinide-poor oxides.

Most chondrules have flat REE patterns but a few show CAI-like patterns and there are rare examples of chondrules that contain recognizable material from CAIs [7]. The presence of zirconolite and loveringite in chondrule ALL-C1 may reflect a similar signature. The original refractory minerals were incorporated into the chondrule precursor but destroyed during melting of the chondrule and reconstituted in the form of apatite, loveringite, and zirconolite upon crystallization. This is a rare event because our preliminary survey of over 100 Allende chondrules yielded no additional examples containing either loveringite or zirconolite.

References: [1] Gatehouse B.M. et al. (1978) *Amer. Mineral.* 63, 28-36. [2] Lorand J.P. et al. (1987) *Can. Mineral.* 25, 683-693. [3] Cabella R. et al. (1997) *Can. Mineral.* 35, 899-908. [4] Peterson R.C. (1998) *Can. Mineral.* 36, 763-774. [5] Haggerty S.E. (1978) *Proc. LPSC 9th*, 1331-1334. [6] Green T.H. and Pearson N.J. (1987) *Mineral. Mag.* 51, 145-9. [7] Lauretta D.S. et al. (2006) *Meteorites and the Early Solar System II*, 431-459.