

# LIEBERMANNITE: A NEW POTASSIC HOLLANDITE ( $\text{KAISi}_3\text{O}_8$ ) FROM THE ZAGAMI BASALTIC

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**Introduction:** Basaltic shergottites provide key insights into igneous processes on Mars [e.g., 1] but they are also highly shocked, thereby providing information about shock conditions during the excavation of samples from Mars and of shock processes in general [e.g., 2-3]. In this work, we describe a new shock-produced mineral, liebermannite (Lieb),  $\text{KAISi}_3\text{O}_8$  in a hollandite-type structure, and coexisting phases from Zagami using SEM, EPMA, EBSD, and synchrotron diffraction. This phase was previously reported in the basaltic shergottites Zagami and NWA 480 based on characterization using ATEM, EPMA, and Raman but not named [2-3]. The name liebermannite (IMA 2013-128) honors the mineral physicist Robert Liebermann for his many contributions to the experimental study of phases at elevated pressures and temperatures.

**Sample and Analyses:** The doubly polished thin section of Zagami used in this study was kindly provided by E.M. Stolper. The section is dominated by augite, pigeonite and maskelynite with minor mesostasis and accessory silica, merrillite, apatite, fayalite, ilmenite, titanomagnetite, baddeleyite, and Fe-sulfide; the basic petrography is consistent with an NZ lithology (“normal Zagami”) [1,4]. Melt pockets are rare and we observed only one shock vein. Thus, high pressure phase assemblages occur sporadically; observed shock phases include stishovite (St), tuite, lingunite, liebermannite and CAS.

**Properties of liebermannite:** Liebermannite is the hollandite-structured polymorph of  $\text{KAISi}_3\text{O}_8$  in which edge-sharing octahedra, containing Al and Si, form chains parallel to the *c*-axis that are corner linked to form cavities containing the K. In Zagami, liebermannite occurs in  $< \sim 15 \mu\text{m}$  aggregates.

We were unable to obtain EBSD patterns on Zagami liebermannite but established the crystal structure through synchrotron diffraction; data were obtained on the regions shown in Fig. 1 using a primary beam energy of 25 keV (0.59494 Å) monochromatized by a double crystal Si 111 monochromator. Based on synchrotron diffraction data, liebermannite is a tetragonal phase crystallizing in the  $I4/m$  space group with cell parameters for the type example (Fig. 1) of  $a = 9.140 \pm 0.036$  (1 $\sigma$ ) and  $c = 2.736 \pm 0.021$  Å, which lead to a cell volume of  $228.56 \pm 0.25 \text{ \AA}^3$ . The *a*-cell dimension is noticeably shorter than values reported in the

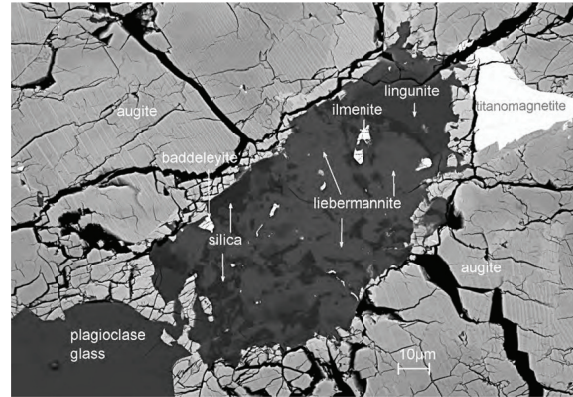


Fig. 1. BSE image showing liebermannite with lingunite, a silica phase (probably stishovite), ilmenite and baddeleyite; the assemblage is surrounded by augite with nearby maskelynite and titanomagnetite.

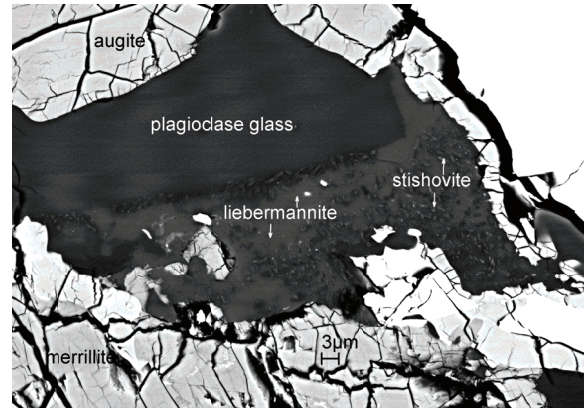


Fig. 2. In this occurrence, liebermannite (based on composition and transparency) with included stishovite is bounded by merrillite, augite, and maskelynite.

literature for synthetic and meteoritic Na/K-hollandites, which are  $\geq 9.26 \text{ \AA}$  [2,5-8]. This may reflect systematic errors for powder diffraction in literature measurements but is more likely to imply different vacancy populations on the M-site or, possibly, different degrees of site disorder or residual strain in the Zagami material. It probably does not suggest strongly negative volumes of mixing along the  $\text{NaAlSi}_3\text{O}_8$  (Ab) -  $\text{KAISi}_3\text{O}_8$  (Or) join, as available experimental data [9] are consistent with ideal volumes of mixing.

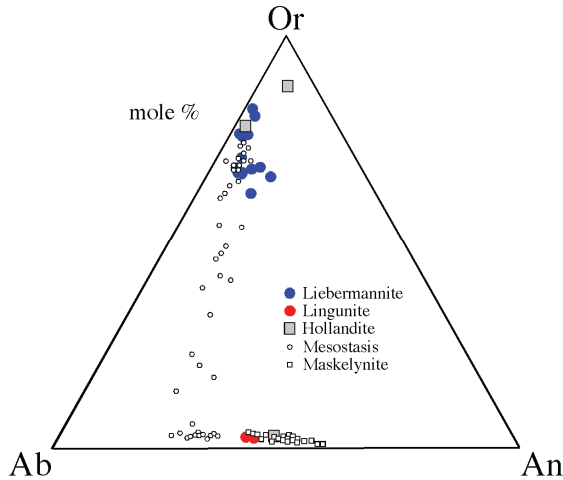


Fig. 3. Compositions of liebermannite and lingunite (this study), Na-K-Ca hollandites [2-3], and mesostasis and maskelynite [1] from Zagami in terms of Or-Ab-CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>(An). Mesostasis compositions are projected from SiO<sub>2</sub>.

The composition of type liebermannite by EPMA is 65.36 wt% SiO<sub>2</sub>, 19.00 Al<sub>2</sub>O<sub>3</sub>, 13.02 K<sub>2</sub>O, 1.62 Na<sub>2</sub>O, and 0.37 CaO (summing to 99.36%), which leads to a formula of (K<sub>0.76</sub>Na<sub>0.14</sub>Ca<sub>0.02</sub>)Al<sub>1.03</sub>Si<sub>3.00</sub>O<sub>8</sub> and a density of 3.975 g/cm<sup>3</sup>. Fig. 3 shows compositions of liebermannite and lingunite (the Na analog of liebermannite) from Zagami together with those of maskelynite and mesostasis [1]. Liebermannite compositions are generally consistent with those of K-rich mesostasis compositions (projected from silica) and it is, therefore, likely that K-rich mesostases were precursors to liebermannite. In contrast, lingunite compositions are substantially more calcic than K-poor mesostases; they plot with maskelynite in Fig. 3, making plagioclase and not K-poor mesostasis the likely precursor.

According to [1], K-rich mesostases are more strongly reddish in plane light than K-poor mesostases (reconnaissance tests confirm their observation for our section). Only one (K-rich) liebermannite occurrence (Fig. 1) was established using synchrotron diffraction but it is optically transparent. It may therefore be possible to identify liebermannite-containing regions in Zagami through the simple artifice of connecting K-mapping by EPMA to determine locations of K-enriched regions and then using color to determine which of these contain liebermannites (e.g., Fig. 2).

**Discussion and Conclusions:** NaAlSi<sub>3</sub>O<sub>8</sub> may not have a hollandite stability field at all (e.g., [10]); meteoritic lingunites may be stabilized by Ca) but liebermannite exists stably under a broad range of P-T and bulk composition [e.g., 5-6,9], as shown in Fig. 4. At 1400°C, the low Ca-liebermannite plus stishovite (no

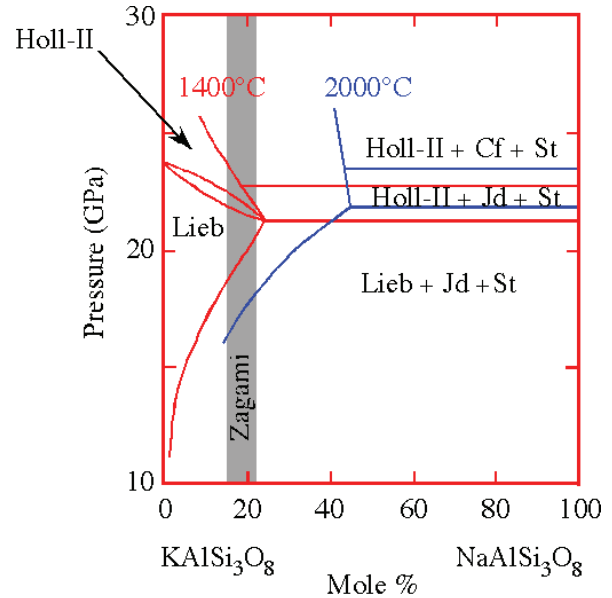


Fig. 4. Phase diagram for the NaAlSi<sub>3</sub>O<sub>8</sub>- KAlSi<sub>3</sub>O<sub>8</sub> join at 1400°C (red & labeled fields) and 2000°C (blue) after [9] with compositions of Zagami liebermannites with <3 mole % An component from this study shaded in gray. Holl-II: *I2/m* hollandite; Jd: jadeite; Cf: Ca-ferrite structured (Na,K)AlSiO<sub>4</sub>.

pyroxene) of Figs. 1-2 would be stable at ~19-21 GPa, bounded at high P by the breakdown of liebermannite to an orthorhombic (K,Na)AlSi<sub>3</sub>O<sub>8</sub> structure and at low P by the formation of pyroxene and stishovite. At higher T, the stability field expands both to low (~17 GPa at 2000°C) and, especially, high P. Most likely, liebermannite crystallized during cooling of high-K mesostasis composition melts that were originally produced during low-P, very late-stage crystallization of Zagami basalt, and then reheated to high P-T during a shock event. The heat source for liebermannite occurrences shown in Figs. 1-2 is uncertain as the melt vein and pockets are >800 μm away. It is possible that a melt pocket or vein out of the plane of the section provided the heat source. Alternatively, cracks or voids in or near rare mesostases collapsed during shock, leading to hot spots that heated the local mesostasis sufficiently so that stishovite and/or silica glass plus liebermannite could form.

**References:** [1] Stolper E. and McSween H.Y. (1979) *GCA* 43, 1475-1498. [2] Langenhorst F. and Poirier J.-P. (2000) *EPSL* 176, 259-265. [3] Beck P. et al. (2007) *GRL* 34, L01203. [4] McCoy T.J. et al. (1992) *GCA* 56, 3571-3582. [5] Boffa Ballaran T. et al. (2009) *Phys. Rev B.*, 80, 214104. [6] Yagi A. et al. (1994) *Phys. Chem. Min.*, 21, 12-17. [7] Ferrior T. et al. (2006) *Am. Min.* 91, 327-332. [8] Gillet P. et al. (2000) *Science* 287, 1633-1636. [9] Liu X. (2006) *EPSL*, 246, 317-325. [10] Deng L. et al. (2010) *EPSL* 298, 427-433.