

Simmonsite, Na₂LiAlF₆, a new mineral from the Zapot amazonite-topaz-zinnwaldite pegmatite, Hawthorne, Nevada, U.S.A.

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ABSTRACT

Simmonsite, Na₂LiAlF₆, a new mineral of pegmatitic-hydrothermal origin, occurs in a late-stage breccia pipe structure that cuts the Zapot amazonite-topaz-zinnwaldite pegmatite located in the Gillis Range, Mineral Co., Nevada, U.S.A. The mineral is intimately intergrown with cryolite, cryolithionite and trace elpasolite. A secondary assemblage of other alumino-fluoride minerals and a second generation of cryolithionite has formed from the primary assemblage. The mineral is monoclinic, $P2_1$ or $P2_1/m$, $a = 7.5006(6)$ Å, $b = 7.474(1)$ Å, $c = 7.503(1)$ Å, $\beta = 90.847(9)^\circ$, $V = 420.6(1)$ Å³, $Z = 4$. The four strongest diffraction maxima [d (Å), hkl , lI_{100}] are (4.33, 111 and $11\bar{1}$, 100); (1.877, 400 and 004, 90); (2.25, $13\bar{1}$, 113, 131 and 311, 70); and (2.65, 220, 202, 022, 60). Simmonsite is pale buff cream with white streak, somewhat greasy, translucent to transparent, Mohs hardness of 2.5–3, no distinct cleavage, subconchoidal fracture, no parting, not extremely brittle, D_m is 3.05(2) g/cm³, and D_c is 3.06(1) g/cm³. The mineral is biaxial, very nearly isotropic, N is 1.359(1) for $\lambda = 589$ nm, and birefringence is 0.0009. Electron microprobe analyses gave (wt%) Na = 23.4, Al = 13.9, F = 58.6, Li = 3.56 (calculated), with a total of 99.46. The empirical formula (based on 6 F atoms) is Na_{4.98}Li_{1.00}Al_{1.00}F₆. The crystal structure was not solved, presumably because of unit-cell scale twinning, but similarities to the perovskite-type structure exist.

The mineral is named for William B. Simmons, Professor of Mineralogy and Petrology, University of New Orleans, New Orleans.

INTRODUCTION

Simmonsite was discovered in 1992 by one of the authors (A.E.S.) while mapping and evaluating the Zapot pegmatite in the Gillis Range, approximately 25 km northeast of Hawthorne, Mineral Co., Nevada, U.S.A. The pegmatite mine is owned and operated by Harvey M. Gordon of Reno, Nevada. For details on the geology and mineralogy of the pegmatite, see Foord et al. (1998).

The mineral and mineral name were approved by the International Mineralogical Association Commission on New Minerals and Mineral Names. The mineral is named for William B. Simmons (1943–), Professor of Mineralogy and Petrology, University of New Orleans, New Orleans, Louisiana 70148, U.S.A., in recognition of his numerous studies on granitic pegmatites and their mineralogy. Type material has been deposited at the U.S. National Museum, Smithsonian Institution.

OCCURRENCE

Simmonsite (Na₂LiAlF₆), cryolite, and cryolithionite occur together as part of a alumino-fluoride assemblage in a late-stage breccia pipe structure (10–25 cm diameter, 2.7 m length) that cuts the Zapot amazonite-topaz-zinnwaldite pegmatite located in the Gillis Range, Mineral Co., Nevada; the assemblage is of pegmatitic-hydrothermal origin. The assemblage occurs with approximately one-third of each phase, and less than 1% elpasolite (Figs. 1a–1d). Phase equilibria studies of synthetic minerals in the system Na₃AlF₆–Li₃AlF₆ (Garton and Wanklyn 1967; Holm and Holm 1970) indicate that at temperatures above 420 °C only cubic phases exist, and that the three-phase assemblage is not an equilibrium assemblage.

The three phases form an intergrowth of anhedral to subhedral grains that range from several micrometers to approximately two- to three-hundred micrometers in maximum dimension. The primary anhydrous alumino-fluorides occur in masses as much as 20 cm or more across, and more than 1 kg in weight. A secondary assemblage of alumino-fluorides, some of which contain water or hydroxyl, includes pachnolite,

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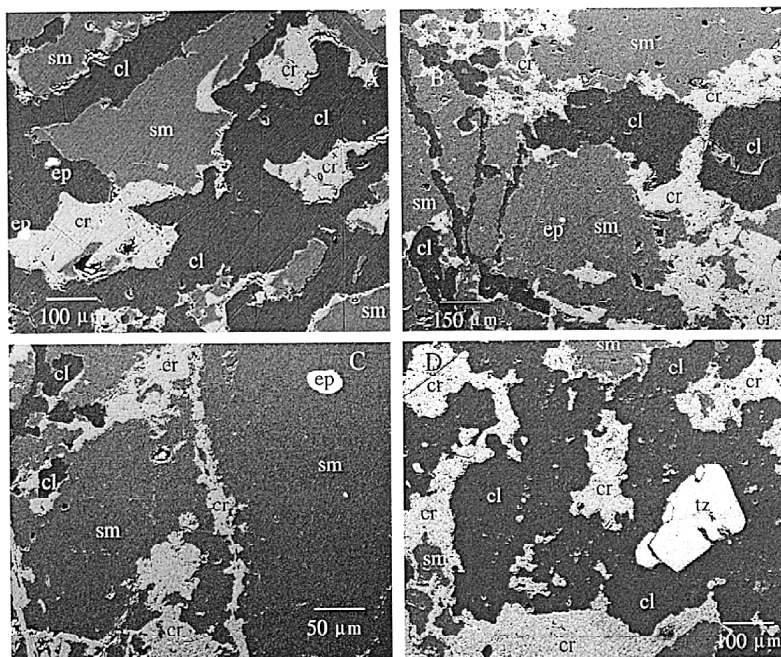


FIGURE 1. (a–d) Backscattered electron images of primary assemblage of cryolite-cryolithionite-simmonsite and trace elpasolite. Part **d** contains an exotic fragment of topaz. Identified phases are: cr = cryolite; cl = cryolithionite; ep = elpasolite; tz = topaz; sm = simmonsite.

weberite, thomsenolite, prosopite, ralstonite, and a second generation of cryolithionite. Fluorite is intimately intergrown with these secondary alumino-fluorides.

METHODS

Electron microprobe analyses were performed at the University of New Orleans (UNO) on a ARL SEMQ microprobe. Standards included melt-crystallized LiF, adularia, and Ivigtut cryolite. Operating conditions were 10 kV, 12 nA, 3 μm beam diameter, 30 s count times on backgrounds, 60 s count times on peaks. Analysis of the primary alumino-fluoride assemblage was undertaken using a Plasmaquad II + LAM-ICP-MS.

Optical properties were determined using standard optical spindle stage procedures in 589 nm light. Birefringence was determined with a Berek compensator. X-ray studies were done using a 114.6 mm Gandolfi camera and Phillips and Siemens powder diffractometers; the single-crystal diffractometer study used an Enraf-Nonius CAD4 diffractometer.

PHYSICAL PROPERTIES

No euhedral crystals of simmonsite were observed (Fig. 1). The mineral shows complex polysynthetic twinning. Simmonsite is pale buff to cream-colored in hand specimen, has a white streak, is somewhat greasy in appearance, and is translucent to transparent in thin section. Its Mohs hardness is 2.5–3. It has no distinct cleavage, a subconchoidal fracture, no parting, and is not extremely brittle. Its density D_m is 3.05(2) g/cm^3 (sink-float in a methylene iodide-acetone mixture), and D_c is 3.06(1) g/cm^3 . Simmonsite is very nearly isotropic, biaxial, N is 1.359(1) for Na light, birefringence is 0.0009. The assemblage of alumino-fluorides is fluorescent (moderate yellow orange) under short-wave UV light but not under longwave UV. Patchy and non-uniform response may be related to incipient alteration. A sec-

ond generation of clear and colorless cryolithionite fluoresces white to pale cream under both shortwave and longwave UV light, and is phosphorescent for several seconds.

CHEMISTRY

Numerous semi-quantitative analyses were carried out on many U.S. Geological Survey instruments. The only elements present in major or minor amounts were Na, Al, Li, and F. Electron microprobe analyses (UNO, average of seven analyses) gave Na = 23.4(2), Al = 13.9(2), F = 58.6(3), (calculated) Li = 3.56, and a total of 99.46 wt%. The empirical formula (based on six F atoms) is $\text{Na}_{1.98}\text{Li}_{1.00}\text{Al}_{1.00}\text{F}_6$. An ICP-MS analysis of a bulk rock sample showed major Na and Al, 0.21% K (as elpasolite inclusions), 2.6 wt% Li, 100 ppm Rb, 13 ppm Sc, and all other elements less than 10 ppm.

Behavior of the four primary alumino-fluorides was distinctly different under the electron beam; elpasolite and cryolithionite showed no beam damage with time, whereas simmonsite showed some and cryolite showed the most damage.

CRYSTALLOGRAPHY

Several previous studies have addressed the complicated crystallography of synthetic $\text{Na}_2\text{LiAlF}_6$. Garton and Wanklyn (1967) proposed that there were two polymorphs of $\text{Na}_2\text{LiAlF}_6$, isometric and hexagonal. Holm and Holm (1970) determined that the hexagonal form of Garton and Wanklyn was in error, as all the reflections could not be indexed on their cell, and suggested that the cell was actually monoclinic, B -centered with $a = 7.54 \text{ \AA}$, $b = 7.52 \text{ \AA}$, $c = 7.53 \text{ \AA}$, and $\beta = 90.81^\circ$ (an erroneous angle, $90^\circ 81'$, is given on the ICDD card, no. 24-653). Our findings on the natural phase, assumed to be isostructural, suggest that both studies are in error and that the low-temperature compound must have crystallized in space group $P2_1$ or $P2_1/m$

TABLE 1. Indexed powder diffraction pattern for simmonsite

| d_{obs} (Å) | hkl | d_{calc} | I_{obs} | $(I/I_{100})_{\text{diff}}$ |
|----------------------|-------------------|-------------------|------------------|-----------------------------|
| 4.33 | 111 | 4.304 | 100 | 22 |
| | $1\bar{1}\bar{1}$ | 4.347 | | 22 |
| 3.78 | 002 | 3.751 | 10 | 90 |
| | 200 | 3.750 | | 99 |
| | 020 | 3.737 | | 5 |
| 3.36 | 210 | 3.352 | 5 | 1 |
| | 012 | 3.353 | | 1 |
| 2.65 | 220 | 2.647 | 60 | 12 |
| | 202 | 2.633 | | 10 |
| | 022 | 2.647 | | 14 |
| 2.37 | 301 | 2.361 | 15 | 9 |
| | 103 | 2.362 | | 9 |
| | 130 | 2.364 | | 1 |
| | $30\bar{1}$ | 2.382 | | 6 |
| | $10\bar{3}$ | 2.383 | | 6 |
| 2.25 | $13\bar{1}$ | 2.258 | 70 | 3 |
| | 113 | 2.252 | | 6 |
| | 131 | 2.252 | | 31 |
| | 311 | 2.252 | | 6 |
| 2.18 | $22\bar{2}$ | 2.173 | 50 | 59 |
| 2.158 | 222 | 2.152 | 40 | 48 |
| 2.076 | 230 | 2.075 | 5 | 4 |
| | 023 | 2.078 | | 1 |
| | 032 | 2.075 | | 4 |
| | 203 | 2.066 | | 1 |
| 2.008 | $32\bar{1}$ | 2.009 | 10 | 5 |
| | $12\bar{3}$ | 2.009 | | 6 |
| | $13\bar{2}$ | 2.004 | | 1 |
| 1.877 | 400 | 1.875 | 90 | 76 |
| | 004 | 1.876 | | 100 |
| 1.824 | 410 | 1.819 | 5 | 2 |
| | 014 | 1.819 | | 2 |
| | 410 | 1.819 | | 2 |
| 1.711 | | | 5 | |
| 1.700 | | | 5 | |
| 1.67x | | | very faint | |
| 1.66x | | | very faint | |
| 1.646 | | | 5 | |
| 1.536 | | | 5 | |
| 1.526 | | | 25 | |
| 1.44x | | | 10 | |
| 1.43x | | | 10 | |
| 1.337 | | | 5 | |
| 1.324 | | | 20 | |
| 1.266 | | | 15 | |
| 1.212 | | | 2.5 | |
| 1.186 | | | 2.5 | |
| 1.138 | | | 2.5 | |
| 1.088 | | | 5 | |
| 1.077 | | | 5 | |

Notes: 114.6 mm gandolfi camera, Cu radiation, Ni filter. Reflections with $d < 1.75$ Å were not indexed because of the many contributing reflections. Lattice parameters from diffractometer: $a = 7.5006(6)$, $b = 7.474(1)$, $c = 7.503(1)$, $\beta = 90.847(9)^\circ$.

in the monoclinic cell, although the violations of B -centering are indeed weak and noted only in detailed work. Holm and Holm (1970) suggested a B -centered lattice based on indexed powder patterns but did not examine single-crystal photographs. Strong pseudo- B -centering is present, but several weak but reliable reflections serve to negate the symmetry. However, because the phase is a low-temperature dimorph of a cubic phase and the high- and low-temperature cells are similar, several cells are possible, as noted by Holm and Holm (1970); ultimately the structure solution will determine the correct cell.

Natural simmonsite is monoclinic, $P2_1$ or $P2_1/m$, $a = 7.5006(6)$ Å, $b = 7.474(1)$ Å, $c = 7.503(1)$ Å, $\beta = 90.847(9)^\circ$, $V = 420.6(1)$ Å³, $Z = 4$, as determined from precession studies and single-crystal diffractometer studies. The indexed powder diffraction data are in Table 1. As shown by the lattice parameters, simmonsite exhibits strong pseudo-cubic symmetry, and several pseudo-symmetries exist. An apparent $h0l$ n -glide results from the pseudo B -centering, but several very weak reflections exist that are in violation of that symmetry, as determined from diffractometer studies. Because $0k0$, $k = 2n + 1$ reflections are absent, we adopt the Holm and Holm (1970) monoclinic cell, in space group $P2_1$ or $P2_1/m$.

Numerous attempts at solving the simmonsite atomic arrangement were unsuccessful, presumably because of unit-cell scale twinning, inversion twinning, or order-disorder phenomena. However, many similarities to the perovskite structure exist that allow speculation on the atomic arrangement. The perovskite structure (CaTiO_3) is based on a framework of TiO_6 octahedra, with the large Ca cation occupying cubic interstices within the framework. Although high-temperature cubic perovskite is known, many distortions of the ideal cubic structure, due to ordering of cations or tilting of the octahedral framework, result in orthorhombic, hexagonal and monoclinic derivatives. Numerous properties of simmonsite suggest that the mineral crystallizes in the "double-perovskite" cell, one that has a cubic unit-cell length ~ 7.5 Å, double the minimum cell length. Parallelism in formulae between

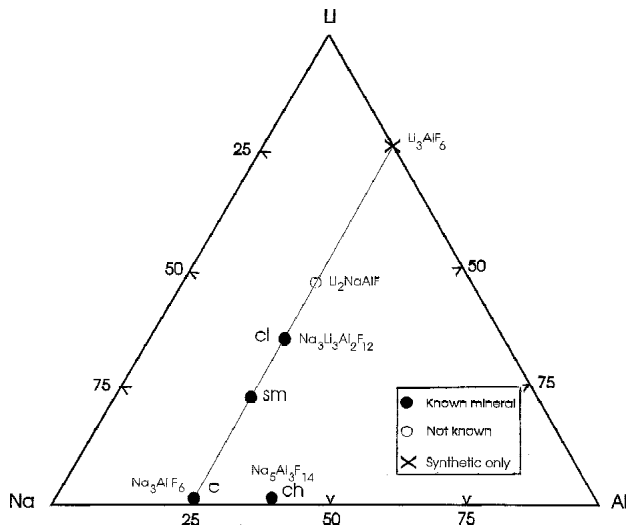


FIGURE 2. Ternary diagram of the system Li-Na-Al fluorides in atomic proportions, including the binary Na_3AlF_6 - Li_3AlF_6 . Cr = cryolite, sm = simmonsite, cl = cryolithionite, ch = chiolite.

perovskite and simmonsite ($\text{Ca}_2[\text{Ti}_2]\text{O}_6$, $\text{Na}_2[\text{AlLi}]\text{F}_6$), in unit cells (perovskite sensu stricto has $P2_1/m$, $b \sim 90.7^\circ$, $a \sim b \sim c \sim 7.65 \text{ \AA}$, whereas simmonsite has $P2_1/m$, $b \sim 90.8^\circ$, $a \sim b \sim c \sim 7.5 \text{ \AA}$), and the presence of high- and low-temperature dimorphs all suggest that simmonsite is a derivative of the perovskite structure. Structure refinement undertaken on single-crystal data using starting parameters of perovskite sensu stricto yields an R factor of $\sim 20\%$, but the refinement will not converge, presumably due to the ubiquitous twinning found in low-temperature perovskite dimorphs. It will ultimately require untwinned single-crystals or more material for Rietveld analysis to support such conjecture.

PHASE EQUILIBRIA STUDIES

Simmonsite is not directly related to any other known mineral. It is part of the ternary system Li-Na-F (Fig. 2) and also part of the binary system Na_3AlF_6 - Li_3AlF_6 that includes cryolite and cryolithionite. A minimum of five phases are possible in this binary system. The compound $\text{Li}_3\text{NaAlF}_6$ is not known naturally nor has it been synthesized, but the compound Li_3AlF_6 has been synthesized.

Synthetic $\text{Na}_2\text{LiAlF}_6$ transforms to a high temperature cubic phase at temperatures above 420°C , with $a = 7.639 \text{ \AA}$ at 445°C (Holm and Holm 1970). Holm and Holm (1970) suggested a B -centered cubic lattice for that phase at 425°C , a lattice which does not exist. It thus may be that the phase is dimensionally cubic but crystallizes in a B -centered orthorhombic cell.

GENESIS

The primary alumino-fluorides at the Zapot pegmatite have only Li and Na as alkali cations with very minor amounts of K present as elpasolite. The secondary alumino-fluorides are dominated by Na, K, Mg, and Ca, the different chemistry being indicative of interaction with host rocks. An elevated level of Li in the Zapot pegmatite is indicated by the presence of late-stage ferroan lepidolite. Sufficient Li was present at the time of crystallization of the primary alumino-fluoride assemblage to form the lithium-bearing phase(s).

Other worldwide occurrences of phases in the system Li_3AlF_6 - Na_3AlF_6 consist of only cryolite and/or cryolithionite. Cryolithionite and associated cryolite are found at Ivigtut, Greenland and Miask, Ural Mountains, Russia, deposits that may also contain (or have contained) simmonsite. Probably because

the Li content was not high enough for its formation, cryolithionite has not been identified from the U.S. occurrences of alumino-fluoride minerals at the Moorefield mine, Amelia, Virginia (Kearns 1995) or St. Peters Dome, El Paso County, Colorado, (Gross and Heinrich 1966; Raade and Haug 1980). When sufficient Li is present, a breakdown reaction of $3\text{Na}_2\text{LiAlF}_6(\text{sm}) = \text{Na}_3\text{AlF}_6(\text{cr}) + \text{Na}_3\text{Li}_3\text{Al}_2\text{F}_{12}(\text{cl})$ may occur, as suggested by Figure 2. The metasomatic exchange operator NaLi_{-1} is an important late-stage (subsolvus) geochemical operator in the petrogenesis of granitic pegmatites (Moore 1973), and the breakdown of the cryolithionite-simmonsite equilibrium assemblage may release that operator into the system. Thus, simmonsite is not stable under the same P, T conditions as cryolite and cryolithionite, perhaps explaining its scarcity.

ACKNOWLEDGMENTS

All those who knew Gene Foord know of his unbending passion for mineralogy. The first draft of this manuscript was prepared by Gene before his untimely death, and it was very important to him that his work be continued. All his co-authors are pleased that his work on simmonsite comes to fruition here, and adds to his innumerable contributions to the discipline.

We thank Harvey M. Gordon of Reno, Nevada for allowing us to complete geological and mineralogical studies of the Zapot pegmatite. The preliminary work benefited from reviews by J. Taggart and G. Meeker of the U.S. Geological Survey, Denver. Reviews of the final manuscript by T.S. Ercit and A.M. McDonald greatly improved the work, particularly the comments on the phase relations, many of which we have incorporated verbatim. Lee Groat provided excellent editorial handling of the manuscript. Partial support for this project was provided by NSF grant EAR-9627222 to J.M.H.

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