

A CLOSER LOOK AT MARTIAN METEORITES: DISCOVERY OF THE NEW MINERAL ZAGAMIITE, $\text{CaAl}_2\text{Si}_{3.5}\text{O}_{11}$, A SHOCK-METAMORPHIC, HIGH-PRESSURE, CALCIUM ALUMINOSILICATE. Chi Ma^{1,*}, Oliver Tschauner², John R. Beckett¹; ¹Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA; ²Department of Geoscience, University of Nevada, Las Vegas, NV 89154, USA; ^{*}chi@gps.caltech.edu.

Introduction: A closer look at shocked martian meteorites with advanced electron-beam and synchrotron techniques, particularly using high-resolution analytical scanning electron microscopy, has revealed more than ten new high-pressure minerals and phases since 2013 [e.g., 1-3]. These phases not only provide new insights into shock conditions and impact processes on Mars, but also inform the study of Earth systems at high pressures and temperatures.

During a nanomineralogy investigation of shock melt pockets in the basaltic shergottites Zagami and NWA 856, we identified a new high-pressure alumino-silicate mineral, $\text{CaAl}_2\text{Si}_{3.5}\text{O}_{11}$, with a $P6_3/mmc$ hexagonal structure [4], named “zagamiite” (Figs. 1-3). We characterized its composition, structure and petrography using high-resolution SEM, electron back-scatter diffraction (EBSD), electron microprobe analysis (EPMA), and synchrotron X-ray diffraction. The mineral zagamiite has been approved by the IMA-CNMNC (IMA 2015-022a) [5]. The name is after the locality Zagami, Nigeria, where the Zagami meteorite fell. In this presentation, we describe this new mineral in greater detail than in [4] and demonstrate how nanomineralogy works and plays a unique role in meteorite and Mars rock research.

Occurrence, chemistry, and crystallography: The Zagami and NWA 856 meteorites consist mainly of pyroxene (mostly zoned augite and pigeonite) and maskelynite (shock-generated plagioclase glass) with

Table 1. EPMA data for zagamiite.

Constituent Wt%	Zagami n=6	NWA 856 n=8
SiO_2	56.95	56.22
Al_2O_3	28.27	27.26
CaO	9.96	10.71
Na_2O	2.67	2.49
FeO	1.01	1.64
K_2O	0.44	0.39
MgO	0.06	0.24
TiO_2	0.05	0.08
MnO	0.03	0.08
Total	99.45	99.10

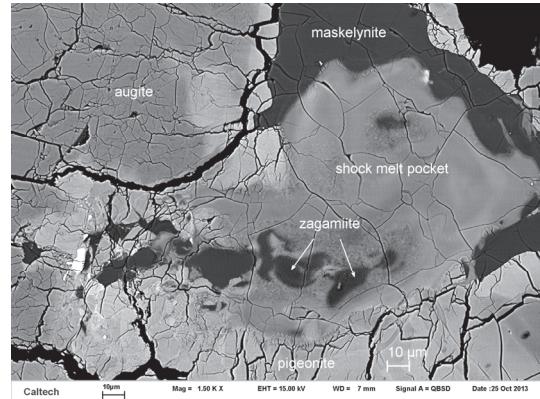


Fig. 1. Backscatter electron (BSE) image showing a zagamiite-bearing shock melt pocket in Zagami.

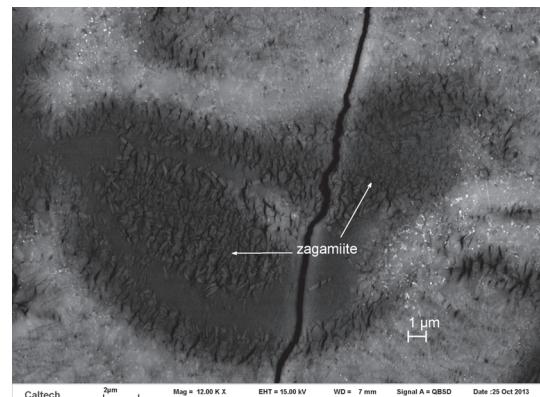


Fig. 2. Enlarged BSE image showing fine-grained zagamiite in the Zagami melt pocket.

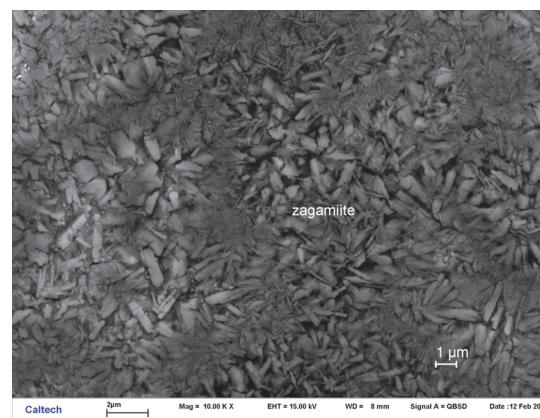


Fig. 3. BSE image revealing a cluster of zagamiite crystals in NWA856.

accessory ilmenite, titanomagnetite, baddeleyite, merrillite, apatite, and Fe sulfide, plus shock melt veins and pockets. In addition to zagamiite, which is de-

scribed below, we observed the high pressure minerals liebermannite, lingunite, stishovite, and a new type of tissintite (*tissinite-II*; $(\text{Ca},\text{Mg},\text{Na},\square_{0.14})(\text{Al},\text{Fe},\text{Mg})\text{Si}_2\text{O}_6$) [6] in Zagami, and stishovite in NWA 856.

Zagamiite occurs as fine-grained prismatic crystals, less than $50 \text{ nm} \times 100 \text{ nm}$ to $400 \text{ nm} \times 1 \mu\text{m}$ in size, within shock melt pockets (Figs. 1-3), often in association with stishovite (St) and maskelynite. The compositions of zagamiite in Zagami and NWA 856 by electron microprobe are similar (Table 1) with empirical formulas based on 11 oxygen *apfu* of $(\text{Ca}_{0.66}\text{Na}_{0.32}\text{K}_{0.03})(\text{Al}_{1.94}\text{Fe}_{0.05}\text{Mg}_{0.01})(\text{Si}_{3.51}\text{Al}_{0.11})\text{O}_{11}$ & $(\text{Ca}_{0.71}\text{Na}_{0.30}\text{K}_{0.03})(\text{Al}_{1.89}\text{Fe}_{0.09}\text{Mg}_{0.02})(\text{Si}_{3.50}\text{Al}_{0.11})\text{O}_{11}$, respectively. The general formula is $(\text{Ca},\text{Na})(\text{Al},\text{Fe},\text{Mg})_2(\text{Si},\text{Al},\square)_4\text{O}_{11}$, leading to an end-member of $\text{CaAl}_2\text{Si}_{3.5}\text{O}_{11}$. Zagamiite is Na-deficient and slightly Ca-enriched relative to plagioclase with the same Al/Si ratio and Al-poor, Si-rich relative to the CAS phase ($\text{CaAl}_4\text{Si}_2\text{O}_{11}$). Fig. 4 shows that the composition of zagamiite lies close to the An-Ab join when projected from Na (~An45) but the Na/Ca ratio (~0.4) is much lower than required (~1.2) for plagioclase with the same Al/Si ratio. This contrasts with tissintite, a highly defective clinopyroxene, where Na/Ca ratios of host maskelynite and tissintite are nearly equal [2]. Conserving Al & Si between a putative plagioclase and zagamiite yields $0.076\text{CaO} + (\text{Na}_{0.75}\text{Ca}_{0.624})(\text{Al}_2\text{Si}_{3.5})\text{O}_{11\text{plagioclase}} \rightarrow 0.451\text{NaO}_{1/2} + (\text{Ca}_{0.7}\text{Na}_{0.3})(\text{Al}_2\text{Si}_{3.5})\text{O}_{11\text{zagamiite}}$. The composition of zagamiite is readily distinguished from that of the phase “CAS” obtained experimentally or as reported by [7] in Zagami and NWA 856 (Fig. 4).

Synchrotron diffraction patterns of zagamiite are powder-like, revealing a dense hexagonal $P6_3/mmc$ structure with unit cell: $a = 5.403(2) \text{ \AA}$, $c = 12.77(3) \text{ \AA}$, $V = 322.9(11) \text{ \AA}^3$, and $Z = 2$. The structure and cell parameters are very similar to those of synthetic CAS ($\text{CaAl}_4\text{Si}_2\text{O}_{11}$; $P6_3/mmc$; 5.42; 12.70; 323.3 [8]). Differences in chemistry vs. CAS (e.g., Fig. 4) are accommodated mostly through differing site occupancies of the 12-coordinated 2c ($\text{Ca}_{4/5}\text{Na}_{1/5}$ in zagamiite vs. Ca_1 in CAS), octahedral 6g ($\sim\text{Si}_{3/4}\square_{1/4}$ vs. $\text{Si}_{2/3}\text{Al}_{1/3}$), and tetrahedral 4f ($\sim\text{Si}_{1/3}\square_{2/3}$ vs. $\text{Al}_{1/2}\square_{1/2}$) sites.

Origin and significance: Zagamiite has significant Fe and Mg and a substantial deficit of Na relative to plagioclase of equivalent Al/Si, suggesting that it formed by crystallization from a melt derived from a plagioclase-rich mixture of plagioclase and clinopyroxene, rather than through solid state transformation of a precursor mineral. Synthetic zagamiite has not been reported. Phase equilibria conducted on plagioclase compositions and natural systems suggest that multi-phase assemblages including CAS and other phases such as grossular are probably stable relative to

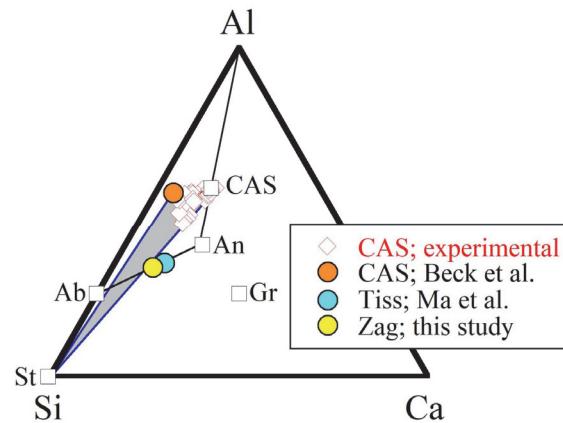


Fig. 4. Compositions of meteoritic tissintite (Tiss), zagamiite (Zag), CAS [2,7, this study] and synthetic CAS [more] in terms of molar Ca-Al-Si. End-member compositions of albite (Ab), anorthite (An), CAS (CAS phase), grossular (Gr), and stishovite (St) are also shown. Gray area encloses region consistent with St+CAS tie lines for plagioclase and plagioclase-like bulk compositions. Zagamiite and Tiss plot on the Ab-An binary when projected from Na and CAS well off of it.

zagamiite but these phases apparently failed to nucleate under the shock conditions for martian meteorites. Instead, it is zagamiite that crystallizes. We have also identified zagamiite in other shergottites, like Tissint.

Since CAS may be important in the Earth’s mantle, it is also important to characterize any natural occurrences. [7] reported natural CAS in Zagami and NWA 856. From Fig. 4, it is possible that CAS (+St) could crystallize from a melt following enrichment of Na and depletion of Ca due to crystallization of zagamiite (gray region), which could explain the occurrence of sodic CAS (+St) such as those reported by [7]. Since the compositions of zagamiite and CAS are distinct (Fig. 4), a cluster of CAS crystals should be easily distinguished from zagamiite. However, we were unable to confirm the presence of any CAS in our samples, even though some regions with zagamiite described here appear to be texturally equivalent to CAS-dominated regions described by [7] from the same meteorites. Confirmation of the identification of CAS in basaltic shergottites [7] is highly desirable.

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- [more] data from 10 papers.