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7   **Donwilhelmsite, [CaAl$_4$Si$_2$O$_{11}$], a new lunar high-pressure Ca-Al-silicate with relevance for**

8   **subducted terrestrial sediments**

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ABSTRACT

We report on the occurrence of a new high-pressure Ca-Al-silicate in localized shock melt pockets found in the feldspatic lunar meteorite Oued Awlitis 001 and discuss the implications of our discovery. The new mineral crystallized as tiny, micrometer sized, acicular grains in shock-melt pockets of roughly anorthitic bulk composition. Transmission electron microscopy based 3 dimension electron diffraction (3D ED) revealed that the $CaAl_4Si_2O_{11}$ crystals are identical to the calcium aluminum silicate, CAS, phase first reported from static pressure experiments. The new mineral has a hexagonal structure, with a space group *of P6$_3$/mmc* and lattice parameters of *a* = 5.42(1) Å; *c* = 12.70(3) Å; *V* = 323(4) Å^3; *Z* = 2. This is the first time 3D ED was applied to structure determination of an extraterrestrial mineral. The International Mineralogical Association has approved this naturally formed CAS phase as the new mineral "donwilhelmsite" [$CaAl_4Si_2O_{11}$], honoring the lunar US geologist Don E. Wilhelms. On the Moon, donwilhelmsite can form from the primordial feldspathic crust during impact cratering events. In the feldspatic lunar meteorite Oued Awlitis 001 needles of donwilhelmsite crystallized in ~200 μm in size shock melt pockets of anorthositic-like chemical composition. These melt pockets quenched within milliseconds during declining shock pressures. Shock melt pockets in meteorites serve as natural crucibles mimicking the conditions expected in the Earth' mantle. Donwilhelmsite forms in the Earths' mantle during deep recycling of aluminous crustal materials, where it is a key host for Al and Ca of subducted sediments in most of the transition zone and in the uppermost lower mantle (460-700 km). Donwilhelmsite bridges the mineralogical gap between kyanite and the Ca-component of clinopyroxene at low pressures and the Al-rich Ca-ferrite phase and Ca-perovskite at high-pressures. In ascending buoyant mantle plumes, at about 460 km depth, donwilhelmsite is expected to break down into minerals such as garnet, kyanite, and clinopyroxene. This may trigger minor

51 partial melting releasing a range of incompatible minor and trace elements contributing to the

52 enriched mantle (EM1 and EM2) components associated with subducted sedimentary lithologies.

53 **Keywords:** High-pressure phase, new mineral, donwilhelmsite, Oued Awlitis 001 lunar

54 meteorite, shock metamorphism, subduction, mantle mineral, enriched mantle component

55

INTRODUCTION

57 The Earth's continental crust and the lunar highlands (i.e., consisting of material derived from

58 many superposed impact ejecta from all crustal levels and covering the lunar surface) are

59 dominantly felsic in composition, including as major elements, O, Si, Al, Ca, Na, and K. Minerals

60 controlling the distribution of these elements are important agents for the origin and fate of

61 planetary crusts. Remnants of a primordial crust are preserved on the Moon, showing the intense

62 mechanical and thermal metamorphism and melting, caused by impacts during the Heavy

63 Bombardment Eon (Wilhelms 1987; Fernandes et al. 2013). Nonetheless, these remnants document

64 initial planetary differentiation processes. Fifty years ago, the Apollo 11 mission collected 21.6 kg

65 of lunar rocks and soils, including anorthosites composed of >90 vol% plagioclase (Wilhelms 1987,

66 1993). Lunar anorthosites contain exceptionally high proportions of the Ca-rich anorthite

67 endmember of the albite – anorthite ($Na[AlSi_3O_8]$ – $Ca[Al_2Si_2O_8]$) plagioclase solid solution, with

68 96-98 mol% anorthite. From these samples, it was concluded that the impact gardened bright lunar

69 highlands derived from a primordial (>4.3 Ga old) anorthositic crust, several tens of kilometers

70 thick (50 ± 15 km, e.g., Wieczorek et al. 2006) that crystallized and floated on a dense lunar magma

71 ocean, several hundred kilometers deep (Wood et al. 1970; Smith et al. 1970).

72   Preservation of a highly fragmented and displaced primary crust (>4.4 Ga), as well as primary

73   mantle heterogeneities resulting from the crystallization of the, likely heterogeneous, lunar magma

74   ocean, is in stark contrast to the geologically active Earth. Earth's oldest preserved oceanic and

75   continental crusts are about 0.2 and 4.0 Gy old, respectively, with the latter being found in very

76   limited areas on Earth. During plate tectonic processes, crustal materials rich in volatiles and other

77   elements incompatible in mantle minerals are reintroduced into the depleted mantle by subduction.

78   The sinking oceanic plates carry continental-derived sediments into the deep mantle (Irifune et al.

79   1994; Plank and Langmuir 1998), and the enriched mantle component EM2 (enriched mantle 2;

80   with high $^{87}Sr/^{86}Sr$ and intermediate $^{206}Pb/^{204}Pb$) is ascribed to the direct terrigenous component

81   with a composition similar to the upper continental crust (White 2015). In contrast, the origin of

82   the enriched mantle component EM1 (enriched mantle 1; with intermediate $^{87}Sr/^{86}Sr$ and low

83   $^{206}Pb/^{204}Pb$) is more elusive but often attributed to pelagic sediments (Garapić et al. 2015).

84   Especially Archean-aged sediments are good candidates for the enriched components in the mantle

85   source of South Pacific Ocean islands like Pitcairn (Delavault et al. 2016). About 75% of the

86   subducted sediment flux is estimated to be direct terrigenous material of average upper crust

87   composition (Plank and Langmuir 1998). Such lithologies can be recycled into the lower mantle

88   and retained there for up to 2-3 Gy, before being sampled by recent plumes and ongoing ocean

89   island volcanism. Deep recycling of continentally derived sediments below 200-300 km depth is

90   facilitated by stepwise densification at 6.5 GPa (~200 km depth), when orthoclase breaks down,

91   and at 9 GPa (~280 km depth), when hollandite and stishovite form, to densities exceeding that of

92   ambient peridotite at the 280-700 km depth range (Irifune et al. 1994). At deeper levels, the

93   sediment and peridotite densities may remain nearly identical to depths beyond 1200 km and ~40

94   GPa (Poli and Schmidt 2002). The densification of terrigenous and pelagic sedimentary lithologies

95   in the mantle transition zone is aided by the occurrence of 7-10 % of a Ca-Al-silicate (CAS) phase

96   with composition $CaAl_4Si_2O_{11}$ at the 460-700 km depth range (Irifune et al. 1994).

97   Natural examples of those minerals composing Earths' deep mantle are rarely accessible. Many

98   minerals stable at deep mantle pressure and temperature conditions decompose into other mineral

99   assemblages stable at lower pressures due to the specific pressure-temperature-time (P-T-t) path

100   during ascent. Notable exceptions include high-pressure phases such as ringwoodite (high-pressure

101   polymorph of olivine), ferropericlase, and Mg-wüstite found as inclusions in diamonds (e.g.,

102   Pearson et al. 2014). The diamond host serves as a pressure vault providing an environment that

103   allows deep mantle high-pressure mineral inclusions to cool to temperatures low enough to inhibit

104   a back reaction into low-pressure mineral assemblages. Localized zones of shock melt in

105   moderately to strongly shocked meteorites present another natural environment in which a hot and

106   compressed melt is quenched at typical deep mantle pressures to temperatures low enough to inhibit

107   a back reaction into low-pressure mineral assemblages during pressure release (Chen et al. 1996;

108   Fritz et al. 2017). A great diversity of natural examples of high-pressure minerals, analogous to

109   those occurring in the Earths' mantle, were first found in local shock melt zones (such as melt veins

110   and melt pockets) of different types of meteorites, including chondrites and achondrites of basaltic

111   and dunitic compositions (e.g., Tomioka and Miyahara 2017). Compared to mafic and ultramafic

112   meteorites, reports of shock melt zones in felsic meteorites are very limited. Although CAS-like

113   phases of various compositions close to the $CaAl_4Si_2O_{11}$-$NaAl_3Si_3O_{11}$ joint have been found in

114   shocked basaltic meteorites from Mars (i.e., in shergottites, Beck et al. 2004; El Goresy et al. 2013),

115   the CAS phase has neither been characterized in felsic meteorites, nor been officially named. Here

116   we report on the discovery and detailed characterization of the natural high-pressure and high-

117   temperature transformation of anorthite in shock melt zones within the feldspathic lunar meteorite

118   Oued Awlitis 001.

MATERIAL AND METHODS

Oued Awlitis 001 meteorite

The main fragment of the lunar meteorite Oued Awlitis 001, originally 382 g, was found on January 15, 2014, in the Western Sahara (25.954°N, 12.493°W). It is largely covered with a green to brownish fusion crust showing features of orientation. Another fragment, 50.5 g, fitting the larger one, was found a few weeks later. About 60% of the recovered meteorite is covered with a crackled fusion crust and shows a rollover lip on one side. Oued Awlitis 001 is classified as an anorthositic lunar impact melt rock, composed of large anorthite clasts set in a poikilitic matrix of plagioclase, olivine, and pyroxene (Ferrière et al. 2017; Ruzicka et al. 2017; Wittmann et al. 2019). The poikilitic matrix indicates a slow cooling history, possibly in a ~100 meter thick impact melt sheet (Wittmann et al. 2019). Later impact event(s) emplaced the rock closer to the lunar surface, and about 0.3 Ma ago it was impact accelerated beyond lunar escape velocity and delivered to Earth (see Ferrière et al. 2017; Wittmann et al. 2019). The sections investigated in this study were prepared from the 50.5 g fragment of this meteorite from the Natural History Museum Vienna (NHMV, Austria) collection (specimen NHMV-N9830).

Optical microscopy

A thin section of Oued Awlitis 001 (NHMV-O105), prepared from the pristine part of the meteorite (i.e., excluding the fusion crust) was studied in transmitted light at the NHMV. A polished thick section mounted in epoxy (NHMV-O104) was studied by optical microscopy in reflected light aided by the use of immersion oil at the Museum für Naturkunde, Berlin, Germany. Such an approach is ideal to recognize potential high-pressure phases within local shock melt zones inside meteorites, as minerals and glass display intense brightness contrast in reflected light. This thick

6

142 section was then studied using a binocular microscope, to acquire depth information of the

143 transparent minerals and their outer surface, visible through the transparent epoxy mount.

144

Micro-Raman spectroscopy

146 Subsequently, micro-Raman spectroscopic analyses were conducted on the uncoated thick section

147 and prior to any disturbances caused by electron beam irradiation during electron microscopic

148 investigations. Raman spectra were collected with the WITec Alpha 300 Raman confocal

149 microscope at the Deutsches Zentrum für Luft und Raumfahrt (DLR), Berlin, Germany, using a

150 Nd:YAG laser with an excitation wavelength of 532 nm, a 100x magnification objective (NA 0.8),

151 and a power of 3 to 7 mW on the sample.

152

Electron microscopy

154 Backscattered electron (BSE) microscopic images were obtained on the polished and carbon coated

155 thick section at the Museum für Naturkunde Berlin (MfN), Germany, using a JEOL JXA 8500F

156 Field Emission Microprobe. For X-ray elemental maps, the microprobe was operated with 15 kV

157 accelerating voltage, a 15 nA beam current, an about 10 nm beam size, and a dwell times of 100

158 ms. Quantitative chemical analyses of the shock melt pocket were obtained with the same

159 instrument using a 10–15 kV accelerating voltage, a 15 nA beam current, and a defocused 10 μm

160 diameter beam. Suitable glass and mineral standards certified by the Smithsonian Museum were

161 used as reference samples for electron microprobe analysis (Jarosewich et al. 1980).

Focused Ion Beam (FIB)

163   FIB foils 20 x 10 x 0.15 μm in size were cut out of the thick section at the Deutsches

164   GeoForschungsZentrum, Sektion 3.5 Grenzflächen-Geochemie Helmholtz-Zentrum (GFZ)

165   Potsdam, Germany, using a FEI TEM 200 FIB system.

166

167   **Transmission electron microscopy (TEM)**

168   Initial TEM characterization was performed using a FEI Tecnai^{TM} G2 F20 X-Twin operated at 200

169   kV with a field emission gun electron source at GFZ Potsdam. The microscope is equipped with

170   an EDAX ultra-thin window EDX system, a Fishione high-angle annular dark-field (HAADF)

171   detector, and a post-column Gatan imaging filter (GIF Tridiem).

172   Additional TEM characterization, including chemical analyses and crystal structure determination,

173   was performed at the Institute of Physics of the Czech Academy of Science (IPCAS), Prague,

174   Czech Republic. The reported chemical analyses were obtained using an FEI Tecnai^{TM} G2 F20 X-

175   Twin attached with an EDAX energy dispersive spectrometer (EDS) operated at 200 kV. The

176   chemical analyses were obtained with a defocused beam with the size of about 300 nm in diameter

177   in TEM mode to avoid the loss of volatile elements such as sodium. Standardless quantification

178   using FEI TIA software version 4.2 was used for the analysis. The empirical formula was calculated

179   on the basis of 7 cations.

180   The crystal structure of donwilhelmsite was determined by 3D electron diffraction (3D ED; Gemmi

181   et al. 2019 and references therein) performed on a Philips CM 120 (LaB$_6$, 120kV), equipped with

182   a NanoMEGAS precession unit DigiStar and an Olympus SIS CCD camera Veleta (2048 x 2048

183   px), in Prague. The diffraction data were collected by means of precession electron diffraction

184   (Mugnaioli et al. 2009). The target crystal was sequentially tilted by 1 deg. step from -50 to +50

185   deg., and at every tilt step a precession diffraction pattern in micro-diffraction mode was acquired

186 using a precession angle of 1 deg. Data processing was carried out using the PETS software

187 (Palatinus et al. 2019). Structure solution and refinement were performed using the computing

188 system Jana2006 (Petříček et al. 2014). The structure was solved by the charge flipping algorithm

189 using the program Superflip (Palatinus and Chapuis 2007), and refined using a dynamical approach

190 (Palatinus et al. 2015a, 2015b).

191

192   **RESULTS**

193 The feldspathic lunar meteorite Oued Awlitis 001 (Fig. 1) is an impact melt rock predominantly

194 composed of up to about 5 mm-sized Ca-rich plagioclase clasts set into a crystallized melt

195 groundmass composed of <100 µm sized olivine and pyroxene grains poikilitically enclosing

196 equally sized anorthite grains. All silicates display strong compositional zoning. Minor phases

197 present include FeNi metal, troilite, ilmenite, Ti-rich spinel, apatite, zircon, baddeleyite, and silica.

198 For the detailed petrology and mineral chemistry of the meteorite the reader is referred to Ferrière

199 et al. (2017) and Wittmann et al. (2019).

200 Oued Awlitis 001 is moderately shocked. The observed shock metamorphic effects developed

201 during a later impact event which affected the already fully crystalline impact melt rock.

202 Plagioclase is mostly crystalline, showing undulatory extinction, reduced birefringence, and well-

203 developed planar deformation features (PDF). In a few places, the plagioclase is transformed into

204 diaplectic glass, so-called maskelynite.

205 Locally, the meteorite contains thin shock melt veins ranging from 50 to 150 µm in thickness, as

206 well as shock melt pockets with diameter typically of about 200 µm (Fig. 2a). Optical inspection

207 with a binocular microscope showed that the melt veins are three dimensional melt sheets with

208 irregular surfaces extending deep into the meteorite sample. The melt veins are recrystallized to

209   extremely fine-grained mineral assemblages. In contrast, the melt pockets appear isolated and

210   contain bundles (acicular texture) of up to 20 µm long and less than 1 µm wide needles that

211   crystallized from the melt (Fig. 2b). Electron microprobe investigation revealed that the shock melt

212   pockets are roughly anorthitic in bulk composition (Table 1). In high-contrast BSE images (Fig.

213   2a-b), the acicular crystals appear slightly brighter than the matrix and are surrounded by a

214   comparatively darker halo when compared to the adjacent anorthite shock melt. Elemental maps

215   show that the needle shaped crystals are enriched in Al and slightly depleted in Ca compared to the

216   glass in the shock melt pocket (Fig. 3). The needles do not incorporate Fe and Mg (the Mg map is

217   not shown). The compositional differences between glass and crystals are such that these phases

218   can be easily overlooked in low-contrast BSE surveys. The localized zones of shock melt and the

219   potential presence of crystallized minerals in polished samples can be identified quickly via

220   reflected light microscopy. In a piece of Oued Awlitis 001 with a polished surface of ~5 x 5 mm in

221   size a total of three shock melt pockets and one shock melt vein were observed. The needle shaped

222   minerals crystallized from all three isolated, roundish, shock melt pockets, but are not observed in

223   the shock melt vein, the latter apparently represents a three dimensional melt sheet.

224   These needle-shaped crystals provided Raman spectra with peaks at 280, 420, 500, 618, and 912

225   cm^{-1} (Fig. 4), and a shoulder indicating an additional peak at ~850 cm^{-1}. The Raman spectra

226   obtained from the needles are in good agreement with Raman spectra reported for synthetic

227    $CaAl_4Si_2O_{11}$ with characteristic peaks at 280, 422, 486, 616, 851, and 910 cm^{-1} Raman shift (Beck

228   et al. 2004). The broad band at 1015 cm^{-1}, together with some contribution around 460-550 cm^{-1},

229   is interpreted to be from the Ca-, Al-, and Si-rich glass surrounding the crystals. A 1015 cm^{-1} band

230   was also observed and relates to the non-bridging vibrations of TO_4 tetrahedra (where T = Si, Al),

231   and its position indicates preferentially more non-bridging Si-O than Al-O tetrahedra compared to

232   anorthite glass with a band at 985 cm^{-1} (Sharma et al. 1983; Matson et al. 1986). The shock melt

pocket of anorthite-like composition (Table 1) displays Raman spectra with a broad feature around

985 cm^{-1} (Fig. 4). In BSE images the brighter needles are surrounded by a dark halo. The halo is

Al-depleted and Si-enriched compared to the anorthitic shock melt pocket, due to crystallization of

the Al-rich needle-shaped crystals (Table 1). The halo contains 20 wt% Al_2O_3 suggesting an

incomplete crystallization sequence. Notably, the glass is not dissociated in phases such as SiO_2,

CaO or $CaSiO_3$, as revealed by the absence of Raman features in the ~800 cm^{-1} spectral region

typical for SiO_2 glass.

Transmission electron microscopy investigation showed that all needles are embedded in a

completely amorphous glassy matrix. No other minerals, such as garnet, corundum, kyanite, or

stishovite were found in the studied shock melt pockets with TEM investigations, elemental maps,

and Raman spectroscopic surveys. An average of ten TEM EDS-analyses of the CAS needles

yielded a chemical composition of 52.7 wt% Al_2O_3, 32.6 wt% SiO_2, and 15.0 wt% CaO (Table 2).

The empirical formula calculated on the basis of 7 cations is $Ca_{1.02}Al_{3.92}Si_{2.06}O_{11}$. The analytical

results show full occupation of Ca and only very slight excess of Si and deficiency of Al with

respect to the stoichiometric composition. Sodium, K, Mg, and Fe contents are below the detection

limit of about 1 wt%.

The crystal structure of the new mineral was determined from eight datasets obtained with TEM

using 3D ED Fig. 5; Table 3). The lattice parameters are $a = 5.42(1)$ Å; $c = 12.70(3)$ Å; $V = 323(4)$

Å^3; $Z = 2$. The hexagonal structure with a space group of $P6_3/mmc$ is identical to that of the CAS

phase synthesized at pressures >14 GPa and temperatures >1773 K (Table 3; Irifune et al. 1994;

Gautron et al. 1999). Moreover, the atomic distribution, inferred from the combination of bond

distances and bond valence sums, is also identical (Table 4). The results presented here are from

256 the dataset 180520-2, which was refined dynamically to *R1(obs)* = 8.95% (Table 5). The crystal

257 structure is composed of di-octahedral M1 layers containing Al and Si in 1:2 proportion, and an

258 interlayer consisting of M2 octahedral positions fully occupied by Al, tetrahedral (T) positions half

259 occupied by Al, and larger cavities occupied by Ca (Fig. 6). The tetrahedral position T-Al3 is

260 disordered between two positions. An ordered model can be built with only one of the two positions

261 occupied. The space group of such a model is *P6₃mc*, and its refinement gave slightly increased

262 figures of merit. This result confirms that the structure is indeed centro-symmetric with a

263 disordered tetrahedral position. The chemical composition derived from the structure model is

264 $CaAl_4Si_2O_{11}$, in good agreement with the measured chemical composition of $Ca_{1.02}Al_{3.92}Si_{2.06}O_{11}$.

265

266 **DISCUSSION**

267 The natural CAS phase ($CaAl_4Si_2O_{11}$) presented in this study is named donwilhelmsite (IMA2018-

268 113; Fritz et al. 2019a), and the holotype is catalogued as NHMV-O104 and preserved in the

269 meteorite collection of the NHMV. Donwilhelmsite is named to honor Dr. Don E. Wilhelms for

270 his seminal and ground-breaking work on the geological history of the Moon (Wilhelms 1987,

271 1993).

272 Donwilhelmsite [$CaAl_4Si_2O_{11}$] was identified within the lunar meteorite Oued Awlitis, 001, and

273 the structure was solved by 3D electron diffraction. The needle shaped minerals are structurally

274 and chemically identical to the CAS phase, first synthesized in static pressure experiments by

275 Irifune et al. (1994), and later characterized in detail by Gautron et al. (1999). Similar and more

276 Na-rich examples of the $CaAl_4Si_2O_{11} – NaAl_3Si_3O_{11}$ solid solution series were previously reported

277 form shock melt veins in basaltic Martian meteorites (Beck et al. 2004). The Na-rich endmember

278 ($NaAl_3Si_3O_{11}$) is energetically in disfavor compared to jadeite or calcium ferrite and, thus, unlikely

279   to form (Akaogi et al. 2010). The phases along the $CaAl_4Si_2O_{11}$ – $NaAl_3Si_3O_{11}$ solid solution series

280   are Al-rich and Si-poor compared to the $CaAl_2Si_{3.5}O_{11}$ high-pressure phase zagamiite (Ma and

281   Tschauner 2017; Ma et al. 2017). Donwilhelmsite forms a complex solid solution series with

282   multiple cation substitution mechanisms including Fe, Mg, K, and Na (Irifune et al. 1994; Beck et

283   al. 2004; Akaogi et al. 2010; El Goresy et al. 2013).

284   In the feldspathic lunar meteorite Oued Awlitis 001, the shock effects in plagioclase (Ferrière et al.

285   2017; Wittmann et al. 2019) indicate whole rock shock pressures of 20-24 GPa (Fritz et al. 2019b).

286   The resulting shock-induced temperature increase of less than 100 K provides sufficiently low

287   whole rock temperatures after shock decompression for the preservation of high-pressure phases

288   when pressure almost instantly drops to zero pressure conditions (Fritz et al. 2017). In the up to

289   200 µm diameter sized isolated shock melt pockets, the shock pressure and temperature, preserved

290   for a short time (milliseconds), mimic the pressure and temperature conditions in parts of the

291   Earth's mantle. In the short period of declining temperature and pressure, donwilhelmsite grains

292   crystallized from the melt. An Al_2O_3 content of ~20 wt% in the glass surrounding donwilhelmsite

293   indicates an incomplete crystallization sequence, and the high Al-abundance suppressed the

294   formation of the SiO_2 high-pressure polymorph stishovite.

295

296   On Earth, donwilhelmsite (the CAS phase, $CaAl_4Si_2O_{11}$) is an important mineral in continental-

297   derived sediments subducted into the deep mantle. Static pressure experiments showed that the

298   minimum pressure to form donwilhelmsite is 13 GPa for a $CaAl_4Si_2O_{11}$ composition (Akaogi et al.

299   2009) and 12 GPa for a less aluminum-rich lunar anorthositic-like composition (Nishi et al. 2018).

300   For compositions corresponding to terrigenous sediments and upper continental crust,

301   donwilhelmsite becomes stable at a pressure of 15.6 GPa (460 km depth) along the transition zone

302 of the adiabatic curve (Irifune et al. 1994; Stixrude et al. 2009). Donwilhelmsite was also recorded

303 in basaltic compositions in near- and super-solidus conditions at about 26 GPa (Hirose and Fei

304 2002), and up to 3% of the mineral might be present in basalts in the lowermost 100 km of the

305 transition zone at temperatures near and above the ambient mantle adiabatic curve (Litasov and

306 Ohtani 2005).

307 Whereas the mineral with a bulk composition of $CaAl_4Si_2O_{11}$ (Akaogi et al. 2009) persists to about

308 36 GPa (950 km depth), at ambient adiabatic conditions (Stixrude et al. 2009) its stability is limited

309 to about 30 GPa (810 km depth) for a composition resembling lunar anorthosites (Nishi et al. 2018).

310 The pressure regime of the Earth's mantle, however, prevents the formation of primary anorthositic

311 magma ocean crust and the accumulation of dense residual melts and associated cumulates in the

312 uppermost mantle (Trønnes et al. 2019). On Earth, aluminum, volatiles, and other elements

313 incompatible in mantle minerals are recycled into the deep mantle via terrigenous and pelagic

314 sediments that plunge down with sinking oceanic plates (Irifune et al. 1994; Plank and Langmuir

315 1998).

316 Within its stability range of about 460-700 km depth, donwilhelmsite comprises 7-10% of

317 terrigenous sediments subducted into the deep mantle and is an important reservoir for Al, Ca, Na,

318 K, and other large-ion lithophile trace elements (Irifune et al. 1994; Litasov and Ohtani 2005). The

319 decompression breakdown in ascending mantle plumes of donwilhelmsite into minerals such as

320 garnet, kyanite, and clinopyroxene might trigger minor partial melting at about 460 km deep,

321 releasing a range of incompatible minor and trace elements. Such melts could be important agents

322 of mantle metasomatism and contribute to the composition of ocean island basalts and kimberlites.

323

324   **IMPLICATIONS**

325 Donwilhelmsite [$CaAl_4Si_2O_{11}$], is a new high-pressure Ca-Al-silicate found in shock melt pockets

326 in the feldspathic lunar meteorite Oued Awlitis 001. The crystal structure of donwilhelmsite was

327 solved with precession assisted 3D ED. The 3D ED approach to solve the crystal structure of

328 minerals, first used by Rozhdestvenskaya et al. (2010), is now often applied to characterize

329 synthetic high-pressure phases of geological interest (Gemmi et al. 2016). Here, for the first time,

330 3D ED technique is used to characterize an extraterrestrial mineral. The method provides new

331 opportunities to study the great variety of minerals with submicrometer size that formed in a broad

332 range of exotic environments (with varying P-T-t) as represented in some meteorites, and in

333 material brought to Earth by "sample-return" space missions.

334 The identification of donwilhelmsite in a lunar meteorite underlines that high-pressure phase

335 formation in localized zones of shock melt in meteorites is a common phenomenon. Meteorites

336 serve as ideal natural crucibles for high-pressure mineral research because 1) they can provide

337 localized zones of shock melt with a broad range of chemical and mineralogical properties, and 2)

338 they were protected from various types of alteration processes in the space environment.

339 The natural occurrence of high-pressure phases is an important asset to understand geological

340 processes affecting the magmatic evolution of terrestrial planets, such as phase-transformations in

341 planetary interiors, magma ocean crystallisation, and plate tectonics. In the Earth's mantle,

342 donwilhelmsite forms during deep recycling of aluminous crustal materials, which in addition are

343 rich in volatiles and other elements incompatible in mantle minerals. In the terrestrial rock cycle,

344 donwilhelmsite is an important agent for transporting crustal sediments through the transition zone

345 and uppermost lower mantle (460-700 km). . The decompression breakdown of donwilhelmsite in

346 pelagic and terrigenous derived components in ascending mantle plumes contributes to the EM1

347 and EM2 geochemical signatures recognized in various mantle derived volcanic lithologies.

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513   Figure 1: Backscattered-electron (BSE) image showing a petrographic overview of the lunar

514   meteorite Oued Awlitis 001 (NHMV-O104). Large plagioclase clasts (pl clast) are embedded in a

515   matrix composed of olivine (ol), pyroxene (px), plagioclase (pl), and silica (not indicated).

516   Figure 2: Backscattered-electron (BSE) image showing a) a shock melt pocket with needles of

517   donwilhelmsite. The grey host rock is mainly composed of anorthite with bright minerals

518   representing olivine and pyroxene. Dark regions are cracks on the surface of the polished thick

519   section. b) BSE image showing bundles of needle-like (acicular) donwilhelmsite crystallized in a

520   ~100 µm wide shock melt pocket of anorthitic chemical composition. The donwilhelmsite needles

521   are surrounded by a darker halo. c) Bright field TEM image showing an almost defect free

522   donwilhelmsite crystal. The dark upper left corner is the platinum strip holding the sample.

523   Figure 3: Ca, Al, and Fe elemental maps and backscattered electron (BSE) image showing needles

524   of donwilhelmsite within a shock melt pocket. Elemental maps of Fe and Mg (not shown) reveal

525   chemical inhomogeneity within the anorthositic-like shock melt pocket, likely related to melted

526   pyroxene or olivine grains.

527   Figure 4: Raman spectra of donwilhelmsite and the glass composing the shock melt pocket. The

528   donwilhelmsite spectra shows peaks at 280, 420, 500, 618, 850, and 912 cm^{-1} together with spectral

529   contributions from the surrounding glass halo providing broad features in the 500 to 560 region

530   and at ~1015 cm^{-1} Raman shift. The shock melt pocket displays a Raman spectra with broad hump

531   with maxima at ~500 and ~560 cm^{-1} and a broad hump with a maxima at ~985 cm^{-1} Raman shift.

532 Figure 5: Precession electron diffraction tomography (PEDT). Displayed are sections through the

533 experimental diffraction dataset 180520-2 in three orientations with the unit cell marked.

534 Figure 6: Structure of donwilhelmsite. a) The structure is composed of b) octahedral M1-layers

535 (dark blue) occupied by Al and Si in 1:2 ratio. c) The interlayers, contain octahedral M2-positions

536 (grey) fully occupied by Al, tetrahedral positions (T, grey) half occupied by Al, and cavities

537 occupied by Ca (green).

538

539 **Table 1** │ Chemical composition of the shock melt pocket given as an average of 10 electron

540 microprobe analyses (Melt) and their standard deviation (S.D.). The chemical composition of the

541 glass halo rimming donwilhelmsite (Gl) and for donwilhelmsite (DW) were obtained by TEM-

542 EDS analytics.

	Melt	S.D.	Gl	DW
SiO_2	44.0	0,75	60.7	32.6
Na_2O	0.35	0.06		
TiO_2	0.10	0.04		
K_2O	0.01	0.01		
Cr_2O_3	0.04	0.02		
Al_2O_3	35.4	1.23	20.8	52.7
MgO	0.52	0.18		
MnO	0.01	0.02		
CaO	18.9	0.51	18.5	15.0
FeO	1.09	0.34		
Total	100.4	0.41	100.0	100.3

543

544 **Table 2** │ **Chemical data (in *weight % of oxides* and *atoms per formula unit = apfu*).** For
545 donwilhelmsite, the empirical formula as calculated on the basis of 7 cations is $Ca_{1.02}Al_{3.92}Si_{2.06}O_{11}$,
546 and the simplified formula is $CaAl_4 Si_2 O_{11}$.

	Al₂O₃	SiO₂	CaO	Al	Si	Ca
	wt%	wt%	wt%	7 apfu	7apfu	7 apfu
sp-01	52.3	32.1	15.7	3.9	2.0	1.1
sp-02	54.0	32.6	14.1	4.0	2.1	1.0
sp-03	46.8	35.2	17.7	3.5	2.3	1.2
sp-04	52.9	34.1	13.9	3.9	2.1	0.9
sp-05	54.0	32.2	14.3	4.0	2.0	1.0
sp-06	51.5	33.1	15.6	3.8	2.1	1.1
sp-07	52.8	32.7	14.9	3.9	2.1	1.0
sp-08	53.3	31.0	15.6	40	2.0	1.1
sp-09	53.2	31.6	15.3	4.0	2.0	1.0
sp-10	56.0	31.4	13.3	4.1	2.0	0.9
average	52.7	32.6	15.0	3.9	2.1	1.0
std. dev.	2.4	1.3	1.2	0.2	0.1	0.1
min.	46.8	31.0	13.3	3.5	2.0	0.9
max.	56.0	35.2	17.7	4.1	2.3	1.2

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Table 3 │ **Comparison of crystal data with hexagonal crystal system.** Diffraction data of the here described new mineral was determined by precession electron diffraction tomography (PEDT), X-ray diffraction data from Gautorn et al. (1999) are obtained on single crystals and Akaogi et al. (2009) used powder samples. The synchrotron diffraction patterns of micrometer-sized high aluminum silica (HAS) zagamiite grains were consider similar to powder-like samples (Ma et al. 2017). The cell parameters of these hexagonal crystals are given as a and c in [Å] Angstrom and the cell volume $V = a^2 c \sin(60°)$ in [Å^3]. The numbers in parentheses () represent the estimated standard deviations in the last digit. *Unit cell parameters from electron diffraction tomography (EDT) are known to have distortions and lower accuracy (Kolb et al., 2008). Z is the number of formula units per unit cell. The calculated density of donwilhelmsite is 3.903 [g/cm^{-3}].

Composition	Space group	a [Å]	c [Å]	V [Å^3]	Z	Reference
Donwilhelmsite **CaAl$_4$Si$_2$O$_{11}$**	$P6_3/mmc$	5.42 (1)	12.70 (3)*	323(4)	2	This work
synthetic **CaAl$_4$Si$_2$O$_{11}$**	$P6_3/mmc$	5.4223 (4)	12.7041 (6)	323.28 (5)	2	Gautron et al. 1999
synthetic **CaAl$_4$Si$_2$O$_{11}$**	$P6_3/mmc$	5.4239 (2)	12.6805 (5)	323.06 (3)	2	Akaogiet al. 2009
Zagamiite **CaAl$_2$Si$_{3.5}$O$_{11}$**	$P6_3/mmc$	5.403 (2)	12.77 (3)			Ma et al. 2017

Table. 4 │ **Characteristics of cation coordination.**

position	occupancy	BVS[1]	ECON[2]	average distance to coordinating oxygen atoms [Å]	*average distance of synthetic CAS [Å] [2]*
Ca	Ca	1.816(3)	11.8945	2.6723	*2.671*
M1	Si1 (2/3)	3.513(7)	5.9876	1.8325	*1.833*
	Al1 (1/3)	3.61(1)			
M2	Al2	2.956(6)	5.6976	1.9159	*1.918*
T	Al3 (1/2)	3.15(2)	3.8164	1.7456	*1.724*

[1]BVS - Bond Valence Sum; [2] ECON - Effective Coordination Number.

566 **Table. 5 │ Analytical conditions for donwilhelmsite.**

Data collection	
Radiation type	electrons, 120 kV
Wavelength [Å]	0.0335
Precession angle φ [°]	1.0
Illuminated area diameter [nm]	1 000
Resolution [Å]	0.7150
No of recorded frames	101
Completeness	100
No. of refined reflections - all/observed [I > 3σ(I)]	3 639/2 574
Dynamical structure refinement	
g^{max} [Å^{-1}], S_g^{max} (matrix), S_g^{max} (refine), R_{Sg}, N$_{or}$	1.6, 0.01, 0.1, 0.4, 128
R1(F), wR(F), GOF - (obs/all) [%]	8.95/11.91, 10.00/10.12, 4.77/4.06
No. of refined parameters	127

567 ^{a} $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; ^{b} $wR = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; ^{c} $GOF = [\Sigma w(F_o^2-F_c^2)^2/\Sigma$
568 $w(F_o^2)^2]^{1/2}$

569

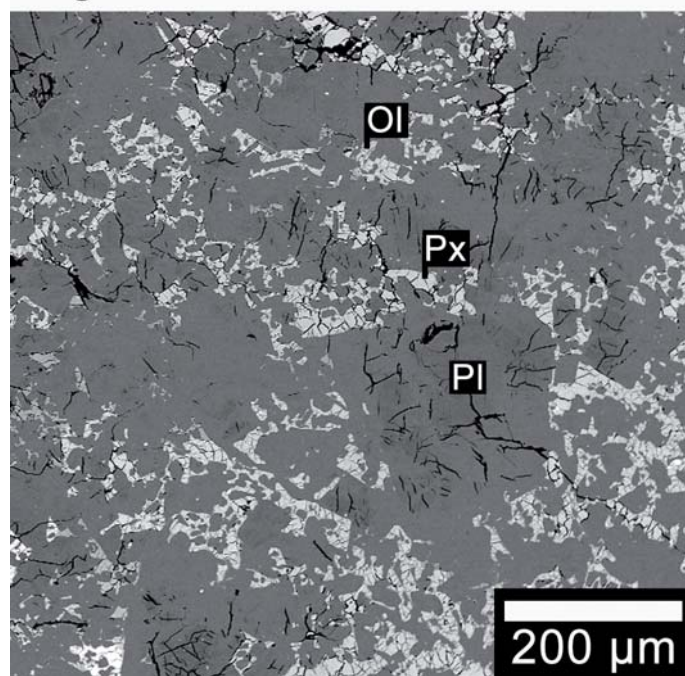570

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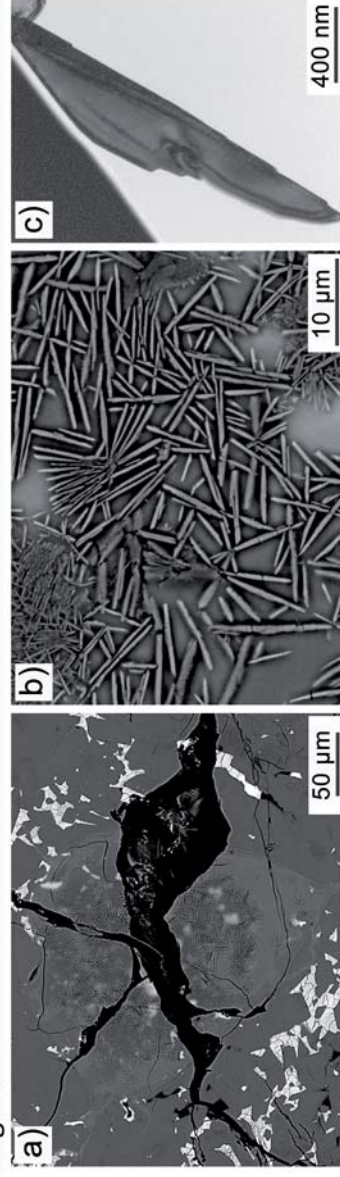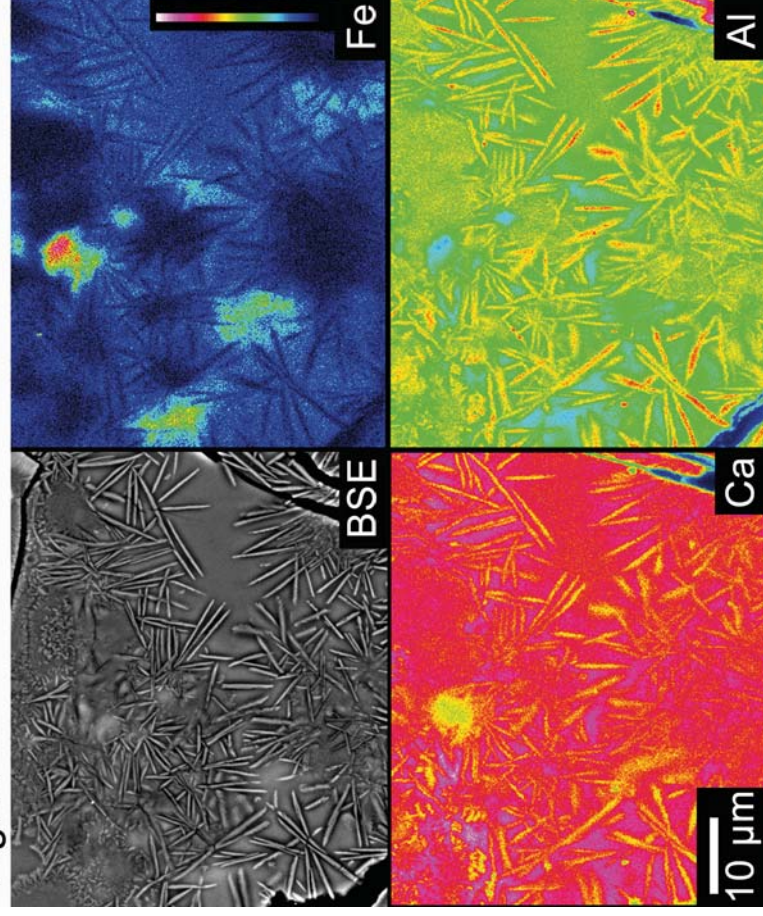
Fig. 1

Ol

Px

Pl

200 μm

Fig. 2

a)

50 µm

b)

10 µm

c)

400 nm

Fig. 3

Fig. 4

Fig. 5

a) h0l 001 100

b) 2̄hl 001 2̄10

c) hk0 010 100

Fig. 6