Caleta el Cobre 022 martian meteorite: increasing nakhlite diversity

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Abstract

Caleta el Cobre (CeC) 022 is a martian meteorite of the nakhlite group, showing an unbrecciated cumulate texture, composed mainly of clinopyroxene and olivine. Augite shows irregular core zoning, euhedral rims and thin overgrowths enriched in Fe relative to the core. Low-Ca pyroxene is found adjacent to olivine. Phenocrysts of Fe-Ti oxides are titanomagnetite with exsolutions of ilmenite/ulvöspinel. Intercumulus material consists of both coarse plagioclase and fine-grained mesostasis, comprising K-feldspars, pyroxene, apatite, ilmenite, Fe-Ti oxides and silica. CeC 022 shows a high proportion of martian aqueous alteration products (iddingsite) in olivine (45.1 vol% of olivine) and mesostasis. This meteorite is the youngest nakhlite with a distinct Sm/Nd crystallization age of 1.215±0.067 Ga. Its ejection age of 11.8±1.8 Ma is similar to other nakhlites. CeC 022 reveals contrasted cooling rates with similarities with faster-cooled nakhlites, such as Northwest Africa (NWA) 817, NWA 5790 or Miller Range (MIL) 03346 nakhlites: augite irregular cores, Fe-rich overgrowths, fine-grained K-feldspars, quenched oxides and high rare earth element content. CeC 022 also shares similarities with slower-cooled nakhlites, including Nakhla and NWA 10153: pyroxene modal abundance, pyroxenes crystal size distribution, average pyroxene size, phenocryst mineral compositions, unzoned olivine and abundant coarse plagioclase. Moreover, CeC 022 is the most magnetic nakhlite and represents an analogue source lithology for the strong magnetization of the martian crust. With its particular features, CeC 022 must originate from a previously unsampled sill or flow in the same volcanic system as the other nakhlites, increasing martian sample diversity and our knowledge of nakhlites.

1. Introduction

Nakhlites constitute a meteorite group originating from Mars (McSween 1985; Treiman et al. 2000). To date, the group comprises 21 meteorites: 10 from Northwest Africa (NWA) including the recently approved NWA 12542, 7 from Antarctica, 1 fall (Nakhla) and 2 other finds from various provenances, with the addition of Caleta el Cobre (CeC) 022. After pairing this number is reduced to 12 meteorites (Udry et al., 2012; Udry and Day, 2018; Meteorite Bulletin Database, https://www.lpi.usra.edu/meteor/). Nakhlites all share broadly similar textures, whole-rock compositions and mineralogy. In addition, they all present a crystallization age within the same range from 1.26 to 1.42 Ga, consistent over four different dating techniques $^{87}Rb/^{86}Sr$, $^{147}Sm/^{144}Nd$, $^{39}Ar/^{40}Ar$ and $^{176}Lu/^{176}Hf$ (from data compilation of Nyquist et al., 2001, Shih et al., 2010, Korochantseva et al., 2011, Cohen et al., 2017, and Udry and Day 2018). Lastly, cosmogenic isotopes yield an exposure age of 9 to 13 Ma, which indicates a single ejection event, strengthening their genetic relationship (Herzog and Caffee, 2013, Nyquist et al. 2001, Wieler et al., 2016, Cohen et al., 2017).

Nakhlites are clinopyroxene-rich cumulates, composed mainly of euhedral clinopyroxene and less abundant olivine. The intercumulus materials consist either of coarse plagioclase, or a fine-grained mesostasis composed of various amounts of fayalite, feldspar, low-Ca pyroxene, titanomagnetite, sulfide, silica and apatite (e.g., Treiman, 2005). Post-eruption alteration phases have also been reported in those meteorites, such as iddingsite which is described as a hydrous iron-magnesium silicate (Bunch and Reid 1975; Bridges and Grady 2000; Treiman and Irving, 2008; Hallis and Taylor, 2011; Lee et al., 2018), as clay minerals referred to as serpentine (Irving et al., 2002) or smectite (Treiman et al., 1993; Gillet et al., 2002), or as jarosite (Noguchi et al., 2009). These secondary phases formed through hydrothermal alteration on Mars (Changela and

64   Bridges 2010) and have been tentatively dated around 633±23 Ma with K-Ar system (Borg and

65   Drake, 2005 and references therein).

66   The formation of the nakhlites started with low-degree partial melting of a long-lived, trace

67   element depleted source that occurred at around 1.34 Ga (McCubbin et al., 2013). The cumulus

68   part of the nakhlites with coarse subhedral crystals suggests slow growth over a long period of time

69   (Lentz et al., 1999) at low pressure in a shallow magma chamber (Day et al. 2006). In contrast, the

70   intercumulus material is composed either of fine-grained mesostasis attesting a relatively fast

71   cooling, or coarse plagioclase crystallized under lower cooling rates. Indeed, nakhlites final cooling

72   would have taken place at the martian surface over short periods of time from 5 to 184 days (Day

73   et al., 2006; Udry and Day, 2018), with cooling rates from 1 to 6°C/hr based on zoning in olivine

74   (Sautter et al., 2002) and intercumulus crystals surface area to volume (Hammer and Rutherford

75   2005). After emplacement as sill or flow, crystal gravitational settling and compaction, as well as

76   dynamical sorting of a phenocryst-rich magmatic mush (Corrigan et al., 2015; Day et al., 2006)

77   and flow dynamics (Daly et al., 2019) have shaped the final texture of nakhlites, based on

78   petrographic textural evidence.

79   The comparable crystallization ages and ejection ages of nakhlites led to the hypothesis of

80   a suite of igneous rocks originating from a single martian volcanic system. The most widely

81   accepted model for the petrogenesis of nakhlites is that the cumulus phases crystallized at depth

82   followed by emplacement at the surface as a flow or shallow subsurface sill (Bunch and Reid 1975;

83   Treiman 1986; Lentz et al., 1999; Mikouchi et al., 2003; Day et al., 2006; Mikouchi et al., 2012,

84   2017; Richter et al., 2016; Udry and Day, 2018). All previously studied nakhlites present slight

85   differences in their modal abundances, intercumulus material and minor minerals, mineral

86   chemistry, crystallinity, rare earth element (REE) enrichment and Ar-Ar ages, which led to various

87   models of emplacement. Based on differences in mineralogy and textures, a stratigraphy of

88   nakhlites within a single cumulate pile was first proposed (Treiman, 1986; Mikouchi et al., 2003,

89   2012; Treiman, 2005; Bridges and Warren, 2006; Day et al., 2006; McCubbin et al., 2013; Corrigan

90   et al., 2015). Based on textural and chemical compositional differences among the various

91   nakhlites, Jambon et al. (2016) proposed nakhlite emplacement in at least three different flows

92   piled on top of one another from Miller range (MIL) 03346 at the uppermost part of the pile, down

93   to Northwest Africa (NWA) 5790. Based on geochemistry and petrography, Balta et al. (2017)

94   proposed another model with one body chamber and two separated lobes. Cohen et al. (2017)

95   proposed a model of multiple flows using geochronological evidences supporting a layered

96   volcanic sequence with at least four discrete eruptive events. Recently, Udry and Day (2018)

97   proposed in a comprehensive study that nakhlites originated from at least six different lava flows

98   or sills, distributed around one or several volcano vents.

99   Caleta el Cobre 022 was approved by the Meteoritical Society Nomenclature Committee in

100 April 2018. It is the 11th unpaired nakhlite (the only one from Atacama Desert) and brings new

101 information to help constrain the diversity, stratigraphy and emplacement conditions of the nakhlite

102 group. This paper is focused on the description of this new nakhlite (petrology, mineralogy and

103 geochemistry) and its comparison with previously studied nakhlites. We observe that CeC 022

104 combines evidence for both high and low cooling rates, with features never observed in other

105 nakhlites. This will open discussion on the crystallization conditions of cumulus minerals, the

106 crystallization sequence and the relation of CeC 022 with the other nakhlites.

107 **2. Analytical Methods**

108   Petrographic observation and elemental micro-analyses were performed on three thick polished

109 sections (referred as A, B and D in the following) and one thin section (C).

2.1. Modal abundances

Modal abundances of major crystals were measured on all sections using hand-drawn grain boundaries in *Adobe Illustrator* (see section 2.1.2.) and pixel counting using the *ImageJ* software. The modal abundances of minor phases were measured using composite elemental maps obtained by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectrometry (EDS) and using pixel counting with the *ImageJ* software. The average modal abundance of CeC 022 is calculated from the 4 sections, all showing similar surface sizes of about 1.5 cm². The total surface analyzed in the 4 sections is 7.1 cm². All phases were characterized using a Leica DM2500P petrographic microscope. An Olympus BH_2 microscope operating in reflected light was used to first characterize Fe-Ni-Cu sulfides. The abundance of sulfides was determined on section B by point counting (2000 points, 50 µm step).

2.2. Quantitative textural analyses

Crystal Size Distribution (CSD) is a quantitative tool defining kinetic textures of a specific mineral crystal population and provides a plot representing the relationship between the natural logarithm of the population density and crystal size (Cashman and Marsh, 1988; Marsh 1988, 1998). Spatial distribution pattern (SDP) analyses investigate ordering and framework of a crystal population and constrain processes of rock formation, such as compaction, flow settling and grain orientation. Spatial distribution pattern analyses are based on both R-value and the porosity or melt content of the thin section, corresponding to the inverse of pyroxene content in the thin section (Jerram et al. 1996, 2003). The R-value is defined- as: $R = 2\sqrt{\rho}\,\Sigma r/N$, where ρ is the observed population density, r is the distance between the center of a crystal and the center of its nearest neighboring crystal and N is the total number of crystals measured (Jerram et al. 1996, 2003). The R-value represents the ratio of the observed versus predicted mean distribution of nearest neighbor

133   distances using the density of the observed distribution. The CSD and SDP analyses were

134   conducted for the pyroxene population of the thin section (C). Pyroxene grains were hand-drawn

135   in *Adobe Illustrator* using mosaic pictures in transmitted and reflected light, X-ray elemental maps

136   and an optical microscope to distinguish grain boundaries. We used the *ImageJ* software to obtain

137   the area of each crystal, the total area of the section, the major and minor axes of ellipses, as well

138   as the centroid location. We followed the same quantitative textural methods as the one described

139   in Udry and Day (2018).

140 **2.3.   Physical properties**

141   Grain density was measured with a Quantachrome helium steropycnometer at Centre Européen

142   de Recherche et d'Enseignement en Géosciences de l'Environnement (CEREGE). Magnetic

143   susceptibility was quantified with MFK1 or KLY2 instruments depending on sample size. Curie

144   temperatures were estimated by measuring the variation of susceptibility with temperature with a

145   CS3 furnace on the MFK1 susceptibility meter. Saturation magnetization was determined with a

146   Princeton model 2900 Micromag vibrating sample magnetometer. All magnetic measurements

147   were performed at CEREGE.

148 **2.4.   Mineral major and minor elements**

149   Backscattered electron (BSE) images, microanalyses by energy dispersive spectroscopy (EDS)

150   and chemical maps were acquired with a Hitachi S3000-N SEM operated at 15 kV and equipped

151   with a Bruker X-ray X-Flash detector and a Spirit analyzer at CEREGE, France. Semi-quantitative

152   analyses used a variety of natural and synthetic standards. Additional field emission gun (FEG)

153   SEM images were obtained on a ZEISS Gemini 500 SEM operated at accelerating voltages from

154   5 to 15 kV at Centre Pluridisciplinaire de Microscopie Electronique et de Microanalyse (CP2M),

155   Marseille. Compositions of sulfides were assessed at the National Museum of Natural History

156   MNHN (Paris) using a Tescan VEGA II LSU SEM operated at 15kV and equipped with an SD3

157   (Bruker) EDS detector.

158   Quantitative major element analyses were conducted using an electron microprobe (EMP)

159   Cameca SX100 at UPMC CAMPARIS facility. The operating conditions were 15 kV accelerating

160   voltage with a current of 10 nA and a counting time of 30 s, with a focused beam (1 µm) for

161   pyroxene, olivine, plagioclase and apatite, and defocused beam (5 µm) for fine-grained mesostasis

162   and alteration phases. Both natural and synthetic standards were used for calibration: albite for Na;

163   anorthite for Al; apatite for P; diopside for Mg, Si, Ca; orthoclase for K; pyrite for S; $MnTiO_3$ for

164   Mn and Ti; Cr_2O_3 for Cr; Fe_2O_3 for Fe; and NiO for Ni. The detection limits are (in ppm): 445 for

165   Na, 466 for Al, 714 for Mg, 669 for Si, 605 for Ca, 602 for K, 392 for S, 1044 for Mn, 419 for Ti,

166   496 for Cr, 1271 for Fe, and 1331 for Ni.

167   Sulfide microphases were analyzed at 15 kV accelerating voltage by a PhiRhoZ EDS

168   standardless procedure. Accuracy of our SEM analytical procedure analyses was checked by

169   repeated analysis of a Del Norte County-DNC (Oregon, USA) natural troilite (stoichiometric FeS),

170   a well-known terrestrial troilite occurrence previously studied by X-ray diffraction and repeatedly

171   analyzed by EMPA and SEM (Chevrier et al., 2011, Lorand et al. 2012, Gattaceca et al., 2013).

172   Gattacceca et al. (2013) shown that the SEM analyses of DNC troilite perfectly match the

173   composition of stoichiometric troilite (FeS). Our own analyses yielded a mean atomic Fe+Ni/S

174   ratios (metal-to-sulfur ratios) of 1.0 ± 0.01 (Figure S2). DNC troïlite was used as external

175   calibration standard and analyzed every 10 to 15 analyses to evaluate potential drifts on metal-to-

176   sulfur ratios of CeC 022 pyrrhotites.

2.5. Major and trace elements bulk analyses

From 200 mg of powdered sample of CeC 022 using an agate mortar, ~50 mg was digested with a 4:1 mixture of lithium metaborate and tetraborate. After heating in a graphite crucible for 10 minutes at 1000°C, the bead was dissolved in 5% HNO_3. After dilution, to control possible instrumental drift, the solution was doped with In for trace elements measurements using an Agilent 7700 inductively coupled plasma mass spectrometry (ICP-MS) and Y for major elements measurements using a Thermoscientific iCA inductively coupled plasma optical emission spectroscopy (ICP-OES) at Laboratoire G-Time (Université Libre de Bruxelle-ULB). In both cases, the calibration curves were obtained on synthetic standards and reproducibility was checked using USGS standard (BHVO-2). For major elements, the relative standard deviation (RSD) is systematically better than 2% (except Na, 5 %), while for trace elements, it is better than 10%, expect for Lu (46%) and U (33%).

2.6. Noble Gases

All noble gas isotopes of He to Xe were extracted in one step and measured at ETH Zurich in a 50.9 mg sample by fusion at ~1700 °C in a Mo crucible according to the established procedures detailed by Riebe et al. (2017). Blank corrections are for ^{3}He, ^{4}He, ^{21}Ne, ^{22}Ne < 0.4 %, for ^{20}Ne, ^{36}Ar, ^{38}Ar, ^{40}Ar, ^{84}Kr and ^{132}Xe 3.3 %, 13 %, 2.1 %, 2.5 %, 8 % and 1.8 %, respectively.

2.7. Isotopic measurements

Mineral separation was carried out at Laboratoire G-Time at Université Libre de Bruxelles. The sample has been crushed and sieved. A first separation using the 150-250 µm fraction was made using dense liquid (methyliodine) and a second one using a Frantz magnetic separator. The different fractions were then crushed and dissolved in a 1/3 mixture of sub-boiled concentrated HF and HNO_3 and left 2 days on hot plate at 120°C using high-pressure vessels. After drying, the

200   fractions were re-dissolved using 12N HCl until the solutions were clear. A 5% aliquot was

201   removed from the initial dissolution and spiked using ^{150}Sm-^{148}Nd spike. REE were first purified

202   using cationic resin, being collected in HCl 6N. For both spiked and unspiked cuts, the REE were

203   further separated using HDEHP resin by increasing the HCl molarity for collecting Nd and spiked

204   Sm. The whole rock fraction was further purified for ^{142}Nd measurements. First, Ce was removed

205   by using HDEHP resin after oxidation of Ce using $NaBrO_3$. The added Na was then cleaned out

206   using cationic resin, similarly to the first purification step. All fractions but the whole rock one,

207   spiked and unspiked, were measured on the HR-MC-ICP-MS Nu-Plasma 2 using an Aridus

208   dessolvator, using 0.05N HNO_3. Spike deconvolution was performed off-line by iteration as

209   described in Debaille et al. (2007). The unspiked fraction were corrected for a Rennes standard

210   value of ^{143}Nd/^{144}Nd of 0.511961 (Chauvel and Blichert-Toft, 2001). Total reproducibility

211   including standards ran at 20 and 5 ppb (n=24) is better than 50 ppm (2σ). The whole rock fraction

212   was measured on the Thermoscientific Triton Plus at ULB in multidynamic mode as in Debaille et

213   al. (2007). The Rennes standard (n=3) gave a value of 0.511957 ± 0.000002 and no correction was

214   required for comparison with the data set measured on the MC-ICP-MS.

215   Oxygen isotopes were measured at the Stable Isotopes Laboratory of CEREGE. Molecular

216   oxygen was extracted using laser fluorination. Aliquots of 1.5 mg obtained from a bulk 12 mg

217   powdered samples were heated with a 30 W CO_2 IR laser in the presence of 100 hPa of BrF_5. The

218   released gas was purified through two cryogenic nitrogen traps and one heated KBr trap. Molecular

219   oxygen was trapped for 10 mn in a molecular sieve cooled at -196°C. The gas was then expanded

220   at 100°C and passed through a molecular sieve cooled at -114°C slush for 5 mn to refreeze possible

221   interfering gases. The gas was then trapped again for 5 mn in the molecular sieve cooled at -196°C,

222   then expanded again at 100°C directly into the bellow of a dual-inlet Thermo-Finnigan Delta Plus

223   mass spectrometer.

224   The isotopic compositions are expressed in standard δ-notation, relative to Vienna standard

225   mean ocean water (VSMOW): $\delta^{18}O = (^{18}O/^{16}O)_{sample} / (^{18}O/^{16}O)_{VSMOW}$ - 1 and $\delta^{17}O = (^{17}O/^{16}O)_{sample}$

226    $/ (^{17}O/^{16}O)_{VSMOW}$ - 1 (expressed in ‰), $\Delta^{17}O$, also expressed in ‰, is defined as $\delta^{17}O - \lambda \times 0.5247$

227    $\delta^{18}O$. For comparison with previous data obtained on Martian meteorites (Franchi et al. 1999), we

228   use $\lambda = 0.52$. Measured $\delta^{18}O$ and $\delta^{17}O$ values of the samples were corrected daily using the

229   laboratory quartz standard itself calibrated against the international standard NBS28 ($\delta^{18}O = 9.60$

230   ‰, $\delta^{17}O = 0.52 \times \delta^{18}O = 4.992$ ‰). Reproducibility (1 sigma) of the quartz laboratory standard are

231   0.119‰ for $\delta^{18}O$, 0.061‰ for $\delta^{17}O$, and 0.024‰ for $\Delta^{17}O$ (n = 63) with a $\Delta^{17}O$ of -0.015 ± 0.024‰.

232   **2.8.   Secondary alteration phases analyses**

233   Infrared (IR) spectroscopy was performed at the Institut de Planétologie et d'Astrophysique

234   de Grenoble (IPAG) using the SHADOWS instrument (Potin et al., 2018). The instrument was

235   used in normal standard mode as well as in a µ-beam mode enabling measurements of IR

236   reflectance spectra of areas of the order of 3 mm². Spectra were measured under nadir incidence

237   and with an observation angle of 30°. Spectra were normalized to infragold™ and spectralon™.

238   The Raman experiments were performed at Laboratoire de Géologie de Lyon (ENS Lyon – France)

239   using a Labram HR800 spectrometer equipped with a Nd ion laser providing 532 nm excitation.

240   The laser spot is <2µm with the used x100 microscope objective. Individual spectra were acquired

241   at various locations in veins of iddingsite, optically localized throughout the sections A and B of

242   CeC 022.

243   **3. Results**

3.1. General description and physical properties

Caleta el Cobre 022 was found casually by tourists traveling in the Atacama Desert, Chile, in November 2016, lying at the surface in the CeC dense collection area, which is part of the densest meteorite collection area in hot deserts (Hutzler et al. 2016). It is a single stone, almost fully crusted. The fusion crust has a few cracks and the typical glassy gloss of achondrites and was identified as such by R. Martinez from the Museo del Meteorito in San Pedro de Atacama (Chile), when he observed the stone a few days after the find. The type specimen of 21g was cut from the main mass of 450 g at the Museo del Meteorito and later given to CEREGE, where the classification was done. Cut face reveals a dark interior with a few fractures penetrating the whole stone. Pinkish-orange mm-sized minerals (altered olivine) are visible over a dark green background (Fig. 1).

Grain density, measured on a 15.42 g sample, is 3.342 ± 0.002 g/cm^3. Magnetic susceptibility, measured on 8 samples ranging from 19.7 mg to 340 g, is homogeneous over this size range with a coefficient of variation of 3.4% and an average mass weighed value of 8.41 10^{-6} m^3/kg. Saturation magnetization is 1.51 Am^2/kg. Saturation remanent magnetization is 4.59 10^{-1} Am^2/kg. Two Curie temperatures are observed at 525°C and 585°C (Fig. S1).

3.2. Petrography

The meteorite shows an unbrecciated cumulate texture with euhedral elongated augite crystals (56.5 vol%) and a lower amount of olivine (4.2 vol%), set in an intercumulus made of coarse plagioclase (19.4 vol%) and fine-grained mesostasis (15.9 vol%).

3.2.1. Phenocrysts

264 *Pyroxene*

265   Clinopyroxene is the major mineral with 52.3-60.3 vol% (average 56.5 vol% among four

266 sections) (Table 1) and measure on average 0.27 mm (up to 2 mm). On BSE images, they present

267 an irregular zoning with rounded cores and a Fe-rich euhedral rim (Fig. 2), surrounded by a thin,

268 sharply delimited Fe-enriched overgrowth, when in contact with the mesostasis. The zoning can be

269 discontinuous or gradual, depending on the orientation of the grains. The sharp overgrowth, usually

270 10-15 µm wide, gets thinner or absent when in contact with other phenocrysts (pyroxene,

271 plagioclase, titanomagnetite, or olivine). Some rounded clinopyroxene (~100 µm) can be found

272 included inside olivine crystals. Also, smaller clinopyroxene (~10 µm) with Fe-oxides are found

273 in linear planes of inclusions, or exsolutions, in the olivine (Fig. 3). Low-Ca pyroxenes (up to 100

274 µm, Fig. 2) were frequently observed adjacent to olivine crystals, sometimes presenting augite

275 irregular cores. Based on grain boundary geometries, low-Ca pyroxene appears to have crystallized

276 after augite rim and olivine.

277 *Olivine*

278   Olivine crystals represent 2.0-8.9 vol% (average 4.2 vol% among four sections) with a

279 maximum measured grain size of 2.5 mm and an average length of 0.66 mm (Table 1). They do

280 not display a euhedral shape, rather a resorbed border. They do not show any zoning on BSE images

281 (Fig. 4). They display large melt inclusions up to 100 µm, rich in Na-K feldspars and apatite.

282 Olivine crystals present high abundance (45.1 vol%) of aqueous alteration products (iddingsite)

283 found in crosscutting veins and sometimes extending to the edge of the olivine and the mesostasis

284 around the olivine. These secondary alteration products are described in more details in part 3.4.

Plagioclase

Caleta el Cobre 022 contains coarse plagioclase with a maximum measured grain size of 1 mm, representing in average 19.4 vol% (17.1-24.2 vol% among three sections) of the meteorite (Table 1). The association of augite cumulate crystals with coarse plagioclase forms a doleritic texture.

Opaque minerals

Intergranular Fe-Ti oxides are abundant (2.6 vol% among three sections) (Table 1) and up to 1 mm size. On BSE images, they show fine-scale (0.5 µm wide) Fe-Ti oxides (ilmenite or ulvöspinel) exsolutions in what appears to be titano-magnetite (Fig. 5, right). At higher resolution (FEG-SEM), finer nanometric (~1-3 nm) exsolutions can be observed in between these micron sized Fe-Ti oxides exsolutions (Fig. 5, left). These oxides phenocrysts show inclusions of augite as well as melt inclusions.

Caleta el Cobre 022 is sulfide-rich (0.15 ± 0.05 vol.%), with sulfides mostly under the form of pyrrhotite. Those intercumulus pyrrhotites are frequently associated with magnetite without ilmenite exsolution. A continuum of textural associations between pyrrhotite and magnetite was observed such as discontinuous or continuous magnetite rims on pyrrhotite (Fig. 6A-B), residual pyrrhotite inclusions in coarse granular magnetite (Fig. 6B), and rounded inclusions of magnetite inside the pyrrhotite coexisting with coarser magnetite grains (Fig. 6C). Plagioclase- or clinopyroxene-hosted pyrrhotite are free from magnetite. Chalcopyrite was observed in only three grains as marginal blebs (Fig. 6D). Pentlandite flames inside pyrrhotite are very scarce.

3.2.2. Mesostasis

Mesostasis in CeC 022 represents on average 15.9 vol% (12.7-16.0 vol% among three sections) of the meteorite (Table 1). Mesostasis pockets contain mainly K-feldspar, silica, dendritic

308 Ti-magnetite, low-Ca pyroxene, apatite and ilmenite. Most oxides in the mesostasis are skeletal Ti-

309 magnetite. Apatite is mainly found as small elongated euhedral crystals embedded in the feldspar.

310 Adjacent to the olivine grains, apatite displays larger sizes (up to 700 µm long) in association with

311 pigeonite rims (Fig. 7). Fine-grained pyrrhotite is hosted in the microcrystalline mesostasis, along

312 with skeletal Ti-magnetite.

3.2.3. Terrestrial weathering

314 Terrestrial weathering is minimal on CeC 022. The meteorite shows a fresh black fusion

315 crust with few alteration products (Fig. 1). Caleta el Cobre 022 is a highly fractured rock (Fig. 1,

316 Fig. 3, Fig. 4). On BSE images, we observed that those fractures are devoid of terrestrial alteration

317 products (e.g., Fig. 1, Fig. 3, Fig. 4), such as evaporite minerals that are classically encountered in

318 meteorites weathered in hot deserts (Bland et al. 2006). Terrestrial weathering is observed only

319 close to the fusion crust and is minimal. It is found as partly altered sulfides and pyrrhotite cracks

320 invaded by iron oxyhydroxides.

3.3.   Quantitative textural analyses

322 We measured a total of 2103 pyroxene grains and obtained a R^2 of 0.88 (Table S1.). Caleta

323 el Cobre 022 pyroxene population displays a best habit ratio of 1.00:1.25:1.80 and shows a CSD

324 slope of -5.31 ± 0.09 mm^{-1}, with an intercept of 6.04 ± 0.05 (Fig. 8). A downturn for the smaller

325 sizes (<0.03 mm) is observed. Spatial distribution analyses show that the pyroxene population of

326 CeC 022 has an R-value of 1.277 and falls within the cluster touching framework, similar to the

327 other nakhlites (Fig. S3, Table S1).

3.4.   Geochemistry

3.4.1. Phenocrysts

330   *Pyroxenes*

331   Electron microprobe analyses reveal augite cores range in composition from $En_{32}Fs_{30}Wo_{38}$

332   to $En_{36}Fs_{24}Wo_{40}$ (average $En_{33}Fs_{27}Wo_{40}$) and FeO/MnO = 35-45 with Mg# [=100 x (Mg/(Fe^{2+} +

333   Mg))] = 55 (Table 2, Fig. 9). They are surrounded by augite richer in Fe of average composition

334    $En_{31}Fs_{29}Wo_{40}$ (Mg# ~ 52). Microprobe traverse analyses across augite crystal reveal that Al, Ti and

335   Mn anticorrelate with Mg#. In contrast, Ca and Cr show a correlation with Mg#, increasing from

336   the rim to the core of the augite, and Na shows no variation throughout the crystal. Augite crystals

337   have relative low Al, Ti and Na concentration (Al_2O_3 = 1.1 ± 0.1 wt%; TiO_2 = 0.4 ± 0.1 wt%; Na_2O

338   = 0.3 ± 0.1 wt%), comparable to terrestrial pyroxene crystallized at low pressure (Harvey and

339   McSween, 1992). The thin overgrowth around the augite rim shows Fe-rich compositions going

340   up to $En_{30}Fs_{31}Wo_{39}$ (Mg# of ~49). This overgrowth is also more enriched in MnO (up to 0.6 wt%),

341   Al_2O_3 (up to 1.5 wt%) and TiO_2 (up to 0.6 wt%), but poorer in Na and Ca. In the olivine, planes of

342   inclusions contain Fe-oxides and augites of composition $En_{31}Fs_{26}Wo_{43}$, similar to cumulus augite

343   irregular cores (Fig. 3).

344   Low-Ca pyroxenes differ from augite by their texture as well as their composition. They

345   are found adjacent to olivine crystals (Fig. 2, Fig. 7). Their augite core compositions are similar to

346   those previously described, but the low-Ca pyroxene overgrowth around the cores has a

347   composition of $En_{36}Fs_{60}Wo_4$ (Fe/Mn = 28; Mg# 38) (Table 2, Fig. 9). The low-Ca overgrowths

348   show an enrichment in Fe, Mn and Mg and lower Ti, Al and Na, compared to the augite pyroxene.

349   *Olivine*

350   Olivine compositions show no zoning, with an average composition of $Fo_{30.3}$ (FeO/MnO =

351   49 ± 3) and minor intragrain variations of $Fo_{27.3}$ to $Fo_{32.5}$ (Table 3, Fig. 10).

Plagioclase

The coarse plagioclase grains found in the meteorite have a homogenous composition of $An_{29.7\pm4.3}Ab_{67.2\pm4.0}Or_{3.1\pm0.5}$ (Fig. 11).

3.4.2. Mesostasis

Mesostasis in CeC 022 is dominated by K-feldspar (Fig. 11) with compositions in the range $An_{6.7}Ab_{84.6}Or_{8.7}$ to $An_{4.5}Ab_{60.4}Or_{35.1}$. Also, some low-Ca pyroxene can be found in the mesostasis with compositions of $En_{31}Fs_{65}Wo_4$ (Fe/Mn = 30) (Table 2). These compositions are similar to the ones of low-Ca pyroxenes rims found next to olivine crystals. Apatite is also observed in the mesostasis with Cl-rich compositions (Table S2).

3.4.3. Bulk rock geochemistry

Major elements in CeC 022 are reported in Table 4, together with other nakhlites. It has a high bulk Mg# of 53.8, with a low FeO/MnO of 38.0 (Table 4). Compared to the other nakhlites, the bulk composition of CeC 022 has low CaO contents (12.8 wt%) but high MgO and Al_2O_3 (12.2 wt% and 3.32 wt% respectively). Sodium and potassium content are low (1.13 wt% and 0.25 wt%).

Rare earth element compositions are reported in Table 4 and Fig. 13 and similar to other nakhlites. Conversely an enrichment in Ce was measured in CeC 022 that is not described in other nakhlites. Bulk $(La/Lu)_{CI}$ is 4.4, within the range of nakhlites (Udry and Day, 2018).

3.4.4. Oxygen isotopes

Analyses of three 1.5 mg aliquots gave $\delta^{18}O$ = 4.683‰ ± 0.428‰, $\delta^{17}O$ = 2.683‰ ± 0.210‰, and $\Delta^{17}O$ = 0.248 ± 0.013‰ (mean ± 1σ).

3.5. Alteration products

3.5.1. Petrography

374   The main martian alteration products in CeC 022 occur in olivine phenocrysts as a reddish-

375   orange phase in optical microscopy in transmitted light. This material is found mainly as veins

376   along cracks in the olivine with Fe-oxides and sulfides situated at the center of the veins, but it can

377   also be located as patches in the mesostasis. This alteration product has already been described in

378   nakhlites under various names such as iddingsite, smectite, illite, saponite, siderite, sulfates (Bunch

379   et al., 1975; Reid and Bunch, 1975; Boctor et al., 1976; Gooding et al. 1991; Gooding, 1992;

380   Treiman et al., 1993; Bridges et al., 2000; Gillet et al. 2002). Caleta el Cobre 022 contains a high

381   abundance of iddingsite, replacing 45.1 vol% of the crystals, found mainly in crosscutting veins

382   inside olivine. A noteworthy feature of CeC 022 is the occurrence of pyrrhotite and Fe-oxides

383   clusters or stringers inside iddingsite veins across olivine (Fig. 4, Fig. 6, Fig. 14). Also, a few

384   deeply altered former sulfides were observed in the vicinity of olivine grains, coexisting with

385   iddingsite aggregates. Such ovoid grains are made from highly porous iron oxyhydroxides-like

386   phases showing detectable amount of sulfur (EDS spectra) (Fig. 6F).

387   Backscattered electron images reveal two types of iddingsite found in association with each

388   other (Fig. 14). Energy dispersive spectrometry (EDS) and EMP analyses show that a brighter type

389   of iddingsite in contact with olivine in the BSE image is enriched in Fe and Mn (~52 wt% FeO)

390   and is poorer in Si (~27 wt% SiO_2), Mg and K, compared to the darker type (~30 wt% FeO and

391   ~50 wt% SiO_2) (Table 5). Low totals (<90 wt%) of the EMP analyses suggest that these phases are

392   hydrated. The Fe-rich type of iddingsite has a Raman spectrum exhibiting well defined and narrow

393   bands in contrast to the spectrum related to the Si-rich type. The Fe-rich iddingsite is also

394   associated, at the micron scale, with a few oxides, possibly hematite or magnetite and possibly

395   carbonates or pyroxene (Fig. S4, right). The wide and poorly defined Raman bands exhibited by

396   the Si-rich iddingsite reflect a degree of crystallization lower than in Fe-rich type (Fig. S4, right).

397   Raman spectroscopy reveals that the Si-rich type of iddingsite is a poorly crystallized hydrated

398   assemblage of minerals (Fig. S4, right). Both Raman and IR (Fig. S4) spectroscopy show weak

399   bands of carbonate and/or phyllosilicate and H_2O bending and H_2O + OH stretching modes,

400   evidencing the hydration of these alteration products. Raman spectra show that each type of

401   iddingsite is homogenous throughout the sample, independent of the location in the meteorite.

402   **3.6.**   **Geochronology**

403   **3.6.1. Sm-Nd systematics and crystallization age**

404   The crystallization age of CeC 022 has been measured at 1215 ± 67 Ma using a Sm-Nd

405   isochron using the Isoplot software (MSWD of 1.2). The initial $^{143}Nd/^{144}N$ using Isoplot is

406   0.511600 ± 0.000069 (Table S3). Expressed in 10^4 deviation to the chondritic average, this

407   corresponds to an $\varepsilon^{143}Nd(i)$ of +10.4 ± 1.4, similar to the $\varepsilon^{143}Nd(i)$ measured on the bulk rock

408   fraction, of +10.5 ± 0.1. Concerning the ^{142}Nd systematics, expressed in 10^6 deviation to the

409   average modern Earth, the $\mu^{142}Nd$ of CeC 022 is equal to +56 ± 3.

410   **3.6.2. Ejection age**

411   Results of the noble gas measurements are given in Table S4. The measured He and Ne

412   isotope ratios indicate that there is no trapped component in He and Ne. Hence, the measured ^3He,

413   ^{21}Ne and $^{21}Ne/^{22}Ne$ are entirely cosmogenic. The (inverse) shielding indicator $(^{21}Ne/^{22}Ne)_{cosm}$ of

414   0.831 ± 0.06 is low. This value suggests low shielding in a small meteoroid, which is often observed

415   for rare meteorites, particularly martian ones (Wieler et al. 2016). Also, the presence of some solar

416   cosmic ray (SCR)-derived Ne cannot be excluded (Wieler et al. 2016). However, using the Mg /

417   (Al + Si) vs. $^{21}Ne/^{22}Ne$ diagram (Wieler et al., 2016), SCR-Ne is most likely not predominant.

418   Nevertheless SCR-Ne could still cause some overestimation of the Cosmic Ray Exposure (CRE)

419   ages and underestimation of shielding. The $^{36}Ar/^{38}Ar$ ratio in CeC 022 is 0.773 and hence close to

420 the expected pure cosmogenic composition of ~0.65 (e.g., Wieler et al., 2016) and a correction for

421 trapped, e.g. atmospheric, ^{38}Ar would be in the order of 2-3%. Trapped ^{38}Ar is thus negligible

422 compared to the other uncertainties related to the determination of CRE ages.

423 Apart from ^{129}Xe/^{132}Xe, the Kr and Xe isotopic compositions are consistent with a mixing

424 of air with — in the light isotopes — cosmogenic Kr and Xe. The presence of a small martian

425 trapped component is visible only in the ^{129}Xe/^{132}Xe ratio = 1.02 ± 0.01. Similarly, the trapped

426 element ratio ^{36}Ar$_{tr}$/^{132}Xe (4.2 ± 1.3) is very low suggesting significant Xe from air, in agreement

427 with the Xe isotopes. The ratios ^{84}Kr/^{132}Xe (1.25 ± 0.05) and ^{129}Xe/^{132}Xe are consistent with

428 previous results for nakhlites and suggest essentially no trapped martian component but merely

429 "Earth fractionated atmosphere" (cf. Fig 3A, Cartwright et al. 2014). The ^{3}He, ^{21}Ne and ^{38}Ar CRE

430 ages of CeC 022 were determined with physical model predictions for cosmogenic noble gas

431 production (Leya and Masarik, 2009) based on the chemistry (Table 4) and the shielding conditions

432 constrained by the shielding parameter given above. As a somewhat arbitrary but safely

433 conservative assumption, we used radii ≤85 cm. Most "allowed" shielding depths, based on

434 cosmogenic ^{22}Ne/^{21}Ne, were in the range 0 to 2 cm. We obtain ^{3}He, ^{21}Ne and ^{38}Ar CRE ages of

435 11.4 ± 0.6 Ma, 9.9 ± 1.6 Ma and 11.8 ± 2.7 Ma, respectively, where the uncertainties include the

436 range of allowed shielding conditions and experimental errors.

437 If using a model specifically created for very small shergottites (see Wieler et al., 2016, based

438 on the original model by Leya and Masarik, 2009), only one shielding condition would be allowed:

439 a perhaps more realistic 7 cm pre-atmospheric radius and 6.4-6.6 cm depth (which excludes any

440 contribution from of SCR). Using that model, the age would slightly increase, to 12.3 ± 0.2 Ma,

441 10.9 ± 0.1 Ma and 14.2 ± 3.3 Ma, respectively. We consider the later data set more reliable and our

442 preferred CRE combined age for CeC 022 is 11.8 ± 1.8 Ma.

443 **4. Discussion**

4.1. Martian origin for CeC 022

All petrographic, geochemical and mineral composition data confirm that CeC 022 is a martian meteorite. Grain density of CeC 022 is 3.342 ± 0.002 g/cm^3, similar to the average of 3.41 ± 0.07 on four nakhlites (Macke et al. 2011), suggesting on overall similar mineralogy. The mineral abundances are in the range observed in nakhlites (Table 1) (Udry and Day, 2018), although image analyses using pixel counting methodology on *ImageJ* gives errors in calculations of modal abundance that are up to 5 vol% (Maloy and Treiman, 2007), due to the heterogeneous nature of the nakhlites sample (Corrigan et al., 2015). Major element bulk compositions are in the range of the nakhlites, with a high FeO (19.0 wt%), Al$_2$O$_3$ (3.32 wt%), MgO (12.2 wt%) and CaO (12.8 wt%) (Table 4), reflecting the abundance of cumulus minerals olivine and pyroxene. Sodium and potassium content are low (1.13 wt% and 0.25 wt%). Likewise, bulk key ratios also confirm the martian origin (Mg#= 53.8, FeO/MnO= 37.9; Na$_2$O/Al$_2$O$_3$ = 0.34; K/La = 450) (Table 4). Bulk REE compositions show a pattern parallel to other nakhlites (Table 4, Fig. 13). Bulk (La/Lu)$_{CI}$ is 4.4, within the range of nakhlites (Udry and Day, 2018).

Oxygen isotopic analyses, with $\Delta^{17}O = 0.248 \pm 0.013$ ‰ (n=3) are close to the Mars fractionation line (MFL), confirming a martian origin. In detail, although this value is compatible with the MFL value $\Delta^{17}O = 0.28 \pm 0.07$ ‰ (31 analyses on 11 meteorites) defined by Clayton and Mayeda (1996), it is significantly lower than the more recent MFL value $\Delta^{17}O = 0.321 \pm 0.013$‰ (34 analyses on 11 meteorites) defined by Franchi et al. (1999). This small discrepancy may originate from the relatively small mass of the initial bulk sample used in our analyses (12 mg), compared to the 50-100 mg used by Franchi et al. (1999).

Caleta el Cobre 022's crystallization age of 1.215 ± 0.067 Ga is close to other nakhlites, even though it is slightly younger than Nakhla (Treiman, 2005, Cohen et al., 2017, Udry and Day,

467 2018). The ejection age of CeC 022 is measured around 11 Ma is similar to other nakhlites (Herzog

468 and Caffee, 2013). Therefore, CeC 022 was sampled by the same ejection event as the other

469 nakhlites.

470 **4.2.   Petrogenesis**

471   **4.2.1. Cumulus crystallization**

472   In a first stage of crystallization, pyroxene cores (Mg# 55) grew in a cumulate layer (Jambon

473 et al., 2016) before the later stage of euhedral rim and overgrowth. These augite cores come from

474 early crystallization of relatively evolved Fe-rich mafic melt, probably in a magma chamber (Imae

475 et al., 2005; Sautter et al., 2002; Jambon et al., 2016). A new injection of magma, with a different

476 composition than the augite cores, could have created a disequilibrium, shown by the resorbed

477 rounded irregular boundaries of the augite cores (Fig. 2). This injection could have enabled the

478 crystallization of the euhedral augite rims, with a composition slightly enriched in Fe and relatively

479 depleted in Mg (Mg# 52) (Table 2). Those euhedral augite with enriched Fe composition could

480 also be explained by a slight drop of the temperature that creates an enrichment in Fe in the minerals

481 (Fig. 15) but would not explain the resorbed rounded cores. Thus, those irregular rounded cores

482 could be rather interpreted as sector zoning or patchy zoning in augite. In both cases, the

483 conservation of zoning indicates that augites cooling was fast enough to preclude diffusive

484 homogenization during augite rim crystallization.

485   Olivine in CeC 022 could have crystallized at the same time as euhedral augite. Olivines in

486 CeC 022 are not zoned and their compositions are homogenous throughout the sample with a Fe-

487 rich composition (Table 3). This agrees with Treiman (2005) who noticed that homogenous

488 olivines are the most ferroan in nakhlites. The sharp petrographic contact between olivine and

489 augite rims show equilibrium and no diffusion (Fig. 4). Using Toplis and Carrol (1995)

experimental data, Jambon et al. (2016) showed the correlation between Mg# of coexisting augite and olivine with decreasing temperature (Fig. 15). As observed in CeC 022, olivine with Mg# ~30 should be in equilibrium with augite euhedral rims of Mg#~50 at ~1075°C (Fig. 15) as seen in other nakhlites (Treiman 1986; Longhi and Pan, 1989; Harvey and McSween, 1992b; Sautter et al., 2002; Jambon et al., 2016). The crystallization of augite alone is possible at higher pressure than the crystallization of both olivine and augite together (Jambon et al., 2016), thus a drop of pressure would initiate the crystallization of olivine and augite rims (Fig. 15). Thence, after the crystallization of pyroxene cores, olivine and augite rims crystallize from a common melt at a shallower depth. Nonetheless, as Fe and Mg diffusion are must faster in olivine than in pyroxene, the homogeneous olivine could be the result of diffusion of initially zoned olivine. The original olivine would have had more magnesian core, with enriched Fe-rim, resembling zoned olivine in other nakhlite, such as NWA 817 or MIL 03346 (core Mg# 40-45) (Sautter et al., 2002; Day et al., 2006; Udry and Day, 2018). Looking at the equilibrium between olivine and pyroxene (Fig. 15), olivine cores richer in Mg would have crystallized at higher temperature, so before augite rim, right after augite cores. The model of crystallization of cumulus minerals in nakhlite has been previously largely discussed in literature. Caleta el Cobre 022 resemble other nakhlites in the crystallization of augite and olivine cumulus, with its differences to other nakhlites described in this paper. For further details about the model of crystallization, we advise the reader to see Day et al. 2006.

Olivine contains planes of inclusions composed of augite and magnetite, which are different in structures and composition from the lamellar symplectite exsolution observed in Nakhla and Governador Valadares (Greshake et al., 2000; Mikouchi et al., 2000). Those augites included in olivine are close in composition to the augite rim, hence likely formed at the same time as the crystallization of augite euhedral rim and olivine, or a slightly after, before final crystallization of intercumulus materials.

4.1.2. Intercumulus phase crystallization

The crystallization of low-Ca pyroxene can be explained by the continuous crystallization of augite and olivine with a decreasing temperature, which would lead to a Ca depleted and Fe enriched melt, enabling the crystallization of low-Ca pyroxene. Also, a drop in the pressure during crystallization could explain the low-Ca pyroxene rim. In basaltic igneous rocks, the peritectic liquidus relationship of olivine and pyroxene is olivine + melt → low-Ca pyroxene (e.g., Kushiro 1969; Morse 1980). Thus, a magma saturated in augite at higher pressure, would become undersaturated in augite and saturated in low-Ca pyroxene at lower pressure (Treiman and Irving, 2008). Hence, low-Ca pyroxene can be found surrounding olivine in nakhlites. This demonstrates that olivine and augite minerals finished growing in a closed system and the last melt crystallized the low-Ca pyroxene rim and the mesostasis pockets with the fine Fe-rich overgrowth.

The thin and sharply delimited Fe-rich overgrowth is found on cumulus augite on their contact with the mesostasis but is absent on low-Ca pyroxene rim. This overgrowth is out of equilibrium with the olivine and augite rim (Fig. 15) and has no gradual transition between the rim and the overgrowth, thus no diffusive exchange occurred in the crystal. Moreover, the euhedral augite rims show no stage of resorption. Therefore, the crystallization of the Fe-rich pyroxene overgrowth is due to rapid cooling and not to a new melt which would have disequilibrated the augite rim and olivine. In the mesostasis, the association of large apatites with low-Ca pyroxene rim around olivines suggests that apatite growth is linked to the crystallization of low-Ca pyroxene, so that the Ca content of apatite might come from the dissolution of augite (Treiman and Irving, 2008) (Fig.7). Intercumulus olivine crystals were not found in the mesostasis, where they have possibly been altered in iddingsite. Indeed, iddingsite is found in the mesostasis as patches that have sometimes shapes reminiscent of olivine crystals.

537   Sulfides in CeC 022 occur in unusually high amount (0.15±0.05 vol.%) compared to other

538   nakhlites and show textural evidence for sulfide mobility and reactivity. The numerous occurrences

539   of sulfide blebs around and inside olivines may reflect a population of sulfide perhaps entrained

540   from deeper levels. In some cases, pyrrhotite-magnetite clusters were brecciated, which may be a

541   shock-related feature. Previous work on MIL's nakhlites has suggested that such large, sub-

542   rounded pyrrhotites, here almost systematically surrounded by magnetite, locally altered, may

543   represent a sulfide population of crustal origin assimilated during magmatic emplacement of the

544   nakhlites and are thus unstable in the matrix (Day et al., 2006; Franz et al., 2014)

545   **4.2.2. Secondary alteration**

546   Caleta el Cobre 022 exhibits one of the most extensive amounts of aqueous alteration

547   products reported in nakhlites (45.1 vol% of olivine crystal replaced by veins of alteration

548   products), resembling NWA 10153 in that regard (around 45.2 vol%). These alteration products,

549   called iddingsite, are assumed to be pre-terrestrial in this study on the basis of the close similarity

550   to iddingsite in other nakhlites, such as Nakhla and Lafayette that contain iddingsite veins truncated

551   by the fusion crust, which prove their extra-terrestrial origin (Gooding et al., 1991; Treiman et al.,

552   1993, Hicks et al., 2014).

553   In CeC 022, at least two types of iddingsite are detected: alteration veins in olivine and

554   patches in mesostasis pockets. The latter are interpreted as relicts of olivine grains in the mesostasis.

555   The Raman analyses reveal a poorly crystalline type and a more crystalline type (Fig. S4). EDS

556   analyses show that in comparison, the less crystalline phase is silicon-rich (~50 wt% SiO_2) and the

557   more crystalline is iron-rich (~52 wt% FeO). Both Raman and IR measurements reflect hydrated

558   alteration phases (Fig. S4). Also, the mesostasis shows alteration into iddingsite at the micrometer

559   scale (Fig. 16), which has been also observed in other nakhlites, but rarely studied compared to

560 iddingsite veins in olivine (Treiman et al., 2005; Daly et al., 2019). The sulfide and oxide stringers,

561 found inside iddingsite veins cross-cutting olivine, indicate that the fluid responsible for this

562 alteration event on Mars could also have transported reduced sulfur inside the nakhlites, after

563 completion of igneous crystallization of CeC 022. Our observation are consistent with previous

564 reports of magmatic sulfides oxidation to sulfate during weathering on Mars during episodic

565 periods of water activity in the vicinity of the nakhlite parent rock that precipitated

566 iddingstite/smectite as recently as 600-650 Ma (Franz et al., 2019 and reference therein). We may

567 surmise that hydrothermalism could have been able to transport sulfur inside the nakhlite while

568 bringing the water that was involved in local replacement of intercumulus sulfides of igneous origin

569 by iron oxyhydroxide-like phases.

570 **4.3.   Geochronology and isotope systematics**

571 Caleta el Cobre 022 crystallization age was determined at 1.215 ± 0.067 Ga (Sm-Nd).

572 Considering only Sm-Nd ages, CeC 022 appears to be slightly younger than the three other

573 nakhlites dated by Sm-Nd (Nakhla, Lafayette and Governador Valadares) with an age range of 1.26

574 $\pm$ 0.07 − 1.37 $\pm$ 0.02 Ga (Nyquist et al., 2001), close to Nakhla within errors. With nakhlite

575 crystallization ages ranging from 1.26 to 1.42 Ga (from compilations of Sm-Nd, K-Ar, ^{40}Ar-^{39}Ar,

576 Rb-Sr, U-Th-Pb data, from Udry and Day, 2018), CeC 022 could be one of the youngest nakhlites

577 found yet. More recently, Cohen et al., 2017 presented an exhaustive study of ^{40}Ar-^{39}Ar dating of

578 nakhlites, proposing four geochronologically distinct eruptions, the youngest age being Lafayette

579 with 1.321 ± 0.009 Ga. While the origin of the systematic offset between older ^{40}Ar-^{39}Ar ages and

580 younger ages obtained with other dating system is not clear, CeC 022 could be the youngest

581 nakhlite found yet and may extend the nakhlite eruptive sequence by about 50 Myr. As only one

582 radiochronologic system has been measured here and because different isotopic systems could lead

583   to different ages for a given nakhlite (Nyquist et al., 2001), this statement should be taken with

584   precaution. Thus, the comparison of CeC 022's Sm-Nd age with ^{40}Ar-^{39}Ar ages is tentative and

585   ^{40}Ar-^{39}Ar dating of CeC 022 is highly desirable.

586   The initial value of $\varepsilon^{143}Nd = +10.5 \pm 0.1$, is clearly lower than the other nakhlites, with an

587   average of $\varepsilon^{143}Nd = +15.7 \pm 1.4$ (2SD), from 14.6 ± 0.1 to 16.9 ± 0.1 (Caro et al., 2008; Debaille

588   et al., 2009). As demonstrated by the positive anomaly in Ce, this lower $\varepsilon^{143}Nd$ could be related to

589   terrestrial contamination in the Atacama Desert. However, the $\mu^{142}Nd$ of CeC 022, of $+56 \pm 3$, is

590   very similar to other nakhlites, with $\mu^{142}Nd$ from $+51$ to $+67$ (Caro et al., 2008; Debaille et al.,

591   2009). Therefore, the decoupling between ^{143}Nd and ^{142}Nd systematics rules out terrestrial

592   disturbance of the Nd systematics as alteration would shift them concomitantly and the ^{142}Nd

593   systematics are identical to other nakhlites. Instead, this decoupling favors a slight change in the

594   source of nakhlite, possibly with time and/or metasomatic agent (McCubbin et al., 2013). However,

595   in any case, the contaminant agent must somehow be related to nakhlites. Indeed, the ^{142}Nd

596   systematics were established during the first 500 Myr of Mars geological history (while ^{146}Sm was

597   extinct) and could not have varied since then, except by mixing with another source. In this case,

598   it would mean that the second source would have had exactly the same ^{142}Nd value, which is highly

599   unlikely. One possibility to reconcile the nakhlite-like ^{142}Nd but slightly lower ^{143}Nd of CeC 022

600   would be that it is actually contaminated by older nakhlites that evolved towards lower $\varepsilon^{143}Nd$

601   during the time between their emplacement and the emplacement of CeC 022. Considering the

602      $^{147}Sm/^{144}Nd$ ratios of nakhlites, a nakhlite-like sill or flow emplaced at least 700 Myr before CeC

603   022 would be able to generate a $\varepsilon^{143}Nd$ low enough to decrease the ^{143}Nd systematics of CeC 022,

604   without changing its REE and ^{142}Nd systematics. This hypothesis is however impossible to test

605   with the current sampling of the nakhlite magmatic system.

606   The shielding indicator $(^{21}Ne/^{22}Ne)_{cosm}$ of ~0.831 is low, as often observed in martian

607   meteorites. With the model specifically created for very small shergottites discussed in paragraph

608   3.6.2., and using a 7 cm pre-atmospheric radius, the recovered mass is estimated to be about 10%

609   of the pre-atmospheric mass of about 4 kg, which corresponds to the mass of the meteorite that was

610   found. The nominal CRE ages for ^3He, ^{21}Ne and ^{38}Ar are all consistent with ages found for other

611   nakhlites: around 11 Ma (Herzog and Caffee, 2013).

612   **4.4.   Relation with other nakhlites**

613   **4.4.1. Nakhlites typology**

614   Independently of the different models of emplacement into a single pile (Treiman, 1986*;*

615   Mikouchi et al., 2003, 2012; Treiman, 2005; Bridges and Warren, 2006; Day et al., 2006;

616   McCubbin et al., 2013; Corrigan et al., 2015) or different units (Jambon et al., 2016; Balta et al.,

617   2016; Cohen et al., 2017; Udry and Day., 2018), nakhlites can be divided into two subgroups based

618   on mineralogy, mineral compositions, REE bulk composition, rock texture and CSD: the slower-

619   cooled nakhlites and the faster-cooled nakhlites.

620   The faster-cooled subgroup comprises NWA 817, MIL's nakhlites, NWA 10645 and NWA

621   5790. They show zoned olivine with a large range of composition Fo_{55}-Fo_{95} (Fig. 10). Pyroxenes

622   show patchy zoning in NWA 10645 (Udry and Day, 2018) and in NWA 5790 (Jambon et al., 2016),

623   with a similar Fe-rich composition (Table 6). They also display Fe-rich overgrowth on augite

624   phenocryst in contact with the mesostasis, produced by rapid cooling of the last residual melt. The

625   zoning observed in pyroxene and olivine is retained due to rapid cooling preventing diffusive

626   homogenization. The mesostasis of faster-cooled nakhlites show quenched oxides with skeletal

627   morphology and fine-grained feldspar, both characteristics of high cooling rates.

628   The slower-cooled subgroup is composed of Nakhla, Lafayette, Governador Valadares,

629   NWA 998, Yamato (Y) 000593 and the pairing group of NWA 10153 (NWA 11013, NWA 10153,

630   NWA 10659 and NWA 10720; Udry and Day, 2018). They present unzoned olivine due to

631   diffusion homogenization enabled by slow crystallization. They also show oxide phenocrysts

632   formed through slow crystallization, in contrast to quenched oxides in faster-cooled nakhlites. The

633   intercumulus materials is mainly composed of coarse plagioclase with very little microcrystalline

634   mesostasis, or none.

635   In addition, REE composition of nakhlites reflects these two different subgroups. The

636   nakhlites with higher cooling rates have a higher content of REE, except for NWA 10113,

637   compared to the nakhlites showing lower cooling rates features, which have lower REE content

638   (Fig. 13), as mentioned by Udry and Day (2018). This grouping is also comparable to the

639   mesostasis grouping by Corrigan et al. (2015), who used modal abundance of major phases and

640   McCubbin et al. (2013) who worked on volatile-bearing minerals morphology and composition to

641   present a model of crystallization sequence of the nakhlites.

642   Caleta el Cobre 022 shows evidence of rapid cooling, as seen in the faster-cooled subgroup

643   and at the same time, shows features consistent with a lower cooling rate, similar to the slower-

644   cooled subgroup. Caleta el Cobre 022 uniqueness is the coexistence of those characteristics of both

645   lower and higher cooling rates.

646   **4.4.2. Slower-cooled nakhlite characteristics**

647   *Olivine*

648   Caleta el Cobre 022 presents a low content of olivine (4.2 vol%), being the second olivine-

649   poorest nakhlite after NWA 10645 (1.2 vol%). Olivines in CeC 022 are the second most fayalitic

650   analyzed (Mg# 30), after the exception of NWA 10645 (Mg# 22), also close to the composition of

651   Lafayette (Mg# of 34) and NWA 998 (Mg# of 36), both slower-cooled nakhlites (Table 7, Fig. 10).

652   Also, olivines do not show any zoning, as seen only in the olivines of NWA 998 and Lafayette, a

653   characteristic explained by a stage of diffusion at low cooling rates.

Pyroxene rims

655   The large rims of augite richer in Fe around the irregular cores of augite show similar

656   mineral compositions ($En_{31}Fs_{29}Wo_{40}$, Mg# ~ 52) as in the slower-cooled nakhlites, such as the

657   Nakhla subgroup (Udry and Day, 2018) (Fig. 9). Also, as seen in both slower and faster-cooled

658   nakhlites, like Nakhla and NWA 817 (Treiman, 2005), pyroxenes are also observed as rounded

659   inclusions (~100 µm) in olivine crystals (Fig. 4).

Plagioclase

661   Caleta el Cobre 022 contains a high proportion of millimeter-sized plagioclase grains (19

662   vol%), also seen in NWA 10153 (32 vol%) and NWA 998 (10.5 vol%) (Table 1). The compositions

663   of those plagioclase are also comparable within errors, for example $An_{35}Ab_{61}Or_4$ for NWA 10153

664   and $An_{25}Ab_{72}Or_3$ for NWA 998 and $An_{29.7\pm4.3}Ab_{67.2\pm4.0}Or_{3.1\pm0.5}$ for plagioclase in CeC 022 (Fig. 11).

665   Those coarse plagioclases are only seen in slower-cooled nakhlites as intercumulus material, and

666   are characteristic of slower crystallization of the last melt, in contrary of fine-grained mesostasis,

667   created by rapid cooling of the last melt.

Pyroxene overgrowth

669   The fine overgrowth of Fe-rich augite is found on the euhedral augite rim and only when in

670   contact with the mesostasis. This stage of final fast cooling is observed on all nakhlites, but the

671   compositions of this pyroxene sharp overgrowths and intercumulus pyroxenes found in the

672   mesostasis are similar to the subgroup of slower-cooled nakhlite Governador Valadares and Nakhla

673   but richer in iron (up to $En_{35}Fs_{61}Wo_4$) (Fig. 9).

Sulfides

The population of large-sized intercumulus sulfides closely associated with magnetite looks

similar to the slower-cooled nakhlite subgroup, such as NWA 998 (Chevrier et al., 2011).

Quantitative textural analysis

The habit ratio and grain sizes of the pyroxene population of slower-cooled nakhlites are

similar to all nakhlites, except NWA 10645, which contains pyroxene double in length than the

nakhlite average (Udry and Day, 2018). The similar CSD slope, CSD intercept and average

pyroxene size of slower-cooled Nakhla and Lafayette with CeC 022 (Fig. 8) demonstrate similar

emplacement histories for the pyroxene population. Based on CSD analysis, CeC 022 might

originate from the same unit as these nakhlites, but closer to the surface as shown by the quenched

oxides and lower content of pyroxene (settling). The SDP analyses show that CeC 022 falls close

to the other nakhlites, especially NWA 11013 (Fig. S3).

4.4.3. Faster-cooled nakhlite characteristics

Pyroxenes cores

Caleta el Cobre 022 contains a low abundance of pyroxene phenocrysts (58 vol%) similar

to NWA 5790 (57.8 vol%) and NWA 11013 (55.0 vol%), which have the lowest pyroxene

abundance in nakhlites (Table 1). The irregular rounded cores with the euhedral rim richer in Fe

are described so far only in the faster-cooled nakhlites NWA 5790 (Jambon et al., 2016) and NWA

10645 (Udry and Day, 2018). The augite cores in CeC 022 are the most Fe-rich measured in

nakhlites yet (16.2 wt%), richer than NWA 5790 (15.7 wt%), NWA 10645 (14.5 wt%), the

nakhlites showing those irregular cores (Table 6; Udry and Day, 2018). The conservation of those

cores, with a different composition than the surrounding rim, is an indicator of rapid cooling, fast

enough to prevent diffusive homogenization (Jambon et al., 2016).

Mesostasis

Caleta el Cobre 022 presents a high abundance (16 vol%) of mesostasis, resembling NWA 5790 (36.3 vol%) and NWA 817 (24.5 vol%), from the faster-cooled subgroup. This abundance of mesostasis can reflect the packing efficiency, thus the burial depth of the rocks. The high abundance of mesostasis in Caleta el Cobre 022 suggests a weak packing efficiency, thus a shallow burial depth, which could induce a higher cooling rate. The abundance of mesostasis could also reflect the crystallization of the nakhlite from dynamically sorted phenocryst-rich magma (Corrigan et al., 2015). The mesostasis pockets contain dendritic cross-shaped oxides, low-Ca pyroxene and apatites, embedded in fine-grained alkali feldspar and silica groundmass, resembling faster-cooled nakhlites NWA 817, MIL 03346 and NWA 5790 (Sautter et al., 2002; Day et al., 2006; Jambon et al., 2016). The fine-grained K-feldspars in the mesostasis has similar composition to the faster-cooled nakhlites NWA 817 and NWA 5790 (Fig. 11). Caleta el Cobre 022's main peculiarity is in those pockets of mesostasis caused by rapid cooling, associated with coarse plagioclase (Fig. 12).

This association of contrasted intercumulus materials has never been observed before in other nakhlites. It could result from a change in cooling rate after crystallization of phenocrysts and plagioclase, during eruption of the magma or emplacement as shallow sill with a drastic temperature drop, leading to fast crystallization of mesostasis pockets and pyroxene overgrowth. Alternatively, this association could be due to a new injection of magma after crystallization of phenocrysts and plagioclase, inducing eruption and faster crystallization.

Sulfides

Caleta el Cobre 022 is sulfide-rich (0.15±0.05 vol.%) compared to other nakhlites so far studied for sulfides (Chevrier et al., 2011; Franz et al., 2014; Dottin et al., 2018; Mari et al., 2019).

719   The sulfide droplets inside skeletal mesostasis minerals coupled with Ni-free pyrrhotite

720   were described in faster-cooled nakhlites as NWA 817 (Chevrier et al., 2011) and MIL's nakhlites

721   (Day et al., 2006; Dottin et al., 2018). Similarly, the high sulfide content, coupled with Ni-free

722   pyrrhotite compositions in CeC 022, also resemble MIL's nakhlites (Day et al., 2006; Franz et al.,

723   2014; Dottin et al., 2018). Assimilation of crustal sulfur during the igneous crystallization stage

724   could account for CeC 022 pyrrhotite modal abundance and Ni-poor composition, as repeatedly

725   documented in nakhlites, especially in the fast-cooled subgroup (Farquhar et al., 2007; Franz et al.,

726   2014; Dottin et al., 2018; Mari et al., 2019; Franz et al., 2019 and reference therein). The mean

727   Fe/S ratio of CeC 022 pyrrhotite (Fe0.89S ; hexagonal pyrrhotite) (Fig. S2), coupled with textural

728   evidence of magnetite, indicates similar oxidizing crystallization conditions near the FMQ

729   synthetic buffer (Chevrier et al., 2011), as usually reported for nakhlite pyrrhotites that inherited

730   abundant crustal sulfur in their S isotopic composition (Farquhar et al., 2007b; Franz et al., 2014;

731   Dottin et al., 2018).

732   ***Rare earth element compositions***

733   Caleta el Cobre 022 shows a high bulk content in REE, resembling faster-cooled nakhlites

734   such as NWA 10645, NWA 817 and MIL 03346 except for a clear positive anomaly in Ce (Fig.

735   13). As mentioned in Pourkhorsandi et al. (2017), a positive Ce anomaly is observed in REE

736   patterns of meteorites from the Atacama Desert, as is CeC 022. This Ce anomaly is likely due to

737   terrestrial alteration specific to Atacama, as Ce in its oxidized form (Ce^{4+}) is a quite mobile element.

738   **4.4.4. Magnetic properties**

739   Magnetic susceptibility average mass weighed value of 8.41×10^{-6} m^3/kg is to be compared

740   to the average value of $4.10 \pm 1.73 \times 10^{-6}$ m^3/kg for the other nine nakhlites (Rochette et al. 2005,

741   Jambon et al. 2016 and our measurement of NWA 10153 at 5.25×10^{-6} m^3/kg). Saturation remanent

742   magnetization (M_{RS}) is 0.459 Am^2/kg, compared to 0.160 ± 0.108 Am^2/kg for the other nine

743   nakhlites (Rochette et al. 2005, Jambon et al. 2016, and our measurement of NWA 10153 at 0.135

744   Am^2/kg,) Saturation magnetization is 1.51 Am^2/kg, to be compared with 0.66 ± 0.37 Am^2/kg for

745   the other nine nakhlites. Caleta el Cobre 022 is the most magnetic nakhlite (Fig. 17).

746   The presence of two Curie temperatures of 525°C and 585°C evidences two families of

747   ferromagnetic iron oxides with compositions $Fe_{2.9}Ti_{0.1}O_4$ (more abundant) and Fe_3O_4, respectively

748   (Lattard et al., 2006). The microprobe analyses on magnetite phenocrysts give a composition richer

749   in Ti of $Fe_{2.6}Ti_{0.4}O_4$. This difference is explained by the exsolutions observed at nanometric scales

750   in these iron oxides grains (Fig. 5). Thus, the microprobe analyses represent a combination of the

751   nanoscale exsolution with the oxide surrounding them. Using the composition $Fe_{2.9}Ti_{0.1}O_4$, the

752   saturation magnetization indicates a magnetite content of 2.90 vol%. This estimate, that does not

753   include the ilmenite/ulvöspinel exsolution since these two minerals are paramagnetic at room

754   temperature, is in good agreement with the modal abundance of oxide phenocrysts estimated from

755   image analyses (2.6 vol%).

756   Besides the petrological implications, the study of magnetic properties of martian

757   meteorites is also of interest for the interpretation of the magnetic anomalies that have been

758   documented over large parts of the Noachian crust at satellite altitude (Acuña et al., 1999). The

759   strong intensity of these anomalies (over 1000 nT at 100 km altitude) imply the existence of a past

760   dynamo operating on Mars, but also the existence of rocks capable of acquiring strong remanent

761   magnetization. It has been estimated that such rocks should satisfy the condition M_{RS}>0.29 Am^2/kg,

762   regardless of their present-day natural remanent magnetization that may have been later modified

763   by a number of processes including shock demagnetization at the surface of Mars, or contamination

764   by magnets by meteorite collectors (Gattacceca et al., 2014). It is noteworthy that this condition is

765   met by only a handful of martian meteorites: MIL 03346, NWA 5790, NWA 7034 and paired

766   stones (Rochette et al., 2005; Gattacceca et al., 2014; Jambon et al., 2016; Herd et al., 2017). With

767   M_{RS}=0.459 Am^2/kg, CeC 022 is only the fourth martian meteorite and the third nakhlite whose

768   magnetic properties may account for the strong intensity of the martian magnetic anomalies (Fig.

769   17). Although nakhlites are obviously younger than the age of the end of the martian dynamo (e.g.,

770   Lillis et al., 2008), CeC 022 still represent an analogue source lithology for the strong

771   magnetization of the martian crust.

772   **4.4.5. Caleta el Cobre 022: a new subgroup**

773   Caleta el Cobre 022 shows similarities with faster-cooled nakhlites, as well with slower-

774   cooled nakhlites. A new characteristic, never observed before in nakhlites, is the presence of both

775   fine-grained mesostasis and coarse millimeter-size plagioclase in CeC 022, showing two different

776   cooling histories in intercumulus materials. In addition, compared to other nakhlites, CeC 022 has

777   the lowest CaO content amongst nakhlites (12.9 wt%), similar to faster-cooled nakhlites NWA

778   5790 (12.9 wt%) or NWA 817 (13.1 wt%). Its low content in FeO (19 wt%) is also close to NWA

779   817, NWA 5790, or MIL nakhlites (Jambon et al., 2016). Caleta el Cobre 022 has high MgO

780   content, similar to Lafayette, NWA 998 and Nakhla (Udry and Day, 2018), with a Mg# of 53.8,

781   closer to the slower-cooled nakhlites (Table 4). This bulk composition and the abundance and

782   composition of mineral phases are a reflection of the presence of both faster and slower-cooled

783   nakhlite subgroup features in CeC 022. In addition, martian aqueous alteration phases are found in

784   high abundance compared to most other nakhlites, and the occurrence of sulfides and Fe-oxides at

785   the core of iddingsite veins is a unique and puzzling feature, giving new insights into the complex

786   thermal and alteration histories of nakhlites.

787   With all its different characteristics, CeC 022 cannot be part of any previously proposed

788   nakhlite subgroup, and therefore increases the diversity of the martian sample suite. In the Udry

789   and Day (2018) model presenting six different units in the nakhlite group based on petrography,

790   crystallinity and composition, CeC 022 may thus represent a 7th subgroup. Also, CeC 022 has a

791   slightly younger Sm-Nd age than other nakhlites. Caleta el Cobre 022 must originate from the same

792   volcanic system as the other nakhlites, according to their similar crystallization age and

793   petrography, compositions and physical properties, but it probably samples a different flow or sill

794   than the other nakhlites.

795   **5. Conclusion**

796   All petrographic, chemicals and isotopic analyses confirm that CeC 022 is a nakhlite,

797   coming from the same volcanic system as other nakhlites, although with characteristics never

798   observed before in other nakhlites. On one hand, it shows similarities with faster-cooled nakhlites,

799   such as NWA 817, NWA 5790 or MIL's nakhlites: conservation of augite irregular cores, Fe-rich

800   overgrowth, high proportion of mesostasis with fine-grained K-feldspars, quenched oxides and

801   high REE content. On the other hand, CeC 022 also shares similarities with slower-cooled

802   nakhlites, like Nakhla and NWA 10153 (Udry and Day, 2018), including: pyroxene modal

803   abundance, CSD slope and intercept, average pyroxene size, phenocrysts minerals composition,

804   unzoned olivine and abundant plagioclase phenocrysts. One unique feature of CeC 022 is the

805   presence of both fine-grained mesostasis and millimeter-size coarse plagioclase, showing different

806   cooling rates of the intercumulus material though time, a feature never observed before in nakhlites.

807   With these characteristics, CeC 022 may thus represent a 7th nakhlite subgroup in Udry and Day

808   (2018) model of six different subgroups. Its slightly younger Sm-Nd age also supports CeC 022

809   was emplaced in a different flow or sill. Moreover, higher abundance of martian aqueous alteration

810   phases compared to other nakhlites, showing sulfides and Fe-oxides at the core of iddingsite veins

811   is a new characteristic. Magnetic susceptibility and saturation remanent magnetization are higher

812   than for other nakhlites, indicating an overall higher content of magnetite. This elevated magnetite

content makes CeC 022 a potential analogue lithology to account for the strong magnetic anomalies observed at the surface of Mars. With its multistage thermal history, its abundant and complex aqueous alteration, its younger age and its unusual magnetic properties, CeC 022 increases the diversity of the martian sample suite and gives new insights into the complex thermal and alteration histories of nakhlites.

6. REFERENCES

Acuna M. H., Connerney J. E. P., Lin R. P., Mitchell D., Carlson C. W., McFadden, J., Anderson K. A., Rème H., Mazelle C., Vignes D.,Wasilewski P. and Clouter P. 1999. Global distribution of crustal magnetization discovered by the Mars Global Surveyor MAG/ER experiment. *Science* 284(5415):790-793.

Balta J. B., Sanborn M. E., Mayne R. G., Wadhwa M., McSween H. Y. and Crossley S. D. 2017. Northwest Africa 5790: a previously unsampled portion of the upper part of the nakhlite pile. *Meteoritics & Planetary Science* 52:36–59.

837   Bland P. A., Zolensky M. E., Benedix G. K., Sephton M. A. 2006. Weathering of chondritic meteorites. *Meteorites*
838   *and the Early Solar System* 943:853-867.

839   Boctor N.Z., Meyer H.O.A. and Kullerud G. 1976. Lafayette meteorite: petrology and opaque mineralogy. *Earth and*
840   *Planetary Science Letters* 32:69–76.

841   Borg L. and Drake M. J. 2005. A review of meteorite evidence for the timing of magmatism and of surface or near-
842   surface liquid water on Mars. *Journal of Geophysical Research: Planets* 110:E12.

843   Bridges J.C. and Grady M.M. 2000. Evaporite mineral assemblages in the nakhlite (Martian) meteorites. *Earth and*
844   *Planetary Science Letters* 176:267-279.

845   Bridges J. C. and Warren P. H. 2006. The SNC meteorites: basaltic igneous processes on Mars. *Journal of the*
846   *Geological Society* 163:229-251.

847   Bunch T. E. and Reid A. M. 1975. The nakhlites Part I: petrography and mineral chemistry. *Meteoritics & Planetary*
848   *Science* 10:303–315.

849   Caro G., Bourdon B., Halliday A. N. and Quitté G. 2008. Super-chondritic Sm/Nd ratios in Mars, the Earth and the
850   Moon. *Nature* 452:336.

851   Cartwright J. A., Ott U., Herrmann S. and Agee C. B. 2014. Modern atmospheric signatures in 4.4 Ga Martian meteorite
852   NWA 7034. *Earth and Planetary Science Letters* 400:77-87.

853   Cashman K. V. and Marsh B. D. 1988. Crystal size distribution (CSD) in rocks and the kinetics and dynamics of
854   crystallization II: Makaopuhi lava lake. *Contributions to Mineralogy and Petrology* 99:292–305

855   Changela H. G. and Bridges J. C. 2010. Alteration assemblages in the nakhlites: Variation with depth on
856   Mars. *Meteoritics and Planetary Science* 45:1847-1867.

857   Chauvel C. and Blichert-Toft J. 2001. A hafnium isotope and trace element perspective on melting of the depleted
858   mantle. *Earth and Planetary Science Letters* 190:137-151.

859   Chevrier V., Lorand J. P. and Sautter V. 2011. Sulfide petrology of four nakhlites: Northwest Africa 817, Northwest

860   Africa 998, Nakhla, and Governador Valadares. *Meteoritics and Planetary Science* 46:769-784

861   Clayton R. N. and Mayeda T. K. 1996. Oxygen isotope studies of achondrites. *Geochimica et Cosmochimica*

862   *Acta* 60:1999-2017.

863   Cohen B. E., Mark D. F., Cassata W. S., Lee M. R., Tomkinson T. and Smith, C. L. 2017. Taking the pulse of Mars

864   via dating of a plume-fed volcano. *Nature communications* 8:640.

865   Corrigan C. M., Velbel M. A. and Vicenzi E. P. 2015. Modal abundances of pyroxene, olivine, and mesostasis in

866   nakhlites: Heterogeneity, variation, and implications for nakhlite emplacement. *Meteoritics and Planetary*

867   *Science* 50:1497-1511.

868   Daly L., Piazolo S., Lee M. R., Griffin S., Chung P., Campanale F., Cohen B. E., Hallis L. J., Trimby P. W.,

869   Baumgartner R., Forman L.V. and Benedix G. K. 2019. Understanding the emplacement of Martian volcanic

870   rocks using petrofabrics of the nakhlite meteorites. *Earth and Planetary Science Letters* 520:220-230.

871   Day J. M., Taylor L. A., Floss C. and Mcsween Jr H. Y. 2006. Petrology and chemistry of MIL 03346 and its

872   significance in understanding the petrogenesis of nakhlites on Mars. *Meteoritics and Planetary*

873   *Science* 41:581-606.

874   Debaille V., Yin Q. Z., Brandon A. D., Jacobsen B. and Treiman A. H. 2007. Lu-Hf and Sm-Nd isotopic studies of

875   shergottites and nakhlites: implications for Martian mantle sources (abstract #1903). 38th Lunar and Planetary

876   Science Conference. CD-ROM.

877   Debaille V., Brandon A. D., O'Neill C., Yin Q. Z. and Jacobsen B. 2009. Early Martian mantle overturn inferred from

878   isotopic composition of nakhlite meteorites. *Nature Geoscience* 2:548.

879   Dottin III J. W., Labidi J., Farquhar J., Piccoli P., Li M. C. and McKeegan K. D. 2018. Evidence for oxidation at the

880   base of the nakhlite pile by reduction of sulfate salts at the time of lava emplacement. *Geochimica et*

881   *Cosmochimica Acta* 239:186-197.

882   Farquhar J., Kim S.-T. and Masterson A. 2007. Implications from sulfur isotopes of the Nakhla meteorite for the origin
883   of sulfate on Mars. *Earth Planetary Science letters* 264:1-8.

884   Franchi I. A., Wright I. P., Sexton A. S. and Pillinger C. T. 1999. The oxygen-isotopic composition of Earth and
885   Mars. *Meteoritics & Planetary Science* 34:657-661.

886   Franz H. B., Kim S. T., Farquhar J., Day J. M., Economos R. C., McKeegan K. D., Schmitt A. K., Irving A.J., Hoek
887   J. and Dottin III J. 2014. Isotopic links between atmospheric chemistry and the deep sulphur cycle on
888   Mars. *Nature* 508:364.

889   Franz H. B., King P. L. and Gaillard F. 2019. Sulfur on Mars from the atmosphere to the core. *Volatiles in the Martian*
890   *crust: Elsevier*.119–183.

891   Gattacceca J., Hewins R. H., Lorand J. P., Rochette P., Lagroix F., Cournède C., Uehara M., Pont S., Sautter V.,
892   Scorzelli R.B., Hombourger C., Munayco P., Zanda B., Chennaoui H., Ferrière L. 2013. Opaque minerals,
893   magnetic properties, and paleomagnetism of the Tissint Martian meteorite. *Meteoritics and Planetary*
894   *Science* 48:1919-1936.

895   Gattacceca J., Rochette P., Scorzelli R. B., Munayco P., Agee C., Quesnel Y., Cournède C. and Geissman J. 2014.
896   Martian meteorites and Martian magnetic anomalies: A new perspective from NWA 7034. *Geophysical*
897   *Research Letters* 41:4859-4864.

898   Gillet Ph., Barrat J. A., Deloule E., Wadhwa M., Jambon A., Sautter V., Devouard B., Neuville D., Benzerara K., and
899   Lesourd M. 2002. Aqueous alteration in the Northwest Africa 817 (NWA 817) Martian meteorite. *Earth and*
900   *Planetary Science Letters* 203:431–444.

901   Gooding J.L. 1992. Soil mineralogy and chemistry on Mars: Possible clues from salts and clays in SNC meteorites.
902   *Icarus* 99:28–41.

903   Gooding J.L., Wentworth S.J. and Zolensky M.E. 1991. Aqueous alteration of the Nakhla meteorite. *Meteoritics*
904   26:135–143.

905 Greshake A. and Stephan R.D.T. 2000. Combined TEM and TOF-SIMS study of symplectiteexsolutions in olivine

906   from the Martian meteorites Nakhla and Governador Valadarez (abstract #1150.). *31th Lunar and Planetary*

907   *Science Conference*. CD-ROM.

908 Grevesse N. and Anders E. 1989. Solar-system abundances of the elements: A new table. *AIP Conference Proceedings*

909   183:1-8

910 Hallis L. J. and Taylor G. J. 2011. Comparisons of the four Miller Range nakhlites, MIL 03346, 090030, 090032 and

911   090136: Textural and compositional observations of primary and secondary mineral assemblages. *Meteoritics*

912   *& Planetary Science* 46:1787–1803.

913 Hammer J. E. and Rutherford M. J. 2005. Experimental crystallization of fe-rich basalt: application to cooling rate and

914   oxygen fugacity of Nakhlite MIL03346 (abstract). 36th Lunar and Planetary Science Conference. CD-ROM.

915 Harvey R.P. and McSween H.Y. 1992. Petrogenesis of the nakhlite meteorites: Evidence from cumulate mineral

916   zoning. *Geochimica et Cosmochimica Acta* 56:1655–1663.

917 Herd C. D. K., Walton E. L., Agee C. B., Mutik N., Ziegler K., Shearer C. K., Bell A. S., Santos A. R., Burger P. V.,

918   Simon J. I., Tappa M. J., McCubbin F. M., Gattacceca J., Lagroix F., Sanborn M. E., Yin Q. Z., Cassata W.

919   S., Borg L. E., Lindvall R. E., Kruijer T. S., Brennecka G. A., Kleine T., Nishiizumi K., Caffee M. W. 2017.

920   The Northwest Africa 8159 martian meteorite: Expanding the martian sample suite to the early

921   Amazonian. *Geochimica et Cosmochimica Acta*, 218:1-26.

922 Herzog G. F. and Caffee M. W. 2013. Cosmic-ray exposure ages of meteorites. *Treatise on Geochemistry: Second*

923   *Edition. Elsevier Inc*. 419-454.

924 Hicks L. J., Bridges J. C. and Gurman S. J. 2014. Ferric saponite and serpentine in the nakhlite Martian

925   meteorites. *Geochimica et Cosmochimica Acta* 136:194-210.

926 Hutzler A., Rochette P., Bourlés D., Gattacceca J., Merchel S., Jull A. J. T. and Valenzuela M. 2016. New Insights in

927   Preservation of Meteorites in Hot Deserts: The Oldest Hot Desert Meteorite Collection (abstract # 6159). 79th

928   Meeting of the Meteoritical Society.

929   Imae N. and Ikeda Y. 2007. Petrology of the Miller Range 03346 nakhlite in comparison with the Yamato-000593

930   nakhlite. *Meteoritics and Planetary Science* 42:171–184.

931   Imae N., Ikeda Y. and Kojima H. 2005. Petrology of the Yamato nakhlites. *Meteoritics and Planetary Science Supplo*

932   40:1581–1598.

933   Irving A. J., Kuehner S. M., Rumble D. III, Carlson R. W., Hupé A. C. and Hupé G. M. 2002. Petrology and isotopic

934   composition of orthopyroxene-bearing nakhlite NWA 998. *Meteoritics and Planetary Science Supplement*

935   37:A70.

936   Jambon A., Sautter V., Barrat J.-A., Gattacceca J., Rochette P., Boudouma O., Badia D. and Devouard B. 2016.

937   Northwest Africa 5790: Revisiting nakhlite petrogenesis. *Geochimica et Cosmochimica Acta* 190:191–212.

938   Jerram D. A., Cheadle M. J., Hunter R. H. and Elliot M. T. 1996. The spatial distribution of grains and crystals inrocks.

939   *Contributions to Mineralogy and Petrology* 125:60–74.

940   Jerram D. A., Cheadle M. J. and Philpotts A. R. 2003. Quantifying the building blocks of igneous rocks: are clustered

941   crystal frameworks the foundation? *Journal of Petrology* 44:2033-2051.

942   Korochantseva E. V., Schwenzer S. P., Buikin A. I., Hopp J., Ott U. and Trieloff M. 2011. 40Ar-39Ar and cosmic-ray

943   exposure ages of nakhlites-Nakhla, Lafayette, Governador Valadares and Chassigny. *Meteoritics and*

944   *Planetary Science* 46:1397–1417.

945   Kushiro I. 1969. The system forsterite-diopside-silica with and without water at high pressures. *American Journal of*

946   *Science* 267A:269–294.

947   Lattard D., Engelmann R., Kontny A. and Sauerzapf U. 2006. Curie temperatures of synthetic titanomagnetites in the

948   Fe-Ti-O system: Effects of composition, crystal chemistry, and thermomagnetic methods. *Journal of*

949   *Geophysical Research: Solid Earth* 111:B12.

950   Lee M. R., Daly L., Cohen B. E., Hallis L. J., Griffin S., Trimby P., Boyce A. and Mark, D. F. 2018. Aqueous alteration

951   of the Martian meteorite Northwest Africa 817: Probing fluid–rock interaction at the nakhlite launch

952   site. *Meteoritics & Planetary Science* 53:2395-2412.

953   Lentz R.C.F., Taylor G.J. and Treiman A.H. 1999. Formation of a Martian pyroxenite: A comparative study of the

954   nakhlite meteorites and Theo's Flow. *Meteoritics and Planetary Science* 34:919–932.

955   Leya I. and Masarik J. 2009. Cosmogenic nuclides in stony meteorites revisited. *Meteoritics and Planetary Science*

956   44:1061–1086.

957   Lillis R. J., Frey H. V. and Manga M. 2008. Rapid decrease in Martian crustal magnetization in the Noachian era:

958   Implications for the dynamo and climate of early Mars. *Geophysical Research Letters* 35:14.

959   Longhi J. and Pan V. 1989. The parent magmas of the SNC meteorites. *Lunar and Planetary Science Conference*

960   *Proceedings* 19:451-464.

961   Lorand J.-P., Barat J.-A., Chevrier V., Sautter V. and Pont S. 2012. Metal-saturated sulfide assemblages in chassignite

962   NWA 2737; evidence for impact-related sulfur devolatilisation. *Meteoritics and Planetary Science Letters*

963   47:1830-1841.

964   Lorand J. P., Hewins R. H., Remusat L., Zanda B., Pont S., Leroux H., Marinova M., Jacob D., Humayun M., Nemchin

965   A., Grange M., Kennedy A. and Gopel C. 2015. Nickeliferous pyrite tracks pervasive hydrothermal alteration

966   in Martian regolith breccia: A study in NWA 7533. *Meteoritics and Planetary Science* 50:2099-2120.

967   Lorand J. P., Pont S., Chevrier V., Luguet A., Zanda B. and Hewins R. 2018. Petrogenesis of Martian sulfides in the

968   Chassigny meteorite. *American Mineralogist* 103:872-885.

969   Macke R. J., Britt D. T. and Consolmagno G. J. 2011. Density, porosity, and magnetic susceptibility of achondritic

970   meteorites. *Meteoritics and Planetary Science* 46:311-326.

971   Maloy A. K. and Treiman A. H. 2007. Evaluation of image classification routines for determining modal mineralogy

972   of rocks from X-ray maps. *American Mineralogist* 92:1781-1788.

973   Mari N., Riches A.J.V., Hallis L.J., Marrocchi Y.,Villeneuve J., Gleissner P., Becker H. and Lee M. 2019. Syneruptive

974   incorporation of martian surface sulphur in the nakhlite lava flows revealed by S and Os isotopes and highly

975   siderophile elements : implication for mantle sources in Mars. *Geochimica et Cosmochimica Acta* 266:416-

976   43.

977   Marsh B. D. 1988. Crystal size distribution (CSD) in rocks and the kinetics and dynamics of crystallization, I. Theory.

978   *Contributions to Mineralogy and Petrology* 99:277–291.

979   Marsh B. D. 1998. On the interpretation of crystal size distributions in magmatic systems. *Journal of Petrology* 39:553–

980   599.

981   McCubbin F. M., Elardo S. M., Shearer Jr C. K., Smirnov A., Hauri E. H. and Draper D. S. 2013. A petrogenetic model

982   for the comagmatic origin of chassignites and nakhlites: Inferences from chlorine-rich minerals, petrology,

983   and geochemistry. *Meteoritics and Planetary Science* 48:819-853.

984   McSween Jr H. Y. 1985. SNC meteorites: Clues to Martian petrologic evolution?. *Reviews of Geophysics* 23:391-416.

985   Mikouchi T., Yamada I. and Miyamoto M. 2000. Symplectic exsolution in olivine from the Nakhla Martian meteorite.

986   *Meteoritics and Planetary Science* 35:937–942.

987   Mikouchi T., Koizumi E., Monkawa A., Ueda Y. and Miyamoto M. 2003. Mineralogy and petrology of Yamato

988   000593: comparison with other Martian nakhlite meteorites. *Antarctic Meteorite Research* 16:34–57.

989   Mikouchi T., Makishima J. and Kurihara T. 2012. Relative burial depth of Nakhlites revisited (abstract #2663). 43rd

990   Lunar and Planetary Science Conference. CD-ROM.

991   Mikouchi T., Righter M., Ziegler K. and Irving, A. J. 2016. Petrology, mineralogy and oxygen isotopic composition

992   of the Northwest Africa 10153 Nakhlite: a sample from a different flow from other Nakhlites? (abstract

993   #6396). 79th Meeting of the Meteoritical Society.

994   Mikouchi T., Takenouchi A. and Zolensky M. E. E. 2017. Multiple igneous bodies for Nakhlites and Chassignites as

995   inferred from olivine cooling rates using calcium zoning (abstract #5739). 80th Meeting of the Meteoritical

996   Society.

997   Miller M. F., Franchi I. A., Thiemens M. H., Jackson T. L., Brack A., Kurat G. and Pillinger C. T. 2002. Mass-

998   independent fractionation of oxygen isotopes during thermal decomposition of carbonates. *Proceedings of the*

999   *National Academy of Sciences* 99:10988-10993.

1000   Morse S. A. 1980. Basalts and phase diagrams: An introduction to the quantitative use of phase diagrams in igneous
1001   petrology. *New York: Springer-Verlag*.

1002   Noguchi T., Nakamura T., Misawa K., Imae N., Aoki T. and Toh S. 2009. Laihunite and jarosite in the Yamato 00
1003   nakhlites: Alteration products on Mars?. *Journal of Geophysical Research: Planets* 114:E10.

1004   Nyquist L. E., Bogard D. D., Shih C.-Y., Greshake A., Stoffler D. and Eugster O. 2001. Ages and geologic histories
1005   of Martian meteorites. Chronology and evolution of Mars. *Springer* 105-164

1006   Potin S., Beck P., Bonal L., Schmitt B., Moynier F., Quirico E. and Garenne A. 2018. Post-Accretion History And
1007   Reflectance Spectroscopy Properties Of The Mukundpura Meteorite. *Journal of Geophysical Research*
1008   113:E12008.

1009   Pourkhorsandi H., D'Orazio M. , Rochette P., Valenzuela M., Gattacceca J., Mirnejad H., Sutter B., Hutzler A. and
1010   Aboulahris M. 2017. Modification of REE distribution of ordinary chondrites from Atacama (Chile) and Lut
1011   (Iran) hot deserts: Insights into the chemical weathering of meteorites. *Meteoritics and Planetary Science*
1012   52:1843–1858.

1013   Reid, A.M. and Bunch, T.E., 1975. The Nakhlites part II: Where, when and how. *Meteoritics* 10:317–324.

1014   Richter F., Chaussidon M., Mendybaev R. and Kite E. 2016. Reassessing the cooling rate and geologic setting of
1015   Martian meteorites MIL 03346 and NWA 817. *Geochimica et Cosmochimica Acta* 182:1–23.

1016   Riebe M. E. I., Welten K. C., Meier M. M. M., Wieler R., Bart M. I. F., Ward D., Laubenstein M., Bischoff A., Caffee
1017   M. W., Nishiizumi K. and Busemann H. 2017. Cosmic-ray exposure ages of six chondritic Almahata Sitta
1018   fragments. *Meteoritics and Planetary Science* 52:2353-2374.

1019   Rochette P., Gattacceca J., Chevrier V., Hoffmann V., Lorand J.P., Funaki M. and Hochleitner R. 2005. Matching
1020   Martian crustal magnetization and meteorite magnetic properties. *Meteoritics and Planetary Science* 40:529-
1021   540.

1022 Sautter V., Barrat J. A., Jambon A., Lorand J. P., Gillet P., Javoy M., Joron J. L. and Lesourd M. 2002. A new Martian
1023   meteorite from Morocco: the nakhlite North West Africa 817. *Earth and Planetary Science Letters* 195:223–
1024   238.

1025 Shih C.-Y., Nyquist L. E., Reese Y. and Jambon A. 2010. Sm-Nd isotopic studies of two nakhlites, NWA 5790 and
1026   Nakhla (abstract #1367). 41st Lunar and Planetary Science Conference. CD-ROM.

1027 Toplis M. J. and Carroll M. R. 1995. An experimental study of the influence of oxygen fugacity on Fe-Ti oxide stability,
1028   phase relations, and mineral—melt equilibria in ferro-basaltic systems. *Journal of Petrology* 36:1137-1170.

1029 Treiman A.H. 1986. The parental magma of the Nakhla achondrite: Ultrabasic volcanism on the shergottite parent
1030   body. *Geochimica et Cosmochimica Acta* 50:1061–1070.

1031 Treiman A.H., Barrett R.A. and Gooding J.L. 1993. Preterrestrial aqueous alteration of the Lafayette (SNC) meteorite.
1032   *Meteoritics* 28:86–97.

1033 Treiman A.H., Gleason J.D., and Bogard D.D., 2000. The SNC meteorites are from Mars. *Planetary and Space Science*
1034   48:1213–1230.

1035 Treiman A.H. 2005. The nakhlite meteorites: Augite-rich igneous rocks from Mars. *Geochemistry* 65:203–270.

1036 Treiman A.H. and Iriving A.J. 2008. Petrology of Martian meteorite Northwest Africa 998. *Meteoritics and Planetary*
1037   *Science* 43:829–854.

1038 Udry A. and Day J.M.D. 2018. 1.34 billion-year-old magmatism on Mars evaluated from the co-genetic nakhlite and
1039   chassignite meteorites. *Geochimica et Cosmochimica Acta* 238:292–315.

1040 Wieler R., Huber L., Busemann H., Seiler S., Leya I., Maden C., Masarik J., Meier M. M. M., Nagao K., Trappitsch
1041   R. and Irving A. J. 2016. Noble gases in 18 Martian meteorites and angrite Northwest Africa 7812-Exposure
1042   ages, trapped gases, and a re-evaluation of the evidence for solar cosmic rayproduced neon in shergottites and
1043   other achondrites. *Meteoritics and Planetary Science* 51:407–428.

1044