

Caleta el Cobre 022 martian meteorite: increasing nakhlite diversity

Lisa Krämer Ruggiu, Jérôme Gattacceca, Bertrand Devouard, Arya Udry, Vinciane Debaille, Pierre Rochette, Jean-Pierre Lorand, Lydie Bonal, Pierre Beck, Violaine Sautter, et al.

▶ To cite this version:

Lisa Krämer Ruggiu, Jérôme Gattacceca, Bertrand Devouard, Arya Udry, Vinciane Debaille, et al.. Caleta el Cobre 022 martian meteorite: increasing nakhlite diversity. Meteoritics and Planetary Science, 2020, 55 (7), pp.1539-1563. 10.1111/maps.13534. hal-02983393

HAL Id: hal-02983393 https://hal.science/hal-02983393v1

Submitted on 31 Aug 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1	Caleta el Cobre 022 martian meteorite: increasing nakhlite diversity
2	L. Krämer Ruggiu ¹ , J. Gattacceca ¹ , B. Devouard ¹ , A. Udry ² , V. Debaille ³ , P. Rochette ¹ , JP.
3	Lorand ⁴ , L. Bonal ⁵ , P. Beck ⁵ , V. Sautter ⁶ , H. Busemann ⁷ , M. M. M. Meier ⁷ , C. Maden ⁷ , G.
4	Hublet ³ , R. Martinez ⁸ .
5	
6	¹ Aix Marseille Univ, CNRS, Coll France, IRD, INRAE, CEREGE, Aix-en-Provence, France
7	(kramer@cerege.fr)
8	² Department of Geoscience, University of Nevada Las Vegas, Las Vegas, NV 89154, USA
9	³ Laboratoire G-Time, Université Libre de Bruxelles, Belgium
10	⁴ LPG, CNRS UMR 6112, Nantes Univ., France
11	⁵ Univ. Grenoble Alpes, CNRS, IPAG, Grenoble, France
12	⁶ IMPMC, MNHN, Paris, France
13	⁷ Inst. of Geochem. and Petrol., ETH Zurich, Zurich, Switzerland
14	⁸ Museo del Meteorito, San Pedro de Atacama, Antofagasta, Chile
15	
16	Corresponding author: <u>kramer@cerege.fr</u>
17	
18	Keywords: nakhlite, martian meteorite, SNC
19	
20	

Abstract

21

22

23

24

25

26

27

28

29

30

31

32

33

34

35

36

37

38

39

40

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

41

42

43

44

45

46

47

48

49

50

51

52

53

54

55

56

57

58

59

60

61

62

63

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 ⁸⁷Rb/⁸⁶Sr, ¹⁴⁷Sm/¹⁴⁴Nd, ³⁹Ar/⁴⁰Ar and ¹⁷⁶Lu/¹⁷⁶Hf (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 finegrained 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 Bridges 2010) and have been tentatively dated around 633±23 Ma with K-Ar system (Borg and Drake, 2005 and references therein).

The formation of the nakhlites started with low-degree partial melting of a long-lived, trace element depleted source that occurred at around 1.34 Ga (McCubbin et al., 2013). The cumulus part of the nakhlites with coarse subhedral crystals suggests slow growth over a long period of time (Lentz et al., 1999) at low pressure in a shallow magma chamber (Day et al. 2006). In contrast, the intercumulus material is composed either of fine-grained mesostasis attesting a relatively fast cooling, or coarse plagioclase crystallized under lower cooling rates. Indeed, nakhlites final cooling would have taken place at the martian surface over short periods of time from 5 to 184 days (Day et al., 2006; Udry and Day, 2018), with cooling rates from 1 to 6°C/hr based on zoning in olivine (Sautter et al., 2002) and intercumulus crystals surface area to volume (Hammer and Rutherford 2005). After emplacement as sill or flow, crystal gravitational settling and compaction, as well as dynamical sorting of a phenocryst-rich magmatic mush (Corrigan et al., 2015; Day et al., 2006) and flow dynamics (Daly et al., 2019) have shaped the final texture of nakhlites, based on petrographic textural evidence.

The comparable crystallization ages and ejection ages of nakhlites led to the hypothesis of a suite of igneous rocks originating from a single martian volcanic system. The most widely accepted model for the petrogenesis of nakhlites is that the cumulus phases crystallized at depth followed by emplacement at the surface as a flow or shallow subsurface sill (Bunch and Reid 1975; Treiman 1986; Lentz et al., 1999; Mikouchi et al., 2003; Day et al., 2006; Mikouchi et al., 2012, 2017; Richter et al., 2016; Udry and Day, 2018). All previously studied nakhlites present slight differences in their modal abundances, intercumulus material and minor minerals, mineral chemistry, crystallinity, rare earth element (REE) enrichment and Ar-Ar ages, which led to various models of emplacement. Based on differences in mineralogy and textures, a stratigraphy of

nakhlites within a single cumulate pile was first proposed (Treiman, 1986; Mikouchi et al., 2003, 2012; Treiman, 2005; Bridges and Warren, 2006; Day et al., 2006; McCubbin et al., 2013; Corrigan et al., 2015). Based on textural and chemical compositional differences among the various nakhlites, Jambon et al. (2016) proposed nakhlite emplacement in at least three different flows piled on top of one another from Miller range (MIL) 03346 at the uppermost part of the pile, down to Northwest Africa (NWA) 5790. Based on geochemistry and petrography, Balta et al. (2017) proposed another model with one body chamber and two separated lobes. Cohen et al. (2017) proposed a model of multiple flows using geochronological evidences supporting a layered volcanic sequence with at least four discrete eruptive events. Recently, Udry and Day (2018) proposed in a comprehensive study that nakhlites originated from at least six different lava flows or sills, distributed around one or several volcano vents.

Caleta el Cobre 022 was approved by the Meteoritical Society Nomenclature Committee in April 2018. It is the 11th unpaired nakhlite (the only one from Atacama Desert) and brings new information to help constrain the diversity, stratigraphy and emplacement conditions of the nakhlite group. This paper is focused on the description of this new nakhlite (petrology, mineralogy and geochemistry) and its comparison with previously studied nakhlites. We observe that CeC 022 combines evidence for both high and low cooling rates, with features never observed in other nakhlites. This will open discussion on the crystallization conditions of cumulus minerals, the crystallization sequence and the relation of CeC 022 with the other nakhlites.

2. Analytical Methods

Petrographic observation and elemental micro-analyses were performed on three thick polished 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 BH₂ 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

distances using the density of the observed distribution. The CSD and SDP analyses were conducted for the pyroxene population of the thin section (C). Pyroxene grains were hand-drawn in *Adobe Illustrator* using mosaic pictures in transmitted and reflected light, X-ray elemental maps and an optical microscope to distinguish grain boundaries. We used the *ImageJ* software to obtain the area of each crystal, the total area of the section, the major and minor axes of ellipses, as well as the centroid location. We followed the same quantitative textural methods as the one described in Udry and Day (2018).

2.3. Physical properties

Grain density was measured with a Quantachrome helium steropycnometer at Centre Européen de Recherche et d'Enseignement en Géosciences de l'Environnement (CEREGE). Magnetic susceptibility was quantified with MFK1 or KLY2 instruments depending on sample size. Curie temperatures were estimated by measuring the variation of susceptibility with temperature with a CS3 furnace on the MFK1 susceptibility meter. Saturation magnetization was determined with a Princeton model 2900 Micromag vibrating sample magnetometer. All magnetic measurements were performed at CEREGE.

2.4. Mineral major and minor elements

Backscattered electron (BSE) images, microanalyses by energy dispersive spectroscopy (EDS) and chemical maps were acquired with a Hitachi S3000-N SEM operated at 15 kV and equipped with a Bruker X-ray X-Flash detector and a Spirit analyzer at CEREGE, France. Semi-quantitative analyses used a variety of natural and synthetic standards. Additional field emission gun (FEG) SEM images were obtained on a ZEISS Gemini 500 SEM operated at accelerating voltages from 5 to 15 kV at Centre Pluridisciplinaire de Microscopie Electronique et de Microanalyse (CP2M), Marseille. Compositions of sulfides were assessed at the National Museum of Natural History

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

Quantitative major element analyses were conducted using an electron microprobe (EMP) Cameca SX100 at UPMC CAMPARIS facility. The operating conditions were 15 kV accelerating voltage with a current of 10 nA and a counting time of 30 s, with a focused beam (1 μm) for pyroxene, olivine, plagioclase and apatite, and defocused beam (5 μm) for fine-grained mesostasis and alteration phases. Both natural and synthetic standards were used for calibration: albite for Na; anorthite for Al; apatite for P; diopside for Mg, Si, Ca; orthoclase for K; pyrite for S; MnTiO₃ for Mn and Ti; Cr₂O₃ for Cr; Fe₂O₃ for Fe; and NiO for Ni. The detection limits are (in ppm): 445 for 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, 496 for Cr, 1271 for Fe, and 1331 for Ni.

Sulfide microphases were analyzed at 15 kV accelerating voltage by a PhiRhoZ EDS standardless procedure. Accuracy of our SEM analytical procedure analyses was checked by

sulfide microphases were analyzed at 15 kV accelerating voltage by a PhiRhoZ EDS standardless procedure. Accuracy of our SEM analytical procedure analyses was checked by repeated analysis of a Del Norte County-DNC (Oregon, USA) natural troilite (stoichiometric FeS), a well-known terrestrial troilite occurrence previously studied by X-ray diffraction and repeatedly analyzed by EMPA and SEM (Chevrier et al., 2011, Lorand et al. 2012, Gattaceca et al., 2013). Gattaceca et al. (2013) shown that the SEM analyses of DNC troilite perfectly match the composition of stoichiometric troilite (FeS). Our own analyses yielded a mean atomic Fe+Ni/S ratios (metal-to-sulfur ratios) of 1.0 ± 0.01 (Figure S2). DNC troilite was used as external calibration standard and analyzed every 10 to 15 analyses to evaluate potential drifts on metal-to-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% HNO₃. 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 HNO₃ and left 2 days on hot plate at 120°C using high-pressure vessels. After drying, the

fractions were re-dissolved using 12N HCl until the solutions were clear. A 5% aliquot was removed from the initial dissolution and spiked using ¹⁵⁰Sm-¹⁴⁸Nd spike. REE were first purified using cationic resin, being collected in HCl 6N. For both spiked and unspiked cuts, the REE were further separated using HDEHP resin by increasing the HCl molarity for collecting Nd and spiked Sm. The whole rock fraction was further purified for ¹⁴²Nd measurements. First, Ce was removed by using HDEHP resin after oxidation of Ce using NaBrO₃. The added Na was then cleaned out using cationic resin, similarly to the first purification step. All fractions but the whole rock one, spiked and unspiked, were measured on the HR-MC-ICP-MS Nu-Plasma 2 using an Aridus dessolvator, using 0.05N HNO₃. Spike deconvolution was performed off-line by iteration as described in Debaille et al. (2007). The unspiked fraction were corrected for a Rennes standard value of 143Nd/144Nd of 0.511961 (Chauvel and Blichert-Toft, 2001). Total reproducibility including standards ran at 20 and 5 ppb (n=24) is better than 50 ppm (2σ). The whole rock fraction was measured on the Thermoscientific Triton Plus at ULB in multidynamic mode as in Debaille et al. (2007). The Rennes standard (n=3) gave a value of 0.511957 ± 0.000002 and no correction was required for comparison with the data set measured on the MC-ICP-MS.

200

201

202

203

204

205

206

207

208

209

210

211

212

213

214

215

216

217

218

219

220

221

Oxygen isotopes were measured at the Stable Isotopes Laboratory of CEREGE. Molecular oxygen was extracted using laser fluorination. Aliquots of 1.5 mg obtained from a bulk 12 mg powdered samples were heated with a 30 W CO₂ IR laser in the presence of 100 hPa of BrF₅. The released gas was purified through two cryogenic nitrogen traps and one heated KBr trap. Molecular oxygen was trapped for 10 mn in a molecular sieve cooled at -196°C. The gas was then expanded at 100°C and passed through a molecular sieve cooled at -114°C slush for 5 mn to refreeze possible interfering gases. The gas was then trapped again for 5 mn in the molecular sieve cooled at -196°C,

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

The isotopic compositions are expressed in standard δ -notation, relative to Vienna standard mean ocean water (VSMOW): $\delta^{18}O = (^{18}O/^{16}O)_{sample}/(^{18}O/^{16}O)_{vSMOW} - 1$ and $\delta^{17}O = (^{17}O/^{16}O)_{sample}/(^{17}O/^{16}O)_{vSMOW} - 1$ (expressed in ‰), $\Delta^{17}O$, also expressed in ‰, is defined as $\delta^{17}O - \lambda \times 0.5247$ $\delta^{18}O$. For comparison with previous data obtained on Martian meteorites (Franchi et al. 1999), we use $\lambda = 0.52$. Measured $\delta^{18}O$ and $\delta^{17}O$ values of the samples were corrected daily using the laboratory quartz standard itself calibrated against the international standard NBS28 ($\delta^{18}O = 9.60$ ‰, $\delta^{17}O = 0.52 \times \delta^{18}O = 4.992$ ‰). Reproducibility (1 sigma) of the quartz laboratory standard are 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‰.

2.8. Secondary alteration phases analyses

Infrared (IR) spectroscopy was performed at the Institut de Planétologie et d'Astrophysique de Grenoble (IPAG) using the SHADOWS instrument (Potin et al., 2018). The instrument was used in normal standard mode as well as in a μ -beam mode enabling measurements of IR reflectance spectra of areas of the order of 3 mm². Spectra were measured under nadir incidence and with an observation angle of 30°. Spectra were normalized to infragoldTM and spectralonTM. The Raman experiments were performed at Laboratoire de Géologie de Lyon (ENS Lyon – France) using a Labram HR800 spectrometer equipped with a Nd ion laser providing 532 nm excitation. The laser spot is <2 μ m with the used x100 microscope objective. Individual spectra were acquired at various locations in veins of iddingsite, optically localized throughout the sections A and B of CeC 022.

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/cm³. 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} m³/kg. Saturation magnetization is 1.51 Am²/kg. Saturation remanent magnetization is 4.59 10^{-1} Am²/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

Pyroxene

Clinopyroxene is the major mineral with 52.3-60.3 vol% (average 56.5 vol% among four sections) (Table 1) and measure on average 0.27 mm (up to 2 mm). On BSE images, they present an irregular zoning with rounded cores and a Fe-rich euhedral rim (Fig. 2), surrounded by a thin, sharply delimited Fe-enriched overgrowth, when in contact with the mesostasis. The zoning can be discontinuous or gradual, depending on the orientation of the grains. The sharp overgrowth, usually 10-15 µm wide, gets thinner or absent when in contact with other phenocrysts (pyroxene, plagioclase, titanomagnetite, or olivine). Some rounded clinopyroxene (~100 µm) can be found included inside olivine crystals. Also, smaller clinopyroxene (~10 µm) with Fe-oxides are found in linear planes of inclusions, or exsolutions, in the olivine (Fig. 3). Low-Ca pyroxenes (up to 100 µm, Fig. 2) were frequently observed adjacent to olivine crystals, sometimes presenting augite irregular cores. Based on grain boundary geometries, low-Ca pyroxene appears to have crystallized after augite rim and olivine.

Olivine

Olivine crystals represent 2.0-8.9 vol% (average 4.2 vol% among four sections) with a maximum measured grain size of 2.5 mm and an average length of 0.66 mm (Table 1). They do not display a euhedral shape, rather a resorbed border. They do not show any zoning on BSE images (Fig. 4). They display large melt inclusions up to 100 µm, rich in Na-K feldspars and apatite. Olivine crystals present high abundance (45.1 vol%) of aqueous alteration products (iddingsite) found in crosscutting veins and sometimes extending to the edge of the olivine and the mesostasis 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

Ti-magnetite, low-Ca pyroxene, apatite and ilmenite. Most oxides in the mesostasis are skeletal Ti-magnetite. Apatite is mainly found as small elongated euhedral crystals embedded in the feldspar. Adjacent to the olivine grains, apatite displays larger sizes (up to $700 \, \mu m$ long) in association with pigeonite rims (Fig. 7). Fine-grained pyrrhotite is hosted in the microcrystalline mesostasis, along with skeletal Ti-magnetite.

3.2.3. Terrestrial weathering

Terrestrial weathering is minimal on CeC 022. The meteorite shows a fresh black fusion crust with few alteration products (Fig. 1). Caleta el Cobre 022 is a highly fractured rock (Fig. 1, Fig. 3, Fig. 4). On BSE images, we observed that those fractures are devoid of terrestrial alteration products (e.g., Fig. 1, Fig. 3, Fig. 4), such as evaporite minerals that are classically encountered in meteorites weathered in hot deserts (Bland et al. 2006). Terrestrial weathering is observed only close to the fusion crust and is minimal. It is found as partly altered sulfides and pyrrhotite cracks invaded by iron oxyhydroxides.

3.3. Quantitative textural analyses

We measured a total of 2103 pyroxene grains and obtained a R^2 of 0.88 (Table S1.). Caleta el Cobre 022 pyroxene population displays a best habit ratio of 1.00:1.25:1.80 and shows a CSD slope of -5.31 \pm 0.09 mm⁻¹, with an intercept of 6.04 \pm 0.05 (Fig. 8). A downturn for the smaller sizes (<0.03 mm) is observed. Spatial distribution analyses show that the pyroxene population of CeC 022 has an R-value of 1.277 and falls within the cluster touching framework, similar to the other nakhlites (Fig. S3, Table S1).

3.4. Geochemistry

3.4.1. Phenocrysts

Pyroxenes

Electron microprobe analyses reveal augite cores range in composition from $En_{32}Fs_{30}Wo_{38}$ to $En_{36}Fs_{24}Wo_{40}$ (average $En_{33}Fs_{27}Wo_{40}$) and FeO/MnO=35-45 with Mg# [=100 x (Mg/(Fe²⁺ + Mg))] = 55 (Table 2, Fig. 9). They are surrounded by augite richer in Fe of average composition $En_{31}Fs_{29}Wo_{40}$ (Mg# ~ 52). Microprobe traverse analyses across augite crystal reveal that Al, Ti and Mn anticorrelate with Mg#. In contrast, Ca and Cr show a correlation with Mg#, increasing from the rim to the core of the augite, and Na shows no variation throughout the crystal. Augite crystals have relative low Al, Ti and Na concentration (Al₂O₃ = 1.1 \pm 0.1 wt%; TiO₂ = 0.4 \pm 0.1 wt%; Na₂O = 0.3 \pm 0.1 wt%), comparable to terrestrial pyroxene crystallized at low pressure (Harvey and McSween, 1992). The thin overgrowth around the augite rim shows Fe-rich compositions going up to $En_{30}Fs_{31}Wo_{39}$ (Mg# of ~49). This overgrowth is also more enriched in MnO (up to 0.6 wt%), Al₂O₃ (up to 1.5 wt%) and TiO₂ (up to 0.6 wt%), but poorer in Na and Ca. In the olivine, planes of inclusions contain Fe-oxides and augites of composition $En_{31}Fs_{26}Wo_{43}$, similar to cumulus augite irregular cores (Fig. 3).

Low-Ca pyroxenes differ from augite by their texture as well as their composition. They are found adjacent to olivine crystals (Fig. 2, Fig. 7). Their augite core compositions are similar to those previously described, but the low-Ca pyroxene overgrowth around the cores has a composition of $En_{36}Fs_{60}Wo_4$ (Fe/Mn = 28; Mg# 38) (Table 2, Fig. 9). The low-Ca overgrowths show an enrichment in Fe, Mn and Mg and lower Ti, Al and Na, compared to the augite pyroxene.

Olivine

Olivine compositions show no zoning, with an average composition of $Fo_{30.3}$ (FeO/MnO = 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 Al₂O₃ (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 $\delta^{18}O=4.683\%\pm0.428\%,\ \delta^{17}O=2.683\%\pm0.210\%$, and $\Delta^{17}O=0.248\pm0.013\%$ (mean \pm 1σ).

3.5. Alteration products

3.5.1. Petrography

The main martian alteration products in CeC 022 occur in olivine phenocrysts as a reddishorange phase in optical microscopy in transmitted light. This material is found mainly as veins along cracks in the olivine with Fe-oxides and sulfides situated at the center of the veins, but it can also be located as patches in the mesostasis. This alteration product has already been described in nakhlites under various names such as iddingsite, smectite, illite, saponite, siderite, sulfates (Bunch et al., 1975; Reid and Bunch, 1975; Boctor et al., 1976; Gooding et al. 1991; Gooding, 1992; Treiman et al., 1993; Bridges et al., 2000; Gillet et al. 2002). Caleta el Cobre 022 contains a high abundance of iddingsite, replacing 45.1 vol% of the crystals, found mainly in crosscutting veins inside olivine. A noteworthy feature of CeC 022 is the occurrence of pyrrhotite and Fe-oxides clusters or stringers inside iddingsite veins across olivine (Fig. 4, Fig. 6, Fig. 14). Also, a few deeply altered former sulfides were observed in the vicinity of olivine grains, coexisting with iddingsite aggregates. Such ovoid grains are made from highly porous iron oxyhydroxides-like phases showing detectable amount of sulfur (EDS spectra) (Fig. 6F).

Backscattered electron images reveal two types of iddingsite found in association with each other (Fig. 14). Energy dispersive spectrometry (EDS) and EMP analyses show that a brighter type of iddingsite in contact with olivine in the BSE image is enriched in Fe and Mn (~52 wt% FeO) and is poorer in Si (~27 wt% SiO₂), Mg and K, compared to the darker type (~30 wt% FeO and ~50 wt% SiO₂) (Table 5). Low totals (<90 wt%) of the EMP analyses suggest that these phases are hydrated. The Fe-rich type of iddingsite has a Raman spectrum exhibiting well defined and narrow bands in contrast to the spectrum related to the Si-rich type. The Fe-rich iddingsite is also associated, at the micron scale, with a few oxides, possibly hematite or magnetite and possibly carbonates or pyroxene (Fig. S4, right). The wide and poorly defined Raman bands exhibited by the Si-rich iddingsite reflect a degree of crystallization lower than in Fe-rich type (Fig. S4, right). Raman spectroscopy reveals that the Si-rich type of iddingsite is a poorly crystallized hydrated

assemblage of minerals (Fig. S4, right). Both Raman and IR (Fig. S4) spectroscopy show weak bands of carbonate and/or phyllosilicate and H_2O bending and H_2O + OH stretching modes, evidencing the hydration of these alteration products. Raman spectra show that each type of iddingsite is homogenous throughout the sample, independent of the location in the meteorite.

3.6. Geochronology

3.6.1. Sm-Nd systematics and crystallization age

The crystallization age of CeC 022 has been measured at 1215 ± 67 Ma using a Sm-Nd isochron using the Isoplot software (MSWD of 1.2). The initial 143 Nd/ 144 N using Isoplot is 0.511600 ± 0.000069 (Table S3). Expressed in 10^4 deviation to the chondritic average, this corresponds to an ϵ^{143} Nd(i) of $+10.4 \pm 1.4$, similar to the ϵ^{143} Nd(i) measured on the bulk rock fraction, of $+10.5 \pm 0.1$. Concerning the 142 Nd systematics, expressed in 10^6 deviation to the average modern Earth, the μ^{142} Nd of CeC 022 is equal to $+56 \pm 3$.

3.6.2. Ejection age

Results of the noble gas measurements are given in Table S4. The measured He and Ne isotope ratios indicate that there is no trapped component in He and Ne. Hence, the measured 3 He, 21 Ne and 21 Ne/ 22 Ne are entirely cosmogenic. The (inverse) shielding indicator (21 Ne/ 22 Ne)_{cosm} of 0.831 ± 0.06 is low. This value suggests low shielding in a small meteoroid, which is often observed for rare meteorites, particularly martian ones (Wieler et al. 2016). Also, the presence of some solar cosmic ray (SCR)-derived Ne cannot be excluded (Wieler et al. 2016). However, using the Mg / (Al + Si) vs. 21 Ne/ 22 Ne diagram (Wieler et al., 2016), SCR-Ne is most likely not predominant. Nevertheless SCR-Ne could still cause some overestimation of the Cosmic Ray Exposure (CRE) ages and underestimation of shielding. The 36 Ar/ 38 Ar ratio in CeC 022 is 0.773 and hence close to

the expected pure cosmogenic composition of ~0.65 (e.g., Wieler et al., 2016) and a correction for trapped, e.g. atmospheric, ³⁸Ar would be in the order of 2-3%. Trapped ³⁸Ar is thus negligible compared to the other uncertainties related to the determination of CRE ages.

Apart from 129 Xe/ 132 Xe, the Kr and Xe isotopic compositions are consistent with a mixing of air with — in the light isotopes — cosmogenic Kr and Xe. The presence of a small martian trapped component is visible only in the 129 Xe/ 132 Xe ratio = 1.02 ± 0.01 . Similarly, the trapped element ratio 36 Ar_{tr}/ 132 Xe (4.2 ± 1.3) is very low suggesting significant Xe from air, in agreement with the Xe isotopes. The ratios 84 Kr/ 132 Xe (1.25 ± 0.05) and 129 Xe/ 132 Xe are consistent with previous results for nakhlites and suggest essentially no trapped martian component but merely "Earth fractionated atmosphere" (cf. Fig 3A, Cartwright et al. 2014). The 3 He, 21 Ne and 38 Ar CRE ages of CeC 022 were determined with physical model predictions for cosmogenic noble gas production (Leya and Masarik, 2009) based on the chemistry (Table 4) and the shielding conditions constrained by the shielding parameter given above. As a somewhat arbitrary but safely conservative assumption, we used radii \leq 85 cm. Most "allowed" shielding depths, based on 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 11.4 ± 0.6 Ma, 9.9 ± 1.6 Ma and 11.8 ± 2.7 Ma, respectively, where the uncertainties include the range of allowed shielding conditions and experimental errors.

If using a model specifically created for very small shergottites (see Wieler et al., 2016, based on the original model by Leya and Masarik, 2009), only one shielding condition would be allowed: a perhaps more realistic 7 cm pre-atmospheric radius and 6.4-6.6 cm depth (which excludes any contribution from of SCR). Using that model, the age would slightly increase, to 12.3 ± 0.2 Ma, 10.9 ± 0.1 Ma and 14.2 ± 3.3 Ma, respectively. We consider the later data set more reliable and our preferred CRE combined age for CeC 022 is 11.8 ± 1.8 Ma.

4. Discussion

4.1. Martian origin for CeC 022

444

445

446

447

448

449

450

451

452

453

454

455

456

457

458

459

460

461

462

463

464

465

466

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/cm³, 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%), Al₂O₃ (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; Na₂O/Al₂O₃ = 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

compared to the 50-100 mg used by Franchi et al. (1999). Caleta el Cobre 022's crystallization age of 1.215 \pm 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,

originate from the relatively small mass of the initial bulk sample used in our analyses (12 mg),

2018). The ejection age of CeC 022 is measured around 11 Ma is similar to other nakhlites (Herzog and Caffee, 2013). Therefore, CeC 022 was sampled by the same ejection event as the other nakhlites.

4.2. Petrogenesis

4.2.1. Cumulus crystallization

In a first stage of crystallization, pyroxene cores (Mg# 55) grew in a cumulate layer (Jambon et al., 2016) before the later stage of euhedral rim and overgrowth. These augite cores come from early crystallization of relatively evolved Fe-rich mafic melt, probably in a magma chamber (Imae et al., 2005; Sautter et al., 2002; Jambon et al., 2016). A new injection of magma, with a different composition than the augite cores, could have created a disequilibrium, shown by the resorbed rounded irregular boundaries of the augite cores (Fig. 2). This injection could have enabled the crystallization of the euhedral augite rims, with a composition slightly enriched in Fe and relatively depleted in Mg (Mg# 52) (Table 2). Those euhedral augite with enriched Fe composition could also be explained by a slight drop of the temperature that creates an enrichment in Fe in the minerals (Fig. 15) but would not explain the resorbed rounded cores. Thus, those irregular rounded cores could be rather interpreted as sector zoning or patchy zoning in augite. In both cases, the conservation of zoning indicates that augites cooling was fast enough to preclude diffusive homogenization during augite rim crystallization.

Olivine in CeC 022 could have crystallized at the same time as euhedral augite. Olivines in CeC 022 are not zoned and their compositions are homogenous throughout the sample with a Ferich composition (Table 3). This agrees with Treiman (2005) who noticed that homogenous olivines are the most ferroan in nakhlites. The sharp petrographic contact between olivine and 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), oliving 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.

490

491

492

493

494

495

496

497

498

499

500

501

502

503

504

505

506

507

508

509

510

511

512

513

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.

Sulfides in CeC 022 occur in unusually high amount (0.15±0.05 vol.%) compared to other nakhlites and show textural evidence for sulfide mobility and reactivity. The numerous occurrences of sulfide blebs around and inside olivines may reflect a population of sulfide perhaps entrained from deeper levels. In some cases, pyrrhotite-magnetite clusters were brecciated, which may be a shock-related feature. Previous work on MIL's nakhlites has suggested that such large, subrounded pyrrhotites, here almost systematically surrounded by magnetite, locally altered, may represent a sulfide population of crustal origin assimilated during magmatic emplacement of the nakhlites and are thus unstable in the matrix (Day et al., 2006; Franz et al., 2014)

4.2.2. Secondary alteration

Caleta el Cobre 022 exhibits one of the most extensive amounts of aqueous alteration products reported in nakhlites (45.1 vol% of olivine crystal replaced by veins of alteration products), resembling NWA 10153 in that regard (around 45.2 vol%). These alteration products, called iddingsite, are assumed to be pre-terrestrial in this study on the basis of the close similarity to iddingsite in other nakhlites, such as Nakhla and Lafayette that contain iddingsite veins truncated by the fusion crust, which prove their extra-terrestrial origin (Gooding et al., 1991; Treiman et al., 1993, Hicks et al., 2014).

In CeC 022, at least two types of iddingsite are detected: alteration veins in olivine and patches in mesostasis pockets. The latter are interpreted as relicts of olivine grains in the mesostasis. The Raman analyses reveal a poorly crystalline type and a more crystalline type (Fig. S4). EDS analyses show that in comparison, the less crystalline phase is silicon-rich (~50 wt% SiO₂) and the more crystalline is iron-rich (~52 wt% FeO). Both Raman and IR measurements reflect hydrated alteration phases (Fig. S4). Also, the mesostasis shows alteration into iddingsite at the micrometer scale (Fig. 16), which has been also observed in other nakhlites, but rarely studied compared to

iddingsite veins in olivine (Treiman et al., 2005; Daly et al., 2019). The sulfide and oxide stringers, found inside iddingsite veins cross-cutting olivine, indicate that the fluid responsible for this alteration event on Mars could also have transported reduced sulfur inside the nakhlites, after completion of igneous crystallization of CeC 022. Our observation are consistent with previous reports of magmatic sulfides oxidation to sulfate during weathering on Mars during episodic periods of water activity in the vicinity of the nakhlite parent rock that precipitated iddingstite/smectite as recently as 600-650 Ma (Franz et al., 2019 and reference therein). We may surmise that hydrothermalism could have been able to transport sulfur inside the nakhlite while bringing the water that was involved in local replacement of intercumulus sulfides of igneous origin by iron oxyhydroxide-like phases.

4.3. Geochronology and isotope systematics

Caleta el Cobre 022 crystallization age was determined at 1.215 ± 0.067 Ga (Sm-Nd). Considering only Sm-Nd ages, CeC 022 appears to be slightly younger than the three other nakhlites dated by Sm-Nd (Nakhla, Lafayette and Governador Valadares) with an age range of $1.26 \pm 0.07 - 1.37 \pm 0.02$ Ga (Nyquist et al., 2001), close to Nakhla within errors. With nakhlite crystallization ages ranging from 1.26 to 1.42 Ga (from compilations of Sm-Nd, K-Ar, 40 Ar- 39 Ar, Rb-Sr, U-Th-Pb data, from Udry and Day, 2018), CeC 022 could be one of the youngest nakhlites found yet. More recently, Cohen et al., 2017 presented an exhaustive study of 40 Ar- 39 Ar dating of nakhlites, proposing four geochronologically distinct eruptions, the youngest age being Lafayette with 1.321 ± 0.009 Ga. While the origin of the systematic offset between older 40 Ar- 39 Ar ages and younger ages obtained with other dating system is not clear, CeC 022 could be the youngest nakhlite found yet and may extend the nakhlite eruptive sequence by about 50 Myr. As only one radiochronologic system has been measured here and because different isotopic systems could lead

to different ages for a given nakhlite (Nyquist et al., 2001), this statement should be taken with precaution. Thus, the comparison of CeC 022's Sm-Nd age with ⁴⁰Ar-³⁹Ar ages is tentative and ⁴⁰Ar-³⁹Ar dating of CeC 022 is highly desirable.

583

584

585

586

587

588

589

590

591

592

593

594

595

596

597

598

599

600

601

602

603

604

605

The initial value of ε^{143} Nd = +10.5 ± 0.1, is clearly lower than the other nakhlites, with an average of ϵ^{143} Nd = +15.7 ± 1.4 (2SD), from 14.6 ± 0.1 to 16.9 ± 0.1 (Caro et al., 2008; Debaille et al., 2009). As demonstrated by the positive anomaly in Ce, this lower ε^{143} Nd could be related to terrestrial contamination in the Atacama Desert. However, the μ^{142} Nd of CeC 022, of +56 \pm 3, is very similar to other nakhlites, with $\mu^{142}Nd$ from +51 to +67 (Caro et al., 2008; Debaille et al., 2009). Therefore, the decoupling between ¹⁴³Nd and ¹⁴²Nd systematics rules out terrestrial disturbance of the Nd systematics as alteration would shift them concomitantly and the 142Nd systematics are identical to other nakhlites. Instead, this decoupling favors a slight change in the source of nakhlite, possibly with time and/or metasomatic agent (McCubbin et al., 2013). However, in any case, the contaminant agent must somehow be related to nakhlites. Indeed, the ¹⁴²Nd systematics were established during the first 500 Myr of Mars geological history (while ¹⁴⁶Sm was extinct) and could not have varied since then, except by mixing with another source. In this case, it would mean that the second source would have had exactly the same ¹⁴²Nd value, which is highly unlikely. One possibility to reconcile the nakhlite-like ¹⁴²Nd but slightly lower ¹⁴³Nd of CeC 022 would be that it is actually contaminated by older nakhlites that evolved towards lower ε^{143} Nd during the time between their emplacement and the emplacement of CeC 022. Considering the ¹⁴⁷Sm/¹⁴⁴Nd ratios of nakhlites, a nakhlite-like sill or flow emplaced at least 700 Myr before CeC 022 would be able to generate a ε^{143} Nd low enough to decrease the ¹⁴³Nd systematics of CeC 022, without changing its REE and 142Nd systematics. This hypothesis is however impossible to test with the current sampling of the nakhlite magmatic system.

The shielding indicator (21 Ne) 22 Ne)

4.4. Relation with other nakhlites

4.4.1. Nakhlites typology

Independently of the different models of emplacement into a single pile (Treiman, 1986; Mikouchi et al., 2003, 2012; Treiman, 2005; Bridges and Warren, 2006; Day et al., 2006; McCubbin et al., 2013; Corrigan et al., 2015) or different units (Jambon et al., 2016; Balta et al., 2016; Cohen et al., 2017; Udry and Day., 2018), nakhlites can be divided into two subgroups based on mineralogy, mineral compositions, REE bulk composition, rock texture and CSD: the slower-cooled nakhlites and the faster-cooled nakhlites.

The faster-cooled subgroup comprises NWA 817, MIL's nakhlites, NWA 10645 and NWA 5790. They show zoned olivine with a large range of composition Fo₅₅-Fo₉₅ (Fig. 10). Pyroxenes show patchy zoning in NWA 10645 (Udry and Day, 2018) and in NWA 5790 (Jambon et al., 2016), with a similar Fe-rich composition (Table 6). They also display Fe-rich overgrowth on augite phenocryst in contact with the mesostasis, produced by rapid cooling of the last residual melt. The zoning observed in pyroxene and olivine is retained due to rapid cooling preventing diffusive homogenization. The mesostasis of faster-cooled nakhlites show quenched oxides with skeletal morphology and fine-grained feldspar, both characteristics of high cooling rates.

The slower-cooled subgroup is composed of Nakhla, Lafayette, Governador Valadares, NWA 998, Yamato (Y) 000593 and the pairing group of NWA 10153 (NWA 11013, NWA 10153, NWA 10659 and NWA 10720; Udry and Day, 2018). They present unzoned olivine due to diffusion homogenization enabled by slow crystallization. They also show oxide phenocrysts formed through slow crystallization, in contrast to quenched oxides in faster-cooled nakhlites. The intercumulus materials is mainly composed of coarse plagioclase with very little microcrystalline mesostasis, or none.

In addition, REE composition of nakhlites reflects these two different subgroups. The nakhlites with higher cooling rates have a higher content of REE, except for NWA 10113, compared to the nakhlites showing lower cooling rates features, which have lower REE content (Fig. 13), as mentioned by Udry and Day (2018). This grouping is also comparable to the mesostasis grouping by Corrigan et al. (2015), who used modal abundance of major phases and McCubbin et al. (2013) who worked on volatile-bearing minerals morphology and composition to present a model of crystallization sequence of the nakhlites.

Caleta el Cobre 022 shows evidence of rapid cooling, as seen in the faster-cooled subgroup and at the same time, shows features consistent with a lower cooling rate, similar to the slower-cooled subgroup. Caleta el Cobre 022 uniqueness is the coexistence of those characteristics of both lower and higher cooling rates.

4.4.2. Slower-cooled nakhlite characteristics

Olivine

Caleta el Cobre 022 presents a low content of olivine (4.2 vol%), being the second olivine-poorest nakhlite after NWA 10645 (1.2 vol%). Olivines in CeC 022 are the second most fayalitic analyzed (Mg# 30), after the exception of NWA 10645 (Mg# 22), also close to the composition of

Lafayette (Mg# of 34) and NWA 998 (Mg# of 36), both slower-cooled nakhlites (Table 7, Fig. 10). Also, olivines do not show any zoning, as seen only in the olivines of NWA 998 and Lafayette, a characteristic explained by a stage of diffusion at low cooling rates.

Pyroxene rims

The large rims of augite richer in Fe around the irregular cores of augite show similar mineral compositions ($En_{31}Fs_{29}Wo_{40}$, $Mg\# \sim 52$) as in the slower-cooled nakhlites, such as the Nakhla subgroup (Udry and Day, 2018) (Fig. 9). Also, as seen in both slower and faster-cooled nakhlites, like Nakhla and NWA 817 (Treiman, 2005), pyroxenes are also observed as rounded inclusions ($\sim 100 \, \mu m$) in olivine crystals (Fig. 4).

Plagioclase

Caleta el Cobre 022 contains a high proportion of millimeter-sized plagioclase grains (19 vol%), also seen in NWA 10153 (32 vol%) and NWA 998 (10.5 vol%) (Table 1). The compositions of those plagioclase are also comparable within errors, for example An₃₅Ab₆₁Or₄ for NWA 10153 and An₂₅Ab₇₂Or₃ for NWA 998 and An_{29.7±4.3}Ab_{67.2±4.0}Or_{3.1±0.5} for plagioclase in CeC 022 (Fig. 11). Those coarse plagioclases are only seen in slower-cooled nakhlites as intercumulus material, and are characteristic of slower crystallization of the last melt, in contrary of fine-grained mesostasis, created by rapid cooling of the last melt.

Pyroxene overgrowth

The fine overgrowth of Fe-rich augite is found on the euhedral augite rim and only when in contact with the mesostasis. This stage of final fast cooling is observed on all nakhlites, but the compositions of this pyroxene sharp overgrowths and intercumulus pyroxenes found in the mesostasis are similar to the subgroup of slower-cooled nakhlite Governador Valadares and Nakhla but richer in iron (up to En₃₅Fs₆₁Wo₄) (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).

The sulfide droplets inside skeletal mesostasis minerals coupled with Ni-free pyrrhotite were described in faster-cooled nakhlites as NWA 817 (Chevrier et al., 2011) and MIL's nakhlites (Day et al., 2006; Dottin et al., 2018). Similarly, the high sulfide content, coupled with Ni-free pyrrhotite compositions in CeC 022, also resemble MIL's nakhlites (Day et al., 2006; Franz et al., 2014; Dottin et al., 2018). Assimilation of crustal sulfur during the igneous crystallization stage could account for CeC 022 pyrrhotite modal abundance and Ni-poor composition, as repeatedly documented in nakhlites, especially in the fast-cooled subgroup (Farquhar et al., 2007; Franz et al., 2014; Dottin et al., 2018; Mari et al., 2019; Franz et al., 2019 and reference therein). The mean Fe/S ratio of CeC 022 pyrrhotite (Fe0.89S; hexagonal pyrrhotite) (Fig. S2), coupled with textural evidence of magnetite, indicates similar oxidizing crystallization conditions near the FMQ synthetic buffer (Chevrier et al., 2011), as usually reported for nakhlite pyrrhotites that inherited abundant crustal sulfur in their S isotopic composition (Farquhar et al., 2007b; Franz et al., 2014; Dottin et al., 2018).

Rare earth element compositions

Caleta el Cobre 022 shows a high bulk content in REE, resembling faster-cooled nakhlites such as NWA 10645, NWA 817 and MIL 03346 except for a clear positive anomaly in Ce (Fig. 13). As mentioned in Pourkhorsandi et al. (2017), a positive Ce anomaly is observed in REE patterns of meteorites from the Atacama Desert, as is CeC 022. This Ce anomaly is likely due to terrestrial alteration specific to Atacama, as Ce in its oxidized form (Ce⁴⁺) is a quite mobile element.

4.4.4. Magnetic properties

Magnetic susceptibility average mass weighed value of 8.41×10^{-6} m³/kg is to be compared to the average value of $4.10 \pm 1.73 \times 10^{-6}$ m³/kg for the other nine nakhlites (Rochette et al. 2005, Jambon et al. 2016 and our measurement of NWA 10153 at 5.25×10^{-6} m³/kg). Saturation remanent

magnetization (M_{RS}) is 0.459 Am²/kg, compared to 0.160 \pm 0.108 Am²/kg for the other nine nakhlites (Rochette et al. 2005, Jambon et al. 2016, and our measurement of NWA 10153 at 0.135 Am²/kg,) Saturation magnetization is 1.51 Am²/kg, to be compared with 0.66 \pm 0.37 Am²/kg for the other nine nakhlites. Caleta el Cobre 022 is the most magnetic nakhlite (Fig. 17).

The presence of two Curie temperatures of 525°C and 585°C evidences two families of ferromagnetic iron oxides with compositions Fe_{2.9}Ti_{0.1}O₄ (more abundant) and Fe₃O₄, respectively (Lattard et al., 2006). The microprobe analyses on magnetite phenocrysts give a composition richer in Ti of Fe_{2.6}Ti_{0.4}O₄. This difference is explained by the exsolutions observed at nanometric scales in these iron oxides grains (Fig. 5). Thus, the microprobe analyses represent a combination of the nanoscale exsolution with the oxide surrounding them. Using the composition Fe_{2.9}Ti_{0.1}O₄, the saturation magnetization indicates a magnetite content of 2.90 vol%. This estimate, that does not include the ilmenite/ulvöspinel exsolution since these two minerals are paramagnetic at room temperature, is in good agreement with the modal abundance of oxide phenocrysts estimated from image analyses (2.6 vol%).

Besides the petrological implications, the study of magnetic properties of martian meteorites is also of interest for the interpretation of the magnetic anomalies that have been documented over large parts of the Noachian crust at satellite altitude (Acuña et al., 1999). The strong intensity of these anomalies (over 1000 nT at 100 km altitude) imply the existence of a past dynamo operating on Mars, but also the existence of rocks capable of acquiring strong remanent magnetization. It has been estimated that such rocks should satisfy the condition M_{RS}>0.29 Am²/kg, regardless of their present-day natural remanent magnetization that may have been later modified by a number of processes including shock demagnetization at the surface of Mars, or contamination by magnets by meteorite collectors (Gattacceca et al., 2014). It is noteworthy that this condition is met by only a handful of martian meteorites: MIL 03346, NWA 5790, NWA 7034 and paired

stones (Rochette et al., 2005; Gattacceca et al., 2014; Jambon et al., 2016; Herd et al., 2017). With M_{RS}=0.459 Am²/kg, CeC 022 is only the fourth martian meteorite and the third nakhlite whose magnetic properties may account for the strong intensity of the martian magnetic anomalies (Fig. 17). Although nakhlites are obviously younger than the age of the end of the martian dynamo (e.g., Lillis et al., 2008), CeC 022 still represent an analogue source lithology for the strong magnetization of the martian crust.

4.4.5. Caleta el Cobre 022: a new subgroup

Caleta el Cobre 022 shows similarities with faster-cooled nakhlites, as well with slower-cooled nakhlites. A new characteristic, never observed before in nakhlites, is the presence of both fine-grained mesostasis and coarse millimeter-size plagioclase in CeC 022, showing two different cooling histories in intercumulus materials. In addition, compared to other nakhlites, CeC 022 has the lowest CaO content amongst nakhlites (12.9 wt%), similar to faster-cooled nakhlites NWA 5790 (12.9 wt%) or NWA 817 (13.1 wt%). Its low content in FeO (19 wt%) is also close to NWA 817, NWA 5790, or MIL nakhlites (Jambon et al., 2016). Caleta el Cobre 022 has high MgO content, similar to Lafayette, NWA 998 and Nakhla (Udry and Day, 2018), with a Mg# of 53.8, closer to the slower-cooled nakhlites (Table 4). This bulk composition and the abundance and composition of mineral phases are a reflection of the presence of both faster and slower-cooled nakhlite subgroup features in CeC 022. In addition, martian aqueous alteration phases are found in high abundance compared to most other nakhlites, and the occurrence of sulfides and Fe-oxides at the core of iddingsite veins is a unique and puzzling feature, giving new insights into the complex thermal and alteration histories of nakhlites.

With all its different characteristics, CeC 022 cannot be part of any previously proposed nakhlite subgroup, and therefore increases the diversity of the martian sample suite. In the Udry

and Day (2018) model presenting six different units in the nakhlite group based on petrography, crystallinity and composition, CeC 022 may thus represent a 7th subgroup. Also, CeC 022 has a slightly younger Sm-Nd age than other nakhlites. Caleta el Cobre 022 must originate from the same volcanic system as the other nakhlites, according to their similar crystallization age and petrography, compositions and physical properties, but it probably samples a different flow or sill than the other nakhlites.

5. Conclusion

789

790

791

792

793

794

795

796

797

798

799

800

801

802

803

804

805

806

807

808

809

810

811

812

All petrographic, chemicals and isotopic analyses confirm that CeC 022 is a nakhlite, coming from the same volcanic system as other nakhlites, although with characteristics never observed before in other nakhlites. On one hand, it shows similarities with faster-cooled nakhlites, such as NWA 817, NWA 5790 or MIL's nakhlites: conservation of augite irregular cores, Fe-rich overgrowth, high proportion of mesostasis with fine-grained K-feldspars, quenched oxides and high REE content. On the other hand, CeC 022 also shares similarities with slower-cooled nakhlites, like Nakhla and NWA 10153 (Udry and Day, 2018), including: pyroxene modal abundance, CSD slope and intercept, average pyroxene size, phenocrysts minerals composition, unzoned olivine and abundant plagioclase phenocrysts. One unique feature of CeC 022 is the presence of both fine-grained mesostasis and millimeter-size coarse plagioclase, showing different cooling rates of the intercumulus material though time, a feature never observed before in nakhlites. With these characteristics, CeC 022 may thus represent a 7th nakhlite subgroup in Udry and Day (2018) model of six different subgroups. Its slightly younger Sm-Nd age also supports CeC 022 was emplaced in a different flow or sill. Moreover, higher abundance of martian aqueous alteration phases compared to other nakhlites, showing sulfides and Fe-oxides at the core of iddingsite veins is a new characteristic. Magnetic susceptibility and saturation remanent magnetization are higher 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.

ACKNOWLEDGMENTS

We acknowledge the support from the Agence Nationale de la recherche (ANR) under the contract ANR-16-CE31-0012 entitled Mars-Prime. VD thanks the FRS-FNRS and ERC StG ISoSyC for present support. GH thanks the Belgian Science Policy (Belspo) for funding under the project BAMM!. VD and GH thank Jérome Roland, Hamed Pourkhorsandi and Sabrina Cauchie for help in the lab and measurements. The Raman facility in Lyon is supported by the Institut National des Sciences de l'Univers (INSU–France). Sylvain Pont is acknowledged for his help with SEM sulfide analyses. Parts of this work (H.B.) have been carried out within the framework of the NCCR "PlanetS" supported by the Swiss National Science Foundation. We thank reviewers L. Daly and Y. Liu and the Associate Editor, Kevin Righter, for helpful comments.

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. <i>Meteorites</i>
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. <i>Meteoritics & Planetary</i>
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. <i>Nature communications</i> 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 ST. 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. <i>Nature</i> 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. <i>Meteoritics</i>
904	26:135–143.

005	
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. <i>AIP Conference Proceedings</i>
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. <i>Treatise on Geochemistry: Second</i>
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 JA., Gattacceca J., Rochette P., Boudouma O., Badia D. and Devouard B. 2016.
937	Northwest Africa 5790: Revisiting nakhlite petrogenesis. <i>Geochimica et Cosmochimica Acta</i> 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? <i>Journal of Petrology</i> 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 JP., Barat JA., 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. <i>Journal of Petrology</i> 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?. <i>Reviews of Geophysics</i> 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). 43 rd
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.

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 CY., 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. <i>Meteoritics</i> 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.

Morse S. A. 1980. Basalts and phase diagrams: An introduction to the quantitative use of phase diagrams in igneous

1000

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 CY., 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. <i>Journal of Petrology</i> 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. <i>Planetary and Space Science</i>
1034	48:1213–1230.
1035	Treiman A.H. 2005. The nakhlite meteorites: Augite-rich igneous rocks from Mars. <i>Geochemistry</i> 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.