Caleta el Cobre 022 martian meteorite: increasing nakhlite diversity

L. Krämer Ruggiu[1], J. Gattacceca[1], B. Devouard[1], A. Udry[2], V. Debaille[3], P. Rochette[1], J.-P. Lorand[4], L. Bonal[5], P. Beck[5], V. Sautter[6], H. Busemann[7], M. M. M. Meier[7], C. Maden[7], G. Hublet[3,] R. Martinez[8].

[1]Aix Marseille Univ, CNRS, Coll France, IRD, INRAE, CEREGE, Aix-en-Provence, France (kramer@cerege.fr)

[2]Department of Geoscience, University of Nevada Las Vegas, Las Vegas, NV 89154, USA

[3]Laboratoire G-Time, Université Libre de Bruxelles, Belgium

[4]LPG, CNRS UMR 6112, Nantes Univ., France

[5]Univ. Grenoble Alpes, CNRS, IPAG, Grenoble, France

[6]IMPMC, MNHN, Paris, France

[7]Inst. of Geochem. and Petrol., ETH Zurich, Zurich, Switzerland

[8]Museo del Meteorito, San Pedro de Atacama, Antofagasta, Chile

Corresponding author: kramer@cerege.fr

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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

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 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

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; $MnTiO_3$ for 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 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 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). Gattacceca 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 troïlite 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% 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

fractions were re-dissolved using 12N HCl until the solutions were clear. A 5% aliquot was removed from the initial dissolution and spiked using ^{150}Sm-^{148}Nd 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 ^{142}Nd measurements. First, Ce was removed by using HDEHP resin after oxidation of Ce using $NaBrO_3$. 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 HNO_3. 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 $^{143}Nd/^{144}Nd$ 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.

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 CO_2 IR laser in the presence of 100 hPa of BrF_5. 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 mm^2. Spectra were measured under nadir incidence and with an observation angle of 30°. Spectra were normalized to infragold™ and spectralon™. 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 <2µm 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/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

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 µm 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 ± 0.09 mm^{-1}, with an intercept of 6.04 ± 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 ($Mg/(Fe^{2+} + Mg)$)] = 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 (Al_2O_3 = 1.1 ± 0.1 wt%; TiO_2 = 0.4 ± 0.1 wt%; Na_2O = 0.3 ± 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%), 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 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 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 $\Delta^{17}O = 0.248 \pm 0.013$‰ (mean ± 1σ).

3.5. Alteration products

3.5.1. Petrography

The main martian alteration products in CeC 022 occur in olivine phenocrysts as a reddish-orange 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% SiO_2), Mg and K, compared to the darker type (~30 wt% FeO and ~50 wt% SiO_2) (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 $\varepsilon^{143}Nd(i)$ of +10.4 ± 1.4, similar to the $\varepsilon^{143}Nd(i)$ measured on the bulk rock fraction, of +10.5 ± 0.1. Concerning the ^{142}Nd systematics, expressed in 10^6 deviation to the average modern Earth, the $\mu^{142}Nd$ of CeC 022 is equal to +56 ± 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 ^3He, ^{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, ^{38}Ar would be in the order of 2-3%. Trapped ^{38}Ar 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 ≤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

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_2O_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_2O/Al_2O_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 ± 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 ± 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 ± 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,

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 Fe-rich 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), 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.

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, sub-rounded 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% SiO_2) 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 ± 0.07 – 1.37 ± 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

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 ε^{143}Nd = +10.5 ± 0.1, is clearly lower than the other nakhlites, with an
587 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
588 et al., 2009). As demonstrated by the positive anomaly in Ce, this lower ε^{143}Nd could be related to
589 terrestrial contamination in the Atacama Desert. However, the μ^{142}Nd of CeC 022, of +56 ± 3, is
590 very similar to other nakhlites, with μ^{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 ε^{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 ε^{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 ^{3}He, ^{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.

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# ~ 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 (~100 µm) 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 $An_{35}Ab_{61}Or_{4}$ for NWA 10153 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). 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 $En_{35}Fs_{61}Wo_{4}$) (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).

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 (Ce^{4+}) is a quite mobile element.

4.4.4. Magnetic properties

Magnetic susceptibility average mass weighed value of 8.41×10^{-6} m^3/kg is to be compared 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, Jambon et al. 2016 and our measurement of NWA 10153 at 5.25×10^{-6} m^3/kg). Saturation remanent

magnetization (M_{RS}) is 0.459 Am^2/kg, compared to 0.160 ± 0.108 Am^2/kg for the other nine nakhlites (Rochette et al. 2005, Jambon et al. 2016, and our measurement of NWA 10153 at 0.135 Am^2/kg,) Saturation magnetization is 1.51 Am^2/kg, to be compared with 0.66 ± 0.37 Am^2/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 $Fe_{2.9}Ti_{0.1}O_4$ (more abundant) and Fe_3O_4, respectively (Lattard et al., 2006). The microprobe analyses on magnetite phenocrysts give a composition richer in Ti of $Fe_{2.6}Ti_{0.4}O_4$. 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 $Fe_{2.9}Ti_{0.1}O_4$, 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 Am^2/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 Am^2/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

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.

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