Formation and transformations of Fe-rich serpentines by asteroidal aqueous alteration processes: a nanoscale study of the Murray chondrite

Agnès Elmaleh^{a,*}, Franck Bourdelle^{a,b,1}, Florent Caste^a, Karim Benzerara^a, Hugues Leroux^c, Bertrand Devouard^d

^a. Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, Université Pierre et Marie Curie, Sorbonne Universités, CNRS UMR 7590, MNHN, IRD UR 206, Campus Jussieu, 4 Place Jussieu, Boîte Courrier 115, 75252 Paris Cedex 05, France Paris, France. Email addresses : elmaleh@impmc.upmc.fr; caste@impmc.upmc.fr; benzerara@impmc.upmc.fr ^b. GeoRessources, Université de Lorraine, CNRS UMR 7359, FST, rue Jacques Callot, BP 70239, 54506 Vandoeuvre-lès-Nancy, France; ¹: Present address: LGCgE, Université Lille 1, SN5, 59655 Villeneuve d'Ascq Cedex, France. Email address : franck.bourdelle@univ-lille1.fr ^c. Unité Matériaux et Transformations, Université Lille 1, CNRS UMR 8207, 59655 Villeneuve d'Ascq, France. Email address : hugues.leroux@univ-lille1.fr ^d. CEREGE UM34, Aix-Marseille Université, CNRS UMR 7330, Europôle Méditerranéen de l'Arbois - Avenue Louis Philibert, BP 80, 13545 Aix en Provence cedex 04, France. Email address: devouard@cerege.fr

* Author to whom correspondence should be addressed (Phone number: +33 1 4427 5061; Fax number: +33 1 4427 3785).

Abstract — Fe-rich serpentines are an abundant product of the early aqueous alteration events that affected the parent bodies of CM carbonaceous chondrites. Alteration assemblages in these meteorites show a large chemical variability and although water-rock interactions occurred under anoxic conditions, serpentines contain high amounts of ferric iron. To date very few studies have documented Fe valence variations in alteration assemblages of carbonaceous chondrites, limiting the understanding of the oxidation mechanisms. Here, we report results from a nanoscale study of a calcium-aluminum-rich inclusion (CAI) from the Murray chondrite, in which alteration resulted in Fe import and Ca export by the fluid phase and in massive Fe-rich serpentines formation. We combined scanning and transmission electron microscopies and scanning transmission X-ray microscopy for characterizing the crystal chemistry of Fe-serpentines. We used reference minerals with known crystallographic orientations to quantify the Fe valence state in Fe-rich serpentines using X-ray absorption spectroscopy at the Fe $L_{2,3}$ -edges, yielding a robust methodology that would prove valuable for studying oxidation processes in other terrestrial or extra-terrestrial cases of serpentinization. We suggest that aqueous Fe^{2+} was transported to the initially Fe-depleted CAI, where local changes in pH conditions, and possibly mineral catalysis by spinel promoted the partial oxidation of Fe^{2+} into Fe^{3+} by water and the formation of Fe-rich serpentines close to the cronstedtite endmember. Such mechanisms produce H_2 , which opens interesting perspectives as hydrogen may have reacted with carbon species, or escaped and yield increasingly oxidizing conditions in the parent asteroid. From the results of this nanoscale study, we also propose transformations of the initial cronstedtite, destabilized by later input of Al- and Mg-rich solutions, leading to Fe^{2+} leaching from serpentines, as well as to random serpentine-chlorite interstratifications. Such transformations towards polysomatic assemblages that are un-equilibrated from the structural, chemical and redox point of views are probably controlled by the various rates of alteration of primary minerals, but also by porosity gradients, as in terrestrial hydrothermal systems. We suggest that the proposed mechanisms may have played a role in the early formation of (Fe^{2+}, Fe^{3+}) -rich serpentines documented in CM chondrites, as well as in their transformation with on-going alteration towards Fe-poorer compositions inferred from previous petrologic, mineralogical and magnetic studies of CM chondrites.

1. INTRODUCTION

Despite their nearly solar chemical composition (highly-volatile elements excluded), the C- and H-rich carbonaceous chondrites of the CI and CM groups are mainly composed of phyllosilicates, attesting to early secondary processing of their parent asteroids (McSween, 1979a; Zolensky et al., 2008). Rare phyllosilicates may have formed in the nebula during passage of shock waves (Ciesla et al. 2003). However, the bulk of the minerals hydration probably occurred in these meteorites parent bodies after ice that accreted with rocky materials have melted. Indeed, there is a wealth of petrologic evidence in CM and CI chondrites showing that primary components (chondrules, metal and refractory inclusions) have been transformed by *in situ* water-rock interactions and demonstrating the alteration of primary anhydrous minerals and their replacement by phyllosilicate-rich assemblages (McSween, 1979a; Bunch and Chang, 1980; Tomeoka and Buseck, 1985; Lee and Greenwood, 1994; Greenwood et al., 1994; Rubin et al., 2007; Velbel et al., 2012). The CM group, where primary features are better preserved than in CI chondrites (Scott and Krot, 2003) is an interesting target for studying the reactions of hydration involved.

The composition of the phyllosilicate assemblages differs among CM chondrites between Fe-rich and Mg-rich endmembers (McSween, 1979b; Browning et al., 1996; Howard et al., 2009) with variable amounts of Al, and large compositional variations at the micro and nano scales (Zolensky et al., 1993; 1997). These changes have been related to varying degrees of aqueous alteration of CM2 chondrites and models of the progression of aqueous alteration involving the transformation from Fe-rich to Mg-rich serpentines have been proposed based on petrography and mineralogy (McSween, 1979b; Tomeoka and Buseck, 1985; Tomeoka et al., 1989; Browning et al., 1996; Rubin et al., 2007). Elmaleh et al. (2012) used the low-temperature bulk magnetic properties of several CM2 chondrites to target specifically the Fe-rich serpentines amongst serpentines. They suggested transformations of Fe-serpentine assemblages predominated by minerals close to the endmember cronstedtite in the Murray chondrite towards predominant Fe-serpentines with a lower FeO/SiO₂ contents in the more highly altered chondrites (such as Cold Bokkeveld), in good agreement with these models. Several hypotheses have been put forward to explain compositional variations including (1) a mass balance effect involving different precursor phases along the fayalite-forsterite joint (Howard et al., 2009) or (2) evolution with the degree of alteration, as some phases (metal, Fe-rich glass in chondrules for instance) would react more rapidly than others (e.g. Mg-olivine) (Tomeoka and Buseck, 1985; Zolensky et al., 1993; Hanowski and Brearley, 2001).

The relationship between the composition of the precursor phase and that of serpentine remains, however, unclear (Velbel et al., 2012) and is still poorly known in the Si-Fe-Mg-Al system. Alternatively, Lee et al. (2013) proposed, from the study of a carbonate-rich CM2 chondrite, the crystallization of Fe-rich serpentines from breunnerite or other Mg- and Fe-bearing carbonates, suggesting possible complex multi-stages reactions. An analogy can be drawn between the evolution of Fe speciation in altered chondrites and changes in Fe partitioning during the serpentinization of abyssal peridotites (Oufi and Cannat, 2002; Klein et al., 2009). From an experimental study of the hydrothermal alteration of peridotite, Marcaillou et al. (2011) have shown that serpentines incorporate Fe^{3+} in tetrahedral sites during the first stages of serpentinization. This early precipitation suggests a kinetic control of the formation of Fe^{3+} -bearing serpentine, which would subsequently transform into Mg-richer serpentines as alteration proceeds, thus bearing similarities to CM chondrites (Elmaleh et al., 2012). The present study aims at better understanding the parameters controlling the composition (Fe^{2+} , Fe^{3+} , Mg, Al contents) of serpentines in the particular case of serpentinization on asteroids by a study at the nanoscale of alteration assemblages in the Murray chondrite (CM2 chondrite). It also aims at evaluating equilibrium/disequilibrium processes and mass transfers on the parent body of this meteorite.

In CM2 chondrites, a clear predominance of Fe-bearing serpentines is observed with significant amounts of cronstedtite, which contains a high proportion of Fe^{3+} in both octahedral and tetrahedral crystallographic sites (Müller et al., 1979; Bunch and Chang, 1980; Tomeoka and Buseck, 1985; Zega et al., 2003). Given that alteration minerals in CM chondrites are Fe-rich and mixed-valent, understanding the alteration processes and the associated redox reactions necessitates the accurate determination of the amount of Fe^{2+} and Fe^{3+} in these samples. Some direct measurements of the Fe valence state have been performed at the micron-scale by X-ray absorption at the Fe K-edge (Beck et al., 2012). Most estimates are provided by charge balance calculations on average, micro-scale data from the matrix, assuming a general stoichiometry for phyllosilicates (e.g. the Mineralogical Alteration Index developed by Browning et al., 1996), which is problematic because the matrix of CM consists of a complex mixture of nanometer-sized minerals (Bland et al., 2006). Therefore, direct nanoscale determinations of Fe speciation in chondritic phyllosilicates appear more relevant. So far, only a few such measurements have been made, by electron energy loss spectroscopy (Zega et al., 2003). Here, in combination with transmission electron microscopy (TEM), scanning TEM and energy dispersive spectroscopy in scanning mode (STEM-EDS), we characterized the Fe valence state of secondary assemblages of a CAI in the Murray chondrite

at the nanoscale by scanning transmission X-ray microscopy and X-ray absorption near edge spectroscopy (STXM-XANES) at the Fe L_{2,3}-edges. For this purpose, we used oriented reference samples of cronstedtite so that dichroic effects were taken into account, as their quantitative importance in phyllosilicates has been demonstrated in the case of micas at the pre-edge of the Fe K-edge (Dyar et al. 2001). From this combined, nanoscale approach, we propose mechanisms for the oxidation of Fe, mineral hydration processes during alteration in asteroids, and transformation of Fe-rich serpentines as alteration proceeds.

2. SAMPLES AND METHODS

2.1. Samples selection, characterization and preparation

Three samples were studied: a petrologic thin section of the Murray meteorite (meteorites collection of Arizona State University, USA, section #365-3) and two millimeter-sized single crystals of cronstedtite: crystal_1 from the Kisbanya mine, Romania (Sorbonne mineral collection, Paris, France) and crystal_2 from the Salsigne mine, France (minerals and meteorites collection of Blaise Pascal University, Clermont-Ferrand, France).

The Murray meteorite is a fall CM2 carbonaceous chondrite that was recovered a few months after its fall in 1950 in Kentucky, USA. It consists of ~74% serpentine according to Howard et al. (2009). The Murray chondrite is characterized by a relatively high preservation of primary chondritic features (Rubin et al., 2007), and contains ~1.6 area% preserved CAIs as evaluated by Hezel et al. (2008) from petrologic data. Rubin et al. (2007) describe a sample where some metal grains contain limonite along their edges and in their interiors, suggesting a low degree of terrestrial weathering, but the petrologic thin section used here has no evidence for such terrestrial products. The refractory inclusion from which we extracted an electron transparent foil was first studied using scanning electron microscopy (SEM) observations, using a field emission gun (FEG) SEM Zeiss Ultra 55 at IMPMC (Paris, France). The image shown in Fig. 3.a was taken using an acceleration voltage of 15 kV, in back-scattered electrons detection mode (BSE mode). Electron Micro-Probe Analyses (EMPA) based on wavelength dispersive spectroscopy (WDS) were performed by chemical mapping using a CAMECA SX-5 micro-probe at CAMPARIS (Paris, France) with an acceleration voltage of 15 kV, a current intensity of 40 nA and acquisition times of 150 ms/pixel at a step size of ~0.4 µm and using a selection of natural and synthetic references. Data reduction was performed using the PAP program (Pouchou and Pichoir, 1985). The uncertainties taken into account are the standard deviation over a series of measurements of the sample.

We studied samples of cronstedtite in order to further test the method setup by Bourdelle et al. (2013) to determine the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in silicates by STXM-XANES at the $\text{L}_{2,3}$ -edges, which proved particularly useful for phyllosilicates, with negligible radiation damages (Fig. 7 of Bourdelle et al., 2013). Here, we tested the method further, paying attention to dichroic effects and their impact on the determination of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ through the analysis of cronstedtite reference crystals. Cronstedtite was chosen because serpentine close to cronstedtite is a major component of the Murray chondrite as well as of other CM2 chondrites (Howard et al., 2009; Elmaleh et al., 2012; Hewins et al., 2014). This serpentine contains Fe at two valence states and in two crystallographic sites, tetrahedral and octahedral: $(\text{Fe}^{2+}_{3-x}\text{Fe}^{3+}_x)(\text{Si}_{2-x}\text{Fe}^{3+}_x)\text{O}_5(\text{OH})_4$. We determined the following structural formula for crystal_1 using EMPA at CAMPARIS (acceleration voltage: 15 kV, current intensity: 40 nA, acquisition times: 10 s/10 s for peak/background): $(\text{Fe}^{2+}_{2.25}\text{Fe}^{3+}_{0.74})(\text{Si}_{1.26}\text{Fe}^{3+}_{0.74})\text{O}_5(\text{OH})_4$. The mean structural for crystals from the Salsigne mine (crystal_2) is: $(\text{Fe}^{2+}_{2.19}\text{Fe}^{3+}_{0.81})(\text{Si}_{1.20}\text{Fe}^{3+}_{0.81})\text{O}_5(\text{OH})_4$ (Elmaleh et al., 2012). The $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratios calculated assuming an ideal formula, with a lack of vacancies in the structure (Hybler et al. 2000, 2002) are therefore 0.41 for crystal_1 and 0.43 for crystal_2 with a standard deviation of 0.03 from multiple measurements (Table 1).

Four ultra-thin foils were prepared for the nanoscale study using focused ion beam (FIB) milling. Two FIB ultra-thin foils were extracted using a FEI strata DualBeam 235 at the Institut d'Electronique, de Microélectronique et de Nanotechnologie (Lille, France): ultra-thin foil 1 from crystal_1, and the Murray ultra-thin foil. These two foils have a thickness ~ 100 nm. The other two (2/1 and 2/2) were cut at IMPMC (Paris, France) using a Zeiss Crossbeam Neon40 (~ 300 nm). Ultra-thin foils 2/1 and 2/2 were cut from crystal_2 with the *c* axis within (2/1) or perpendicular (2/2) to the plane of the foils. We used a lift-out procedure as described by Heaney et al. (2001). A FIB-assisted Pt deposit was first made. A 30 kV Ga^+ beam operated at ~ 5 nA was then used for the initial milling steps, consisting in rough excavations from both sides of the thin foil. An in situ micromanipulator was attached to the foil by FIB-assisted platinum deposition prior to separation of the foil (at ~ 100 pA). The thin foil was transferred to a TEM grid and welded to it. The thinning of the ultra-thin foil was performed with the beam operated at a ~ 100 pA current. A last cleaning step was performed at low acceleration tension (~ 3 kV). After milling, the ultra-thin foils were sealed in a glove box and X-ray absorption experiments were performed prior to transmission electron microscopy.

2.2. X-ray absorption spectroscopy

2.2.1. STXM-XANES data collection

STXM-XANES measurements were mainly carried out on Molecular Environmental Science 11.0.2.2 beamline at the Advanced Light Source (ALS, Berkeley, USA) (Murray chondrite, angular dependent measurements on ultra-thin section 1). The ALS storage ring was operated at 1.9 GeV and 500 mA current. Measurements were performed at the Fe $L_{2,3}$ -edges in the 690-730 eV energy range. Methods used for STXM data acquisition and analysis can be found for example in Cosmidis and Benzerara (2014). Spectra were acquired at a resolution of ~ 0.2 eV and calibrated in energy by fixing the maximum of the L_2 -edge (which energy has been shown to be constant among various Fe^{2+} and/or Fe^{3+} -compounds, see Table 1 in Bourdelle et al., 2013) at 723.54 eV. Ultra-thin foils 2/1 and 2/2 were analyzed at the Canadian Light Source (CLS) with STXM on beamline 10ID-1. The beamline 10ID-1 at the CLS was described in detail by Kaznatcheev et al. (2007). For both experiments, focus was achieved for each sample, and precision in the determination of the focus position was better than the focus depth. For each sample, we acquired maps of the whole FIB foils (at 702, 707.9, 709.7, 708.2, 717.9, 720.7 and 723.2 eV for ALS experiments) and a few image stacks (one image at each energy point between 690 and 730 eV) in smaller areas of the ultra-thin foils (in the case of Murray section, the area is shown in Fig. 4).

2.2.2. STXM-XANES data analysis

AXis2000 software (Hitchcock, 2014) was used to align images, extract XANES spectra from image stacks and for STXM map construction. For spectra, the optical density (OD) was chosen between 0.5 and 1.5. At higher OD, distortions of the spectra are observed. In ultra-thin areas of the FIB foils, with very low OD, we observed a reduction of Fe, and no dichroic effect in cronstedtite: beam damage is suspected. At the L_2 -edge, the $Fe^{3+}/\Sigma Fe$ ratio is calculated using (i) the ratio between an integration window with a 2 eV width centered around the maximum of the L_2 -edge (labeled 2 in Fig. 2.b) and the total L_2 -edge intensity obtained by integrating the area under the X-ray absorption spectra, and (ii) an experimental calibration, established from reference samples analysis by Bourdelle et al. (2013). These authors used 14 silicate references including phyllosilicates with variable compositions (see their Table 1). In particular, phyllosilicates with variable amounts of Fe, Mg and Al (various chlorites, smectite, micas) were used, all of which fall in single calibration lines at the L_2 edge and at the L_3 edge (Fig. 3 and Fig. 5 of Bourdelle et al., 2013).

The spatial resolution is about 50 nm for maps (Fig. 7), and ~150 nm for reconstructing spectra of Fe-rich serpentines with a good signal to noise ratio (Fig. 6.b), although larger areas were also used for averaging purposes or to increase the signal to noise ratio (Fig. 1, 2 and values given at the beginning of section 3.2.2). The semi-quantitative Fe valence map of the whole Murray FIB ultra-thin foil (Fig. 7) was built using a sequence of images at the L₂ edge (at 717.9, 720.7 and 723.2 eV), following a procedure analogous to that described by Bourdelle et al. (2013) at the L₃-edge. The map was obtained using the ratio of 723.2 eV to 720.7 eV images after background subtraction (717.9 eV image). Furthermore, the map was corrected using the image stack obtained on the full energy range. Consistency was evaluated and the scale of the map was set using a series of discrete spectra. Distortions of the images are observed, due to slight deformations of the FIB foil acquired between the STXM experiments and microscopic observations.

2.3. Transmission electron microscopy (Murray ultra-thin foil)

High-resolution TEM (HRTEM) and selected area electron diffraction (SAED patterns) were performed with a JEOL JEM-3010 at CINAM (Marseille, France). Areas selected for SAED are 280 nm in diameter. For measurement of d-spacing, we took care of keeping a constant objective current. Under these conditions, the precision on d-spacing measurements proved to be better than $\pm 5\%$. STEM and microanalysis by STEM-EDS on the Murray ultra-thin foil were performed using a Philips CM30 equipped with a Bruker EDS (Esprit software) at the electron microscopy center of the University of Lille. STEM-EDS maps shown are semi-quantitative. For these maps, binning for quantification using k-factors (O, Si, Al, Mg and Fe determined experimentally) and absorption correction, which results are given in Table 2 and Fig. 4, yielded a resolution of ~120 nm; quantitative analyses are expressed for 100 % on an anhydrous basis. The uncertainties taken are standard deviations from multiple measurements.

3. RESULTS

3.1. Linear polarization dependent X-ray absorption spectroscopy of reference cronstedtite at the Fe L_{2,3}-edges

The estimation of the Fe³⁺/ΣFe ratio from XANES spectra at the Fe L_{2,3}-edges (dipole 2p-3d transitions) is based on the ~2 eV chemical shift between the absorption edges of Fe²⁺ (*d*⁶) and Fe³⁺ (*d*⁵), and relies on the measurement of ratios of different peak heights or areas (e.g. Cressey et al., 1993; Bourdelle et al., 2013). However, the relative height of different peaks in

the XANES spectrum measured on a given crystal may change, independently of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio, with the orientation of the crystallographic axes with respect to the polarization of light. This angular dependence of X-ray absorption depends on the symmetry of the crystal, as investigated in detail by Brouder (1990). In order to assess quantitatively the impact of variations due to crystal orientation on the estimation of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio, we measured the XANES spectra of cronstedtite at the Fe $L_{2,3}$ -edges using linearly polarized light on FIB ultra-thin foil 1 (with the **c** axis within the plane of the foil) for two directions of the linear polarization vector $\mathbf{\epsilon}$, vertical and horizontal. Hence, with a normal incidence of the beam (**k** vector perpendicular to the **c** axis), we measured the spectrum for $\mathbf{\epsilon}$ either parallel or perpendicular to the **c** axis. The spectra displayed in Fig.1 and in Fig 2.a (close up at the L_2 -edge, after a double-arctangent background subtraction and normalization to the maximum), present a strong linear dichroism (Fig. 1.a). The same applies to FIB ultra-thin foil 2/1, measured in similar conditions (Fig. 2.b, L_2 -edge data). On the contrary, no azimuthal angular dependence is observed for ultra-thin foil 2/2, where the polarization vector is oriented along two mutually perpendicular orientations in the (**a**,**b**) plane (Fig. 2.c, L_2 -edge data). This observation is consistent with the dipolar electric approximation for a crystal with a trigonal point group symmetry, such as the samples studied here (space group $P31m$ in Salsigne crystals – Elmaleh et al., 2012 – and in Kisbanya crystals – Hybler et al., 2000 and Elmaleh et al., 2012). Crystals with a trigonal symmetry are indeed expected to show dichroism, with an absorption cross section depending only on the angle between the three-fold rotation axis (the **c** axis) and $\mathbf{\epsilon}$ (Brouder, 1990). As shown in the inset of Fig. 1, measurements at 708 eV for different values of θ , the angle between the polarization vector and the three-fold, **c** axis, show that the absorption obeys at first order the electric dipole expression of the angular dependence (Heald and Stern, 1977): $\sigma(\theta) = \sigma_{\text{perp}} \cdot \sin^2 \theta + \sigma_{\text{par}} \cdot \cos^2 \theta$, where σ is the absorption cross-section, and σ_{perp} and σ_{par} correspond to the cross sections measured with $\mathbf{\epsilon}$ respectively perpendicular and parallel to the unique high-symmetry axis of the crystal, here the three-fold symmetry axis (corresponding respectively to the $\mathbf{\epsilon}_{\text{vert}}$ and the $\mathbf{\epsilon}_{\text{hor}}$ cases in Fig. 1).

In transmission mode, it may sometimes be better to measure the L_2 -edge rather than the more intense L_3 -edge, because of saturation effects arising when the sample is too thick, which distorts the L_3 -edge as described by Hanhan et al. (2009) for the STXM technique. Close-ups of spectra at the L_2 -edge are displayed in Fig. 2. Three main structures can be identified at the L_2 edge, at ~ 719.4 eV, ~ 721 eV (subdivided into two peaks) and 723.2 eV, respectively labeled 1 to 3. Comparison with published experimental or calculated X-ray

absorption spectra (van der Laan and Kirkman, 1992; Cressey et al., 1993; Kuiper et al., 1997) or with electron energy loss spectra (Gloter et al., 2003) suggests that peak 1 corresponds to Fe^{2+} , peak 2, to a mixture and peak 3, to Fe^{3+} . In order to quantify the effect of the polarization on the determination of the valence state of iron, the ferric iron ratio was calculated using the calibrations of Bourdelle et al. (2013) in different cases (Table 1), and compared to the estimates provided by the structural formulae established using EMPA. We find higher apparent Fe^{3+} concentrations when ϵ is parallel to c . Values obtained for the same polarization, but in different experimental conditions are analogous within the 5-10% error of the method (van Aken and Liebscher, 2002; Bourdelle et al., 2013). In the electric dipole approximation, the isotropic spectra can be evaluated considering a 2/3 contribution of the absorption with ϵ perpendicular to c and a 1/3 contribution of the absorption with ϵ parallel to c . It is therefore possible to evaluate the valence state of Fe in the isotropic case as the weighted average of these two extreme cases. The valence obtained by this approach is in good agreement with the expected value, within error (Table 1). Taken literally, data in Table 1 may suggest an uncertainty of over $\pm 20\%$ on the Fe valence state of a crystal of unknown orientation. However, the largest difference between the isotropic and apparent $\text{Fe}^{3+}/\Sigma\text{Fe}$ values is observed for a single orientation of the polarization vector with respect to the c axis, i.e. $\epsilon//c$. The probability to encounter such an orientation is low. Moreover, we recorded the spectra of the meteorite sample using circularly polarized light, which is equivalent to averaging out ϵ orientations (partial depolarization) with respect to c in the plane of polarization, which is the plane of the ultra-thin foil. Taking also into account the uncertainty on the quantification at the $L_{2,3}$ -edges, the total uncertainty is of the order of 10-15%.

3.2. Primary minerals and alteration assemblages of the altered refractory inclusion (Murray chondrite)

3.2.1. Electron microscopy, EDS and WDS analyses

We studied a small ($<100\ \mu\text{m}$ wide) and heavily altered CAI (Fig. 3). The area displays a few primary relicts of micrometer sized Mg,Al-spinel (MgAl_2O_4) and of micrometer to $10\ \mu\text{m}$ sized Ca,Ti-perovskite (CaTiO_3). A FIB foil was cut across such relicts (Fig. 4). Spinel contains minor elements such as V ($1.2\pm 0.05\ \text{wt}\%$), Fe ($0.6\pm 0.1\ \text{wt}\%$), Ti ($0.2\pm 0.1\ \text{wt}\%$) and Si ($0.2\pm 0.08\ \text{wt}\%$). Minor Al ($0.8\pm 0.2\ \text{wt}\%$) and Si ($0.3\pm 0.2\ \text{wt}\%$) were found in perovskite. The altered CAI mostly consists of Fe,Mg,Al-phyllsilicates that are found around and in between the relicts, which suggests that these secondary minerals replaced the primary ones. No clear rim was observed around the altered inclusion, but in a $\sim 20\ \mu\text{m}$ wide area, abundant

micrometer-sized crystals of Fe-poor and Mg-rich pyroxene and olivine (marked by asterisks in Fig. 3.b), Fe,Ni-sulfides and rare Fe,Cr-oxides are observed. Additionally, dense patches of nanometer-sized Fe,Ni-sulfides are found at the edge of the CAI (Fig. 3 and 4). As visible in compositional maps displayed in Fig. 3.b and Fig. 4.b and c, the altered CAI is characterized by Al enrichment, Fe enrichment, and Mg depletion with respect to the surrounding matrix. On the contrary, Ca concentrations are low (< 1 wt% CaO in average), but Ca-enriched phases, either phosphates or S-rich phases, are observed within and especially around the CAI. Calcium as well as Ti-rich rims are also observed around and within fractures of the spinels (Fig. 4 and Fig. 5.b). Sulfur and Ni are globally less concentrated in the CAI area (1.1 ± 1.1 wt% and 0.56 ± 0.26 wt%, respectively) than in the surrounding matrix (4.6 ± 2.8 wt% and 2.2 ± 1.04 wt%). Rare S-rich phases, sulfates and sulfides, are observed in the CAI. In particular, a few lamellae of a Fe,Mg,Al- and S rich- phase, interpreted as tochilinite, are present among the phyllosilicates (Fig. 4). Most areas of the CAI are depleted in Si with respect to the matrix, except for a Si rich aggregate (Fig.3.a). The EMPA yielded low totals for this aggregate (70 to 80 oxides wt%), suggesting that it corresponds to a Na-bearing hydrous aluminosilicate, containing up to ~ 0.3 wt% Cl and ~ 0.7 wt% F, which exact nature could not be determined. Moreover, this aggregate presents a high chemical heterogeneity, with values of ~ 25 - 35 wt% SiO_2 , ~ 20 - 30 wt% Al_2O_3 , ~ 2 - 10 wt% Na_2O and ~ 3 - 20 wt% FeO with increasing Fe towards the edges, and with about 6-8 wt% MgO .

Two main populations of phyllosilicates are identified within the altered CAI, based on their grain size and morphology (Fig. 4). One population composed of coarse phyllosilicates (up to >1 μm) with planar morphologies is found in large areas of the CAI, which appear brighter in Fig. 3.a and red in Fig. 4.b, due to their high Fe content (Table 2). A second population is composed of phyllosilicates with fine grain sizes, and more fibrous and curved morphologies, which mostly surround the primary anhydrous minerals, spinel and perovskite being enclosed within a ribbon of fibrous phyllosilicates (bluish – yellowish -greenish in Fig. 4.b, depending on their relative Mg and Al content). SAED patterns and high-resolution TEM images of both the coarse and fine phyllosilicate areas show the predominance of ~ 0.7 nm basal layer spacing, typical of the (001) lattice plane of serpentine-kaolin group as shown by the examples displayed in Fig. 5.a and 5.b (areas analyzed located in Fig. 4.a). The coarse phyllosilicates are well ordered, despite frequent streaking due to stacking faults (Fig. 5.a, upper part). SAED patterns of fine phyllosilicates areas show spotty rings, reflecting both the small size of the crystallites and their low amount of orientation (Fig. 5.b). TEM images of a fine-grained area with a very high Al content, moderate S enrichment, and conversely low Si

content are shown in Fig. 5.c (location in Fig. 4.a, composition in Table 2). They show that well ordered, ~ 0.7 nm basal spacing areas predominate. However, they only occur as packets of ~ 10 layers. Some layers of the 1:1 phase are bent (Fig. 5.c). Packets of ~ 0.7 nm layers are separated by disordered and / or beam damaged areas, as well as domains displaying larger spacings, mostly ~ 1.4 , ~ 2.1 and ~ 2.8 nm, suggesting intergrowth with brucite-type layers and serpentine-chlorite interstratifications as observed in terrestrial hydrothermal systems (Banfield et al., 1994; Mellini et al., 2005). A well-ordered domain with a d-spacing of ~ 0.5 nm was observed at the edge of a coarse crystal surrounded by an Al-, Mg- and S-enriched aureole (Fig. 5.a, lower part; compositional data in Fig. 4.b). This d-spacing value, typical of a hydroxide, is very close to the basal spacing of brucite (0.48 nm).

Compositions determined by STEM-EDS analyses distinguish the two morphological groups: the coarse grains are enriched in Fe and depleted in Mg and Al with respect to the fine ones, whereas the Si contents are statistically identical, with mean SiO_2 concentrations of 14.31 ± 0.17 wt% and 15.13 ± 1.83 wt% respectively (Table 2, coarse and fine grained phyllosilicates, area analyzed located in Fig 4.a). We expressed the atom % composition of phyllosilicates (or packets of secondary phases, predominated by phyllosilicates) for a total of 5 cations (Fig. 6a, Table 2). Note that if occupancy of the octahedral sites were only partial, the total number of cations would be comprised between 4 and 5 for 7 O. As discussed below, the data rather suggests trioctahedral structures (serpentine structures). In both the fine and coarse groups, the number of Si for 5 cations is generally close to one, as in cronstedtite (1 Si and 1 Fe^{3+} for 2 tetrahedral sites), or in amesite (1 Si, 1 Al), but it falls below 1 in some instances (note that this is not readily visible from Fig. 6 as we represented Al+Si). The Si tetrahedral occupancy of phyllosilicates is observed to be at least $\frac{1}{2}$ (with the exception of clintonite, Sanz et al., 2003), which is interpreted as a consequence of local charge equilibrium constraints (also called Al-avoidance or Loewenstein's rule). The situation is even clearer in Al-rich patches (Table 2, Fig. 5.c). Mixing with a Si-poor phase is therefore likely, in agreement with TEM observations, which suggest the presence of hydroxide layers. Small but consistent amounts of S (1.34 ± 0.24 in the fine grained areas, 0.79 ± 1.12 wt% S in coarse grains, and 1.75 ± 0.43 wt% S in Al-rich assemblages, Table 2) also suggest limited mixing with a S-bearing phase. Tochilinite, which was observed in association with coarse phyllosilicates (Fig. 4), was not identified in the fine-grained phyllosilicates areas, so that if present, it is only as packets of a few layers. Note that on the basis of 5 cations, S values represent a maximum of 0.2 S, contributing to the scattering of data in Fig. 6.a. On this figure, two compositional groups are clearly defined: the coarse-grained and the fine-grained

phyllosilicate populations. Their compositions plot along an anti-correlation trend linking the Mg and Fe contents. Similarly, the Al+Si content is anti-correlated to the Fe content. Such trends suggest that the two populations shared common processes of formation during aqueous alteration on the parent body of the Murray chondrite.

3.2.2. STXM measurements

Large variations of the valence state of Fe are observed throughout the altered CAI area, from purely ferrous in the spinel, which contains ~0.6 wt% FeO (image stack analysis), to largely ferric in the fine-grained matrix (Fig. 7). The average ferric iron percentages estimated the matrix surrounding the altered CAI and the CAI itself are, however, very close, ~70% and ~75% respectively (from image stack). Within the matrix, the L₂-edge spectrum of Fe,Ni-sulfides yielded mostly Fe²⁺ with ~25% Fe³⁺. Given the size of the sulfide grains (aggregates of <100 nm grains), it is unclear whether this actually corresponds to the valence state of Fe in the minerals, in which case it would have partly oxidized after formation, or whether it is that of a mixture with the adjacent fine-grained matrix. We mostly focused here on the phyllosilicate assemblages that replaced the primary anhydrous phases of the CAI. Examples of X-ray absorption spectra of the coarse-grained and fine-grained phyllosilicates areas at the Fe L₂-edge are shown in Fig. 6.b. L₃ spectra are not shown here, because most of the spectra obtained are above the saturation levels (optical density > 1.5). All spectra show a relative intensity of the L₂-3 peak higher than the reference cronstedtite sample, which contains ~40% Fe³⁺, suggesting higher Fe³⁺/ΣFe. Variations are observed, due both to orientation and valence changes. According to the electron diffraction study, the spectra were taken from coarse grains with various orientations (c axis either contained in the plane of the FIB foil or out of the plane) and as mentioned earlier, the orientation of fine crystallites is random. Yet, systematic differences are observed between the coarsest phyllosilicates, showing Fe³⁺/ΣFe ratios (between 45 to 65% Fe³⁺; 50% in average) significantly lower than the fine-grained areas where Fe³⁺/ΣFe ratios of about 70-80% are measured (determined from the spectra shown in Fig. 6.b). This also appears clearly in the semi-quantitative Fe valence map of Fig. 7, where coarse-grained phyllosilicates have a greenish color, whereas the fine-grained assemblages including the Al-rich assemblages mentioned earlier (see location in Fig. 4.a) appear bluish as they contain more Fe³⁺.

4. DISCUSSION

4.1. Mass transfers during aqueous alteration

It is difficult to evaluate the reactions of alteration, particularly in meteorites, because the composition of the precursor phase is poorly known. Calcium-aluminum-rich inclusions (CAIs) are of particular interest from this point of view because the mineralogy of most refractory inclusions in chondrites is limited to relatively few essential minerals. Spinel, melilite, perovskite, hibonite, calcic pyroxene are the most common minerals, with anorthite and olivine also often present as rim phases, and with less common metal (MacPherson, 2003). Accordingly, the chemical composition of CAIs mainly consists in a small number of refractory elements, so that a geochemical budget of alteration can be proposed. Assessing mass transfers is a key to understanding the alteration pathways in chondrites. We compared the average elemental composition of the alteration assemblages of the CAI and average compositions of more pristine CAIs from CV chondrites, which have been extensively studied (Table 3). Although secondary processes have affected CV chondrites (Hashimoto and Grossman, 1987; Krot et al., 1995; Krot et al., 1998), they remain limited in comparison with those that impacted CM chondrites (Krot et al., 1998; Zolensky et al., 2008). Russell et al. (1998) noticed textural and mineralogical similarities between the pristine CAIs found in the least metamorphosed CO CAIs and CM CAIs, which would have made the former an appropriate reference in this context. Bulk data from CO CAIs are, however, very scarce. As a consequence, we used CV CAIs data instead, but we did not consider data from the large igneous type B CAIs that are found only in CV chondrites (MacPherson, 2003). Due to secondary processing, the concentrations of Fe, alkalis and halogens are very heterogeneous in CV chondrites. The literature data presented in Table 3 come from CV CAIs studied by Simon and Grossman (2004, see their Table 1) and by Krot et al. (2004, see their Table 7), which largely lack secondary mineralizations, and have low Fe concentrations. One of the most prominent features of the Murray CAI alteration assemblages is, therefore, the enrichment in Fe. Iron, mostly included here in phyllosilicates, was thus imported by the fluid phase. As Ni is also enriched, Fe in the altered CAI likely originates at least partly from the alteration of the Fe,Ni-alloy kamacite from chondrules or the matrix, via corrosion of the metal by water, similar to earlier suggestions (Tomeoka and Buseck, 1985). The second striking feature is Ca depletion. Note that the conclusion holds true if we include the perovskite relicts in the average (Ca concentration is then <3 wt%). Looking at elemental maps (Fig. 3.b and 4.c), Ca exported from the CAI may in fact have partly precipitated at the

rim of the CAI (see section 3.2.1). The case of Al is more complicated. Indeed, large variations of the Al content are observed among the alteration assemblages (Table 2, and section 3.2.1.), although the total relative content of Al is low compared to average CAIs (Table 3). Aluminum has a complex chemistry: it is very insoluble at circumneutral pH but its solubility is significantly increased under acidic ($\text{pH} < 6.0$) or alkaline ($\text{pH} > 8.0$) conditions, and strongly depends on the formation of complexes with various inorganic or organic ligands (Driscoll and Schecher, 1990). As a consequence, we have no definite interpretation of the apparent Al depletion, but this point would deserve further investigation. Concentrations of Mg and Si measured here are within the range of CAI concentrations, but Si stands in the lower range. This would suggest a rather low SiO_2 activity in the fluid, which is consistent with the predominance of serpentine over smectite. The only identified primary relicts are perovskite and spinel, suggesting that if any primary Si-bearing phases were present, they had been totally consumed. The most common Si-bearing phase preserved in CAIs of CM chondrites is Ca-pyroxene (Lee and Greenwood, 1994; Rubin, 2007), which was not detected here, followed by olivine, which is usually present as a rim phase. Micrometer-sized olivine observed here around the altered CAI might be a remnant of this rim. Rubin (2007) linked the lack of melilite in CAIs from CM chondrites to the high degree of alteration of the meteorites. Indeed, observations (Hashimoto and Grossman, 1987) and experiments (Nomura and Miyamoto, 1998) show that melilite is highly susceptible to alteration. The fact that Hewins et al. (2014) observed partly preserved melilite in the Paris chondrite is actually consistent with these observations, as the authors propose that this chondrite is significantly less altered than other known CM chondrites. The Na-bearing hydrated aluminosilicate described in section 3.2.1 is the most Si-rich phase of the secondary assemblage of Murray' CAI and is analogous to the alteration phase of melilite observed in the Paris meteorite (interpreted by Hewins et al., 2014, as a zeolite) and to the secondary assemblages obtained by Nomura and Miyamoto (1998). Further investigation of this phase would be important as such phases (for instance zeolite, hydrogarnet or hydromelilite) form at temperatures higher than that generally inferred for the alteration of CM2 chondrites ($< 100^\circ\text{C}$, Zolensky et al., 2008).

4.2. Oxidation of iron and implications for parent body alteration processes

The matrix and alteration assemblages of the CAI contain mostly ferric iron. It is possible that some terrestrial oxidation occurred either before or during FIB sampling. The preservation of the oxidation state of Fe in the cronstedtite reference after ion beam milling suggests a limited impact of the preparation of the samples, as suggested previously (e.g.

Bourdelle et al., 2013), although the effects would depend on the size of the particles and their crystallinity. Additionally, the ferric iron ratio determined by Sephton et al. (2004) for the Murray chondrite, ~ 70%, agrees well with the matrix values of ~ 60 to 75% determined by Beck et al. (2012) using XANES at the Fe K-edge, and with the ~ 75% matrix average presented here. In a Mössbauer study of bulk fragments of several CM chondrites, either recovered in Antarctica or collected shortly after their fall, Sephton et al. (2004) have shown that iron in Antarctic chondritic finds is generally nearly completely oxidized (up to 90% Fe^{3+}), reflecting terrestrial weathering, whereas meteorite falls, such as the Murray chondrite, show lower ferric iron ratios, as well as a higher preservation of the organic matter. Lee and Bland (2004) evaluated terrestrial weathering processes in meteorites by comparing falls and finds of L5 and L6 equilibrated ordinary chondrites, which are interesting from that point of view because falls do not show evidence for any significant parent body aqueous alteration. They concluded that whereas terrestrial Fe^{3+} -bearing mineralogical assemblages occurred in finds, they were absent in falls. Among the CM2 falls, the Murray chondrite is generally considered as one of the least terrestrially weathered (e.g. Bland et al., 2006; Rubin et al. 2007). So even though a terrestrial overprint is possible, and should be further tested using a methodology such as the one developed here, ideally in the future framework of asteroid samples return missions, high ferric iron ratios are observed consistently in the Murray chondrite, as well as in other CM2 falls (Sephton et al., 2004), hence the question of the processes of Fe oxidation on the parent body.

Prior to parent body aqueous alteration, the initial mineralogical assemblages formed by nebular processes would mainly comprise Fe^0 and Fe^{2+} (Zolensky et al., 1989; Rosenberg et al., 2001) due to the reducing character of the solar nebula gas. The oxidation state of the gas is controlled by the concentration of water relative to hydrogen, which would have fluctuated from values producing only metallic iron to higher values inducing the incorporation of FeO in silicates and oxides (Krot et al., 2000; Ciesla and Cuzzi, 2006). Therefore, Fe is partially oxidized during aqueous alteration in the anoxic environment of asteroids. It has been proposed that the radiolysis of ices accreted to chondritic parent bodies generates strong oxidants, such as H_2O_2 (Cody and Alexander, 2005). Hydrogen peroxide can oxidise Fe^{2+} via Fenton reactions. Oxidation of Fe^{2+} by water is another possibility, but the process and rate of electron transfer from aqueous Fe^{2+} to water are not well understood. Mayhew et al. (2013) suggest a catalytic role of minerals of the spinel group in the oxidation of aqueous Fe^{2+} during laboratory hydrothermal alteration of ultramafic and mafic assemblages at 55-100°C under strictly anoxic conditions. Indeed, even though spinels are accessory phases (<1 vol%) in the

initial assemblages considered by these authors, the surface of these minerals would efficiently promote electron transfers that would be otherwise kinetically inhibited. This may provide a mechanism by which aqueous Fe^{2+} released by the alteration of primary ferromagnesian minerals for instance is oxidized in chondrites, particularly in spinel bearing CAIs – i.e. in most CAIs. Alternatively, a large number of studies document the corrosion of metallic iron by water in anoxic conditions, yielding both ferrous and ferric iron species. The analogy between the corrosion of metal and iron-silicate reactions in confined nuclear waste disposal (e.g. Lantenois et al., 2005) and asteroidal alteration has been outlined by a number of authors (Perronnet et al., 2008, Morlok and Libourel, 2013). Legrand et al. (2000) showed that an increase of pH (8.5-9), and/or temperature, and moderate concentrations of dissolved carbonate promoted the production of Fe^{3+} species under anoxic conditions. Conditions for this mechanism to occur are likely met in chondritic parent bodies, where alkaline and carbonated fluids would be produced by the inferred rock and ice precursors (Rosenberg et al., 2001). In the present case, the geochemical budget of the alteration of the CAI supports the supply of Fe from the fluid. Transport as Fe^{3+} would have required strongly acidic conditions, whereas numerical modeling suggests that alkaline conditions prevailed (Zolensky et al., 1989; Rosenberg et al., 2001). But if Fe was transported as Fe^{2+} then either a local increase of pH or catalysis by minerals such as spinel might have promoted the oxidation and precipitation of Fe in phyllosilicates – not necessarily simultaneously. Nomura and Miyamoto (1998) monitored the pH during the alteration of primary CAI phases, and observed increasing pH, especially in the case of melilite. The mechanisms discussed above generate hydrogen, which opens an important question: given the low density and the high rate of diffusion of hydrogen, would the system have evolved toward increasingly oxidizing conditions, through H_2 escape? Studies of the global Fe valence state in chondrites are still scarce (Sephton et al., 2004; Bland et al., 2006; Beck et al., 2012) and it is still difficult to decipher whether or not there is a trend towards a higher Fe^{3+} content with a higher degree of parent body alteration, which might have been induced by H_2 escape as discussed previously (Alexander et al., 2010; Zolotov, 2014; Howard et al., 2015). Alternatively, if H_2 was produced, it may have reacted locally with carbon species for instance (e.g. Guo and Eiler, 2007), and hence played a role in prebiotic organosynthesis.

4.3. Parameters controlling the crystal-chemistry of Fe-rich serpentines

The alteration assemblages of the CAI, containing mixed-valence serpentines, Fe,Ni-sulfides and sulfates suggest redox disequilibrium, which is expected given the slow electron

transfer rates. Among the serpentine assemblages, $\text{Fe}^{3+}/\Sigma\text{Fe}$ is inversely correlated with the Fe content (comparison between Fig. 4.b and Fig. 7). This suggests a local mobility of Fe^{2+} together with Mg and Al, and not only a redox process. The compositional and structural variability of serpentines reflects metastability and suggests transformations in response to nanoscale differences in the composition of the fluid. Establishing whether the phyllosilicates of the altered CAI evolved toward Al- and Mg-rich compositions or the contrary is not straightforward. However, in assemblages with higher Al and Mg concentrations, bending of 1:1 layers and random interstratifications with hydroxide layers may suggest the destabilization of an initial, Mg- and Al-poorer, serpentine phase. The effect can be better evaluated using both compositional and X-ray absorption data, in areas where the full L_2 -edge spectra were obtained (data displayed in Fig. 6). Here we bear in mind that data for the fine-grained assemblages are often Si deficient, suggesting inter-layering with Mg,Al-rich hydroxides. The structural formula calculated for the coarse serpentine is close to that of cronstedtite, with Al and Mg substitution limited to less than 1 per formula unit. As an example, the composition shown by the green dot in Fig. 6.a, and the corresponding Fe L_2 -edge spectrum in Fig. 6.b (green line) gives high amounts of tetrahedral Fe^{3+} :

$(\text{Mg}_{0.39}\text{Al}_{0.36-x}\text{Fe}^{2+}_{1.74}\text{Fe}^{3+}_{0.48+x})(\text{SiAl}_x\text{Fe}^{3+}_{1-x})_2\text{O}_5(\text{OH})_4$ with a x value within the range 0-0.36, depending on the distribution of Al over tetrahedral and octahedral sites. Calcium, Ti and Mn yield a total of ~ 0.02 per 5 cations, and other cations yield even smaller concentrations, and are not shown in the structural formula. The total cationic charge calculated using the Fe valence state is 13.83, which suggests that the structural model is correct. In fact, data for fine assemblages also seem compatible with a serpentine model. Indeed, we found for instance a cationic charge of 14.18 (pink symbol and curve in Fig. 6) suggesting that there are 5 cations for 7 O (and, therefore, no cation vacancy). This is consistent with structural data (Fig. 5.b). Thereby calculating the number of Fe^{3+} cations for 5 cations using X-ray absorption spectra at the L_2 -edge, we obtain about 1.5 Fe^{3+} in the previous case, a maximum of 2 Fe^{3+} in fine-grained phyllosilicates and 0.9 to 1.8 in coarse-grained phyllosilicates.

The low amount of Al in the coarse, cronstedtite-type phyllosilicates of the altered CAI is striking, and comparable to the Al content of other meteoritic cronstedtite, regardless of the context. Lee and Greenwood (1994) measured 0.12 Al and 0.7 Mg for 5 cations in Fe-rich serpentine rimming an altered CAI of the Murray chondrite. In the Paris chondrite, ATEM analyses of matrix cronstedtite crystals yield about 0.3 Al and 0.8 Mg for 5 cations (Hewins et al. 2014, see their Table 9). Zega and Buseck (2003) studied fine-grained rims around

chondrules in one of the most heavily altered CM2 chondrites, the Cold Bokkeveld meteorite. There, cronstedtite crystals have about 0.4 Al and 0.9 Mg for 5 cations. In all cases, cronstedtite is intergrown with variable amounts of tochilinite (higher than in the present study). Similarly, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of cronstedtite determined using electron energy loss spectroscopy by Zega et al. (2003) in fine-grained rims around chondrules and in the matrix of Murray, Murchison (presenting an alteration degree comparable to that of Murray) and Cold Bokkeveld are very close to one another (0.45 to 0.54) and to the one found here in the coarse phyllosilicates. Cronstedtite has long been proposed as an early alteration phase (e.g. McSween, 1979b). This observation, and the fact that a Fe-rich phyllosilicate phase, sometimes identified as cronstedtite, is frequently observed around more pristine spinel and perovskite bearing CAIs, for instance in the Paris chondrite (Hewins et al., 2014) support their formation at early stages of alteration. Our results support the hypothesis of a primary Fe oxidation and precipitation of a cronstedtite-type phase containing small but consistent amounts of Al and Mg in CM. The early formation of Fe^{3+} -rich serpentine may be kinetically controlled, similarly to the early formation of Fe^{3+} -bearing serpentine during the experimental alteration of peridotite observed by Marcaillou et al. (2011).

This primary formation of cronstedtite would then be followed by destabilization by input of Al- and Mg-rich solutions, and Fe^{2+} leaching in the CAI, thus providing a possible mechanism for the transformation from Fe-rich to Mg-richer serpentines with alteration observed in CM chondrites. Fe^{2+} leaching was possibly followed by Fe precipitation as nanometer-sized Fe,Ni-sulfides at the edge of the CAI, maybe along a sulfur gradient, as observed in terrestrial hydrothermal systems (e.g. mid-ocean vent sulfide deposits, Haymon, 1983). Indeed, we expect variations of the fluid's properties in and out of the CAI, partly because of differences in permeability, hindering homogenization. The matrix has a very low permeability, so that water flux might have been more important along grain boundaries (Bland et al., 2009), for instance in CAIs. Also, chemical gradients are expected in a heterogeneous system where incomplete reactions take place in a similar way to hydrothermal alteration of mafic and ultramafic rocks where reactions are limited temporally and spatially by the fluid flux (Alt et al., 2010). As outlined by Bland et al. (2009), aqueous alteration in chondrites would be isochemical because of the localized scale of circulation ($< 1\text{mm}$), as opposed to open-system convection. Similar conclusions were reached by Andreani et al. (2007) from a chemical microanalysis of oceanic serpentinites. As outlined by these authors, important feedbacks are expected between the hydrodynamic properties (permeability, porosity) of a system and physico-chemical processes such as dissolution, diffusion and

crystallization. In peridotites, serpentine crystallization in veins may result from local, out-of-equilibrium, diffuse mass transfer (Andreani et al., 2007). Here, similar mechanisms may be at play at grain boundaries. It is important to identify such processes and to evaluate their quantitative influence relative to equilibrium processes in the control of the crystal-chemistry of alteration phases.

5. CONCLUSIONS

This study provides new insights into the processes of formation of Fe-rich serpentines and of Fe oxidation in carbonaceous chondrites. The combination of analytical electron microscopy and STXM-XANES techniques used here gave an accurate account of the crystal-chemistry of Fe-rich serpentine assemblages in the Murray chondrite, yielding details about the complex chemical and mineralogical transformations associated with the aqueous alteration of a refractory CAI inclusion. Spinel and perovskite are the only remaining primary phases, suggesting a total consumption of any initial Si-bearing phases. The altered CAI is highly enriched in Fe, depleted in Ca relative to the average CAIs, and mostly replaced by Fe-bearing serpentines, suggesting alteration by a fluid with a low Si activity and a high Fe activity. Serpentines are Fe³⁺-rich, indicating an oxidation phase likely promoted by local changes in pH, which are known to occur during the alteration of primary phases of CAIs and / or by mineral catalysis, for instance by spinel phases. We observed the coexistence of two main populations of Fe-serpentines. The first is Al- and Mg-bearing cronstedtite, with a composition very close to that of cronstedtite found in other chondrites, either in CAIs, fine-grained rims or matrix. The second consists in finer grained Fe,Mg,Al-serpentines, containing significantly less Fe²⁺ per formula unit. Association with brucite-type layers and random interstratification is frequent in assemblages with the highest Al and Mg content. Chemistry, redox and structure of the serpentine-rich assemblages reveal strong disequilibria, similar to polysomatic assemblages observed in hydrothermal terrestrial systems. The partial oxidation of Fe²⁺ in Fe³⁺ and the subsequent formation of Mg- and Al-bearing cronstedtite occurred first and was followed by a destabilization by small-scale inputs of Al and Mg-rich solutions, thus providing possible mechanisms by which the Fe content of Fe-rich serpentines decreases as alteration proceeds. Associated changes in the valence state of Fe would have been at least partly controlled by the mobility of Fe²⁺. Ferrous iron may then have re-precipitated as Fe,Ni-sulfides at the edge of the refractory inclusion along porosity and presumably fluid composition gradients. Overall, kinetic factors and disequilibrium mass transfers played an important role in the formation of Fe³⁺-rich serpentines and their transformations in the parent

661 body of the meteorite. Finally, the generation of hydrogen by the reactions proposed for Fe
662 oxidation, and its possible interaction with the abundant carbon species present in the parent
663 body of carbonaceous chondrites deserve further attention.

664

665

Acknowledgements

This study was funded by an Agence Nationale de la Recherche (ANR) JC program (“Water-rock interactions in the early Solar system: clues from Fe-serpentines in CM2 chondrites”, coordinated by A. Elmaleh). The SEM and FIB facilities at IMPMC were supported by Région Ile de France grant SESAME 2006 I-07-593/R, INSU-CNRS, INP-CNRS, UPMC, Paris. The EMP facility at CAMPARIS is supported by INSU-CNRS and UPMC. The TEM national facility in Lille (France) is supported by the Conseil Regional du Nord-Pas de Calais, the European Regional Development Fund (ERDF), and INSU-CNRS. Advanced Light Source (ALS) Molecular Environmental Science beamline 11.0.2 is supported by the Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences and Materials Sciences Division, U.S. Department of Energy, at the Lawrence Berkeley National Laboratory. The Canadian Light Source, Saskatoon, Canada (CLS) is supported by NSERC, CIHR, NRC and the University of Saskatchewan. We thank Tolek Tylicszak (LBNL) at the ALS STXM, and Jian Wang, Jay Dynes and Yingshen Lu at the CLS STXM, for their expert support. We also thank Julie Cosmidis and Sylvain Bernard for their help in data collection at ALS and CLS respectively. We thank David Troadec and Imène Estève for the FIB foils, Jean-Claude Boulliard for the cronstedtite samples, ASU Center for Meteorite Studies and Peter R. Buseck for providing the Murray petrological section, Michel Fialin for his help at the EMP (CAMPARIS), and Delphine Cabaret for helpful discussions. We thank Sara S. Russell for her editorial handling, as well as the three reviewers, an anonymous reviewer, Martin R. Lee and Kieren T. Howard for their comments that helped to improve the manuscript.

References

- Alt J. C., Laverne C., Coggon R. M., Teagle D. A. H., Banerjee N. R., Morgan S., Smith-Duque C. E., Harris M. and Galli L. (2010) Subsurface structure of a submarine hydrothermal system in ocean crust formed at the East Pacific Rise, ODP/ IODP Site 1256. *Geochem. Geophys. Geosyst.* **11**, Q10010.
- Alexander C. M. O'. D, Newsome S. D., Fogel M. L., Nittler L. R., Busemann H. and Cody G. D. (2010) Deuterium enrichments in chondritic macromolecular material - Implications for the origin and evolution of organics, water and asteroids. *Geochim. Cosmochim. Acta* **74**, 4417–4437.
- Banfield J. F., Bailey S. W. and Barker W. W. (1994) Polysomatism, polytypism, defect microstructures and reaction mechanisms in regularly and randomly interstratified serpentine and chlorite. *Contrib. Mineral. Petr.* **117**, 137–150.
- Beck P., De Andrade V., Orthous-Daunay F. R., Veronesi G., Cotte M., Quirico E. and Schmitt B. (2012) The redox state of iron in the matrix of CI, CM and metamorphosed CM chondrites by XANES spectroscopy. *Geochim. Cosmochim. Acta* **99**, 305–316.
- Bland P. A., Zolensky M. E., Benedix G. K. and Sephton M. A. (2006) Weathering of chondritic meteorites. In *Meteorites and the early solar system II* (eds. D. S. Lauretta. and H. Y. McSween). The University of Arizona Press, Tucson. pp 853–867.
- Bland P. A., Jackson M. D., Coker R. F., Cohen B. A., Webber J. B.-W., Lee M. R., Duffy C. M., Chater R. J., Ardakani M. G., McPhail D. S. and Benedix G. K. (2009) Why aqueous alteration in asteroids was isochemical: high porosity – high permeability. *Earth Planet. Sci. Lett.* **287**, 559–568.
- Bourdelle F., Benzerara K., Beyssac O., Cosmidis J., Neuville D.R., Brown G.E. and Paineau E. (2013) Quantification of the ferric/ferrous iron ratio in silicates by scanning transmission X-ray microscopy at the Fe L_{2,3}-edges. *Contrib. Mineral. Petr.* **166**, 423–434.
- Brouder C. (1990) Angular dependence of X-ray absorption spectra. *J. Phys.-Condens. Mat.* **2**, 701-738.
- Browning L. B., McSween H. Y. J. and Zolensky M. E. (1996) Correlated alteration effects in CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **60**, 2621-2633.
- Bunch T. E. and Chang S. (1980) Carbonaceous chondrites: II. Carbonaceous chondrite phyllosilicates and light element geochemistry as indicators of parent body processes and surface conditions. *Geochim. Cosmochim. Acta* **44**, 1543–1577.
- Ciesla F. J. and Cuzzi J. N. (2006) The evolution of the water distribution in a viscous protoplanetary disk. *Icarus* **181**, 178–204.

724 Ciesla F. J., Lauretta D. S., Cohen B. A. and Hood L.L. (2003) A nebular origin for chondritic
 725 fine-grained phyllosilicates. *Science* **299**, 549–52.

726 Cody G. D. and Alexander C. M. O'. D. (2005) The history of early solar system processes
 727 recorded in the structure of meteoritic organic solids. *Geochim. Cosmochim. Acta* **69**,
 728 1085–1097.

729 Cosmidis J. and Benzerara K. (2014) Soft X-ray scanning transmission micro-spectroscopy.
 730 In *Handbook of Biomineralization* (eds. L. Gower and E. DiMasi). Taylor and Francis,
 731 London.

732 Cressey G., Henderson C. M. B. and van der Laan G. (1993) Use of L-edge X-Ray-absorption
 733 spectroscopy to characterize multiple valence states of 3d transition-metals: a new probe
 734 for mineralogical and geochemical research. *Phys. Chem. Miner.* **20**, 111–119.

735 Driscoll C. T. and Schecher W. D. (1990) The chemistry of aluminum in the environment.
 736 *Environ. Geochem. Health* **12**, 28–49.

737 Dyar M. D., Delaney J. S. and Sutton S. R. (2001) Fe XANES spectra of iron-rich Micas.
 738 *Eur. J. Mineral.* **13**, 1079–1098.

739 Elmaleh A., Tarantino S. C., Zema M., Devouard B. and Fialin M. (2012) The low-
 740 temperature magnetic signature of Fe-rich serpentine in CM2 chondrites, comparison with
 741 terrestrial cronstedtite and evolution with the degree of alteration. *Geochem. Geophys.*
 742 *Geosyst.* **13**, Q05Z42.

743 Gloter A., Douiri A., Tence M. and Colliex C. (2003) Improving energy resolution of EELS
 744 spectra: an alternative to the monochromator solution. *Ultramicroscopy* **96**, 385–400.

745 Greenwood R. C., Lee M. R., Hutchison R. and Barber D. J. (1994) Formation and alteration
 746 of CAIs in Cold Bokkeveld (CM2). *Geochim. Cosmochim. Acta* **58**, 1913–1935.

747 Guo W. and Eiler J. M. (2007) Temperatures of aqueous alteration and evidence for methane
 748 generation on the parent bodies of the CM chondrites. *Geochim. Cosmochim. Acta* **71**,
 749 5565–5575.

750 Hanhan S., Smith A. M., Obst M. and Hitchcock A. P. (2009) Optimization of analysis of soft
 751 X-ray spectromicroscopy at the Ca 2p edge. *J. Electron. Spectrosc. Relat. Phenom.* **173**,
 752 44–49.

753 Hanowski N. P. and Brearley A. J. (2001) Aqueous alteration of chondrules in the CM
 754 carbonaceous chondrite, Alan Hills 81002: implications for parent body alteration.
 755 *Geochim. Cosmochim. Acta* **65**, 495–518.

756 Hashimoto A. and Grossman L. (1987) Alteration of Al-rich inclusions inside amoeboid
 757 olivine aggregates in the Allende meteorite. *Geochim. Cosmochim. Acta* **51**, 1685–1704.

758 Haymon R. (1983) Growth history of hydrothermal black smoker chimneys. *Nature* **301**,
759 695–698.

760 Heald S. M. and Stern E. A. (1977) Anisotropic X-ray absorption in layered compounds.
761 *Phys. Rev. B: Condens. Matter* **16**, 5549-5559.

762 Heaney P. J., Vicenzi E. P., Giannuzzi L. A. and Livi K. J. T. (2001) Focused ion beam
763 milling: a method of site-specific sample extraction for microanalysis of earth and
764 planetary materials. *Am. Min.* **86**, 1094–1099.

765 Hewins R.H., Bourot-Denise M., Zanda B., Leroux H., Barrat J.-A., Humayun M., Gopel C.,
766 Greenwood R. C., Franchi I. A., Pont S., Lorand J.-P., Cournede C., Gattacceca J.,
767 Rochette P., Kuga M., Marrocchi Y. and Marty B. (2014) The Paris meteorite, the least
768 altered CM chondrite so far. *Geochim. Cosmochim. Acta* **124**, 190-222.

769 Hezel D. C., Russell S., Ross A. and Kearsley A. T. (2008) Modal abundances of CAI's:
770 implications for bulk chondrite element abundances and fractionations. *Meteorit. Planet.*
771 *Sci.* **43**, 1879–1894.

772 Hitchcock A. (2014) *aXis 2000 – Analysis of X-ray Images and Spectra*. Available at:
773 <<http://unicorn.mcmaster.ca/aXis2000.html>>.

774 Howard K. T., Benedix G., Bland P. A. and Cressey G. (2009) Modal mineralogy of CM2
775 chondrites by X-ray diffraction (PSD-XRD). Part 1: Total phyllosilicate abundance and the
776 degree of aqueous alteration. *Geochim. Cosmochim. Acta* **73**, 4576-4589.

777 Howard K. T., Alexander C. M. O'. D., Schrader D. L. and Dyl K. A. (2015) Classification of
778 hydrous meteorites (CR, CM and C2 ungrouped) by phyllosilicate fraction: PSD-XRD
779 modal mineralogy and planetesimal environments. *Geochim. Cosmochim. Acta* **149**, 206-
780 222.

781 Hybler J., Petricek V., Ďurovič S. and Smrcok L. (2000) Refinement of the crystal structure of
782 the cronstedtite-1T. *Clays Clay Miner.* **48**, 331-338.

783 Hybler J., Petricek V., Fabry J. and Ďurovič S. (2002) Refinement of the crystal structure of
784 cronstedtite-2H₂. *Clays Clay Miner.* **50**, 601-603.

785 Kaznatcheev K. V., Karunakaran C., Lanke U. D, Urquhart S. G., Obst M. and Hitchcock A.
786 P. (2007) Soft X-ray spectromicroscopy beamline at the CLS: Commissioning results.
787 *Nucl. Instrum. Methods Phys. Res., Sect. A* **582**, 96-99.

788 Klein F., Bach W., Joens N., McCollom T. M., Moskowitz B. and Berquo T. (2009) Iron
789 partitioning and hydrogen generation during serpentinization of abyssal peridotites from
790 15°N on the Mid-Atlantic Ridge. *Geochim. Cosmochim. Acta* **73**, 6868–6893.

791 Krot A. N., Scott E. R. D. and Zolensky M. E. (1995) Mineralogical and chemical
 792 modification of components in CV3 chondrites: Nebular or asteroidal processing.
 793 *Meteoritics* **30**, 748-775.

794 Krot A. N., Petaev M. I., Scott E. R. D., Choi B.-G., Zolensky M. E. and Keil K. (1998)
 795 Progressive alteration in CV3 chondrites: More evidence for asteroidal alteration. *Meteorit.*
 796 *Planet. Sci.* **33**, 1065–1085.

797 Krot A. N., Fegley B., Lodders K. and Palme H. (2000) Meteoritical and astrophysical
 798 constraints on the oxidation state of the solar nebula. In *Protostars and Planets IV* (eds.
 799 V. Mannings, A. P. Boss, S. S. Russell). Univ. of Arizona Press, Tucson, pp. 1019–1054.

800 Krot A. N., MacPherson G. J., Ulyanov A. A. and Petaev M. I. (2004) Fine-grained, spinel-
 801 rich inclusions from the reduced CV chondrites Efremovka and Leoville: I. Mineralogy,
 802 petrology, and bulk chemistry. *Meteorit. Planet. Sci.* **39**, 1517-1553.

803 Kuiper P., Searle B., Duda L.-C., Wolf R. and van der Zaag P. (1997) Fe $L_{2,3}$ linear and
 804 circular magnetic dichroism of Fe_3O_4 . *J. Electron. Spectrosc. Relat. Phenom.* **86**, 107-113.

805 Lantenois S., Lanson B., Muller F., Bauer A., Jullien M. and Plançon A. (2005) Experimental
 806 study of smectite interaction with metal iron at low temperature: 1. Smectite destabilization.
 807 *Clays Clay Miner.* **53**, 597-612.

808 Lee M. R. and Greenwood R. C. (1994) Alteration of calcium- and aluminium-rich
 809 inclusions in the Murray (CM2) carbonaceous chondrite. *Meteoritics* **29**, 780-790.

810 Lee M. R. and Bland P. A. (2004) Mechanisms of weathering of meteorites recovered from
 811 hot and cold deserts and the formation of phyllosilicates. *Geochim. Cosmochim. Acta* **68**,
 812 893-916.

813 Lee M. R., Sofo M. R., Lindgren P., Starkey N. A. and Franchi I. A. (2013) The oxygen
 814 isotope evolution of parent body aqueous solutions as recorded by multiple carbonate
 815 generations in the Lonewolf Nunataks 94101 CM2 carbonaceous chondrite. *Geochim.*
 816 *Cosmochim. Acta* **121**, 452-466.

817 Legrand L., Savoye S., Chausse A. and Messina A. (2000) Study of oxidation products
 818 formed on iron in solutions containing bicarbonate/carbonate. *Electrochim. Acta* **46**, 111–
 819 117.

820 MacPherson G. J. (2003) Calcium-aluminum-rich inclusions in chondritic meteorites. In
 821 *Meteorites, Planets, and Comets* (ed. A. M. Davis), *Treatise on Geochemistry, Vol. 1* (eds.
 822 H. D. Holland and K. K. Turekian). Elsevier- Pergamon, Oxford. pp 201-246.

823 Marcaillou C., Muñoz M., Vidal O., Parra T. and Harfouche M. (2011) Mineralogical
824 evidence for H₂ degassing during serpentinization at 300 degrees C/300 bar. *Earth*
825 *Planet. Sci. Lett.* **303**, 281-290.

826 Mayhew L. E., Ellison E. T., McCollom T. M., Trainor T. P. and Templeton A. S. (2013)
827 Hydrogen generation from low temperature water–rock reactions. *Nat. Geosci.* **6**, 478–484.

828 McSween H. Y. (1979a) Are carbonaceous chondrites primitive or processed? A review. *Rev.*
829 *Geophys. Space Phys.* **17**, 1059–1078.

830 McSween H. Y. (1979b) Alteration in CM carbonaceous chondrites inferred from modal and
831 chemical variations in matrix. *Geochim. Cosmochim. Acta* **43**, 1761-1770.

832 Mellini M., Rumori C. and Viti C. (2005) Hydrothermally reset magmatic spinels in
833 retrograde serpentinites: formation of ‘ferritchromit’ rims and chlorite aureoles. *Contrib.*
834 *Mineral. Petrol.* **149**, 266–275.

835 Morlok A. and Libourel G. (2013) Aqueous alteration in CR chondrites: Meteorite parent
836 body processes as analogue for long-term corrosion processes relevant for nuclear waste
837 disposal. *Geochim. Cosmochim. Acta* **103**, 76–103.

838 Müller W.F., Kurat G. and Kracher A. (1979) Chemical and crystallographic study of
839 cronstedtite in the matrix of the Cochabamba (CM2) carbonaceous chondrite. *Tschermaks*
840 *Mineral. Petrogr. Mitt.* **26**, 293–304.

841 Nomura K. and Miyamoto M. (1998) Hydrothermal experiments on alteration of Ca-Al-rich
842 inclusions (CAIs) in carbonaceous chondrites: Implications for aqueous alteration in parent
843 asteroids. *Geochim. Cosmochim. Acta* **62**, 3575–3588.

844 Oufi O. and Cannat M. (2002), Magnetic properties of variably serpentinized abyssal
845 peridotites, *J. Geophys. Res.* **107 B5**, 2095.

846 Perronnet M., Jullien M., Villieras F., Raynal J., Bonnin D. and Bruno G. (2008) Evidence of
847 a critical content in Fe(0) on FoCa7 bentonite reactivity at 80 degrees C. *Appl. Clay Sci.*
848 **38**, 187–202.

849 Pouchou J.-L. and Pichoir F. (1985) “PAP” phi-rho-Z procedure for improved quantitative
850 microanalysis. In *Microbeam Analysis* (ed. J.L. Armstrong). San Francisco Press Inc, San
851 Francisco, California. pp 104-106.

852 Rosenberg N.D., Browning L. and Bourcier W.L. (2001) Modeling aqueous alteration of CM
853 carbonaceous chondrites. *Meteorit. Planet. Sci.* **36**, 239–244.

854 Rubin A. E (2007) Petrography of refractory inclusions in CM2.6 QUE 97990 and the origin
855 of melilite-free spinel inclusions in CM chondrites. *Meteorit. Planet. Sci.* **42**, 1711-1726.

856 Rubin A. E., Trigo-Rodríguez J. M., Huber H. and Wasson J. T. (2007) Progressive aqueous
 857 alteration of CM carbonaceous chondrites. *Geochim. Cosmochim. Acta* **71**, 2361-2382.

858 Russell S. S., Huss G. R., Fahey A. J., Greenwood R. C., Hutchison R. and Wasserburg G. J.
 859 (1998) An isotopic and petrologic study of calcium-aluminum-rich inclusions from CO3
 860 meteorites. *Geochim. Cosmochim. Acta* **62**, 689–714.

861 Sanz J., Herrero C. P. and Robert J.-L. (2003) Distribution of Si and Al in clintonites: a
 862 combined NMR and Monte Carlo study. *J. Phys. Chem. B* **107**, 8837-8342.

863 Scott E. R. D. and Krot A. N. (2003) Chondrites and their components. In *Meteorites, Comets,*
 864 *and Planets* (ed. A. M. Davis), *Treatise on Geochemistry, Vol. 1.* (eds. H. D. Holland and
 865 K. K. Turekian). Elsevier- Pergamon, Oxford, pp. 143–200.

866 Sephton M. A., Bland P. A., Pillinger C. T. and Gilmour I. (2004) The preservation state of
 867 organic matter in meteorites from Antarctica. *Meteorit. Planet. Sci.* **39**, 747–754.

868 Simon S. B. and Grossman L. (2004) A preferred method for the determination of bulk
 869 compositions of coarse-grained refractory inclusions and some implications of the results.
 870 *Geochim. Cosmochim. Acta* **68**, 4237–4248.

871 Tomeoka K. and Buseck P. R. (1985) Indicators of aqueous alteration in CM carbonaceous
 872 chondrites : Microtextures of a layered mineral containing Fe, S, O and Ni. *Geochim.*
 873 *Cosmochim. Acta* **49**, 2149-2163.

874 Tomeoka K., McSween H. Y. and Buseck P. R. (1989) Mineralogical alteration of CM
 875 chondrites: a review. *Proc. NIPR Symp. Antarct. Meteorites* **2**, 221–234.

876 van Aken P. A. and Liebscher B. (2002) Quantification of ferrous/ferric ratios in minerals:
 877 new evaluation schemes of Fe L-23 electron energy-loss near-edge spectra. *Phys. Chem.*
 878 *Miner.* **29**, 188–200.

879 van der Laan G. and Kirkman I. W. (1992) The 2p absorption spectra of 3d transition metal
 880 compounds in tetrahedral and octahedral symmetry. *J. Phys. Condens. Matter* **4**, 4189-
 881 4204.

882 Velbel M. A., Tonui E. K. and Zolensky M. E. (2012) Replacement of olivine by serpentine
 883 in the carbonaceous chondrite Nogoya (CM2). *Geochim. Cosmochim. Acta* **87**, 117–135.

884 Zega T. J. and Buseck P. R. (2003) Fine-grained rim mineralogy of the Cold Bokkeveld CM
 885 chondrite. *Geochim. Cosmochim. Acta* **67**, 1711-1721.

886 Zega T. J., Garvie L. A. J. and Buseck P. R. (2003) Nanometer-scale measurements of iron
 887 oxidation states of cronstedtite from primitive meteorites. *Am. Mineral.* **88**, 1169-1172.

888 Zolensky M. E., Bourcier W. L. and Gooding J. L. (1989) Aqueous alteration on the hydrous
 889 asteroids: results of EQ3/6 computer simulations. *Icarus* **78**, 411–425.

Zolensky M. E., Barrett R. and Browning L. (1993) Mineralogy and composition of matrix and chondrule rims in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **57**, 3123-3148.

Zolensky M. E., Mittlefehldt D. W., Lipschutz M. E., Wang M.-S., Clayton R. N., Mayeda T. K., Grady M. M., Pillinger C. T. and Barber D. (1997) CM chondrites exhibit the complete petrologic range from type 2 to 1, *Geochim. Cosmochim. Acta* **61**, 5099-5115.

Zolensky M. E., Krot A. N. and Benedix G. (2008) Low-temperature alteration in asteroids. *Rev. Mineral. Geochem.* **68**, 429-462.

Zolotov M. (2014) Formation of brucite and cronstedtite-bearing mineral assemblages on Ceres. *Icarus* **228**, 13-26.

Figure captions

Fig. 1: X-ray absorption spectra of cronstedtite (ultra-thin foil 1) at the Fe $L_{2,3}$ -edges measured in transmission mode (STXM, ALS) (no background correction, no normalization, same area of the FIB foils for both polarizations, $0.6 < O.D. < 0.9$). We used a linear polarization with the polarization vector ϵ either perpendicular or parallel to the c axis. The evolution of the absorption at 708.2 eV for intermediate positions of ϵ with respect to the c axis is shown in the inset, as well as a fit (see section 3.1. for explanation). The experimental setup is shown in the upper part of the graphics.

Fig. 2: Fe L_2 -edge data obtained for cronstedtite using linear polarization, in different orientations and from different samples, after background correction and normalization to the maximum. **a.** Data from Fig. 1 (ALS, ultra-thin foil 1), with peak assignment (see section 3.1. for explanation). **b.** STXM data from ultra-thin foil 2/1 (measured at CLS), same experimental setup as in **a.** **c.** STXM data from ultra-thin foil 2/2 (measured at CLS), with c perpendicular to k .

Fig. 3: SEM and EMPA data from the altered Murray. **a.** SEM backscattered electron image showing the location of the FIB ultra-thin foil (a-b). The frame refers to the EMP composition maps displayed in **b.** Note the high density of Ca-rich phases and Ni-rich sulfides around the CAI. White asterisks highlight olivine (closed symbol) and pyroxene (open symbol). In **a.** and **b.** the white arrows indicate Ca,Ti-perovskite. In **a.**: the black arrows

indicate Al,Mg-spinels. The black double arrows point towards dense patches of nanometer sized Fe,Ni-sulfides (visible in the bottom right of the Ni map in **b.**), and the white double arrow indicates the Na-bearing hydrated aluminosilicate mentioned in section 3.2.1.

Fig. 4: STEM image and STEM-EDS composition maps of the FIB foil taken from the Murray chondrite (*italic a and b* refer to Fig. 3). **a.** STEM image. White arrow: perovskite; yellow arrows: spinels, the tip of the arrows signals Ti and Ca-enriched rims. The asterisks and numbers 1, 2 and 3 refer respectively to Fig. 5.a and 5.b. and 5.c. White rectangle: area where STXM stack images were taken. **b.** and **c.** STEM-EDS maps. In **b.**, Fe is in red, Mg, in blue and Al, in green. In **c.**, Si is in turquoise, Ca in yellow, Ni in dark blue and S in red. The Fe-sulfides appear red and the Fe,Ni-sulfides appear purple on the image. The Pt edge appears in **c.** as a pink band. Note the patchy distribution of Ca, mostly as phosphate grains (P not shown here) and S-rich lamellae. Ca-rich phases are more abundant at the edge the CAI. White arrows in **b.** and **c.**: examples of Fe, Mg, Al and S-rich lamellae interpreted as tochilinite lamellae.

Fig. 5: Electron microscopy observations and analyses of phyllosilicate assemblages, in areas labeled 1, 2 and 3 in Fig. 4.a. **a.** Bright field TEM image of a coarse grained serpentine (labeled 1, dark lath; the image is rotated by 120° with respect to Fig. 4), and corresponding SAED pattern, displaying a 0.7 nm basal spacing. Below is a higher resolution image of the left edge of the crystal (white rectangle in the image upper), showing the 0.7 nm spacing on the right, and a faint but regular 0.48 nm spacing on the left. **b.** Bright field TEM image (left), selected area (white circle), and corresponding electron diffraction pattern (right) of fine grained serpentine from the area labeled 2 in Fig. 4.a, surrounding one of the spinels. Indexing is as follows: 0.73 nm / 001, 0.44 nm / 020, 0.36 nm / 002, 0.26 nm / 200 and 0.24 nm / 003. Note the tiny black crystals at the edge of the spinel crystal and within the fracture, corresponding to the Ca- and Ti-enriched rim mentioned in section 3.2.1. **c.** HRTEM image of the area labeled 3 in Fig 4.a. Packets with a 0.7 nm basal spacing are shown by brackets; domains with different spacing are shown in the images below, which are higher magnification images of the framed areas.

Fig. 6: STEM-EDS and STXM-XANES (ALS) data of phyllosilicate assemblages. Data come from within the white rectangle in Fig. 4.a. **a.** Variations in the Fe, Mg and Al+Si content of the phyllosilicates from the altered CAI in the Murray chondrite, obtained by

STEM-EDS, and expressed as the number of atoms for a total of 5 cations. **b.** Examples of corresponding normalized X-ray absorption spectra (X.A.S.) at the Fe L₂-edge. The reference spectra of cronstedtite obtained using linear polarization (ϵ parallel and perpendicular to the **c** axis, same as Fig. 2.a) are shown as dotted lines. In all figures, the coarse grained and fine-grained populations are distinguished. The composition data and spectra discussed in section 4.3 are shown in pink and green in both **a.** and **b.**

Fig. 7: Semi-quantitative map of the valence state of iron in the Murray ultra-thin foil based on STXM Fe L₂-edge data (ALS). Black areas, including spinel, perovskite and the Pt deposit of the FIB foil contain very low amounts of Fe and yielded a high noise over signal ratio at this resolution. Fe²⁺-rich minerals such as nanometer size Fe,Ni-sulfides observed at the edge of the CAI appear bright green on that map. The coarse serpentine minerals close to the endmember cronstedtite appear pale green or turquoise on the map whereas the fine-grained serpentines appear blue due to their higher Fe³⁺ content.

Table 1: Valence of Fe in cronstedtite deduced from STXM and EMPA measurements

Sample	EMPA	STXM			
	Deduced $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}^{\text{a}}$	Ultra-thin section	Polarization ^b	Apparent $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}^{\text{c}}$	$2/3(\text{Fe}^{3+}/\text{Fe}_{\text{tot}})_{\varepsilon \perp \text{c}} +$ $1/3(\text{Fe}^{3+}/\text{Fe}_{\text{tot}})_{\varepsilon // \text{c}}$
Crystal_1	0.41				0.41
		1 ^d	$\varepsilon // \text{c}$	0.50	
		1 ^d	$\varepsilon \perp \text{c}$	0.37	
Crystal_2	0.43				0.45
		2/1 ^e	$\varepsilon // \text{c}$	0.56	
		2/1 ^e	$\varepsilon \perp \text{c}$	0.40	

^a: deduced from the structural formula obtained by EMPA.
^b: STXM measurements, quantification at the L₂-edge using the calibration of Bourdelle et al. (2013).
^c: Orientation of the polarization vector ε relative to the c axis.
^d: Measured at ALS; ^e: Measured at CLS.

Table 2: STEM-EDS analyses of alteration assemblages of the altered CAI in the Murray chondrite

	Coarse-grained phyllosilicates ^a		Fine-grained phyllosilicates ^a		Al- and Mg rich assemblages ^b	
	Average	S.D.	Average	S.D.	Average	S.D.
wt%						
SiO ₂	14.31	0.17	15.13	1.83	8.32	1.82
Al ₂ O ₃	5.11	2.25	14.21	2.74	26.36	2.4
FeO	73.86	2.93	53.22	4.51	49.82	2.38
MgO	5.03	0.49	15.24	2.28	12.72	3.28
CaO	0.43	0.44	0.23	0.21	0.34	0.29
TiO ₂	0.08	0.12	0.18	0.13	0.22	0.16
MnO	0.39	0.1	0.21	0.13	0.24	0.14
K ₂ O	< 0.4 ^c		0.07	0.11	0.08	0.1
Cr ₂ O ₃	< 0.4 ^c		0.06	0.1	0.07	0.11
S	0.79	1.12	1.34	0.24	1.75	0.43
Ni	< 0.2 ^c		0.08	0.07	0.06	0.07
Number of atoms for a total of 5 cations ^o						
Si	1.02	0.01	0.98	0.11	0.55	0.95
Al	0.32	0.14	0.79	0.14	1.49	1.09
Fe	3.23	0.11	2.12	0.22	2.00	0.76
Ca	0.02	0.02	0.01	0.01	0.02	0.12
Mg	0.39	0.04	1.07	0.14	0.91	1.88
Mn	0.02	0.01	0.01	0.01	0.01	0.04
S	0.08	0.11	0.12	0.02	0.16	0.31

Analyses in wt % normalized to 100% on an anhydrous basis. S.D.: standard deviation from multiple measurem

^a Average of analyses performed in the area highlighted by the rectangle in Fig. 4.a, fully displayed in Fig. 6.

^b Average of analyses from the Al- and Mg-rich region of the alteration assemblages marked by *3 in Fig. 4.a.

^cThe average is close to 0, the maximum values are given here; ^o only values ≥ 0.01 are shown.

Table 3: Mean major element composition of alteration assemblages of the Murray CAI compared to the compositions of CAIs in CV chondrites

	<i>Literature data, CV chondrites</i>				<i>This study</i>	
	<i>Simon & Grossman (2004)[*]</i>		<i>Krot et al. (2004)^{**}</i>		<i>Alteration assemblages^{***}</i>	
	Average	<i>S.D.</i>	Average	<i>S.D.</i>	Average	<i>S.D.</i>
wt%						
SiO ₂	23.44	<i>1.45</i>	31.37	<i>5.87</i>	21.51	<i>4.67</i>
Al ₂ O ₃	35.22	<i>2.70</i>	33.13	<i>6.13</i>	10.75	<i>3.74</i>
FeO	0.68	<i>0.30</i>	1.33	<i>0.97</i>	53.33	<i>9.37</i>
MgO	8.26	<i>2.81</i>	13.40	<i>3.01</i>	9.05	<i>2.32</i>
CaO	30.68	<i>4.93</i>	19.62	<i>4.13</i>	0.74	<i>1.04</i>
TiO ₂	1.70	<i>0.48</i>	0.81	<i>0.47</i>	0.44	<i>0.21</i>
MnO	0.0040	<i>0.0031</i>	<0.08		0.35	<i>0.06</i>
Na ₂ O	0.06	<i>0.03</i>	0.12	<i>0.04</i>	0.85	<i>0.58</i>
K ₂ O	n.d.		<0.04		0.11	<i>0.07</i>
Cr ₂ O ₃	n.d.		0.15	<i>0.09</i>	0.33	<i>0.04</i>
S	n.d.		n.d.		1.12	<i>0.37</i>
Ni	n.d.		n.d.		0.43	<i>0.21</i>
Cl	n.d.		n.d.		0.41	<i>0.21</i>

^{*} Average of INAA data from type A and CTA CAI from Allende, Leoville and Efremkova meteorites from Simon & Grossman (2004, Table 1). ^{**} Average of CAI EMPA data from fine-grained CAIs from Leoville and Efremkova, from Krot et al. (2004, Table 7). n.d.= no data.

^{***} This study, EMPA. Surface analyzed $\approx 2200\mu\text{m}^2$.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7