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# The old, unique C1 chondrite Flensburg – Insight into the first processes of aqueous alteration, brecciation, and the diversity of water-bearing parent bodies and lithologies

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## Abstract

On September 12, 2019 at 12:49:48 (UT) a bolide was observed by hundreds of eye-witnesses from the Netherlands, Germany, Belgium, Denmark and the UK. One day later a small meteorite stone was found by accident in Flensburg. The presence of short-lived cosmogenic radionuclides with half-lives as short as 16 days proves the recent exposure of the found object to cosmic rays in space linking it clearly to the bolide event. An exceptionally short exposure time of  $\sim 5000$  years was determined. The 24.5 g stone has a fresh black fusion crust, a low density of  $< 2 \text{ g/cm}^3$ , and a magnetic susceptibility of  $\log \chi = 4.35$  ( $\chi$  in  $10^{-9} \text{ m}^3/\text{kg}$ ). The rock consists of relict chondrules and clusters of sulfide and magnetite grains set in a fine-grained matrix. The most abundant phases are phyllosilicates. Carbonates ( $\sim 3.9 \text{ vol.}\%$ ) occur as calcites, dolomites, and a Na-rich phase. The relict chondrules (often surrounded by sulfide laths) are free of anhydrous silicates and contain abundant serpentine. Lithic clasts are also surrounded by similar sulfide laths partly intergrown with carbonates.  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  ages of carbonates in Flensburg indicate that brecciation and contemporaneous formation of the pyrrhotite-carbonate intergrowths by hydrothermal activities occurred no later than  $4564.6 \pm 1.0 \text{ Ma}$  (using the angrite D'Orbigny as the Mn-Cr age anchor). This corresponds to  $2.6 \pm 1.0$  or  $3.4 \pm 1.0 \text{ Ma}$  after formation of CAIs, depending on the exact absolute age of CAIs. This is the oldest dated evidence for brecciation and carbonate formation, which likely occurred during parent body growth and incipient heating due to decay of  $^{26}\text{Al}$ .

In the three oxygen isotope diagram, Flensburg plots at the  $^{16}\text{O}$ -rich end of the CM chondrite field and in the transition field to CV-CK-CR chondrites. The mass-dependent Te isotopic composition of Flensburg is slightly different from mean CM chondrites and is most similar to those of the ungrouped C2 chondrite Tagish Lake. On the other hand,  $^{50}\text{Ti}$  and  $^{54}\text{Cr}$  isotope anomalies indicate that Flensburg is similar to CM chondrites, as do the  $\sim 10 \text{ wt.}\%$   $\text{H}_2\text{O}$  of the bulk material. Yet, the bulk Zn, Cu, and Pb concentrations are about 30% lower than those of mean CM chondrites. The He, Ne, and Ar isotopes of Flensburg show no solar wind contribution; its trapped noble gas signature is similar to that of CMs with a slightly lower concentration of  $^{20}\text{Ne}_{\text{tr}}$ .

Based on the bulk H, C, and N elemental abundances and isotopic compositions, Flensburg is unique among chondrites, because it has the lightest bulk H and N isotopic compositions of any type 1 or 2 chondrite investigated so far. Moreover, the number of soluble organic compounds in Flensburg is even lower than that of the brecciated CI chondrite Orgueil.

The extraordinary significance of Flensburg is evident from the observation that it represents the oldest chondrite sample in which the contemporaneous episodes of aqueous alteration and brecciation have been preserved. The characterization of a large variety of carbonaceous chondrites with different alteration histories is important for interpreting returned samples from the OSIRIS-REx and Hayabusa 2 missions.

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**Keywords:** C1 chondrite; Carbonaceous chondrite; Aqueous alteration; Carbonates; Early solar system; Oldest carbonates in solar system; Unique chondrite; Ungrouped C chondrite

## 1. INTRODUCTION

On September 12, 2019 at 12:49:48 UT a daylight fireball was seen by hundreds of eye-witnesses from the Netherlands and Belgium and a few observers in Northern Germany, Denmark, and the UK. Soon after the event some incidental video recordings (dash, action and security cams) from the Netherlands and Germany appeared in the social media (e.g., Fig. 1a).

More than 580 reports by witnesses were collected by the International Meteor Organization (IMO) via their fireball reporting website operated by Mike Hankey of the American Meteor Society. The bolide at 14:49:48 CEST local time was also observed by one of the authors (A.P.) and was

registered by one German AllSky6 meteor camera from Herford (AMS21), which can operate even during daylight hours (Fig. 1b; Fig. S1).

NASA-JPL's Center for Near Earth Object Studies (CNEOS) has released some basic data of the bolide event: The peak brightness of the fireball was reached over  $54.5^\circ \text{ N}$ ,  $9.2^\circ \text{ E}$  at an altitude of about 42 km. The US Government Sensors determined that the meteoroid had an entry velocity of 18.5 km/s, and a total impact energy of 0.48 kt TNT; however, this latter value can only be regarded as a completely unexaminable estimate, since no details about the calculations are known.

One day after the fireball event, on Friday the 13<sup>th</sup> of September, a small meteorite was found by accident by Mr. Erik Due-Hansen on the lawn of his front garden in the southwestern part of Flensburg, Schleswig-Holstein, Germany (Fig. S2; coordinates:  $54^\circ 45.6873' \text{ N}$ ,  $9^\circ 22.7353' \text{ E}$  =  $54.761455^\circ \text{ N}$ ,  $9.378922^\circ \text{ E}$ ) and on September 15<sup>th</sup>

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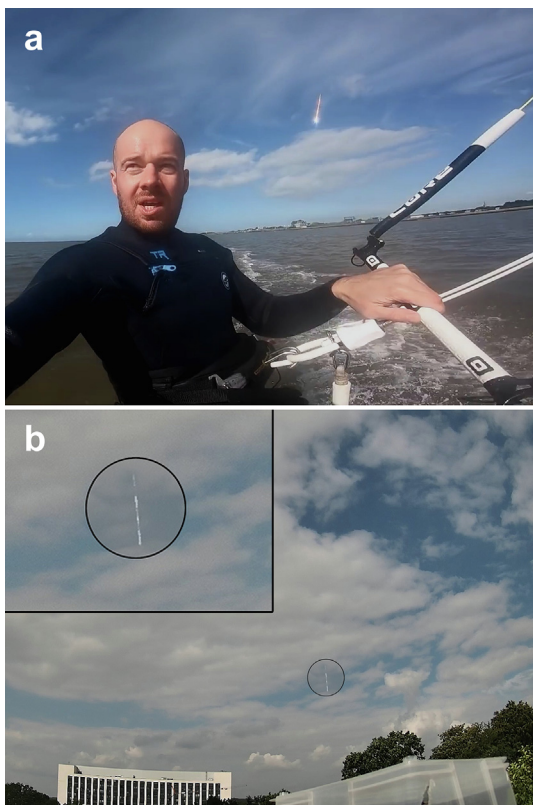


Fig. 1. The observed fireball of the meteoroid entering the atmosphere. (a) A kiteboarder from Bremerhaven recorded the fireball by accident from the mouth of the Weser river near Wremen. He did not hear a detonation sound and did not notice the bolide while filming and editing the action cam video. Image: Dorian Cieloch. (b) The daylight fireball is visible between clouds on this stacked image of a video recorded by the AllSky6 meteor camera AMS21 from Herford. The distance between the meteor camera and the visible part of the bolide is 230 km. Image: Jörg Strunk, Mike Hankey (American Meteor Society).

he reported the meteorite find to the IMO website. More details on the fireball event and on the post-recovery procedures are given in the “Supplementary Material” (SM). The finding of a fresh meteorite is supported by short-lived cosmogenic radionuclide detection by gamma-spectrometry.

In this study, details of the characteristics of Flensburg regarding its mineralogy, chemistry, isotopic and (cosmogenic) nuclide composition are summarized. In addition, some physical properties of the rock will be discussed, as well as details on its soluble organic components.

It was quickly recognized by electron microscopy that Flensburg consists almost entirely of hydrated phases or minerals precipitated from fluids (e.g., phyllosilicates, magnetite, carbonates, pyrrhotite, etc.). Thus, the meteorite was initially classified as an ungrouped C1 chondrite (*The Meteoritical Bulletin* no. 109). In this respect, Flensburg bears some similarities to those CI, CM, and CR chondrites that have also suffered high degrees of aqueous alteration (e.g., Fuchs et al., 1973; McSween, 1979a; Mackinnon and Zolensky, 1984; Rubin and Wasson, 1986; Tomeoka and Buseck, 1988; Zolensky and McSween, 1988;

Fredriksson and Kerridge, 1988; Grimm and McSween, 1989; Zolensky et al., 1989a,b, 1997, 2002; Endress and Bischoff, 1993; Johnson and Prinz, 1993; Browning et al., 1996; Bischoff, 1998; Brearley, 2006; Morlok et al., 2006; Rubin et al., 2007; Howard et al., 2009; Alexander et al., 2012, 2013; Tonui et al., 2014; Garenne et al., 2014; Visser et al., 2018).

However, as already stated in the *Meteoritical Bulletin Database* (<https://www.lpi.usra.edu/meteor/metbull.php?code=71098>), differences exist between Flensburg and CI, CM, and CR chondrites, which will be discussed in detail in this study in order to achieve an appropriate classification.

## 2. SAMPLES AND SUMMARY OF METHODS

To date (October 2020), only one piece with a total mass of 24.5 g has been recovered within the fall area (Fig. 2; Fig. S2). Several thin and thick sections were prepared and stored at the Institut für Planetologie, Wilhelms-Universität Münster (two large ones PL19171 (~71 mm<sup>2</sup>) and PL19172 (~132 mm<sup>2</sup>) and two small sections (PL19173 (~13 mm<sup>2</sup>) and PL19174 (~16 mm<sup>2</sup>)).

Different analytical methods were applied to analyze the rock and to classify this meteorite. Here, a brief summary of most of the methods applied is given, and further details are included in the Supplemental Material (SM).

After initial scanning electron microscopic (SEM) studies on the complete piece in Münster, the meteorite was cut with a saw into two pieces. The smaller piece of about 6.5 g was broken. To provide representative material for a number of bulk analytical methods, a fusion-crust-free chip from the broken 6.5 g piece of approximately 1 g was crushed using an agate pestle and mortar.

Detailed SEM studies on polished thin and thick sections were performed in Münster and at the Friedrich-Schiller-Universität in Jena, while focused ion beam (FIB) work and transmission electron microscope (TEM) studies on the section PL19173 were performed only in Jena using a FEI Quanta 3D FEG FIB-SEM workstation and a FEI Tecnai G2 with a field emission gun (FEG), respectively. Microprobe analyses (EPMA) were done with a JEOL JXA 8530F in Münster, whereas X-ray computed microtomography (CT) studies were performed at the Helmholtz Institute Freiberg for Resource Technology. By this technique, the 3D microstructures within the rock were deciphered and several phases could be distinguished, e.g. sulfides, silicates, and pores, based on the phase density. A CT scan with 11.7 μm voxel size of the larger part (17.0 g) of the meteorite was performed and processed.

Cosmogenic as well as primordial radionuclide concentrations were analyzed on the complete piece by non-destructive gamma-spectrometry in the underground laboratory “Felsenkeller” (Niese et al., 1998) of the VKTA Rossendorf, and thereafter using a 35.60 mg aliquot of the ~1 g bulk powder by destructive accelerator mass spectrometry (AMS) at the Helmholtz-Zentrum Dresden-Rossendorf for <sup>10</sup>Be and <sup>26</sup>Al (Rugel et al., 2016), and at the Australian National University, Canberra for <sup>41</sup>Ca and <sup>60</sup>Fe (Wallner et al., 2015), respectively. Additionally, <sup>14</sup>C was measured on a 25 mg homogenized bulk aliquot

at the University of Arizona AMS Laboratory (Jull et al., 2008).

A 104 mg aliquot taken from the homogenized  $\sim 1$  g sample of the Flensburg meteorite was analysed for major and trace element concentrations by inductively-coupled plasma atomic emission spectrometry (ICP-AES) and inductively-coupled plasma sector field mass spectrometry (ICP-SFMS). The procedure is described by Barrat et al. (2012, 2015, 2016). The concentration reproducibility is generally much better than 5% at the chondritic level.

Several aliquots of the  $\sim 1$  g bulk powder, totalling about 40 mg were used to determine the bulk water/OH content and C concentration at the University of Bochum (see details in SM). Roughly 4 mg and 16 mg aliquots were used to determine, respectively, the bulk H and the bulk C and N elemental and isotopic abundances using the methods outlined in Alexander et al. (2012, 2013; details in SM).

Bulk oxygen isotope compositions of three  $\sim 2$  mg samples were obtained by means of laser fluorination. The details on the latter technique and normalization are reported in the SM and previously published studies (see Pack et al. (2016) and Peters et al. (2020) for the protocol and standardization).

Titanium and Cr isotope analyses on 20–50 mg samples of Flensburg were performed in Münster and at the ETH Zürich. Chromium and Ti analyses at the ETH Zürich were carried out on a single 26 mg aliquot of the Flensburg meteorite and used a Thermo Scientific Neptune Plus

multi-collector inductively-coupled plasma mass spectrometer (MC-ICPMS). The analytical procedure is described in Bischoff et al. (2019b). In Münster, the Cr isotope data were obtained using a Thermo Scientific Triton Plus Thermal Ionization Mass Spectrometer, while the Te and Ti data were obtained using a Thermo Scientific Neptune Plus MC-ICPMS (details in SM).

The noble gas (He-Xe) isotopic compositions were analyzed in a small “S” and a large “L” aliquot ( $4.83 \pm 0.03$  and  $18.880 \pm 0.014$  mg) of the  $\sim 1$  g powder at ETH Zürich. For details on the techniques see Riebe et al. (2017). The noble gases were extracted by fusion at  $\sim 1700^\circ\text{C}$ , which was confirmed to be complete by repeat extractions at  $\sim 1750^\circ\text{C}$ . Blank corrections were  $<0.5\%$  for He in both samples,  $<5\%$  for Ne,  $<3.5\%$  for  $^{36,38}\text{Ar}$ ,  $\sim 33\%$  for  $^{40}\text{Ar}$ ,  $\sim 10\%$  for  $^{84}\text{Kr}$ ,  $\sim 2\%$  for  $^{132}\text{Xe}$  in the small sample and  $<1.5\%$  for Ne,  $\sim 1\%$  for  $^{36,38}\text{Ar}$ ,  $\sim 6\%$  for  $^{40}\text{Ar}$ ,  $\sim 3\%$  for  $^{84}\text{Kr}$ ,  $\sim 0.6\%$  for  $^{132}\text{Xe}$  in the large sample, respectively.

Mn-Cr, C, and O isotope analyses of carbonates were performed by ion probe (SIMS; Cameca IMS 1280-HR) on thin section PL19172 at the Institute of Earth Sciences (University of Heidelberg), while infrared (IR) spectroscopy was performed in vacuum on thin sections at the IR/IS laboratory (Institut für Planetologie, Münster) using a Bruker Vertex 70v instrument with a Bruker A513 bidirectional reflectance stage with varying observation geometries to measure a bulk sample signal (details in SM). The magnetic properties of the rock were studied in

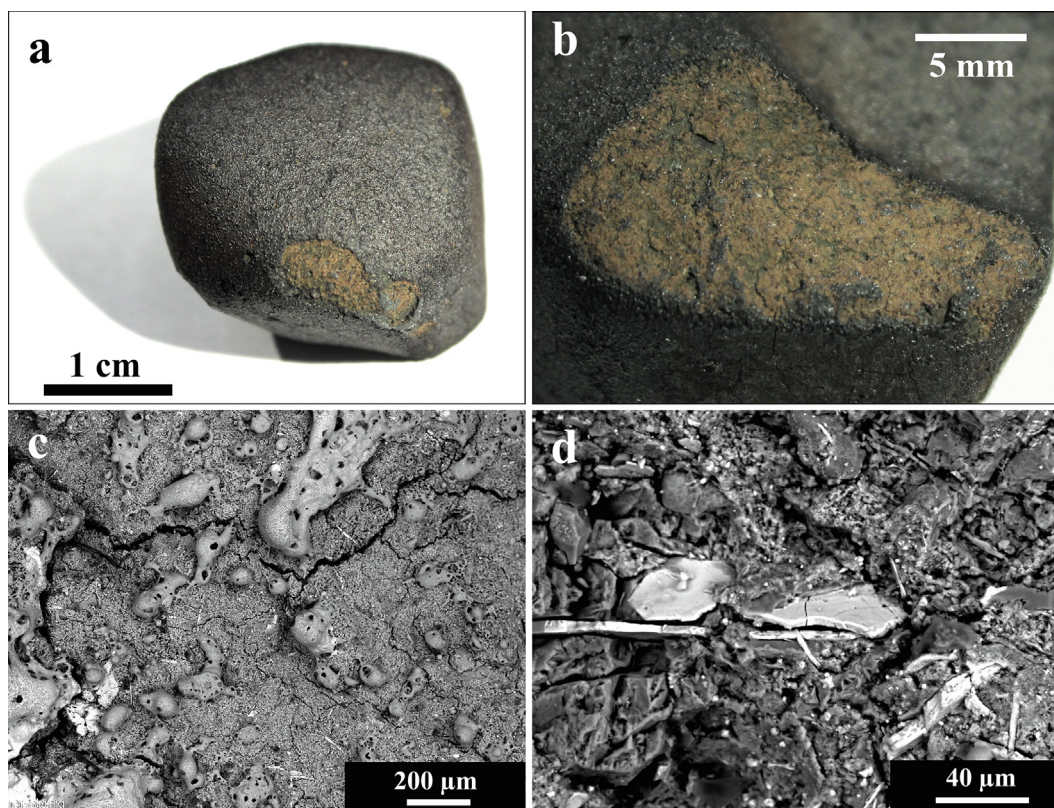


Fig. 2. (a) Bulk meteorite of Flensburg. (b) On parts of the rock, the fusion crust has been broken off. (c) BSE-image of a thin new (secondary) fusion crust that developed on the region where the primary fusion crust had broken off as shown in (b). Porous melt lumps partly cover the modified surface. (d) Sulfide plates (sheets) are visible on the rough broken surface of Flensburg (BSE-image).

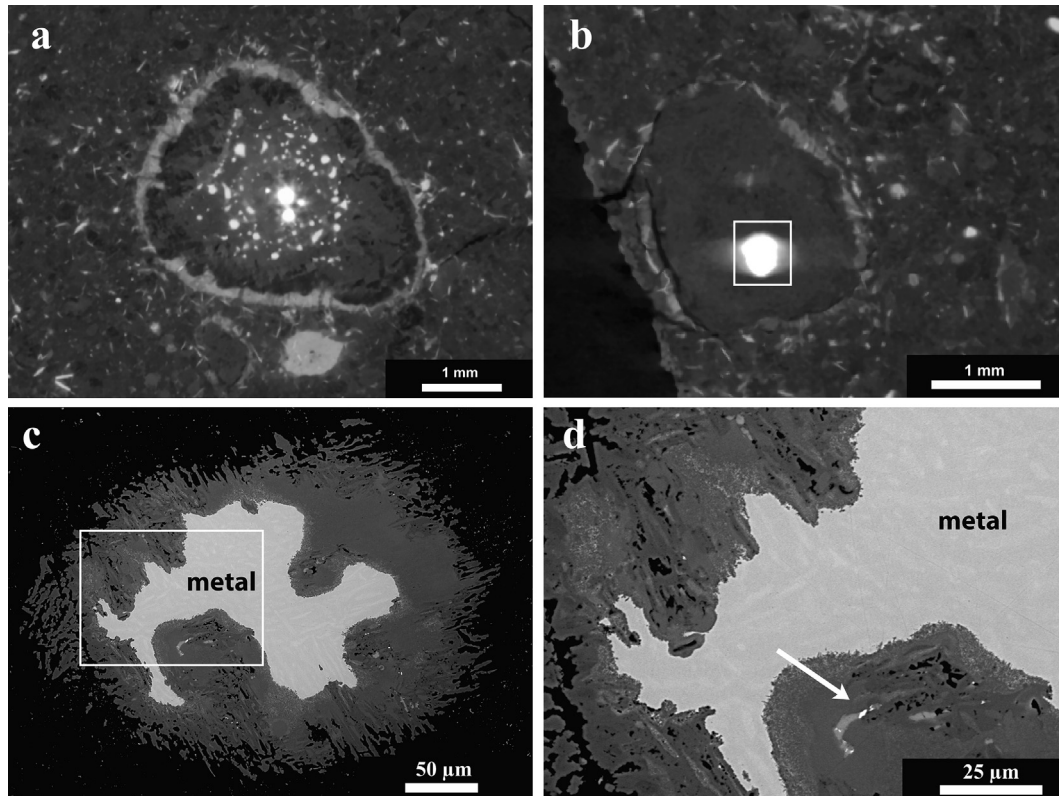


Fig. 3. (a) The largest object in Flensburg (about 3 mm) contains abundant small bright rounded particles indicating heavy element-rich phases. Heavy phases (but less dense than the white round particles) also surround the clast as visible by the light corona; CT-cross section; (b) A similar clast that appears to be internally homogeneous (except for the white blob), is surrounded by a light corona; CT-cross section; this object will be discussed in detail below; (c) within a polished thick section the large rounded, heavy element-rich inclusions of (b) consist of kamacite in its center surrounded by an Fe-oxide also containing considerable amounts of Si, S, and Ni; BSE-image. (d) Area of (c) showing an internal texture within the metal. The brighter areas have on average 8.5 wt.% Ni, while the darker metal has about 6 wt.% Ni. The Fe-rich oxides surrounding the metal core are very heterogeneous in terms of texture and composition. An As,S-rich Fe,Ni-grain is indicated by an arrow; BSE-image.

Aix-en-Provence and Nördlingen using different sample aliquots (bulk sample and later subsamples of 17.0 g, 3.5 g, and ~0.3 g; details in SM).

The diversity of soluble organic components in the meteorite was obtained from the solid specimen as previously done for Murchison and other extraterrestrial soluble organic matter (SOM; Schmitt-Kopplin et al., 2010, 2012; Popova et al., 2013; Hertkorn et al., 2015). A single 20.6 mg fragment of Flensburg was divided into several aliquots; two pieces (~5 mg each) were used for Fourier transform ion cyclotron resonance (FTICR) mass spectrometry and nuclear magnetic resonance (NMR) spectroscopy.

The thermal evolution of the Flensburg parent planetesimal was modelled using a 1D thermal evolution code (Neumann and Kruse, 2019; Neumann et al., 2020) adapted to a carbonaceous chondritic composition specific to the Flensburg meteorite (see details in SM).

### 3. MINERALOGY AND PETROGRAPHY

#### 3.1. Hand specimen observations

A meteorite with a total mass of 24.5 g (roughly 3.5 cm × 3.2 cm × 2.4 cm in size) and a density of 1.984

± 0.016 g/cm<sup>3</sup> was recovered. The rock has a fresh black fusion crust that contains brownish patches (Fig. 2a and b), where the crust has been broken off. SEM studies of these brownish areas revealed that these parts must have been removed in the atmosphere and covered by a thin new secondary fusion crust (Fig. 2c) that only partially covers the internal features and minerals (e.g., sulfide plates; Fig. 2d). No clear indication was found as to why these areas appear brownish in hand specimen.

#### 3.2. CT-observation

The X-ray computed tomography studies showed a fine-grained-rock with some large obvious lithic clasts several mm in size (Fig. 3a and b). CT-cross sections revealed that the densest phase occurs as round inclusions (bright blobs) inside these objects, which are surrounded by light grey coronas including phases having relatively high atomic numbers (Fig. 3). The bright blob studied in a polished thick section from the object shown in Fig. 3b was identified as kamacite surrounded by an unidentified Fe-oxide containing some percent of Si, S, and Ni (Fig. 3c). The coexistence of isolated metal blobs and silicate components is a typical feature of CR chondrites, although the size

Table 1

The mean modal abundances (vol.%) and standard deviations (SD) of various phases in Flensburg determined here and in four CI chondrites (Alfing et al., 2019) by point-counting and through PSD-XRD analysis of a ~50 mg powdered sample. Ranges for CM1s are taken from King et al. (2017).

Phases	Point Counting			PSD-XRD*	
	Mean	SD	4 CIs (range in CIs) <sup>#</sup>	Flensburg	CM1s
Calcite	2.6	± 0.6		0.9 ± 0.6	
Dolomite	1.3	± 0.4		0.6 ± 0.5	
“Carbonates”	3.9	± 1.0	0.48 (0.08–0.99)	1.5 ± 1.1	0.4–1.7
Magnetite**	1.9	± 0.3	4.3 (3.4–5.0)	3.9 ± 2.2	2.0–3.3
Sulfides	3.8	± 0.9	1.01 (0.4–1.7)	3.1 ± 1.7	0.1–4.4
Others (metals, ilmenite, phosphate)	<0.2				
Phyllosilicates	90.2	± 0.8 <sup>##</sup>	94.0 (93.2–94.9)	91.5 ± 4.4	84.3–90.0

<sup>#</sup> Alfing et al. (2019) determined only grains >5 µm.

<sup>##</sup> Phyllosilicates and porosity were determined by difference.

\* Uncertainties for the PSD-XRD analysis are relatively high due to the short measurement time and overlap between diffraction peaks (e.g., magnetite and Fe-sulfide peaks, since Flensburg has a relatively high abundance of sulfides).

\*\* Includes traces of chromite.

ranges of the constituents are different. The kamacite consists of two lamellae-like areas of different compositions. Both contain about 0.5 wt.% Si, but the brighter areas have about 8.5 wt.% Ni, while 6 wt.% Ni were analyzed for the darker ones.

### 3.3. General petrology and mineralogy

Based on SEM and EPMA analyses of the thin sections, here we summarize the main petrological and mineralogical features of Flensburg. Rounded to ellipsoidal relict chondrules (~0.05–1 mm in apparent diameter) and clusters of sulfide and magnetite grains are set in a dark, fine-grained matrix. Ca,Al-rich inclusions (CAIs) were not found, but irregularly-shaped, phyllosilicate-rich aggregates are present that optically resemble fine-grained CAIs or AOAs (Fig. S3; Holm, 2020). In an area of 15 mm<sup>2</sup>, the sizes and abundances of all relict chondrules were determined: The 134 relict chondrules have a mean size of 168 µm revealing an abundance of ~20 vol.% (see SM for details). The most abundant phases are phyllosilicates (~90 vol.% (including porosity); Table 1). TEM studies (see below) indicate that tochilinite is rare or absent. Locally the matrix contains some S, but this may result from the presence of nano-sized sulfide grains. Magnetite mainly occurs as aggregates. Carbonate grains exhibit a diverse mineralogy, including calcites, Mn-bearing dolomites, and a Na-rich phase. The relict chondrules are free of any anhydrous silicates (such as olivine and pyroxene), contain abundant phyllosilicates and carbonates, and are often surrounded by sulfide laths (Fig. 4). These laths consist of exsolved troilite within non-stoichiometric pyrrhotite. Pentlandite is absent in the laths, but occurs as separate grains in the matrix. In addition to the relict chondrules, lithic fragments are also present (Fig. 4e and f). The lithic fragment shown in Fig. 4f has a well-preserved chondritic texture and is surrounded by abundant sulfide laths that are similar to those around relict chondrules. The relevance of these observations will be discussed in Section 7.11.

The modal mineral abundances obtained by optical means given in Table 1 are the averages of four independent

analyses determined by means of point counting (in all cases more than 1500 points were registered on areas of different sizes ranging from 8 mm<sup>2</sup> to 20 mm<sup>2</sup> covering a total area of about 56 mm<sup>2</sup>). The data are slightly different to the results obtained by X-ray techniques. A total abundance of ~3.8 vol.% sulfides and ~1.9 vol.% magnetite was obtained from point counting. All these phases are heterogeneously distributed throughout the Flensburg meteorite. Minor amounts of chromite, ilmenite, Ca-phosphate (Fig. S3; Holm, 2020), and traces of a Fe,Ni,As(Te,S)-rich phase (see below) were also detected.

#### 3.3.1. Carbonates

The point counting suggests that carbonate abundances total about 4 vol.%, making them the second most abundant mineral group after that of the phyllosilicates (Table 1). Three different carbonates occur: calcite, dolomite and a (rare) Na-rich carbonate (Fig. 5). Representative carbonate compositions are given in Table S1.

#### 3.3.2. Sulfides

Three major sulfides are observed in Flensburg: Pyrrhotite, troilite, and pentlandite. Their total abundance is about 3.8 vol.%. In general, pyrrhotite and troilite occur as small-scale lamellar intergrowths (Fig. 6), whereas the pentlandites occur as individual grains in the matrix. Representative compositions determined by EPMA are given in Table S2. The composite crystals of pyrrhotite/troilite are tabular to lath-shaped and are distributed in the matrix as well as rimming chondrules and larger objects (Fig. 4). Often, the crystals are surrounded by phyllosilicate sheaths and occasionally they are embedded in carbonates (Fig. 5a). In order to obtain details on the pyrrhotite/troilite intergrowth and to resolve their relationship to the surrounding phyllosilicates, three FIB sampling sites were selected to target sulfide crystals and adjacent phyllosilicates of interest. Representative compositions of sulfide minerals are given in Table S2.

The tabular to lath-shaped, low-Ni iron sulfide crystals are predominantly non-stoichiometric pyrrhotite [(Fe,Ni)<sub>1-x</sub>S; x ≤ 0.09] with variable amounts of exsolved troilite (FeS). The sizes and morphologies of the troilite

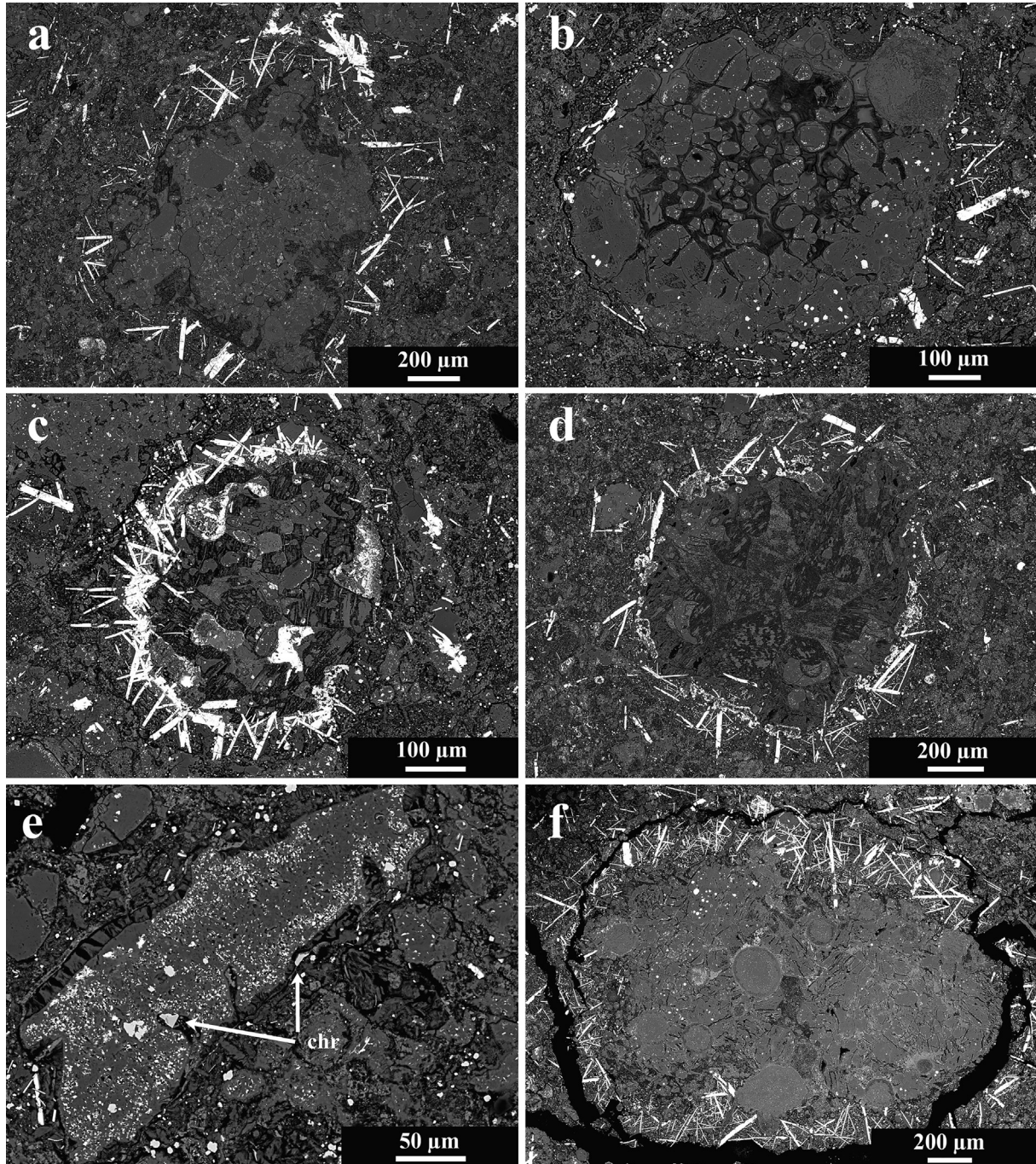


Fig. 4. BSE images of representative relict chondrules and fragments in Flensburg. The chondrules in (a)–(d) do not contain any olivine or pyroxene and often show abundant sulfide laths at their boundaries. (e) Vein-like fragment with abundant small magnetite grains and some large chromites. A reaction zone is clearly visible on the left-hand side. (f) One of the largest objects (shown in Fig. 3b; different slice) in the Flensburg meteorite. The clast has an internal “chondritic” texture that differs from that of the Flensburg host. The clast is consisting of about 20 relict chondrules of various sizes (all mafic silicates have been transformed into phyllosilicates). Thus, it is an impact-generated fragment in the bulk rock and completely surrounded by a zone that is rich in sulfide laths.

exsolution lamellae vary considerably (Figs. 6 and 7), from lenticular bodies just a few nm wide to flame-like lamellae several  $\mu\text{m}$  wide and up to 30  $\mu\text{m}$  long. The former are hardly visible even in TEM images (sample F02), but become apparent as diffuse superstructure reflections in selected area electron diffraction (SAED) patterns

(Fig. 7). The coexisting pyrrhotite shows diffuse reflections, indicating that troilite exsolved from an initial monosulfide solid solution (MSS), which was the original state of the sulfide crystals during formation.

The superstructure reflections of pyrrhotite arise from the ordering of Fe-site vacancies and can be understood



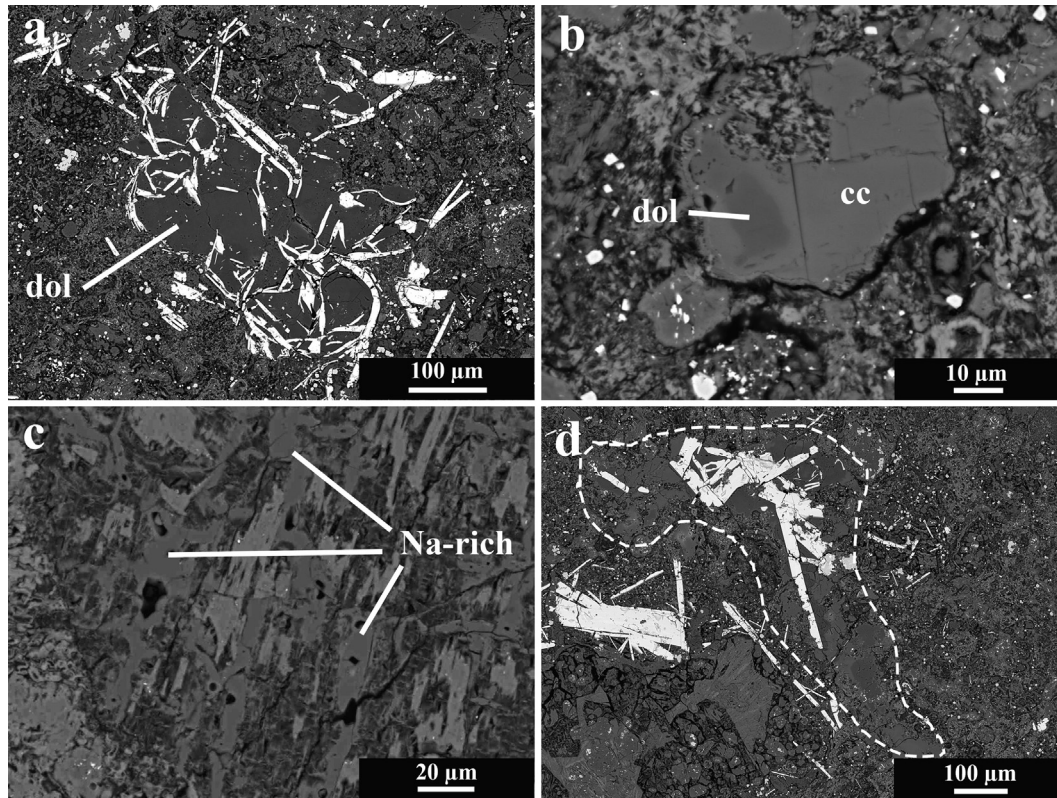


Fig. 5. Carbonates in Flensburg; (a) dolomite-pyrrhotite intergrowth; (b) dolomite (dol) embedded within calcite (cc); (c) oriented Na-rich carbonates (Na-rich) in a replaced radial-pyroxene chondrule (?); (d) carbonate vein (indicated by dashed lines) consisting of dolomite and calcite embedding sulfide laths. BSE-images.

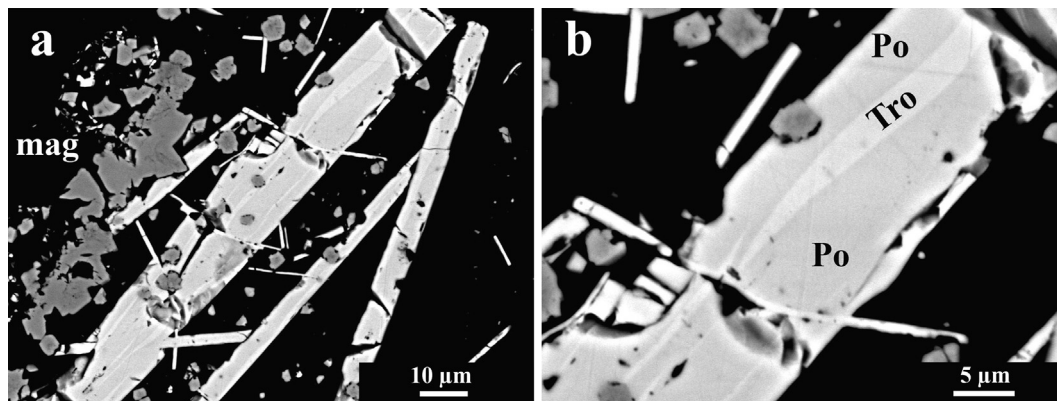


Fig. 6. (a) Typical appearance of exsolved troilite (Tro) within pyrrhotite (Po); (b) detail of (a); mag = magnetite; BSE-image.

as a quasi-periodic structural modulation that is characterized by the repeat parameter  $N$  along the crystallographic  $c$  axis (Harries et al., 2011). As in many cases of NC-pyrrhotites (Harries and Langenhorst, 2013),  $N$  is a non-integral number between 4 and 6. TEM samples F01 and F03 show unusual and variable superstructure reflections of pyrrhotite that cannot be indexed consistently (Fig. 7a–c). In sample F02, the observed  $N$  value is consistently about 5.39 (Fig. 7c) and corresponds to an Fe-rich pyrrhotite composition close to  $(\text{Fe,Ni})_{0.91}\text{S}$ , i.e. intermediate between  $(\text{Fe,Ni})_9\text{S}_{10}$  (5C-pyrrhotite) and  $(\text{Fe,Ni})_{11}\text{S}_{12}$

(6C-pyrrhotite). This agrees well with the compositions measured by EPMA (Table S2). Because the pyrrhotite-troilite exsolution assemblage contains abundant stoichiometric troilite, the metal/sulfur ratio must be  $>0.91$  in the bulk sulfide and is estimated to be  $\sim 0.95$  in most cases (i.e., about equal volume fraction of pyrrhotite and troilite).

The bulk Ni content of the pyrrhotite crystals typically ranges between 0.18 and 0.57 wt.% (Table S2; Fig. S4; mean molar  $\text{Ni}/(\text{Fe} + \text{Ni}) \approx 0.004$ ), but some crystals show zones with no Ni detectable by TEM-EDS. No evidence for exsolved pentlandite was found in the pyrrhotite crystals

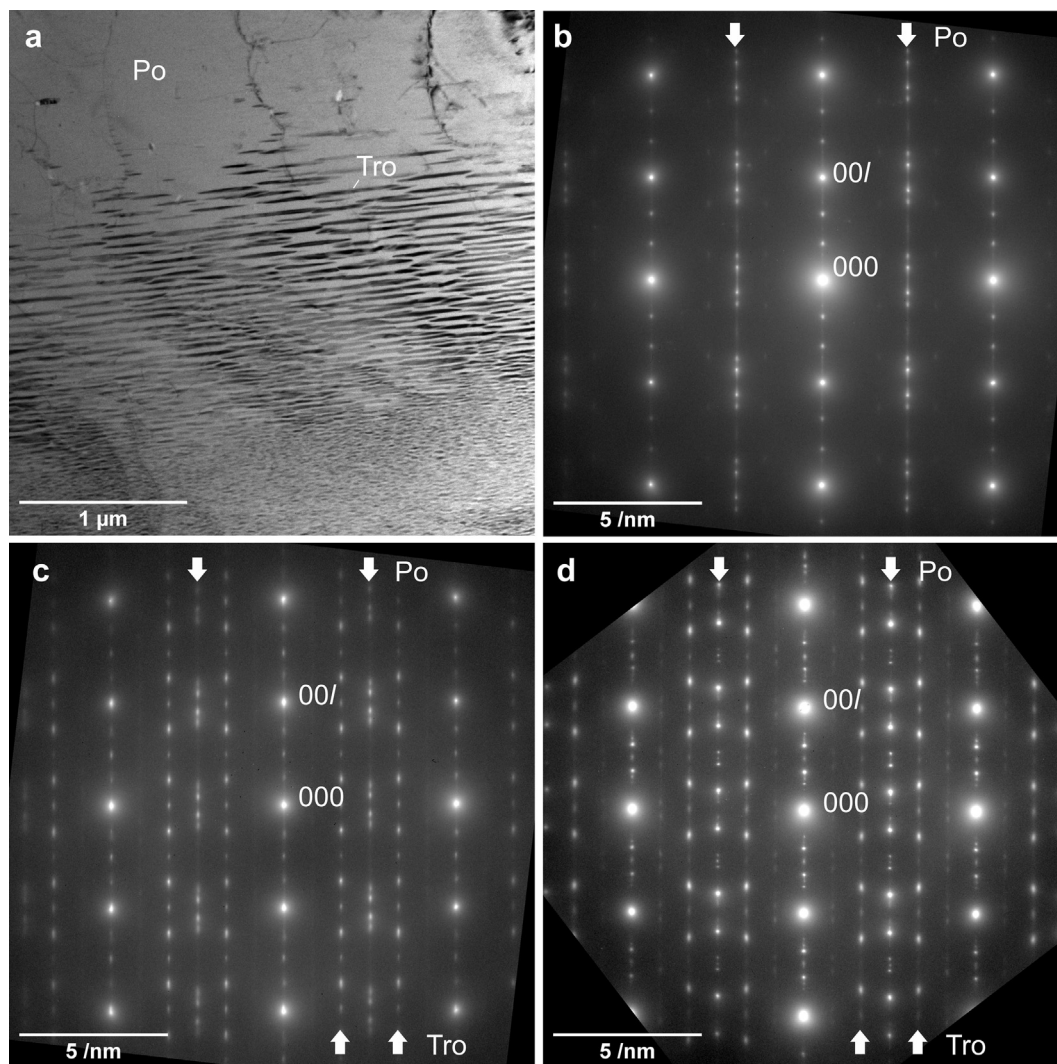


Fig. 7. TEM analysis of low-Ni iron sulfide in Flensburg. Po: pyrrhotite, Tro: troilite. (a) TEM bright-field image of dark (diffracting) troilite lamellae within pyrrhotite. The center of the crystal is at the top, the rim is close to the bottom. The change of troilite size and abundance likely reflects a chemical gradient of the metal/sulfur ratio. (b) SAED pattern of the troilite-poor region showing diffuse pyrrhotite reflections (arrows). (c) SAED pattern of the troilite-rich region showing additional troilite reflections. The pyrrhotite superstructures in (b) and (c) are distinct, but cannot be indexed with typical NC-pyrrhotite, possibly due to poor vacancy ordering or unusual coexisting ordering schemes. (d) SAED pattern from a different low-Ni iron sulfide crystal showing reflections of pyrrhotite and troilite. Here, the pyrrhotite can be consistently indexed as NC superstructure with  $N \approx 5.39$ , suggesting a bulk metal/sulfur ratio  $>0.91$ .

of Flensburg. In Flensburg, pentlandite only occurs as separate grains with molar Ni/(Fe + Ni) of 0.42 (EPMA) to 0.48 (TEM-EDS). Even at the TEM scale pentlandite grains show sharp boundaries with the surrounding matrix and no signs of alteration to other Ni-rich sulfides.

### 3.3.3. Phyllosilicates

TEM samples included phyllosilicates of three distinct compositional and morphological types within the Flensburg chondrite: sheath, vein, and matrix serpentine (Fig. S5; Table 2).

*Sheath serpentine* surrounds pyrrhotite as well-formed crystal stacks (Fig. 8a and b) that are subparallel to the tabular faces of the pyrrhotite crystals. It predominantly consists of lizardite-type serpentine that shows the characteristic 0.7 nm basal interplanar spacing. The sheath-

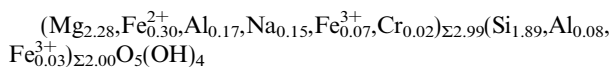
ing phyllosilicates of Flensburg do not display any intimate intermixing of serpentine and chlorite. Only one  $\sim 120$  nm wide chlorite stack showing the characteristic 1.4 nm basal lattice spacing was found in sample F03 (Fig. 8c–f). A narrow stack showing  $\sim 1$  nm basal lattice spacing in sample F01 is possibly a talc-like structure or a dehydrated/collapsed smectite-group phyllosilicate, but these appear to be rare. EDS measurements show that the sheath serpentine has a high atomic Mg/(Mg + Fe) ratio of  $\sim 0.85$  and contains additional Na and Al. Attempts to quantify the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio by electron energy loss spectroscopy (EELS) failed due to rapid oxidation of the sample, probably due to H loss (Garvie et al., 2004). During cumulative spectrum acquisition, some initial Fe edge spectra showed evidence for  $\text{Fe}^{2+}$ , which rapidly changed to dominant  $\text{Fe}^{3+}$ . Based on TEM-EDS measurements (Table 2), crystal

Table 2

Averaged TEM-EDS analyses of distinct serpentine types in Flensburg. All data in wt.%; n.d. = not detected; O calculated assuming a molar  $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$  that results in filled octahedral and tetrahedral sites, H calculated by stoichiometry (totals normalized to 100 wt.%). Detection limits of Ca, V, Ti, and Ni are about 0.05 to 0.1 wt.%, Mn is not detected below about 0.2 wt.% due to overlap of Cr K $\beta$ .

	O	Na	Mg	Al	Si	$\text{Fe}^{2+}$	$\text{Fe}^{3+}$	Cr	H	Total
Sheath low-Al (n = 9)	49.4 ± 0.2	1.15 ± 0.25	18.9 ± 0.6	1.94 ± 0.13	18.4 ± 0.23	6.40 ± 0.41	2.13 ± 0.14	0.25 ± 0.06	1.38 ± 0.01	100
Sheath high-Al (n = 17)	49.6 ± 0.3	1.18 ± 0.45	19.1 ± 0.8	2.65 ± 0.21	18.1 ± 0.6	5.56 ± 0.51	1.85 ± 0.17	0.44 ± 0.21	1.39 ± 0.01	100
Vein high-Fe (n = 9)	48.9 ± 0.3	<0.05	19.0 ± 0.7	1.61 ± 0.23	18.4 ± 0.4	10.3 ± 0.81	n.d.	0.34 ± 0.11	1.37 ± 0.01	100
Vein low-Fe (n = 6)	50.8 ± 0.2	<0.05	23.7 ± 0.8	1.07 ± 0.10	19.2 ± 0.5	3.82 ± 0.30	n.d.	<0.05	1.42 ± 0.01	100
Matrix high-Fe (n = 10)	45.1 ± 2.0	~0.2	12.8 ± 3.2	1.40 ± 0.46	15.6 ± 1.1	18.2 ± 5.4	5.12 ± 1.5	~0.2	1.26 ± 0.06	100
Matrix low-Fe (n = 2)	48.1	0.46	16.6	1.03	18.9	13.1	n.d.	0.28	1.35	100

stoichiometry can be established by assuming ~25% of the total Fe being  $\text{Fe}^{3+}$  on octahedral and tetrahedral sites:

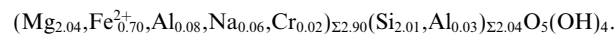


The high Na contents of 1–2 wt.%  $\text{Na}_2\text{O}$  are unusual for serpentines, but are balanced stoichiometrically via a coupled substitution with Al: The high Si occupancy on the tetrahedral sites does not allow for much Tschermak-type charge compensation ( $\text{M}_{\text{oct}}^{2+} + \text{Si}_{\text{tet}}^{4+} = \text{M}_{\text{oct}}^{3+} + \text{M}_{\text{tet}}^{3+}$ ) and, therefore, the high Al contents must be assigned to the octahedral sites. This is consistent with the observed Na contents, which provide additional charge compensation by monovalent ions on the octahedral sites ( $2 \text{M}_{\text{oct}}^{2+} = \text{M}_{\text{oct}}^{3+} + \text{M}_{\text{oct}}^{+}$ ).

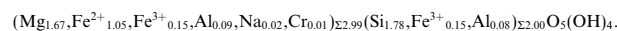
*Vein serpentine* forms short, vein-like structures several tens of  $\mu\text{m}$  in length within the matrix and is composed of interlocking stacks of lizardite-type serpentine crystals reaching sizes on the order of 10  $\mu\text{m}$  (Fig. 8g and h). Compared to the sheathing phyllosilicates, the vein serpentine contains almost no Na and shows zonal variations of the Mg/Fe ratio, from  $(\text{Mg}_{2.76}, \text{Fe}_{0.19}^{2+}, \text{Al}_{0.06})_{\Sigma 3.01} (\text{Si}_{1.94}, \text{Al}_{0.06})_{\Sigma 2.00} \text{O}_5(\text{OH})_4$  in the Mg-rich center of crystals to  $(\text{Mg}_{2.30}, \text{Fe}_{0.54}^{2+}, \text{Al}_{0.08}, \text{Cr}_{0.02}, \text{Na}_{0.01})_{\Sigma 2.95} (\text{Si}_{1.93}, \text{Al}_{0.09})_{\Sigma 2.02} \text{O}_5(\text{OH})_4$  in Fe-rich outer zones (Table 2). As described above, EELS quantification of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio was inconclusive. Stoichiometric balancing suggests that there is little  $\text{Fe}^{3+}$ , as it would produce excess occupancy of the tetrahedral sites and a deficit on the octahedral sites. This observation also points to a distinct phase of phyllosilicate formation relative to the sheath serpentine.

*Matrix serpentine* constitutes fine-grained, highly porous material (Fig. 9a and b; Table 2). Most of it appears to be lizardite-type stacks of <1  $\mu\text{m}$  in size, often randomly arranged to form interlocking, felty aggregates (Fig. 9c

and d). TEM investigations did not show unambiguous evidence for chrysotile-type serpentine, although some smaller, elongated particles (<200 nm long) in the matrix might be tubular or curled serpentine. The matrix serpentine contains more Fe than the other two occurrences of serpentine described above, but the Mg/Fe ratios vary considerably. In the Mg-rich matrix serpentine there seems to be little to no  $\text{Fe}^{3+}$ , indicated by high Si contents:



The Fe-rich matrix serpentine appears to have about 20–25% of its total Fe as  $\text{Fe}^{3+}$ , as indicated by its low Si contents:



### 3.3.4. Magnetite and chromite

Based on point-counting, magnetite makes up about 1.9 vol.% of Flensburg (Table 1), whereas chromite is much less abundant ( $\ll 0.5$  vol.%; Fig. 10). A high Si content was found in the magnetite, as well as high Ti in chromite (Table S3). Small grains of magnetite are dispersed throughout the matrix or occur in relict chondrules probably replacing metals.

In the FIB section (Fig. 11), magnetite occurs as small crystals in the matrix and as an overgrowth on a chromite grain. The magnetite is Si-bearing. In the composite grain, the magnetite epitactically overgrows the chromite grain. The chromite grain contains substantial amounts of Mg-spinel and ulvöspinel components, but no apparent  $\text{Fe}^{3+}$ . The average composition of the chromite is



At the TEM-scale, parts of the magnetite grains are chemically heterogeneous due to nanoscale inclusions

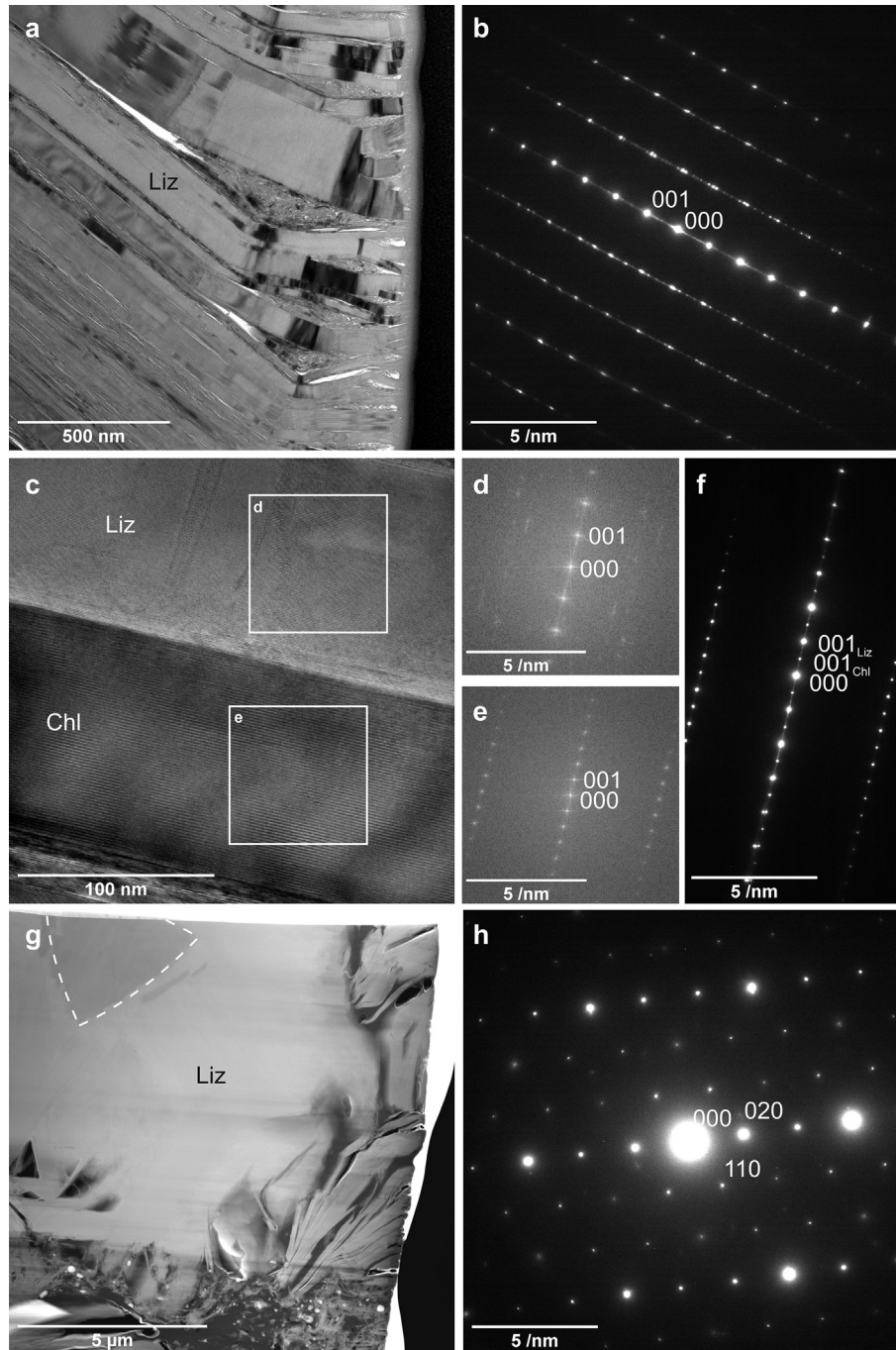


Fig. 8. TEM analysis of coarse-grained phyllosilicates in Flensburg. Liz: lizardite, Chl: chlorite. (a) Sheath serpentine surrounding a pyrrhotite crystal (out of view). The bending of lizardite stacks is probably due to the preparation of the thin section. (b) SAED pattern of the lizardite in (a), showing the characteristic 0.7 nm 001 interplanar spacing. (c) Isolated stack of chlorite about 120 nm thick in sheathing serpentine of Flensburg. The chlorite shows the characteristic 1.4 nm interplanar spacing and sharply borders lizardite. The boxes mark locations of Fast Fourier Transform (FFT) patterns shown in (d) and (e). (d) FFT pattern of lizardite in (c). (e) FFT pattern of chlorite in (c). (d) and (e) demonstrate the doubling of the periodicity in the chlorite stack. (f) SAED pattern of the mixed region of lizardite and chlorite. (g) Scanning TEM high-angle annular dark-field (STEM-HAADF) image of vein serpentine. The dashed line marks the Mg-rich core of the crystal, and the outer zone is Fe-rich. (h) SAED pattern of the serpentine crystal in (g) in the same orientation. The zone axis is perpendicular to the basal layer stacking and indexed for a monoclinic polytype due to the asymmetric intensity distribution.

(Fig. 11b). These inclusions appear to be Fe-rich silicates, but their compositions and mineralogies have not been determined conclusively. Regions of apparently inclusion-

free magnetite also show elevated Si contents of about 0.22 atoms per formula unit, suggesting that Si is substituted into the structure.

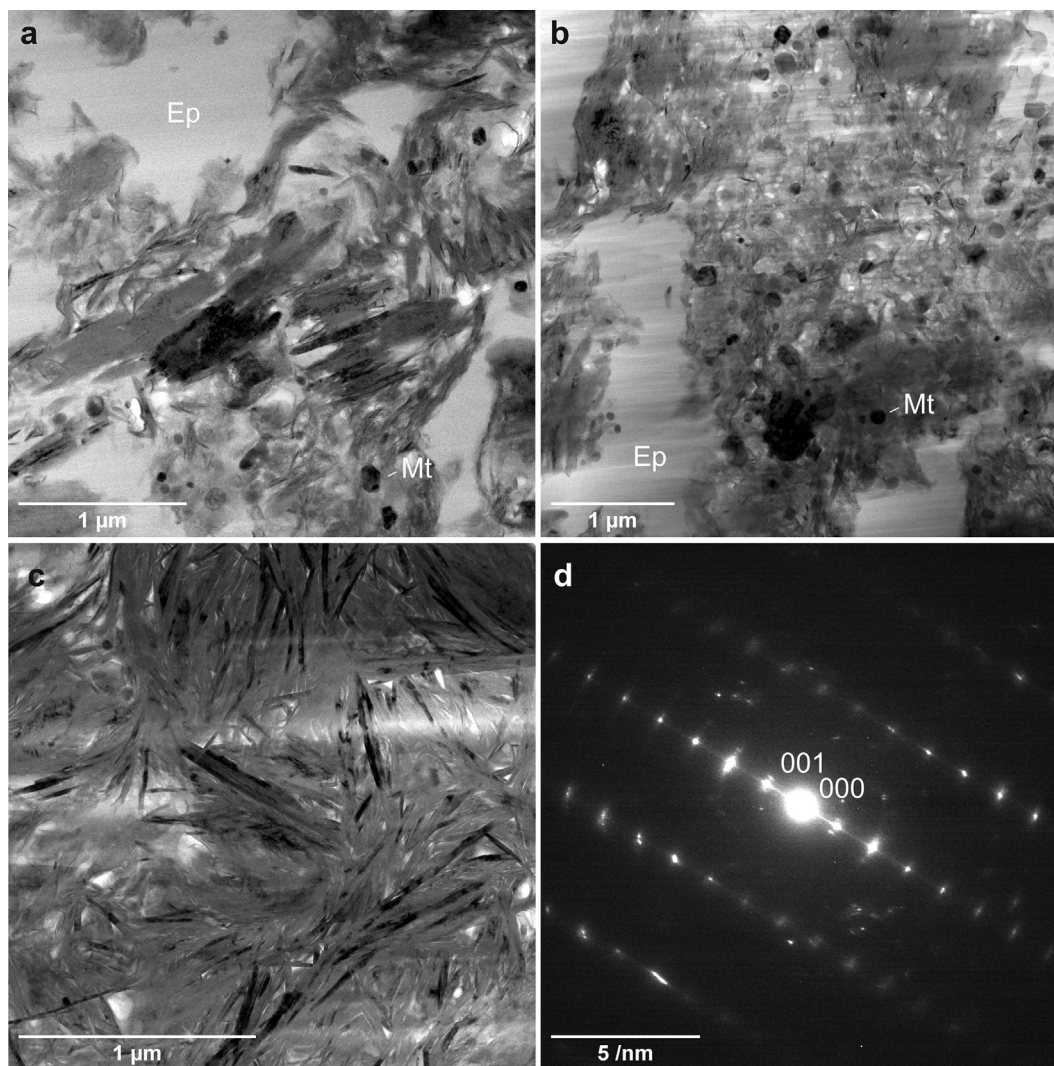


Fig. 9. TEM analysis of fine-grained matrix phyllosilicates in Flensburg. Ep: epoxy, Mt: magnetite. Subhorizontal streaks are due to FIB sample preparation. (a) Small stacks of lizardite and possibly tubular forms of serpentine. Small, rather isometric grains are mostly magnetite. The pore space is filled by epoxy resin. (b) Different location than in (a) showing smaller serpentine aggregates and more abundant magnetite. (c) Coarser-grained, relative Mg-rich matrix serpentine forming felty aggregates. These may be curled aggregates, but no clearly tubular cross-section has been found. (d) SAED pattern of the serpentine crystal in the center of (c).

### 3.4. Isotopic studies on carbonates

Concerning the O isotopes, the analyzed calcite grains in Flensburg range in  $\delta^{18}\text{O}_{\text{VSMOW}}$  from +13.5‰ to +32.4‰ with  $\Delta^{17}\text{O}_{\text{VSMOW}}$  ranging from -3.8 to -1.1‰ defining a line with a slope of  $\sim 0.62$  (Fig. 12a, Table 3). There is no apparent systematic difference between calcite grains with different petrologic context, i.e. sulfide-associated calcite and zoned calcite grains overlap significantly. Typical calcite grains (in the matrix) exhibit a rather small range in  $\delta^{18}\text{O}_{\text{VSMOW}}$  from +13.5 to +24.3‰ (Fig. 12b). The O isotope compositions of dolomite grains in Flensburg range from +11.8 to +17.9‰ in  $\delta^{18}\text{O}_{\text{VSMOW}}$  with  $\Delta^{17}\text{O}_{\text{VSMOW}}$  ranging from -4.1 to -2.4‰ defining a line with a slope of  $\sim 0.39$  (Fig. 12a, Table 3). On average, the dolomite grains that are associated with sulfides tend to be more enriched in  $^{16}\text{O}$  when compared to other dolomite grains (Fig. 12c).

Fig. 13a displays single spot simultaneous measurements of both C and O isotopic compositions (Schmidt, 2020; Table S4). Flensburg dolomites do not only show a limited range in O isotopic composition (+11.8‰ to +17.9‰ in  $\delta^{18}\text{O}_{\text{VSMOW}}$ ), but are also restricted in C compositions (+48‰ to +60‰ in  $\delta^{13}\text{C}_{\text{VPDB}}$ ), with sulfide associated dolomites tending to have both lighter O and C isotopic compositions. The calcites are compositionally more variable, extending to higher  $\delta^{18}\text{O}_{\text{VSMOW}}$  and lower  $\delta^{13}\text{C}_{\text{VPDB}}$  values in a seemingly uncorrelated and unsystematic way. There is no clear difference between isolated calcites or those associated with sulfides.

The decay system  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  can be used to constrain the formation age of carbonates, because the carbonates are characterized by very high Mn/Cr ratios and, provided that they formed during the lifetime of  $^{53}\text{Mn}$ , highly radiogenic  $^{53}\text{Cr}/^{52}\text{Cr}$  ratios. Calcites and dolomites from the

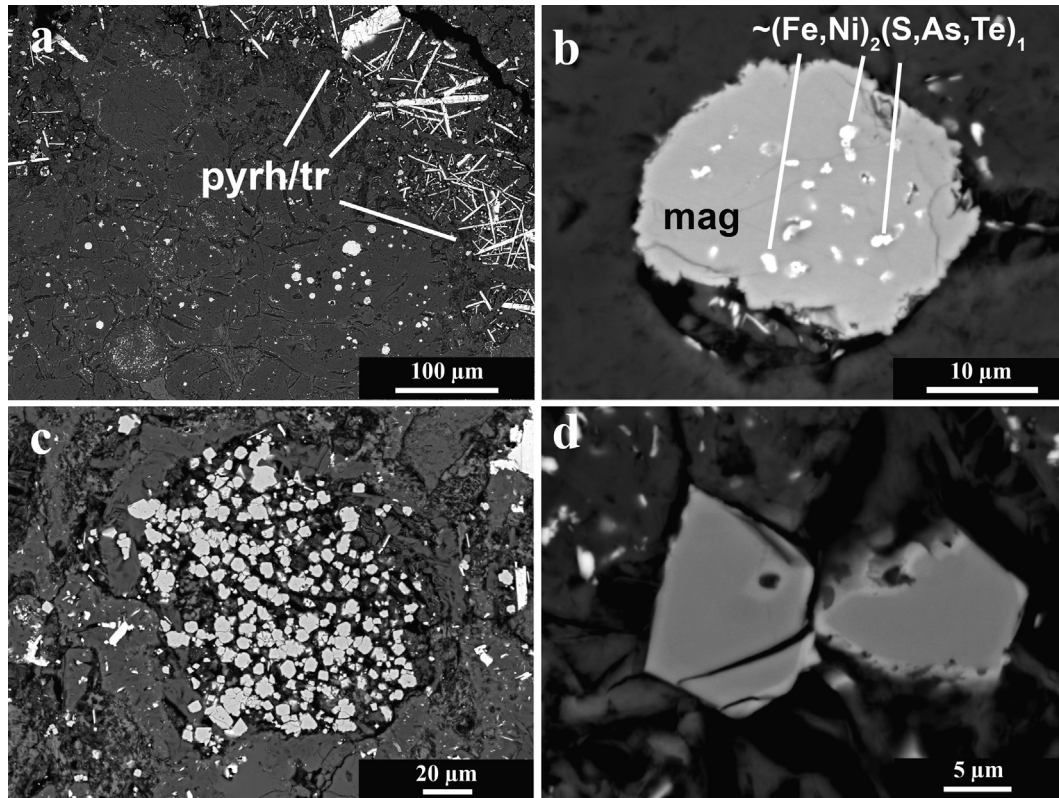


Fig. 10. (a) Part of a clast within the Flensburg meteorite showing a relict chondrule-like object with round magnetite-rich inclusions (lower right) embedded in phyllosilicates. The clast is surrounded by a zone of pyrrhotite/troilite laths (pyrh/tr). (b) Magnetite grains contain small inclusions of an Fe,Ni,As-rich phase that may be close to  $(\text{Fe,Ni})_2\text{As}$ ; (c) aggregate of small magnetite grains, texturally different to the typical magnetite framboids in CI chondrites; (d) chromite grains; BSE-images.

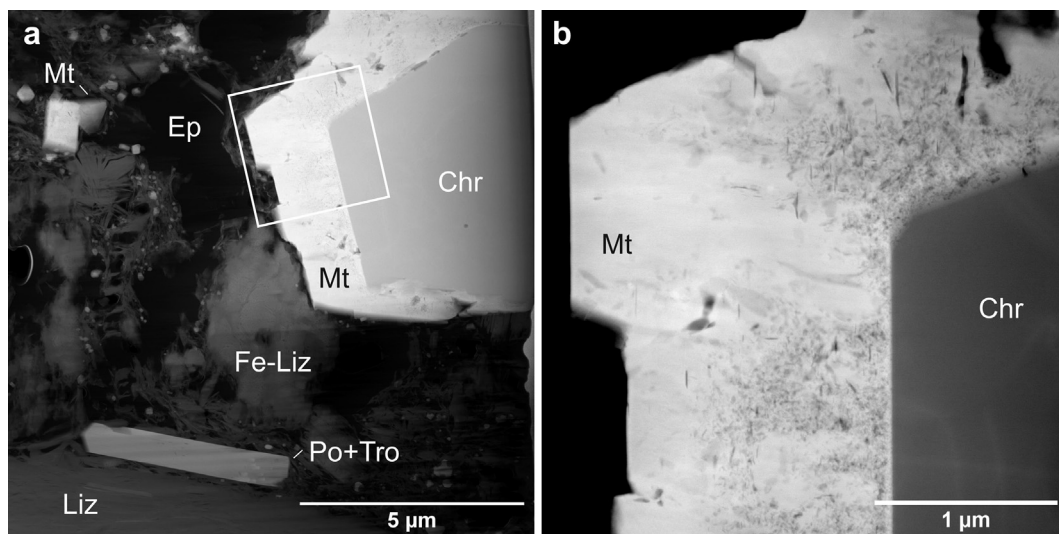


Fig. 11. Scanning TEM high-angle annular dark-field (STEM-HAADF) images of a composite magnetite-chromite grain in Flensburg. Chr: chromite, Ep: epoxy, Liz: lizardite, Mt: magnetite, Po: pyrrhotite, Tro: troilite. a) Overview image with sheath serpentine at the bottom, an attached low-Ni iron sulfide crystal, and adjacent Fe-rich matrix serpentine (Fe-Liz). Magnetite occurs as small octahedral crystals in the matrix and as an overgrowth on a chromite grain. b) Detail of (a) showing the internally heterogeneous structure of the magnetite rim. Nanoscale inclusions are likely a Fe-rich silicate, possibly with a spinel-like structure, as there are no obvious extra reflections in SAED patterns.

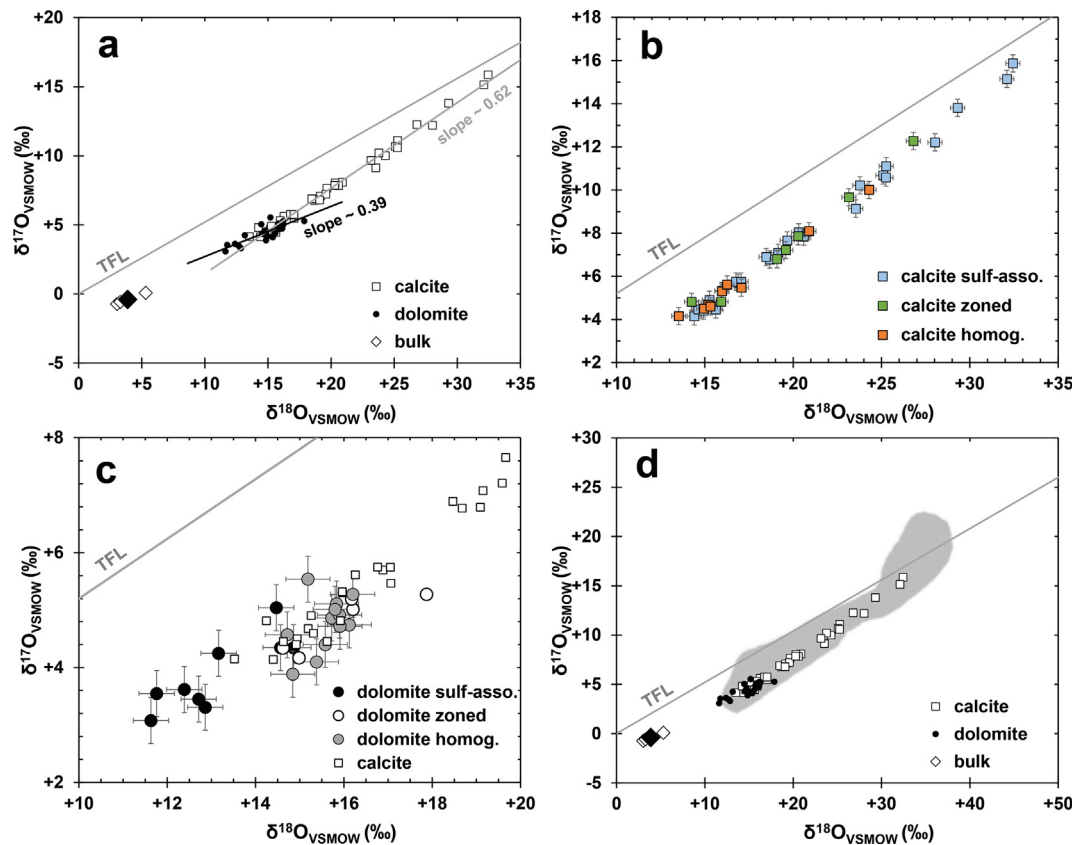


Fig. 12. Three O isotope diagrams of calcite and dolomite grains from Flensburg. (a) Overview of calcite and dolomite grains and the bulk values obtained for Flensburg. (b) Detailed view of calcite grains of different petrologic context. (c) Detailed view of dolomite grains of different petrologic context. (d) Overview of calcite and dolomite grains compared to literature data of calcites in CM chondrites. Literature data from Tyra et al. (2012, 2016), Horstmann et al. (2014b), Verdier-Paoletti et al. (2017), and references therein (grey field). TFL = terrestrial fractionation line; sulf-asso. = sulfide-associated; homog. = homogeneous.

Flensburg chondrite display well-defined isochrons (Fig. 14; Table S5a,b), which yield initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios at the time of carbonate formation of  $(4.43 \pm 0.80) \times 10^{-6}$  and  $(4.50 \pm 1.08) \times 10^{-6}$ , respectively. Note that uncertainties on the  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios include errors of relative ion yields (RIY) determined on HIGP calcite (Donohue et al., 2019, see SM), and dolomite (the same calibration, but corrected for dolomite-calcite matrix effect using data from Steele et al., 2017).

As the solar system initial  $^{53}\text{Mn}/^{55}\text{Mn}$  is not well constrained, the initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios of the carbonates cannot be directly translated into ages relative to the beginning of the solar system (i.e., to the time of CAI formation), but they must first be converted to absolute ages. Relative to the angrite D'Orbigny with an initial  $^{53}\text{Mn}/^{55}\text{Mn} = (3.54 \pm 0.18) \times 10^{-6}$  (McKibbin et al., 2015) and a (U isotope corrected) Pb-Pb age of  $4563.37 \pm 0.25$  Ma (Brennecka and Wadhwa, 2012), the initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios of the Flensburg carbonates correspond to absolute ages of  $4564.6 \pm 1.0$  Ma for calcites and  $4564.6 \pm 1.3$  Ma for dolomites ( $2\sigma$  errors, including uncertainties on RIY, the absolute age of D'Orbigny, and the  $^{53}\text{Mn}$  decay constant). Relative to an absolute Pb-Pb age of  $4567.16 \pm 0.30$  Ma for CAIs (Connelly et al., 2012; Amelin et al.,

2010), the Mn-Cr ages of the carbonates correspond to relative ages of  $2.6 \pm 1.0$  Ma and  $2.5 \pm 1.3$  Ma after CAI formation, respectively. These ages would change to  $3.4 \pm 1.0$  Ma and  $3.3 \pm 1.3$  Ma if the Pb-Pb age of  $4567.94 \pm 0.31$  Ma for CAIs reported by Bouvier et al. (2011) is used. Note that both Pb-Pb ages have been calculated using the measured U isotope composition of the CAIs, although the U isotope composition of Bouvier et al. (2011) has only been reported in an abstract. Further, the CAI used by Bouvier et al. (2011) was analysed also for  $^{26}\text{Al}/^{27}\text{Al}$  systematics, which yield an initial  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $(5.5 \pm 0.3) \times 10^{-6}$  (Wadhwa et al., 2013), which is consistent with canonical  $^{26}\text{Al}/^{27}\text{Al}$  at the start of the solar system and indicates that the Al-Mg system in this particular CAI has not been disturbed by post-formation processes.

Prior studies have shown that carbonates from CM and CR chondrites have initial  $^{53}\text{Mn}/^{55}\text{Mn}$  ratios of between  $\sim 0.8 \times 10^{-6}$  and  $\sim 3.7 \times 10^{-6}$  (Fujiya et al., 2012, 2013; Jilly-Rehak et al., 2017 – only studies using carbonate standards for RIY evaluation are considered, see SM), indicating that these carbonates formed  $\sim 1.0$ – $9.2$  Ma later than the carbonates in Flensburg. As such, the carbonates in Flensburg carbonates are the oldest yet identified in carbonaceous chondrites.

Table 3

$\delta^{18}\text{O}_{\text{VSMOW}}$ ,  $\delta^{17}\text{O}_{\text{VSMOW}}$ , and  $\Delta^{17}\text{O}_{\text{VSMOW}}$  values for calcites and dolomites within the unique Flensburg carbonaceous chondrite. C. = code; N = homogenous grains; S = sulfide-associated grains; Z = zoned grains. Errors are  $\pm 1$  s.

Calcite	C.	$\delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)	Dolomite	C.	$\delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
#004	N	+5.3 ± 0.3	+16.0 ± 0.1	-3.1 ± 0.3	#021	N	+4.9 ± 0.2	+15.7 ± 0.2	-3.4 ± 0.3
#121	N	+4.7 ± 0.5	+15.2 ± 0.3	-3.3 ± 0.6	#023	N	+3.9 ± 0.3	+14.8 ± 0.2	-3.9 ± 0.3
#137	N	+4.2 ± 0.3	+13.5 ± 0.2	-3.0 ± 0.3	#173	N	+4.1 ± 0.3	+15.4 ± 0.2	-4.0 ± 0.3
#166	N	+8.1 ± 0.4	+20.9 ± 0.5	-2.9 ± 0.5	#183	N	+4.4 ± 0.4	+15.6 ± 0.1	-3.8 ± 0.4
#198	N	+10.0 ± 0.4	+24.3 ± 0.5	-2.8 ± 0.5	#214	N	+5.1 ± 0.3	+15.8 ± 0.2	-3.2 ± 0.4
#206	N	+4.5 ± 0.3	+14.9 ± 0.3	-3.4 ± 0.3	#218	N	+4.7 ± 0.3	+16.1 ± 0.2	-3.7 ± 0.3
#277	N	+4.6 ± 0.3	+15.3 ± 0.3	-3.5 ± 0.3	#257	N	+4.9 ± 0.3	+15.9 ± 0.2	-3.5 ± 0.3
#328	N	+5.6 ± 0.3	+16.3 ± 0.3	-2.9 ± 0.3	#260	N	+4.6 ± 0.3	+14.7 ± 0.2	-3.2 ± 0.3
#350	N	+5.5 ± 0.3	+17.1 ± 0.2	-3.5 ± 0.3	#268	N	+5.5 ± 0.2	+15.2 ± 0.1	-2.4 ± 0.2
#002	S	+13.8 ± 0.3	+29.3 ± 0.3	-1.6 ± 0.3	#273	N	+4.7 ± 0.3	+15.9 ± 0.2	-3.6 ± 0.3
#016	S	+11.1 ± 0.5	+25.3 ± 0.4	-2.2 ± 0.5	#283	N	+5.0 ± 0.2	+15.8 ± 0.2	-3.3 ± 0.2
#025	S	+6.8 ± 0.4	+18.7 ± 0.3	-3.0 ± 0.4	#301	N	+5.3 ± 0.2	+16.2 ± 0.2	-3.2 ± 0.3
#038	S	+4.5 ± 0.3	+14.6 ± 0.2	-3.2 ± 0.4	#045	S	+3.6 ± 0.2	+12.4 ± 0.2	-2.9 ± 0.3
#061	S	+4.4 ± 0.2	+14.9 ± 0.2	-3.4 ± 0.2	#080	S	+4.3 ± 0.3	+14.9 ± 0.2	-3.5 ± 0.3
#062	S	+7.8 ± 0.4	+20.6 ± 0.6	-3.0 ± 0.5	#131	S	+3.5 ± 0.3	+11.8 ± 0.2	-2.6 ± 0.3
#078	S	+9.1 ± 0.3	+23.5 ± 0.5	-3.2 ± 0.4	#168	S	+3.5 ± 0.2	+12.7 ± 0.2	-3.2 ± 0.3
#082	S	+5.3 ± 0.3	+16.0 ± 0.3	-3.1 ± 0.4	#201	S	+3.1 ± 0.3	+11.6 ± 0.2	-3.0 ± 0.3
#099	S	+12.2 ± 0.4	+28.0 ± 0.3	-2.5 ± 0.4	#211	S	+3.3 ± 0.3	+12.9 ± 0.2	-3.5 ± 0.3
#120	S	+10.2 ± 0.3	+23.8 ± 0.3	-2.3 ± 0.3	#261	S	+5.0 ± 0.3	+14.5 ± 0.2	-2.6 ± 0.3
#153	S	+6.9 ± 0.4	+18.5 ± 0.4	-2.8 ± 0.4	#325	S	+4.3 ± 0.3	+14.6 ± 0.2	-3.3 ± 0.3
#161	S	+10.7 ± 0.4	+25.1 ± 0.4	-2.5 ± 0.5	#330	S	+4.2 ± 0.3	+13.2 ± 0.2	-2.7 ± 0.3
#167	S	+15.9 ± 0.3	+32.4 ± 0.3	-1.1 ± 0.3	#011	Z	+4.3 ± 0.3	+14.6 ± 0.2	-3.3 ± 0.3
#167a	S	+15.1 ± 0.3	+32.1 ± 0.3	-1.7 ± 0.3	#101	Z	+5.0 ± 0.3	+16.2 ± 0.2	-3.5 ± 0.3
#177	S	+4.5 ± 0.3	+15.6 ± 0.3	-3.8 ± 0.3	#175	Z	+4.2 ± 0.3	+15.0 ± 0.2	-3.7 ± 0.3
#181	S	+5.7 ± 0.3	+16.9 ± 0.3	-3.2 ± 0.4	#179	Z	+5.3 ± 0.3	+17.9 ± 0.2	-4.1 ± 0.3
#184	S	+4.1 ± 0.3	+14.4 ± 0.3	-3.4 ± 0.3	#250	Z	+5.2 ± 0.2	+16.2 ± 0.2	-3.3 ± 0.2
#208	S	+7.1 ± 0.3	+19.1 ± 0.4	-3.0 ± 0.4					
#215	S	+4.9 ± 0.3	+15.3 ± 0.3	-3.1 ± 0.4					
#234	S	+5.7 ± 0.3	+17.1 ± 0.2	-3.2 ± 0.3					
#272	S	+7.7 ± 0.3	+19.7 ± 0.5	-2.7 ± 0.4					
#306	S	+8.0 ± 0.4	+20.3 ± 0.4	-2.6 ± 0.4					
#312	S	+10.6 ± 0.3	+25.2 ± 0.3	-2.7 ± 0.3					
#323	S	+5.7 ± 0.3	+16.8 ± 0.2	-3.1 ± 0.3					
#010	Z	+4.8 ± 0.3	+15.9 ± 0.3	-3.6 ± 0.3					
#020	Z	+4.8 ± 0.3	+14.2 ± 0.3	-2.7 ± 0.4					
#107	Z	+12.3 ± 0.3	+26.8 ± 0.3	-1.8 ± 0.4					
#180	Z	+7.2 ± 0.3	+19.6 ± 0.2	-3.1 ± 0.3					
#205	Z	+7.9 ± 0.4	+20.3 ± 0.4	-2.8 ± 0.5					
#231	Z	+6.8 ± 0.4	+19.1 ± 0.4	-3.2 ± 0.5					
#264	Z	+9.7 ± 0.4	+23.2 ± 0.3	-2.5 ± 0.5					

## 4. CHEMISTRY AND ISOTOPIC COMPOSITIONS

### 4.1. Bulk composition

The chemical bulk composition determined by ICP-AES and ICP-SFMS is given in Table 4. The composition of Flensburg is very similar to the median composition of 14 CM chondrites analyzed by Braukmüller et al. (2018), except for somewhat lower concentrations of Zn, Cu, and Pb (about 30%) in Flensburg. These data will be discussed below.

### 4.2. Bulk H, C, and N abundances and isotopic compositions

The bulk H, C and N elemental abundances and isotopic compositions of the Flensburg meteorite are given in Table 5. The H abundances were determined by two different techniques and agree very well. They clearly show that

Flensburg is a carbonaceous chondrite of the petrologic types 1–2. A H concentration of  $1.10 \pm 0.03$  wt.% was obtained at the Earth and Planets Laboratory (CIW), whereas in Bochum the water-content of the meteorite was determined as being 10.15, 9.56 and 9.92 wt.% for three dried samples (mean:  $9.88 \pm 0.5$  wt.%) revealing a very similar H concentration (Table 5).

The C contents were also determined by two different techniques on approximately the same amounts of material taken from the large powdered sample of Flensburg. Unlike for H, there is significant disagreement in the two measured C contents for reasons that are unclear.

As illustrated in Figs. 15–17, compared to other type 1 and 2 chondrites (Robert and Epstein, 1982; Kerridge, 1985; Eiler and Kitchen, 2004; Alexander et al., 2012, 2013) Flensburg is unique. It has the lightest bulk H isotopic composition of any measured type 1 or 2 chondrite (Fig. 15). Its bulk H content is similar to a fairly typical



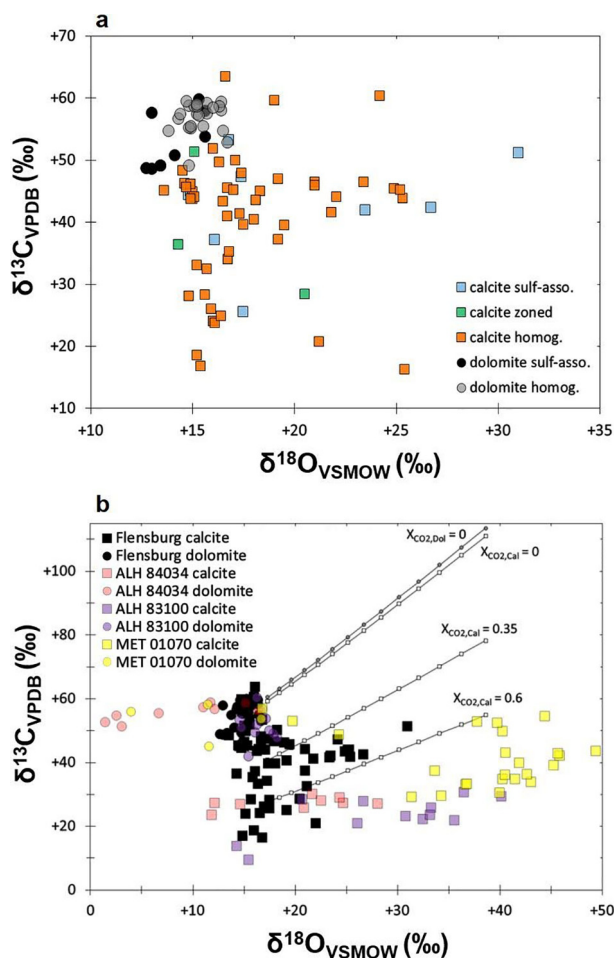


Fig. 13. (a) Simultaneous single-spot carbon and oxygen isotope analyses of Flensburg dolomites and calcites. (b) Comparison with CM carbonate data by [Telus et al. \(2019\)](#). Scatter of dolomite data is lower than for calcites, which may have formed from gas with varying CO/CO<sub>2</sub> ratios resulting in significant  $\delta^{13}\text{C}$  variation as indicated by model curves calculated according to [Alexander et al. \(2015\)](#). Most dolomites and Flensburg calcites formed at rather high temperatures (i.e., low  $\delta^{18}\text{O}$  values), when compared to the majority of CM calcite data.

unheated CM chondrite, and significantly less than in type 1 CI, CM or CR chondrites. Its bulk C content, on the other hand, is lower than most unheated CMs, as well as all CIs and Tagish Lake, but higher than all CRs except the anomalous Al Rais. Its  $\delta^{13}\text{C}$  value is higher than that for almost all CMs, CRs, and CIs ([Fig. 16](#)). Only the Tagish Lake lithologies have higher bulk  $\delta^{13}\text{C}$  values. There is a crude correlation between bulk N content and bulk  $\delta^{15}\text{N}$  ([Fig. 17](#)) amongst type 1 and 2 chondrites, except for the very  $^{15}\text{N}$ -rich CRs and the anomalous CM Bells. Flensburg has the lowest bulk N content and  $\delta^{15}\text{N}$  value of any measured type 1 and 2 chondrites ([Fig. 17](#)).

#### 4.3. Bulk O isotope compositions

The O isotope compositions of the three analyzed chips are listed in [Table 6](#). The data for Flensburg plot within the

field of CM chondrites, but at the  $^{16}\text{O}$ -rich end and marginally overlap with data from CV and CR chondrites ([Fig. 18](#)). The possible relationships between Flensburg and other carbonaceous chondrite groups will be considered in the discussion.

#### 4.4. Noble gas components

The results of the noble gas measurements for the two samples are summarized in [Tables 7a–7d](#). All noble gases consist almost entirely of trapped (tr) components with a very small cosmogenic (cos) contribution, which renders decomposition and determination of the latter difficult. The composition of the pure Ne<sub>tr</sub> endmember was determined by extrapolating a line from a mean Ne<sub>cos</sub> through the measured data points and finding the intercept with the Ne-E-Ne-Q mixing line ([Fig. 19](#)).

As the gas mixture is dominated by trapped components, the cosmogenic  $^{22}\text{Ne}/^{21}\text{Ne}$  cannot be determined. Therefore, a mean cosmogenic  $^{21}\text{Ne}/^{22}\text{Ne}$  of 1.11 was assumed, following [Scherer and Schultz \(2000\)](#). This ratio commonly serves as a shielding indicator, and is e.g., used in the depth- and chemistry-dependent model of Leya and Masarik “LM” (2009) applied here to determine production rates. The chemistry was taken from [Table 4](#) (ICP-SFMS, where ICP-AES data are not available assuming an average 42.5 wt.% O, see section “bulk composition”).

[ReVelle \(1979\)](#) estimated mass loss due to atmospheric ablation for ordinary chondrites. The authors concluded that a minimum of 35% of the mass is lost during flight through the atmosphere, and modelled for a velocity of 18 km/s a mass loss between 85 and 95%. These estimates are probably still conservative considering that Flensburg is more fragile and more volatile than the ordinary chondrites used in the model. [Alexeev \(2003\)](#) estimated a mean ablation percentage of  $91.5^{+2.1}_{-2.6}\%$  for ordinary chondrites.

A most probable range of production rates was calculated assuming 85% of the mass has been lost in ablation. Additionally, production rates were restricted by excluding 22% of the inner radius for each allowed size. The volume of this part of a sphere only makes up <1% of the total volume. Very large radii above 200 cm were not included, as Flensburg’s size and density makes such a pre-atmospheric size highly unlikely. A range of possible production rates is given in [Table S6](#). All measured isotope ratios for He, Ne, and Ar are consistent with essentially no exposure to cosmic rays (e.g. [Fig. 19](#)). Maximum possible cosmogenic  $^3\text{He}$ ,  $^{21}\text{Ne}$ , and  $^{38}\text{Ar}$  were determined and maximum CRE ages calculated accordingly and are given in [Table S7](#). Large variations in the determined CRE ages are due to the unknown  $^{22}\text{Ne}/^{21}\text{Ne}$  ratio.

The density used in the LM model is 2.25 g/cm<sup>3</sup>, whereas Flensburg’s density is lower ( $1.984 \pm 0.016$  g/cm<sup>3</sup>), leading to an increase of all calculated possible pre-atmospheric sizes by 13.4%. [Fig. S7](#) shows the Xe isotopic composition of Flensburg and that air contamination due to weathering or oxidation is negligible as might be

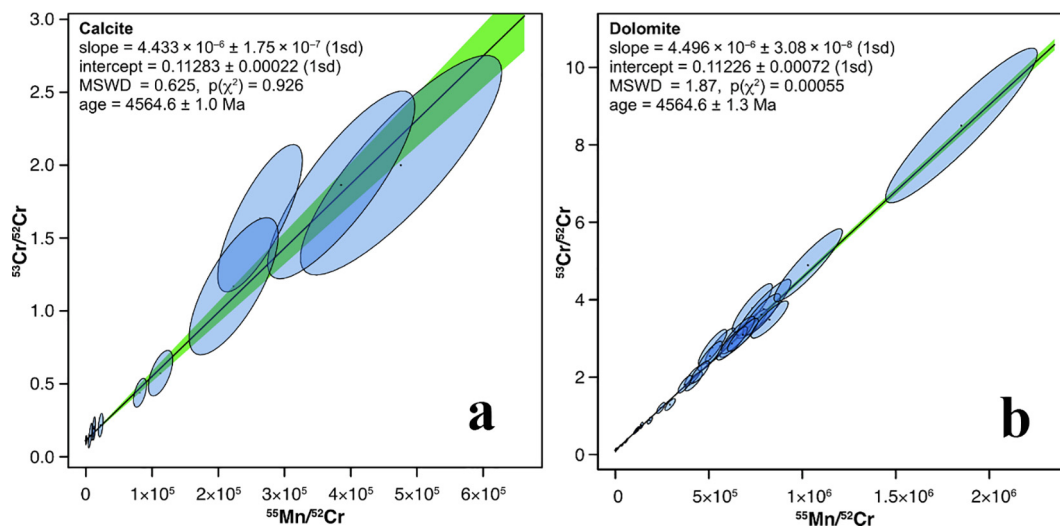


Fig. 14. (a)  $^{53}\text{Cr}$ - $^{53}\text{Mn}$ -age of calcites from the unique C1 chondrite Flensburg. Calcites formed very early in the planetesimal from which Flensburg originated. (b)  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  age of dolomites. As confirmed by mineralogical observations, particularly calcite overgrowth of dolomite, most dolomites formed before calcite. The remarkably nearly perfect alignment of dolomite data along the isochron (corresponding to a 0.7% error of the slope) indicates dolomite formation in a narrow time interval of about 70 000 years.

Table 4

The bulk chemical composition of Flensburg compared with CM data. Oxides in wt.%, all other elements in ppm ( $\mu\text{g/g}$ ).

wt.%	ICP-AES	ICP-SFMS	CM*	ppm	ICP-SFMS	CM*
$\text{SiO}_2/\text{S}^{**}$						
$\text{TiO}_2$	0.09	0.099	0.093	Zr	4.91	4.73
$\text{Al}_2\text{O}_3$	2.20		2.25	Nb	0.375	0.368
FeO	27.4		28.3	Cs	0.119	0.119
MnO	0.22	0.202	0.229	Ba	3.24	2.98
MgO	19.7		20.1	La	0.343	0.290
CaO	1.82	1.78	1.76	Ce	0.876	0.758
$\text{Na}_2\text{O}$	0.64		0.356	Pr	0.131	0.122
$\text{K}_2\text{O}$	0.05	0.050	0.046	Nd	0.661	0.624
$\text{P}_2\text{O}_5$	0.23	0.245	0.226	Sm	0.215	0.204
ppm				Eu	0.0813	0.0773
Cr	3036		3176	Gd	0.296	0.321
Li				Tb	0.055	0.0515
Be		0.0287		Dy	0.296	0.351
K		413	382	Ho	0.082	
Sc		8.37		Er	0.240	0.221
V		65.4	67.3	Tm	0.0375	0.0346
Mn		1568	1775	Yb	0.235	0.229
Co		536	597	Lu	0.0352	0.0346
Ni	13,000		13,236	Hf	0.152	0.139
Cu		102	140	Ta	0.0194	
Zn		154	197	W	0.130	0.125
Ga		7.15	6.86	Pb	1.166	1.50
Rb		1.70	1.60	Th	0.0433	0.0369
Sr		10.33		U	0.0099	0.0087
Y		2.26				

\* Median CM data ( $n = 14$ ) of Braukmüller et al. (2018).

\*\*  $\text{SiO}_2$  and S concentrations of  $\sim 28$  and  $\sim 2.3$  wt.%, respectively, were calculated from microprobe analysis (controlled and correlated by the ICP-AES data for Mg, Al, and Ca; see SM).

expected given the short period of one day between fall and find. The Xe isotopic composition is similar to Q with possibly a small HL contribution ( $\sim 2\%$ ). Corrections for a cosmogenic contribution to the heavy noble gases are therefore not necessary.

#### 4.5. Radionuclide activities

Gamma-lines were detected from primordial radionuclides, members of the natural decay series of  $^{238}\text{U}$  and  $^{232}\text{Th}$ , as well as of  $^{40}\text{K}$  (Table 8), and short-lived

Table 5

The bulk H, C, and N elemental abundances and isotopic compositions. The uncertainties are  $1\sigma$ .

H (wt.%) <sup>1</sup>	$1.10 \pm 0.03$	$\delta D$ (‰)	$-311 \pm 4$
H (wt.%) <sup>2</sup>	$1.10 \pm 0.03$		
C (wt.%) <sup>1</sup>	$1.54 \pm 0.01$	$\delta^{13}C$ (‰)	$+3.5 \pm 0.9$
C (wt.%) <sup>2</sup>	$1.14 \pm 0.2$		
N (wt.%) <sup>1</sup>	$0.027 \pm 0.001$	$\delta^{15}N$ (‰)	$-25 \pm 2$

<sup>1</sup> Analysed at the Earth and Planets Laboratory (CIW).

<sup>2</sup> Analysed at the University of Bochum. The uncertainties are based on the measurements of standards and results for 2–3 sample aliquots.

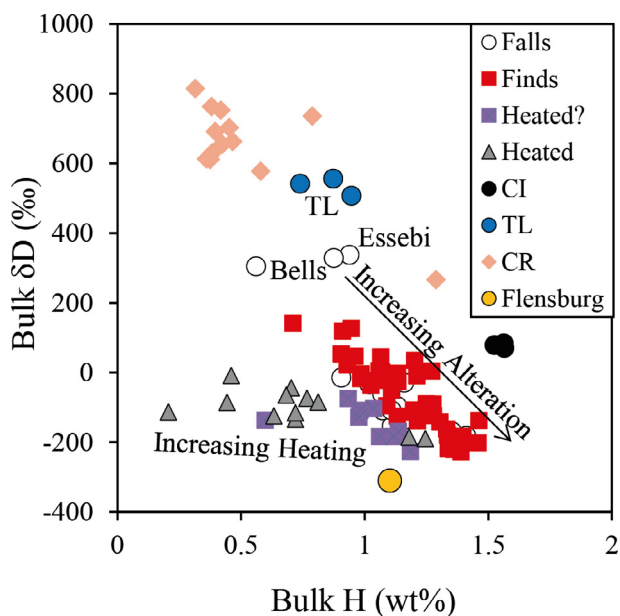


Fig. 15. The bulk H elemental abundances and isotopic compositions of type 1–2 carbonaceous chondrites (Alexander et al., 2012, 2013), including Flensburg. In general, for unheated members of a chondrite group, the H contents increase and the  $\delta D$  values decrease with increasing degree of alteration. This is due to the mixing of H in two components, a D-rich organic matter and D-poor  $H_2O/OH$ . Where a meteorite plots in this figure depends on its water/organic ratio and the initial H isotopic compositions of these two components. Almost all type 1–2s seem to have accreted water and organic matter with similar compositions (roughly  $-450‰$  and  $3000$ – $3500‰$ , respectively). The principle exceptions are the CRs whose water was significantly more D-rich ( $\sim 100‰$ ). Heating of altered meteorites, mostly through shock, drives them to lower H contents. Flensburg occupies a unique position in this diagram, being isotopically lighter than any other measured type 1–2 chondrite. It cannot be ruled out from this figure that Flensburg has been heated and partially dehydrated, but from other evidence this seems unlikely. TL = Tagish Lake.

cosmogenic nuclides. All given specific activities in units of disintegration per minute (dpm) per kg are corrected to 12<sup>th</sup> September 2019 including decay-correction during the measurement time itself.

The radionuclide data do not allow any statement about possible disequilibria in the decay series. However, assuming an equilibrium state of the decay series, the terrestrial

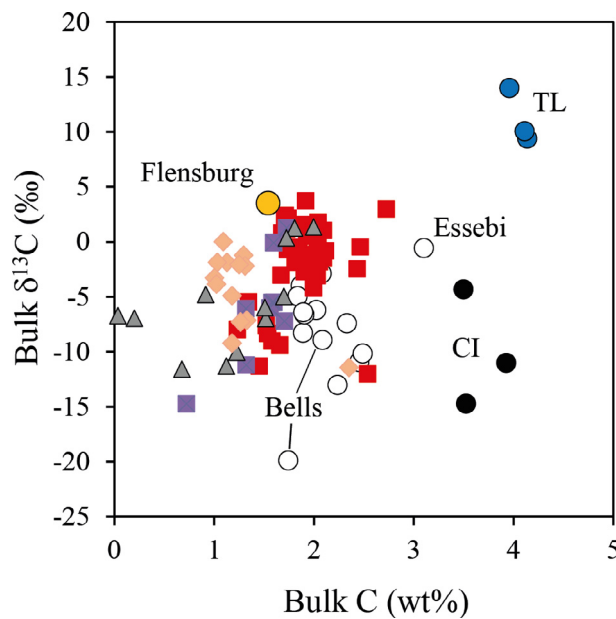


Fig. 16. The bulk C elemental abundances and isotopic compositions of type 1–2 carbonaceous chondrites (Alexander et al., 2012, 2013), including Flensburg. The symbols are as in Fig. 15. Where unheated meteorites plot in this figure depends on their relative abundances of isotopically light organic material (typically  $-34‰$  to  $-14‰$ ) and isotopically heavy carbonate (typically  $23$ – $80‰$ ). Heating will destroy both organic matter and carbonates, though probably not always in the same proportions. Flensburg has a bulk C content that is intermediate between most CMs and CRs, but a high  $\delta^{13}C$  value that is consistent with the fact that Flensburg is carbonate-rich. TL = Tagish Lake.

isotope ratios and a homogenous distribution in the sample, the U, Th, and K concentrations of the sample would be  $(18 \pm 3) \text{ ng g}^{-1}$ ,  $(68 \pm 9) \text{ ng g}^{-1}$ , and  $(420 \pm 40) \mu\text{g g}^{-1}$ , respectively. A comparison of the gamma-spectrometric values to those from ICP-SFMS for Flensburg presented in Table 4 show clearly higher values for U and Th.

For the only long-lived cosmogenic radionuclide usually detectable by gamma-spectrometry,  $^{26}\text{Al}$ , only an upper limit of  $1.7 \text{ dpm kg}^{-1}$  could be given, providing evidence for a short or complex exposure history of the meteoroid.

The relevant AMS data for Flensburg and corresponding processing blanks, and specific activities for  $^{10}\text{Be}$ ,  $^{26}\text{Al}$ , and  $^{41}\text{Ca}$  for Flensburg have been calculated from AMS ratios, ICP-MS results of the liquid aliquot ( $^{27}\text{Al}$  and  $^{nat}\text{Ca}$ ) or carrier addition ( $^9\text{Be}$ ), sample weight and half-lives. The concentrations of the three lighter radionuclides are extremely low ( $^{10}\text{Be}$ :  $0.0539 \pm 0.0016 \text{ dpm kg}^{-1}$ ,  $^{26}\text{Al}$ :  $0.209 \pm 0.030 \text{ dpm kg}^{-1}$ ,  $^{41}\text{Ca}$ :  $0.37_{-0.26}^{+0.32} \text{ dpm kg}^{-1}$ ). These values are one to more than two orders of magnitude lower than saturation activities under typical irradiation geometries. The  $^{26}\text{Al}$  specific activity, determined from the AMS data, is about a factor of ten lower than the detection limit of gamma-spectrometry. These results suggest a very short exposure age. The concentration of  $^{14}\text{C}$  is  $31.3 \pm 1.3 \text{ dpm kg}^{-1}$ , which can be e.g. compared to the expected saturation of  $\sim 60 \text{ dpm kg}^{-1}$  for a CI meteorite (Jull et al., 1998) for a meteoroid of a radius of  $\sim 30 \text{ cm}$ . The measured  $^{60}\text{Fe}/\text{Fe}$  ratio of Flensburg is not distinguishable from that

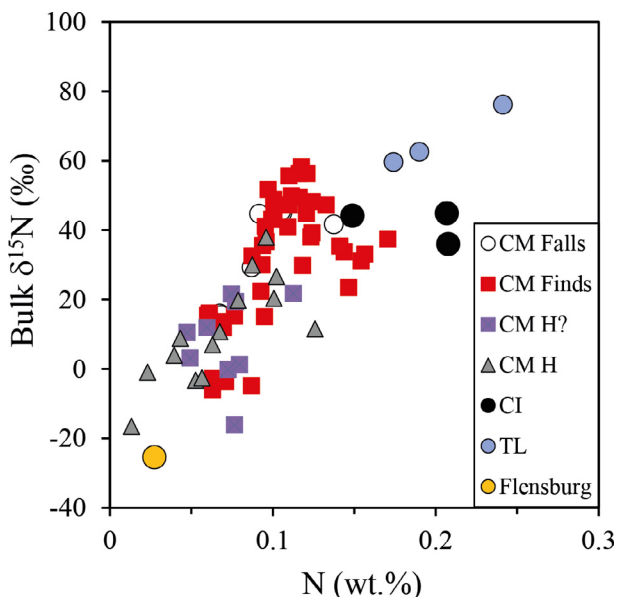


Fig. 17. The bulk N elemental abundances and isotopic compositions of type 1–2 carbonaceous chondrites (Alexander et al., 2012, 2013), including Flensburg (Table 5). The anomalous CM, Bells, and the CRs are not shown because their bulk isotopic compositions are >100‰. There is a rough correlation between N abundance and isotopic composition, but the cause of this is unknown. Flensburg occupies a unique position in this figure having both the lightest N isotopic composition and the lowest N content of any unheated type 1–2 chondrite (compare Fig. S6). TL = Tagish Lake; CM H = heated CM chondrite; CM H? = possibly heated CM chondrite.

Table 6

Results of O isotope analyses of three different chips of the Flensburg meteorite. The  $\delta^{17,18}\text{O}$  values are reported relative to VSMOW, and the  $\Delta^{17}\text{O}$  is reported relative to a mass dependent isotope fractionation reference line with a slope of 0.528 (equation 1; SM).

Analysis ID	Mass (mg)	$\delta^{17}\text{O}$ (‰)	$\delta^{18}\text{O}$ (‰)	$\Delta^{17}\text{O}$ (‰)
6871	1.943	-0.730	3.03	-2.33
6870	2.036	-0.578	3.30	-2.32
6718	2.181	0.081	5.30	-2.72

of the processing blank ( $(4\text{--}6) \times 10^{-17}$ ). The value is about three orders of magnitude lower than that expected for saturation values for stony meteorites (e.g. Knie et al., 1999) and by far the lowest  $^{60}\text{Fe}/\text{Fe}$  ratio ever measured in any meteorite so far.

#### 4.6. Titanium, Cr, and Te isotope compositions

The Cr and Ti isotope compositions of Flensburg were obtained in Zürich and Münster and the data are very similar (Table 9). The Cr isotope data show the best overlap with CM chondrites. The Ti isotope data from Zürich fall close to the field of CV/CO chondrites, whereas the Münster data overlaps with CM chondrites (Table 9, Fig. 20; Figs. S8 and S9). The combined  $^{54}\text{Cr}$  and  $^{50}\text{Ti}$  isotope data

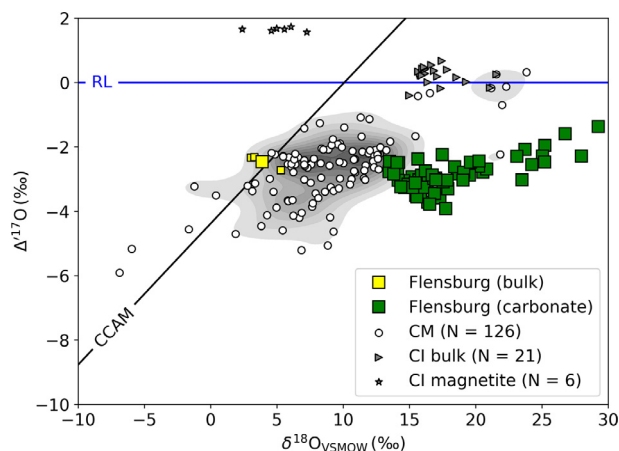


Fig. 18. Plot of the O isotope composition of Flensburg in comparison to published compositions of CM and CI chondrites and components. The  $\Delta^{17}\text{O}$  data have been calculated using Equation 1 (Supplement). The chondrite data were obtained from the Meteoritical Bulletin database (<https://www.lpi.usra.edu/meteor/>, access February 2020; Clayton et al., 1976; Clayton and Mayeda, 1984; Mayeda et al., 1987; Rowe et al., 1994; Clayton and Mayeda, 1999). The carbonaceous chondrite anhydrous minerals mixing line (CCAM,  $\delta^{17}\text{O}_{\text{VSMOW}} = 0.9467 \delta^{18}\text{O}_{\text{VSMOW}} - 4.3674\text{‰}$ ) is taken from Clayton (2008). Terrestrial samples plot on the mass fractionation line termed “RL” (reference line).

place Flensburg between the CM and CV chondrites, with the closest link to CM chondrites (Fig. 20).

It has recently been shown that carbonaceous chondrites (except CR chondrites) exhibit correlated variations of mass-dependent Te isotope composition and Te concentration, indicating that increasingly volatile- and, hence, Te-depleted samples are increasingly isotopically light (Hellmann et al., 2020). This correlation reflects varying amounts of CI-like matrix in the different groups of carbonaceous chondrites and, as such, can be used as an additional tool to assess genetic relationships among and between different carbonaceous chondrites. The Te isotopic data obtained in this study reveals that Flensburg has one of the heaviest Te isotopic composition observed among carbonaceous chondrites ( $\delta^{128/126}\text{Te} = 0.12 \pm 0.02$ ), overlapping only with CI chondrites and Tagish Lake. Compared to CM chondrites, Flensburg has a slightly higher  $\delta^{128/126}\text{Te}$  value, yet its Te concentration of  $1399 \pm 51 \text{ ng/g}$  is very similar to that of CM chondrites (Fig. 21). The Te isotopic data, therefore, link Flensburg to CM-like and other volatile-rich carbonaceous chondrites.

## 5. ORGANICS

The volatile elements C, H, O, N, and S were the most abundant elements in the early Solar nebula, and many accreted as ices or organic compounds on planetesimals (Calvin, 1999), with a continuum ranging from small defined molecules (e.g.  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{NH}_3$ ,  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2$ , in decreasing order of freezing temperature) to larger  $\text{C}_n\text{H}_m\text{O}_p\text{N}_q\text{S}_r$  molecules of considerable mass range and chemical diversity (Schmitt-Kopplin et al., 2010). The

Table 7a

He and Ne isotope concentrations (in  $10^{-8}$  cm<sup>3</sup> STP/g) and isotopic ratios in the two samples.

	<sup>3</sup> He <sub>(cos)</sub>	<sup>4</sup> He	<sup>3</sup> He/ <sup>4</sup> He × 10,000	<sup>20</sup> Ne	<sup>20</sup> Ne/ <sup>22</sup> Ne	<sup>21</sup> Ne/ <sup>22</sup> Ne	<sup>21</sup> Ne <sub>cos</sub>
S	0.365 ± 0.011	3052 ± 45	1.195 ± 0.040	8.45 ± 0.26	8.86 ± 0.19	0.0348 ± 0.0013	0.0332 ± 0.0014
L	0.2873 ± 0.0025	2442 ± 21	1.177 ± 0.014	7.71 ± 0.10	8.866 ± 0.081	0.03233 ± 0.00062	0.02813 ± 0.00059

Table 7b

Ar isotope concentrations (in  $10^{-8}$  cm<sup>3</sup> STP/g) and isotopic ratios in the two samples.

	<sup>36</sup> Ar	<sup>36</sup> Ar/ <sup>38</sup> Ar	<sup>40</sup> Ar/ <sup>36</sup> Ar	<sup>36</sup> Ar <sub>Ir</sub>	<sup>38</sup> Ar <sub>cos</sub>
S	47.64 ± 0.94	5.34 ± 0.11	19.1 ± 5.0	48.37 ± 0.95	0.01 ± 0.01
L	41.851 ± 0.034	5.339 ± 0.019	41.6 ± 2.6	41.846 ± 0.0034	0.007 ± 0.001

Table 7c

Kr isotope concentrations (in  $10^{-10}$  cm<sup>3</sup> STP/g) and isotopic ratios in the two samples (×100).

	<sup>84</sup> Kr	<sup>78</sup> Kr/ <sup>84</sup> Kr	<sup>80</sup> Kr/ <sup>84</sup> Kr	<sup>82</sup> Kr/ <sup>84</sup> Kr	<sup>83</sup> Kr/ <sup>84</sup> Kr	<sup>86</sup> Kr/ <sup>84</sup> Kr
S	53.2 ± 3.7	0.597 ± 0.058	3.83 ± 0.39	20.0 ± 2.0	20.0 ± 1.9	31.1 ± 3.1
L	50.0 ± 1.1	0.611 ± 0.017	3.90 ± 0.11	20.10 ± 0.55	20.14 ± 0.53	30.86 ± 0.84

Table 7d

Xe isotope concentrations (in  $10^{-10}$  cm<sup>3</sup> STP/g) and isotopic ratios in the two samples (×100).

	<sup>132</sup> Xe	<sup>124</sup> Xe/ <sup>132</sup> Xe	<sup>126</sup> Xe/ <sup>132</sup> Xe	<sup>128</sup> Xe/ <sup>132</sup> Xe	<sup>129</sup> Xe/ <sup>132</sup> Xe	<sup>131</sup> Xe/ <sup>132</sup> Xe	<sup>134</sup> Xe/ <sup>132</sup> Xe	<sup>136</sup> Xe/ <sup>132</sup> Xe
S	59.8 ± 1.3	0.4754 ± 0.0100	0.4275 ± 0.0091	8.29 ± 0.12	108.5 ± 1.6	81.9 ± 1.3	38.56 ± 0.62	32.37 ± 0.51
L	48.53 ± 0.75	0.4785 ± 0.0057	0.4102 ± 0.0051	8.122 ± 0.056	107.62 ± 0.78	80.97 ± 0.58	37.82 ± 0.25	31.97 ± 0.20

Table 8

Specific activities of radionuclides determined by gamma-spectrometry. All activity data are referenced to the date of fall, 12<sup>th</sup> September 2019. Half-lives are from the Decay Data Evaluation Project (DDEP, 2020) or for <sup>26</sup>Al from Norris et al. (1983); d = days; a = years.

Radionuclide	Half-life	Specific activity (dpm kg <sup>-1</sup> )	σ (%)
<i>Cosmogenic</i>			
<sup>7</sup> Be	53.22 d	121	14
<sup>22</sup> Na	2.6029 a	65	8.8
<sup>26</sup> Al	7.05 10 <sup>5</sup> a	<1.7	
<sup>46</sup> Sc	83.787 d	12.6	13
<sup>48</sup> V	15.9735 d	26	17
<sup>51</sup> Cr	27.704 d	116	21
<sup>54</sup> Mn	312.19 d	150	8
<sup>56</sup> Co	77.236 d	7.3	19
<sup>57</sup> Co	271.81 d	13.5	13
<sup>58</sup> Co	70.85 d	16.4	13
<sup>60</sup> Co	5.2711 a	98	8.1
<b>Primordial &amp; decay series</b>			
<sup>238</sup> U decay series			
<sup>238</sup> U	4.468 10 <sup>9</sup> a	<22	
<sup>226</sup> Ra	1600 a	13.3	18
<sup>210</sup> Pb	22.23 a	<27	
<sup>232</sup> Th decay series			
<sup>228</sup> Ra	5.75 a	<24	
<sup>228</sup> Th	1.9126 a	16.6	13
<sup>40</sup> K	1.2504 10 <sup>9</sup> a	780	8.4

Fourier Transform mass spectra (FTMS) obtained from the Flensburg methanolic extract showed ~1400 assigned molecular compositions, substantially fewer than those obtained for the CM2.5-CM6 chondrite breccia Murchison (n = 9850), CM1 Meteorite Hills (MET)01070 or CI

Orgueil, as well as selected metamorphosed ordinary chondrites (Fig. 22). No CHOMg-species were observed in the Flensburg soluble organic matter (SOM), in contrast to the ~60 samples previously analyzed by FT mass spectrometry (Ruf et al., 2017).

Table 9  
Titanium and Cr isotope compositions of the Flensburg meteorite.

Sample	$\epsilon^{46}\text{Ti}$	2 SE	$\epsilon^{48}\text{Ti}$	2 SE	$\epsilon^{50}\text{Ti}$	2 SE	n*	$\epsilon^{53}\text{Cr}$	2 SE	$\epsilon^{54}\text{Cr}$	2 SE	n*
Flensburg (Zürich)	+0.53	0.05	-0.02	0.02	+3.31	0.08	11	+0.20	0.04	+0.95	0.05	17
Flensburg (Münster)	+0.54	0.11	$\pm 0.00$	0.08	+2.98	0.10	13	+0.19	0.05	+1.06	0.11	6

\* n: Number of measurements; SE = Standard Error.

Table 10

The  $^1\text{H}$  NMR section integrals for key substructures of Flensburg and Murchison methanolic extracts of soluble organic matter (SOM) (asterisk \*: sizable proportions of formic acid,  $\text{HCOOH}$ ). Murchison data were extracted from Fig. 2 in [Hertkorn et al. \(2015\)](#); this reference includes detailed interpretations on aliphatic branching patterns in Murchison SOM, which are grossly similar for Flensburg SOM as well.

$\delta$ ( $^1\text{H}$ ) [ppm]	key substructures	Flensburg %	Murchison %
10 ... 5.2	$\text{C}_{\text{ar}}\underline{\text{H}}_n = \underline{\text{C}}\underline{\text{H}}_2, \text{O}_2\underline{\text{C}}\underline{\text{H}}$	3	5.0*
4.7 ... 3.1	$\text{O}\underline{\text{C}}\underline{\text{H}}$	7	7.6
3.1 ... 2.0	$\text{C}_{\text{ar}}\underline{\text{C}}\underline{\text{H}}_2, \text{OC}\underline{\text{C}}\underline{\text{H}}$	19	14.7
2.0 ... 1.85	$\underline{\text{H}}_3\underline{\text{C}}\text{COH}$	12	5.3
1.85 ... 1.35	$\text{OCC}\underline{\text{C}}\underline{\text{H}}_2$ , alicyclic $\text{CC}\underline{\text{C}}\underline{\text{H}}$	15	19.8
1.35 ... 1.25	$\text{C}_2\underline{\text{C}}\underline{\text{H}}_2$ , complex branching	17	20.8
1.25 ... 0.30	$\text{OC}_n\underline{\text{C}}\underline{\text{H}}_3$ ; $n \geq 3$	25	26.4
$\sim 0$	$\text{Si}(\text{O}\underline{\text{H}})_4$ derivatives	2	minuscule

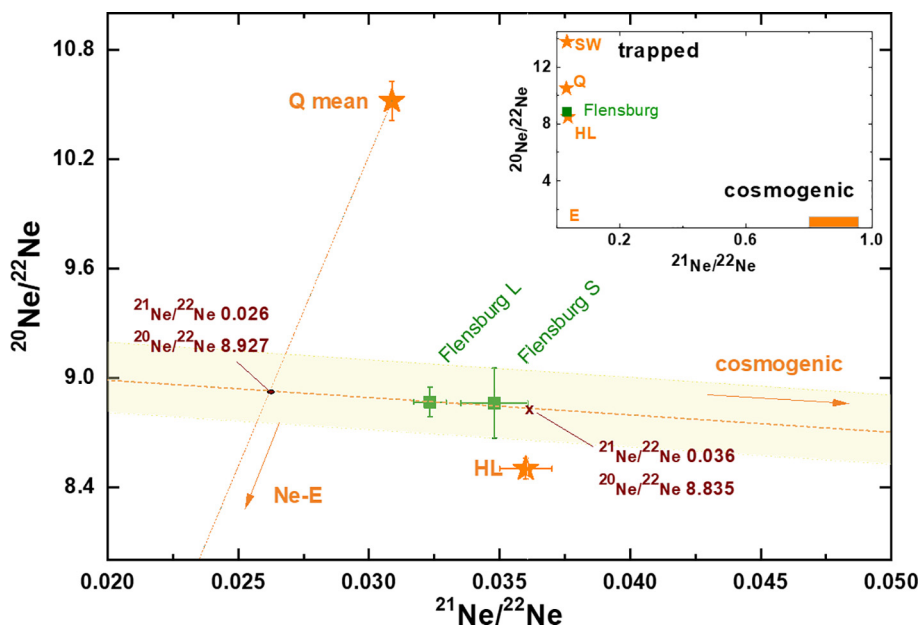


Fig. 19. Three-isotope plot showing the Ne isotopic composition of Flensburg, plotting very close to trapped Ne compositions found in carbonaceous chondrites (see inset for typical cosmogenic endmember composition ( $^{20}\text{Ne}/^{22}\text{Ne}$ )<sub>cos</sub> =  $0.83 \pm 0.11$  and ( $^{21}\text{Ne}/^{22}\text{Ne}$ )<sub>cos</sub> =  $0.87 \pm 0.08$  ([Wieler, 2002](#)). The isotopes plot within a triangle of the trapped Ne components Q ([Busemann et al., 2000](#)), Ne-E ([Amari et al., 1995](#)) and HL ([Huss and Lewis, 1994](#)) and can thus be explained entirely without a cosmogenic contribution. The position of the data point that allows us to determine a maximum contribution of cosmogenic  $^{21}\text{Ne}$  is marked by “x”. The composition of the pure trapped endmember in Flensburg ( $(^{20}\text{Ne}/^{22}\text{Ne})_{\text{tr}} = 8.93 \pm 0.29$  and  $(^{21}\text{Ne}/^{22}\text{Ne})_{\text{tr}} = 0.03 \pm 0.01$ ) is determined by the crossing of the extrapolated line from  $\text{Ne}_{\text{cos}}$  through the measured data points and the Ne-E-Ne-Q mixing line.

The  $^1\text{H}$  NMR spectra (Fig. S10) demonstrated that both Murchison and Flensburg SOM shared analogous fundamental aliphatic branching units. However, Flensburg SOM showed higher proportions of hump-like background NMR resonances from  $\delta_{\text{H}} \sim 0.7$ – $2.7$  ppm that in part repre-

sent remote O functionalization (OCCH<sub>2</sub>-units;  $\delta_{\text{H}} > 2$  ppm) and alicyclic rings (Table 10). Acetic acid represents  $\sim 12\%$  of the total  $^1\text{H}$  NMR integral, and in combination, directly (OCH<sub>3</sub> units;  $\delta_{\text{H}} \sim 3.1$ – $4.7$  ppm) and remotely (OCCH<sub>2</sub> units;  $\delta_{\text{H}} \sim 2.0$ – $3.1$  ppm) oxygenated aliphatic compounds were

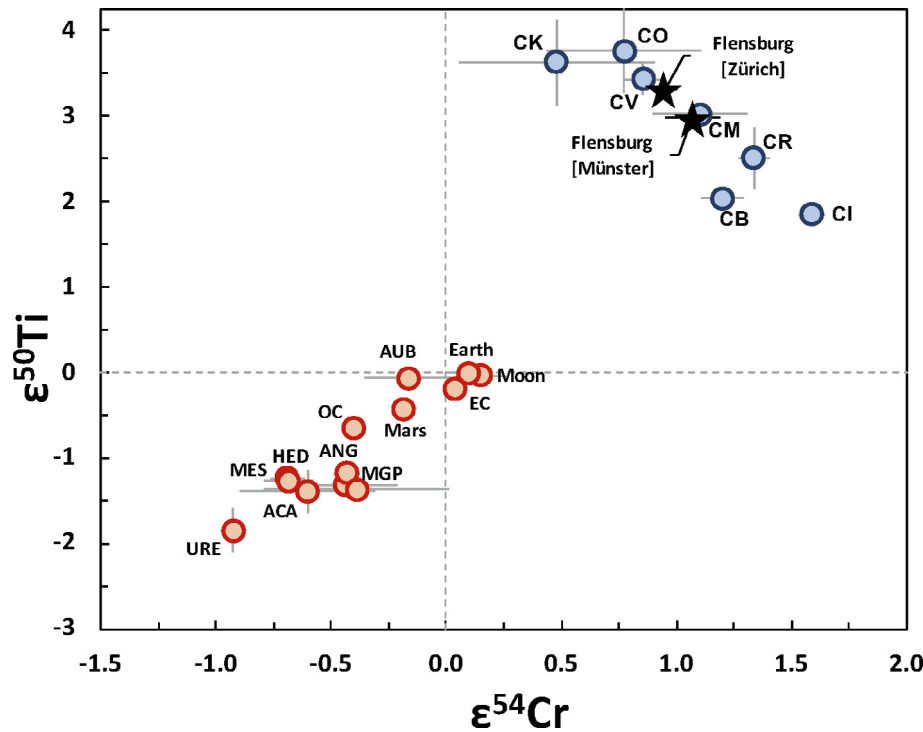


Fig. 20. Titanium versus Cr isotope compositions obtained in this study compared to literature data of various meteorite groups. Epsilon values are given relative to Earth. Uncertainties are 2 SE for data of this study (or 95% CI) and 2 SD for averages of meteorite groups in order to illustrate the scatter of the data in each meteorite group. EC: enstatite chondrites, OC: ordinary chondrites, AUB: aubrites, ANG: angrites, ACA: acapulcoites, BRA: brachinites, HED: howardite-eucrite-diogenite group, MGP: main group pallasites, MES: mesosiderites, URE: ureilites. Literature data: e.g., Niederer et al., 1981; Shukolyukov and Lugmair, 2006; Trinquier et al., 2007, 2008a, 2008b, 2009; Qin et al., 2010; Yamashita et al., 2010; Yamakawa et al., 2010; Göpel and Birck, 2010; Zhang et al., 2011, 2012; Petit et al., 2011; Larsen et al., 2011; Schiller et al., 2014; Sanborn et al., 2015; Williams, 2015; Göpel et al., 2015; Burkhardt et al., 2017, 2019; Bischoff et al., 2017a; Goodrich et al., 2017; Gerber et al., 2017; Mougél et al., 2018; Sanborn et al., 2019; Zhu et al., 2019.

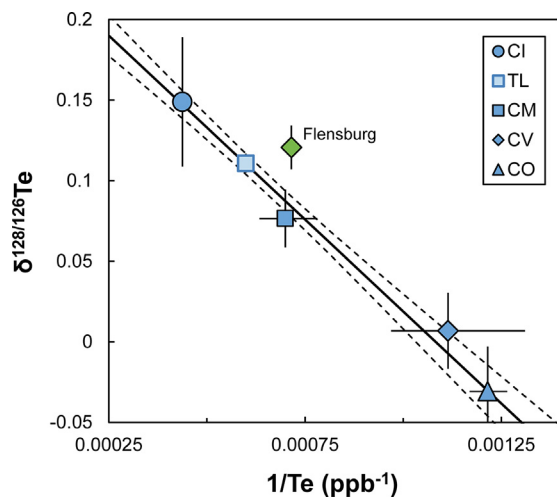


Fig. 21. Te isotope characteristics of Flensburg. The  $\delta^{128/126}\text{Te}-1/\text{Te}$  mixing line is defined by carbonaceous chondrite groups. TL: Tagish Lake. Data from Hellmann et al. (2020). Uncertainties on  $\delta^{128/126}\text{Te}$  and  $1/[\text{Te}]$  represent two standard deviation (2 s.d.).

more abundant in Flensburg SOM than in Murchison SOM (Fig. S10).

## 6. PHYSICAL CHARACTERISTICS

### 6.1. IR-spectroscopy

The infrared (IR) reflectance spectra between 8  $\mu\text{m}$  and 18  $\mu\text{m}$  (spectral resolution of 4  $\text{cm}^{-1}$ ) of a thin section of the Flensburg meteorite were compared to those from selected CI, CM, CV and CH chondrites (Fig. 23a). Details about the analyzed samples are given in Table S8.

The Christiansen feature (CF) is visible as a characteristic minimum in reflection spectra (maximum emission spectra). Its wavelength can be related to several different sample properties, e.g. the chemical composition of the sample (e.g., Pieters and Englert (1993), and references therein). The CF of the Flensburg sample measured with an angle of incidence ( $i$ ) of 25° and angle of emergence ( $e$ ) of 15° is at 8.98  $\mu\text{m}$ . Measured at  $i20;e15$ , the CF shifts slightly to 9.07  $\mu\text{m}$ . Both values are comparable to the wavelength of the CF of the two CI1 samples Alais (CF = 8.83  $\mu\text{m}$ ) and Orgueil (CF = 8.90  $\mu\text{m}$ ). For comparison, in the Murchison thin section the CF is at 8.80  $\mu\text{m}$  and in that of Cold Bokkeveld at 8.85  $\mu\text{m}$ . The samples of Allende (CV) and Acfer 182 (CH) show CFs at shorter wavelengths.

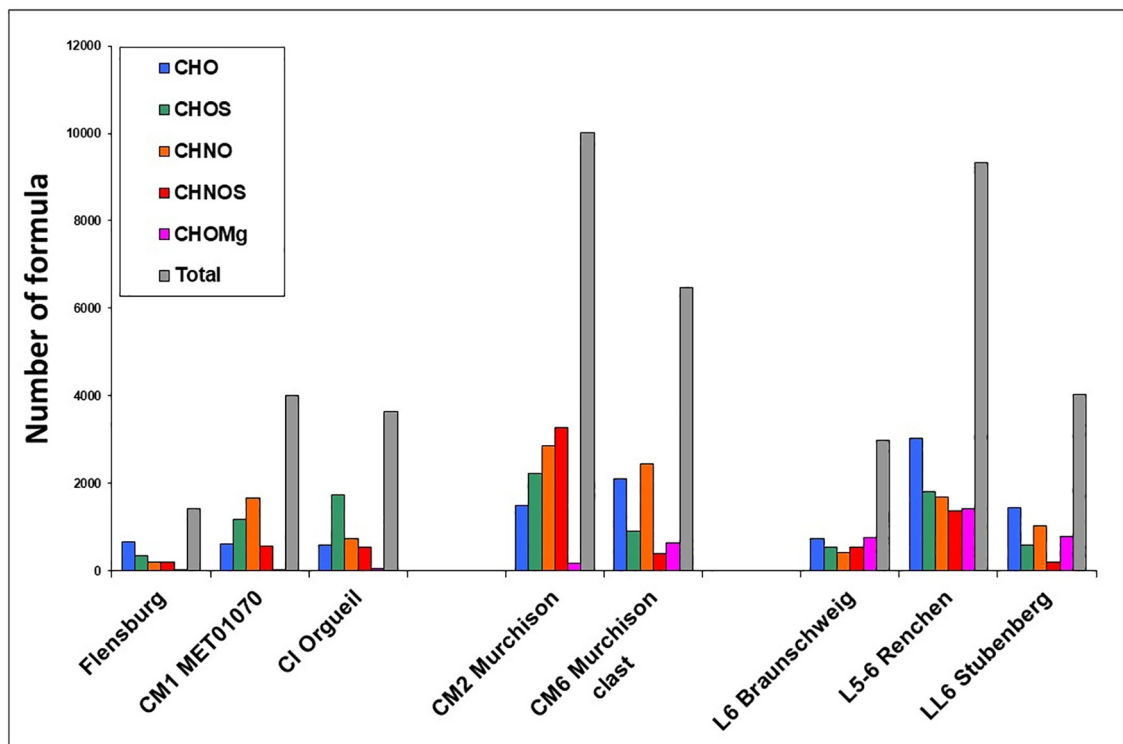


Fig. 22. Number of distinct FTMS-derived molecular compositions indicating the relatively minor number of species for soluble organic matter (SOM) of Flensburg in comparison with that of bulk Murchison and its CM6 fragment. In addition, the number of species for selected CM1, CI, and metamorphosed ordinary chondrites of recent German meteorite falls (Bartoschewitz et al., 2017; Bischoff et al., 2017a, 2019b) are provided.

Reststrahlen bands (RBs) are characteristic IR bands related to the stretching and bending of the Si-O ions and therefore to the chemical composition of the sample (e.g., Pieters and Englert (1993) and references therein). The most intense RB is at  $9.92 \mu\text{m}$ , which is again comparable to the CII samples analyzed. The other four samples clearly display different RB in terms of position and shape. Measured at the i20:e15 geometry, the most intense RB of the Flensburg thin section is at  $10.11 \mu\text{m}$ .

The spectrum of Flensburg contains three shoulders between  $10 \mu\text{m}$  and  $12 \mu\text{m}$  that are not present in the spectra of Alais and Orgueil. However, the Flensburg spectrum has a small feature at  $12.08 \mu\text{m}$  which is also seen in the CII spectra.

Fig. 23b shows the IR spectra of Flensburg, Alais, Orgueil and Cold Bokkeveld in the wavelength region between  $2 \mu\text{m}$  and  $4 \mu\text{m}$ . All four spectra contain a sharp absorption trough at around  $2.7 \mu\text{m}$  with varying “intensity”. Especially in the spectra of Alais and Cold Bokkeveld between approximately  $2.7 \mu\text{m}$  and  $3.2 \mu\text{m}$  a broad trough is visible, but also a very shallow one in Orgueil and Flensburg. At around  $3.48 \mu\text{m}$ , three absorption bands arise that are associated with aliphatic C-H bonds.

## 6.2. Magnetic properties

*Magnetic mineralogy.* The most characteristic magnetic properties of Flensburg are summarized in Fig. S11. The

coercivity spectrum of Flensburg shows a simple coercivity distribution peaking at  $11 \text{ mT}$ , suggesting that the magnetic mineralogy is dominated by a single and relatively low coercivity mineral. The presence of a magnetic Verwey transition observed at  $120 \text{ K}$  in the low temperature magnetic measurements indicate that this mineral is magnetite. The  $S_{-300}$  value of  $0.985$  indicate the absence of any significant amount of high-coercivity ferromagnetic minerals, such as monoclinic pyrrhotite, in the meteorite, which is consistent with TEM observations. This is also suggested by the low  $B_C$  and  $B_{CR}$  values ( $10.9 \text{ mT}$  and  $33.0 \text{ mT}$ ). The  $M_{RS}/M_S$  ratio of  $7.96 \times 10^{-2}$ , and  $B_{CR}/B_C$  ratio of  $3.02$  indicate a pseudo-single domain grain size, i.e., magnetite grains in the micron size range. This small grain size also accounts for the rather smooth and small Verwey transition observed in the magnetic susceptibility signal.

Saturation magnetization  $M_S$  is  $3.52 \text{ Am}^2/\text{kg}$ , corresponding to  $3.83 \text{ wt.}\%$  of magnetite using  $M_S = 92 \text{ Am}^2/\text{kg}$  for the magnetite. Indeed, the substitution by a few wt.% of  $\text{SiO}_2$  has an insignificant effect on  $M_S$  at room temperature (Yamanaka and Okita, 2001). Thus, Flensburg contains much more magnetite than CM chondrites. This value of  $3.83 \text{ wt.}\%$ , combined with the meteorite bulk density of  $1.98 \text{ g/cm}^3$  (see above), corresponds to a magnetite abundance of  $1.46 \text{ vol.}\%$ , in reasonable agreement with the  $1.9 \text{ vol.}\%$  obtained by point-counting (Table 1). The magnetic susceptibility of Flensburg is  $\log \chi = 4.35$  (where  $\chi$  is in  $10^{-9} \text{ m}^3/\text{kg}$ ; Fig. S12). It was measured on five



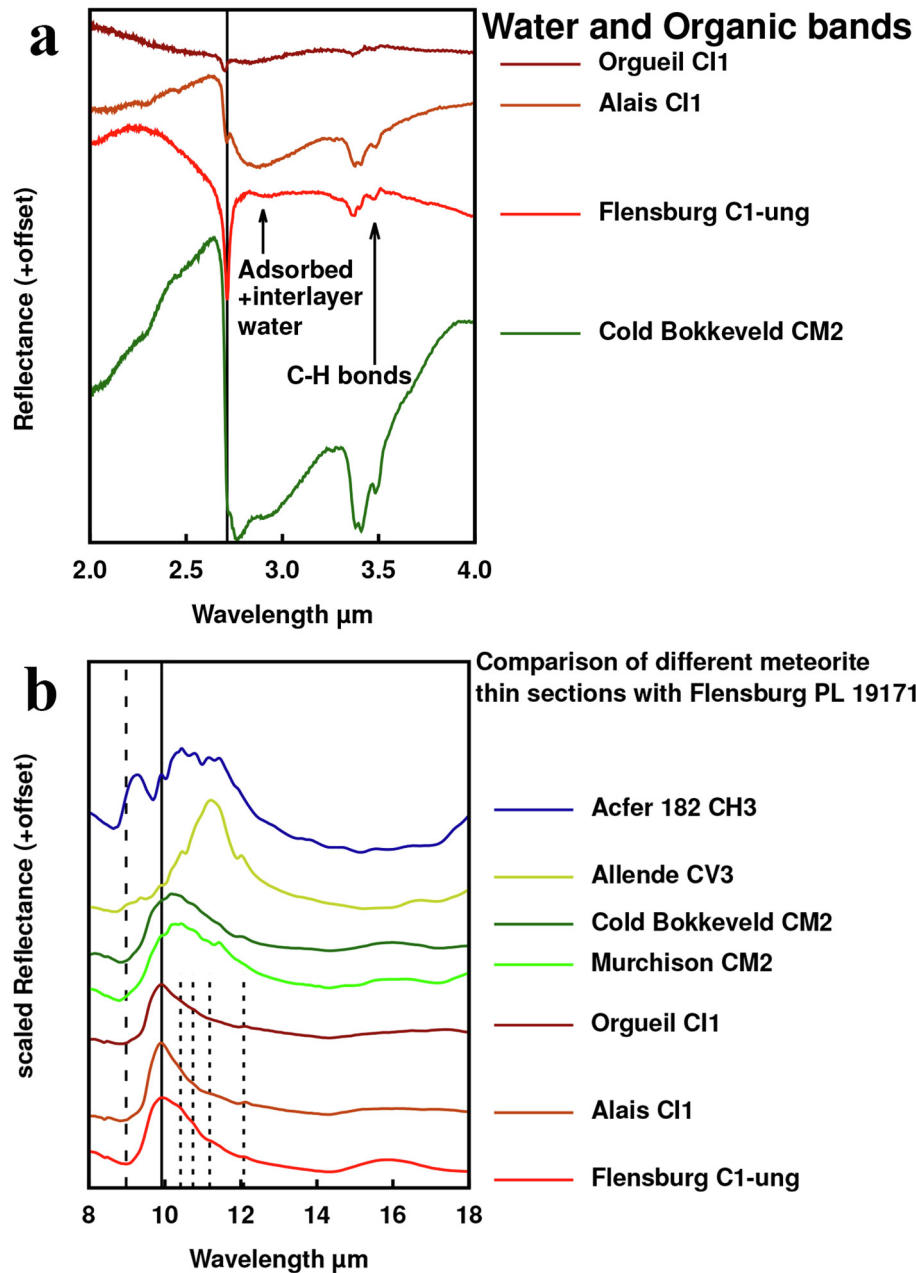


Fig. 23. (a) The infrared spectra of Flensburg, Alais, Orgueil, and Cold Bokkeveld in the wavelength region between 2  $\mu\text{m}$  and 4  $\mu\text{m}$ . (b) The infrared spectrum (IR) between 8  $\mu\text{m}$  and 18  $\mu\text{m}$  of a thin section of the Flensburg meteorite compared to spectra of other meteorites.

samples with mass ranging from 267 mg to 24.5 g (the main mass and sub-samples from the main mass), with identical results (standard deviation: 0.011). This is evidence of a very homogeneous magnetite concentration down to small size (a few dozens of mg at least).

**Paleomagnetism.** The paleomagnetic record of meteorites is a unique tool to estimate the past magnetic field in the solar systems. In particular, the paleomagnetism of meteorites that have suffered intense aqueous alteration, like Flensburg, has given insights to the intensity of the disk magnetic fields generated within the solar nebula (Cournède et al., 2015), or to the location of formation of meteorite

parent asteroids (Bryson et al., 2020). However, although the meteorite sample reached the laboratory within days after its fall, the natural remanent magnetization (NRM) of the studied 267 mg Flensburg sample show all the characteristics of complete remagnetization by a strong magnetic field originating from a magnet: curved demagnetization paths, and high NRM/sIRM ratio (0.21; sIRM = saturation isothermal remanent magnetization). The evolution of the remnant magnetization  $\text{REM}^*$  with an alternating field (see Gattacceca and Rochette (2004) for a detailed explanation about this method) shows that the strong field remagnetization affects the whole coercivity

spectrum of the meteorite, up to 100 mT. In other words, any extraterrestrial magnetic record has been erased. This is unfortunate and highlights the extremely bad habit of testing meteorites with magnets. It is noteworthy that the measurement of magnetic susceptibility that is more quantitative than any “magnet test”, does not result in any remagnetization, and is easy to perform even in the field (e.g., [Folco et al., 2006](#)); this should be encouraged among meteorite hunters, collectors and dealers.

## 7. DISCUSSION

### 7.1. General remarks

The short-lived radionuclides of the complete Flensburg meteorite measured from October 11 until October 28 clearly confirmed the connection of the Flensburg meteorite with the bolide event over Schleswig-Holstein on September 12, 2019. Thus, Flensburg is the 33<sup>rd</sup> meteorite fall in Germany and the fourth recovery fall in the last seven years after Braunschweig (2013), Stubenberg (2016), and Renchen (2018) ([Bartoschewitz et al., 2017](#); [Bischoff et al., 2017a, 2019b](#)).

### 7.2. Significance of mineralogical features for classification

As shown in the results, many different aspects of the mineralogical, chemical, and isotopic data suggest that Flensburg is best classified as a unique carbonaceous chondrite rather than a member of the CI, CM, or CR groups. Considering the primary petrographic properties for classification, this assessment is based on (a) the lack of olivine and pyroxene grains (transformed into phyllosilicates; main characteristic of a type 1 chondrite), (b) the rather small mean size ( $\sim 170 \mu\text{m}$ ) of relict chondrules and their abundance (chondrules in CM and CR chondrites are larger and their abundances in CR chondrites are much higher ([Weisberg et al., 2006](#); [Weisberg and Huber, 2007](#)), and (3) the high abundance and mineralogy of carbonates compared to those in CI and CM1 chondrites ([Table 1](#)). These mineralogical features alone indicate that Flensburg is a CI-ung chondrite. The following discussion will further describe different mineralogical, chemical, and isotopic aspects of Flensburg that clearly prove Flensburg is a unique CI chondrite.

The overall texture of Flensburg is chondritic with aqueously-altered chondrules embedded in a fine-grained groundmass. The chondrules do not have typical accretionary dust mantles as found in CM chondrites (e.g., [Metzler et al., 1992](#); [Metzler and Bischoff, 1996](#)), but often contain areas rich in sulfide laths ([Fig. 4](#)). The average size of the relict chondrules in Flensburg ( $\sim 170 \mu\text{m}$ ) is certainly significantly lower than that of CM chondrites ( $270 \mu\text{m}$ ) as determined for Murray by [Rubin and Wasson \(1986\)](#). Thus, Flensburg cannot result from further alteration of a Murray-type carbonaceous chondrite. Apparent differences also exist considering the matrix texture and mineralogy. While in primary accretionary clasts of Maribo and Cold Bokkeveld ([Fig. 24](#)) an internal matrix texture is visible – the TCI-objects (Tochilinite-Cronstedtite-Intergrowth) are

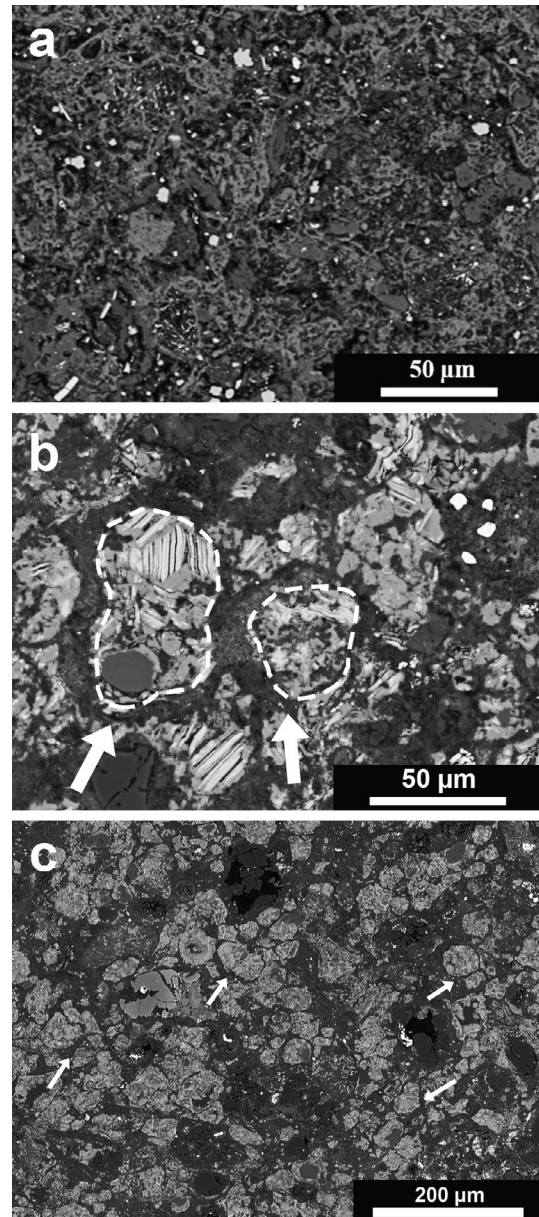


Fig. 24. Comparison between the internal matrix textures of (a) Flensburg, (b) Maribo, and (c) Cold Bokkeveld. The matrix of Flensburg is almost featureless, whereas in Maribo TCI-rich objects are coarse-grained and surrounded by thin layers of accretionary dust (arrows). Some of these objects are indicated by dashed lines. In a clast of the Cold Bokkeveld (CM-breccia) the TCI-objects (light grey) are well-separated from each other by thin rims (dark grey; arrows). BSE-images.

surrounded by thin dust rims – no distinct features can be recognized in the matrix of Flensburg ([Fig. 24a](#)). The absence of these TCI-objects is related to the scarcity or even complete absence of tochilinite in Flensburg as determined by TEM-studies. This observation is in good agreement with the high abundance of sulfides in Flensburg ([Table 1](#)), since most S is present in sulfides rather than in tochilinite. The 3.8 vol.% of sulfides within the bulk

meteorite obtained by point-counting indicate a S concentration of roughly  $1.4 \pm 0.4$  wt.%, which is similar to the value of  $\sim 2.0$  wt.% obtained by defocused-beam microprobe analysis ( $n = 135$ ; *The Meteoritical Bulletin no. 109*).

The abundances and sizes of troilite lamellae in TEM sample F01 are strongly variable and suggest that there are gradients of the bulk Fe,Ni/S ratio across the crystals. This is also consistent with the variability of pyrrhotite diffraction patterns observed. The variable troilite/pyrrhotite volume ratios indicate that the bulk Fe,Ni/S ratios of the original MSS spanned a wide range and suggests changing  $fS_2$  during crystal growth.

The unique breccia Kaidun contains clasts that may be related to Flensburg (e.g., [Zolensky and Ivanov, 2003](#); [Zolensky et al., 1996](#)). The microstructures of the exsolved troilite and the overall appearance of the phyllosilicate-sheathed low-Ni iron sulfide crystals in Flensburg are strikingly similar to those observed in the Kaidun CM1 lithology ([Harries and Zolensky, 2016](#)). In analogy to their results, the formation temperature of the sulfide must have been greater than  $100^\circ\text{C}$ , because troilite exsolution requires that the initially MSS precursor formed homogeneous above this solvus temperature.

The TEM samples F01 and F03 show unusual and variable superstructure reflections of pyrrhotite that cannot be indexed consistently ([Fig. 7a–c](#)). They are streaked out along the reciprocal  $c^*$  direction and appear to represent poor or atypical vacancy ordering from initially disordered MSS (1C-pyrrhotite). This is possibly a result of insufficient time during cooling through temperatures below the onset of vacancy ordering ( $<200^\circ\text{C}$  for Fe,Ni/S ratios  $> 0.91$  at.).

The observation that no exsolved pentlandite was found in the pyrrhotite crystals of Flensburg is in sharp contrast to the composite sulfide crystals in the Kaidun CM1 lithology, which contain about 1.8 at.% Ni in bulk (molar Ni/(Fe + Ni)  $\approx 0.04$ ). In principle, the Flensburg pyrrhotite should have exsolved pentlandite ([Fig. S4](#)), but the process was apparently hindered by slow kinetics.

Because the pyrrhotite crystals in Flensburg have substantially lower Ni contents than those in Kaidun, it appears that they formed at lower temperatures – possibly at  $150$ – $200^\circ\text{C}$ , if the original sulfide before troilite exsolution was in equilibrium with the separately coexisting pentlandite and had intermediate metal/sulfur ratios around 0.95 ([Fig. S4](#)). Using the relations of [Harries and Zolensky \(2016\)](#), the bulk composition of the sulfide and its co-formation with magnetite suggest S fugacities ( $fS_2$ ) between about  $-20$  ( $150^\circ\text{C}$ ) and  $-17$  ( $200^\circ\text{C}$ ) log units (bar) and O fugacities ( $fO_2$ ) between about  $-50$  ( $150^\circ\text{C}$ ) and  $-44$  ( $200^\circ\text{C}$ ) log units (bar). This points to high  $fS_2$  that should have stabilized pentlandite against other Ni-rich sulfides such as heazlewoodite (e.g., [Klein and Bach, 2009](#)).

The temperature interval of  $150$ – $200^\circ\text{C}$  requires hydrostatic pressures of  $>4$  to  $>18$  bar, respectively, to stabilize liquid water along its vapor pressure curve. Hence, catastrophic decompression by collision events or pressure-driven disruption might have led to volatile degassing and rapid cooling ([Wilson et al., 1999](#)).

Unlike similar sheath serpentines surrounding the pyrrhotite of the Kaidun CM1 lithology, the sheathing phyl-

losilicates of Flensburg do not display the frequent intermixing of serpentine and chlorite. The sheath phyllosilicates of two previously studied Kaidun FIB samples ([Harries and Zolensky, 2016](#)) were re-analyzed using the same conditions as the Flensburg samples. They are considerably less Na-rich ( $\sim 0.01$  atoms per formula unit) and contain more Fe ( $\sim 10\%$  Fe<sup>3+</sup> in total Fe).

In a Mg-Fe-(Si + Al) ternary compositional diagram ([Fig. S5](#)), the Flensburg serpentines extend the compositional trend of serpentines observed in CM2 and Kaidun CM1 lithologies ([Zolensky et al., 1996](#)) toward Mg- and Al-rich compositions. This is consistent with a high degree of hydrothermal alteration in which serpentines progressively become enriched in Mg relative to Fe ([Browning et al., 1996](#)).

The variable compositions of serpentine in Flensburg, the Mg-Fe zoning of vein serpentine, and the dolomite to calcite transition in composite carbonate grains suggest variable fluid compositions during alteration. The remarkable Na content in the sheath serpentines of Flensburg suggests a large Na activity in the aqueous fluid (e.g., as Na carbonate) that formed them during sulfide precipitation. This was apparently distinct from the conditions in the clast of Kaidun. Sodium could have been leached from the altered chondrule mesostases and subsequently been concentrated in the fluid after a significant amount of water had already been incorporated into the previously formed phyllosilicates.

Considering magnetite and chromite, the high Ti content of the chromite and the high Si content of the magnetite are unusual in chondrites (e.g., [Johnson and Prinz, 1991](#); [Wlotzka, 2005](#); [Björnberg and Schmitz, 2013](#)). Because chromite is strongly resistant to aqueous alteration, the chromite core of the composite grain likely represents a primary mineral of the chondritic lithology prior to alteration and served as a site of heterogeneous nucleation for later magnetite growth. In TEM, the contact between the chromite core and the magnetite rim is very sharp on the nm scale. It shows no resolvable diffusion profile, suggesting that virtually no chemical equilibration took place. The lack of detectable Fe<sup>3+</sup> and the elevated Mg, Al, and Ti abundances in the chromite core suggest formation under reducing nebula conditions from refractory-rich material.

At the TEM-scale, parts of the magnetite rims and larger grains are heterogeneous due to nanoscale inclusions ([Fig. 11b](#)). These appear to be Fe-rich silicates, but these have not been identified conclusively. Regions of apparently inclusion-free magnetite also show elevated Si contents of about 0.22 atoms per formula unit, suggesting that Si is substituted into the structure. A review of the earlier studied Kaidun samples also revealed one magnetite grain that contains very similar nanoscale inclusion of Fe-rich silicates. However, the inclusion-free regions of this grain contain little Si. Silicon-bearing magnetite and nanoscale segregation of Si-rich phases are quite common in terrestrial samples, but little is known about the physicochemical conditions that facilitate Si substitution ([Xu et al., 2014](#)). This requires further study to understand the significance for the hydrothermal environment.

### 7.3. Significance of the isotopic study of carbonates

A comparison of O and C isotopic compositions with CM literature values (Fig. 13b) by [Telus et al. \(2019\)](#) demonstrates that dolomites in Allan Hills (ALH) 83100 are quite similar to those of Flensburg, while ALH84034 and MET01070 dolomites scatter to lower  $\delta^{18}\text{O}_{\text{VSMOW}}$  values rather but comparable  $\delta^{13}\text{C}_{\text{VPDB}}$  values. This indicates similar dolomite formation conditions concerning temperature and oxygen fugacity and/or carbon source(s). The isotopic compositions of calcites in these Antarctic carbonaceous chondrites frequently range to significantly higher  $\delta^{18}\text{O}_{\text{VSMOW}}$  values (+50‰) and many of them (particularly ALH calcites) are at the low end of the Flensburg calcite  $\delta^{13}\text{C}_{\text{VPDB}}$  values (+10 to +30‰). Obviously, Flensburg calcites therefore appear to fill the gap between dolomite and most CM calcite data with  $\delta^{13}\text{C}_{\text{VPDB}}$  values of +30 to +50‰ and  $\delta^{18}\text{O}_{\text{VSMOW}}$  values of +15 to +25‰. This indicates a somewhat closer genetic relationship between Flensburg dolomites and calcites than for CM chondrite carbonates. The very similar Mn-Cr ages and very similar  $\delta^{18}\text{O}_{\text{VSMOW}}$  values indicate that there was most probably a shorter formation time interval between Flensburg calcites and dolomites at similar conditions (particularly similar formation temperatures) during prograde carbonate formation. The modeling curves in Fig. 13b were calculated according to [Alexander et al. \(2015\)](#) from a starting composition of  $\delta^{13}\text{C} = +5$  and  $\delta^{18}\text{O} = +5$  and indicate that many Flensburg calcites formed at relatively higher temperatures than those present in CM chondrites. Flensburg carbonate data could be explained by a scenario involving early formation of dolomite and many calcites from a CO dominated fluid at high temperatures, followed by calcite formation from fluids with higher CO<sub>2</sub> content, and partly lower temperatures.

A distinction between type 1 and type 2 calcites in Flensburg, as is observed for CM chondrites (e.g., [Tyra et al., 2012, 2016; Lee et al., 2013](#)) was not found in this study. The  $\delta^{18}\text{O}_{\text{VSMOW}}$  composition of calcites in Flensburg does not extend to values as high as those observed for the least altered CM chondrites Paris and Maribo, but are at the lower end of the compositional range of calcites in other CM chondrites of lower petrologic type ([Verdier-Paoletti et al., 2017](#)). There is no simple correlation between the O and C isotope composition of homogenous calcites, zoned calcites, and sulfide-associated calcites, but the latter occasionally extend to higher  $\delta^{18}\text{O}$  values indicating that some Flensburg calcite grains possibly formed continuously from an evolving aqueous solution. However, episodic fluid pulses cannot be excluded, particularly if the difference in  $\delta^{18}\text{O}_{\text{VSMOW}}$  of sulfide-associated dolomites and other dolomite grains is considered (Fig. 12c). This would imply that they formed during different events, probably starting with the sulfide-associated dolomites from slightly different fluids. This may require an interruption of the aqueous alteration possibly induced by a slight discontinuity of the thermal evolution possibly caused by early brecciation and relocation of the Flensburg sample in the parent body during the collisional growth of the parent body (see below).

The Mn-Cr ages for Flensburg calcite and dolomite of  $4564.6 \pm 1.0$  Ma and  $4564.6 \pm 1.3$  Ma, respectively, are nominally the oldest carbonate ages obtained so far for carbonaceous chondrites, if compared to previous studies using carbonate standards for determinations of the RIY ([Jilly-Rehak et al., 2017; Fujiya et al., 2012, 2013](#)). The intergrowth relationships suggest that the carbonates formed more or less contemporaneously with the pyrrhotites. Carbonate formation in CI or CM chondrites is generally considered to have occurred before or close to reaching peak temperatures of aqueous alteration in CI and CM parent bodies ([Krot et al., 2015](#)). Formation temperatures were estimated based on their O isotopic composition and thermodynamic modelling ([Clayton and Mayeda, 1984; Zolensky et al., 1989a,b; Guo and Eiler, 2007](#)) suggesting 100–150°C for CI chondrites, and 20–70°C for CM chondrites. [Verdier-Paoletti et al. \(2017\)](#) inferred even higher average formation temperatures of 110°C for CM chondrites, perhaps ranging from 50°C to 300°C. However, the Flensburg planetesimal was likely heated to higher peak metamorphic temperatures, i.e., >200°C based on the evidence from the pyrrhotites (see above). We suggest that the Mn-Cr age of  $4564.6 \pm 1.0$  Ma is the age of prograde formation of carbonates, soon after accretion of the parent body followed by metamorphic heating due to <sup>26</sup>Al decay (see below). Although Mn-Cr ages of calcite and dolomite are indistinguishable by means of Mn-Cr chronology – mainly due to the relatively large errors associated with relative ion yields from the two types of carbonates – mineralogical observations, particularly calcite overgrowth of dolomite, indicate that most dolomites formed before calcite. Remarkably, the SIMS analyses of the dolomites yield a nearly perfect alignment of dolomite data along the isochron, corresponding to a 0.7% error of the slope only. This indicates dolomite formation in a narrow time interval of ca. 70 000 years and would be consistent with an intense and short pulse of dolomite formation, preceded by a period of aqueous alteration allowing significant alteration to drive the pH of fluids sufficiently up.

### 7.4. Significance of bulk chemical and isotopic properties

#### 7.4.1. Minor and trace elements

As described above, for most elements the concentrations in Flensburg are very similar to those of the median composition of 14 CM chondrites analyzed by [Braukmüller et al. \(2018\)](#). However, there are some distinct differences. Flensburg has about 30% lower concentrations of Zn, Cu, and Pb and slightly higher Na concentrations than the concentrations of these elements in other CM chondrites given by [Braukmüller et al. \(2018\)](#). However, Na does not seem anomalous because the abundances are similar to those for the CM chondrites Boriskino, Nogoya, and Paris (~0.6 wt.% Na<sub>2</sub>O; [Hewins et al., 2014](#)) and of literature data from Murchison (0.58; [Kallemeyn and Wasson, 1981](#)). Of course, Cu, Zn, and Pb in Flensburg seem marginally low considering the data of [Hewins et al. \(2014\)](#), but the data are certainly not sufficiently different enough to make Flensburg chemically a completely different rock, when comparing it with the values for other

CM chondrites. The C content (Table 5) is also lower than is typical for a CM (~2 wt.%; Kerridge, 1985; Alexander et al., 2012, 2013). The low Zn and C may suggest a low initial matrix content, although it is possible that the organic C has been destroyed somehow. A low matrix content would raise the issue of why the water/OH content is so high.

#### 7.4.2. Hydrogen, C, and N elemental and isotopic compositions

As illustrated in Figs. 15–17 the Flensburg carbonaceous chondrite is unique. Its H content (Table 5) is similar to that of a fairly typical CM2 (Kerridge, 1985; Alexander et al., 2012, 2013; Braukmüller et al., 2018). If Flensburg was carbonate-free, then using a C content of 1.54 wt.% and assuming a CM-like H/C ≈ 0.055 (wt.) for its organics, the H in H<sub>2</sub>O/OH would be roughly 1.02 ± 0.03 wt.% (9.2 ± 0.2 wt.% H<sub>2</sub>O) and it would have a petrologic type of 1.5 on the 1–3 scale of Alexander et al. (2013). The 1σ uncertainties only take into account the uncertainties in the bulk measurements (Table 5) because at present there is no information on the H/C ratio of the bulk organics. This H<sub>2</sub>O/OH content is probably a minimum estimate, not only because it uses the higher of the two measured C contents but also because in situ measurements suggest that Flensburg may contain 3.9 ± 1.0 vol.% carbonate (Table 1). Assuming a density of 2.71 g/cm<sup>3</sup> and a C content of 11.98 wt.% for the carbonate (those of calcite) and a bulk rock density of 1.98 g/cm<sup>3</sup> (see above), the volume fraction of carbonate would account for ~0.63 wt.% C in the bulk meteorite. Hence, it is possible that about half of the bulk C is in carbonate, which would translate to a somewhat higher proportion of the H in OH/H<sub>2</sub>O than estimated above. The bulk H content is lower than those of typical CIs, CMs, and CRs (1.3–1.5 wt.%; Kerridge, 1985; Alexander et al., 2012, 2013; Braukmüller et al., 2018). This is surprising because olivine and pyroxene have been completely altered to phyllosilicates in Flensburg, whereas other chondrites classified as CM1 and CI1 still contain several vol.% of olivine and pyroxene (Howard et al., 2015; King et al., 2015, 2017). The relatively low H<sub>2</sub>O might be due to the absence of saponite-like clay minerals, which contain additional interlayer H<sub>2</sub>O.

The range of H abundances and isotopic compositions amongst the unheated type 1–2s can, to first order, be explained by mixing between D-rich organic matter and D-poor H<sub>2</sub>O/OH (Alexander et al., 2012). This can be seen in plots of δD vs. C/H (Fig. 25). Here, the C content determined at the Earth and Planets Laboratory (CIW) is used for consistency with the other data shown. The initial isotopic composition of the organic material appears to have been quite similar for all type 1–2s (δD ≈ 3000–3500‰). For the CIs, CMs, and Tagish Lake the H<sub>2</sub>O/OH seems to have had a composition of δD ≈ -450‰, but in the CRs it must have been significantly heavier (δD ≈ 100‰). The bulk H in Flensburg is not only isotopically lighter than even the most altered CM, but it is also displaced to higher C/H than the CM trend. Taken at face value, this would imply that Flensburg accreted water, and possibly organics, that was even more D-poor than that accreted

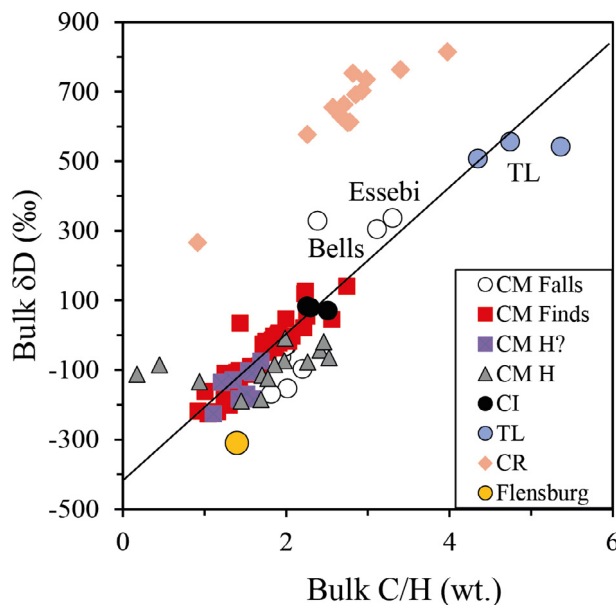


Fig. 25. The bulk δD vs. bulk C/H for type 1–2 carbonaceous chondrites (Alexander et al., 2012, 2013), including Flensburg. This figure illustrates how the H isotopic compositions are primarily determined by mixing of H in C- and D-rich organic matter with C- and D-poor H<sub>2</sub>O/OH. The line is a linear fit to the unheated CM finds, but the CIs, the anomalous CMs Bells and Essebi, and the Tagish Lake (TL) lithologies all scatter about this line. The CRs form a separate trend apparently because they accreted more D-rich water ice than the other type 1–2s. Flensburg has a lighter H isotopic composition than any other measured type 1–2. It also falls well to the right of the CM fall line, but this could be due, at least in part, to its apparently high carbonate content. CM H = heated CM chondrite; CM H? = possibly heated CM chondrite.

by the CIs, CMs, and Tagish Lake. However, if Flensburg contains about 0.6 wt.% carbonate C, almost half of the bulk C is in carbonate, which is a higher proportion than in any other type 1–2 chondrite, except perhaps some Tagish Lake lithologies (Grady et al., 2002; Zolensky et al., 2002). Since the δD vs. C/H trend strictly only applies to organic C, after subtracting the carbonate C Flensburg's C/H would decrease by roughly half and it would then fall quite close to the CM trend. Hence it is possible that Flensburg accreted water with a similar isotopic composition to the other type 1–2 chondrites, excluding the CRs.

The bulk C content of Flensburg is intermediate between CMs and CRs. Generally, in chondrites most of the C is in organic material (Alexander et al., 2015). However, in Flensburg almost half of its bulk C might be in carbonate, in which case its organic C content is similar to or less than that in CR and CO chondrites. It has been suggested that the organic C in chondrites is carried by CI-like matrix, which would imply a matrix abundance that is similar to or less than that in CR and CO chondrites (i.e., ≤30 vol.%). Alexander (2019) concluded that water-ice was also accreted in the matrix and generally in roughly CI-like abundances. However, to explain the range of degrees of alteration amongst the CMs and CRs requires either rather heterogeneous accretion of ices or post

accretion redistribution of water. One or other of these processes is also needed to explain the high H to organic C ratio of Flensburg.

Carbonates in unheated C1-2 chondrites typically have high average  $\delta^{13}\text{C}$  values (23–80‰) (Grady et al., 1988; Alexander et al., 2015), while their bulk organic matter is much lighter (–13‰ to –36‰) (Robert and Epstein, 1982; Yang and Epstein, 1983, 1984; Alexander et al., 2007). Flensburg does have one of the highest bulk  $\delta^{13}\text{C}$  values of any type 1–2.

#### 7.4.3. O isotopes

Two principal processes controlled the O isotope compositions of early solar system materials. One process is the exchange between silicate/oxides and  $^{16}\text{O}$ -poor  $\text{H}_2\text{O}$  that was produced by CO self-shielding (Clayton, 2002). Materials that were affected by this process fall roughly on a trend with slope 1 in the  $\delta^{17}\text{O}$  vs.  $\delta^{18}\text{O}$  space, which is well-defined by the carbonaceous chondrite anhydrous mixing line (CCAM, e.g., Clayton, 2008). The other process is mass-dependent fractionation, which leads to a correlated shift in  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  roughly along a trend with slope 0.528 (see e.g., Pack and Herwartz (2014) for more details of mass-dependent triple isotope fractionation). The two trends are indicated in Fig. S13a. The CM chondrites span a wide range in both  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$ , neither following the pure mass-independent nor the pure mass-dependent trend and were affected by exchange with a  $^{16}\text{O}$ -poor reservoir and mass-dependent enrichment in  $\delta^{18}\text{O}$  typical of interaction with liquid water.

Clayton and Mayeda (1984) presented an evolution model to understand the composition of components in the CM2 chondrite Murchison. They suggested that the primordial dust fell on the CCAM line and that interaction with liquid water in the CM chondrite parent body shifted the isotope compositions towards higher  $\delta^{18}\text{O}$  values. Depending on the water/rock ratio (W/R), either the rocks shift in  $\delta^{18}\text{O}$  towards higher values (high W/R) or the water shifts towards higher  $\delta^{18}\text{O}$  (low W/R).

The O isotope composition of Flensburg falls on the CCAM (Clayton, 2008) in the field of CM chondrites (Fig. 18), and only marginally overlaps with CR and CV chondrites (Figs. S13a and b). The isotope composition of Flensburg does not overlap with published data on CO chondrites (Fig. S13c). Recently a CM1 clast in Mukundpura was found that also has a light O isotope composition (Findlay et al., 2020).

Assuming similar anhydrous silicate and water O isotopic compositions to those in the CMs, as well as similar alteration conditions, the formation of the hydrous minerals in Flensburg must have occurred at low W/R ratios. Otherwise, its bulk O isotopic composition would have been mass-fractionated away from the CCAM line towards higher  $\delta^{18}\text{O}$  values, which is not the case (Fig. 18).

In terms of the O isotopes only, it is feasible that Flensburg silicates and oxides exchanged O at high temperatures with a  $^{16}\text{O}$ -poor  $\text{H}_2\text{O}$  reservoir produced by CO self-shielding (Clayton, 2002). A low-temperature process would lead to mass-fractionation and hence move the materials toward higher  $\delta^{18}\text{O}$  values, away from the CCAM line.

#### 7.4.4. Titanium, Cr, and Te isotopes

The Cr isotopes indicate that Flensburg is similar to CM chondrites. The Ti isotope data analyzed in Münster is also consistent with a CM chondrite affinity, while the Zürich data show a slightly higher, more CV-like, enrichment in  $^{50}\text{Ti}$ . This could be due to a nugget effect in the sample aliquot analyzed at ETH Zürich. Hibonites are well documented in CM chondrites and they have been shown to contain highly variable and extreme  $^{50}\text{Ti}$  compositions (e.g., Kööp et al., 2016). Mass balance considerations show that a single additional 30–50  $\mu\text{m}$  hibonite grain in the Zürich aliquot could explain the small deviation from the average CM value.

The analyses of the Te concentration and isotopes revealed that Flensburg has a  $\delta^{128/126}\text{Te}$  value different to that of mean CM chondrites (Hellmann et al., 2020), but similar to that of Tagish Lake (C2-ungrouped); however, its Te concentration is indistinguishable to that of CM chondrites (Fig. 21).

### 7.5. Significance of the noble gas budget

The extremely low abundance of cosmogenic noble gases in Flensburg implies a very short CRE age. All measured noble gases can be explained entirely by trapped components within error, meaning that, on the basis of the noble gases, the CRE age could be anywhere between zero and a maximum age of 0.20 Ma. This upper limit CRE age is consistent with CRE ages determined by long-lived radionuclides (see discussion in Section 7.6) and, therefore, there is no evidence for a complex exposure history. The maximum CRE age falls within the main age cluster of around 0.2 Ma found for CMs (Krietsch, 2020), although the more precisely determined exposure ages in Section 7.6 suggest Flensburg was exposed to cosmic rays in space for much less than any asteroidal meteorite that we know of. Only the lunar meteorite Kalahari 008/009 has a shorter CRE age (Sokol et al., 2008).

Helium, Ne, and Ar isotopes show no solar wind (SW) contributions, as demonstrated by the low  $^4\text{He}$ ,  $^{20}\text{Ne}$ , and  $^{36}\text{Ar}$  concentrations that are comparable to those in CM chondrites unaffected by SW (Krietsch, 2020). This combined with the low CRE ages implies that Flensburg does not stem from a regolith environment.

Flensburg's trapped noble gas signature is similar to that of CMs, with a major difference being a comparatively low concentration of  $^{20}\text{Ne}_{\text{tr}}$ . The low  $^{36}\text{Ar}$ ,  $^{84}\text{Kr}$ , and  $^{132}\text{Xe}$  concentrations fit with those found in strongly aqueously altered CRs and CMs of type 1–2, consistent with the classification of Flensburg as a type 1 carbonaceous chondrites.  $^{36}\text{Ar}/^{132}\text{Xe}$  ( $80.0 \pm 0.1$ ) and  $^{84}\text{Kr}/^{132}\text{Xe}$  ( $0.98 \pm 0.09$ ) plot close to Q:  $(^{36}\text{Ar}/^{132}\text{Xe})_{\text{Q}} = 76 \pm 7$  and  $(^{84}\text{Kr}/^{132}\text{Xe})_{\text{Q}} = 0.81 \pm 0.05$  (Busemann et al., 2000) with no evidence of an additional Ar-rich component that is observed in many of the least aqueously altered CMs.

The  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio is in the typical range for CO3 chondrites (Scherer and Schultz, 2000), and slightly higher than typical CM chondrites. The higher normalized  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio compared to other  $\text{Xe}/^{132}\text{Xe}$  ratios can be explained by  $^{129}\text{I}$ -derived  $^{129}\text{Xe}$ .

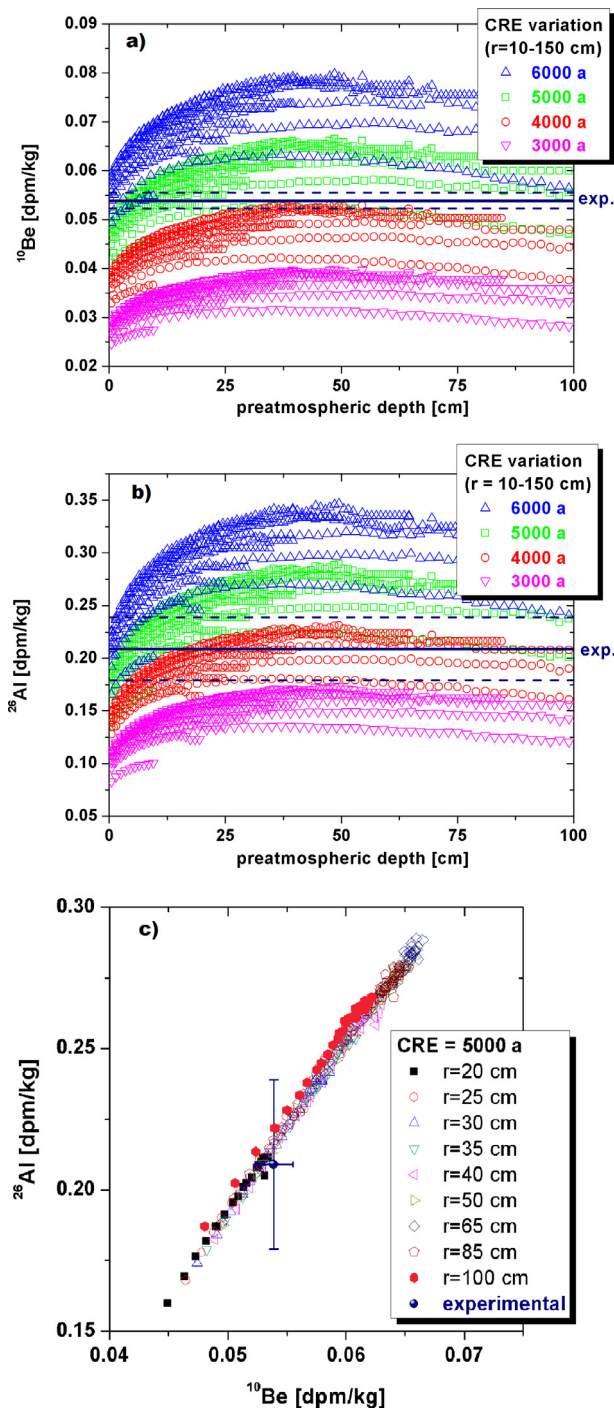


Fig. 26. Comparison of  $^{10}\text{Be}$  (a) and  $^{26}\text{Al}$  (b) experimental data with theoretical depth- and radius-dependent ( $r = 10\text{--}150\text{ cm}$ ) production rates for different cosmic ray exposure (CRE) ages (Leya and Masarik, 2009). Conclusive shielding-conditions for both nuclides are found for a CRE of  $\sim 5000\text{ a}$  (c).

## 7.6. Significance of radionuclide concentrations

The presence of short-lived cosmogenic radionuclides with half-lives as short as 16 days prove the recent exposure to cosmic rays in space of the Flensburg stone (Table 8).

The U, Th, and K concentrations of the Flensburg chondrite are in the same range as those found in gamma-spectrometric studies of recent ordinary chondrite falls like Stubenberg (Bischoff et al., 2017a) or Renchen (Bischoff et al., 2019b).

The short-lived cosmogenic radionuclides are also in the range of values measured for the Braunschweig (Bartoschewitz et al., 2017), Stubenberg (Bischoff et al., 2017a), or Renchen (Bischoff et al., 2019b) meteorites with the exception of  $^{60}\text{Co}$ , which is more than two orders of magnitude higher in Flensburg. Such high  $^{60}\text{Co}$  activity can only be explained by a rather shielded position of the Flensburg specimen following the arguments of Povinec et al. (2015). Taking density differences between Flensburg and ordinary chondrites into consideration, the  $^{60}\text{Co}$  specific activity of  $98\text{ dpm kg}^{-1}$  can only be explained if the sample was situated in a minimum depth of 25 cm within a meteoroid – at least for the last 30 years or so.

Results for  $^{41}\text{Ca}/\text{Ca}$  are based on four counts only, hence, have a high statistical uncertainty. This hinders further interpretation apart from the fact that the low concentrations of both,  $^{41}\text{Ca}$  and  $^{60}\text{Fe}$  are consistent with the very short exposure of Flensburg in space that can be already deduced from the  $^{10}\text{Be}$  and  $^{26}\text{Al}$  data alone.

Comparison of  $^{10}\text{Be}$  and  $^{26}\text{Al}$  data with depth- and radius-dependent ( $r = 10\text{--}150\text{ cm}$ ; Fig. 26) production rates based on the work of Leya and Masarik (2009) are presented in Fig. 26. In a first step,  $^{10}\text{Be}$  and  $^{26}\text{Al}$  theoretical production had been modified for highly-variable exposure, i.e. 500–50,000 a, then followed by exposure for 3000–6000 a only. Both radionuclides point to a short exposure around 5000 a (Fig. 26), if we exclude very small pre-atmospheric radii  $\leq 10\text{ cm}$ , which is valid based on the  $^{60}\text{Co}$  data. With a very simple density adjustment of the model to Flensburg's density, the meteoroid must have had a minimum size of  $r > 15\text{ cm}$ .

Using a size of  $r = 30\text{ cm}$ , consistent with the  $^{60}\text{Co}$  data, the  $^{14}\text{C}$  result confirms that the exposure age of Flensburg should be  $\sim 6000\text{ a}$ , which assumes a density similar to an ordinary chondrite. Some more detailed calculations were undertaken, since Flensburg has a sufficient nitrogen content of 0.027 wt.% to produce  $^{14}\text{C}$  from thermal neutron reactions on  $^{14}\text{N}$  at a rate of 12.5 atoms/min kg. The production rates from the spallation of O can be determined from scaling ordinary chondrite production rates to be  $\sim 40\text{ dpm/kg}$  ( $r = 15\text{ cm}$ ) to  $56.5\text{ dpm/kg}$  ( $r = 30\text{ cm}$ ) based on Wieler et al. (1996) and Leya and Masarik (2009). Using these values, we can estimate a  $^{14}\text{C}$  exposure age of 5.0 to 7.5 ka. If we further note that the density of Flensburg is  $\sim 2.0\text{ g/cm}^3$  as opposed to the typical value of  $\sim 3\text{ g/cm}^3$  for an ordinary chondrite, then we would obtain values of 7.4–11.6 ka. Hence, we can constrain the  $^{14}\text{C}$  exposure age to be  $\sim 7\text{ ka}$  (for  $r = 30\text{ cm}$ ), consistent with the  $^{10}\text{Be}$  and  $^{26}\text{Al}$  estimates of  $\sim 5\text{ ka}$  and the  $^{60}\text{Co}$  shielding depth estimate, bearing in mind that these age estimates make several assumptions and are unlikely to be more accurate than  $\pm 2\text{ ka}$ . This makes Flensburg besides the desert find Kalahari 008/009 (Sokol et al., 2008) to a sample with one of the shortest known CRE ages; thus, Flensburg is the meteorite fall with the shortest known CRE age. We note that Brown

et al. (1984) gave a similar exposure age estimate for Farmington (an L5 chondrite that fell in 1890) based on  $^{14}\text{C}$  and  $^{26}\text{Al}$  to be 8.5–11.3 ka. This is the only other meteorite fall, which has been measured, that was not in radioactive saturation for  $^{14}\text{C}$ .

### 7.7. Significance of physical characteristics

Based on the value for the saturation magnetization ( $M_S = 3.52 \text{ Am}^2/\text{kg}$ ) Flensburg contains 3.83 wt.% (1.46 vol.%) of magnetite. For comparison, it contains much more magnetite than typical CM chondrites: the average  $M_S$  for CM chondrite falls is  $1.01 \pm 0.55 \text{ Am}^2/\text{kg}$  ( $N = 9$ , Cournède et al. (2015) and data for Boriskino, Pollen and Santa Cruz), corresponding to  $1.10 \pm 0.60 \text{ wt.}\%$  of magnetite. On the other hand, Flensburg contains less magnetite than CI chondrites like Orgueil ( $M_S = 9.55 \text{ Am}^2/\text{kg}$ ), Ivuna ( $M_S = 8.85 \text{ Am}^2/\text{kg}$ ), or the C2-ung Tagish Lake ( $M_S = 9.9 \text{ Am}^2/\text{kg}$ ). These three latter values are averages from previous studies (Brecher and Arrhenius, 1974; Thorpe et al., 2002; Tikoo et al., 2019).

Magnetic susceptibility ( $\log\chi = 4.35$ , where  $\chi$  is in  $10^{-9} \text{ m}^3/\text{kg}$ ; Fig. S12) is in the upper range of CM2s that have an average  $\log\chi = 3.90 \pm 0.43$  ( $n = 52$ ; Rochette et al., 2008). The only CM1 measured in Rochette et al. (2008), MET01070, has a much lower susceptibility,  $\log\chi = 3.63$ . Flensburg has similar susceptibility to the C2-ung chondrite like NWA 5958 ( $\log\chi = 4.12$ , measured on a 4.53 g sample). Other C2-ung chondrites like Acfer 094, Adelaide, Bells, and Essebi have much higher susceptibility, with  $\log\chi = 4.62, 4.76, 4.82,$  and  $4.85$ , respectively (Rochette et al., 2008).

Sulfides do not contribute significantly to the magnetic properties, implying that only a very minor fraction can be in the form of monoclinic pyrrhotite, which is confirmed by TEM studies.

The IR-spectroscopic characteristics of a Flensburg thin section were analyzed and compared with the spectra with other carbonaceous chondrites. Salisbury et al. (1991) found in powder reflectance spectra of Orgueil a CF between  $8.64 \mu\text{m}$  and  $8.55 \mu\text{m}$  and in Alais a value of  $8.85 \mu\text{m}$ . The slight shifts between our measurements on Flensburg compared with those of Salisbury et al. (1991) and the shift of the CF between the two different measurements with varying viewing geometry are most likely due to a change in the sampled surfaces. A small change in the viewing geometry results in a change of the analyzed area which probably has a different bulk mineralogical composition. Therefore, the wavelength of the CF around  $9.03 \mu\text{m}$  in the spectra of the Flensburg sample reflects its mineralogical similarities to those of the CII samples.

In addition, the strongest RB found at around  $10.02 \mu\text{m}$  in the spectrum of the Flensburg meteorite, is comparable to the spectra of the measured CII meteorites. This peak position is a result of the presence of phyllosilicates occurring in the samples (Beck et al., 2010).

The CM, CV, and CH samples show other distinct RBs, which demonstrates the difference between these meteorites and Flensburg. The shoulder in the spectrum of Flensburg at about  $11.29 \mu\text{m}$  is probably due to the presence of calcite

or ankerite (Green and Schodlok, 2016). Olivine has also a strong feature at this wavelength (e.g., Morlok et al., 2020) and, therefore, the feature may indicate the presence of minor amounts of olivine; however, olivine was not positively detected by optical microscopy, SEM, and TEM, but maybe by X-ray techniques (see SM). It is also possible that all observed shoulders are an effect of pentlandite. In this wavelength region, pentlandite also has some weak features (seen in a pentlandite spectrum laag02 taken from RELAB spectral database). In contrast to this assumption, the most intense RB peak of pentlandite is at  $\sim 9.5 \mu\text{m}$ . At this wavelength no clear peak or shoulder could be observed in the spectrum of Flensburg.

In the wavelength region around  $3 \mu\text{m}$ , water absorption bands with varying depths are present in the spectra of Flensburg, Orgueil, Alais, and Cold Bokkeveld (Salisbury et al., 1991). The water bands can be differentiated into OH that is bound within the crystal structures and water either between layers in minerals or that is adsorbed at the surface (Beck et al., 2010). The depths of the band for the adsorbed water in Flensburg are much shallower than in Alais and Cold Bokkeveld indicating that these samples have some terrestrial water adsorbed (Beck et al., 2010). In contrast to the study of Beck et al. (2010), our sample of the Orgueil meteorite does not show a strong band due to adsorbed water indicating that this sample is probably “fresher” and less contaminated than the samples used by Beck et al. (2010).

The strong absorption band at  $2.71 \mu\text{m}$  in the spectra of Flensburg and Alais, (which is slightly shifted in Orgueil and weakly visible in the spectrum of Cold Bokkeveld) is due to OH stretching in phyllosilicates (Beck et al., 2010). The strongest and clearest visible absorption feature in the Cold Bokkeveld sample measured in this study is at about  $2.76 \mu\text{m}$ . Beck et al. (2010) argue that this strong absorption band around  $2.7 \mu\text{m}$  originates from Mg-rich serpentines. The wavelength of this feature is also affected by the total amount (wt.%) of phyllosilicates in the probed sample (Beck et al., 2010). According to visual inspection of the figures presented in Beck et al. (2010), the intensity at a wavelength of  $2.71 \mu\text{m}$  observed in the spectrum of Flensburg meteorite is due to approximately 80 wt.% of phyllosilicates.

The total water content of CM chondrites can be determined by the depth of the  $2.7 \mu\text{m}$  absorption band (Beck et al., 2018). Applying this method to the Flensburg spectrum leads to an assumed water content of around 8.5 wt.% ( $H = 0.94 \text{ wt.}\%$ ), which is in good agreement with the measured mean value of 9.88 wt.% ( $H = 1.10 \text{ wt.}\%$ ) (Table 5).

Both analyzed IR spectral regions indicate that the Flensburg meteorite is comparable to CI meteorites because of their overall similar mineralogical compositions; however, the Flensburg spectrum exhibits some characteristics in the wavelength region between  $8 \mu\text{m}$  and  $18 \mu\text{m}$  that are not present in the spectra of the CI chondrites.

The results for Flensburg presented here can also be used to interpret remote observations of asteroids, and can help to determine the surface mineralogy as well as the degree of aqueous alteration on asteroids. Bates et al.



(2020), who also studied highly altered carbonaceous chondrites, suggest after comparing IR spectra of highly altered carbonaceous chondrites with the preliminary results from Hayabusa2 and OSIRIS-REx that aqueously altered chondrites may be suitable analogues to the surface materials of the asteroids Ryugu and Bennu (e.g., Kitazato et al., 2019; Hamilton et al., 2019).

### 7.8. Mineralogical and textural similarities to other C1 and CI chondrites and related fragments in breccias

Recently, an increasing number of xenoliths within brecciated meteorites have been described and characterized. This also includes a number of aqueously altered clasts in numerous achondrite and chondrite groups such as ureilites, howardites, CR, CH, and ordinary chondrites (e.g. Zolensky et al., 1996; Endress et al., 1994; Gounelle et al., 2005; Patzek et al., 2018a,b). Although the general mineralogies of the clasts are similar to those of CI and CM chondrites, there are differences in the mineral composition (Patzek et al., 2018a). Comparing the mineralogical features of Flensburg to those of CI chondrites and C1 clasts in several brecciated meteorites, the high abundances of sulfide laths are unique to Flensburg and CM1 clasts in the carbonaceous micro breccia Kaidun (Zolensky et al., 1996; Harries and Zolensky, 2016). The abundance of magnetite grains is lower than that of CI chondrites as determined using similar techniques, whereas the abundance of carbonates is clearly higher (Table 1; Alfing et al., 2019). Magnetite and carbonate grains are less abundant or even absent in the CM1 lithologies of Kaidun. The distribution of the different mineral phases within the sample is somewhat heterogenous, but – although some clasts in Flensburg exist (see below) – the obvious and typical brecciation features as observed for CI chondrites, where several lithologies can have highly variable abundances of different minerals (Endress and Bischoff, 1993; Morlok et al., 2006; Alfing et al., 2019), are not observed. There is also a clear difference between Flensburg and CI chondrites and C1 clasts in the abundance of chondrules (or relict chondrules): While the texture of Flensburg is dominated by abundant relict chondrules that are often rimmed by sulfide laths, these features are lacking in the CI chondrites and all observed C1 clasts. Although the CM1 clast in Kaidun is the closest analogue to Flensburg, the clast only shows a limited abundance of relict chondrules with sulfide rims (Harries and Zolensky, 2016). Additionally, the magnetite grains in Flensburg contain considerable concentrations of Si (~4 wt.% SiO<sub>2</sub>), which is much higher than for magnetite in the CM1 clast in Kaidun. Silicon is below detection limits in magnetite in CI chondrites and C1 clasts in brecciated meteorites (compare with Section 3.3.4).

In summary, Flensburg is an outlier among aqueously-altered carbonaceous chondrites with its notably different mineralogy and texture, implying a diversity of parent bodies with slightly different elemental and isotopic composition within the early solar system that ultimately led to slightly different alteration conditions. This is also suggested as a possibility by a recent study considering the O

isotopic composition of chondrite meteorites (Greenwood et al., 2019; see below).

### 7.9. Classification of Flensburg

For an appropriate classification of Flensburg, all characteristics (mineralogical, textural, physical, chemical and isotopic) discussed above will be considered.

Several different mineralogical-textural schemes have been developed to quantify the degree of aqueous alteration seen in CI and CM chondrites and to define distinct lithologies (e.g., McSween, 1979b; Endress and Bischoff, 1993; Browning et al., 1996; Rubin et al., 2007; Morlok et al., 2006; Howard et al., 2009, 2015; Lindgren et al., 2013; Garenne et al., 2014; Alfing et al., 2019; Lentfort et al., 2020). In Flensburg, mafic minerals (olivine, pyroxenes) have been completely transformed into secondary phases. This clearly requires a type 1 classification. A relationship to CII chondrites can be ruled out based on several mineralogical parameters (e.g., the occurrence of relict chondrules, the modal abundance of minor phases, Si in magnetites). Flensburg – although having clasts – does not have the typical brecciated texture observed in almost all CI and CM chondrites (e.g., McSween, 1979b; Endress and Bischoff, 1993; Morlok et al., 2006; Lindgren et al., 2013; Alfing et al., 2019; Lentfort et al., 2019, 2020). As shown in Fig. 24, the internal texture of the fine-grained material is completely different to those in typical lithologies from CM chondrite breccias.

Based on the value for the saturation magnetization ( $M_S = 3.52 \text{ Am}^2/\text{kg}$ ), Flensburg contains 3.83 wt.% of magnetite, which is much more magnetite than typical CM chondrites have, but less than in CI chondrites (Table 1).

Although the composition of Flensburg is very similar to the median composition of 14 CM chondrites analyzed by Braukmüller et al. (2018), there are some differences such as the lower concentrations of Zn, Cu, and Pb (about 30%) in Flensburg. Considering the H, C, and N elemental and isotopic compositions as illustrated in Figs. 15–17, clearly, the Flensburg carbonaceous chondrite is unique. Other isotopic studies show that Flensburg has a  $\delta^{128/126}\text{Te}$  value that is different from that of mean CM chondrites.

Since Flensburg contains carbonates that formed very early, it can certainly be postulated that the rock represents a unique parent body not sampled by other carbonaceous chondrite samples. Thus, Flensburg is a very old and unique carbonaceous chondrite breccia.

### 7.10. Flensburg and the abundance and nomenclature of organic components

*FTICR mass spectrometry.* The FTICR mass spectra of Flensburg soluble organic matter (SOM) show comparatively smaller numbers of mass peaks than those of Murchison SOM (CM2.5-CM6 breccia; Fig. S14) and offer mass spectra profiles that are very similar to those observed for the CM1 MET01070 (Fig. S14b). Flensburg SOM shows a group of intense mass peaks that are attributed to highly oxidized poly-sulphur compounds (Fig. S14a). Expansions

of nominal mass clusters (e.g.  $m/z$  311; Fig. S14b) also show fewer signals than those of Murchison extracts. Of the ~1400 assigned molecular compositions of the Flensburg extract, CHO compounds are most abundant. This is in clear contrast to Murchison SOM, in which only <20% of the ~9850 assigned molecular compositions accounted for CHO compounds, whereas heteroatom-containing compounds follow the order  $\text{CHNOS} > \text{CHNO} > \text{CHOS}$  (Fig. S15). Low abundances of soluble organics in CM1 chondrites have been attributed to aqueous alteration at higher temperatures (e.g., Botta et al., 2007; Aponte et al., 2011; Glavin et al., 2011).

The van Krevelen diagram is a widely used tool to characterize SOM of terrestrial (Meckenstock et al., 2014; Hertkorn et al., 2013, 2016) and extraterrestrial origin (Schmitt-Kopplin et al., 2010; Hertkorn et al., 2015). Commonly, thousands of assigned CHNOS and CHOMg (Ruf et al., 2017) molecular compositions, which each may represent many isomers (Hertkorn et al., 2007), are plotted according to their H/C versus O/C atomic ratios; in addition, the area of the data points indicates the relative proportions of these compounds.

Flensburg, with its large extent of aqueous alteration shows the highest proportions of CHO compounds, whereas the solubilization of heteroatoms N and S appears to require more elevated temperatures. This seems reasonable, given that the synthesis of CHNO compounds probably preceded that of CHO compounds (Schmitt-Kopplin et al., 2010). Primordial CHNO compounds can carry much more numerous and molecularly diverse coordination motifs (Derenne et al., 2012) than CHO compounds (in particular for hydrogen-deficient molecules). Hence, cohesion of intricate mixtures of CHNO compounds in the presence of mineral matrices is larger than that of CHO, while hydrogen-deficiency in general attenuates water solubility in the case of CHO and CHNO compounds (Hertkorn et al., 2015). However, oxygenated CHOS compounds commonly carry O-rich, S-containing functional groups, which facilitate water solubility. Furthermore, these compounds ionize well in negative electrospray ionization (Gonsior et al., 2011). Organomagnesium compounds (CHOMg) that were shown previously as a marker for metamorphism (Ruf et al., 2017) and were abundant in the metamorphosed chondrites Braunschweig, Stubenberg, and Renchen and in the CM6 clast in Murchison (Bartoschewitz et al., 2017; Bischoff et al., 2017a, 2019b; Kerraouch et al., 2019) were entirely absent in the solvent extract of Flensburg (Fig. 22). This absence of CHOMg compounds is consistent with mass spectra obtained for MET01070 (CM1) and Orgueil (CI1) extracts, reflecting the supposedly low temperatures and high degree of aqueous alteration. This also excludes later annealing by impact. Van Krevelen diagrams revealed a relative depletion of certain sections of elemental ratios in the Flensburg extracts in contrast to SOM in Murchison (and other CM2 meteorites), which occupy rather contiguous molecular series for CHO, CHNO, CHOS and CHNOS compounds (Fig. S15). These patterns indicate rather selective processing of SOM in Flensburg, which can be divided into abundant saturated CHO (H/C ratio from 1.7 to 2.0) and considerably less abundant but

clearly visible series of unsaturated CHO compounds (H/C ratio from 0.7 to 1.5). Some of these probably represent mono-, di- and tri-oxygenated polyaromatic hydrocarbons, which remained in solution owing to their functionalization (Fig. S15).

*The  $^1\text{H}$  NMR spectroscopy.* The  $^1\text{H}$  NMR spectra of Flensburg C1 methanolic extracts show substantial line broadening compared with those of Murchison (Hertkorn et al., 2015) and other meteorites, most likely arising from the increased proportions of dissolved minerals and metal ions. This is probably related to the increased degree of aqueous alteration, which induces corrosion of metals and transformation into soluble salts (Morlok and Libourel, 2013). Paramagnetic transition metal ions (e.g.,  $\text{Fe}^{2/3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ ) induce considerable line broadening in  $^1\text{H}$  NMR spectra (Bertini et al., 2005). Acetic acid (12% of  $^1\text{H}$  NMR integral), methanol (not shown) and formic acid (<2% of  $^1\text{H}$  NMR integral) are recognizable in Flensburg extracts. While the fundamental aliphatic branching units, which represent an averaging of many similar chemical environments (Hertkorn et al., 2015), were similar for Murchison and Flensburg (Fig. S10), the latter shows higher proportions of background NMR resonances indicative of more elaborate aliphatic branching patterns. This includes substituted alicyclic rings and remote O functionalization (Table 10), in accordance with a higher degree of aqueous alteration. By analogy to the FTICR mass spectra, the proportions of distinct NMR resonances in Flensburg are smaller than those in Murchison, indicative of smaller amounts of specific recognizable species (molecules) in Flensburg. The region of the NMR spectrum populated by aromatic protons is dominated by resonances indicative of fused aromatic compounds with two rings (polyaromatic hydrocarbons, i.e. naphthalene derivatives) and polycarboxylated benzene derivatives confirming the FTICR-MS results; on the other hand, the proportions of single aromatic compounds are smaller than those in Murchison SOM (Fig. S10).

### 7.11. The genetic relationships of aqueous alteration, hydrothermal activity, and brecciation

The petrogenesis of the final Flensburg chondrite likely started with the accretion of water-rich ices intermixed with mineral dust, chondrules and mineral and lithic clasts including substantial amounts of Fe,Ni metal and Fe,Ni sulfides (Harries and Langenhorst, 2013; Singerling and Brearley, 2018). Subsequent and substantial heating after accretion led to aqueous (low-temperature) and hydrothermal (high-temperature, >100°C) alteration. This caused the progressive and total conversion of the primary ferromagnesian silicates to phyllosilicates and the dissolution of primary metal and Fe-rich sulfides. Only a few primary phases survived this stage, such as chromite grains and, possibly, pentlandite that appears to be more resistant to alteration than low-Ni Fe sulfides (Singerling and Brearley, 2020) and often occurs as clusters of fragmented or aligned grains in Flensburg. At the low-temperature stage, comparable to alteration observed in CM2 chondrites, much of the fine-grained, Fe-rich matrix serpentine may have formed. As

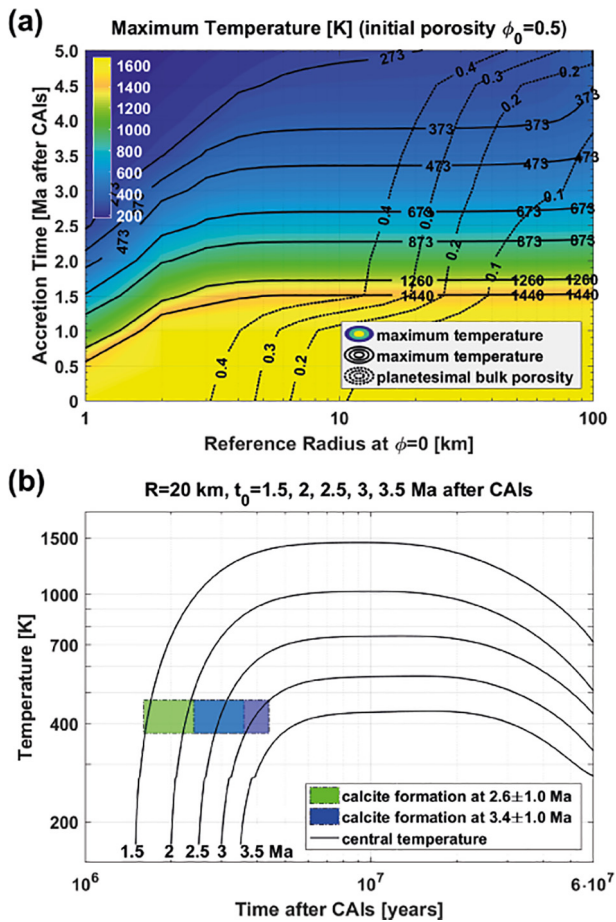


Fig. 27. (a) Maximum temperature and bulk porosity as functions of the accretion time and size of the parent body. A maximum temperature of 400°C is obtained for planetesimals with an accretion time of  $\sim 2.7$  Ma after CAIs. The thermal evolution of these bodies is consistent with the Mn-Cr data. Bulk porosities of 30%, 20%, and 10% are obtained for radii of  $\sim 20$  km,  $\sim 30$  km, and  $\sim 60$  km, respectively. (b) Thermal evolution of the Flensburg parent body at the center assuming accretion at 1.5, 2, 2.5, 3, and 3.5 Ma after CAIs, and a radius of 20 km. Calcite formation of 2.6 Ma or 3.4 Ma after CAIs can be fitted on prograde temperature evolution paths. High maximum temperatures obtained assuming accretion at 1.5 and 2 Ma after CAIs imply phyllosilicate dehydration or partial melting, contradicting Flensburg mineralogy. Maximum temperatures of 350–400°C (623–673 K) obtained in the Flensburg parent body assuming accretion at  $\sim 2.7$  Ma after CAIs agree with mineralogical observations, and this accretion time is compatible with both calcite formation ages.

the temperature increased up to  $\sim 200^\circ\text{C}$  (perhaps higher, see below) Fe- and S-rich hydrothermal fluids (possibly from the breakdown of tochilinite at  $\sim 120^\circ\text{C}$ ; Zolensky et al., 1997) led to the crystallization of magnetite and pyrrhotite. Some pyrrhotite crystals were sheathed by Mg-rich serpentine or enclosed by co-precipitating carbonates. The dolomite cores in many carbonate grains (calcites) further suggest elevated temperatures (Lee et al., 2014). The enhanced formation of pyrrhotite at the rims of chondrules and lithic clasts may have been due to high internal Fe concentrations from the alteration of metallic inclusions and

the slow release of Fe to the outside, where it reacted with S-bearing fluids transported through the more permeable meteorite matrix.

The primary heat sources besides enthalpy of hydration might have been internal radiogenic heat production and impact heating. Based on the early carbonate (and implicit pyrrhotite) formation (Fig. 14), radiogenic heating would have played a dominant role. It is assumed here that the impacts responsible for creating the fragments in Fig. 4 did not cause significant heating within the porous planetesimal, since no shock-features like chondrule flattening were observed within the chondritic clast (Fig. 4f and b). As fragment formation predates carbonate and pyrrhotite formation, it likely occurred by brecciation due to low velocity impacts during planetesimal growth.

Radiogenic heating by mainly  $^{26}\text{Al}$  could have heated small bodies with a few tens of km radius to temperatures well in the range of  $>100^\circ\text{C}$  if accretion occurred at about 3.5 Ma relative to CAIs (Fujiya et al., 2012; Bland and Travis, 2017). A more detailed calculation demonstrates that a thermal pulse triggering carbonate formation in a time interval prescribed by Mn-Cr dating (1.6–4.4 Ma after CAIs) requires a formation time at ca. 1.5–3.0 Ma after CAIs (see thermal evolution curves in Fig. 27, and model description in SM). This formation time – assuming a homogeneous  $^{26}\text{Al}/^{27}\text{Al}$  ratio of  $5.23 \times 10^{-6}$  at the time of CAI formation – would inevitably lead to internal heating by  $^{26}\text{Al}$  up to maximum temperatures of ca. 550–1500 K in a 40 km sized planetesimal ( $r = 20$  km), depending on accretion time. As Flensburg did not experience significant thermal metamorphism as described for some CI and CM chondrites, we may consider 400°C as heating limit according to Tonui et al. (2014). This would be sufficient to trigger pyrrhotite and magnetite crystallization, but insufficient to lead to dehydration of serpentine, in agreement with mineralogical observations and pressure estimates. Flensburg started with a relatively low water/rock ratio as indicated by O isotope data, such that at  $>200^\circ\text{C}$  most liquid water may have been used up by phyllosilicate formation and Fe oxidation. This probably stalled further hydrothermal processing, but preserved serpentine through peak temperatures by remaining high partial pressures of  $\text{H}_2\text{O}$  vapor.

Taking 400°C as the upper limit, Fig. 27 indicates that parent body formation occurred slightly later than 2.5 Ma after CAIs, followed by carbonate formation ca. 3 Ma after CAIs, which is in agreement with Mn-Cr dating, no matter if carbonate formation constraints of  $3.4 \pm 1.0$  Ma after CAIs (with a CAI Pb-Pb age by Bouvier et al. (2011) or  $2.6 \pm 1.0$  Ma after CAIs (using the Connelly et al. (2012) CAI age) are applied. Earlier carbonate formation can be excluded, as parent body temperatures up to 1500 K would be incompatible with the hydrated mineralogy of Flensburg. An exception could be very small bodies with a few km radius: these could escape severe heating; however, they would keep a very high porosity, again incompatible with Flensburg's porosity. There remains another – more speculative – possibility that could reconcile both early formation and lack of too severe heating effects which is a lower than canonical  $^{26}\text{Al}/^{27}\text{Al}$  ratio in the formation region of the Flensburg parent body. This would imply a heterogeneous

distribution of  $^{26}\text{Al}$  (or of the short-lived nuclide  $^{53}\text{Mn}$  used here for dating) in the solar nebula.

In summary, the optimum parent body model with 400°C maximum temperature and 10–20% porosity prescribes 20–30 km radius, and a formation time of 2.5 Ma after CAIs, implying carbonate formation ca. 3 Ma after CAIs.

Clearly, shock processing has also played a role in the history of Flensburg; however, the degree of shock metamorphism is uncertain, since typical shock effects in mafic silicates (olivine, pyroxenes) and plagioclase, which are considered to be excellent indicators of shock metamorphism (Stöffler et al., 1991; Scott et al., 1992; Bischoff and Stöffler, 1992; Bischoff et al., 2019a) do not exist anymore within this strongly, aqueously-altered chondrite. Strong arguments for early shock processes are given by the occurrence of lithic clasts (Fig. 4e and f). The shape, mineralogy, and the boundary of the magnetite-rich object in Fig. 4e clearly indicate that it did not form in-situ.

The most convincing argument for an early brecciation comes from one of the largest objects in Flensburg having an internal chondritic texture (Fig. 4f). This object can clearly be considered as an independent clast, since its texture is completely different from the texture of the bulk rock. As shown in Fig. 4f, the fragment has a well-preserved chondritic texture. The phases surrounding this clast and similar objects include abundant sulfide laths (light grey coronas in the CT-cross sections of Fig. 3a and b) and carbonates.

The most considerable explanation for the formation of this clast is that the object (of course without the sulfide-rich zone) formed by soft impact brecciation and that the resulting clast was mixed with (altered) chondrules and matrix components (like phyllosilicates) within the (still fluid-rich) parent body. As documented by the sulfides, the temperature of their formation was high (definitely >100°C). As shown in Figs. 5 and 14, carbonate precipitation must be contemporaneous with hydrothermal pyrrhotite formation within 3.4 Ma after CAIs. If the clasts originated from the same parent body, only very soft impact activity is considered since the fragment did not escape from the parent body. Alternatively, this clast and probably similar ones represent a chondritic lithology from an impacted and (partly) destroyed, independent parent body and can be considered as (a) projectile(s) softly added to the “Flensburg planetesimal”.

In any case, the clast shown in Fig. 4f suffered a second episode of aqueous alteration. The collision-induced fragmentation and re-accretion of the components resulted in a loosely-compacted, brecciated parent body with high porosity and significant pore space especially between larger objects. Thus, this pore space enabled the formation of the completely circumferential zone of sulfides (Fig. 4f; often intergrown with carbonates) at elevated  $fS_2$  (from breakdown of tochilinite or primarily  $\text{H}_2\text{S}$ -rich fluids). It is suggested that many other large objects (e.g., chondrules; Fig. 4a–d) received similar sulfide-rich areas at the same time as the chondritic clast (Fig. 4f). This kind of breccia formation is certainly different to processes in the formation history of typical CM breccias as recently discussed (e.g., Metzler et al., 1992; Bischoff et al., 2006, 2017b; Lindgren

et al., 2013; Zolensky et al., 2017; Lentfort et al., 2019, 2020).

### 7.12. The diversity of (water-bearing) parent bodies and lithologies in the early Solar System

The primordial planetesimal disk likely consisted of thousands to millions of independent primary planetesimals that formed within the first few Ma of the solar system and have been altered and modified by thermal and aqueous processes and impact activities. Many have probably been destroyed by impact, delivered precursor materials for consecutive second generation parent bodies or materials that accreted together with chondrules, forming new parent bodies. In this respect, the CR chondrites that accreted C1-like components, are an excellent example. Since the CR chondrite parent body(ies) formed late (~4 Ma after CAIs; e.g., Budde et al., 2018), sufficient time was available to form the C1-like “dark inclusions” (e.g., Endress et al., 1994; Patzek et al., 2018a) by aqueous alteration processes on water-rich precursor planetesimals possibly at similar heliocentric distances based on similar D enrichments, that were later fragmented (Patzek et al., 2020). Subsequently, clasts were transported, mixed, and accreted with components (chondrules, metals) formed under completely different (reducing) conditions to form the CR planetesimal(s). It is often considered that specific groups of chondrites derive from only one “primordial” asteroid as it existed in the first tens of Ma of solar system history (e.g., “the H chondrite parent body”; “the CM chondrite parent body”; e.g., Tieloff et al., 2003; Blackburn et al., 2017) and that fragmentation and re-assembly occurred later. Since ~1,000,000 asteroids in the main belt with sizes >1 km exist, Burbine et al. (2002) point out that no direct evidence rules out multiple primordial chondritic asteroids of essentially identical material. In detail, for the ordinary chondrites, Vernazza et al. (2014) argued that large groups of compositionally similar asteroids are a natural outcome of planetesimal formation.

On the other hand, the impact-related formation of several generations of planetary bodies is evident and has been discussed earlier mostly for “water-free” rocks (e.g., Urey, 1959, 1967; Zook, 1980; Hutchison et al., 1988; Hutchison, 1996; Sanders, 1996; Bischoff, 1998; Zolensky and Ivanov, 2003; Bischoff and Schultz, 2004; Bischoff et al., 2006, 2010, 2019b; Sokol et al., 2007a,b; Horstmann et al., 2014a; Goodrich et al., 2014; Horstmann and Bischoff, 2014; Weyrauch et al., 2018). To explain certain mineralogical and textural features in CR, CM, CI, and similar chondrites, the necessity of the occurrence of precursor planetesimals has been previously proposed (e.g., Metzler et al., 1992; Weisberg et al., 1993; Bischoff, 1998; Bischoff et al., 2006, 2018a, 2018b; Patzek et al., 2019a,b, 2020; Greenwood et al., 2020).

This should also be the case for CM chondrites and many chondrites having similar mineralogical characteristics (e.g., abundant phyllosilicates). It is completely unclear, whether all the different rocks represent a single parent body. It is even not clear, if the very different clasts in CM chondrites represent different lithologies of a single

parent body or whether the brecciated CM chondrites are formed by re-accretion of fragments that originally formed on primordial or first-generation precursor planetesimals (CM2.0-CM6; e.g., [Kerraouch et al., 2019, 2020](#); [Lentfort et al., 2020](#)).

[Bischoff et al. \(2006\)](#) report abundant evidence from meteoritic breccias that early-formed asteroids were rapidly destroyed and resulting fragments were incorporated into the second generation “daughter” bodies as confirmed by several recent studies (e.g., [Bonal et al., 2010](#); [Lindgren et al., 2013](#); [Bischoff et al., 2018a, 2018b](#); [Patzek et al., 2018a, 2020](#); [Greenwood et al., 2020](#)). The concept of the existence and evolution of primary vs. secondary parent bodies is also discussed by [Greenwood et al. \(2020\)](#). They suggest that this relationship has important implications for early Solar System evolution, since chondritic parent bodies are known to have accreted between 1 and 4 Ma after CAIs. This difference in time may reflect the fact that their source asteroids, particularly those of the carbonaceous chondrites, are secondary bodies, with the original CAI-bearing primary bodies destroyed during early collisional processing ([Greenwood et al., 2020](#)).

As also well summarized by [Greenwood et al. \(2020\)](#), dark inclusions in carbonaceous chondrites preserve evidence of complex evolutionary processes. These clasts preserve information about the aqueous alteration that took place prior to incorporation within the final host parent body (e.g., [Bischoff et al., 2006, 2018a](#); [Sokol et al., 2007a,b](#); [Bonal et al., 2010](#); [Patzek et al., 2018a](#)). [Bischoff et al. \(2006, 2018a\)](#) and [Patzek et al. \(2018a\)](#) suggested that the evidence from meteoritic breccias and dark inclusions is consistent with the formation and destruction of multiple generations of precursor asteroids prior to the accretion of the final parent body. [Patzek et al. \(2018a\)](#) suggest that the volatile-rich clasts in CR, CH, and (perhaps) in H chondrites represent components of primary accretion and not pieces of projectiles that impacted the host parent bodies much later. [Bonal et al. \(2010\)](#) come to a very similar conclusion after studying different aqueously altered clasts in Isheyevo: The characteristics of the clasts do not match those of any of these aqueously altered meteorite classes, nor do they match those of similar material in various types of chondritic clasts present in other meteorite groups. The Isheyevo clasts are considered as being fragments of previously unsampled parent bodies ([Bonal et al., 2010](#)).

Considering the aqueously-altered matter in carbonaceous chondrites, the formation of these rocks and the evolution of their parent bodies is even more complex. Clear evidence exists that the phyllosilicates in the dust-rims surrounding chondrules and the TCI formation must result from alteration processes prior to accretion onto the chondrules and chondrite accretion ([Metzler et al., 1992](#); [Bischoff, 1998](#)). This early episode is illustrated in Fig. 19 of [Metzler et al. \(1992\)](#). After accretion of CM parent bodies, collisions between similar and/or with different planetesimals played a fundamental role in the evolution of the CM parent bodies. By far, most CM chondrites are breccias that consist of lithic clasts with different alteration stages ([Metzler et al., 1992](#); [Lindgren et al., 2013](#); [Bischoff et al., 2017b](#); [Kerraouch et al., 2019, 2020](#); [Lentfort et al.,](#)

[2020](#)) mixed together in the same breccia. The observation that all lithic clasts still show their original accretionary texture (see also [Fig. 24b](#) and [c](#)) indicate that a single starting material was affected by liquid water under different alteration conditions, followed by impact brecciation and mixing.

[Greenwood et al. \(2019\)](#) suggested the possibility that “the CM parent body” is more isotopically heterogeneous than previously thought or, alternatively, that CM-related material is present on multiple bodies and formed from similar starting materials and then experienced variable degrees of hydrothermal processing. They also concluded that CMs and COs – except for the O isotopes – show a range of textural and geochemical similarities and, perhaps, a close genetic relationship. The main difference relates to the amount of water that would have been accreted to the parent bodies of the two groups ([Chaumard et al., 2018](#)), with COs being essentially dry and CMs having experienced significant aqueous alteration ([Clayton and Mayeda, 1999](#)). [Greenwood et al. \(2019\)](#) interestingly noticed that the CO-CM oxygen isotope “gap” is effectively filled by a significant number of CM and C2-like chondrites which show transitional features between CO and CM chondrites (e.g., EET 87522, GRO 95566, LEW 85311, MAC 87300, MAC 88107, NWA 7821, NWA 11556, Y-82054, NWA 5958, NWA 7821 and NWA 11556, Adelaide, and ALH 77307).

Flensburg is presenting another case. Concerning the low number of different meteorite groups and the present-day existence of ~1,000,000 asteroids in the main belt >1 km, which are most likely fragments of once larger planetesimals, it is suggested that many more CM and ungrouped C1 or C2 chondrite parent bodies exist than typically considered. CM-related material should have been present on many different parent bodies, which may have formed from similar starting materials and evolved in a similar environment as indicated by similar, but not identical mineralogy and isotopic characteristics.

### 7.13. Final aspects

#### 7.13.1. Flensburg as an analogue for asteroidal samples returned by the OSIRIS-REx and Hayabusa 2 missions

In general, the rocks heavily affected by aqueous alteration (e.g., CI and CM chondrites) are highly-brecciated (e.g., [Metzler et al., 1992](#); [Morlok et al., 2006](#); [Bischoff et al., 2006, 2017b](#); [Lindgren et al., 2013](#); [Zolensky et al., 2015, 2017](#); [Alfing et al., 2019](#); [Lentfort et al., 2020](#)). All these rocks and breccias provide insight into the formation processes of their parent bodies as well as into the evolution of asteroid surfaces. Considering the current NASA and JAXA missions to the asteroids (101955) Bennu and (162173) Ryugu, respectively, the work on the strongly aqueously-altered Flensburg chondrite may help to decipher distinct features on Bennu and Ryugu that can be studied after the sample return. Both asteroids are regarded as consisting of materials affected by aqueous alteration (e.g., [Hamilton et al., 2019](#); [Kitazato et al., 2019](#)). Ryugu is described as having a very low density and an estimated high porosity of >50% in its interior ([Watanabe et al., 2019](#)). A very low density of <2 g/cm<sup>3</sup> is also observed

for Flensburg. Considering asteroid Bennu, early spectral data of OSIRIS-REx show evidence for abundant hydrated minerals on the surface as demonstrated by the absorption feature at  $\sim 2.7 \mu\text{m}$  (Hamilton et al., 2019) indicating similarities to aqueously-altered carbonaceous chondrites. In addition, Bennu also has a low density, which is consistent with a high porosity and particle density characteristic of CM chondrites (Lauretta et al., 2019; McCoy et al., 2019) and perhaps the Flensburg carbonaceous chondrite. In summary, the mineralogical, textural, and chemical work on CM and CI breccias will certainly help to evaluate and understand the returned samples from the OSIRIS-REx and Hayabusa 2 missions.

### 7.13.2. Flensburg and the meteorite fall statistics in Central Europe

Considering the meteorite falls of Braunschweig (L6; Bartoschewitz et al., 2017), Žďár nad Sázavou (L3; Spurný, 2016; Spurný et al., 2016), Ejby (H5/6; Spurný et al., 2017; Haack et al., 2019), Stubenberg (LL6; Ebert and Bischoff, 2016; Spurný et al., 2016; Bischoff et al., 2017a), Hradec Králové (LL5; 2016; *The Meteoritical Bulletin*), Broek in Waterland (L6, 2017; *The Meteoritical Bulletin*), and Renchen (L5-6; Bischoff et al., 2019b), Flensburg is the eighth recovered meteorite fall since 2013 impacting on Earth in an area less than 500 km in radius. As estimated from meteorite entries within the Database (*The Meteoritical Bulletin*), on average, less than ten meteorite falls are recovered globally per year. Hence, this number of recorded falls in Central Europe is remarkable. Although the Flensburg meteorite was found accidentally one day after the fireball event, the high concentration of recorded falls partly demonstrates the great success of the European Fireball Network and crowd sourcing initiatives of the IMO and AMS in recording fireball events and calculating possible meteorite strewn fields. This led to ultimately finding the respective/associated meteorites by well-informed amateurs and scientists.

## 8. CONCLUSIONS

Flensburg is a phyllosilicate-rich rock that does not contain any olivine and pyroxenes and is classified here as a unique type 1 carbonaceous chondrite. The rock consists of relict chondrules, clusters of sulfide and magnetite grains, and carbonates (often intergrown with sulfides) set in a fine-grained matrix.

In particular, based on its bulk H, C, and N elemental abundances and isotopic compositions, Flensburg is clearly unique among previously analyzed chondrites as it has the lightest bulk H and N isotopic compositions of any type 1 or 2 chondrite. The bulk O isotope composition of Flensburg reveals that it plots at the  $^{16}\text{O}$ -rich end of the CM chondrite field and in the transition field to the CV-CK-CR chondrites. Normally this is the area, where most of the least altered type 2 chondrites plot.

Mineralogical observations demonstrate that there was brecciation and contemporaneous formation of the pyrrhotite-carbonate intergrowths. The  $^{53}\text{Mn}$ - $^{53}\text{Cr}$  ages of carbonates in Flensburg indicate that their formation hap-

pened no later than  $4564.6 \pm 1.0 \text{ Ma}$  (using D'Orbigny as the Mn-Cr anchor). This corresponds to  $2.6 \pm 1.0$  or  $3.4 \pm 1.0 \text{ Ma}$  after CAIs, depending on the exact CAI age assumed, representing the oldest carbonates measured in any chondrite. This result indicates that aqueous activity occurred very early in the solar system and that the primary parent body must have been very small in order to retain water-bearing phases and escape dehydration based on heating from the decay of  $^{26}\text{Al}$ .

In summary, the extraordinary significance of Flensburg is given by the observation that it represents the oldest chondrite sample, in which the contemporaneous episodes of aqueous alteration and brecciation from the time of the growth of the parent body by low velocity collisions are perfectly visible. The Flensburg meteorite is evidence for the existence of small water-rich parent bodies in the early solar system and might be similar to planetesimals that delivered (as building blocks) water to Earth.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## APPENDIX A. SUPPLEMENTARY MATERIAL

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