Abstract

Meteoroid entry physics remain poorly understood, owing to the extreme conditions experienced by the meteoroid during hypervelocity atmospheric passage, which are not reproducible in ground-test facilities. Therefore, much of our knowledge of fundamental processes is based on bolide lightcurve inference and a posteriori analysis of recovered meteorites. Here, novel in situ microtomography experiments at entry-relevant temperatures were performed on samples of two ordinary chondrites: Tandakht (H5) and Tenham (L6). The two meteorites were imaged while undergoing a temperature ramp from room temperature to 1200°C. A machine-learning mediated analysis of the microstructural evolution reveals incongruent melting of the meteorite, initiated by the meteoritic iron and iron sulfide grains, and subsequent flow through microcracks that leads to the evolution of large voids. This behavior is correlated to a broad, high-temperature endotherm, noted from differential scanning calorimetry analysis, indicative of the heat of fusion of the melting grains. Correspondingly, a surface elemental analysis indicates that the sulfur species in iron sulfide are highly mobile, which can result in the formation of nonstoichiometric iron–sulfur compounds with melting points that span the temperature range of the observed endotherm. The implications for entry phenomena, in particular meteoroid ablation, are discussed.

1. Introduction

Several thousand meteorites blast the Earth’s atmosphere each year (Bland et al. 1996). Most of the cosmic material ablates completely during atmospheric entry, though a significant number of micrometeorites (Genge et al. 2008) and fragments produced by larger objects survive the impact and reach the ground as meteorite falls. Larger objects (>10 m), while very rare, pose safety hazards to human populations and infrastructure, ranging from minor damage, to regional catastrophe, to mass extinction, depending on the magnitude, location, and dynamics of the event. Since the Chelyabinsk event in 2013 (Popova et al. 2013), there has been a renewed interest and research in high-fidelity modeling of meteoroid entry phenomena to aid in the assessment of asteroid risk (Johnston et al. 2018; Chen et al. 2019; Haskins et al. 2019; Johnston & Stern 2019; Pittarello et al. 2019; Bariselli et al. 2020; Register et al. 2020; Dias et al. 2020a, 2020b; Johnston et al., 2021). Assessing asteroid threats and implementing mitigation strategies are active pursuits of space agencies and require reliable models for meteoroid entry physics.

Destructive and nondestructive experiments on recovered meteorites are vital to the development of predictive models that detail surface heating, fragmentation/breakup, and ablation during entry. (Opeil et al. 2010, 2012; Ostrowski & Bryson 2020). Structural characteristics, such as density and porosity, and mechanical properties, such as moduli and failure strengths, are critical for characterizing both fragmentation during entry and airburst events (Consolmagno et al. 2008; Kimberley & Ramesh 2011; Hogan et al. 2015; Cotto-Figueroa et al. 2016). A detailed review of such thermal, structural, and mechanical properties for a variety of meteorite classes can be found in the work of Ostrowski & Bryson (2019). Additionally, campaigns in high-enthalpy wind tunnels that expose meteorite samples to air plasma provide direct insight into the heating and ablation associated with some entry regimes—see, for example, the works by Agrawal et al. (2018), Helber et al. (2019), and Loehle et al. (2017) and references therein.

While destructive testing provides insight into the bulk response of meteorites during entry, details of internal phenomena, such as microstructural evolution, are more elusive and have primarily relied on a posteriori inference from sectioned meteorite falls (Sears & Mills 1973; Genge & Grady 1998; Genge et al. 2008). In this regard, high-resolution X-ray μ-CT has emerged as a promising technique for the nondestructive evaluation of meteorite, as well as many other, microstructures (Baruchel et al. 2000; Maire & Withers 2014). Although the nondestructive nature of the technique has been questioned with regard to the contamination of the natural radiation record of cosmic material (Sears et al. 2016), several authors have successfully applied μ-CT to probing the internal features of meteorites without the need for destructive sectioning. Specific applications for chondrites include the work of Jenniskens et al. (2012) to provide populations and distribution of brecias and microcracks and that of Alwmark et al. (2011) to localize grains with specific chemical and...
optical signatures. Related applications include the study of cracks and porosity in the Chelyabinsk meteorite by Popova et al. (2013) and the study of the microstructure of asteroidal regolith from the Hayabusa mission by Tsuchiyama et al. (2011). While there are many benefits to μ-CT analysis, one notable challenge is the difficulty in characterizing large volumes of scan data, with a common approach being visual inspection of reconstructions to identify specific features, which is laborious (Ebel & Rivers 2007).

In this work, we study the microstructural evolution of ordinary chondrites—samples of Tamdakht (H5) and Tenham (L6)—at temperatures in excess of 1000°C using X-ray μ-CT and complementary thermal and surface analysis techniques. Earth impactors heat up during entry owing to the large aerodynamic heating and shock layer radiation, experiencing surface temperatures of a few thousand Celsius and sharp temperature gradients. The fusion crust can go from temperatures of >2000°C to below 800°C within a thickness of the order of the millimeter (Sears & Mills 1973). Peak surface temperatures depend on composition and rate of sublimation/evaporation of the exposed material. Whereas past μ-CT examinations of meteoritic material have been performed on static samples in equilibrium conditions, the present heating experiments are performed at a synchrotron source to allow in situ observation of microstructural phenomena during heating. Known challenges in the analysis of large volumes of scan data are overcome by applying tailored machine-learning techniques to accurately identify and track the evolution of specific grains. Tomographic reconstructions of the meteorites during heating reveal that melting is incongruent and initiated in iron sulfide and meteoritic iron grains, which leads to the creation of internal voids. A detailed description of the thermochemical nature of the melting behavior is provided through additional scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) studies. The implications of the identified internal degradation mechanism for the ablation and fragmentation behavior of meteorite materials during entry, as well as observed fusion crust properties, are discussed.

The paper is structured as follows. Section 2 describes material samples (Section 2.1) and methods for μ-CT experiments (Section 2.2), tomography segmentation (2.3), and material characterizations (Section 2.4). We present the main observations from in situ μ-CT in Section 3.2, supported by grain composition (Section 3.1) and thermal degradation (Section 3.3) analyses. Implications for atmospheric entry are discussed in Section 4.

2. Experimental and Numerical Approach

2.1. Materials

We investigated samples of representative meteorite materials typical of common near-Earth asteroids, specifically machined for the experimental setup described in Section 2.2. Samples were extracted from large (~10 cm characteristic length) recoveries of the Tamdakht H5 chondrite (Weisberg et al. 2006) and from the Tenham L6 chondrite. Bulk densities of 3.4 and 3.3 g cm\(^{-3}\) were computed from mass and volume measurements for the Tamdakht and Tenham samples, respectively, which are in family with average values for ordinary H chondrites (Consolmagno et al. 2008; Cotto-Figueroa et al. 2016) and data by Ostrowski & Bryson (2020) reported for the two materials. Average porosities, mostly made of closed pores, were reported at 8.7%–8.8% for Tamdakht and 5.5%–4.8% for Tenham, calculated from measurements of mass and laser-based volume scans of large samples (Ostrowski & Bryson 2020). Our samples were machined as rectangular cuboids of 3.5 × 3.5 mm cross section and variable length (between 10 and 15 mm), from regions at depth of at least 5 cm below the fusion crust. Specific locations were selected so that samples had minimal apparent macro-porosity to ensure structural integrity during machining. Tomographic measurements on the samples prior to heating yielded porosity values below 1%, mainly in the form of microcracks randomly distributed throughout the volume.

2.2. In Situ X-Ray Microtomography Experiments

In situ X-ray μ-CT experiments were conducted on samples of Tamdakht and Tenham meteorites at the beamline 8.3.2 of the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory. Tests were performed in different reactors designed to collect μ-CT data under extreme heating.

The Tamdakht meteorite was tested in a hot cell setup initially developed for investigations on high-temperature ceramics (Bale et al. 2013; Haboub et al. 2014), as shown in Figures 1(a)–(d). The system features six halogen lamps powered by an external power supply (Acopian, Easton, PA, USA), which are focused on a ∼10 mm diameter spherical region at uniform temperature that embeds the entire μ-CT field of view (FOV). X-ray access to the region of interest in the reactor is provided by a 300 µm thick, 7 mm high aluminum window located along the equatorial plane of the cell. The window allows X-ray transmission above 90%. All elements of the cell are water cooled, and supply lines for water, in- and outflow gases, and electrical connections are interfaced such that the whole system can translate and rotate on the tomography stage with minimal interference. In our experiments, the sample (Figure 1(b)) was mounted at the center of the cell at the focal point of the lamps using stainless steel mounts connected to water-cooled copper posts.

The Tenham meteorite was tested in a newer experimental arrangement not available at the time in which the Tamdakht was tested, as shown in Figures 1(a′)–(d′). The system consists of a 1 kW tube furnace (Micropyretics Heaters International Inc., Woodlawn, OH, USA) with a 6 × 6 mm beam port and a vertical 50 cm diameter bore heated by a MoS\(_2\) heating element. A sample is mounted at the extremity of a quartz (fused silica) tube using a high-temperature ceramic cement. The interior of the tube is atmosphere controlled via a vacuum regulator and mass flow controllers for test gas. The furnace is anchored to an optical table having a tomography setup and can be positioned with respect to the beam and sample by means of a translational horizontal–vertical stage overhanging the rotating tomography stage. The entire sample/quartz tube assembly is mounted on the tomography stage and can be inserted and freely rotated into the bore of the furnace. Further details of this experimental arrangement can be found in Barnard et al. (2018). Compared to the hot cell setup used for Tamdakht, this system allows the entire sample to be at uniform temperature but is limited by the softening temperature of the fused silica assembly.

In both reactors, a dedicated LabVIEW program was used to control and record test parameters. Feedback control was established for temperature by regulating the current to the IR lamps or to the furnace heating element. Temperature was
measured with ±5% accuracy using a type-K thermocouple placed in contact with the sample. Different temperature schedules were used, as reported in Table 1 and shown in Figure 2. All tests were performed in ambient air at atmospheric pressure. The virgin (“as recovered”) material was first imaged at room temperature, and then consecutive scans were collected at increasing temperatures, up to >1000°C. At each temperature, the sample was allowed to equilibrate for at least 10 minutes prior to performing μ-CT, which ensured that constant conditions were achieved during imaging. This was required to accommodate for the long scan times and obtain good-quality tomographic data. In all experiments the maximum temperature was “1100°C, which is substantially lower than peak surface temperatures attained during meteorite entry, thus preventing the formation of a melted external crust in our experiments. It is also noted that transient effects of an actual atmospheric entry are not captured here, although rapid advances in imaging techniques anticipate the possibility to time-resolve decomposition events in future studies.

In all cases, tomography scans were collected in white-light mode, with the beam filtered through a 0.65 mm thick Cu plate and collected through a 50 μm LuAG scintillator. The details of the X-ray camera systems are provided by MacDowell et al. (2012). For the present work, we used a 5× magnification, long working distance objective (Mitutoyo Plan Apo) that provided a 1.303 μm voxel size and CMOS camera (PCO Edge, PCO AG, Germany) rendering a 2560 × 2160 pixel FOV. At each scan, 1313 radiographs were acquired over a continuous 180° rotation. Exposure time was set to between 500 and 650 ms, resulting in scan times of approximately 20 minutes at each temperature.

### 2.3. Tomographic Reconstruction and Data Analysis

X-ray radiographic projections needed to be reconstructed into three-dimensional images. Reconstruction was executed using the classical Fourier grid reconstruction algorithm (Dowd et al. 1999) implemented in the TomoPy software (Gürsoy et al. 2014; Pelt et al. 2016). TomoPy reconstruction was configured using a custom Python script for processing ALS
8.3.2 data. A bilateral filter implemented in Fiji (Schindelin et al. 2012) was applied to the reconstructed data sets to improve edge detection. Data sets of the Tenham meteorite were further denoised using an anisotropic diffusion filter (Perona & Malik 1990).

Data analysis and visualization were performed using the Dragonfly software (Object Research System, Montreal, Quebec, Canada; Makovetsky et al. 2018). Accurate segmentation is essential in the first place to distinguish the different phases. The process needs to be efficient to cope with the size of data to analyze. Images were segmented by means of the U-Net convolutional neural network architecture (Ronneberger et al. 2015) implemented in Keras (Chollet et al. 2015), configured through the deep learning plugin of Dragonfly. U-Net training in Dragonfly/Keras is based on the TensorFlow suite (Abadi et al. 2015). A five-layer U-Net trained using a total of 17 manually segmented slices was used as the training set, nine of the slices being selected randomly from a virgin data set and the remaining eight being selected randomly from the highest-temperature data set, which presented the largest difference from the virgin materials. Two independent networks were trained for the two meteorites; remarkably, each respective network was observed to perform very accurate segmentation on the other material.

2.4. Surface Analysis and Thermal Characterizations

Surface and thermal characterization of the meteorite samples was performed to further analyze the material composition and behavior at temperature. SEM images were collected with a Thermo Fisher Helios 5 Dual Beam equipped with an Oxford 100 mm detector. Energy-dispersive X-ray spectroscopy (EDS) was used to map the surface and track the spatial distribution of elements before and after each experiment.

TGA and DSC data were collected with a TA Instruments SDT Q600 to provide variation of mass during heating at temperatures comparable to those investigated with μ-CT. Two cubes of Tamdakht (~3 × 3 × 3 mm), extracted from adjacent regions to the sample used for μ-CT, were heated at a continuous rate of 10°C·min−1 to final temperatures of 1000°C (Sample 1 or S1) and 600°C (Sample 2 or S2). Additionally, the samples were subjected to an isothermal soak for the duration of 4.2 hr (Sample 1) and 4.8 hr (Sample 2) after the initial heating ramp (Figure 13(b) in the Appendix). TGA experiments were conducted in air with the flow rate set at 30 mL·minute−1. The TGA-DSC was coupled to a Fourier transform infrared (FTIR) spectrometer via a capillary for the low-temperature experiment (S2) to characterize evolved gases that may be produced during heating.

3. Results

3.1. Grain Composition and Segmentation

Tamdakht and Tenham are both ordinary chondrites, the most common type of meteorites to fall (Sears 1997), and are equilibrated varieties (H5 and L6, respectively) having experienced metamorphism on their parent asteroids. These meteorites, like other chondrites, have compositions of nonvolatile elements similar to the solar photosphere and thus are dominated by silicon, iron, oxygen, and magnesium, with lesser amounts of Al, Ca, Ni, Na, K, and Cr. Mineralogically these meteorites are dominated by the ferromagnesian silicates olivine and pyroxene, with lesser abundances of the aluminosilicate plagioclase. Iron–nickel metal and sulfide are common in ordinary chondrites and are more abundant in H (high-iron) chondrites than in L (low-iron) chondrites. As equilibrated meteorites, Tamdakht and Tenham have experienced crystal growth during metamorphism, leading to crystalline textures and homogeneous mineral compositions owing to diffusive exchange of Fe and Mg.

An example of typical H5 and L6 chondrite chemical compositions is found in the work of Jarosewich (1990), which is reconstructed in Figure 3. Ordinary chondrites are dominated by silicates. Oxides have been shown to be present as various minerals such as olivine ([Mg, Fe]2SiO4) and pyroxene ([Mg, Fe]SiO3). Both chondrites also have significant weight percentages of metallic iron (Fe) and iron sulfide (FeS). Iron has been shown to be present in chondrites as grains of meteoritic iron (Fe with a small percentage of siderophiles like Ni), while iron sulfide is present in grains of stoichiometric troilite (FeS) and in the sulfur-deficient pyrrhotite (FeS1−x). Inspection of the data also reveals differences between the two classes of chondrites. In particular, L6 chondrites are composed of higher percentages of oxides and lower percentages of iron and related siderophiles than H5 chondrites. Thus, fewer grains of meteoritic iron are expected in L6 compared to H5 chondrites.

The chemical composition can be cross-referenced with μ-CT scans to characterize the microstructure of the chondrites. In Figure 4 we present the reconstructed scans of the virgin Tamdakht and Tenham meteorite samples. The grayscale intensity of the images is proportional to the local material attenuation, with the highest attenuation regions displayed in white, low-to-mid-attenuation regions in light to dark gray, and voids with no attenuation in black. Previous studies have demonstrated that grains with high atomic number elements (e.g., Fe) exhibit the highest attenuation, while lower atomic number elements (e.g., Si, S, and O) exhibit lower attenuation (Ebel & Rivers 2007). Thus, for chondrites attenuation can be correlated directly with Fe concentration and volumetric mass density. Both meteorites show well-defined grains of high and low attenuation, which correspond to meteoritic iron and troilite/pyrrhotite, respectively. Comparatively, the matrix appears as a heterogeneous background of low attenuation and is composed of low-density silicates. Variations in the
density and thus the iron content of the silicates were observed in the Tenham meteorite. Both meteorites show typical micron-sized void regions in the form of microcracks and pores, although a few larger initial pores are observed in the Tenham meteorite.

The grain structure, microcracks, and voids were found to evolve during heating, as described in Section 3.2. The convolutional neural network segmentation described in Section 2.3 was applied to track the grains and voids across the μ-CT data sets acquired at increasing temperatures. Specifically, the algorithms were tailored to identify the four attenuation regions identified from visual inspection of the μ-CT reconstructions: high-attenuation grains (meteoritic iron), low-attenuation grains (troilite and pyrrhotite), matrix (silicates), and voids/cracks. Figure 5 shows examples of this segmentation approach on slices from data sets collected during Test 2 at room temperature (Figures 5(a) and (a′)) and at 1027°C (Figures 5(b) and (b′)) for the Tamdakht meteorite. Notably, the segmentation distinguishes the four selected densities accurately and efficiently. The success of this approach allows the interrogation of large volumes of μ-CT data that are not feasible to analyze manually.

3.2. In Situ X-Ray Microtomography Analysis

The thermal behavior of the two meteorites was examined as a function of temperature using the μ-CT setup described in Section 2.2. In Test 1 a Tamdakht sample was imaged at room temperature and ~1000°C. Two representative slices (cross sections) are shown in Figure 6. Variation in intensity of the high-attenuation phase is observed, with small bright spots suggesting the presence of inclusions or microstructural features such as Widmanstätten. A comparison between the data collected at high and room temperature reveals decomposition of the low-attenuation troilite/pyrrhotite grains (yellow arrows in Figure 6), which vanish from the sample. A number of cracks, previously empty in the virgin material, are filled by higher-attenuation compounds (green arrows in Figure 6), indicating flow of molten iron sulfide material that migrated to adjacent microcracks via capillary action. The presence of metal veins was observed by Ramdohr (1967) in the thermally altered substrate of meteorites, and they have been proposed as early products of partial melting on differentiated asteroids. Genge & Grady (1998) observed extrusion of sulfide-metal liquids into the fusion crust and suggested expansion on melting driving the extrusion process. The formation of large voids suggests production of decomposition gases during melting, which depletes the concentration of sulfides as temperature increases. High-attenuation grains of
needed to corroborate this hypothesis. The exsolution of taenite from the kamacite, associated with a specimen. This microstructural change could be attributed to an increase in temperature, although banding is observed in the heated meteoritic iron remain, by and large, unaffected by the increase in temperature, although banding is observed in the heated specimen. This microstructural change could be attributed to the exsolution of taenite from the kamacite, associated with a volume change resulting in fracturing. Further studies are needed to corroborate this hypothesis.

During heating, slow growth of blisters (Figure 7(a)) was observed around the sample surface, suggesting the presence of an outflow of melt material and gas generation. Growth rate was estimated to be of the order of several minutes. Black oxide blisters were clearly evident in post-test inspections of the heated surface (Figures 7(b), 7(c)), and their composition (hematite and magnetite) is further discussed in Section 3.3.

The decomposition of the low attenuation grains was further investigated as a function of temperature during Tests 2 and 3 for the Tamdakht and Tenham materials, respectively. Three-dimensional visualizations of the Tamdakht sample during heating are shown in Figure 8. In order to highlight the behavior of grains and voids, the matrix is rendered transparent in these visualizations. As the temperature exceeds ∼850°C, the low-attenuation grains appear to progressively shrink as heating increases. At higher temperatures, portions of the high-attenuation, meteoritic iron grains (Fe- and Ni-rich compounds) also melt and evaporate, vanishing from the region of interest. The loss of both the low- and high-attenuation grains results in large voids.

A quantification of the grain evolution for the two meteorites is presented in Figure 9, and representative cross sections are shown in Figure 10. The volume fraction of all grains is computed from the segmented images and plotted as a function of temperature. First looking at the data point at room temperature, one notices that the virgin Tamdakht has ≈7% and 4% volume fractions of low- and high-attenuation grains, respectively, while the Tenham has ≈8% volume fraction of low-attenuation grains and minimal high-attenuation structures. Void fractions (micropores and microcracks) are slightly below 1% for both materials. These data are consistent with expected compositions of H5 and L6 chondrites, specifically Tenham having a lower volume fraction of meteoritic iron than Tamdakht (see Figure 3). Porosities are small (∼1%) because of the samples selected in regions of low porosity. In addition, they could be slightly underestimated owing to limitations in image resolution with the μ-CT settings used in this work. In particular, the voxel size of 1.3 μm implies that sub-micrometer pores and structures are unresolved. It is also noted that portions of the molten material that fill submicron pores and cracks could be excluded.

For Tamdakht, the low-attenuation grains begin decomposing at temperatures between 700°C and 800°C and are effectively lost by 1100°C. High-attenuation grains begin degrading at slightly higher temperatures, above 800°C, and their volume fraction is nearly halved at temperatures exceeding 1100°C. Material porosity (void fraction) concurrently increases with temperature as grains decompose, reaching values up to 12%. A similar behavior is observed for the Tenham meteorite. The low-attenuation grains begin decomposing at slightly higher temperatures compared to the Tamdakht and lead to the formation of large pores as they progressively shrink.

3.3. Thermochemical and Surface Analysis

The observation of significant thermal evolution of the Tamdakht and Tenham microstructures from reconstructions of μ-CT can be interrogated further by analysis of the thermochemistry and changes in elemental distribution during heating. The thermochemical signatures of microstructural changes are evaluated using simultaneous TGA and DSC experiments on two Tamdakht samples: Sample 1 being taken to 1000°C, and Sample 2 being taken to 600°C. Combined TGA-DSC results are provided in Figure 11 for Sample 1 (see Figure 13 in the Appendix for thermal profiles and TGA results on a per-time basis for both samples). Correspondingly, elemental distributions are characterized through SEM-EDS both before and after the TGA-DSC experiments were conducted. The SEM-EDS analysis targets S, Fe, and O on select regions of the sample surfaces corresponding to meteoritic iron and iron sulfide grains, as shown in Figure 12.

The TGA results show that Samples 1 and 2 both experienced a minimal degree of mass loss (0.3%–0.4%) at
low temperature (27°C to 400°C), followed by an increase in mass at high temperature ($T > 400°C$) as indicated in Figure 11(b). Water vapor was detected and was present until Sample 2 reached ~$600°C$. Therefore, mass loss between ambient and ~$400°C$ is partially due to the vaporization of water. The mass gain at $T > 400°C$ can be attributed to the oxidation of iron in the silicate matrix, as well as from the meteoritic iron and iron sulfide grains at the surface (Pittarello et al. 2019; Helber et al. 2019). Meteoritic iron at the surface becomes oxidized by $600°C$, as evidenced by the increase in oxygen coverage on the surface of each grain, as shown in the EDS images of Figure 12(c) and (c'). Furthermore, blisters begin to form on the surface of the sample, which are covered with whiskers and blades of hematite (see Figure 7 and Figure 12(c')).

A survey of other studies of heating chondrites provides supporting evidence for our interpretation of the TGA results. For instance, water vapor has been detected upon heating of L/LL class chondrites over similar temperature ranges, specifically for the Holbrook meteorite (Gooding & Muehlner 1977). The formation and growth of hematite whiskers have been observed during the oxidation of iron, and their growth is enhanced in the presence of H$_2$O vapor (Voss et al. 1982). Furthermore, iron present in silicate minerals, specifically olivine ($\text{Mg}_2\text{SiO}_4$), has been shown to oxidize to
form layers of iron-rich surface hematite (Fe₂O₃) and subsurface magnetite (Fe₃O₄) and enstatite (MgSiO₃) (Goode 1974; Mackwell 1992).

The DSC results show a variety of discrete endotherms that can be associated with phase transitions of species present in chondrites. The data show that domains of FeS persist at low temperatures, as evidenced by the endotherms at 154°C and 325°C (points 2 and 3; Figure 11(a)). Endothermic transitions have been detected at similar temperatures during DSC experiments that were carried out on the Soltmany (L6) meteorite and have been assigned to the low-temperature phase transitions of troilite (FeS) (Walden & Pelton 2005; Szurgot et al. 2012). Furthermore, a distinct phase transition is detected between 744°C and 780°C, as evidenced by the broad endotherm at point 4 in Figure 11(a). This endotherm is partially attributed to the transition of the low-temperature plessite structure of meteoritic iron, which is composed of α-kamacite and γ-taenite phases, to the γ-taenite phase. Such a phase transition has been noted at similar temperatures in the Akyumak iron meteorite (Fe with 8–9 wt. % Ni; Aksoy et al. 1996).

The DSC results show a broad exotherm between 50°C and 300°C (Figure 11(a)). The oxidation of iron, which is exothermic, is one source of the noted low-to-mid-temperature behavior and is corroborated by clear evidence from the EDS images. Furthermore, the oxidation of iron sulfide compounds, such as pyrrhotite and troilite (Fe₃S₄), is highly exothermic and produces gaseous sulfur oxides. Such reactions have been analyzed in detail for stoichiometric FeS powder via TGA and X-ray diffraction, with a strong SO₂ signal being noted (Kim & Themelis 1987). Unfortunately, the FTIR signal was weak (absorbance < 10⁻³) during the present TGA-DSC experiments, challenging the direct evidence of the production of such gases.

The DSC data in Figure 11(a) reveal a broad endotherm between 300°C and 1000°C. This endotherm is partially attributed to the high-temperature vaporization of volatile species from grains of iron sulfide, meteoritic iron, and the silicate matrix. This is corroborated by past studies on the thermal degradation of chondrites, which revealed evidence of alkali elements (e.g., Na and K), metallic species (e.g., Fe, Ni), and S₂ and H₂O volatilization at high temperatures. Using mass spectroscopy, Gooding & Muenow (1977) detected the presence of S₂ between 900°C and 1300°C during heating of the Holbrook meteorite. Therefore, it is reasonable to suggest that the void formation in our experiments corresponds to progressive vaporization of disulfur upon melting of the troilite/pyrrhotite phases in the investigated chondrites.

Concurrently, the endotherm might indicate a transition of the plessite structure of meteoritic iron, composed of α-kamacite and γ-taenite, to the γ-taenite phase, which supports the hypothesis on the microstructure banding of the metal phase discussed in Section 3.2.

**Figure 10.** Temperature evolution of representative cross sections for the Tamdakht (top row) and Tenham (bottom row) samples from μ-CT.

**Figure 11.** (a) DSC and (b) TGA curves of Sample 1 during the heating ramp phase of the experiment.
An additional contributing factor to the large endotherm at high temperatures is the melting of iron sulfides and meteoritic iron. While in lower concentration compared to troilite, pyrrhotite begins to melt incongruently when the sulfur content is higher than 53%, with melting initiating at 743°C and complete liquefaction by 1100°C (Kubaschewski 1993; Walden & Pelton 2005; Shishin & Decterov 2015). Furthermore, meteoritic iron forms a eutectic with FeS (Kitakaze et al. 2016; Jantzen et al. 2017) that can lower the melting point, dependent on the concentration of Ni. For meteoritic iron found in L, LL, and H chondrites, the melting point can be lowered to ~900°C, although Ni-rich grains can melt at temperatures down to 850°C (Tomkins 2009). Melt behavior of these eutectics at the interface of meteoritic iron and iron sulfide grains has been observed in heated chondrite samples (Mare et al. 2014; Moreau et al. 2018).

The high dependence of the melting point of iron-bearing grains on sulfur concentration is complicated by the high mobility of sulfur. The EDS images of Figure 12 reveal that sulfur is no longer spatially correlated with the original grain after heating. Lauretta et al. (1997) also demonstrated the high-temperature mobility of sulfur by heat-treating beads of artificial type LL chondrites in inert conditions at 500°C and 900°C. Post-test inspection of the beads revealed the development of large pores within sulfide grains and the transport of sulfur to adjacent surfaces. Spatial correlation of sulfide- and nickel-bearing grains of taenite and kamacite was shown via microscopy and scanning electron microprobe analysis of polished Guarena (H6) and Colby (L6) meteorites by Willis & Goldstein (1983). The diffusion-driven changes of sulfur compositions in meteoritic iron and iron sulfide, or at the interface of the two, could trigger melting.

### 4. Discussion

#### 4.1. Near-surface Microstructural Evolution

The above results provide some unique insights into the evolution of the meteorite interior during entry heating. Previous detailed a posteriori examinations of sectioned fusion crusts have been used to map out the temperature gradient near the surface of the meteoroid. Sears & Mills (1973) examined the fusion crust of an ordinary chondrite (Barwell, L5) and identified several zones within a region 0.4–0.8 mm from the meteorite surface, corresponding to inferred temperatures associated with those features. Similar strata identification for ordinary chondrites was reported in earlier studies by Ramdohr (1967) and by Genge & Grady (1998), while Genge & Grady (1999) analyzed the fusion crust of stony meteorites. Of interest to the current study, Sears & Mills (1973) identified a region where nonstoichiometric concentrations of Fe and FeS appear to have flowed into microcracks and pores in the unaltered structure. The temperature range associated with this region is between 900°C and 1100°C. Our results of the current work are consistent with their finding that a so-called “impregnation zone” occurs within this temperature range. μ-CT measurements, supported by calorimetric analysis, reveal a macroscopic-scale melting of iron sulfide and meteoritic iron. The high mobility of S observed in EDS measurement can lead to eutectic formation that lowers the melting point and can progressively erode grains with high iron content. The molten material flows into microcracks through capillary action. Upon
melting, the progressive evaporation of sulfur at increasing temperatures generates gases and leads to void formation and overall increase of the subsurface porosity.

4.2. Implications for Fragmentation

In addition to providing first-of-its-kind in situ confirmation of the metallic impregnation process identified in previous meteorite studies, the morphological evolution observed in the current work may have implications for the complex process of meteoroid fragmentation. Popova et al. (2011) observed, in a study of 13 meteorite falls, that the strength corresponding to the aerodynamic pressure at the first observed fragmentation event, in all cases, was much less than the compressive or tensile strength measured for those meteorite classes in the laboratory. This is a well-known and fundamental issue impeding a complete physically consistent treatment of the meteoroid entry problem. While there are not sufficient data here to make the claim that the observed internal degradation is responsible for the required reduction in strength to match observations, it is reasonable to expect that porosity formation would reduce the robustness of material near the surface and make it more susceptible to crack growth and resultant fracture.

In addition to enhanced structural failure explanations for low-strength fragmentation of meteoroids, several authors have presented alternative hypotheses involving permeation of compressed atmospheric gases into the microstructure. Park & Brown (2012) studied the fragmentation of resin-bonded graphite samples in ballistic range experiments. Based on experimental observation, they introduced the hypothesis of an incubation process for meteorite-like objects where permeation of fluid would lead to interior pressurization of material prior to splitting. The incubation time was determined by the ratio of permeability of the fragment to the fluid viscosity and found to be much longer than the time for splitting given by the fragmentation theory of Hills & Goda (1993). Tabetah & Melosh (2017) performed numerical simulation of air penetration into entering meteoroids using a 2D Eulerian finite-difference model for the exchange of momentum and energy between two phases, representing a porous meteoroid and the surrounding air, respectively. They concluded that material permeability and porosity enhance breakup and dispersion in the fragmentation process. Our experimental observations suggest an increase in near-surface porosity, increasing permeability and thereby facilitating air penetration. Filling of microcracks with melt flow could further contribute by sealing escape pathways for volatile products formed at high temperatures, leading to an increase in internal pressure that further affects the breakup process. It should be noted that the timescale associated with any of these hypothesized phenomena is rather large relative to the timescale of mass loss due to ablation, particularly for a large meteoroid, where the recession velocity of the surface may be on the order of tens of centimeters per second. Therefore, the described processes must be assumed to be confined to the first few millimeters of material near the surface of the meteoroid. From this perspective, it is unlikely that these mechanisms could be the primary instigator for breakup of larger monolithic fragments. However, it could remain a contributor for fragmentation of smaller/higher-altitude meteoroids where heating and ablation onset occur more gradually. In addition, for larger meteoroids for which catastrophic disruption has already been initiated, these phenomena could contribute to weakening and terminal disintegration of smaller fragments that may be partially shielded by the parent body.

5. Conclusions

We have presented an experimental study of the morphological evolution of ordinary chondrites at entry-relevant temperatures. Our characterizations revealed incongruent melting of iron sulfide and meteoritic iron grains when temperatures exceeded 800°C. This behavior is consistent with past observations of an impregnation zone at the inner region of the fusion crust for recovered meteorites. The decomposition process altered the interior morphology of the tested materials, leading to the creation of internal voids. Formation of porosity would result in an increased permeability and affect the mechanical strength of the agglomerate, in turn promoting fragmentation. The observed process is correlated to the iron sulfide content in the material, suggesting that chondrites with larger pyrrhotite volume fraction would be subjected to enhanced internal decomposition and consequent fragmentation. Although the techniques applied in the present work have limitations in sample size and time resolution, advances in optics and in time-resolved in situ μ-CT will enable observation of dynamic processes at extreme temperature, furthering our understanding of meteoroid ablation and breakup phenomena. Finally, evidence of high-temperature decomposition in our work reveals the need for mechanical measurements at relevant temperatures when investigating fracture mechanics of meteorite materials, as it is highly likely that mechanical properties will be altered in laboratory-scale coupons owing to morphological changes within the material.

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Appendix

Supplementary Material

Figure 13 shows percent mass variation measured during TGA tests for both samples 1 and 2 (Figure 13(a)) and the correspondent thermal time profiles (Figure 13(b)).
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Figure 13. TGA curves of Tamdakht samples as a function of temperature (panel (a)) and their associated heating profiles (panel (b)).

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