Full Title: Incremental Laser Space Weathering of Allende Reveals non-lunar like Space Weathering Effects

Short Title: Laser Weathering of Allende Reveals non-lunar Effects

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Abstract

We report findings from a series of laser-simulated space weathering experiments on Allende, a CV3 carbonaceous chondrite. The purpose of these experiments is to understand how spectra of anhydrous C-complex asteroids might vary as a function of micrometeorite bombardment. Four 0.5-gram aliquots of powdered, unpacked Allende meteorite were incrementally laser weathered with 30 mJ pulses while under vacuum. Radiative transfer modeling of the spectra and Scanning Transmission Electron Microscope (STEM) analyses of the samples show lunar-like similarities and differences in response to laser-simulated space weathering. For instance, laser weathered Allende exhibited lunar-like spectral changes. The overall spectra from visible to near infrared (Vis-NIR) redden and darken, and characteristic absorption bands weaken as a function of laser exposure. Unlike lunar weathering, however, the continuum slope between 450-550 nm does not vary monotonically with laser irradiation. Initially, spectra in this region redden with laser irradiation; then, the visible continua become less red and eventually spectrally bluer. STEM analyses of less mature samples confirm submicroscopic iron metal (SMFe) and micron sized sulfides. More mature samples reveal increased dispersal of Fe-Ni sulfides by the laser, which we infer to be the cause for the non-lunar-like changes in spectral behavior. Spectra of laser weathered Allende are a reasonable match to T- or possibly K-type asteroids; though the spectral match with a parent body is not exact. The key take away is, laser weathered Allende looks spectrally different (i.e., darker, and redder or bluer depending on the wavelength region) than its unweathered spectrum. Consequently, connecting meteorites to asteroids using unweathered spectra of meteorites would result in a different parent body than one matched on the basis of weathered spectra. Further, spectra for these laser weathering experiments may provide an explanation for inconsistencies observed in both laboratory (e.g., Hiroi et al., 2003 & 2001;

Lazzarin et al., 2006; Moroz et al., 2004 & 1996; Shingareva et al., 2004) and telescopic data (Lazzarin et al., 2006; Marchi et al., 2006; Nesvorný et al., 2005).

1. Introduction

Space weathering encompasses several processes that affect rocks and regoliths on airless bodies. The two principal processes are solar-wind irradiation and micrometeorite impacts. Knowledge of the effects of these processes primarily comes from analyzing and comparing lunar samples and spectra. This body of research yields a lunar-based space-weathering model, whereby physical features such as nanophase iron bearing rims on silicate minerals (Keller and McKay, 1993; Keller and McKay, 1997; Noble et al., 2005) and agglutinates (Duke et al., 1970) increase as a function of surface exposure (i.e., maturity). The accumulation of these products cause increased reddening, darkening, and reduced spectral contrast (Domingue et al., 2014; Fischer and Pieters, 1996; Hapke, 2001; Hapke et al., 1975; Noble et al., 2001; Pieters et al., 1993; Pieters et al., 2000). Inherent in this model are lunar specific elements of target composition (e.g., plagioclase, pyroxene, and olivine (e.g., Taylor et al., 1991)), surface environment (acceleration due to gravity is 1.62m/s^2 , H^+ flux of $\sim 1 \times 10^8$ ions/cm²/s (Pillinger, 1979), gardening rates, and micrometeorite velocity distribution and flux (Cintala and Hörz, 1987; Grün et al., 2001)). As all of these factors are different between asteroids and the Moon, and even among asteroids themselves, a single model for how spectra should change and the space-weathering products formed is not possible. Hence, these lunar specific space weathering components must be taken with certain caveats when applied to other airless bodies.

For instance, S- and V-type asteroids in general follow lunar spectral trends, but in detail these asteroids seem to weather differently (Chapman, 2004; Clark et al., 2002; Pieters et al., 2012) despite being approximately lunar in composition. The optical properties of carbonaceous chondrites are dominated by fine-grained opaque phases such as sulfides and organics. The response of sulfides and organics to space weathering could be significantly different from that of silicates (Moroz et al., 2004). On this basis, the vastly different composition and environment of C-type asteroids would suggest that a lunar space-weathering model, which was developed to predict the spectral response and space weathering effects of lunar materials under lunar conditions, is not likely an accurate model for C-type asteroids.

The possibility of a non-lunar type of space weathering motivates our experimental approach. The premise of our experiments is further formed by three other factors. First, associations between asteroid types (analyzed remotely in space) and meteorite classes (analyzed in laboratories) are made on the basis of spectral similarities. There are multiple factors that must be considered when comparing spectra of the two (e.g., phase angle, grain size, type and amount of space weathering). Laboratory analyses allow systematic examination of a single parameter or multiple parameters at a time. The aim of this research is to provide insight as to how the surfaces of anhydrous C-complex asteroids evolve in response to space weathering – future work will investigate the spectral response of aqueously altered meteorites (e.g., CI1, CM1-2 and CR1-2). Hence we limit our experimental set up to laser space weathering while holding other factors constant. Second, asteroid reflectance spectra only “scratch the surface” of what can be known about them, while information about asteroid interiors (e.g., chemistry, mineralogy and thermal history) can be provided by meteorites. Our results are intended to facilitate connections

between meteorites and asteroid parent bodies in order to better understand the interiors of anhydrous C-complex asteroids, one of the largest asteroid groups (Bus and Binzel, 2002; DeMeo and Carry, 2014; Gradie et al., 1989). And lastly, spectra of carbonaceous materials subjected to step-wise laser-weathering are vital for spectral interpretation and sample site selection for missions investigating C-complex asteroids (e.g., OSIRIS-Rex (Lauretta et al., 2015), Dawn at Ceres (e.g., Bland et al., 2016; Nathues et al., 2015), and Hayabusa-2 (Tachibana et al., 2014)). These experimental data may have further applicability to remote sensing estimates of carbonaceous material intimately mixed within non C-type asteroids like Vesta (Reddy et al., 2012), and also serve as a comparison for spectral data of other potential carbonaceous bodies (e.g., Phobos and Deimos (Fraeman et al., 2012; Pajola et al., 2013) and Trojan asteroids (Yang and Jewitt, 2011)). To achieve these goals, we conducted a series of simulated space weathering experiments on the classic carbonaceous chondrite Allende.

2. Methods

2.1 Laser Simulated Space Weathering

High-velocity dust impacts were simulated with a pulsed laser beam produced by a Continuum Surelite I-20 Nd:YAG laser (1064 nm, 20 Hz pulse rate, ~6 ns pulse width). Laser spot size on the sample is 0.25 mm with an incident energy of 30 mJ. Irradiation was done in a vacuum between 10^{-6} and 10^{-7} torr. The 6-7 ns pulse duration is comparable to the timescale of dust impacts (Yamada et al., 1999). The experimental apparatus at the University of Hawaii is similar to Yamada et al. (1999), but there are two key differences. First, we use uncompressed powder for our sample because it is more representative of the physical properties of asteroid surfaces, which are expected to have comminuted regoliths dominated by fine particles (Dollfus et al.,

1989). The laser pulses stir and garden the loose powder. Hence the experiment processes the whole volume of material. In comparison, compressed powders exclude space-weathering products from the volume of the sample, altering, and potentially reducing their effect due to multiple scattering, as the packed power only permits alteration of the sample's surface (Moroz et al., 2014). The second key difference, which is related to the volume and state of the sample, is the number of laser shots needed to modify the spectra. Sasaki et al. (2001) performed up to 5 laser pulses on their pressed pellet sample. When we irradiated 0.5 g of San Carlos olivine powder with $<75\ \mu\text{m}$ grain size, it took between 36,000 and 48,000 laser pulses to match the albedo, visible continuum slope, and reduced spectral contrast of the San Carlos olivine in the Sasaki et al. (2001) experiments (Fig. 1). Spectra of laser weathered San Carlos match well in the visible out to 1200 nm for both techniques; However, beyond 1200 nm, spectra of the Sasaki et al. weathered San Carlos are much brighter and continuum redder than our experiments. We attribute the difference to the production of agglutinate like surface on grains in our experiments (Section 3.3). The large difference in number of required laser shots between the two experimental setups is attributed to the fact that we use five times the mass of the Yamada et al., (1999) and Sasaki et al. (2001) experiments and the whole volume of material must be processed, not just the upper surface. On the bases of similar spectral properties between the two sets of experiments, we equate a 40,000-laser pulse experiment in our setup to the 5-shot laser experiment of Yamada et al. (1999) and Sasaki et al. (2001). Sasaki et al. (2001) argued on the basis of energy flux equivalence between laser heating and micrometeorite impacts, that their 5-shot laser experiments corresponds to dust-impact heating of approximately 5^8 years. Thus, it is reasonable to conclude that our experiments represent an equivalent exposure age.

Laser irradiation experiments were performed on Allende, an oxidized CV3 carbonaceous chondrite, which is comprised mainly of fine-grained Fe-rich olivine and relatively a small amount of aqueously altered goethite or phyllosilicate minerals (Bland et al., 2004; Mason, 1963; Oliver et al., 1984). This sample is of petrologic grade 3.2 (Guimon et al., 1995), which indicates unaltered chondrules and a lack of metamorphism, and shock grade S1 for completely unshocked. The sample was categorized as W(0), meaning it was not weathered, and our inspection confirmed that it exhibited no observable terrestrial weathering. Although there are many carbonaceous chondrite types (e.g., CI, CV, CM, CR, CH, CK, ungrouped, etc.) and different petrologic types (i.e., exhibiting various amounts of aqueous alteration, where petrologic types 1 and 2 represent high- and moderate-degrees of aqueous alteration respectively and petrologic type 3 meteorites do not have extensive aqueous or thermal alteration). Allende is an ideal choice for our experiments because: It has been widely studied and is thus well characterized; it is available in large quantities; and it is readily available to other researchers for further correlation of results.

A 7.15 g sample was obtained from the Arizona State University Center for Meteorite Studies pristine collection through Big Island meteorites. The Allende fragment was ground in a quartz mortar and pestle. The sample was then dry-sieved so that the grain size was $<150\text{ }\mu\text{m}$. Grain sizes for asteroids in the range of $30\text{--}300\text{ }\mu\text{m}$ are measured using polarization studies (Dollfus et al., 1989). In order to characterize experiment reproducibility, four 0.5 g aliquots of the sample were taken for pulsed laser irradiation experiments. Each sample aliquot was laser irradiated in multiple increments so that spectral trends as a function of exposure could be observed. Two of the Allende samples were irradiated by up to 12,000 laser pulses in 1,200 pulse, or 1-minute

increments (or a total energy of 720 J/g of material). Two long duration experiments, to match the time increment of Sasaki, of 48,000 pulses (or a total energy of 2,880 J/g of material) were performed in two 6,000 pulse, or 5-minute increments, followed by three 12,000 pulse or 10-minute increments, for a total of 48,000 laser pulses.

2.2 Radiative Transfer modeling

We conducted radiative transfer modeling to characterize the spectral changes of the laser irradiated Allende powder. We use the radiative transfer model developed by Hapke (2001) with modifications by Lucey and Riner (2011). The radiative transfer model transforms the fresh Allende spectra in an attempt to reproduce each laser-weathered spectrum by increasing the spectral effects of two sizes of submicroscopic iron metal (SMFe) in single-scattering albedo space. The first size fraction, called nanophase here, about 3 nm, is similar to the average grain size of submicroscopic iron metal found in rims on lunar materials, about 1-5 nm (Keller and McKay, 1993). The nanophase grain size is much smaller than the wavelength of visible light and scatters shorter wavelengths of light preferential to longer wavelengths (Hapke, 2001); hence nanophase iron imparts a red slope to the material. The second size fraction, called microphase, was initially set at 1 μm , but was allowed to vary. The microphase iron initial size was taken from Lucey and Riner (2011) who determined that 1 μm was the most optically active grain size that, because of its size relative to wavelengths of light, causes darkening and not reddening. A mean grain size of 75 μm is used in modeling the fresh Allende spectra, which is the presumed mean value for our dry sieved grain size distribution of <150 μm .

2.3 STEM Analyses

Microanalyses of two samples were carried out using the University of Hawaii FEI 80 – 300 kV Titan dual aberration-corrected (Scanning) Transmission Electron Microscope (STEM). The STEM is equipped with a monochromator and high-resolution Gatan imaging filter electron energy-loss spectrometer. We acquired High-Angle Annular Dark Field (HAADF) images (~1 Å resolution) in STEM mode as well as conventional bright-field and dark-field images and diffraction patterns. Elemental distributions and compositions were analyzed using energy filtered imaging and mapping via Energy Dispersive X-rays (EDX). For most measurements, relative error, determined chiefly by counting statistics and peak fitting, is < 1% for O, Mg, Al, Si, Ca, S and Fe. Electron transparent thin sections were prepared at the University of Oregon and the Molecular Foundry (Lawrence Berkeley National Laboratory) using standard Focused Ion Beam (FIB) microscopy techniques: A 1-2 μm thick section was removed from the laser-irradiated grain by Ga-ion milling with a Pt-protective layer over the region of interest to limit ion damage to the top surface. Following extraction from the bulk, samples were further thinned to ~60 nm.

3. Spectral, Modeling, and STEM Results

3.1 Reflectance Spectra

Spectra of four, 0.5 g, powdered and unweathered Allende samples exhibit low reflectance, 7.8-8.5% at 550 nm, with an ultraviolet absorption below 500 nm causing a steep visible continuum (Fig. 2 and Supplement Fig. 1). The overall spectral character of fresh Allende is comparable for all experiments, however, reflectance values for aliquots/experiments 1 and 3 are systematically brighter by 5% on average than aliquots/experiments 2 and 4. The brighter reflectance is probably due to a higher abundance of Calcium-Aluminum-rich Inclusions (CAIs). A broad

shallow absorption feature is present centered beyond 1 μm , which is characteristic of Fe-bearing olivine. There is also a broad, shallow 2- μm absorption feature, extending from 1.6 μm to 2.4 μm . The broad 2- μm absorption, centered at about $\sim 1.9 \mu\text{m}$, is characteristic of pyroxene, Fe^{2+} spinel (Cloutis et al., 2004) or possible minor contribution from hydrated phases (Cloutis et al., 2012). These spectra lie within the range of spectra for Allende measured by Brown University's REflectance LABoratory (RELAB) and Mike Gaffey's Laboratory and reported in Cloutis et al. (2012) (Supplementary Fig. 2).

Three spectral changes occurred as a function of laser exposure (Figs. 2 & 3). First, the powder became darker. Second, the sample lost spectral contrast with increasing laser irradiation. And finally, the Vis-NIR continuum slope became redder (i.e., reflectance increasing as a function of increasing wavelength). These spectral changes are a lunar-like spectral response to space weathering. Over a limited wavelength range (450-550 nm), however, the visible continuum slope did not vary monotonically with exposure. In the early stages of maturation by the laser, up to $\sim 12,000$ laser shots, reflectance of all four samples decreased faster at 450 nm relative to 550 nm, causing the 450/550 ratio to become redder, or decrease (Figs. 3 & 4; Table 1). Experiments 3 and 4, which were exposed to a greater number of laser shots and for longer multi-minute pulsed laser exposures, exhibited an initial period of becoming redder in the 450/550 ratio, like experiments 1 and 2, but then unpredictably changed and became flatter or bluer. This continuum slope change was brought about by a larger decrease in reflectance at 550 nm relative to reflectance at 450 nm as maturation of the powder continued. Incrementally weathered soil spectra from these two experiments exhibited slightly different continuum changes (Figs. 3 & 4). In experiment 3, the 450/550 ratio started increasing or becoming bluer after only 6,000 shots,

then decreased again between 12,000 and 24,000 laser shots, and increased again in the last two spectral measurements of 36,000 and 48,000 shots. On the other hand, spectra of samples from experiment 4 showed that the 450/550 nm ratio decreased between 0 and 12,000 shots and then gradually increased/bluer for laser shots 24,000, through 48,000. Fig. 4 compares the two components of the visible continuum (i.e., 450/550 and 550/750 ratio) and illustrates that 450/550 values at first decrease and then slightly increase after about 10,000 laser shots, while values for the 550/750 ratio only decrease as a function of total number of laser shots.

Characterizing slope changes in this narrow wavelength range is important because most asteroid spectral data is normalized to 550 nm and the UV absorption edge is used as a criterion for spectral classification.

3.2 Radiative Transfer Modeling

Radiative transfer modeling provides insight into size and abundance of SMFe that control the spectral response of the laser space weathered materials. For instance, we specifically examine whether increasing the size of the SMFe could account for the change in the spectral response of the samples in experiments 1–3. As the nanophase-sized SMFe particles impart a red slope to the material, the microphase-sized SMFe, which acts as a darkening agent, could account for flattening or bluing of the spectra if their abundance greatly increased relative the nanophase reddening particles.

The model fits to the altered material spectra are reasonable, reproducing the overall slopes and albedos of the altered material spectra (Fig. 5A). As the model uses optical properties SMFe to alter the fresh spectrum to create a modeled weathered spectrum that best matches the laboratory

measure spectrum of a laser weathered material, we can infer that most of the change in the continuum and 1- μ m absorption is accounted for by slight, steady increases in the SMFe abundance, which is a lunar-like characteristic of space weathering. There are, however, noticeable differences in spectral shape between the model and actual spectra that indicate alteration beyond simple addition of nanophase/microphase iron.

Other observations made from the weight percent of SMFe output from the model is that the percentage of nanophase iron the longer experiment 3 agrees with the shorter experiments 1 and 2, for similar number of laser shots, and maintains the same proportional increase with greater laser shots (Fig. 5B). In comparing both the nanophase- and microphase- iron we find that the abundance of the microphase iron increases more rapidly than the nanophase iron (Fig. 5B). In addition, while the model size of the microphase iron was allowed to vary, it became only slightly larger during the process of modeling all three experiments (Table 2). The result is that the relative abundances of the nano and microphase iron are not in lunar-like proportions. Radiative transfer modeling of lunar soils estimates that the two sizes of SMFe are in approximately equal proportion (Lucey and Riner, 2011), while the results here suggest the larger microphase iron is between 20 and >100 times more abundant (Table 2).

Interestingly, experiments 1 and 2 exhibit a more rapid increase in microphase abundance than experiment 3. The cause for the greater percentage of microphase abundance for experiments 1 and 2 relative to experiment 3 is unknown. The rapid increase in microphase iron for experiments 1 and 2 result in more microphase iron while remaining spectrally redder, in the narrow spectral range from 450 to 550 nm, than experiments 3 and 4 in the 6,000-12,000 laser

shot region. On the basis of this observation we suggest that bluing of the spectra between 450 to 550 nm for the long duration experiments is not due to an increase in the size or abundance of microphase iron. It is possible that alteration of a non-lunar phase is influencing the UV slope and may play a role in changing the visible continuum. We will test this hypothesis through STEM studies.

3.3 STEM Analyses

Samples for STEM analyses were taken from the Allende power at 12,000 laser shots (10-min) and 48,000 laser shots (40-min). Figures 6, 7 and 9 show FIB sampling sites and sections from these two Allende grains (Supplement Figs. 3 and 4). The surfaces of both grains are covered by melt but their surface texture and degree of melt coverage varies with laser irradiation. The first FIB section, which is 30 μm long, is from the less space weathered Allende aliquot (i.e., 12,000 laser pulses). A large sulfide particle is stuck in the melt on the surface of this grain (Fig. 6). In the SEM secondary electron image the sulfide appears bright (Fig. 6), and in the STEM bright field and HAADF images it is a mix of bright, dark and gray tones (Fig. 7). The sulfide particle is approximately 2-3 μm across, and based on the SEM image, we infer that all the bright surface particles associated with the melt, which are 1-2 μm in size, are sulfides. As confirmed by STEM EDX analyses the sulfide particle is a mix of FeS (e.g. troilite or pyrrhotite) and FeNiS (e.g., pentlandite) (Supplemental Fig. 5, Supplemental Table 1). STEM imagery of the FIB section shows two olivine grains (Fig. 7) with an EDX determined composition of Fo_{53-58} (Supplemental Table 2). The zone between the two olivine grains appears comminuted or brecciated, and may have been generated by a laser hit (Supplemental Fig. 6). Characterization of the melt/vapor rim away from the sulfides indicate a rim thickness of approximately 100 nm with a concentration of

SMFe in the lower half of the rim (Fig. 8). Identification of SMFe was confirmed by EDX and lattice fringe imaging. The SMFe blebs appear as gray and dark gray circles with most diameters in the 7-10 nm range, and two of the bigger grains are ~30 nm. Also apparent in Fig. 8 are two locations within the olivine that contain chrome spinel.

The second FIB section is from the more laser-weathered aliquot (i.e., 48,000 laser shots) and is 6 μm long. In the SEM secondary electron image, the melt surface looks texturally much different than the rim of the less laser-weathered particle. The melt on the less mature particle is smooth and relatively flat with sulfide grains cemented in it. In contrast, the melt on the more weathered particle occurs as multiple generations of rounded bubbly blobs that appear to have been more viscous when deposited (Fig. 9). The area of the FIB section, ~6x6 μm , is comprised of laser generated melt, vesicles and mineral pieces. It is texturally similar to a lunar agglutinate. Minerals within the melt are predominately olivine grains that exhibit reverse zoning (Fig. 10), which means that the proportion of magnesium increases rather than decreases relative of iron. The composition of the nanophase particles is also different from those in the less laser-weathered particle rim. EDX maps of this more exposed rim shows that nanophase particles are mostly nickel, iron and sulfur (Fig. 10). These iron-nickel-sulfides are concentrated along some melt/mineral boundaries in the bottom part of the FIB section but are also dispersed homogenously through the melt in the upper part of the FIB section. This size of the iron-nickel-sulfides is on the order of 5 nm, however, their concentration along grain boundaries may allow them act like larger grain absorbers by preventing photons of all wavelengths from being transmitted through the minerals they surround; Thus causing darkening rather than reddening. While iron-sulfide particles have previously been observed in space weather exposed (Noguchi

et al., 2011) and laboratory irradiated particles (Matsuoka et al., 2015; Noble et al., 2011), this is the first observation of nanophase iron-nickel-sulfide particles.

4. Discussion

Our pulse-laser irradiation experiments brought about spectral, mineralogical, compositional and physical changes to the Allende powder. Radiative transfer modeling and STEM analyses together reveal that the Allende samples have two space weathering components. The first component is lunar like, i.e., spectral reddening, darkening, and loss of absorptions bands due to ~100 nm thick melt/vapor deposited rims that contain SMFe. The second component, is an eventual halt to reddening at 450/550 ratio, which we attribute to the generation of nanophase NiS, FeNiS, and FeS through the breakdown of larger sulfide grains. On the basis of the two FIB sections, we infer that the sulfides in the sample with <12,000 laser shots remain fairly large at 1-3 μm , and as a result, the abundance of nanophase size SMFe control the spectral properties of the sample. With increased laser exposure (i.e., >12,000 laser shots), sulfide grain size is significantly decreased by dissolution in melt, vapor redeposition, and potential comminution in samples – a similar effect of sulfide dispersion into small droplets was noticed in laser irradiation of ordinary chondrites (Noble et al., 2011) and the kinetic experiments of Hörz et al. (2005). Because NiS, FeNiS, and FeS, are dark opaque minerals, a reduction in their grain size results in an increase their ability to absorb light. The pervasive distribution of NiS, FeNiS, and FeS through the melt rim and particularly along the interface between melt and mineral grains would increase their capability to absorb light at all wavelengths. Hence we infer that the spectral properties of these particles overwhelm the spectral signature of the nanophase sized SMFe. Moreover, the greater volume of sulfide containing rim material compared to the thin SMFe

containing rim would also contribute an important factor in the takeover of the spectral properties of the sample. We are unsure at this time whether the NiS or NiFeS metal sulfides could be responsible for blueing of the spectra in 450-550 nm region. Optical constants or reflectance spectra of these minerals will be needed to test whether one or a combination of the two sulfides is responsible for flattening the spectra of Allende samples with >12,000 laser shots.

The change in the 450/550-nm ratio trend has important implications for telescopic and mission spectral data, as well as for optimizing science value for mission sample site selection of carbonaceous asteroids. Hence, we compare our Allende spectra with spectra from the Small Main-Belt Asteroid Spectroscopic Survey II (SMASS II, with continuous spectra from 440-920 nm) (Binzel et al., 2001; Burbine and Binzel, 2002; Bus and Binzel, 2002). We compare our results with SMASS using the 750/550 ratio and 450/550 ratios because these ratios capture the biggest spectral differences between different asteroid spectral classes in the SMASS data, which is normalized to 550 nm (Supplement Fig. 7).

A comparison of mean reflectance values and standard deviation for 13 SMASS II taxonomic classes (DeMeo et al., 2009) illustrates a spectral trend as a function of asteroid composition (Fig. 11A). With the spectrally bluer end member represented by B-, C-, Cb- and Ch-type asteroids, and the spectrally redder end member comprised of L-, R-, and S-type asteroids. Spectra of the fresh Allende laboratory sample lie in the middle of the overall spectral trend, close to Cg-, Cgh-type asteroids. In contrast, spectral ratios of the more weathered Allende are more consistent with D-, K-, and T-type asteroids.

Average spectra of these spectral types (Cg-, Cgh-, D-, K- and T-) are plotted with spectra of Allende (Fig. 11B). Spectra of Cg-, and Cgh-types overlap with spectra of the fresh and relatively low space weathered Allende. However, the 1- μm absorption feature of Cg- is too broad, while Cgh- has an absorption feature at 0.8- μm . Both spectral types lack a 2- μm feature. D-type asteroid spectra match the visible portion of the most space weathered but become increasing much redder at wavelengths longer than 0.8- μm . K-type asteroids have characteristic absorption bands at 1- μm from olivine and 2- μm from spinel (Sunshine, 2008), which is spectrally/compositionally similar to Allende. However, the visible continuum is steeper/flatter than any of the Allende spectra. The most weathered Allende sample exhibits a similar continuum and albedo T-type asteroids – with noted differences being a shorter than 1 μm absorption and a flatter continuum beyond 2 μm .

The state (e.g., rock, power, fresh, and weathered) of the meteorite that spectra are acquired from matters. A spectral association between Allende and L-type asteroids (Trigo-Rodríguez et al., 2013) and spectral link between the CV3 chondrite Mokoia and K-type asteroids (i.e., (221) Eos, (599) Luisa, and (653) Berenike (Bell, 1988; Burbine et al., 2001)) has been made in the past. In these pairings, spectra were acquired from unweathered meteorites pieces or powders and compared to telescopic spectra of asteroids. Comparing spectra of laser weathered Allende with mean spectra of asteroid types reveals some similarities with darker and redder asteroid types. Hence, this is the first time a spectral connection between Allende and D- and T-types asteroids has been suggested. D-type asteroids have been linked to CI chondrites (Trigo-Rodríguez et al., 2013) and Tagish Lake (Hiroi et al., 2001), both meteorites are inherently darker (4% reflectance at 550 nm) than fresh Allende. However, beyond about 0.8- μm the spectra of D-type asteroids

are quite different than weathered Allende (Fig 10B); hence it is not considered a parent body candidate for Allende. Spectra of T-type asteroids such as (96) Aegle and (308) Polyxo exhibit similar spectral slope in the visible and NIR, however, the 1 μm absorption and a flatter continuum beyond 2 μm do not replicate weathered Allende spectra (Supplement Fig. 8). In conclusion, the point is not that K- or T-type asteroids are the parent body of Allende, but that Allende looks spectrally different than the parent body one would predict based on its unweathered spectrum. In addition, the large and non-lunar spectral variations with increased weathering of our Allende samples (Fig. 10) suggest the most spectrally similar parent body candidate is space-weathering dependent. Hence, iterative space weathering experiments are essential for understanding a material's spectral response to space weathering from Near Earth Asteroids to Main Belt Asteroids.

Our incrementally space weathered spectra may also have bearing on the astronomical issue of how the spectra of C-complex asteroids are affected by space weathering. Two recent studies of asteroid families find opposite trends in spectral slope with age for C-type asteroids. Principal component analyses of Sloan Digital Sky Survey (SDSS) photometric data (5-band spectra with bands centered at 355, 482, 626, 767, and 910 nm) showed that C-type asteroids decrease in their mean spectral slopes (become spectrally “bluer”) with age (Nesvorný et al., 2005). Spectral bluing space weathering trends of dark asteroids and CM chondrites is also supported by Lantz et al. (2013). An opposite trend was observed in the spectral slopes from the SMASS II. In this study (Lazzarin et al., 2006), C-type asteroids exhibit an increase in spectral slope (become spectrally “redder”) with time. It was suggested (Lazzarin et al., 2006) that the decrease in spectral slope with age found in the SDSS data (Nesvorný et al., 2005) may be a result of

compositional differences among different C-type families and not a result of space weathering, but it is then difficult to explain the apparent change as a function of family age which should not be correlated with compositional difference. Our results suggest that it is possible for an asteroid family, or in this case, a laboratory simulated asteroid family of a single composition to become spectrally bluer within a narrow wavelength range as a function of exposure to micrometeorite bombardment. A future test of this hypothesis is whether, like our Allende data, only spectra within the 450-550 nm range become bluer with exposure age for the C-type families studied by Nesvorný et al. (2005), or whether all spectral ratios would exhibit a flatter slope.

5. Conclusions

We conducted incremented space weathering experiments of Allende, a CV3 carbonaceous chondrite, using pulsed laser irradiation. Spectral changes in response to the laser were compared between each time step, and each spectrum was analyzed using a radiative transfer model. While the spectral response to laser weathering tend to follow lunar-like trends (i.e., materials redden, darken, and reduce the spectral contrast when laser space weathered). Radiative transfer modeling reveals that of the two populations of SMFe, nanophase iron particles predominantly control the spectral properties of the sample (Fig. 5B). The relative abundances of the nano- and microphase-iron, however, are not in lunar-like proportions. In further examining the incrementally laser weathered spectra, we uniquely find that the visible continuum slope between 450-550 nm does not vary monotonically with laser exposure. Initially, spectra redden with laser irradiation; then, the visible continuum in this region begins to become less red while the overall spectra continue to darken (Figs. 3B, 4 and 11A). We suggest that the addition of SMFe alone cannot fully reproduce laser weathered Allende spectra (Fig. 5A), and that other nanophase

materials must be affecting the spectra.

STEM analyses shows that the nanophase component is primarily SMFe in samples experiencing low degrees of laser space weathering, but that FeNiS, FeS and NiS become dominant and control the spectral properties of the sample with increasing weathering. A test of this hypothesis is to do the Hapke modeling with proper but not yet obtained optical constants for these phases.

On the basis of modeling and STEM imaging and compositional analyses, it appears that a non-lunar like space weathering effect influences the color of our laser space weathered Allende samples between 450-550 nm. Therefore, applying a carbon copy of the lunar space-weathering model to C-type asteroids is not suitable to understand the physical, chemical and spectral response of these carbon-bearing asteroids to space weathering. A space-weathering model specific to C-complex asteroids must be developed.

We find a reasonable match between our weathered Allende spectrum and K- and T-type asteroids. Typically these asteroid spectral types would be considered too dark to be a spectral match with unweathered Allende, which highlights the importance of comparing laboratory space weathered spectra of meteorites to telescopic spectra of asteroids. Furthermore, our Allende spectra show that the 450/550 nm slope can be variably altered by the space weathering process, which has direct impact on telescopic observations for three reasons: (1) The 550 nm wavelength is typically used as a normalization wavelength in telescopic spectra in order to remove albedo and phase angle effects; (2) different C-complex asteroids are distinguished by their 450/550 nm ratio (e.g., B-, C-, and Cb-type are spectrally bluer than Cg-, Cgh-, T-, and K-

type); and (3) our laboratory simulated asteroid family suggests that an asteroid family of a single composition can become spectrally bluer as a function of exposure to micrometeorite bombardment. An intriguing application of the determined weathering rates is the possibility to estimate surface ages for individual C-complex asteroids from their color.

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Fig 1. (A) a comparison of spectra of altered San Carlos olivine of similar grain size ($< 75 \mu\text{m}$) between laser irradiation experiments done previously (Sasaki et al., 2001) and those done at our laser space weathering facility. (B) Comparison of spectral ratios similar to Figures 3 and 10. On the basis of these data we find that it takes between 36,000 and 48,000 laser shots in 0.5 grams of material to reproduce the spectral change observed in 5 laser shots into the pressed pellet (Sasaki et al., 2001). We include an un-irradiated pressed pellet spectrum to show the reproducibility of our spectrometer and sample with the experimental setup of Sasaki et al. (2001).

Fig 2. Reflectance spectra of Allende illustrating how spectra change as a function of laser irradiation. Spectra of Allende are from experiment 1 (solid lines) for fresh through 12,000 laser pulses and from experiment 3 (dashed lines) for fresh to 48,000 shots. To keep the graph from becoming overly busy data for Experiments 1 and 4 are not plotted. Spectra for experiments 2 through 4 are plotted in Supplementary Figure 1.

Fig 3. (A) Ratio of 750/550 nm reflectance versus reflectance at 750 nm for the four experiments reported here. All four experiments show that the 750/550 nm ratio increased or became redder, while reflectance at 750 nm decreased with increase number of laser shots. Lines connect the experiment series in order from fresh Allende to 12,00 laser shots. Experiments 3 & 4, the long exposure series, were weathered in two 6,000 shot increments (shown) but reflectance data for laser shots 24,000, 36,000 and 48,000 are not shown. (B) 750/550 vs. 450/550 data showing that with more extreme space weathering (i.e., >12,000 shots) the visible continuum as represented by the 450/550 ratio changed from getting redder, or steepening, to becoming bluer. The effect is not present for the 750/550 nm ratio. Error bars are not shown because they are smaller than the size of the symbols used, see supplementary data.

Fig 4. A comparison between the blue-green continuum (450/550 ratio) and the green-red continuum (550/750 ratio) and accumulated number of laser shots for each experiment. Cold colors depict how 450/550 ratio values at first decrease and slightly increase after about 10,000 laser shots. In contrast values for the 550/750 ratio, portrayed by warm colors, only decrease in relation to total number of laser shots.

Fig 5. (A) Radiative transfer modeling (model fit represented by lighter colors) to laser space weathered Allende spectra (darker colors) from experiments 1, 2 and 3. Continuum and albedo variations are reproduced by lunar-like steady increases in the submicroscopic iron abundance. The divergence between the model spectra and weathered spectra in the visible portion suggests a non-lunar like space-weathering component (e.g., chemical, physical, and or mineralogical). (B) Illustrates the weight percent submicroscopic iron, which is split into two populations nanophase (small) and microphase (~1 micron), which are used to produced the model fit spectra. The relative abundances of the nano and microphase iron are not in lunar-like proportions.

Fig 6. An SEM secondary electron image of the 12,000 shot laser space weathering Allende grain. The area was selected for sampling because of the smooth melt texture and bright grains, which are inferred to be sulfides. The line depicts location and length (30 μm) of the FIB site.

Fig 7. STEM HAADF (top) and bright field image (bottom) of FIB section from Fig 5. Bulbous area at top of section (outlined in cyan in the bright field image) is the sulfide grain transected by the line in Fig 5. There is a brightness artifact in both STEM images (outlined in yellow in the bright field image) caused by the top of the section being thinned during the FIB process more than bottom. The two areas outlined in green in the bright field image are olivine grains that are separated by a brecciated zone that we suggest was created by a laser shot. The pink square depicts the location of Fig 7. Supplement Fig. 5 shows a close-up view of the brecciated zone separating the two olivine grains. Orange squares are locations where EDX compositional measurements for the olivine were acquired (Supplement Table 1).

Fig 8. Images of the host grain and rim with embedded SMFe. (A) is a zero-loss brightfield image, which shows the iron as dark circles and a spinel within the olivine and below the vapor/melt deposited rim. (B) and (C) are compositional maps showing the distribution and population of SMFe as measured by K-alpha (Oxygen) and L-alpha (Iron) x-ray energies – SMFe is rich in iron while deficient in oxygen. And (D) is a dark field image of the rim showing the size range of SMFe.

Fig 9. A) An SEM secondary electron image of the 48,000 shot laser space weathering Allende grain. The area was selected for sampling because of the blobby melt texture. The line depicts location and length (6 μm) of the FIB site. B) FIB section prior to being thinned. White line denotes boundary between deposited Platinum (Pt) and actual rock sample. Multiple vesicles are present in the FIB section, which is in contrast to the FIB section shown in Fig 6.

Fig 10 TEM EDX compositional maps of a $2 \times 2\text{-}\mu\text{m}$ portion of the FIB section in Fig 8. The compositional maps reveal an abundance of nanometer-sized NiS, FeNiS, and Fe grains along with reversely zoned olivine grains. The diagonal brightness variations, called curtaining, are the result of slight differences in thickness from FIB ion thinning triggered by material property differences (i.e. juxtaposed vesicles and silicates) within the section.

Fig 11. a) Spectral comparison of iteratively laser weathered Allende, from Fig. 3B, along with mean reflectance values and their standard deviations for 13 SMASS II taxonomic classes (Burbine and Binzel, 2002). Spectra of the most weathered Allende sample are comparable to spectra of D-, K-, and T-type asteroids. Spectral data for experiment 1, which included 12,000 laser shots, and experiments 3 and 4, up to 48,000 laser shots, are shown. Experiment 2 data are not shown because they over plot experiment 1 data. B) Comparison of spectral data for Allende, unweathered through 48,000 laser shots, and mean spectra of asteroids from five taxonomic classes (Cg, Cgh, D, K and T). While K-type asteroids have a 1-μm absorption band due to olivine, which is much stronger than observed in Allende, K-type asteroids do not exhibit the 2-μm spinel related absorption, and they are not as spectrally red as weathered Allende. T-type asteroids are a comparable match the spectral slope of the most weathered Allende sample their spectra do not exhibit the 2-μm spinel absorption. Spectra of both T-type asteroids and the most weathered Allende sample lack the olivine 1-μm feature. Spectra of D-type asteroids are much steeper than the most weathered Allende are spectrally similar to some comets and ice bearing or

715 aqueously altered asteroids (Fitzsimmons et al., 1994; Jones et al., 1990; Kanno et al., 2003), so
716 are not a good candidate for space weathered anhydrous Allende.

1 Table 1 Reflectance data used to make Figures 3, 4 and 11.

Laser shots	450 nm	550 nm	750 nm	450/550	750/550	550/750
Experiment 1						
0	0.07272	0.08070	0.08524	0.90116	1.05627	0.94673
1,200	0.06839	0.07620	0.08107	0.89757	1.06397	0.93988
2,400	0.06494	0.07228	0.07686	0.89845	1.06331	0.94046
3,600	0.06437	0.07159	0.07629	0.89918	1.06568	0.93837
4,800	0.05943	0.06647	0.07149	0.89397	1.07542	0.92987
6,000	0.05841	0.06512	0.07015	0.89688	1.07731	0.92824
7,200	0.05357	0.06019	0.06553	0.88998	1.08866	0.91856
8,400	0.05184	0.05842	0.06407	0.88734	1.09669	0.91183
9,600	0.05090	0.05705	0.06239	0.89224	1.09363	0.91439
10,800	0.04802	0.05419	0.05988	0.88606	1.10486	0.90510
12,000	0.04721	0.05319	0.05892	0.88747	1.10762	0.90283
Experiment 2						
0	0.06739	0.07519	0.07977	0.89625	1.06091	0.94259
1,200	0.06354	0.07100	0.07564	0.89486	1.06525	0.93875
2,400	0.06089	0.06855	0.07384	0.88825	1.07712	0.92840
3,600	0.05698	0.06388	0.06927	0.89194	1.08439	0.92218
4,800	0.05220	0.05895	0.06461	0.88547	1.09595	0.91245
6,000	0.05226	0.05883	0.06449	0.88834	1.09616	0.91228
7,200	0.04985	0.05599	0.06181	0.89040	1.10400	0.90580
8,400	0.04460	0.05058	0.05655	0.88168	1.11811	0.89437
9,600	0.04392	0.04970	0.05546	0.88363	1.11598	0.89608
10,800	0.04090	0.04641	0.05232	0.88131	1.12735	0.88704
12,000	0.03992	0.04515	0.05089	0.88413	1.12703	0.88729
Experiment 3						
0	0.07418	0.08156	0.08544	0.90955	1.04764	0.95452
6,000	0.06073	0.06751	0.07220	0.89967	1.06955	0.93497
12,000	0.05179	0.05789	0.06311	0.89469	1.09019	0.91727
24,000	0.04093	0.04573	0.05110	0.89502	1.11741	0.89492
36,000	0.03542	0.03953	0.04475	0.89600	1.13189	0.88348
48,000	0.03054	0.03407	0.03950	0.89637	1.15941	0.86251
Experiment 4						
0	0.06976	0.07675	0.08064	0.90898	1.05079	0.95166
6,000	0.05770	0.06413	0.06886	0.89982	1.07380	0.93127
12,000	0.04852	0.05393	0.05916	0.89978	1.09712	0.91148
24,000	0.03759	0.04210	0.04745	0.89283	1.12715	0.88720
36,000	0.03119	0.03487	0.04004	0.89441	1.14834	0.87082
48,000	0.02782	0.03089	0.03583	0.90090	1.16004	0.86204

4 **Table 2.** Abundance of nanophase and microphase iron, and size of microphase iron used in radiative transfer modeling shown in Fig
5 4b.

	Number of laser shots	1,200	2,400	3,600	4,800	6,000	7,200	8,400	9,600	10,800	12,000	24,000	36,000	48,000
Experiment 1	Nanophase Abundance (wt. %)	0.000071	-0.000010	-0.000149	-0.000018	0.000016	0.000149	0.000264	0.000216	0.000395	0.000323	--	--	--
	Microphase Abundance (wt. %)	0.001413	0.003035	0.004158	0.005783	0.006101	0.008290	0.009132	0.010198	0.011902	0.012544	--	--	--
	Microphase Size (microns)	1.04	1.03	1.08	1.04	1.03	1.05	1.05	1.07	1.09	1.09	--	--	--
Experiment 2	Nanophase Abundance (wt. %)	0.000028	-0.000070	0.000027	0.000020	-0.000013	0.000192	0.000067	0.000152	0.000154	0.000313	--	--	--
	Microphase Abundance (wt. %)	0.001166	0.002446	0.003272	0.005613	0.005773	0.007284	0.008767	0.010367	0.011426	0.013245	--	--	--
	Microphase Size (microns)	1.14	1.18	1.18	1.19	1.19	1.18	1.17	1.16	1.18	1.18	--	--	--
Experiment 3	Nanophase Abundance (wt. %)	--	--	--	--	0.000155	--	--	--	--	0.000409	0.000886	0.001277	0.001626
	Microphase Abundance (wt. %)	--	--	--	--	0.005301	--	--	--	--	0.009863	0.016974	0.023167	0.030071
	Microphase Size (microns)	--	--	--	--	1.06	--	--	--	--	1.11	1.07	1.12	1.15

6