THE SPATIAL DISTRIBUTION OF ORGANIC MATTER AND MINERALOGICAL RELATIONSHIPS IN CARBONACEOUS CHONDRITES. S. J. Clemett[1], S. Messenger[2], K. L. Thomas-Keprta[1] & K. Nakamura-Messenger[1]; [1]ESCG / NASA Johnson Space Center, Mail Code JE-23, Houston TX 77058, [2]Robert M. Walker Laboratory for Space Science, ARES, NASA JSC, Mail Code KR, Houston TX 77058.

Introduction: Organic matter present within primitive carbonaceous meteorites represents the complex conglomeration of species formed in a variety of physically and temporally distinct environments including circumstellar space, the interstellar medium, the Solar Nebula & Jovian sub-nebulae and asteroids. In each case, multiple chemical pathways would have been available for the synthesis of organic molecules. Consequently these meteorites constitute a unique record of organic chemical evolution in the Universe and one of the biggest challenges in organic cosmochemistry has been in deciphering this record [1].

While bulk chemical analysis has provided a detailed description of the range and diversity of organic species present in carbonaceous chondrites [2], there is virtually no hard experimental data as to how these species are spatially distributed and their relationship to the host mineral matrix (with the notable exception of [3]). The distribution of organic phases is nevertheless critical to understanding parent body processes. The CM and CI chondrites all display evidence of low temperature (< 350K [4]) interaction with aqueous fluids, which based on O isotope data [5], flowed along thermal gradients within the respective parent bodies. This pervasive aqueous alteration may have led to aqueous geochromatographic separation of organics and synthesis of new organics coupled to aqueous mineral alteration (e.g., [6]).

To address such issues we have applied the technique of microprobe two-step laser desorption / photoionization mass spectrometry (L^2MS) to map *in situ* the spatial distribution of a broad range of organic species at the micron scale in the freshly exposed matrices of the Bells, Tagish Lake and Murchison (CM2) carbonaceous chondrites.

Technique & Methods: The L^2MS technique [7] has a high sensitivity and requires little to no sample preparation. However, a limitation of our current L^2MS instrument has been the range of organic species that can analyzed. This is a consequence of the ionization mechanism used that of (1+1) resonance enhanced multi photon ionization (REMPI). In this scheme, absorption of a 266 nm photon causes excitation of a molecule into a rovibrational manifold of the first electronic excited state and resonant adsorption of a second photon then leads to ionization. This technique is exquisitely sensitive to and selective for aromatic compounds but is not effective in ionizing other types of organics.

To overcome this restriction we have designed and constructed a vacuum UV (VUV) ionization source capable of non-resonant single-photon *soft* ionization of essentially all organics. The VUV light is generated by frequency tripling the 3rd harmonic of a Nd:YAG at 355 nm to produce the 9th harmonic at 118.2 nm. Tripling is achieved through non-linear 4-wave sum mixing ($3\lambda_{355} \rightarrow \lambda_{118}$) in a phase matched low pressure Xe/Ar gas cell. The tripling cell is directly integrated into the L^2MS vacuum chamber and separation of the 3rd and 9th harmonics is effected by utilizing the chromatic aberration of an *in vacuo* MgF_2 focusing lens. The optical design retains the ability to simultaneously utilize the previous multiphoton ionization scheme using the same optical path.

Using VUV photoionization with the L^2MS instrument we have been able to demonstrate detection of alkanes, alkenes, alkynes, alcohols, ethers, amines, aldehydes, ketones with comparable sensitivity (subfemtomole) to that previously obtained for aromatic hydrocarbons. Furthermore ionization generally results in the formation of intact molecular ions, rather than fragments, simplifying mass spectral analysis.

In our previous studies [8], meteorite samples were prepared by embedding small matrix fragments (~500 μm) in epoxy (Embed 812™). From this, a fresh sample surface could be exposed using a diamond knife ultramicrotome. Unfortunately during curing, reagents present in the epoxy resin were observed to react with indigenous matrix organics. To avoid this problem in the current study, samples were instead prepared by gently compressing a freshly fractured matrix fragment onto Au foil with a fused silica window. The highly porous nature of the meteorite matrix means that is easily compacted without significant loss of spatial integrity. After removing the silica window the flattened surface can be analyzed directly without any further sample preparation. Prior to L^2MS mapping, samples were imaged both optically and under UV illumination using a Nikon BX-50 fluorescent microscope equipped with a 330-385 nm excitation filter in combination with a 420 nm long-pass emission filter.

Results & Discussion: The results from three *in situ* surface maps of a small fragment of Bells matrix are illustrated in Figures 1-3. These were obtained by rastering the sample under the beam focus of pulsed CO_2 desorption laser and photoionizing neutrally desorbed organic species using 118 nm VUV light. At each anal-

ysis spot a complete mass spectrum out to 800 amu is acquired, and the spatial resolution of all three maps is ≤ 10 μm. Figure 1 shows the mass spectrum obtained by summing the individual shots from all three maps and represents the average organic composition of a ~0.5 mm^2 surface of the Bells matrix. The spectrum is characterized by $C_2 - C_{10}$ hydrocarbons with a variety of functionalities, but which are dominated by $-CO_2H$ and $-OH$. This is consistent with recent bulk chemical analyses using solvent extraction [9]. S-containing species (including H_2S and S_2) also appear to be prevalent in the mass spectra. Some caution is necessary, however, as their apparent abundance is likely over emphasized in the mass spectra because of the very large photoionization cross-section of S-containing species at 118 nm.
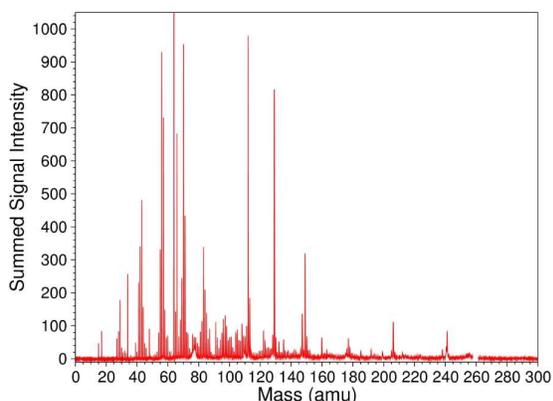

Figure 1: Averaged L^{2}MS organic mass spectrum of Bells matrix obtained using non-resonant singlephoton VUV photoionization. The break in the spectrum at 258-260 amu is due to the removal of internal mass calibration peak.

Figure 2 shows the distribution of the polar thiol methanethiol (the S analog of methanol) and provides an illustration of the ~mm scale spatial heterogeneity we commonly observed among various organic species. This should be compared with Figure 3 which illustrated the spatial distributions of the non-polar C_6 hydrocarbons hexane and hexene which in contrast show a far more homogenous distribution over similar length scales. This disparity may reflect hydrothermal mobilization of small polar organics. On a large scale such processes could also explain the dearth of amino acids in Tagish Lake [1] or the absence of three-ring aromatic hydrocarbons in Ivuna.

The capability to probe the detailed, broad spectrum organic chemical composition of astromaterials in situ will greatly enhance our ability to investigate the relationships between the petrological evolution of meteorite matrix and the evolution of primitive organic matter. Another important line of investigation will be probing the organic compositions of micrometer-scale H, C, and N-isotopic hotspots and organic nanoglob-

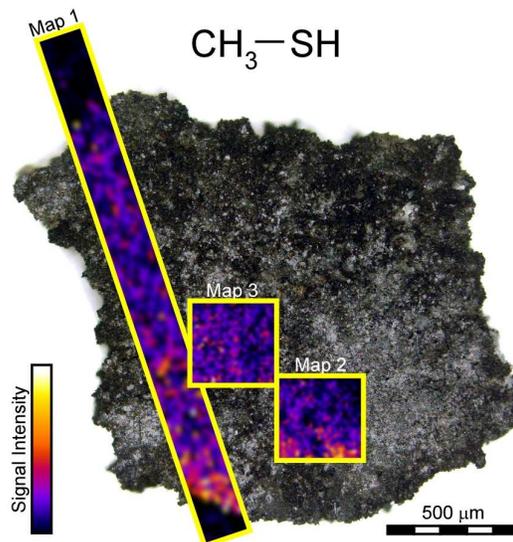ules [12], potentially the best preserved remnants of the primordial Solar System organic matter.

Figure 2: Spatial distribution maps for the polar thiol methanethiol (CH$_3$SH; 48 amu) on the surface of Bells matrix.
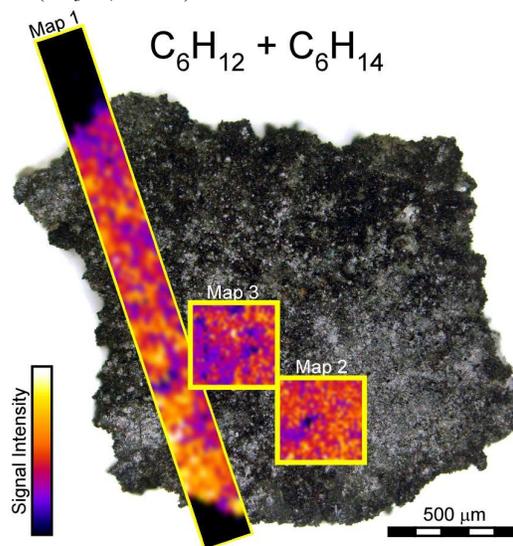

Figure 3: Spatial distribution maps for the non-polar C_6 hydrocarbons hexane (C_6H_{14}) and hexene (C_6H_{12}) on the surface of Bells matrix

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