

COORDINATED CHEMICAL AND ISOTOPIC IMAGING OF BELLS (CM2) METEORITE MATRIX.

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Introduction: Meteoritic organic matter is a complex conglomeration of species formed in distinct environments and processes in circumstellar space, the interstellar medium, the Solar Nebula and asteroids. Consequently meteorites constitute a unique record of primordial organic chemical evolution [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 little information as to how these species are spatially distributed and their relationship to the host mineral matrix (excepting [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]) aqueous alteration that may have led to aqueous geochromatographic separation of organics and synthesis of new organics coupled to aqueous mineral alteration (e.g., [5]).

Here we present the results of the first coordinated in situ isotopic and chemical mapping study of the Bells meteorite using a newly developed two-step laser mass spectrometer (μ -L²MS) capable of measuring a broad range of organic compounds.

Methods: Samples were prepared by pressing grains of Bells matrix (up to several 100 μ m in size) into Au foil using an optically flat sapphire window. This provided the requisite flat sample surface for chemical and isotopic mapping while still preserving the local spatial relationships of the matrix materials. The samples were not otherwise chemically treated and no embedding medium such as epoxy was used, in order to avoid contamination.

Samples were first imaged by white-light and UV fluorescence microscopy. We used a Nikon BX-50 fluorescent microscope equipped with a 330-385 nm excitation filter and a 420 nm long-pass emission filter as well as a higher spatial resolution Leica TCS SP8 confocal laser scanning microscope system to acquire fluorescence emission spectra. The fluorescence imaging non-destructively shows the distribution of aromatic and conjugated organic moieties and can quickly reveal the presence and distribution of μ m-scale organic grains such as carbonaceous nanoglobules [6].

Organic chemical mapping was then performed using the JSC μ -L²MS instrument. The μ -L²MS uses a pulsed IR laser to desorb molecules from sample surfaces that are then ionized by a second UV or VUV laser [7]. The wavelength of the laser photoionization source allows targeting of different types of organic

species. The 266 nm laser is selective for aromatic/conjugated organic species, while the 118 nm laser is used to measure essentially any organic species. We used both 266 nm UV and 118 nm VUV photoionization sources to map the abundance and distribution of organics with a spatial resolution of \sim 5 μ m.

Lastly, selected regions of one particle were mapped for C and N isotopic compositions with the JSC NanoSIMS 50L ion microprobe. A total of 13 areas of 20x20 micrometers in size were imaged for ^{12,13}C, ¹⁶O, ^{14,15}N (as CN), ²⁸Si, and ²⁴Mg¹⁶O as negative secondary ions using a 16 KeV, 1 pA Cs⁺ primary ion beam. NBS 24 graphite and terrestrial 1 hydroxy benzotriazole hydrate grains were measured before each run as C and N isotopic standards. An electron flood gun was used for charge compensation. Isotopic images were processed using custom-written software to correct for instrumental mass fractionation, QSA, and to derive isotopic and elemental ratios from regions of interest.

Visible, UV fluorescent, chemical, and isotopic image maps were carefully aligned by using large and small scale features in the samples to within < 3 μ m. Isotopic compositions were then derived for chemically distinct regions and integrated μ -L²MS chemical mass spectra were derived for isotopically distinct regions.

Results: Figure 1 shows optical and UV fluorescent images of the area analyzed by both μ -L²MS and NanoSIMS. The spatial distribution of organics in the range of 17-250 amu is shown in Fig 2. Within the grain interior the distribution of organics in VUV-L2MS maps shows broad variations at 10-to-100 μ m scales. Comparison with mapping of similar matrix grains using UV photoionization indicates that the aromatic and aliphatic organics are partially segregated, with the aromatic fraction closely following the fluorescence intensity. Distributed through the grain surface are organic 'hot-spots' which show wide spectral distributions of organics.

All areas of the Bells matrix imaged by NanoSIMS contained μ m-scale domains having significant ¹⁵N-enrichments, with δ^{15} N values ranging from a few hundred to >5,000 ‰. δ^{15} N enrichments exceeding 1,000 ‰ were common (Fig. 2). These ¹⁵N-rich hotspots were exclusively associated with μ m-scale carbonaceous domains, although the method of measuring N isotopes as CN introduces an observational bias. Only a few areas showed significant C isotopic anomalies, including two ¹⁵N-rich spots having δ^{13} C depletions (-

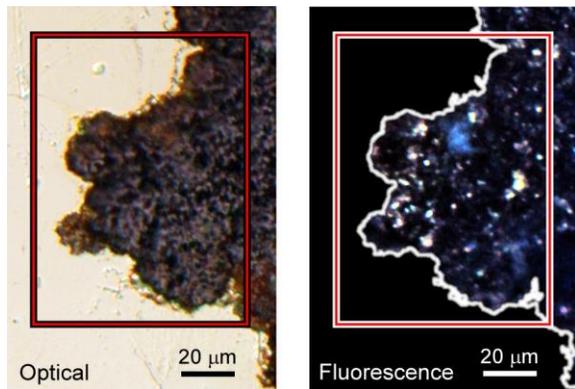


Fig. 1: Optical and UV fluorescence images of a fragment of Bells matrix on Au

200 ‰) and one probable presolar carbonaceous grain (possibly graphite) with $\delta^{13}\text{C} = 1,200 \pm 200$ ‰. Fig. 3 shows VUV- μ -L²MS spectra of two regions with low bulk $\delta^{15}\text{N}$ (~100 ‰) and high bulk $\delta^{15}\text{N}$ (570 ‰) containing a 5,000 ‰ hotspot. Considerably greater spectral complexity is observed in the ¹⁵N-rich region.

Discussion: The magnitude and diversity of ¹⁵N-enrichments observed in this sample are on par with the most isotopically primitive meteoritic and cometary (IDP) samples [8,9]. Previous in situ transmission electron microscopy and NanoSIMS studies found the highest N and H isotopic anomalies in Bells and Tagish Lake meteorites to be associated with morphologically distinct carbonaceous grains, often organic nanoglobules [10-12]. Such isotopic distributions cannot be accommodated by formation in the meteorite parent body and point to origins in the outer regions of the protoplanetary disk or presolar molecular cloud. From the isotopic standpoint, the anomalous carbonaceous grains are among the best preserved among meteoritic materials. In this work we find strong chemical evidence of preserved differences at micro-scales. These distinct chemical fingerprints may preserve records of pre-accretion chemical processes. Future studies will focus on establishing isotopic and chemical trends.

References: [1] Pizzarello S.J. et al. (2006) *Meteorites & the Early Solar System II*, 625. [2] Sephton M.A. (2002) *Nat. Prod. Rep.*, 19, 292. [3] Pearson V.K. et al. (2007) *PSS* 55, 1310. [4] Guo & Eiler J (2007) *GCA* 71, 5565 [5] Schulte M. & Shock E. (2004) *MAPS* 39, 1577. [6] Clemett S.J. et al. (2009) *MAPS*, 44, A52. [7] Clemett S.J. & Zare R.N. *IAUS* 178,305-320. [8] Floss [9] Busemann [10] Nakamura-Messenger K. et al. (2006) *Science*, 314, 1439 [11] Matrajt, G. et al (2012) *MAPS* 47, 525. [12] De Gregorio, B.T. et al.(2013) *MAPS* 48, 904.

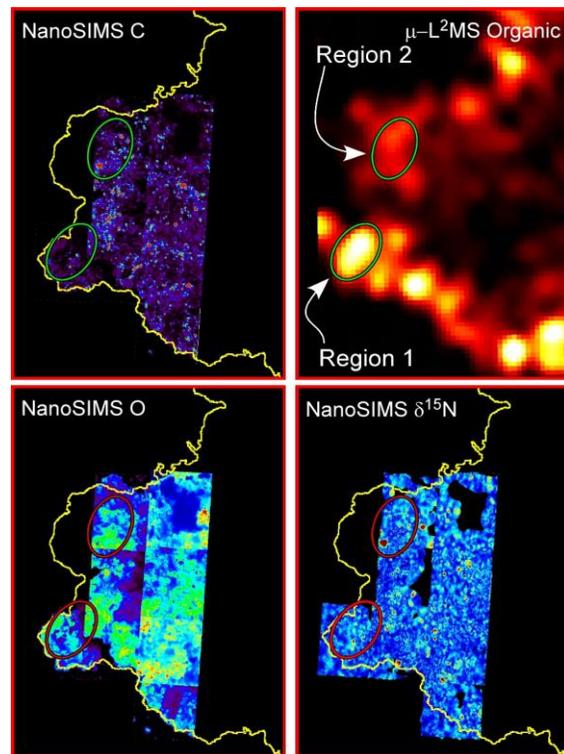


Fig. 2: NanoSIMS elemental C and O images together with $\delta^{15}\text{N}$ image scaled from -200 – 1000 ‰ compared with integrated VUV-L²MS map of the region.

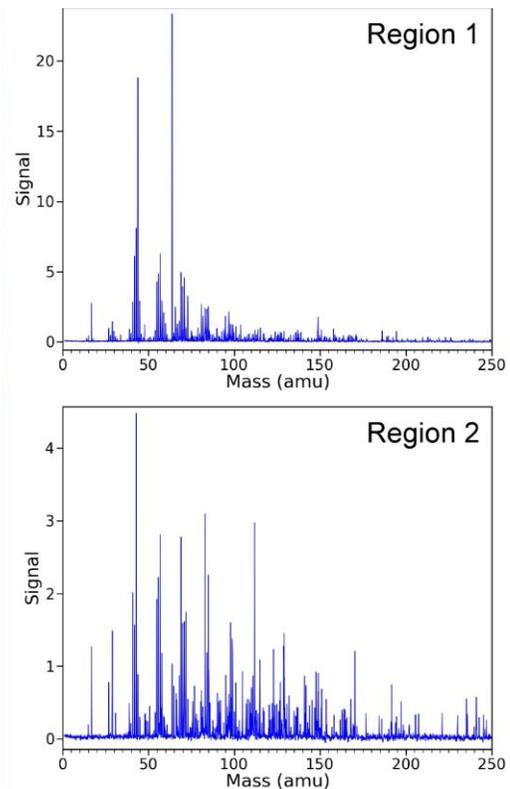


Fig. 3: VUV- μ -L²MS spectra of regions 1&2 above.