

REASSESSING THE ORGANIC CONTENT OF ANTARCTIC ICE AND METEORITES. O. Botta^{1,2}, Z. Martins³, C. Emmenegger⁴, J. P. Dworkin¹, D. P. Glavin¹, R. P. Harvey⁵, R. Zenobi⁴, J. L. Bada⁶ and P. Ehrenfreund³, ¹Goddard Center for Astrobiology, NASA Goddard Space Flight Center, Greenbelt, MD 20771, USA (obotta@pop600.gsfc.nasa.gov), ²Goddard Earth Sciences and Technology Center, University of Maryland Baltimore County, 5523 Research Park Drive, Baltimore, MD 21228, USA, ³Astrobiology Laboratory, Leiden Institute of Chemistry, University of Leiden, Einsteinweg 55, 2300 RA Leiden, The Netherlands, ⁴Department of Chemistry and Applied Biosciences, ETHZ Hönggerberg, Wolfgang-Paulistrasse 10, 8093 Zürich, Switzerland, ⁵Dept. of Geology, Case Western Reserve University, Cleveland, OH 44106, USA, ⁶Scripps Institution of Oceanography, University of California at San Diego, 9500 Gilman Drive, La Jolla, CA 92093, USA.

Introduction: A variety of organic molecules have been identified in carbonaceous chondrites such as Murchison. Except for the CMs and CIs, all other chondrites contain only low abundances of organic molecules. Only a few Antarctic carbonaceous chondrites have been analyzed for their organic content [1]. Although organic contamination from the long residence time in the ice was believed to be a problem, the abundances of indigenous organic compounds such as amino acids and polycyclic aromatic hydrocarbons (PAHs) in meteorites are so high that no terrestrial contribution could be recognized.

Terrestrial contamination starts to become a problem for meteorites with only very low organic content, including, for example, SNC meteorites. Clemett *et al.* [2] concluded in their study of possible sources of terrestrial contamination for PAHs in Antarctic meteorites that it is unlikely that these specimens contain significant amounts of organic compounds originating from the surrounding ice. This study concentrated on PAHs, and only a small ice sample (150g) from a unspecified location of the Allan Hills Ice sheet was analyzed. On the other hand, studies of EETA79001 and ALH84001 have shown that the relative abundances of amino acids [2,3] and PAHs [1] in the druse (carbonate) material resembled those in an Antarctic ice sample from the Allan Hills region, suggesting that the source of these amino acids may be the ice melt water.

We report on a systematic study of the contribution of amino acids and PAHs of Antarctic meteorites from terrestrial sources. In order to investigate the relationship between the meteorite and its surrounding ice with respect to the organic composition, we collected both meteorite and ice samples at the same time and location.

Sample collection and processing: During the 2003/2004 ANSMET field season, six ice samples from the LaPaz ice field stranding region were cut out using a chain saw. Five of these samples were each taken directly underneath a meteorite that was collected at the same time, while the sixth ice sample was collected from a location where there was no

meteorite. The ice samples were wrapped in nylon bags and stored frozen for transport. The samples (initial volumes 2250 to 4000 ml) were melted and concentrated using a rotary evaporator to volumes between 12 and 19 ml. These solutions were filtered through 100 μ m PVDF filters to isolate any particulate material. These filters were not investigated for micrometeorite content. Dissolved PAHs were extracted from the resulting filtrates using solid-phase extraction with PVC membranes [4]. The resulting solutions were concentrated under vacuum, and the residues dissolved in 100 μ l high-purity water. A 1-liter aliquot of doubly distilled water (proc. blank) was carried through the same procedure as the ice samples.

The meteorites samples LAP03624 (LL5), LAP03573 (LL5), LAP03637 (LL5), LAP03784 (CK5) were obtained from the NASA JSC Antarctic meteorite collection. For each specimen, one surface sample and three interior samples representing different distances from the surface were analyzed. PAH analysis of the meteorites was carried out directly on the chips without further sample preparation.

Sample Analysis: *Polycyclic Aromatic Hydrocarbons (PAHs).* PAHs were measured using two-step laser mass spectrometry (L2MS) [5]. The filters (containing the particulate material), PVC membranes (containing the soluble PAHs), and the meteorite chips were directly placed into the L2MS system. 72 laser shots were performed on each of the filter and membrane sample, while the meteorites were shot five times at five different locations. All the spectra were averaged.

Amino Acids. The amino acid concentrations in the ice samples were determined using OPA/NAC pre-column derivatization combined with HPLC separation coupled to both UV fluorescence and time-of-flight mass spectrometry (ToF-MS) detection [6,7]. Peak identification was achieved by retention time comparison with known standards (for fluorescence) and retention time plus exact mass (for

MS). Abundances were averaged over at least three measurements.

Results and Discussion: PAHs. The L2MS spectra of the filters containing the particulate matter look very similar for all ice samples. Dominant signals are m/z 178, as well as its alkylated homologs at m/z 192, 206, 220 and 234, plus a signal at m/z 212. Masses higher than m/z 280 are mostly lacking. Extensive alkylation is characteristic for anthropogenic emissions, indicating that the particulate matter could be terrestrial dust. In contrast to the filter spectra, the L2MS spectra of the PVC membranes are much lower in intensity. The PAH concentrations in the ice samples lie below 10-80 pg/l, depending on the concentration factors of the individual samples and the m/z signal. This is in the range of the upper limit as determined for Greenland ice [7]. The L2MS spectra of the meteorites depict similar overall characteristics, although the signal intensities vary between the different specimens. The highest intensities were detected in interior sample LAP03637,8 (Figure 1). The most prominent signals are two omnipresent peaks at m/z 226, which can be assigned to a skeletal PAH, and m/z 211, a nitrogen-containing compound. Furthermore, peaks corresponding to m/z 178, 192, 206, 220 and 234, were detected, as well as a peak at m/z 202.

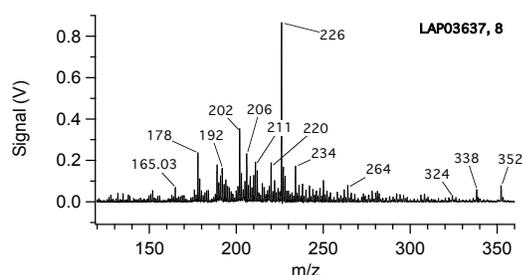


Figure 1. L2MS spectrum of the interior piece LAP03637,8 (LL5 ordinary chondrite).

Amino Acids. The concentration levels of the amino acids in the Antarctic ice samples are found to be close to blank levels. Due to the large ice sample size the detection limit was about 1 part per trillion (ppt). However, we observed some variability between the ice samples with regard to their amino acid composition. Most importantly, the signals corresponding to α -amino-isobutyric acid (AIB), an extremely rare compound on Earth, and its co-eluting homolog β -AIB were found to correspond to concentration levels between 10 ± 1 and 24 ± 6 ppt in three of the ice samples. Interestingly, one of these is associated with a LL5 OC (LAP03624), one of them

with the CK5 chondrite LAP03784, and one of them is the ice blank sample, with no meteorite collected at the same time. This finding suggests that the AIB in the ice is not a result of leaching of the meteorite during its residence time in the ice. We speculate that micrometeorites embedded in the ice could be the source of the material.

Conclusions and Future Work. Highly-sensitive PAH and amino acid abundances measurements of Antarctic ices collected directly under meteorites show very low level of terrestrial contamination for both compound classes. The PAHs in the particulate matter indicate a terrestrial origin of these compounds. The concentration levels of dissolved PAHs in all the ice samples are below 10-80 pg/l. The amino acid concentrations in the ice samples are near blank level. However, some of the ices samples contain α - and/or β -AIB at concentration levels of 10-25 ppt.

The PAH composition of the meteorites is variable between and within the specimens. A direct comparison with the soluble PAHs in the ice was not possible due to the low levels of these compounds in the PVC membrane extracts of the ice samples. However, the detection of alkylated homologs of skeletal PAHs in the meteorites indicates that some of these compounds could have a terrestrial origin. Amino acid analyses of the meteorite samples using HPLC/fluorescence/ToF-MS are currently underway.

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Acknowledgment: We like to thank the ANSMET 03/04-expedition field team for support in the collection of the ice samples. The NASA Astrobiology Institute and the Goddard Center for Astrobiology (DPG, JPD, OB) and the NASA Specialized Center for Research and Training in Exobiology (JLB) are acknowledged for grant support. This research was also supported by Fundação para a Ciência e a Tecnologia (scholarship SFRH/BD/10518/2002), the European Space Agency and Verniewingsimpuls (NOW-VI 016023003).