EXTENDED IN-SITU SEARCH OF AMINO ACIDS IN THE MURCHISON METEORITE.

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Introduction: Amino acids are thought to have played a vital role in the formation of life on the early Earth. Primitive meteorites are therefore of great interest because they contributed to the early Earth's budget of organic material. Previous characterization of organic matter in meteorites [e.g. 1] has almost exclusively been carried out on bulk samples by physically extracting organic material from the meteorite, usually by hot water extraction. This extraction process can alter the abundances of amino acids as shown by [2] and it is unclear to what extent amino acids are produced by the extraction process [3].

In this study, C_{60}-time-of-flight secondary ion mass spectrometry (C_{60}-TOFSIMS) was used to analyze the organic content of Murchison in-situ. C_{60} primary ions split up on impact, distributing the kinetic energy between the sixty carbon atoms. This means that no primary ion impacts deeply into the sample causing a collision cascade. Instead the impact produces a nanometer-sized crater and molecular secondary ions are lifted from the sample surface surrounding the crater with high efficiency and little fragmentation. Because no significant amount of energy is deposited below the impact crater, any organic material below the surface layer survives which enables depth profiling of organic material.

Sample: A ~4mm-sized flake from the Murchison CM2 meteorite was broken off to expose a fresh surface and used for C_{60}-TOF-SIMS analysis. A previous initial study [4] which analyzed three areas 128µm in size, did not find any amino acid signal above the background level that results from handling the sample in air. We now systematically extended the search for amino acids in this sample of the Murchison meteorite by analyzing more areas on a different part of the fragment. The surface was not coated or analyzed by other techniques which could have contaminated it before the C_{60}-TOFSIMS analysis. We studied eight areas of 150×150microns.

We also studied 22 different amino acids standards and found that the typical fragmentation pattern is the loss of the NH_2-group which is easily understandable because the C-N bond typically has the lowest bond energy and therefore breaks off first. Amino acids are therefore identifiable by the presence of the whole molecule and their carboxylic fragment.

Instrumentation: Our C_{60}-TOFSIMS instrument is described in more detail in [5,6]. Recording a whole mass spectrum up to mass 2000 allows for parallel detection of almost all organic matter found in primitive meteorites and mapping it with a spatial resolution of 2-3µm. A mass resolution of up to 10,000 together with a mass accuracy of a few tens of ppm allows for the unambiguous identification of organic molecules.

Because the sample has been handled in air it has a layer of air contamination on its surface which mainly consists of simple organic molecules like aliphatic hydrocarbons plus traces of aromatic and N- or O-bearing hydrocarbons. Blank measurements were therefore performed on the surroundings of the sample holder. Because topographic effects of the sample lead to large variations in sputter rate, it's necessary to divide the sample results by this blank. This results in a base line different from unity but any organic material indigenous to the meteorite is clearly visible above the background.

Results: Similar to our previous results, we find amines (methylamine, ethylamine and propylamine) well above the background level. There is also an over-abundance of relative heavy aliphatic hydrocarbons as detected previously. On the other other amino acids and their carboxylic fragments have not been detected or are not above the background level.

Discussion: Amines and amino acids have similar abundance in the Murchison meteorite according to previous studies [1]. The ionization efficiencies of both are similar and therefore amino acids or their carboxylic fragments should have been detected with similar efficiency to the amines. One explanation for their absence would be that the amino acids are not homogeneously distributed and are localized in very small areas. However, they are very water-soluble and would therefore easily migrate during aqueous alteration in the Murchison parent body. Another explanation could be that the amino acids reported in bulk studies are mainly produced during the hot water extraction and that indigenous abundances are below our detection limit. The production of most or almost all amino acids during the extraction process would seem hard to explain. Another explanation could be the air contamination of the meteorite sample. Volatile organic material does settle on any surface and can move along surfaces. We did break up a flake of the meteorite to create a fresh surface to avoid this problem but redistribution of air contamination over several decades since the fall of Murchison cannot be fully excluded.

References: [1] Sephton, M. A. 2002. *Natural product reports* 19:292-311. [2] Cronin J. R. and Moore C. B. 1971. *Science* 172:1327-1329. [3] Burton, A. S. et al. 2012. *Chem. Soc. Rev.* 41:5459-5472. [4] Henkel T. and Lyon I. C. 2015. *Met. Soc. Meeting* #5256. [5] Henkel, T. et al. 2007. *Rev. of Sci. Instr.* 78:055107. [6] Henkel, T. et al. 2009. *Rapid Com. in Mass Spec.* 23:3355-3360.