

**The Impact and Oxidation Survival of Selected Meteoritic Compounds: Signatures of Asteroid Organic Material on Planetary Surfaces.** George Cooper<sup>1</sup>, Fred Horz<sup>2</sup>, Alanna O'Leary<sup>1,3</sup>, Sherwood Chang<sup>1</sup>. <sup>1</sup>NASA-Ames Research Center, Space Science Division, MS 239-4, Moffett Field, CA 94035. <sup>2</sup>NASA Johnson Space Center, Houston, Texas, USA. <sup>3</sup>University of California, Davis, Davis, CA 95616

**Introduction:** Polar, non-volatile organic compounds may be present on the surfaces (or near surfaces) of multiple Solar System bodies. If found, by current or future missions, it would be desirable to determine the origin(s) of such compounds, e.g., asteroidal or in situ. To test the possible survival of meteoritic compounds both during impacts with planetary surfaces and under subsequent (possibly) harsh ambient conditions, we subjected known meteoritic compounds to relatively high impact-shock pressures and/or to varying oxidizing/corrosive conditions. Tested compounds include sulfonic and phosphonic acids (S&P), polyaromatic hydrocarbons (PAHs) amino acids, keto acids, dicarboxylic acids, deoxy sugar acids, and hydroxy tricarboxylic acids (Table 1). Meteoritic sulfonic acids were found to be relatively abundant in the Murchison meteorite and to possess unusual <sup>33</sup>S isotope anomalies (non mass-dependent isotope fractionations) [1]. Combined with distinctive C-S and C-P bonds, the S&P are potential signatures of asteroidal organic material.

**Methods:** Impact studies were performed on S&P and selected protein amino acids: a known amount of each compound was added to a sample of powdered Murchison meteorite. Water was then added to the mixture followed by vortexing and thorough drying of the mixture. The shock experiment was done in the Experimental Impact Laboratory of NASA's Johnson Space Center. Basic details of impact apparatus and sample handling procedures are similar to previous work [2]. Our methods resulted in the samples experiencing shock pressures up to 42.9 GPa – relatively high impact pressure in the testing of organic compounds. After impact, the samples were analyzed by a combination of ion chromatography, HPLC, and gas chromatography-mass spectrometry. Oxidation tests were performed on all groups of compounds. Standards were placed in excess 3:1 HCL:HNO<sub>3</sub> (aqua regia) at either 22 °C or 100 °C for various times. In the case of S&P, compounds at 22 °C were exposed to aqua regia for up to ~ 7.5 months.

**Results:** Figure 1 shows one impact-shock experiment of sulfonic and phosphonic acids. In the same shock mixture were the (protein) amino acids glycine,  $\alpha$ -aminoisobutyric acid and glutamic acid: only trace levels (<1%) of these amino acids survived above ~18 gigapascals (GPa) (not shown). This is consistent with earlier impact work on amino acids that also used solid matrices: less than 1% of a variety of amino acids (in a

meteorite matrix) survived at shock pressures of ~ 30 GPa [2]; amino acids embedded in a saponite clay matrix showed survivals of ~ 0% to 4% near 30 (28.9) GPa [3]. In the present experiments, impact shocks of PAHs (data not shown) resulted in 4 to 8% survival at the highest test pressure of 36 GPa. Some fraction of the majority of S&P survive at higher (30.7 and 42.9 GPa) pressures.

Table 1 shows the remarkable stability of S&P towards oxidation (and hydrolysis). The one and two-carbon compounds (MSA, MPA, and ESA, EPA) show survivals of at least 86 % up to ~ seven months at 22 °C in aqua regia. The phosphonic acids appear to be slightly more stable than the sulfonic acids at seven months (~100% survival vs ~ 87%, respectively). The 52% survival of tBPA is the lowest survival of all S&P and may reflect the lower relative stability of branched compounds, however, like the other phosphonic acids, it also survives quantitatively for at least seven months at 22 °C. Amino acid survival depends on structure. Tested compounds included the “alpha” amino acids (i.e., compounds with the amino group on a carbon adjacent to a carboxyl group), glycine, alanine, glutamic acid,  $\alpha$ -aminoisobutyric acid, proline (proline contains an aliphatic-cyclic side chain) and phenylalanine. The other amino acids were “non-alpha” (Table 1). It can be seen that at 22 °C only proline and the non-alpha amino acids survived (to a measureable level) the extremely oxidizing mixture: 100 °C trials of amino acids are not complete although it is apparent that they (with the possible exceptions of proline and 4-Methyl- $\gamma$ -aminobutyric) are far less resistant to oxidation than S&P. These results (the relative stability of the non-alpha amino acids) may qualitatively relate to the phenomenon of some carbonaceous meteorites having a higher relative abundance of non-alpha to alpha amino acids [4, 5] although the present test conditions are not meant to simulate meteorite parent-body conditions. If amino acids are discovered on other planets/moons it would be interesting to examine their relative abundances.

Citric acid and its isomer isocitric acid have vastly different survival rates. The much greater survival of isocitric acid (including possible citric-isocitric isomerization) is in contrast to the low isocitric/citric ratio in meteorites, perhaps adding to the case for a prolonged and specific synthesis of citric acid and certain other compounds [6]. The deoxy sugar acids and dicarboxylic acids also have significant levels of survival (at 22 °C – 17 hours), however, the % survival of the

latter group may be influenced by the production of dicarboxylic acids from the keto acids. However, the unique molecular/isotopic properties, meteoritic abundances, and impact and chemical stability of the S&P point to them as potentially significant markers of asteroidal (and possibly cometary) delivery of organic material.

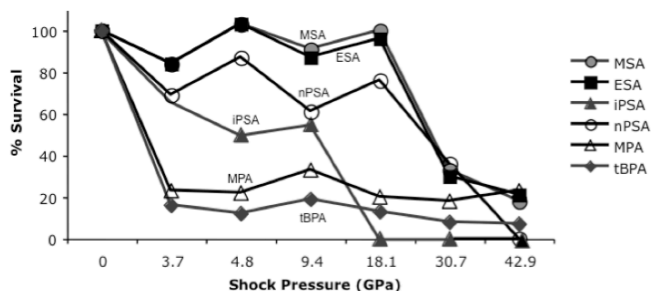


Figure 1. Impact survival of sulfonic and phosphonic acids vs shock pressure. MSA = methanesulfonic acid; ESA = ethanesulfonic acid; iPSA= isopropanesulfonic acid; nPSA = n-propanesulfonic acid; MPA = methylphosphonic acid; tBPA = tert-butylphosphonic acid.

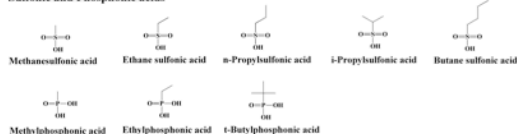
Table 1. Oxidation stability (% survival) of selected meteoritic compounds. Compounds were treated with excess aqua regia (3:1 HCL:HNO<sub>3</sub>) for the times and temperatures indicated. The dicarboxylic acid results were likely influenced by the production of additional dicarboxylic acids from oxidation of keto acids.

| Compound | time (hrs/mos) | temp (°C) | % Survived |
|----------|----------------|-----------|------------|
| MSA      | 7 mos          | 22        | 86 (±1)    |
|          | 40 hrs         | 100       | 97         |
| ESA      | 7 mos          | 22        | 88 (±3)    |
|          | 40 hrs         | 100       | 73         |
| MPA      | 7 mos          | 22        | 99 (±2)    |
|          | 42 hrs         | 100       | 100        |
| EPA      | 7 mos          | 22        | 100 (±3)   |
|          | 42 hrs         | 100       | 97         |
| tBPA     | 42 hrs         | 100       | 52         |
|          | 7.5 mos        | 22        | 100        |

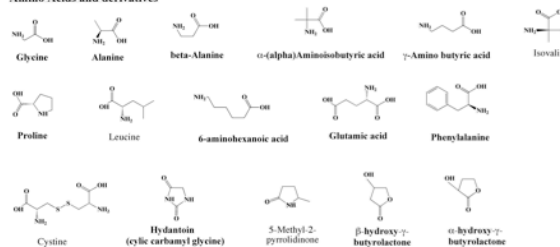
|                                    | Time = hours | temp (°C) | % Survived |
|------------------------------------|--------------|-----------|------------|
| <b>Protein/α-amino acids</b>       | various      | 22        | 0          |
| <b>Keto acids</b>                  | 17           | 22        | 0          |
| <b>Non- α amino acids</b>          |              |           |            |
| Beta-alanine                       | 16           | 22        | 16 (± 7)   |
| 6-Aminohexanoic acid               | 16           | 22        | 50 (± 20)  |
| γ-Aminobutyric acid                | 16           | 22        | 77 (± 7)   |
| Proline                            | 16           | 22        | 97 (± 3)   |
| 4-Methyl-γ-aminobutyric acid       | 17           | 22        | 100        |
| <b>Tricarboxylic-hydroxy acids</b> |              |           |            |
| Citric acid                        | 17           | 22        | 9          |
| Isocitric acid                     | 17           | 22        | 71         |
| <b>Deoxy sugar acids</b>           |              |           |            |
| 3,4-Dihydroxybutanoic acid         | 17           | 22        | 92         |
| 2,4-Dihydroxybutanoic acid         | 17           | 22        | 79         |
| <b>Dicarboxylic acids</b>          |              |           |            |
| Succinic acid                      | 17           | 22        | (100)      |
| Methylsuccinic acid                | 17           | 22        | 86         |
| Pimelic acid                       | 17           | 22        | (89)       |

**References:** [1] Cooper, G.W., Onwo, W.M. and Cronin, J.R. (1992) *Geochim. Cosmochim. Acta* 56, 4109-4115. [2] Peterson, E., Horz, F., Chang, S. (1997) *Geochimica et Cosmochimica Acta* 61, 3937-3950. [3] Bertrand, M., Van der Gaast, S., Vilas, Hörz, F., Haynes, G., Chabin, A., Brack, A., Westall, F. (2009) *Astrobiology* 9, 943-951. [4] Burton, A.S., Elsila, J. E., Callahan, M.P., Martin, M.G., Glavin, D.P., Johnson, N.M., and Dworkin, J.P. (2012) *Meteoritics & Planetary Science* 47, 374-386. [5] Glavin, D.P., Aubrey, A.D., Callahan, M.P., Dworkin, J.P., Elsila, J.E., Parker, E.T., Bada, J.L., Jenniskens, P., Shaddad, M.H., (2010) *Meteoritics & Planetary Science* 45, 1695-1709. [6] Cooper G, Reed C, Nguyen D, Carter M, Wang Y (2011) *P Natl Acad Sci USA* 108, 14015-14020.

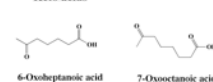
**Sulfonic and Phosphonic acids**



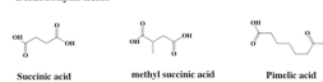
**Amino Acids and derivatives**



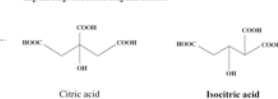
**Keto acids**



**Dicarboxylic acids**



**Hydroxy tricarboxylic acids**



**Polyaromatic hydrocarbons**

