HIGH ABUNDANCE OF METHYLAMINE IN THE ORGUEIL (CI1) METEORITE. J. C. Aponte^{1,2}, J. P. Dworkin¹ and J. E. Elsila¹, ¹Solar System Exploration Division, Code 691, NASA Goddard Space Flight Center, Greenbelt, Maryland 20771, USA, ²Department of Chemistry, Catholic University of America, Washington, DC 20064, USA. Email: jose.c.aponte@nasa.gov

Introduction: The Orgueil meteorite is a type 1 primitive chondrite from the CI group that experienced extensive aqueous alteration inside its parent body. Orgueil has been well studied, and diverse families of organic compounds including amino acids, aromatic hydrocarbons and nucleobases have been previously extracted from its matrix along with varying degrees of terrestrial contamination [1]. CI meteorites contain a higher water-to-rock ratio and higher abundance of hydrated minerals relative to other carbonaceous chondrite groups (e.g. CM). The high water content, the lack of chondrules, and other chemical and mineralogical characterisites observed in Orgueil and other CI1 chondrites have led to the suggestion that their parent body was cometary [2].

In contrast to the well-studied Murchison (CM2) meteorite, Orgueil is significantly depleted in amino acids. Both, Orgueil and Murchison appear to have remained below 150°C during their alteration histories; therefore, differences in their organic composition by the larger degree of aqueous alteration observed in Orgueil, which may have led to oxidation or other chemical destruction of the amino acids [3]. It is unclear whether the differences in amino acid abundances between Murchison and Orgueil reflect initial differences in parent body composition or the effects of the more extensive aqueous alteration of the CI chondrites [4].

We have developed an analytical method to investigate the abudance, molecular distribution, and $\delta^{13}C$ isotopic composition of aliphatic amines in carbonaceous chondrites and applied it to the Murchison meteorite [5]. Here, we report on results from our investigation of Orgueil and compare these results to those from Murchison. Our work is the first study of the amine composition in Orgueil and sheds light on the characteristics of the CI parent body and the chemical processes that may have led to its organic content.

Methodology: We analyzed a sample of Orgueil (931.6 mg) obtained from the Musée National, Paris, a procedural blank and a pyrolyzed serpentine blank were subjected to the same procedures. The Orgueil sample, which did not show any visual evidence of fusion crust was analyzed by gas chromatography mass-spectrometry (GC-MS) and GC-isotope ratio mass spectrometry (GC-IRMS), after extraction and derivatization of amines for chiral and compound-

specific ¹³C-isotopic analyzes using previously published methods [5].

Results and Discussion: We investigated a range of aliphatic amines in Orgueil, finding large amounts of methylamine (331.5 \pm 0.5 nmol/g of meteorite) and other small molecular weight aliphatic amines (Figure 1, Table 1). Furthermore, we analyzed the amine to amino acid ratio, finding that methylamine and ethylamine in Orgueil are about 30 times more abundant than their structurally analogous amino acids, glycine and α -alanine respectively (amino acids concentration taken from [6]).

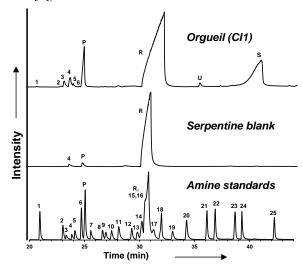


Figure 1. Partial GC-MS chromatogram showing the separation of aliphatic amines present in Orgueil (CI1). The identities of the peaks are presented in Table 1; U: unknown compound, P: phthalate, R: reagent (*S*-TPC acid), S: sulfur.

The amounts of methylamine in Orgueil are almost 4 times higher than those we reported in Murchison using the same analytical procedure (85.1 \pm 7.7 nmol/g of meteorite; [5]). Additionally, the total amount of amines in Orgueil (395.9 nmol/g of meteorite) are 2.5 times higher than that found in the Murchison meteorite. Methylamine represents 84% of total amine content found in Orgueil, and 54% of the total amine content in Murchison. However, the molecular diversity in Orgueil is substantially lower than that in Murchison, which exhibited a complete suite of molecular isomers [5]. We also measured the δ^{13} C composition of the aliphatic amines in Orgueil (Table 1); their 13 C-

enrichment suggests these molecules are indigenous to the meteorite, not the result of terrestrial contamination, and that these amines may have formed in cold interstellar environments [7].

Table 1. Abudance (nmol/g of meteorite) and δ^{13} C (‰VPDB) values of aliphatic amines in Orgueil.

Aliphatic amine	Orgueil (CI1) ^a	
	[C]	δ ¹³ C
1- tert-Butylamine	1.3 ± 0.2	n.d.
2- Isopropylamine	5.1 ± 0.1	10 ± 3^{b}
3- Methylamine	331.5 ± 0.5	43 ± 10
4- Dimethylamine	13.0 ± 4.9	-6 ± 9^{b}
5- Ethylamine	27.3 ± 2.4	59 ± 10
6- tert-Pentylamine	1.1 ± 0.2	n.d.
7- Ethylmethylamine	2.3 ± 0.4	n.d.
8- (R)-sec-Butylamine	2.4 ± 0.3	n.d.
9- Diethylamine	3.2 ± 0.4	n.d.
10- (S)-sec-Butylamine	2.5 ± 0.3	n.d.
11- <i>n</i> -Propylamine	4.8 ± 0.1	-20 ± 5^{b}
12- (R)-3-Methyl-2-butylamine	n.f.	n.d.
13- Methylpropylamine	n.f.	n.d.
14- Isobutylamine	n.f.	n.d.
15- (R)-sec-Pentylamine	n.f.	n.d.
16- (S)-3-Methyl-2-butylamine	n.f.	n.d.
17- Ethylpropylamine	n.f.	n.d.
18- 3-Pentylamine	n.f.	n.d.
19- (S)-sec-Pentylamine	n.f.	n.d.
20- <i>n</i> -Butylamine	1.39 ± 0.1	n.d.
21- (<i>R</i> , <i>S</i>)-2-Methylbutylamine	n.f.	n.d.
22- Isopentylamine	n.f.	n.d.
23- <i>n</i> -Pentylamine	n.f.	n.d.
24- Pyrrolidine	n.f.	n.d.
25- <i>n</i> -Hexylamine	n.f.	n.d.
Total Abundance	395.9	-

^aCompounds were identified by comparison with elution time and mass spectra of standards. ^bPartially contaminated with the derivatization reagent.

Meteoritic aqueous processes have been suggested to be detrimental to the abundance of amino acids in meteorites [8], because aliphatic amines are less polar and significantly more volatile than amino acids (especially methylamine), it was expected that amines would be less abundant than amino acids in the aqueously altered Orgueil meteorite. However, amines may be produced by the decomposition of their corresponding amino acids by decarboxylation, a process that may explain the large abundance of methylamine in Orgueil. Similar to the molecular differences found in the amino acid abundances of Orgueil and Murchison, the higher amine content in Orgueil than in Murchison suggest that their parent bodies are chemically different and faced distinctive degrees of aqueous processing [3]. However, it is difficult to assess whether the differences between Orgueil and Murchison reflect primarily

parent body differences or effects of the more extensive aqueous alteration in Orgueil. The difference in molecular abundance between amines and amino acids in Orgueil and Murchison may be explained by two different, but not mutually exclusive, hypotheses: a) the CI parent body (which has been conjectured to be fragments of comets or extinct cometary nuclei [2,3]) may be richer in aliphatic amines relative to amino acids and their molecular precursors than the CM parent body; and b) aliphatic amines are more resistant to the aqueous processes that result in the depletion of amino acids in meteorites.

The lower polarity of amines may have aided their survival in water-rich CI chondrites relative to the more polar amino acids. These compounds may also be more abundant in CI parent bodies. Continued analyses of amines and other organic classes in diverse meteorite groups will further illuminate the synthesis and development of these organic compounds.

References: [1] Sephton M. A. 2002. Nat. Prod. Rep. 19:292-311. [2] Campins H. Swindle T. D. 1998. Meteorit. Planet. Sci. 33:1201-1211. [3] Ehrenfreund P., Glavin D. P., Botta O., Cooper G., Bada J. L. 2001. Proc. Natl. Acad. Sci. U.S.A. 98:2138-2141. [4] Cobb A. K., Pudritz R. E. 2014. Ap. J. 783:140 (12pp). [5] Aponte J. C., Dworkin J. P., Elsila J. E. 2014. Geochim. Cosmochim. Acta 141:331-345. [6] Glavin D. P., Callahan M. P., Dworkin J. P., Elsila J. E. 2011. Meteorit. Planet. Sci. 45:1948-1972. [7] Sandford S. A., Bernstein M. P., Dworkin J. P. 2001. Meteorit. Planet. Sci. 36:1117-1133. [8] Burton A. S., Grunsfeld S., Elsila J. E., Glavin P. D., Dworkin J. P. 2014. Polar Sci. 8:255-263.

n.f.: Compound not found.

n.d: Value could not be determined due to coelution or limited amount of sample.