

ISOTOPIC COMPOSITIONS OF H, C, AND N IN C δ DIAMONDS FROM THE ALLENDE AND MURRAY CARBONACEOUS CHONDRITES; A. Virag⁺, E. Zinner⁺, R. S. Lewis^{*}, Tang M.^{*†}; ⁺McDonnell Center for the Space Sciences and Physics Dept., Washington University, St. Louis, MO 63130, USA; ^{*}Enrico Fermi Institute and Department of Chemistry, University of Chicago, Chicago, IL 60637, USA; [†]present address: Dept. of Management Science, University of Minnesota, Minneapolis, MN 55455, USA.

Sophisticated chemical isolation steps have been developed to isolate the carrier phases of exotic noble gas components in meteoritic materials [1-3]. Whereas C δ , the carrier of Xe-HL, consisting of extremely fine-grained diamond, was found in both CM2 and CV3 meteorites [4], C β and C ϵ (SiC), the carriers of Xe-S and Ne-E(H) have only been found in CM2 chondrites [2,5] and, if present in CV3 chondrites, must occur at substantially lower concentration. Here we report ion probe isotopic analyses of H, C, and N isotopes in C δ separates from the Murray CM2 and Allende CV3 carbonaceous chondrites, undertaken to look for any differences in the C δ from these meteorite classes. The N- and Xe-anomalies indicate that C δ is of presolar origin but curiously its carbon isotopic composition is within the terrestrial range. A hint of different components in C was indicated by Xe-measurements on Allende residues DK, DM, and DN [6]. The second goal was therefore to investigate whether these differences are accompanied by differences in other isotopic systems. The separation of C δ from all other phases of the Murray meteorite was described in detail by Tang and Anders [2]. Two Murray residues, CE and CN, and three Allende residues DK, DM and DN were analyzed according to their H, C, and N isotopic compositions. Si isotopes were measured only in Murray residue CE.

Sample CN was obtained by treating CE with H₃PO₄ at 220°C, followed by a mixture of HNO₃ and HClO₄ at 75°C. This procedure was used to dissolve residual spinels and other non-diamond materials. The tendency of C δ to form a stable colloid at pH>5 and to agglomerate into large flocs at pH<3 was used to fractionate the C δ D-series samples from each other. Three fractions, DK, DM, and DN, were separated by centrifugation at a pH > 3.7, pH 3.0-3.7, and pH <3 [6]. Sample Allende CJ was a C δ -residue obtained by a previous separation experiment [4].

Residue agglomerates of about 20 μ m were mounted on a gold foil together with terrestrial standard samples WU-amphibole (H/D), NBS-21 graphite (¹³C/¹²C), and 1-hydroxy-benzotriazol-hydrate (¹⁵N/¹⁴N). WU-amphibole was also used as standard for Si isotopic measurements. All isotopic measurements were made with a CAMECA IMS 3F secondary ion microprobe, detecting negative secondary ions produced by a Cs⁺-primary ion beam except for Si isotopes which were measured as positive secondary ions, sputtered with an O⁻-beam. D/H and ¹³C/¹²C measurements were performed according to McKeegan *et al.* [7]. Experimental details of the ¹⁵N/¹⁴N- and Si-isotope measurements can be found in Zinner *et al.* [8]. The Si isotopic composition in Murray CE is highly anomalous, very similar to that measured in coarser-grained SiC [8, 9]. The presence of SiC in Murray CE was also confirmed by TEM observation [10]. During the C isotopic measurements the ²⁸Si⁻/¹²C⁻ ratio was also measured in order to determine the maximum amount of SiC left in the C δ residues. The SiC content was evaluated by normalizing the measured Si⁻/¹²C⁻ ratios to that of the SiC standard. Since SiC of Murchison and Murray was shown to have $\delta^{13}\text{C}$ values of about +1250‰, even small amounts of residual SiC would strongly affect the measured $\delta^{13}\text{C}$ value. All isotopic compositions are normalized for instrumental mass fractionation and are given as δ -values relative to the usual terrestrial standards (SMOW, PDB, air, NBS-28).

The effect of terrestrial contamination has to be evaluated carefully. Although contamination during ion probe analysis from the residual gas in the sample chamber probably is not significant under our analysis conditions, H isotopic exchange during sample preparation is a distinct possibility. The residues were treated with strong acid solutions at high temperatures which can lead to deuterium exchange [11] and perhaps changes in the H and N concentrations. Titration data [6 and unpublished] show that part of the H (H/C = .007) is acidic (apparently in the form of COOH groups) and thus readily exchangeable with H from water. In addition, C δ forms a very bulky gel in water [6 and unpublished]. Thus, samples could have adsorbed humidity during storage in air prior to analysis. An indication for this was given by the fact that in several samples the first analyses on a given spot yielded normal D/H ratios whereas later analyses provided clear evidence for D excess. As a consequence, all quoted δD values represent only lower limits. There is the possibility of N contamination during the colloidal separation step of C δ in NH₃ [6]. Furthermore, Murray CE was treated with H₃PO₄ and a mixture of HClO₄ and HNO₃, yielding Murray CN. It is not known if this has an influence on the N-isotope composition. The effect of N from the residual gas during ion probe analysis on the N isotopic ratio was estimated from measurements of NBS-21 graphite and was found to be maximally 2.4 ‰, smaller than the precision of the $\delta^{15}\text{N}$ -measurements (see table 1). The chemicals used to prepare the residue samples did not contain carbon. Therefore, alteration of the ¹³C/¹²C-values can be ruled out.

A summary of the results is given in Table 1 which contains also the results of earlier measurements on

Allende separate CJ [12]. Cδ of Allende and Murray shows isotopic carbon compositions within the terrestrial range. The $\delta^{13}\text{C}$ values of the different Allende samples show no significant differences. The carbon isotopic composition of Murray CE also agrees very well with that of the Allende residues. Remarkably, there is a difference of 7.9‰ between Murray CE and CN. This means that the chemical treatment of CE yielding CN, intended to remove residual spinels and other impurities, also removed some heavier carbon. This could not have been only Cθ contained in spinels because Cθ is isotopically lighter ($\delta^{13}\text{C} = -50$ ‰). This difference between the two samples also cannot be explained by different amounts of SiC because the difference of the Si content is maximally 0.063 at.% corresponding to a shift in $\delta^{13}\text{C}$ of at most 0.8‰. The Si isotopes in CE indicate that Si is present in the form of SiC. If we assume that all Si is bound to C in both samples we expect that the true values of $\delta^{13}\text{C}$ for C are shifted by 2.5‰ or 2.2‰ for Murray CE and CN respectively. The Si concentration in the Allende D samples are an order of magnitude lower than in the Murray separates. The chemical form of this Si is still unknown.

All residues are depleted in ^{15}N . A significant difference between the Allende samples DK, DM, and DN was found for $\delta^{15}\text{N}$ which is, in addition to Xe-measurements [6] and previous $\delta^{15}\text{N}$ results [13], a further hint that Cδ contains several components, but no correlation of the $\delta^{15}\text{N}$ values with any other property of the samples has been established. There also is a difference in $\delta^{15}\text{N}$ values of CE and CN, but we do not know whether it is intrinsic or the result of the chemical history of the samples. The mean of the $\delta^{15}\text{N}$ values of the Allende and Murray residues agrees well with the $\delta^{15}\text{N}$ value of Cδ of -164 ‰ measured by R. S. Lewis *et al.* [13] in Allende CC but falls way short of the minimum of -375 ‰ measured by R. D. Ash *et al.* [14] in Allende CJ.

Cδ residues of Allende are enriched in Deuterium. All samples contain high amounts of hydrogen of about 10-40 at % which was estimated from the analysis of a graphite standard containing 45 ppm wt hydrogen. The new results, especially the $\delta^{15}\text{N}$ and δD values, support a presolar origin of Cδ. The $\delta^{15}\text{N}$ values of Allende residues DK, DM, and DN and the difference of the $\delta^{13}\text{C}$ -values of Murray residues CE and CN indicate that Cδ is heterogeneous. But because the chemical treatment of the samples may strongly affect the measured isotopic compositions, more detailed conclusions are not possible.

References: [1] Tang M. *et al.* (1988) *GCA* 52, 1221; [2] Tang M. and Anders E. (1988) *GCA* 52, 1235; [3] Tang M. and Anders E. (1988) *GCA* 52, 1245; [4] Lewis R. S. *et al.* (1987) *Nature* 326, 160; [5] Bernatowicz T. *et al.* (1987) *Nature* 330, 728; [6] Lewis R. S. and Anders E. (1987) *Lunar Planet. Sci. XIX*, 679; [7] McKeegan K. D. *et al.* (1985) *GCA* 49, 1971; [8] Zinner E. *et al.* (1987) *Nature* 330, 730; [9] Tang M. *et al.* (1987) *Lunar Planet. Sci. XIX*, 1177; [10] Bernatowicz T., private communication; [11] Kerridge J. F. and Chang S., (1988) *GCA* 52, 2251; [12] Carey W. *et al.* (1987) *Meteoritics* 22, 349; [13] Lewis R. S. *et al.* (1983) *Nature* 305, 767; [14] Ash R. S. *et al.* (1987) *Meteoritics* 22, 319.

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Table 1: Isotopic compositions of Allende and Murray Cδ separates

Sample	$\delta^{13}\text{C}$			C_{Si}		$\delta^{15}\text{N}$			δD		
	(‰)	1 σ_m	n	(at%)	1 s.d.	(‰)	1 s.d.	n	(‰)	1 s.d.	n
DK	-34.4 ± 0.8		10	0.030 ± 0.014		-129.7 ± 9.6		4	-		-
DM	-35.4 ± 1.9		8	0.018 ± 0.006		-169.1 ± 8.4		5	180.0 ± 11.2		4
DN	-35.1 ± 0.7		6	0.028 ± 0.004		-144.6 ± 7.7		7	-		-
CJ	-33.1 ± 2.3		3	-		$-165.0^* \pm 26.5$		3	283.7 ± 51.4		3
CE	-32.3 ± 0.7		14	0.197 ± 0.023		-199.2 ± 9.2		5	-		-
CN	-40.2 ± 1.4		12	0.173 ± 0.031		-145.4 ± 8.6		7	-		-

* For these measurements NBS-21 (assumed to have terrestrial N-isotopic composition) was used as standard
n.... number of agglomerates measured