

Isotopic and molecular analysis of Antarctic CR chondrites

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Introduction: The CR (Renazzo-type) chondrite has characteristic mineralogical and chemical compositions, showing the most pristine signatures of the solar system materials [e.g. 1]. The CR chondrite is generally enriched in heavy isotopes such as hydrogen (D) and nitrogen (^{15}N) [2], including extremely D- and/or ^{15}N -enriched organic globules known as “hot spot” [3, 4]. In spite of its unique features in carbonaceous chondrite, organic molecular study is limited only for amino acids and amines. The hot water extract of some CR chondrites including EET92042 yielded amino acids (up to ~ 320 ppm) after hydrolysis [5]. However, soluble organic compounds in CR chondrites are largely unknown. Recently, many CHN compounds were identified in the methanol extract of the Murchison meteorite (CM2) using liquid chromatography/high resolution mass spectrometry (LC/HRMS) [6], in which homologous series of alkylated pyridines and imidazoles were predominant. In this study, Antarctic CR chondrites were examined for bulk isotopic compositions and molecular occurrence for methanol-soluble organic matter.

Sample and Methods: Three Antarctic CR chondrites (Y-002540, Y-8449 and A-881828) were used in this study. The interior part of the meteorite was powdered using an alumina mortar and pestle in a clean room. A part of the meteorite powder was subjected to an elemental analyzer-isotope ratio mass spectrometer to determine bulk carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotope values by combustion and bulk hydrogen (δD) isotope value by high-temperature pyrolysis. The sample powder (~ 20 mg) was sequentially extracted with hexane and methanol by sonication. The methanol extract was analyzed by nanoLC using a C18 column ($75\ \mu\text{m}$ i.d. \times 15 cm) coupled with a hybrid quadrupole-Orbitrap MS (Q-Exactive Plus, Thermo Scientific). The eluent was $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ with 0.1%(v/v) HCOOH at a flow rate of 200 nL/min and was electrically charged to ~ 3 kV followed by spraying into MS using nano electrospray ionization (nanoESI). The positive ions were collected in full scan mode from m/z 60 to m/z 600 with mass resolution of $\sim 140,000$ ($m/\Delta m$ at m/z 200).

Results and Discussion: Bulk C, H and N contents of the CR chondrites are shown in Table 1 with their stable isotopic compositions. The three CR chondrites have a similar $\delta^{13}\text{C}$ value ($\sim -5\%$), which is identical to the average value of CM chondrites [7]. In contrast, hydrogen and nitrogen are enriched in heavy isotope ($\delta\text{D} \sim +540\%$ and $\sim +160\%$), which are consistent with previous studies [2]. The nanoESI/HRMS revealed alkylated CHN and CHN_2 homologues in the Y002540 in the range between m/z 140 and 300 with the maxima of $m/z \sim 180$. In contrast to abundant alkylated pyridine ($\text{C}_n\text{H}_{2n-5}\text{N}$) and imidazole ($\text{C}_n\text{H}_{2n-2}\text{N}_2$) homologues in the CM chondrites such as the Murchison and Murray meteorites, the distribution of the alkylated N-heterocycles in the CR chondrite was different from that of the CM2 chondrites. The hydrogenated cyclic homologues (alkylated piperidines as $\text{C}_n\text{H}_{2n+1}\text{N}$) were more predominant in the Y002540 meteorite. Because the alkylated N-heterocycles could be produced from simple aldehydes (i.e. formaldehyde and acetaldehyde) and ammonia [6], the N-heterocycles of the CR chondrite were likely formed under more reducing conditions. The molecular distribution is consistent with the common occurrence of reduced metal in CR chondrites. The results of this study indicate that the redox conditions of meteorite parent bodies could control formation pathways of extraterrestrial organic compounds probably during the aqueous alteration.

Table 1. Bulk contents and isotopic compositions of C, H and N of three Antarctic CR chondrites.

Meteorite	Carbon		Hydrogen		Nitrogen	
	wt%	$\delta^{13}\text{C}$ (‰, PDB)	wt%	δD (‰, SMOW)	wt%	$\delta^{15}\text{N}$ (‰, Air)
Y-002540 (CR)	0.89	-6.1	0.53	+467	0.072	+151
Y-8449 (CR2)	1.26	-4.8	0.52	+538	0.047	+145
A-881828 (CR2)	1.03	-4.9	0.56	+245	0.071	+163

References: [1] Krot A. N. et al. 2002. *MAPS* **37**:1451–1490. [2] Kerridge J. K. et al. 1985. *GCA* **49**:1707–1714. [3] Busemann H. et al. 2006. *Science* **312**: 727–730. [4] Hashiguchi M. et al. 2015. *Geochem. J.* **49**: 377–391. [5] Glavin D. P. et al., 2011. *MAPS* **45**: 1948–1972. [6] Naraoka H. et al. 2017. *ACS Earth Space Chem.* DOI: 10.1021/acsearthspacechem.7b00058. [7] Naraoka H. et al. 1997. *Geochem. J.* **31**: 155–168.