



Chiral molecules in space and their possible passage to planetary bodies recorded by meteorites

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ABSTRACT

We searched the ethanol extracts of the Murchison meteorite for propylene oxide (PrOx), the only chiral molecule discovered so far outside solar environments, and detected its likely derivative after isolation of the low boiling components of the extract. This compound is also chiral and, upon hydrolysis, produces propylene glycol (PrGl), the expected product of PrOx under these conditions. Both the PrOx derivative and PrGl were detected with variable enantiomeric excesses (*ee*) averaging at ~10% and to have the (R)(+) configuration, i.e., for the same optical isomer as for sugars in the biosphere and sugar derivatives in meteorites. Besides PrGl, the hydrolysates also contained homologous compounds and polymeric materials with the combined δD (‰) of +235 and +65, respectively, suggesting a yet unknown compositional complexity in meteorites. The occurrence of *ee* in interstellar PrOx cannot be ascertained with current spectroscopic methodologies, however, the overall data reported here would allow to imply it.

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1. Introduction

Carbonaceous chondrite meteorites may contain a large variety of organic molecules (e.g., Sephton, 2002; Schmitt-Kopplin et al., 2010; Callahan et al., 2011; Glavin et al., 2012; Koga and Naraoka, 2017), whose precursors have in several instances been traced to presolar environments (e.g., Pizzarello and Huang, 2005). That a number of these compounds are also chemical components of the terrestrial biosphere have led to discussions of whether their exogenous delivery might have aided the origin of terrestrial life. However, the stochastic abundances and distributions shown by all known organic components in meteorites, in contrast to the functional selectivity of life's molecules (Pizzarello, 2006; Burton et al., 2012), appeared at first to hinder the search of their likely prebiotic pathways.

Yet, at least one biomolecular trait was later found to be common to meteoritic as well as biological compounds and that is the presence in meteorites of chiral organic molecules carrying enantiomeric excesses (*ee*) (Cronin and Pizzarello, 1997). These *ee* have been found so far to be of the L-configuration for amino acids and amines while hydroxyacids and sugar derivatives have the D-configuration mimicking, albeit to a different degree, those

present in the biosphere and renewing the discourse about the possible importance of exogenous delivery to the early Earth of molecules essential for the origins of life (Pizzarello and Groy, 2011; Pizzarello et al., 2012; Pizzarello et al., 2010; Pizzarello and Yarnes, 2016; Cooper and Rios, 2016).

Until recently, no chiral molecule had been observed directly in space environments, either solar or presolar, and the recent gas-phase detection of propylene oxide (PO) in protostellar clusters of the Sagittarius B2 star-forming region by McGuire et al. (2016) was the first report of such molecule and a major step towards understanding the possible cosmic distribution of chirality. However, the enantiomeric ratios of this and other space molecules are not known and, so far, have not been possible to acquire with available spectroscopic methods.

We searched for PO in ethanol extracts of the Murchison (MN) meteorite by using their low-T transfer under vacuum and Gas Chromatographic–Mass Spectrometric (GC–MS) analysis, a method based on the low boiling point of PrOx (34 °C) relative to that of the ethanol solvent (78 °C), which was successful when tested with a standard. Although PO's high volatility made its measurements difficult, e.g., its injection in a GC–MS is detected *before* the solvent front, during a time usually not recorded by the detector (known as “solvent delay”), these near-solvent elutions of PrOx still allowed sufficient separation for the GC–MS analyses shown in Fig. 1 but prevented any attempt of isotopic measurements.

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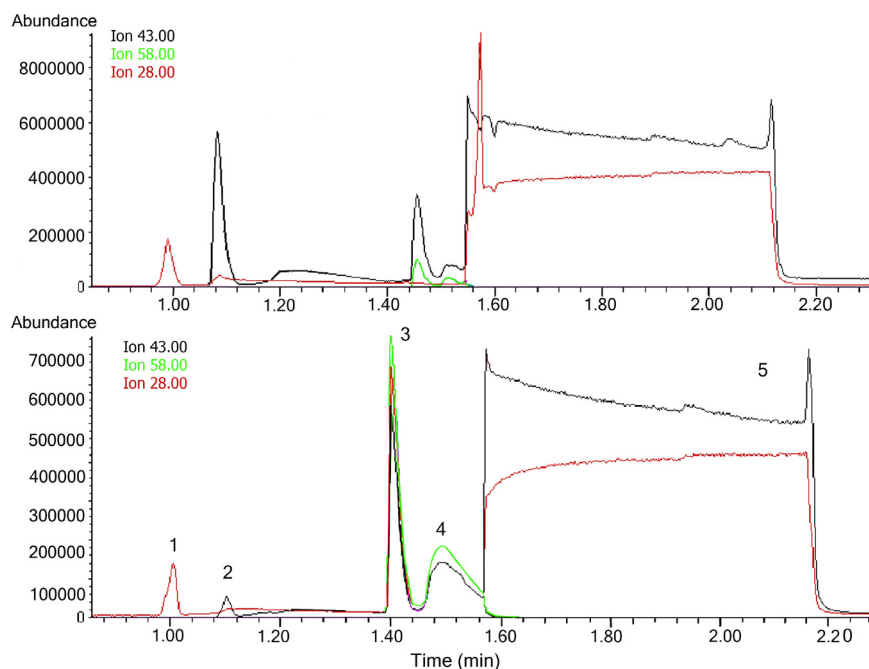
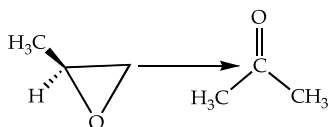


Fig. 1. Single ion traces from GC-MS analysis of a low T transferred Murchison ethanol extract (top) and a standard PrOx. 1: CO₂; 2: ethylene oxide (m/z 43, shown here for simplicity, is ~46% of base peak m.z. 44); 3: (R) PrOx, 4: (S) PrOx, 5: solvent ethanol. Here and in all figures, Abundances refer to arbitrary units. (For interpretation of the colors in the figure(s), the reader is referred to the web version of this article.)

PrOx is a very reactive molecule that can easily isomerize, i.e., change into a compound with the same chemical formula but different structure via C–O bond breaking and H-atom shifts (Parker and Isaacs, 1959; Dubnikova and Lifshitz, 2000). There are several known compositional isomers of PrOx: acetone, shown in the scheme below, methyl vinyl ether, propanal, allyl alcohol and trimethylene oxide.



These isomers were searched for in the meteorite extracts' chromatograms and both the one with boiling point similar to that of PrOx, as methyl vinyl ether (b.p. 35–36 °C), and four others either have unambiguously different molecular spectra (see also the National Institute of Standards: NIST Chemistry Web Book) or showed different retention times upon injection of standards. Between these, only propanal was detected, with elution time past the solvent peak, a detection suggesting that other aldehydes may be present in MN as previously seen in CR2 meteorites (Pizzarello and Holmes, 2009).

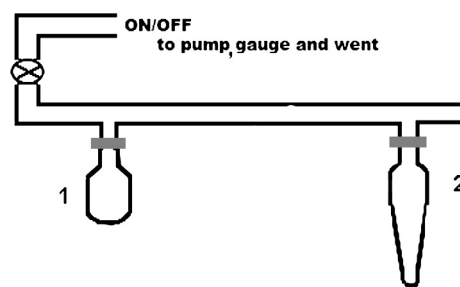
However, injection of standard acetone (b.p. 56 °C) showed this compound to have both a spectrum and eluting time similar to those of PO. Even though the injection of standards showed that acetone could show partial resolution from PO at lower injection temperatures (29 °C), elute after (S) PrOx (Fig. 1) and was not detected in the meteorite extracts using the same conditions, in light of the elution shift of the detected PrOx derivative compared to PO, we have to assume that acetone, if present in the meteorite, could have altered the *ee* ratios determined in our chromatograms.

Because none of PrOx isomers are chiral or would behaved upon hydrolysis as PO, we hydrolyzed directly another low T transfer of MN ethanol extracts and searched for propylene glycol (1,2 propane-diol; PrGI), which is the expected hydrolytic product of propylene oxide, is chiral and could have formed during the water alteration phase known to have occurred in the asteroidal par-

ent bodies of this and similar meteorites (Zolensky and McSween, 1988; Takeuchi et al., 1993). PrGI is comparable to polyols, compounds carrying OH-moieties on every carbon but lacking a keto-, or aldehyde-group of sugars; they were first described in MN and Murray by Cooper in 2001 (Cooper et al., 2001), but using a derivatization step preparatory to GC-MS analyses that impeded chiral recognition while a more recent study (Cooper and Rios, 2016) did not search for possible *ee* in this particular diol.

We report here on the finding of both a PrOx likely derivative and PrGI in several samples of the MN meteorite and that both display variable *ee* of the (R) configuration. These detections were surprising because the detection of PrOx was not expected, in view of its high volatility, and PrGI *ee* seem to conflict with other results showing 4C and 5C sugar alcohols to be racemic in multiple carbonaceous chondrite meteorites (Cooper et al., 2001).

2. Experimental conditions



A MN fragment of ~2 g was obtained from the Center for Meteorite Studies at Arizona State University, freed of fusion crust and surrounding layers and split in half. Three larger fragments of 250–300 mg plus several smaller fragments of about 50 mg each were then chiseled from their centers. The larger samples were used for the search and separation of PrOx, while analyses of the smaller ones were used to measure the possible presence of PrGI *ee* and the variability of their distributions. Two of the larger fragments were powdered in an agate mortar and extracted in dis-

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