Organic indicators of alteration in the CR chondrites

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Introduction: Petrographic and mineralogical evidence indicates that the CR chondrites have been subjected to aqueous processes [1,2,3]. Such processes also play an essential role in the development of organic materials within carbonaceous chondrites [4] so that an understanding of the organic reactions that take place in hydrous environments is crucial when reconstructing the aqueous conditions that existed on the meteorite parent body. Under certain environmental conditions such as elevated temperatures and/or pressures, water can act as a solvent or reactant, enhancing organic transformations and reactions. A further complicating factor is that there is evidence to suggest that the CR chondrite parent body may have been subjected to a period of anhydrous heating [2].

This study intends to assess the macromolecular fraction of a suite of CR chondrites (Al Rais, Renazzo, EET87770 and Y790112) to better understand the effects of pre-terrestrial alteration on the CR parent body.

Experimental: Whole rock meteorite samples were powdered and ultrasonically extracted with a 93:7 dichloromethane/methanol mixture (4 times 25 min with additional 15 min centrifugation following each sonication). The extract was removed and the residue dried. 25 mg of residue was loaded into a pre-cleaned quartz glass tube. The sample was flash pyrolysed at 610°C using a CDS 1000 pyroprobe (CDS Analytical, Oxford, PA) for 15 s in a flow of helium. The heating rate of pyrolysis was 20°C ms⁻¹. The interface was held at 260°C. The pyrolysate was analysed on an Agilent Technologies 5973 GCMS and the GC injector maintained at 250°C. GC conditions as in [5].

Results and Implications: Al Rais, Renazzo and Y790112 displayed an homologous series of C₁ through C₄ alkyl substituted benzenes (only up to C₃ in Y790112). All samples contained C₁ to C₄ alkylated benzenes. Unsubstituted benzene was evident in all except EET87770.

Naphthalene is the dominant compound in each sample. C₁ to C₃ alkyl substituted naphthalenes are present, with traces of C₄ substituted naphthalenes evident in Al Rais.

Phenanthrene (and its monomethyl substituted isomers), fluorene, fluoranthene and pyrene were found in all samples. Methylpyrenes, and further 4 ring compounds, including benzanthracene, were found only in Al Rais.

Compounds indicative of alteration: Several compounds have been identified that are indicative of an aqueous event in the CR chondrites’ pre-terrestrial history. Phenol was present in substantial quantities in all samples except EET87770 where it is present only in trace amounts. No alkylphenols were identified in any sample.

Using water as a donor, hydroxylation of toluene or other alkyl-substituted aromatics can lead to the development of phenols. It has been noted that in hydrothermal environments an intermediate product of this reaction may be benzaldehyde [6]. Benzaldehyde was found in all samples, again with the exception of EET87770. The ratios of toluene:benzaldehyde and toluene:phenol indicate that, if occurring, toluene transformation to phenol is most pronounced in Al Rais, a sample known to have endured more extensive aqueous alteration than the other samples analysed here [1]. Further to this acetophenone was detected in Al Rais and Renazzo.

The lack of phenolic compounds in EET87770 casts doubts on the hydroxylation of toluene as a reaction pathway for the generation of phenol, however several other factors may responsible for this deficiency. EET87770 contains a higher proportion of 2-methylnaphtalene, which is stable at high temperatures, relative to 1-methylnaphtalene. This suggests that EET87770 may have been subjected to a thermal event following aqueous processing, which would cause the dehydration of hydroxyl groups, and the loss of phenol.

In addition, EET87770 showed no traces of benzene, and thiophene was found to elute in its place. It is also the only sample to contain the S-heterocycle thienothiophene. Thiophenes have
been previously recorded in other carbonaceous chondrites [7]. In this study, benzothiophene, dibenzothiophene and methyl dibenzothiophene (not in Renazzo) are evident in all CRs. Their formation has been attributed to the incorporation of reduced inorganic sulphur [8]. At elevated temperatures, carbonyl groups and double bonds can break down and facilitate sites for sulphur incorporation. Similarly, hydroxyl groups can be dehydrated, generating a site for sulphur introduction [8].

A homologous suite of C_4 through C_{13} n-alkyl substituted thiophenes is present in Renazzo and Al Rais but interestingly is absent from EET87770 or Y790112.

A mild thermal alteration event on the EET87770 parent body was not entirely reductive since high molecular weight hydroxylated species were retained.

A temperature constraint can be placed on this event due to the presence of dibenzofuran. Present in all samples, including EET87770, it is stable even up to temperatures of 460 °C [9]. Dibenzofuran is a heteroatomic analogue of fluorene and is seen in all samples. Several other fluorene-derived compounds have been detected including 9H-fluoren-9-one, benzophenone, biphenylene and diphenylmethane.

Biphenyl is a prime component in each sample and traces of methyl- and dimethyl-biphenyls are evident. Interestingly, polychlorinated biphenyls (PCBs) have been detected in the macromolecule of Y790112. These may be indicative of terrestrial contamination [10]. In Y790112, this could result from weathering in the Antarctic environment by melt-waters rich in salts. However, the 2 ring chlorine compound o,p’-DDE has been found in the non-Antarctic chondrite Al Rais. The origin of this chlorine-bearing compound remains undetermined.

Few nitrogen-bearing compounds were detected. Benzonitrile and the isomers of naphthalencarbonitrile were present in all samples but Renazzo. These compounds are significant since their formation may be intimately linked with the liberation of macromolecular-bound organic nitrogen during parent body aqueous alteration [11].

Conclusions: The organic components present within the macromolecular fraction of the CR chondrites suggest a complex pre-terrestrial history. All indicate a period of aqueous alteration that has resulted in the oxidation of organic compounds. However, EET87770 may have been subjected to a period of anhydrous heating.