

COMPARATIVE IODINE GEOCHEMISTRY OF EARTH AND MARS: A POSSIBLE BIOMARKER?

J. D. Gilmour, J. A. Whitby and G. Turner. Dept of Earth Sciences, University of Manchester, Manchester M13 9PL, United Kingdom. Email jamie.gilmour@man.ac.uk

Introduction: Terrestrial iodine geochemistry is dominated by processes involving life. The details of the mechanisms involved are not well known, but their ultimate effects are to incorporate iodine into marine sediment and release methyl iodide to the atmosphere [1]. As a consequence, the I/Cl ratio of seawater has been reduced by a factor of ~ 40 over geological time [2]. Furthermore, mobilisation of iodine during diagenesis and metamorphism produces pore waters enriched by factors as high as 10^4 in I/Cl ratios over seawater that cannot be accounted for by evaporation [3]. This signature is readily detected in terrestrial ground waters, and its effect should also be recorded in aqueous alteration products.

It is thus expected that iodine geochemistry would be radically different from the terrestrial system on a planet on which life had never evolved. Whether the

converse is true, that life always alters iodine geochemistry, is less certain.

Two effects can be distinguished. First, elevated concentrations of iodine may be associated with minerals that contain other traces of extinct life. Secondly, high iodine concentrations (or I/Cl ratios) of circulating waters, determined either directly from fluid inclusions or indirectly by analysis of aqueous alteration products, may indicate a contribution from once-living organisms to the water's source region.

Here we discuss some of our data from previous studies of SNC meteorites in this context and outline some of the outstanding problems that must be addressed before definitive conclusions can be reached.

Results and Discussion: Iodine, bromine and chlorine all produce noble gas isotopes after neutron irradiation. For this reason, noble gas analysis of neutron irradiated samples (the method employed here) is the most sensitive available method of determining halogen ratios.

ALH84001 Carbonate: Carbonate decrepitation was identified in step heating analysis of irradiated whole rock samples of ALH84001 through the evolution of carbon dioxide (fig 1.). This coincided with a significant release of iodine-derived $^{128}\text{Xe}^*$ that was not observed in samples that did not evolve CO_2 (and so is unlikely to represent terrestrial contamination). We attributed this release to iodine associated with the carbonate and calculated a bulk iodine concentration in carbonate of ~ 0.5 ppm in this $20 \mu\text{g}$ sample [4]. (For comparison, the bulk iodine concentrations of the whole rock samples varied between 10 and 40 ppb). There was some evidence of a decrease in iodine concentration in carbonate from ~ 2.5 ppm in the first release to ~ 400 ppb in the second. While it is possible that xenon diffusion contributed to this apparent gradient, variation in iodine concentration from centre to rim of a carbonate rosette is expected given the well known major element zoning.

Average iodine concentrations of deep sea carbonates and continental limestones are 30 ppm and 2.5 ppm respectively [5]. However, while biological activity is implicated in their formation, these samples are not analogues of ALH84001 carbonates. Furthermore, an elevated iodine concentration in Martian carbonates may reflect parent waters not depleted in iodine by the mechanisms operating on Earth. Thus the observed iodine concentration need not be attrib-

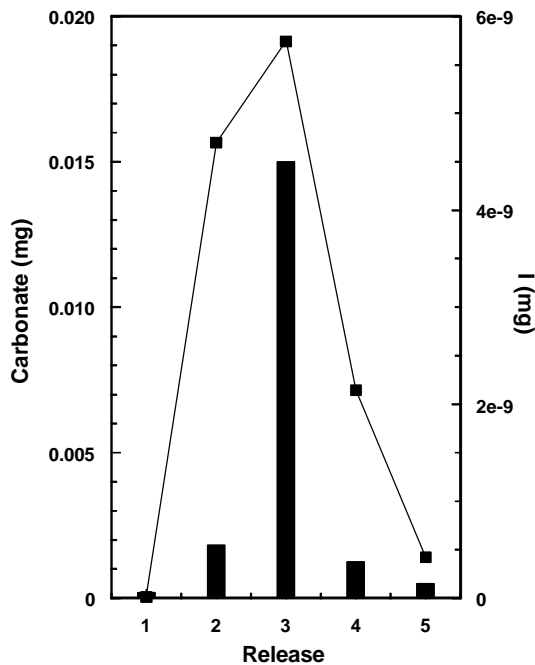


Figure 1: Low temperature release profiles of carbonate (bars: measured as CO_2) and iodine (line: measured as $^{128}\text{Xe}^*$ after neutron irradiation) during filament step heating of ALH84001. No iodine derived gas was observed in releases from the equivalent temperature steps of samples that did not contain carbonate. Data from [4].

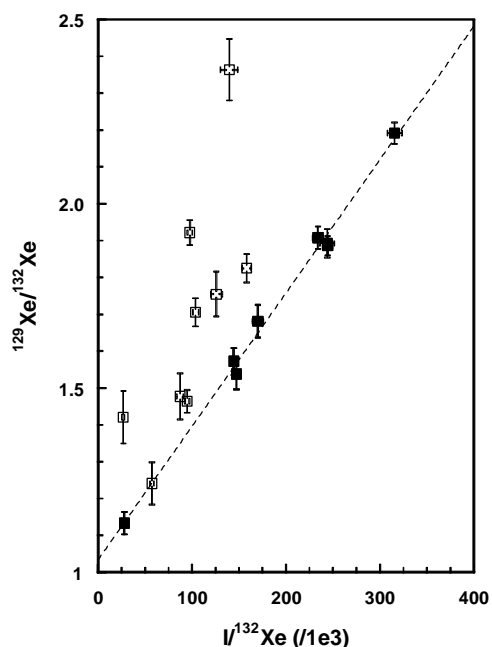


Figure 2: A correlation between iodine and Martian atmospheric $^{129}\text{Xe}_{\text{XS}}$ is observed in low temperature releases during step heating of water-treated Nakhla (solid symbols). Treatment with HNO_3 (before irradiation) destroys the correlation without removing the Martian atmospheric xenon (open symbols).

uted to the action of life.

Nakhla Low temperature releases in step heating of Nakhla reveal a correlation between iodine and excess ^{129}Xe from the Martian atmosphere (Fig. 2). This correlation was destroyed, apparently by removal of iodine, when a second aliquot of the same sample was etched with acid [6]. The correlation corresponds to a $^{129}\text{Xe}_{\text{XS}}/\text{I}$ ratio of 3.6×10^{-6} .

Water in equilibrium with the present day Martian atmospheric xenon partial pressure would contain $4 \times 10^{-11} \text{ cm}^3 \text{ STP g}^{-1} \text{ }^{129}\text{Xe}_{\text{XS}}$. Thus, if the Xe/I ratio represents unfractionated Martian groundwater, its iodine concentration was ~ 60 ppb. This is very low, in fact comparable to modern terrestrial seawater. However, to accommodate all the $^{129}\text{Xe}_{\text{XS}}$ associated with this correlated component in trapped fluid would require the meteorite to be $\sim 5\%$ water [7]. Thus the actual trapping mechanism and the fractionation between xenon and iodine it introduced are unknown.

The close correlation between iodine and xenon requires that they be similarly distributed within a common phase. Bulk incorporation is precluded since removal of iodine during etching would require dis-

solution of the host phase, inevitably removing trapped xenon as well. Surface trapping of both iodine and xenon may explain the observed similar release patterns for iodine-derived and Martian atmosphere-derived xenon and the preferential mobilisation of iodine during the acid etching process. Iodine adsorption on mineral surfaces depends on pH and the iodine oxidation state, but is associated with Fe^{2+} sites [8]. Thus oxidation of mineral surfaces during the HNO_3 etching process may explain the observed loss of iodine. This suggests that (this) xenon component is sited close to the surface of its host mineral and retained during the acid etching. Since olivine was dissolved during our acid etch, we believe the most likely site for this component is the surface of pyroxene grains. This is consistent with the conclusion of our previous analyses of mineral separates [7].

Discussion:

Although the global effect of life on iodine geochemistry is well known, the detailed mechanisms by which iodine enrichment occurs and the evolutionary benefit that accrues to the organism have not been determined. Enzymes (haloperoxidases) that catalyse halogenation of hydrocarbons have been identified, and a link with nitrogen fixation has been suggested, but the range of halogen-bearing metabolites found cannot as yet be accounted for [8].

It is also not known when organisms capable of producing iodine-rich metabolites first evolved. Those species in which iodine enrichment has been measured are eukaryotes (e.g. red, brown, green algae), but halometabolites have been identified in bacteria [8] and the I/Cl ratio in 3.2 Ga seawater [2] is less than the CI value, perhaps suggesting that iodine concentration into sediments commenced early in the evolution of life.

It is thus not yet clear whether biotic activity is required to explain the iodine concentrations observed in either ALH84001 carbonate or Nakhla. Future work on terrestrial analogues and the iodine geochemistry of the Archean may provide an answer.

References: [1] Wong, G. T. F (1991) *Rev. Aq. Sci.*, 4, 45-73. [2] Channer D. M. DeR et al. (1997) *Earth Planet. Sci. Lett.*, 150, 325-335. [3] Worden, R. H. (1996) *Chem. Geol.*, 60, 259-274. [4] Gilmour, J. D. et al. (1998) *Geochim. Cosmochim. Acta*, 62, 2555-2571. [5] Muramatsu, Y. and Wedepohl, K. H. (1998) *Chem. Geol.*, 147, 201-216. [6] Gilmour, J. D. et al. (1998) in: *Martian Meteorites: Where do we stand and where are we going*, *LPI Cont. no 956*, 18-19. [7] Gilmour J. D. et al., (1999) *Earth Planet. Sci. Lett* (in press). [8] Furhman, M. et al., (1998) *App. Geochem.*, 13, 127-141. [8] Neidelman S. L. and Geigert J. (1986) *Biohalogenation*, Ellis Horwood Ltd., Chichester.