NITRATES IN SNCs: IMPLICATIONS FOR THE NITROGEN CYCLE ON MARS;

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Nitrogen is the second most abundant constituent of the martian atmosphere, after CO_2, present at a level of *ca.* 2.7%. Several authors have hypothesised that earlier in the planet's history, nitrogen was more abundant, but has been removed by processes such as exospheric loss from the atmosphere [*e.g.* 1]. However, an alternative sink for atmospheric nitrogen is the regolith; model calculations have predicted that, *via* the formation of NO_x, HNO_2 and HNO_3 in the lower layers of the martian atmosphere, the regolith might trap nitrite and nitrate anions, leading to the build-up of involatile nitrates [2]. Integrated over 4.5×10^9 yr, such a mechanism would contribute the equivalent of a layer of nitrates up to 0.3 cm thick distributed across the martian surface [2]. Features in thermal emission spectra of the surface of Mars have been interpreted tentatively as emanating from various anions (carbonates, bicarbonates, sulphates, *etc.*), and the presence of nitrates has also been addressed as a possibility [3]. The identification of carbonates in SNC meteorites has allowed inferences to be drawn concerning the composition and evolution of the martian atmosphere in terms of its carbon isotope systematics [4]; if nitrites, nitrates, or other nitrogen-bearing salts could be isolated from SNCs, similar conclusions might be possible for an analogous nitrogen cycle.

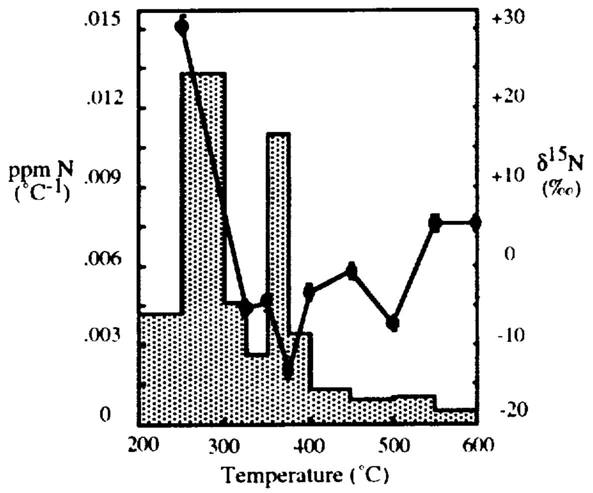
Nitrates are unstable, being readily soluble in water, and decomposed at temperatures between 50°C and 600°C, depending on composition. Any nitrates present in SNCs might be removed during ejection from the planet's surface, passage to Earth, or during the sample's terrestrial history, by weathering *etc.* The same might have been said for carbonates, but pockets of shock-produced glass (lithology C) from within the EET A79001 shergottite and bulk samples of other SNCs contain this mineral, which did apparently survive [5-7]. Nitrates occuring within the glassy melt pockets of lithology C in EET A79001 might likewise be protected. Lithology C glass was therfeore selected for nitrate analysis, first by non-destructive infra red spectroscopy, and then by stepped combustion.

Infra red spectroscopy: several nitrates (both AnalaR-grade chemicals and natural minerals, powdered in a matrix of KBr) were subjected to FTIR, in order to provide a calibration against which lithology C glass could be matched. In all cases, the most prominent feature in the spectrum was a very sharp singlet peak at approximately 1375 cm^{-1}. Comparison of the standard nitrate spectra with those from carbonates indicated that the two types of salt were well resolved, with the strongest carbonate feature at *ca.* 1425 - 1450 cm^{-1}. Analysis of powdered lithology C black glass yielded a spectrum with several features: a sharp peak at 1375 cm^{-1}, and a doublet between 1400 and 1450 cm^{-1}. The data imply the presence of both nitrates and carbonates in the specimen, although the technique used gave no indication of the relative concentrations of the two species.

Stepped combustion: having ascertained that nitrates might indeed be present in lithology C glass, *ca.* 5 mg of material were subjected to a high-resolution stepped combustion analysis, using FINESSE, a new gas source mass spectrometer, capable of measuring the nitrogen isotopic composition of samples as small as 100 pg; results for the combustion between 200°C and 600°C are shown in the figure. The yield histogram can be interpreted as indicating the presence of two components with discrete combustion/decomposition temperatures. The least stable component (≈ 1 ppm), labile below *ca.* 320°C, is not isotopically well-defined due to an analytical problem, but has a $\delta^{15}N$ between -8‰ and +30‰. The second component (≈ 0.25 ppm) is released between 350°C and 400°C, with $\delta^{15}N$ *ca.* -14‰. The first component might be a mixture of fractionated terrestrial atmosphere with organic material, whilst the higher temperature species, which had a lower atomic C/N ratio, could also be organic in origin or the predicted nitrates. Above 400°C, nitrogen is released in gradually decreasing quantities with generally increasing nitrogen isotopic composition.

A second sample from EET A79001, enriched in white druse (carbonates and sulphates) of postulated martian origin, also exhibited a release of nitrogen with $\delta^{15}N$ *ca.* -14‰ at temperatures below 400°C [8]. There has, however, been some discussion on the provenance of the salts, whether they are indeed martian, or simply Antarctic weathering products. The recognition of carbonates in Nakhla [6] argued against a terrestrial origin for the salts, and the same could also be applied to any nitrates present.

Implications: there appear to be two nitrogen-bearing phases in Lithology C from EET A79001 released below 400°C, either of which might be the nitrate identified by FTIR, and both of which have $\delta^{15}N$ values much lower than that estimated for the martian atmosphere [5]. It might therefore be inferred that the nitrates were not formed by direct implantation into the regolith of nitrogen (as NO_x, HNO_2 or HNO_3) from the current atmosphere. An alternative source of nitrogen for the nitrates is from recycling of martian "mantle" nitrogen into the regolith, although the mechanism for the reaction is not clear.



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