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Oxygen isotopic composition of carbonate in the Nakhla meteorite: Implications for the hydrosphere and atmosphere of Mars

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Abstract—We have located small areas of siderite within the mesostasis of the Nakhla meteorite. High concentrations of Mn (up to ~50% rhodochrosite) and elevated D/H ratios indicate that the siderite is not a terrestrial alteration product. The isotopic composition of oxygen in the siderite has been determined with the Manchester ISOLAB 54 ion microprobe. The siderite has $\delta^{18}O = +34 \pm 1‰$, which is higher than any other martian carbonate yet reported. If the $\delta^{18}O$ value is the result of equilibration with water at $<60°C$, then the carbonate could have formed from CO_2/H_2O produced during the degassing of Mars, and not modified subsequently isotopically. Formation from a water rich fluid at $>60°C$ requires that the fluid was heavy isotope enriched relative to fluids produced during planetary degassing. An enrichment of 8–15‰ is consistent with theoretical outgassing models that are able to account for enhancements of $\Delta^{17}O$ in martian alteration products. Estimated deposition temperatures would be raised to 80–170°C. The effect of a global scale fixation of martian CO_2 as carbonate operates in the opposite direction and could lead to a reduction in $\delta^{18}O$ of the martian hydrosphere of a few permil. *Copyright © 2000 Elsevier Science Ltd*

1. INTRODUCTION

The martian meteorites are igneous rocks, some of which contain trace quantities of secondary minerals that are potentially of great importance for understanding the aqueous geochemistry of Mars. Secondary phases have been observed in several of the martian meteorites, the most conspicuous example being ALH84001 (Mittlefehldt, 1994). Secondary alteration—in the form of films of reddish-brown alteration product—is readily apparent in optical examination of Nakhla and Lafayette. Aqueous alteration of Nakhla and Lafayette has been described by Gooding et al. (1991) and Treiman et al. (1993), respectively. Smectite clays, ferrihydrite, and magnetite were identified among the alteration products in Lafayette. In Nakhla, Gooding et al. tentatively identified smectite in the veins of reddish-brown material and demonstrated its preterrestrial origin (because it is truncated by fusion crust). They also reported other secondary phases in Nakhla: a Ca-carbonate (probably calcite), a Ca-sulphate, Mg-sulphate, and NaCl. Carbonates (possibly calcite) have been also reported in EET79001; however, Jull et al. (1992) suggest that the carbonate is of terrestrial origin, or has at least suffered terrestrial contamination, on the basis of its ^{14}C activity. Calcite has been observed in Chassigny (Wentworth and Gooding, 1994), although its extraterrestrial origin remains unproven. Chatzitheodoridis and Turner (1990) reported the occurrence Fe-Mn carbonate in Nakhla. Recently, Bridges and Grady (1999) have argued that the siderite was derived by melting of martian sediment. Very small amounts of Fe-Mn carbonate have also been reported in Lafayette (Vincenzi et al., 1997).

Oxygen isotope data for these secondary phases are valuable, as many exchange processes between different reservoirs of

martian volatiles will introduce isotope fractionation. Isotopic data are thus crucial parameters of any comprehensive model of martian volatile evolution. Processes expected to fractionate isotopes include formation of minerals from fluid reservoirs at different temperatures, water–rock isotope exchange, and evolution of the martian atmosphere through time. Current data, from spacecraft, earth-based spectroscopic observations, and meteorites, indicate that atmospheric H, C, and N are enriched in their heavy isotopes. This enrichment may be the result of atmospheric loss to space (e.g., Nier et al., 1976; Nier and McElroy, 1977; Owen et al., 1988; Wright et al., 1990; see also review by Owen, 1992). It is desirable to know whether atmospheric oxygen is similarly heavy isotope enriched; lack of an enrichment would indicate buffering of atmospheric oxygen by another oxygen reservoir (e.g., polar cap ice, subsurface H_2O/ice, isotopic exchange with crust through hydrothermal activity).

Most previous oxygen isotopic studies of the carbonates in martian meteorites have used dissolution in phosphoric acid. Clayton and Mayeda (1988) used oxygen isotope data from calcite in EET79001 to infer possible ratios of outgassed H_2O/CO_2 for Mars. Wright et al. (1988) studied both EET79001 and Nakhla; their Nakhla data indicated the presence of carbonate, with $\delta^{18}O$ ranging from 22 to 30‰ in different analyses. Jull et al. (1995) also studied Nakhla; their data also indicated the presence of an isotopically heavy carbonate, but showed a large scatter and the presence of ^{14}C, which suggested at least some terrestrial contamination.

We have used the Manchester ISOLAB 54 ion microprobe to study Fe-Mn carbonates in Nakhla. In contrast to earlier isotopic studies of Nakhla (e.g., Wright et al., 1988; Jull et al., 1995), the ion microprobe allows us to study individual mineral grains; interpretation of the oxygen isotope data may then be aided by both petrographic and chemical (electron microprobe) observations. This is important as Nakhla contains different types of carbonates, possibly including terrestrial contamina-

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Table 1. Chemical analysis of carbonate grains.

Grain	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	FeO	MnO	CaO	MgO	Na_2O	K_2O	P_2O_5	Cl	CO_2	Total
C1	3.1	0.0	0.0	0.0	47.7	4.5	1.5	2.8	3.2	n.a.	4.1	n.a.	37.4	104.2 NHM
C2	1.4	0.0	0.0	0.1	51.7	7.3	0.5	1.7	2.6	n.a.	1.7	n.a.	39.4	106.3 NHM
C2	0.3	0.0	0.0	0.0	42.6	14.8	0.8	0.9	1.9	n.a.	0.6	n.a.	37.5	99.3 NHM
C3	0.3	0.2	0.0	0.2	47.8	4.7	0.7	3.4	0.8	n.a.	1.2	n.a.	37.1	96.4 NHM
C3	1.7	0.1	0.0	0.0	49.8	2.8	0.4	4.3	1.7	n.a.	1.2	n.a.	38.0	99.9 NHM
C4	5.0	0.0	0.1	0.0	22.1	20.7	2.1	5.8	1.4	0.3	0.0	1.0	35.6	96.3 W
C8	4.8	—	—	0.1	48.6	1.0	2.7	9.9	0.4	—	—	—	43.6	111.1 NHM
C8	4.0	0.0	0.0	n.a.	47.9	1.1	2.0	7.2	0.8	0.1	0.0	0.3	39.8	103.3 EDX
C8	4.8	0.0	0.0	n.a.	45.1	1.1	2.8	9.5	0.7	0.0	0.0	0.3	41.2	105.4 EDX
C8	5.4	0.0	0.0	n.a.	50.1	1.3	2.4	7.7	0.7	0.0	0.0	0.3	42.0	109.9 EDX
C8	5.6	0.0	0.0	n.a.	44.8	1.1	2.7	9.1	1.0	0.0	0.0	0.2	40.5	105.0 EDX
C8	1.6	0.0	0.0	n.a.	34.6	0.8	2.4	16.4	0.8	0.0	0.0	0.1	41.7	98.3 EDX
C8	2.6	0.0	0.0	n.a.	41.4	1.0	2.3	10.8	0.5	0.0	0.0	0.1	39.8	98.5 EDX
C9	1.5	—	—	0.1	36.2	0.9	2.9	12.2	0.2	0.0	—	—	38.5	91.0 NHM
C9	3.0	0.0	0.2	n.a.	41.3	1.0	2.3	10.3	0.6	0.0	0.0	0.2	39.4	98.4 EDX
C9	0.2	0.0	0.0	n.a.	32.5	0.8	2.7	16.4	0.8	0.0	0.0	0.0	40.7	94.0 EDX
C9	5.5	0.0	0.4	n.a.	46.9	1.2	2.4	7.1	0.4	0.0	0.0	0.1	39.6	103.6 EDX
C9	1.8	0.0	0.0	n.a.	33.4	0.8	2.9	15.6	0.0	0.0	0.0	0.1	40.2	94.8 EDX
C10	0.3	0.0	0.0	n.a.	32.6	1.1	2.2	13.7	0.0	0.1	0.0	0.1	37.4	87.5 EDX
C10	1.6	0.0	0.0	n.a.	41.5	1.3	1.2	10.1	0.9	0.1	0.0	0.1	38.5	95.2 EDX
C10	0.8	0.0	0.0	n.a.	35.5	1.1	1.3	14.7	0.5	0.0	0.0	0.1	39.6	93.5 EDX
C10	1.7	0.0	0.2	n.a.	40.2	1.2	2.1	11.4	0.8	0.0	0.0	0.1	39.9	97.6 EDX
C10	0.2	0.0	0.0	n.a.	33.2	1.0	2.5	15.6	0.4	0.1	0.0	0.0	40.1	93.1 EDX
C10	0.9	0.0	0.3	n.a.	40.4	1.2	1.7	8.6	1.1	0.1	0.0	0.2	36.8	91.4 EDX

CO_2 calculated assuming all metals present as carbonates.

tion; this may explain the large scatter in acid–dissolution results. A preliminary report of this work is given in Saxton et al. (1997).

2. SAMPLES AND METHODS

2.1. Samples

We studied three polished thin sections between 1989 and 1998. The first carbonates (C1 to C4) were discovered in a polished thin section prepared from sample BM 1913, 369 (Chatzitheodoridis and Turner, 1990). The first two occurrences of carbonate found (hereafter C1 and C4) were found using optical microscopy and EDX/WDS analyses. Because these occurrences of carbonate appeared orange in transmitted light and were Mn-rich, more examples were sought by setting a spectrometer of the Camebax electron probe (see below) to the Mn Kα line and connecting its output to a loudspeaker, while the sample was searched optically in transmitted light. In this way it was easy to distinguish between orange carbonate (containing Mn) and the more abundant iddingsite. Carbonates C2 and C3 were found by this procedure.

In 1998, two more Nakhla polished thin section (P7635 and P7403) were kindly supplied by Dr. John Bridges of the Natural History Museum, London. These contained more examples of Fe-carbonate, of which three were analysed for oxygen (C8 in P7635 and C9 and C10 in P7403). The carbonates in these sections were located by examination of back-scattered electron images in conjunction with EDX analysis.

Chemical Analyses

Chemical analyses of the carbonates have been obtained using a variety of instruments. The earliest work (on C1 and C4) was performed with the JEOL 6500 electron microscope, which is equipped with an EDX analysis facility, and also the Cameca Camebax electron probe at the University of Manchester. Most observations and analyses were made with the JEOL SEM and EDX, partly because this provided the easiest way of studying the grains at high spatial resolution, and also because WDS facilites were not available at Manchester in mid-1998, when much of the work described here was done.

The Cameca SX 50 electron probe at the Natural History Museum, London, has also been used. This instrument was used for analyses of C8 and C9 in Table 1 (which were analysed by Dr. J. C. Bridges), and also for analyses of C1 and C3. The analyses of C1 and C3 were made after ion probe analysis on the remaining carbonate that still retained a flat polished surface. Analysis was performed using the Cameca-supplied PAP routine, which assumes C and O to be the unmeasured elements.

Oxygen Isotope Analyses

Oxygen isotope analyses were made with the Manchester ISOLAB 54 ion microprobe (Saxton et al., 1996). A beam of Cs^+ ions was used to sputter the sample, producing a crater of diameter ~ 10 μm. Low energy secondary ions are admitted to the double focusing mass spectrometer, and ^{16}O, ^{17}O, and ^{18}O are measured simultaneously using a Faraday collector and two CDS multipliers, respectively. A piece of siderite (composition $Cc_1Mg_9Sd_{74}Rh_{15}$, which is intermediate to carbonates C1 and C3) was used as a day-to-day standard. Carbonates C8, C9, and C10 contain more Mg and less Fe, but previously we have demonstrated that negligible matrix effect is observed between magnesite and siderite with our ion microprobe (Saxton et al., 1998). Oxygen isotope measurements were made from 21 to 24

March 1997, 16 to 18 April 1997, and 8 to 14 July 1998. The 1s reproducibilities of $^{18}O/^{16}O$ for n of measurements of the siderite standard in each dataset were 1.1‰ (n = 14), 2.1‰ (n = 10), and 1.7‰ (n = 39), respectively. We assume the 1s uncertainty associated with any Nakhla carbonate measurement to be equivalent to the scatter of the standard measurements.

D/H Analyses

We also attempted to measure the D/H ratio of the carbonates by peak jumping between the nearly isobaric species ^{16}OD and ^{17}OH. The main aim of these measurements was to seek evidence of the high martian D/H ratio (up to five times terrestrial) and thus verify that the carbonates are not terrestrial alteration products. This pair of species yielded low count rates (6–17 cps for ^{17}OH), but was chosen as it did not require large (i.e., whole mass unit) jumps in mass at high mass resolution. The precise D/H ratio of our siderite standard is not known, but is assumed to be within a few percent of standard mean ocean waters (SMOW). Five measurements of the terrestrial siderite standard yielded mean $^{16}OD/^{17}OH$ = 0.42, 1s = 0.02 (for comparison, the expected ratio—in the absence of matrix effects and instrumental fractionation—would be 0.41 for a sample having both H and O of SMOW isotopic composition). Because we expect the OH^- signal to be derived from both the sample itself and also water deposited from the vacuum, the measured $^{16}OD/^{17}OH$ ratio may represent a mixture of these two sources; this would act to dilute a martian signature in the Nakhla siderite. Therefore, some measurements were also made with a pulsed Cs^+ beam having a duty cycle of ~30%. Pulsing the beam increased the OH/O ratios (by a factor of 1.4–2.6) in both cases. We interpret this as due to increased contamination from terrestrial water that accumulates on the spot while the beam is off. It was found that pulsing the beam made no significant difference to the $^{16}OD/^{17}OH$ ratio from the terrestrial standard, but reduced the ratio from the Nakhla carbonates; for this reason we expect our reported values yield lower limits to the true D/H ratios of the Nakhla carbonate. We stress that no change in measured *oxygen* isotopic ratio of the siderite standard has been observed after allowing water to accumulate on the surface, although the $^{16}OH/^{16}O$ ratio was doubled.

3. CARBONATE PETROGRAPHY, CHEMISTRY, AND ISOTOPIC COMPOSITION

All the carbonates so far found occur in the mesostasis. Fe-rich carbonate is a minor phase; we estimate that Fe-rich carbonates constitutes on the order of 30–100 ppm of the rock. Some examples are shown in Figure 1. They mostly occur as blocky grains or masses—typically 5–15 μm in size—among the mesostasis minerals. Only one example, C4, has a texture that suggests it may be fracture filling. The texture of the carbonate is generally different to that of the Fe-rich hydrated silicate (hereafter called rust; Gooding et al., 1991). In sections P7635 and P7403 we noted many occurrences of rust, but the rust occurred as thin veins cutting both mesostasis and cumulus minerals, and the vein thickness was less than that of the many of the carbonate "masses." In these two sections there are many examples of rust and carbonate occurring together; in these

instances, the rust is often a film between the carbonate and the surrounding minerals.

All occurrences of carbonate we studied are orange in transmitted light, suggesting some staining by ferric iron. The carbonates are too small ($\ll$thickness of the section) and too irregular in shape to determine satisfactorily whether the whole grain goes into extinction at once, and thus whether or not it is polycrystalline.

The carbonates are chemically heterogeneous, both within grains and between grains. High magnification backscattered electron (BSE) images show the grains have a mottled appearance, which energy dispersive X-ray spectroscopy (EDX) analyses show to be due to variations in cation chemistry on a scale of microns. Owing to the limited precision of the EDX results, at least some variation could be due to an admixture of an Fe-oxyhydroxide mineral such as goethite, rather than cation substitution in siderite. Nevertheless, we stress that, on the basis of the Cameca wavelength dispersive spectroscopy (WDS) results and the EDX totals, we are confident that the materials we analysed are predominantly carbonate and the amount of oxide, if any, is minor (less than ~10%). Assuming no ferric oxides, then the variation shown by C10 corresponds to variation between $Mg_{43}Cc_5Rh_2Sd_{51}$ and $Mg_{26}Cc_4Rh_2Sd_{68}$ over a distance of several microns. The "thick" end of area C1, where the ion probe analyses were obtained, is more Mn-rich ($Mg_3Cc_1Sd_{71}Rh_{26}$, average of nine EDX analyses) than the central "bar" where the WDS analyses were made, although one EDX analysis from the other end has the highest Mg content ($Mg_{19}Cc_2Sd_{72}Rh_7$). The variations in chemistry between grains are even larger than those within grains. All the Mn-rich examples occur in the first section studied, whereas the carbonates in natural history museum (NHM) sections P7635 and P7403 are predominantly Fe-Mg carbonates. The most Mn-rich carbonate, C4, contains ~50% rhodochrosite, but unfortunately was too small for ion probe analysis.

WDS analyses of the carbonates are shown in Table 1. A few spots show increased silicon and lower carbon, which we believe is due to fluorescence of surrounding silicate. The data for C8 and C9 are copied from Bridges and Grady (1999). The stoichometry from these analyses is our primary evidence that the analysed phases are indeed carbonate.

For C10 only EDX measurements made at Manchester are available (but the analysis totals are not significantly different to those obtained from C8 and C9). The oxygen isotope measurements are listed in Table 2. Excluding C8, the six measures are identical within error and yield mean $\delta^{18}O_{SMOW}$ = 33.8 ± 0.7‰ (error is $s/(n - 1)^{1/2}$). The lower apparent $\delta^{18}O$ of C8 is plausibly due to oxide contamination, which is expected to lower the apparent $\delta^{18}O$ of the carbonate for two reasons: first, goethite is lighter than carbonate with which it is in equilibrium (at 50°C, the difference is ~23‰, using fractionation factors from Yapp, 1987, and Carothers, 1988); second, the matrix effect we have measured for goethite will reduce the apparent $^{18}O/^{16}O$ ratio further still (the only Fe oxide minerals we have measured are magnetite and goethite, but we assume here that other Fe oxides will have similar matrix effects). We estimate that a 10% admixture of goethite would result in our underestimating the $\delta^{18}O$ of the siderite by ~5‰ if the carbonate formed at low temperature (<70°C). For the remainder of this
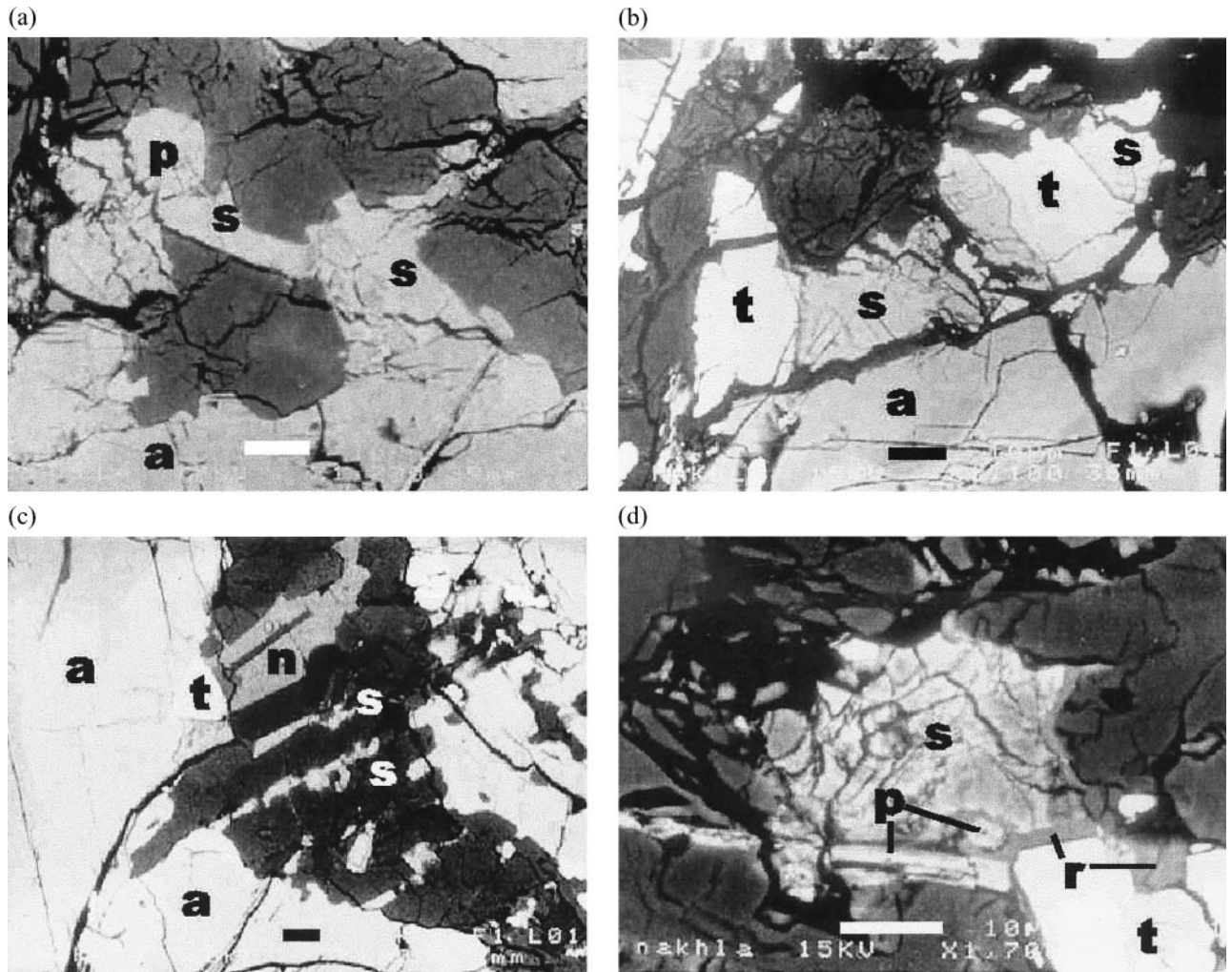
Fig. 1. Back-scattered electron images of four areas of siderite. All occur in the mesostasis. (a) C1, showing ion probe analysis crater at one end; (b) C3; (c) C4, Mn-rich siderite that might be filling fractures in mesostasis; (d) Fe–Mg-rich grain C10. C10 shows some mottling in the BSE image indicating it is chemically inhomogeneous. Note the films of rust partially surrounding grain C10, this may be interpreted either as rust replacing carbonate along grain boundaries or precipitation of rust on the surface of a cavity, followed by filling of the cavity with carbonate. Surrounding minerals are a = augite, n = anhydrite, p = phosphate, r = rust, s = siderite, t = Ti-bearing magnetite. All scale bars are 10 μm.

article we will assume no oxide contamination and take the carbonate $\delta^{18}O$ to be $+34$‰.

Our D/H measurements are listed in Table 3. $^{16}OD/^{17}OH$ from the Nakhla carbonate is consistently higher than from the

Table 2. Oxygen isotope analyses of carbonate grains.

Measurement	Mg	Ca	Sd	Rh	$\delta^{18}O$ SMOW
C1 spot 1	3	1	71	26	32.5
C1 spot 2	3	1	71	26	34.9
C1 spot 3	3	1	71	26	33.9
C3	10	1	81	8	35.3
C8	27	5	66	2	26.2
C9	38	5	55	1	31.2
C10	33	3	62	2	35.2

MgCaSdRh is average of several EDX analyses in area of ion probe craters.

terrestrial standard; the highest value is 2.4 times that from the standard. As noted previously, the true D/H ratio of the Nakhla carbonate may be >2.4 times terrestrial, owing to the possibility of some mixing with terrestrial water. Despite the uncertainties in the measurements, the clearly elevated ratio of D/H—relative to terrestrial—is our primary evidence that the Nakhla carbonates are indeed martian and not terrestrial contamination.

4. DISCUSSION

4.1. Carbonate Chemistry and Petrography

A variety of carbonate minerals has now been reported in the martian meteorites, but high Mn-carbonates appear to be restricted to Nakhla. Gooding et al. (1991) reported trace amounts of carbonate in Nakhla, but Ca appeared to be the only cation. This material was found as both globules and veins

Table 3. D/H analyses of carbonate grains.

Material	$^{16}OD/^{17}OH$ On	$^{16}OD/^{17}OH$ Pulsed
C8 (a)	0.84 ± 0.02	0.65 ± 0.03
C8 (b)	0.54 ± 0.02	0.53 ± 0.06
C9	0.83 ± 0.02	0.70 ± 0.04
C10 (a)	0.92 ± 0.03	0.70 ± 0.07
C10 (b)	1.00 ± 0.03	—
siderite standard	0.42 ± 0.02	0.41 ± 0.02

Fig. 2. Isotopic composition of CO_2 and H_2O in instantaneous equilibrium with siderite having $\delta^{18}O = +34‰$. CO_2 in equilibrium with the siderite had $38 < \delta^{18}O < 42‰$; as discussed in the text, this places a lower limit on the $\delta^{18}O$ of martian atmospheric CO_2.

within rust, but the occurrences were very small (a few microns). Fe-rich carbonate has recently been reported from another nakhlite, Lafayette (Vincenzi et al., 1997); however, the Lafayette material has <11% Mn and far more Ca (up to 25–26 mole % calcite) than the Nakhla carbonates.

As noted, the textures of the carbonate and rust differ; the former usually occurs as small blocky masses, whereas the latter is found as films along fractures and grain boundaries. This may suggest the carbonate and rust formed in different events. Unfortunately the textures of the rust and carbonate do not permit an unambiguous determination as to which formed first. For example, the carbonate surrounded by rust in Figure 1 could be the result of rust formation at the boundaries between preexisting carbonate and feldspar grains; alternatively, it could result from rust deposition on the open surfaces of a cavity (interstitial to the cumulus minerals), followed by filling of the pore space with fine-grained carbonate.

Although chemically heterogenous, the carbonate masses do not show conspicuous zoning such as that exhibited by the ALH84001 carbonates. All the carbonates are orange in transmitted light, indicating some staining by ferric oxides. We note that alteration of siderite to ferric oxides is common terrestrially (Deer et al., 1966) and may, plausibly, also be common on Mars.

4.2. Oxygen Isotopes

Oxygen isotopes have been measured from carbonates in EET79001, ALH84001, and Nakhla and Lafayette. Jull et al. (1995) studied Nakhla by acid dissolution. Their results show considerable scatter in both $\delta^{18}O$ and ^{13}C having $10‰ < \delta^{18}O < 29‰$ and $15‰ < \delta^{13}C < 55‰$; the highest values occurred together. Nevertheless, they noted that the presence of significant ^{14}C in their samples might be indicative of some terrestrial contamination. The acid dissolution data of Wright et al. (1988) also suggest the presence of heavy carbonate in Nakhla with $22‰ < \delta^{18}O < 30‰$. There was also some indication that the carbonate had $\delta^{13}C \sim 49‰$ (Romanek et al., 1994). High $\delta^{13}C$ values are noteworthy as they are probably derived from the martian atmosphere (Romanek et al., 1994). Recently Vincenzi and Eiler (1998) reported $\delta^{18}O$ values for the Lafayette siderite ranging from 31 to 36‰.

The consistently high $\delta^{18}O$ (+34‰) of our carbonate analyses clearly demonstrates that it is not part of the primary igneous assemblage, as the olivine and pyroxene have much lower $\delta^{18}O$ (4.1‰ and 4.6‰ SMOW, respectively; Clayton and Mayeda, 1996). Using fractionation factors from Chiba et al. (1989), we estimate that the siderite would have $\delta^{18}O < 7‰$
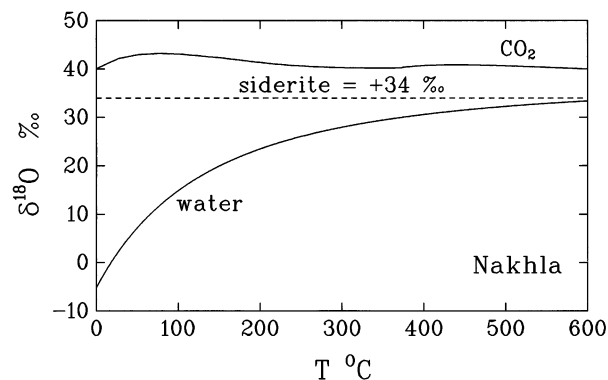
if it were equilibrated with the silicate at temperatures above 750°C.

In Figure 2 we show the isotopic compositions of CO_2 and water in isotopic equilibrium with +34‰ siderite as a function of temperature. Construction of this figure uses the formulae for the reduced partition function of water given by Rosenbaum (1997) (lines 2, 3, and 8 of his Table 8), the reduced partition function for carbon dioxide tabulated by Chacko et al. (1991), and siderite–water fractionation as described by Carothers et al. (1988). This figure is the starting point for any interpretation of the carbonate $\delta^{18}O$ and our aim is to consider processes that will generate these compositions. These processes could be low or intermediate temperature interactions involving plausible martian CO_2 and water reservoirs, or could be fluids modified by high temperature interaction of these reservoirs with the crust, for example, in a high temperature hydrothermal circulation. Before attempting to do this in detail we summarise the theoretical and experimental basis for current ideas concerning the isotopic composition of the martian hydrosphere and atmosphere.

4.3. The Isotopic Composition of the Martian Hydrosphere and Atmosphere

No in-situ measures of the martian atmosphere, of sufficient accuracy, exist for detailed comparison with the laboratory analyses of martian carbonate. A $^{16}O/^{18}O$ ratio of 490 ± 25 for CO_2 in the martian atmosphere was obtained by the Viking mass spectrometers (Nier and McElroy, 1977). This corresponds to $\delta^{18}O = +20 \pm 50‰$. Krasnopolsky et al. (1996) used IR spectroscopy to derive $\delta^{18}O = -130 \pm 80‰$ for atmospheric CO_2.

In the absence of more precise analyses of martian water and CO_2 reservoirs, interpretations of the isotopic composition of secondary minerals produced from these reservoirs in martian meteorites must rely on comparison with various theoretical models. A convenient starting point is the model of Clayton and Mayeda (1988), which is based on the premise that the hydrosphere and atmosphere were initially outgassed from the interior of Mars with an isotopic composition determined by interaction with the crust. Changes to this primitive isotopic

composition may have arisen subsequent to outgassing from a number of processes, including fixation of atmospheric CO_2 as carbonate and loss of oxygen from the upper atmosphere by photochemical processes. These processes are discussed below. Regional differences may also have arisen, as on the Earth, as a result of atmospheric processes involving evaporation and precipitation or condensation of water and CO_2.

4.3.1. Clayton and Mayeda model

In the model of Clayton and Mayeda (1988), early Mars is considered to outgas, at high temperature, a mixture of CO_2 and H_2O, whose isotopic composition is fixed by interaction with the silicate crust. At high temperature, the equilibrium isotopic fractionation between CO_2, H_2O, and silicate rock is small. (Clayton and Mayeda give $\delta^{18}O$ = 4.2, 8.5, and 6.4‰ for silicate, CO_2, and H_2O, respectively, at 1000°C.) During the subsequent cooling of the CO_2 and H_2O, they are assumed to remain in isotopic equilibrium with each other but to be isotopically decoupled from the silicate. In consequence the isotopic composition of the bulk fluid (CO_2 + H_2O) reservoir remains fixed as the fluid cools, leading to the simple relationship:

$$X_0 H_0 + (1 - X_0)C_0 = X_0 H_{1000} + (1 - X_0)C_{1000}, \qquad (1)$$

where H_0, C_0, are the $\delta^{18}O$ values of the water and CO_2 in the hydrosphere and atmosphere at low temperature (for the moment assumed to be 0°C), and H_{1000} (= +6.4‰), C_{1000} (= +8.5‰) are the $\delta^{18}O$ values at equilibrium with silicate at 1000°C. X_0 is the mole fraction of oxygen as water in the total (H_2O + CO_2) fluid. Clayton and Mayeda demonstrated that for X_0 = 0.8, the water–CO_2 reservoirs formed could yield the carbonate observed in EET79001 as a low temperature alteration product. They noted that X_0 = 0.8 is consistent with some models of the initial volatile inventory of Mars. In a subsequent section we shall consider to what extent the Nakhla measurements may be used to constrain X_0.

4.3.2. Fixation of CO_2 as carbonate

It is possible that by the time of formation of the Nakhla siderite, much of the CO_2 originally in the martian atmosphere had been incorporated into carbonate minerals in the crust. The effect of this process on $\delta^{18}O$ of water in the hydrosphere is small, but not negligible, as we shall now demonstrate. To fix CO_2 as carbonate, a source of metal ions is required. We assume the relevant reaction is

$$2X_0[H_2O] + (1 - X_0)[CaSiO_3 + CO_2] \rightarrow 2X_0[H_2O]$$
$$+ (1 - X_0)[CaCO_3 + SiO_2]. \quad (2)$$
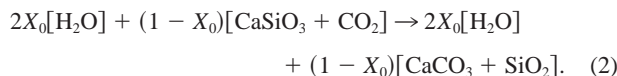
For simplicity, we assume that the whole atmosphere is fixed so that X_0 refers to the total atmosphere + hydrosphere system, as defined above. We include water in the equation as it affects the isotope mass balance, as the reactant CO_2 and product $CaCO_3$ and SiO_2 are assumed to be isotopic equilibrium with it. The multiplier 2 is arbitrary, but is chosen to make the definition of X_0 consistent with that in the previous section. The choice of Ca as the metal is arbitrary; Fe and Mg may partly substitute for Ca, although this makes little difference isotopically. Because

$\delta^{18}O$ of the total oxygen in the above reaction remains constant we may write:

$$X_0 H_i + (1 - X_0)(C_i + \tfrac{3}{2}S_0) = X_0 H_f + (1 - X_0)(\tfrac{3}{2}C_f + Q), \qquad (3)$$

where H_i = initial $\delta^{18}O$ of hydrosphere; C_i = initial $\delta^{18}O$ of atmospheric CO_2; H_f = $\delta^{18}O$ of hydrosphere after fixation of CO_2 as carbonate; S_0 = $\delta^{18}O$ of silicate; C_f = $\delta^{18}O$ of carbonate, Q = $\delta^{18}O$ of quartz. Substituting $C_f = H_f + F_{CarbH}(T)$, $C_i = H_i + F_{CH}(T)$ and $Q = H_f + F_{QH}(T)$, where F_{CarbH}, F_{CH}, and F_{QH} are the carbonate–water, CO_2–water, and quartz–water fractionation at the appropriate temperature T and solving for H_f we obtain

$$H_f = \frac{H_i + (1 - X_0)\{F_{CH}(T) + \tfrac{3}{2}S_0 - \tfrac{3}{2}F_{CarbH}(T) - F_{QH}(T)\}}{\tfrac{5}{2} - \tfrac{3}{2}X_0}.$$
$$(4)$$

For X_0 near 0.8, the effect of fixation of CO_2 as carbonate is to lower the $\delta^{18}O$ of the hydrosphere. Clearly there is no effect for X_0 = 1, but as X_0 is reduced, $\delta^{18}O$ of the hydrosphere also decreases. For example, with fixation as $CaCO_3$ at 0°C, and with S_0 = +4.2, $\delta^{18}O$ of the hydrosphere is reduced by 6‰ for X_0 = 0.8 and by 4‰ for X_0 = 0.9.

4.3.3. Effects of atmospheric loss

The above discussion indicates that the globally averaged $\delta^{18}O$ of the hydrosphere can probably be estimated to within a few per mill provided we know X_0 and assume high temperature equilibration with the crust at some stage. However, one potentially large effect, which we have so far ignored, is heavy isotope enrichment due to preferential loss of the lighter isotopes to space. D/H in the atmosphere is enriched by a factor of 5 over the terrestrial ratio (Bjoraker et al., 1989), and $^{15}N/^{14}N$ by a factor of 1.6 (Nier and McElroy, 1977). Wright et al. (1990) argued that $^{13}C/^{12}C$ in the atmosphere was enriched by ~40‰ over that in magmatic minerals; this could be increased to ~70‰ in the light of the more recent observation of Romanek et al. (1994) of heavy carbon in ALH84001 carbonate.

Heavy isotope enrichment can be modelled quantitatively as a Rayleigh fractionation process (e.g., see Jakosky, 1993), and is related to present-day isotope ratios by three essential parameters: (1) the loss rate of a species from the atmosphere, (2) the size of the reservoir which is being depleted, and (3) the ratio of loss rates for different isotopes of a given element.

With regard to loss rates, a number of nonthermal loss mechanisms for O loss have been identified, but the total flux is uncertain. O loss due to dissociative recombination has been estimated at 3–6 × 10^6 cm^{-2}/s (Lammer and Bauer, 1991; Fox, 1993). Loss due to sputtering by O^+ pickup ions has been estimated at up to 3 × 10^6 cm^{-2}/s by Kass and Yung (1996). Fox (1997) estimated the loss of O ions and concluded that the flux from the day-side ionosphere could be as high as 5.5–18 × 10^7 cm^{-2} s, depending on solar activity. However, Fox notes that part of this flux could well return to the atmosphere on the night-side of the planet. Fluxes of ions (O^+ and O_2^+) detected by instruments on Phobos 2 have also been used to derive a global escape flux as high as 2 × 10^7 cm^{-2}/s (Lundin et al.,

1989). Thus, flux estimates cover a range from a few $\times$ 10^6 cm^{-2}/s to a little over 10^8 cm^{-2}/s, an uncertainty of more than an order of magnitude.

Estimates of the size of the exchangeable O reservoir are also uncertain. It has been estimated that the present-day North Cap System contains enough water to cover the planet to a depth of 10–40 m (Fanale et al., 1992), whereas Clifford (1984) estimated that 70–700 m of H$_2$O could be stored in the pore space of a 10-km deep megaregolith, in the upper layers as permafrost, and at depth as liquid water. Given the uncertainties in these parameters, it is clear that any δ^{18}O enrichment of the atmosphere could range from significant to negligible. For example, a current reservoir of 10 m H$_2$O and a constant loss of 10^8 cm^{-2}/s over 4.5 Ga would correspond to loss of 30% of the initial oxygen and, using the relative escape fluxes for ^{16}O and ^{18}O from Jakosky (1993), would raise δ^{18}O by ~130‰. A current reservoir of 40 m of H$_2$O and a flux of only 10^7 cm^{-2}/s would lead to a loss of only 1% and produce a ~3‰ increase in δ^{18}O. If the exchangeable reservoir were larger the increase in δ^{18}O would be even less. The Viking observations, ^{16}O/^{18}O = 490 $\pm$ 25 (Nier and McElroy, 1977), compared to a terrestrial ocean value of 499, would seem to rule out an increase in δ^{18}O of as large as 130‰, but the uncertainty would still permit a small effect.

The fractionation factor of the escaping species is usually expressed in the form $\alpha = b^{-\Delta A}$, where α is the isotope ratio of the component being lost from the atmosphere divided by the ratio in the well mixed lower atmosphere (Wallis, 1989; Jakosky, 1993). ΔA is the mass difference in amu between the isotopes in question. b is factor that expresses the change in relative abundance of different isotopes with height above the turbopause and any additional fractionation, arising, for example, from velocity differences associated with the photo-dissociation processes. For a simple isothermal atmosphere segment, b would be equal to exp(mgh/kT), where m is the mass of 1 amu and h the height above the turbopause. Current estimates, based on atmospheric models and taking into account the details of the photochemistry, lead to values of b in the range 1.20–1.25 (Wallis, 1989), although some estimates are based solely on gravitational separation and do not take in account photochemical effects, and therefore may be lower limits.

Jakosky (1993) has modelled the loss process in terms of the Rayleigh fractionation formula, $R = f^{(\alpha - 1)}$, where R is the isotope ratio in the residual atmosphere divided by its initial value, and f is the fraction of the initial atmosphere remaining. The corresponding *change* in δ values is given by; $\delta = 1000 \cdot (R - 1)$. An important feature of the loss process pointed out by Jakosky is that the ratio of the fractionation factors, for ^{18}O/^{16}O and ^{17}O/^{16}O, can be larger than those associated with the familiar chemical equilibrium fractionation processes, and that this can lead to significant departures of the isotopic composition from the "normal" isotope fractionation line. Evidence for such an effect on Mars comes from the observation that some alteration products in martian meteorites have Δ^{17}O values (=δ^{17}O − 0.515 · δ^{18}O) some 0.3 to 0.5‰ greater than that of the host rock (Karlsson et al., 1992; Farquhar et al., 1998; Romanek et al., 1998).

Using Jakosky's model, the observed value of Δ^{17}O can be used to estimate both the offset in δ^{18}O for the martian hydrosphere brought about by atmospheric loss processes and the
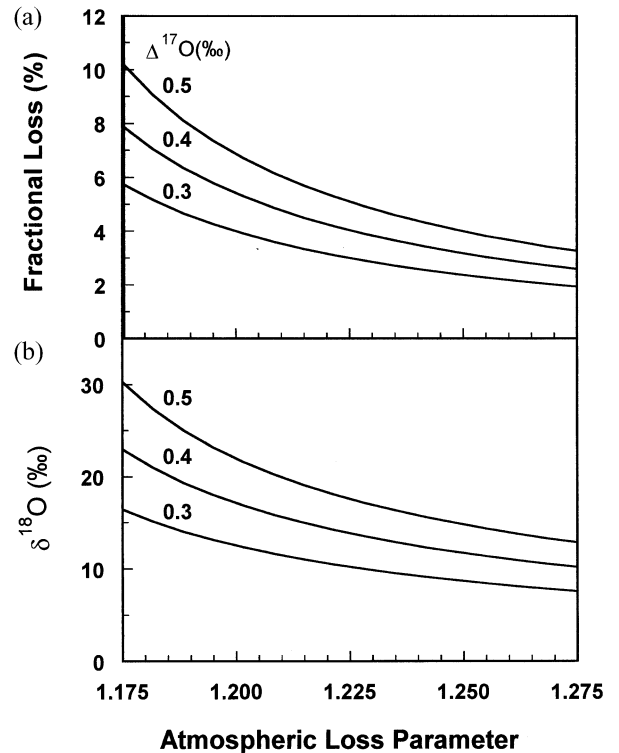

Fig. 3. (a) Calculated fraction of martian atmospheric loss required to account for increases in Δ^{17}O between 0.2 and 0.4‰, plotted as a function of isotope fractionation parameter b (see text). (b) Calculated enhancement of δ^{18}O in martian hydrosphere/atmosphere arising from losses in (a).

extent of the loss. The results of this calculation are shown in Figure 3a, b, as a function of the parameter b and for Δ^{17}O offsets of 0.3, 0.4, and 0.5‰. On the basis of values of b covering the range 1.20–1.25, the increase in δ^{18}O is probably in the range 9‰ (Δ^{17}O offset = 0.3, b = 1.25) to 21‰ (Δ^{17}O offset = 0.5, b = 1.20). Figure 3b suggests that between 3 and 7% of oxygen has been lost to space. This estimate of oxygen loss would be increased if isotopic exchange between hydrosphere and the silicate crust had taken place. However, the relationship between Δ^{17}O and δ^{18}O would not be affected significantly. The estimates of both effects would be reduced if photochemical effects led to higher levels of fractionation associated with the loss (increased value for b).

4.4. Formation of Nakhla Siderite

4.4.1. No isotopic exchange with silicates

There is no unique interpretation of the measured δ^{18}O of the Nakhla siderite and therefore, we are constrained to explore a range of plausible options that could give rise to fluids with the isotopic compositions indicated in Figure 2. We shall consider two extreme possibilities. In this section we examine the possibility that the siderite was deposited from fluids taken from a global martian water and atmospheric CO$_2$ reservoir, at temperatures where no significant isotopic exchange occurs with the silicate crust.

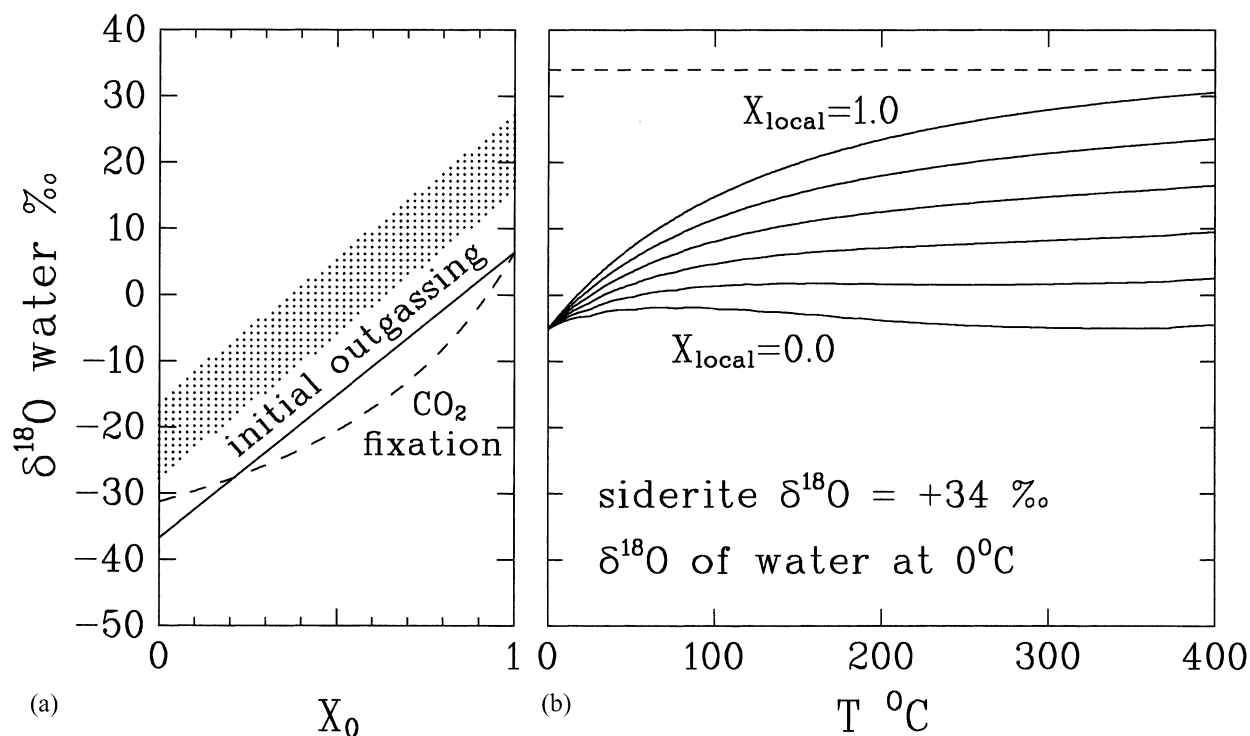To estimate the range of permitted isotopic compositions for

Fig. 4. A comparison of (a) theoretical estimates of the possible isotopic composition of the martian hydrosphere, with (b) source reservoir compositions required to generate the Nakhla siderite. (a) Solid line: theoretical estimates of $\delta^{18}O$ of H_2O (=H_0) produced by initial outgassing of Mars for various molar fractions of oxygen as water, X_0. Lower dashed line: theoretical estimate of effects of fixation of atmospheric CO_2 as carbonate. Upper shaded band: calculated enhancement of $\delta^{18}O$ in martian hydrosphere/atmosphere arising from loss processes capable of producing increases in $\Delta^{17}O$ between 0.2 and 0.4‰. (b) $\delta^{18}O$ of H_2O reservoir at 0°C (=H_1) of a martian H_2O reservoir at 0°C, which, when heated to temperature T in the presence of various proportions of CO_2, would be in isotopic equilibrium with the Nakhla siderite. X_{local} is the molar fraction of oxygen present as water in the water–CO_2 fluid. Comparison of the two sides of the figure shows under what conditions the theoretical models of the martian hydrosphere/atmosphere system can be reconciled with the Nakhla analyses and, conversely, the constraints that would be placed on the deposition conditions of the Nakhla siderite if the composition of the martian hydrosphere were known. Specifically, comparison of (a) and (b) indicates that the siderite could have formed from fluids produced by initial outgassing only if it formed below 60°C. Hydrothermal formation of the siderite in a hot water-rich system (e.g., 200–300°C, X ~1, conditions under which some terrestrial siderite is known to have formed) would require fluids more enriched in ^{18}O than can be provided by initial outgassing.

this reservoir we consider a situation in which a sample of water and CO_2, at 0°C, with $\delta^{18}O_{H2O} = H_1$ and having a mole fraction X_{local} of oxygen as water, is isolated from the global reservoir and heated (e.g., in a hydrothermal system) to some temperature, T, at which the carbonate in Nakhla is deposited. During the heating equilibrium between CO_2 and H_2O causes the $\delta^{18}O$ of each to change, while keeping the average $\delta^{18}O$ unchanged. The amount of siderite is assumed to be negligible in comparison with the fluid. The starting isotopic composition of water at 0°C (=T_0), H_1, is plotted in Figure 4b as a function of the carbonate deposition temperature, T, for different values of X_{local}, according to the expression:

$$H_1 = H(T) + (1 - X_{local})(F_{CH}(T_0) - F_{CH}(T)), \qquad (5)$$

where $H(T)$ is the isotopic composition of water in equilibrium with 34‰ siderite (see Fig. 2). Note that when $X_{local} = 1$, $\delta^{18}O_{H2O}$ remains constant and $H_1 = H(T)$.

For comparison, the theoretical estimates of the isotopic composition of the martian hydrosphere and CO_2, discussed in section 4.3, are summarised in Figure 4a as a function of X_0,

the global fraction of oxygen in the hydrosphere/atmosphere system. Comparison of the two sides of Figure 4 indicates under what conditions the theoretical models are consistent with the Nakhla analyses.

To make use of the figures we simply regard Figure 4b as indicating the isotopic composition of the hydrosphere (referred to a 0°C baseline) required to generate the Nakhla carbonate at different deposition temperatures and H_2O/CO_2 ratios. Figure 4a, on the other hand, indicates what compositions may be "available" on Mars, based on the Clayton and Mayeda model, appropriately modified by CO_2 fixation and atmospheric loss. This approach has the advantage of separating out the local factors, related to the formation of Nakhla siderite, from the global factors, associated with the formation of the major martian reservoirs. It provides a way of testing the various models by answering the question: What would the isotopic and elemental composition of the H_2O and CO_2 in a 0°C hydrosphere/atmosphere have to be, such that when a sample of this fluid is isolated and heated to temperature T, it would be in equilibrium with +34‰ siderite?

We see that at low temperatures, H_1, C_1 required to generate the carbonate lie within the range of values of H_0, C_0, which may be produced by the initial outgassing of Mars, provided X_0 is sufficiently high. Specifically, if the siderite were equilibrated with water at 0°C, then $X_0 = 0.74$ and $H_0 = -5.2$‰. Water–siderite equilibration at $0 < T < 60$°C requires $X_0 > 0.74$, up to $T = 60$°C where $X_0 = 1$ and $H_0 = 6.4$. As noted by Clayton and Mayeda (1988), these values of X_0 are plausible. The effect of CO_2 fixation is to increase the value of X_0 corresponding to deposition of the siderite at 0°C, i.e., $X_0 = 0.85$. Thus, our data on Nakhla do not of themselves require a hydrosphere/atmosphere highly enriched in ^{18}O, which might otherwise have been expected by analogy with atmospheric H, C, and N.

We also see that if the siderite formed from a water rich fluid ($X_{\text{local}} \to 1$) with $T > 60$°C, the inferred values of H_1 and C_1 are too high to be consistent with fluids produced by initial outgassing and subsequently unmodified. If the siderite did form in a water-rich system at $T > 60$°C, e.g., is of hydrothermal origin, then a hydrosphere–atmosphere with a modest enrichment in ^{18}O is implicated. Enrichments at a level able to account for the high $\Delta^{17}O$ observed in some martian weathering products are consistent with these higher temperatures.

On the assumption of no isotopic exchange with silicate, our data can be used place limits on $\delta^{18}O_{H2O}$ and $\delta^{18}O_{CO2}$ for the martian hydrosphere and atmosphere. On the basis of a reference temperature of 0°C the upper limits are ∼+31 and +76‰, respectively, and the lower limits −5 and +41‰. The upper limit has assumed that deposition temperatures were no higher than 400°C, to be consistent with the requirement of no exchange with silicate. As the curves in Figure 4b level off above 400°C, this assumption is not critical. Romanek et al. (1998) suggested $\delta^{18}O_{H2O}$ lay within the range −15 to +5‰ based on their analyses of Lafayette iddingsite.

Similar arguments can be applied to other martian carbonates that may have formed in equilibrium with the martian hydrosphere. In particular, the +22‰ Mg-rich rims on the carbonate globules in ALH84001 correspond to an upper limit for $\delta^{18}O_{H2O}$ of 19‰. It is probably not appropriate to apply this argument to the carbonate cores in ALH84001 as the formation temperature was (probably) higher (Saxton et al., 1997, 1998; Leshin et al., 1998). Also, given the apparent antiquity of the ALH84001 carbonates (Pb-Pb age of 4.0 Ga; Borg et al., 1999), this limit can only be applied to the martian hydrosphere of 4.0 Ga ago.

Figure 4 was constructed assuming that 0°C is an appropriate temperature for the martian hydrosphere. Reducing this temperature changes the curves only slightly; the main effect is to permit lower equilibration temperatures, which implies lower values of H_1 and C_1. For example, for at −20°C, H_1 is reduced to −12.4‰ and C_1 to +35.6‰.

It is instructive to compare the Nakhla observations with those of terrestrial siderite, bearing in mind that $\delta^{18}O$ of the martian mantle (Franchi et al., 1997) is only about 1‰ lower than the terrestrial mantle. The most common occurrence of siderite on Earth is in bedded sedimentary rocks (Deer et al., 1966). $\delta^{18}O$ values of a large number of carbonates of marine origin were summarised by Mozley and Burns (1993); the majority of siderite had $22 < \delta^{18}O < 30$‰. The high end of this range is consistent with deposition from seawater at

∼25°C, whereas the lower values may reflect the influence of meteoric water (Mozley and Burns, 1993). The Nakhla siderite is heavier than typical terrestrial marine siderites, but the difference is small enough to be accounted for by lower formation temperatures and possible lack of meteoric water on Mars, and without requiring a martian hydrosphere isotopically very different from the terrestrial one. Terrestrial siderite is also known from hydrothermal systems and has lower $\delta^{18}O$ (e.g., 13 to 17‰; Carothers et al., 1987; Criss et al., 1995); these studies found formation temperatures from 150 to 300°C. If the Nakhla siderite formed at similar temperatures and from a water-rich fluid ($X_{\text{local}} \to 1$), then Figure 4 implies that a CO_2–H_2O reservoir exists on Mars with $\delta^{18}O$ values significantly higher than is consistent with initial outgassing.

Recently, Bridges and Grady (1999) have suggested that the siderite formed from a halide–carbonate–sulphate-rich melt that was incorporated into, but immiscible with, the Nakhla parent magma. They postulate that the halide–carbonate–sulphate melt was itself derived by melting of an evaporite. It is conceivable that siderite in an evaporite might have $\delta^{18}O = +34$‰, but we doubt that this would be preserved once the carbonate was incorporated into an igneous melt (typical diffusion rates in a basaltic melt would homogenise oxygen over a 10-μm distance in <15 min, using the data tabulated by Brady, 1995). The tight clustering of the siderite $\delta^{18}O$ also seems inconsistent with partial exchange of an initially isotopically heavy carbonate with a light reservoir such as a silicate melt. The oxygen isotopic composition of the anhydrite (∼+7‰; Saxton et al., 1999) also precludes formation of the anhydrite and siderite in the same melt, unless the siderite alone was subsequently altered.

4.4.2. Silicate buffered

The previous model assumes that the composition of the hydrothermal fluid from which the carbonate was deposited was not modified by exchange with the silicate. Such exchange could occur if the fluids were part of a high temperature hydrothermal circulation before carbonate deposition. The effect of complete equilibration with the silicate would be to erase any information about the isotopic composition of the hydrosphere and atmosphere of Mars and result in a fluid composition similar to that predicted by the Clayton and Mayeda model (Fig. 4a). Comparison with Figure 4b shows that in this case the carbonate would need to be deposited from the fluid after it cooled below 60°C. However, equilibration with silicate would erase the anomaly in $\Delta^{17}O$ (Farquhar et al., 1999) and can be ruled out on those grounds.

4.5. Nakhla and the Contemporary Martian Environment

We conclude with some general remarks on the possible significance of the Nakhla analyses in the light of measurements of $\delta^{18}O$ of martian ice, which might possibly be made later this year by Mars Polar Lander. On the one hand, the Nakhla data and the preceding arguments can be used to make predictions regarding the Mars Polar Lander results. On the other hand, a direct measurement of the isotopic composition of martian water would allow us to better constrain the formation conditions of the Nakhla siderite and of other martian carbon-

ates. First, however, a note of caution; it is necessary to assume no isotopic evolution between the time of formation of the siderite (some time in the past 1.3 Ga) and the present day.

Provided the fluids from which the siderite formed underwent no exchange with the crust, the discussion in section 4.3 indicates that $\delta^{18}O$ of (globally averaged) ice probably lies in the range $-6‰$ (Nakhla siderite formed at $0°C$) to $+34‰$ (Nakhla siderite formed in water-rich environment at $\sim400°C$. The lower limit is reduced to $-12‰$ if the siderite formed at $-20°C$. Fixation of CO_2 as carbonate subsequent to siderite formation (which we think unlikely if the carbonate is younger than 1.3 Ga) would reduce the lower end of the above range by several per mil. Conversely, a much higher value may indicate that atmospheric loss occurred after the Nakhla siderite $\delta^{18}O$ was established. A direct analysis of the isotopic composition of martian ice will clearly allow us to constrain the formation temperature of the Nakhla siderite, provided we can assume that it formed in a water-dominated environment.

5. CONCLUSIONS

1) Small grains of siderite exist within the mesostasis of Nakhla. The high and variable Mn content suggest that the carbonate formed during conditions of open system (to cations) alteration on Mars and is not terrestrial alteration. This conclusion is reinforced by the observation of high D/H ratios ($\delta D \geq +1000‰$) in the siderite.
2) The siderite has $\delta^{18}O_{SMOW} = +34 \pm 1‰$ and is the heaviest martian carbonate yet observed.
3) Assuming no isotopic exchange between fluid and silicate, and a minimum temperature of formation of $0°C$, then $\delta^{18}O$ of the water from which the siderite formed was between -5 and $\sim+34‰$.
4) If the siderite formed in equilibrium with aqueous fluids produced during planetary outgassing (for which $\delta^{18}O_{H2O} \leq +6‰$) and not subsequently modified, then the equilibration temperature was $<60°C$. This conclusion also applies if the siderite formed in equilibrium with aqueous fluids that had undergone high temperature isotopic exchange with silicates in a hydrothermal system before deposition.
5) Equilibration with a water-rich fluid at temperatures above $60°C$ is only possible if the fluid is heavy isotope enriched. Enrichments of $\delta^{18}O$ by $9–21‰$, arising from atmospheric loss processes, are consistent with published $\Delta^{17}O$ enhancements of $0.3–0.5‰$. If the siderite formed in equilibrium with aqueous fluids enriched in this way, estimated deposition temperatures would be raised to $80–170°C$.
6) The effect of a global scale fixation of martian CO_2 as carbonate would lead to a reduction in $\delta^{18}O$ of the martian hydrosphere. The effect is small, amounting to a 6‰ reduction if the ratio of oxygen in water to CO_2 is 4:1.
7) We estimate that the $\delta^{18}O$ of martian ice is in the range -5 to $+34‰$. The lower limit is based on the Nakhla siderite and assumes a minimum formation temperature of $0°C$. The corresponding lower limit on the $\delta^{18}O$ of martian atmospheric CO_2 is $\sim+40‰$. This limit is compatible with Earth-based measurements of $^{18}O/^{16}O$ in martian water vapour.
8) The suggestion that the Nakhla siderite formed from a halide–carbonate–sulphate-rich melt is only possible provided that the melt was already heavy oxygen enriched and did not undergo significant isotopic exchange with the Nakhla silicate.

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