

time on photon energy found from the fit is given by  $E_\gamma^{-2.04 \pm 0.31}$ , in agreement with the dependence expected from equation (7). For the reasons already stated and because of the finite threshold, the fitted line corresponds to somewhat smaller delay times than the analytical limit (by about a factor of three in this case). Although the way in which the region below the 'maximal delay limit' is filled in is very model-dependent, the shape of the maximal envelope is not and is therefore a robust signature of FIDs.

By performing observations on different timescales and at energies above  $\sim 10$  MeV, one can search over a large range of IGMF strengths. For example, a timescale of seconds with photons of 100 MeV energy would be appropriate for field strengths of  $\sim 10^{-24}$  G. For field strengths above  $\sim 10^{-15}$  G the delay times become very large for all energies below 10 TeV, even for relatively near sources. In this range of IGMF strengths it is possible to observe the deflection directly as a diffuse image with an angular extension of the source  $< \theta$  from equation (5). If the IGMF is strong enough ( $> 10^{-11}$  G), the cascade radiation from the electron/positron pairs will appear as a halo around the  $\gamma$ -ray source<sup>19</sup> because the magnetic field is strong enough to make the distribution of these pairs isotropic.

Recently, delayed VHE emission following a  $\gamma$ -ray burst has been reported<sup>7</sup>. The photon with the highest energy (18 GeV) arrived 0.05 d after the main burst. It is tempting to speculate that the delayed signal was due to an FID. By assuming<sup>17</sup> the total energy of a typical cosmological  $\gamma$ -ray burst to be  $10^{51}$  erg, and using the total fluence<sup>7</sup> from this burst ( $6.6 \times 10^{-4}$  erg/cm<sup>2</sup>) one estimates a distance  $x \approx 100$  Mpc to this GRB. By inserting this distance, the energy and a field strength<sup>3</sup> of  $B = 10^{-16}$  G into

equation (7) and correcting for the coherence length of  $f$  pc, a 'maximal delay limit' of 25/d is obtained. For  $f > 2 \times 10^{-3}$  (consistent with theoretical expectations<sup>3</sup>) the inequality (7) would hold for all delayed events. The question as to whether such an interpretation is consistent with all the data deserves further study. The detection of FIDs in  $\gamma$ -ray bursts would also be strong evidence for the cosmological origin of the latter. The event statistics necessary to clearly identify the 'maximal delay limit' will probably be reached<sup>18</sup> by future ground-based  $\gamma$ -ray telescopes with thresholds below 100 GeV.  $\square$

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## Evolution of water reservoirs on Mars from D/H ratios in the atmosphere and crust

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ANCIENT fluvial networks on the surface of Mars suggest that it was warm and wet over three billion years ago. Surface features resembling massive outflow channels provide evidence that, even more recently, the martian crust contained the equivalent of a planet-wide reservoir of water several hundred metres deep<sup>1,2</sup>. But arguments based on the isotopic fractionation<sup>3,4</sup> and present-day escape rate of hydrogen in the martian atmosphere require only 0.5 metres of crustal water today and about six metres in the past<sup>5</sup>. An additional constraint on the evolution of the isotopic composition of martian water has recently been obtained<sup>6</sup> from measurements of the deuterium to hydrogen ratio of hydrous minerals in the SNC meteorites—meteorites that almost certainly originated on Mars. Here I show that these new data require that the modern crustal reservoirs of martian water must be quite large, at least several metres in global-equivalent depth. The deuterium enrichment of the present martian atmosphere then implies that the reservoir of crustal water on ancient Mars was several hundred metres deep, consistent with the geological evidence<sup>3,4</sup>.

The ratio,  $R$ , of deuterium to hydrogen in martian atmospheric water vapour is  $(8.1 \pm 0.3) \times 10^{-4}$  (refs 3, 4;  $R$  is half the abundance ratio of HDO and H<sub>2</sub>O) and is greater than in terrestrial ocean water by a factor of  $5.2 \pm 0.2$ . Given the large size of the reservoirs on Earth, it is reasonable to assume that the D to H ratio has not changed appreciably in terrestrial water in 4.5 billion years. Moreover, this ratio is likely to have originally been the same for martian and terrestrial water. (Measure-

ments in SNC meteorites set an upper limit for  $R$  in magmatic martian water only 1.5 times that of terrestrial water<sup>6</sup>.) The simplest interpretation of this enrichment of deuterium in the martian atmosphere is that an appreciable amount of hydrogen associated with the original water reservoir on Mars has escaped (most escape processes discriminate against loss of the heavier isotope).

I consider martian water at an arbitrary time in the past,  $t$ , as residing in two reservoirs, one crustal,  $c(t)$ , the other atmospheric,  $a(t)$ ;  $c(t)$  is large compared to  $a(t)$ , and the water content is expressed as the total number of hydrogen atoms in a vertical water column of 1 cm<sup>2</sup> cross-section. (I shall consider the effect of storage of water in the polar caps later). I shall assume that the two reservoirs exchange freely with each other; as hydrogen and deuterium are lost from the atmosphere, the deuterium to hydrogen ratio in the crustal and atmospheric reservoirs change together. Loss of hydrogen and deuterium at different efficiencies leads to fractionation, and  $R$  increases with time. The ratio of  $R$  at one time,  $t_2$ , to that at an earlier time,  $t_1$ , is independent of the escape fluxes themselves, and depends only on the ratio,  $r(t)$ , of the size of the reservoirs,  $[H(t_1)]/[H(t_2)]$ , and the efficiency of fractionation. This follows from integration of the relationship

$$f = \phi_2 / \phi_1 R = \frac{d[D]/[D]}{d[H]/[H]} \quad (1)$$

which defines the fractionation factor  $f$ .  $\phi_1$  and  $\phi_2$  are, respectively, the hydrogen and deuterium escape fluxes;  $[D]$  and  $[H]$  are the abundances of D and H in the combined reservoirs in atoms per cm<sup>2</sup>. Integration gives

$$r(t_1, t_2) = \frac{[H(t_1)]}{[H(t_2)]} = \left( \frac{R(t_2)}{R(t_1)} \right)^{\frac{1}{1-f}} \quad (2)$$

Hydrogen is being lost from the upper atmosphere of Mars today by a thermal process called Jeans escape. The fractionation factor for loss of martian hydrogen by Jeans escape has been calcu-

lated to be 0.32 (ref. 5). It follows that if  $R$  is 5.2 times its original value 4.5 billion years ago, there was 11.3 times more hydrogen (and thus water) in the early martian crust and atmosphere than there is today, no matter how much hydrogen has been lost.

A constraint on the actual size of the reservoirs can be obtained from the escape rate. For a fixed escape rate, the smaller the change in  $R$  over a given period of time, the larger must be the size of the reservoir compared to the amount of hydrogen (and deuterium) lost. In fact, it is easy to show<sup>5</sup> that this ratio is equal to the reciprocal of  $r - 1$ , assuming that  $c(t)$  is always much larger than  $a(t)$ .

Measurements and modelling<sup>7</sup> put  $\phi_1$ , the present rate of loss of hydrogen in the form of H and H<sub>2</sub>, averaged over a solar cycle, at  $2.4 \times 10^8 \text{ cm}^{-2} \text{ s}^{-1}$ . This should be very much larger than any injection rate resulting, for example, from comet impacts. Assuming that the escape rate of hydrogen has been constant for 4.5 billion years immediately leads to the conclusion (from the value of  $r - 1$ ) that the present-day crustal reservoir,  $c(0)$ , contains hydrogen equivalent to 0.5 m of liquid water. The original reservoir, 11.3 times larger according to equation (2), would then be about 5.6 m (ref. 5). This is very small compared to the 500 m or so required by the surface geology of Mars. As others have pointed out<sup>5,8</sup>, increasing  $\phi_1$  would cause both reservoirs to increase correspondingly. There are several ways to increase  $\phi_1$ . One is to increase the temperature of the upper atmosphere, which, as I discuss below, by itself can lead to at most a rough doubling of present-day escape flux. Another is to increase the amount of water vapour in the atmospheric reservoir. It is also necessary, at least in the present-day atmosphere, to dispose of the atomic oxygen associated with the disappearing water<sup>9-11</sup>. Otherwise, changes in the redox state of the atmosphere will affect the rate at which water vapour dissociates to give H and H<sub>2</sub>. In fact, changing the oxygen loss rate is a third way to change the hydrogen loss rate without changing anything else in the system.

The recent measurement of D to H ratios in hydrous minerals contained in three SNC meteorites<sup>6</sup> seems, in fact, to demand that  $c(0)$  be much larger than 0.5 m and points the way to estimating by how much. There is abundant evidence that these meteorites are samples of the martian crust ejected by the impact of a massive object, and they may therefore provide us with measurements of the D to H ratio in crustal water interacting with intrusive igneous rock at the time of its crystallization. This time has been set at 0.18–1.3 billion years ago. The D to H ratio of the water in the mineral apatite from one SNC, Zagami, is in some cases as large as that in the martian atmosphere today, whereas in other minerals in this and other SNCs, the isotopic ratios range downward to values only about 1.5 times that of terrestrial water. This range in D to H ratios is thought<sup>6</sup> to result from the exchange of highly deuterated ground water with deuterium-poor magmatic water in the recently formed crystals. The degree of exchange ranges from apparently complete in the case of some Zagami apatites to little in the case of other minerals. Hydrothermal alteration should not have significantly post-dated primary crystallization of the magmas<sup>6</sup>. Thus, the largest ratio found in Zagami minerals would reflect the degree of atmospheric deuterium enrichment at the time of apatite crystallization in Zagami,  $t_z$ , or at an earlier time when the water last exchanged freely with the atmosphere. Thus, it appears that the D to H ratio in martian crustal and atmospheric water was about as high at time  $t_z$  as it is today, whereas estimates based on the assumption of a constant escape rate (for 4.5 Gyr) predict a D to H ratio only 80% as large 180 Myr ago and 40% as large 1.3 Gyr ago. From the published data and the precision claimed for the measurements<sup>6</sup>, it is difficult to see how  $R(t_z)$  could have been more than 4% lower than the present-day value; 20% lower is certainly excluded. If, indeed,  $R(t_z)$  was within 4% of the present value at the time when the Zagami apatites crystallized, the amount of hydrogen and deuterium that have since escaped

from Mars must be small compared to the amount in the reservoir 0.18–1.6 Gyr ago. But in 0.18 or 1.3 Gyr, hydrogen associated with 0.2 m or 1.4 m of water would have escaped at present-day escape rates. These amounts of water are larger than or comparable to the present-day reservoir of 0.5 m calculated for a constant escape flux over 4.5 Gyr.

Assuming a change in  $R$  of only 4% between  $t_z$  and the present day, and taking  $t_z$  to be 1.3 Gyr, it follows from equation (2) and the resulting value of  $r - 1$  that  $c(0)$  is 25 m and  $c(t)$  at 4.5 Gyr is 280 m. If  $t_z$  is only 180 Myr, these crustal reservoirs would be reduced to 3.4 m and 42 m of liquid water, respectively. But a change in  $R$  of 4% between  $t_z$  and the present day is only an upper limit; the Zagami measurements allow an arbitrarily close match. So it is legitimate to ask whether the Zagami measurements also permit a much larger hydrogen reservoir, say 500 m. In that case  $c(0)$  would be 44 m and  $R(t_z)$  would be 0.997 of the present-day value for a  $t_z$  of 180 Myr, and 0.978 for  $t_z = 1.3$  Gyr. The escape fluxes before  $t_z$  would need to have been, on average, larger than the present-day value:  $3 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$  in the first case and  $2.2 \times 10^{10} \text{ cm}^{-2} \text{ s}^{-1}$  in the second. If escape was effected mainly in the first billion years, as the geological record suggests, these rates could approach  $10^{11} \text{ cm}^{-2} \text{ s}^{-1}$ , roughly 400 times the current escape rate. This would suggest that Mars was once much warmer and wetter than it is today, but it also requires a mechanism for disposing of a correspondingly large amount of oxygen. One possible such mechanism is vigorous sputtering of oxygen atoms and other non-thermal processes in the presence of high extreme ultraviolet luminosity in the young Sun<sup>12,13</sup>.

Because the measurements do not constrain how little  $R$  has changed after  $t_z$ , a lower limit to  $c(0)$  might be obtained if the minimum amount of water required to drive a hydrothermal system could be estimated. On the other hand, an upper limit is set by the maximum permissible hydrogen escape flux. One limit of about  $5 \times 10^{11} \text{ cm}^{-2} \text{ s}^{-1}$  is set by the solar photon insolation available below 185 nm to photolyse H<sub>2</sub>O at 1.4 AU after correction for enhanced ultraviolet radiation from the young Sun, solar cycle effects, absorption by other atmospheric species, and solar zenith angle variation. If escape occurred mainly during the first billion years, the crustal reservoir 4.5 Gyr ago could not exceed 2,200 m and  $c(t)$ , today and for most of the past 3.5 Gyr, about 190 m. If the minimum amount of crustal water reservoir required to drive hydrothermal convection or cause the large outflow channels should turn out to be larger than 190 m, there is a difficulty. Extending the period of enhanced escape would not change this limit appreciably because declining solar luminosity would reduce the allowable escape rate.

Another fundamental limitation to the escape flux is set by the amount of hydrogen (atomic and in compounds) available in the well mixed atmosphere just below the homopause, and by the rate at which this hydrogen reaches the level from which escape occurs<sup>14,15</sup>. The escape flux today is about half the maximum possible, given the amount of hydrogen present near the homopause. Increasing the temperature at the escape level could therefore only double the escape flux unless the supply of hydrogen should also increase. If the escape flux once was 400 times its present value, the mixing ratio of H<sub>2</sub> (the dominant hydrogen compound near the homopause) must then have been at least 200 times the present value of  $2 \times 10^{-5}$  by volume. This enhancement could have been caused by an appropriate increase in the tropospheric water vapour concentration and in the oxygen loss rate. Heating of the upper atmosphere by enhanced ultraviolet radiation from the young Sun could have caused the requisite temperature increase. It could also have enhanced the rate of oxygen loss<sup>12,13</sup>. Careful study of these processes involving self-consistent modelling of the atmosphere based on up-to-date chemistry needs to be carried out<sup>10,16,17</sup>.

There may be the planet-wide equivalent of 30 m of water stored today in the polar caps<sup>18</sup>. This water may be mobilized at intervals of  $10^5$ – $10^6$  years because of changes in obliquity

and eccentricity. Because these interludes are short on planetary timescales or the crystallization age of Zagami, this polar cap water can be taken to exchange effectively with atmospheric and crustal water. The treatment presented here would still be valid except that  $c(0)$  would have to be at least as large as the polar cap reservoir. If, on the other hand, the polar caps sequester a large amount of water, which has only infrequently been mobilized, the planet's exchangeable water would have been occasionally diluted with water having a low D to H ratio. The present  $R$  would be lower than it would have been if uninterrupted fractionation had occurred, in which case the reservoir enhancement given by equation (2) would be larger than 11.3. Numerical modelling would be required to explore this contingency further, but the basic conclusions reached here, that an early large crustal reservoir is allowed by deuterium to hydrogen ratio measurements, would not change. This is true also, of course, for any sizeable reservoir that might ordinarily be sequestered but is mobilized occasionally.

The measurements of the D to H ratio for Zagami thus allow for very large crustal reservoirs in the past as well as today; reservoirs large enough to account at least for early geological features associated with flowing water<sup>18</sup>, regardless of the uncertainties in the age of Zagami. Escape fluxes would have been large, and the atmosphere at least occasionally considerably warmer and wetter than it is today. A lot of work needs to be done to understand the physics and chemistry of this early wet martian atmosphere. No suitable radiative convective model based on a greenhouse effect that could account for early warm-

ing currently exists<sup>19</sup>. Furthermore, the mechanisms for disposal of the very large amount of oxygen associated with the escaping hydrogen and how they affect atmospheric chemistry, need to be much better understood. There is a challenge also to understand the hydrothermal systems that apparently permit the exchange of water between atmosphere and interior, and to reconcile the large amount of crustal water they may need with the correspondingly huge early reservoirs and escape fluxes that would then be implied by the current D to H ratio. □

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## Importance of phase fluctuations in superconductors with small superfluid density

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**THE superconducting state of a metal is characterized by a complex order parameter with an amplitude and a phase. In the BCS–Eliashberg mean-field theory<sup>1</sup>, which is a very good approximation for conventional metals, the phase of the order parameter is unimportant for determining the value of the transition temperature  $T_c$  and the change of many physical properties brought about by the transition. Here we argue that superconductors with low superconducting carrier density (such as the organic and high- $T_c$  oxide superconductors) are characterized by a relatively small phase ‘stiffness’ and poor screening, both of which imply a significantly larger role for phase fluctuations. As a consequence, in these materials the transition to the superconducting state may not display typical mean-field behaviour, and phase fluctuations, both classical and quantum, may have a significant influence on low-temperature properties. For some quasi-two-dimensional materials, notably underdoped high-temperature superconductors, the onset of long-range phase order controls the gross value of  $T_c$  as well as its systematic variation from one material to another.**

The importance of phase fluctuations for a variety of superconductors may be assessed by using experimentally determined quantities to evaluate the temperature  $T_\theta^{\text{max}}$  at which phase order would disappear if the disordering effects of all other degrees of freedom were ignored. If  $T_c \ll T_\theta^{\text{max}}$ , phase fluctuations are relatively unimportant, and  $T_c$  will be close to the mean-field transition temperature,  $T^{\text{MF}}$ , predicted by BCS–Eliashberg theory. On the other hand, if  $T_\theta^{\text{max}} \approx T_c$ , then the value of  $T_c$  is determined

primarily by phase ordering, and  $T^{\text{MF}}$  is simply the characteristic temperature below which pairing becomes significant locally.

To evaluate  $T_\theta^{\text{max}}$ , the system must be divided into regions of linear dimension  $a$  which are large enough for the order parameter to be well defined locally. A region  $j$  is characterized by a phase angle  $\theta_j$  and its dynamically conjugate variable<sup>2</sup>, the number of electrons  $N_j$ . There are essentially three types of fluctuations about the BCS ground state which can ultimately destroy the superconducting order: classical phase fluctuations, which are the primary concern of this paper, quantum phase fluctuations, and the effects of all other degrees of freedom which affect the local magnitude of the order parameter. The stiffness of the system to classical phase fluctuations is determined by the superfluid density,  $n_s(T)$ ; the smaller the superfluid density, the more significant the classical phase fluctuations. Quantum phase fluctuations are associated with the number–phase uncertainty relation, according to which phase coherence between neighbouring regions implies large relative number fluctuations and correspondingly large Coulomb energies unless there is adequate screening. Thus the smaller and dielectric function, or equivalently the frequency-dependent conductivity, the more significant the effects of quantum phase fluctuations. We have shown<sup>3</sup> that the classical limit is achieved for infinite conductivity, and that quantum phase fluctuations are sufficient to destroy superconductivity even at zero temperature unless  $\sigma(T_c)$  (the conductivity at  $T_c$ ) exceeds a non-universal critical value proportional to  $\sigma_C \equiv (2e)^2/hb$ , where  $b$  is an appropriate microscopic length. The degrees of freedom other than the phase of the order parameter are usually well treated by mean-field theory.

The hamiltonian ( $H$ ) governing the thermodynamic effects of long-wavelength phase fluctuations at low temperature is the kinetic energy of the superfluid:

$$H = \frac{1}{2} m^* n_s(0) \int dr v_s^2 \quad (1)$$

where  $v_s = \hbar \nabla \theta / 2m^*$  is the superfluid velocity, and  $m^*$  is the effective mass of an electron. If  $\theta$  could take any value between  $\pm\infty$ , the system described by  $H$  would not undergo a phase transition. However  $\theta$  is a periodic variable (with period  $2\pi$ ),