

Experimental study of D/H fractionation between water and hydrogen gas during the oxidation of Fe-bearing silicates at high temperatures (600 °C–1200 °C)

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Hydrogen gas is produced during the oxidation of the FeO component of silicates by water. This redox reaction occurs during the high-temperature (400 °C–800 °C) hydrothermal alteration of oceanic crustal rocks, and is responsible for H₂ production at mid-ocean ridges. Samples of international reference biotite NBS30 ($\delta D = -65.7\text{‰}$) were reacted at high temperatures (600–1200 °C) in a high-vacuum line, releasing both structural water and hydrogen gas. An apparent fractionation factor α , derived from D/H measurements of water and hydrogen gas, is linearly dependent on T^{-2} following the equation $\alpha = 1.024 + 2477296 \cdot T^{-2}$ with a residual standard deviation $\sigma = 0.023$. The apparent D/H fractionation factors between water vapor and hydrogen gas during biotite oxidation show a dependency on T^{-2} that resembles those measured either by equilibration experiments or calculated from partition functions. Moreover, the apparent fractionation factors we measured are close to those determined at equilibrium in the same temperature range by Cerrai et al. (1954). This observation suggests that the D/H fractionation between H₂O and H₂ could be close to equilibrium during the reduction of water to hydrogen by the FeO component of silicates.

Key words: δD , oxido-reduction, high-temperature, isotopic fractionation, iron-bearing silicate, Archean ocean

Introduction

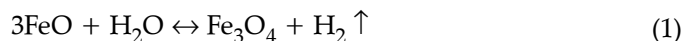
D/H ratios have been widely used to study the water evolution of terrestrial planet atmospheres. The D/H ratio of surficial water intimately depends on the evolution mode of the atmosphere and its interactions with inner envelopes of terrestrial planets. Water dissociation and hydrogen escape are responsible for high deuterium enrichment of Martian's and Venusian's atmospheres relative to

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Earth's hydrosphere (Owen 1992; Donahue 1999). On Earth, the δD value of the oceans is mainly controlled by the isotopic exchange between mantle and seawater (Lécuyer et al. 1998) that occurs at mid-ocean ridges and the release of water to subduction zones. During the hydrothermal alteration of the oceanic crust, the D/H fractionation between hydrous silicates and seawater ($\alpha \sim 0.960$; Wenner and Taylor 1973; Suzuoki and Epstein 1976; Sakai and Tsutsumi 1978) leads to a deuterium enrichment of the hydrosphere while the outgassed mantle water $\delta D = -80\text{‰}$ to -30‰ ; Javoy 1980; Kyser and O'Neil 1984; Chaussidon et al. 1991; Deloule et al. 1991) contributes to decrease the D/H ratio of surficial waters.

During seawater-basalt interactions, the fayalite component of the basaltic rocks is oxidized to pyrite and magnetite by marine sulfates (Shanks et al. 1981). The oxidation of ferrous to ferric iron by sulfates results in a net flux of ferric iron to the mantle (Lécuyer and Ricard 1999). However, before the rise of O_2 in the Earth's atmosphere (2.4 to 2.2 Ga; Holland 1984; Rye and Holland 1998; Bau et al. 1999; Canfield et al. 2000; Farquhar et al. 2000), more reducing conditions prevailed in the oceans as witnessed by the occurrence of Banded Iron Formations (James and Trendall 1982; Kump and Holland 1992). Sulfur species in Precambrian seawater were both in reduced and oxidized states as suggested by the high variability of sulfur isotope ratios of both sulfides and sulfates in Precambrian rocks older than 2.4 Ga (Farquhar et al. 2000; Farquhar and Wing 2003; Ono et al. 2003). If marine sulfates were not the dominant oxidizing agent in seawater, the ferrous iron component of the oceanic crustal rocks could have been oxidized to Fe^{3+} by water during seawater-basalt interactions according to the reaction:



This reaction promotes the reduction of water to H_2 . On an O_2 -free planet, such as Mars and early Earth, the rate of hydrogen escape is proportional to the H_2 mixing ratio in the atmosphere (Hunten 1973). Thus, H_2 produced by reaction (1) may enhance hydrogen escape. Water reduction and hydrogen escape finally contribute to the evolution of the redox state of surficial planetary envelopes, potentially increasing the oxidation state of the atmosphere and surficial rocks.

Oxidation of silicates during seawater-basalt interactions is able to modify the D/H ratio of surficial water because of the high magnitude of D/H fractionation that occurs between water and H_2 , even at high temperatures (Suess 1949; Cerrai et al. 1954; Richet et al. 1977). For example, during on-axis mid-ocean ridge hydrothermal alteration (200 °C to 350 °C), the equilibrium fractionation factor $\alpha_{H_2O-H_2}$ between water and H_2 ranges from 1.567 to 1.962 (Richet et al. 1977). In order to quantify the effect of the oxidation of rocks by water on the hydrogen isotope composition of terrestrial atmospheres, experiments were performed to determine the isotopic fractionation between water and H_2 that accompanies silicate oxidation.

During heating and breakdown of biotite, water is released according to the following equation:



then a fraction of this water is partly reduced by Fe^{2+} into H_2 (Feldstein et al. 1996; Righter et al. 2002; Demény et al. 2006). These experimentally-determined apparent fractionation factors, most likely resulting from kinetic effects, are finally applied to mass balance calculations for estimating the D/H ratios of Earth's ocean and Mars' atmosphere through time.

Experimental methods

Experiments have been conducted in a high-vacuum extraction line. Selected material to promote the redox reaction is the biotite international reference standard NBS30 ($\delta\text{D} = -65.7\text{‰}$) which contains 4 wt.% of water. An amount of 30 mg to 60 mg of biotite was loaded into a quartz reactor and heated at 150 °C for 1 hour in vacuum to remove any atmospheric adsorbed water on the sample. Temperatures of reaction were selected between 600 °C and 1200 °C. At temperatures lower than 600 °C, we did not observe any production of hydrogen gas during sample heating. The vacuum extraction line made of Pyrex was maintained at a temperature of 80 °C over the complete manipulation to avoid water condensation on the inner sides of the experimental apparatus.

Biotite samples were instantaneously heated at the temperature of interest for 5 minutes when temperatures exceeded 900 °C, and up to 20 minutes when temperatures were lower than 700 °C. The amount of water released by the dehydration of biotite was qualitatively monitored using the pressure gauge. Water vapor was collected at liquid nitrogen temperature into a glass tube containing zinc metal. The residual gases, not condensable in liquid nitrogen, were mainly composed of H_2 produced by the oxidation of the FeO component of biotite by water. The hydrogen gas was quantitatively oxidized to water in a CuO furnace (500 °C), and the water was finally trapped in liquid nitrogen.

H_2 gas for isotopic measurement was obtained from both water samples following the off-line method of water reduction by hot zinc to produce hydrogen gas (Vennemann and O'Neil 1993). D/H isotopic analyses were then performed by using a dual-inlet MAT-Finnigan Delta E mass spectrometer. External reproducibility of D/H measurements was 3‰ relative to the SMOW-SLAP scale.

After expansion of H_2 into a constant volume of the mass spectrometer sample inlet, the amount of gas was estimated from the voltage of mass 2 collector (Vennemann and O'Neil 1993). We thus observed that during the experiments the H_2 production ranged between 3 and 8 μmol , at least one order of magnitude lower than the amount of water collected at the same time (20–70 μmol).

Statistical analyses were performed using JMP 7 software (SAS, Cary, NC, USA). Significance of all statistical tests was accepted at $\alpha < 0.05$.

Results

D/H ratio is expressed relative to SMOW and noted δD_{H_2O} for water and δD_{H_2} for hydrogen. The calibration of the procedure is achieved using SMOW and SLAP water aliquots (cf. Table 1). The isotopic fractionation factor $\alpha_{H_2O-H_2}$ is expressed as:

$$\alpha_{H_2O-H} = (1000 + \delta D_{H_2O}) / (1000 + \delta D_{H_2}) \quad (3)$$

The fractionation factors α between water and hydrogen gas have a linear dependence on $10^6 \cdot T^{-2}$ (Fig. 1), as follows:

$$\alpha = 1.024(\pm 0.022) + 0.247729(\pm 0.027705) \cdot 10^6 \cdot T^{-2}$$

with $r^2 = 0.83$, $P < 10^{-6}$ and the residual standard deviation of the linear regression $\sigma = 0.023$. This linearity of α vs. T^{-2} is accounted for by the property

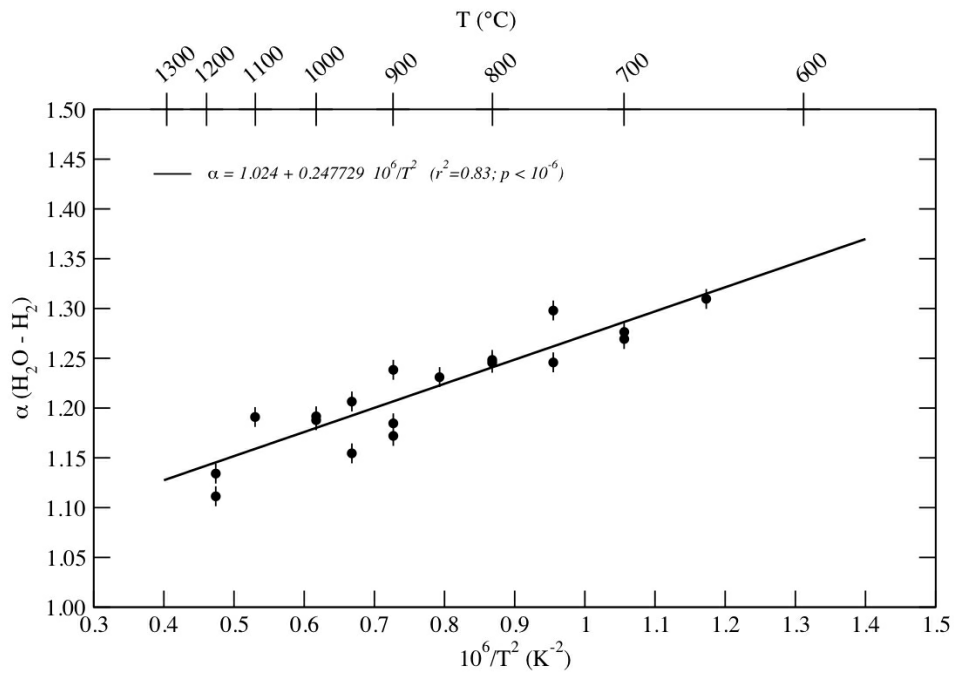


Fig. 1
Apparent fractionation factors $\alpha_{H_2O-H_2}$ reported as a function of $10^6 \cdot T^{-2}$

Table 1
D/H measurements of water and hydrogen gas released during the high-temperature oxidation of biotite NBS30. Apparent fractionation factors $\alpha_{\text{H}_2\text{O}-\text{H}_2}$ between H_2O and H_2 were determined in the temperature range 600–1200 °C. $\sigma = 3\text{‰}$ for the δD values

Experiment	T (K)		$\delta\text{D} (\text{H}_2\text{O})$	$\delta\text{D} (\text{H}_2)$	$\alpha_{\text{H}_2\text{O}-\text{H}_2}$
			(‰ SMOW)	(‰ SMOW)	
E – 23	923	±10	–49	–273	1.31
E – 05	973	±30	–42	–249	1.275
E – 08	973	±40	–51	–251	1.270
E – 16	1023	±10	–35	–256	1.297
E – 22	1023	±10	–47	–234	1.245
E – 01	1073	±10	–25	–218	1.247
E – 04	1073	±15	–42	–230	1.245
E – 17	1123	±25	–41	–220	1.230
E – 07	1173	±10	–50	–189	1.172
E – 15	1173	±10	–33	–184	1.185
E – 20	1173	±25	–27	–213	1.237
E – 21	1223	±20	–39	–167	1.154
E – 24	1223	±25	–35	–200	1.206
E – 19	1273	±40	–29	–182	1.187
E – 26	1273	±20	–25	–181	1.191
E – 18	1373	±30	–24	–179	1.190
E – 25	1453	±40	–36	–132	1.111
E – 27	1453	±45	–29	–143	1.133

of the partition functions of isotopically substituted H_2 and H_2O (Horibe and Craig 1995).

The slope of this apparent fractionation line is not significantly different from that obtained for the equilibrium fractionation factors between water and H_2 calculated by Richet et al. (1977) (Fig. 1; Analysis of Covariance, "Study" x "T" interaction effect, $P=0.358$). Nevertheless, these apparent fractionation factors are significantly higher than those deduced either from calculations (Bardo and Wolfsberg 1976; Richet et al. 1977, Analysis of Covariance, "Study" effect, $P<10^{-7}$)

or from equilibrium experiments between water vapor and hydrogen gas (Suess 1949). Our measured fractionation factors between water and hydrogen gas are, however, higher than those obtained by equilibrium experiments between H_2O and H_2 (Cerrai et al. 1954). Discrepancies between these experimental fractionation factors suggest that H_2 production during hydrothermal reactions are dominated by kinetic fractionation effects. Our results are also in agreement with those obtained by Kuroda et al. (1998) who have shown that at temperatures higher than 700°C , a small amount of water in minerals may react with ferrous iron to produce deuterium-depleted H_2 gas.

The results of our experiments can be compared to the isotopic compositions of high temperature hydrothermal gases. H_2 gas is produced by abiogenic processes in the high-temperature hydrothermal vents of the East Pacific Rise at 21°N (Welhan and Craig 1983). This H_2 gas has a mean δD value of about -395‰

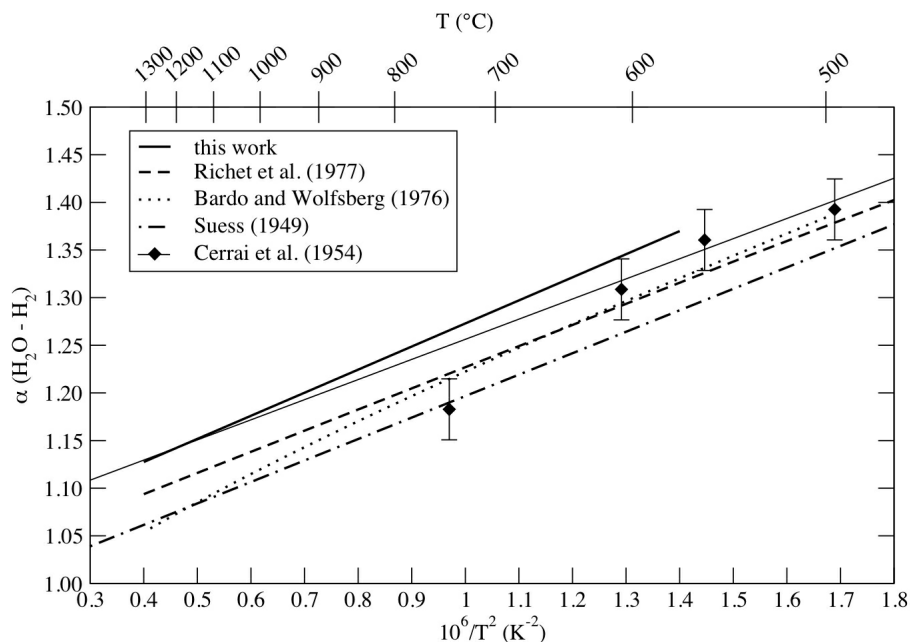


Fig. 2

Comparison of apparent fractionation factors $\alpha_{\text{H}_2\text{O}-\text{H}_2}$ between water and hydrogen gas released during our high-temperature oxidation experiments (plain line) with equilibrium fractionation factors determined from equilibrium experiments (dotted-dashed line: Suess 1949; thin line and diamonds: Cerrai et al. 1954) and theoretical considerations (dotted line: Bardo and Wolfsberg 1976; dashed line: Richet et al. 1977)

with a δD of the liquid water close to 0‰ (Welhan and Craig 1983; Horibe and Craig 1995). Using equation (3), the temperature calculated from the D/H ratio of H_2 is 350°C, matching well the measured regional base temperature of the vent field (Welhan and Craig 1983).

Implications on the D/H ratio of Early Earth and Mars volatile envelopes

D/H evolution of the Early Earth

D/H fractionation between water and hydrogen is expected to be associated with the hydrothermal reaction between basaltic rocks and water. A corresponding flux of water lost during silicate oxidation equals $1.3 \cdot 10^3 \text{ kg} \cdot \text{s}^{-1}$ (equivalent to $10^{10} \text{ atom H} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) according to reaction (1) and also based on the net flux of Fe^{3+} subducted into the mantle ($12 \cdot 10^3 \text{ kg} \cdot \text{s}^{-1}$) proposed by Lécuyer and Ricard (1999). Integrating this flux over 4 Gy provides a maximum water mass of $1.6 \cdot 10^{20} \text{ kg}$, corresponding to about 10% of the present-day oceanic masses which would have escaped from Earth's atmosphere as hydrogen. Such a rate of water escape is two orders of magnitude higher than the present-day escape H_2 flux in the upper atmosphere which equals about $2 \cdot 10^8 \text{ atom H} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$, corresponding to a water flux of $8 \cdot 10^8 \text{ kg} \cdot \text{a}^{-1}$ (Hunten and McElroy 1974). Two reasons could be invoked to explain this difference: (i) the present-day Earth's atmosphere contains oxygen gas which rapidly oxidizes H_2 to water during atmospheric reactions and (ii) most of the Fe^{3+} in the subducted oceanic crust results from the oxidation of basaltic rocks by marine sulfates. As far as (i) is concerned, the absence of oxygen gas in the Precambrian atmosphere (before 2 Ga) prevents any atmospheric oxidation of H_2 , hence enhancing the escape flux of H_2 . The flux of ferric iron (ii) that entered the mantle remains still impossible to quantify because of the lack of available $Fe^{3+}/\Sigma Fe$ data for Precambrian hydrothermally-altered oceanic rocks. Nevertheless, the net flux of Fe^{3+} subducted to the mantle, calculated by Lécuyer and Ricard (1999), could be used for the Precambrian if we consider two counterbalancing processes that are (i) a lower sulphate concentration less than 200 μM (Habicht et al. 2002) in seawater and (ii) a higher rate of oceanic crust production from 6 to 10 times the present-day value of $3 \text{ km}^2 \cdot \text{y}^{-1}$ (Kröner 1985; Hargraves 1986; Catling et al. 2001). The resulting net flux of hydrogen escape from the atmosphere of $10^{10} \text{ atom H} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ is bracketed by the two boundary values ($1.9 \cdot 10^9$ – $1.9 \cdot 10^{10} \text{ atom H} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$) of hydrogen fluxes released by the volcanic activity into the early atmosphere (Holland 1984). According to the relationship that links the escape flux to the total mixing ratio of hydrogen in an oxygen-free atmosphere (Walker 1977; Holland 1984), a total hydrogen mixing ratio of $4 \cdot 10^{-4}$ is calculated and is compatible with a negligible content of O_2 in the lower atmosphere (Kasting and Walker 1981; Holland 1984).

The change of the D/H ratio of the hydrosphere caused by the oxidation of the mantle rocks can be modeled by a Rayleigh-type distillation in which H_2 is

instantaneously removed after its production from water reduction. The isotopic evolution of the residual water is:

$$d \ln(D/H)_{H_2O} = (\alpha_{H_2O-H_2} - 1) d \ln f \quad (4)$$

where f is the fraction of water remaining, $(D/H)_{H_2O}$ is the D/H isotope ratio of water, and $\alpha_{H_2O-H_2}$ the fractionation factor between hydrogen gas and water. Considering again the calculated hydrogen flux of 10^{10} atom $H.cm^{-2}.s^{-1}$ escaping from Earth's atmosphere as a consequence of hydrothermal reactions, calculated δD values of the remaining ocean mass vary between $+17\text{‰}$ (assuming a mean temperature of hydrothermal reaction of 400 °C and $f=0.95$, i.e. 5% of the hydrosphere was lost) and $+55\text{‰}$ (for $T=200\text{ °C}$ and $f=0.9$). In combination to the hydrogen isotope fractionation that takes place between water and OH-bearing minerals during the alteration of the oceanic crust ($-15\text{‰} < \delta D \text{ seawater} < 10\text{‰}$; Lécuyer et al. 1998), the primordial ocean was deuterium-depleted relative to SMOW, possibly down to -70‰ .

D/H evolution of the Martian atmosphere

The D/H ratio of Martian atmospheric water vapor is $8.1 \pm 0.3 \cdot 10^{-4}$ (Owen et al. 1988), a value 5.4 times greater than the D/H terrestrial ratio. Without any strong supporting evidence, the pristine D/H ratio of Mars water could be assumed to be close to the terrestrial ratio (e.g. Donahue 1995; Krasnopolsky 2000; Boctor et al. 2003). D/H ratios of apatite grains from Martian meteorites (Leshin 2000) suggest that the initial D/H value could have been about 1.9 times the terrestrial value. The dynamical simulations of Mars accretion performed by Lunine et al. (2003) suggest a primitive D/H ~ 1.2 to 1.6 times the Earth's D/H ratio. Analyses of Martian meteorite NWA817 reveal that a primitive component of Martian surface water with a low δD value of -170‰ could have been recorded by alteration products (Gillet et al. 2002). Present-day estimates of the amount of surficial water mainly trapped in ice caps would represent a 30 m-thick layer of water covering totally the Martian surface. The physical properties of the Martian regolith suggest that it could contain an amount of water equivalent to a homogeneous layer comprised between 50 and 450 m (Carr 1986; Clifford 1993; Jankovski and Squyres 1993; Mangold et al. 2002; Boyce et al. 2005). Taking into account the presence of a large amount of ice stored near the Martian surface combined to a volcanic activity documented during nearly all Mars' history (Hartmann et al. 1999; McEwen et al. 1999), hydrothermal systems should have been active on Mars (Soderblom and Wenner 1978; Mouginiis-Mark 1985; Squyres et al. 1987). They could be responsible for a storage of about 30 m of water in hydrous minerals (Griffith and Shock 1997).

The Deuterium-enrichment of SNC meteorites may be related to high-temperature isotope exchange with Martian atmospheric water that was strongly

isotopically fractionated during the mechanism of hydrogen escape (Bjoraker et al. 1989). Demény et al. (2006) have shown, however, that dehydrogenation and dehydration of hydrous silicates such as amphiboles can account for the δD values that were measured in Martian meteorites.

If hydrothermal systems have existed on Mars, crustal oxidation by water could have changed the D/H of residual water circulating in the crust. Because the atmosphere of Mars is oxygen-free, H_2 produced from water reduction can escape to space. The maximum ability of Martian crust to oxidize, hence to change its water D/H ratio, can be tested by using the Rayleigh distillation equation (eq. 4). The D/H ratio of residual water is calculated as a function of the fraction of remaining water for mean temperatures of hydrothermal reactions ranging from 100 to 400 °C (Fig. 3). A 5.4-fold increase of D/H ratio is achieved by a loss of water of about 93% (100°C) to more than 99% (400 °C). If the present-day Martian D/H ratio is the result of a 4-fold enrichment, a 89–98.5% range of water loss is then required (Fig. 3). Considering the mechanism of hydrogen escape, comparable fractions of water losses (80–90%) have been proposed to explain the present-day D/H ratio of the Martian's atmosphere (Carr 1996). Consequently, the

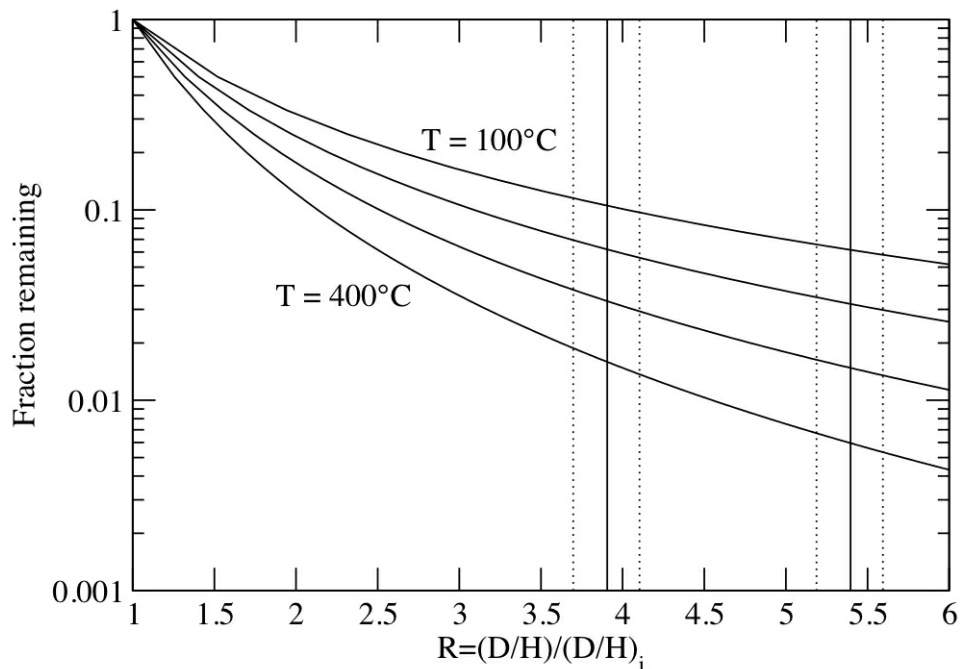


Fig. 3 Influence of water loss by silicate oxidation in hydrothermal conditions on the D/H ratio of Martian atmosphere. The fraction of original water remaining is reported as a function of the D/H enrichment for temperatures ranging from 100 °C to 400 °C (curves each 100 °C). Vertical lines represent enrichments of 3.9 ± 0.2 and 5.4 ± 0.2 , corresponding to a primitive D/H ratio of 210×10^{-6} (~ 1.4 SMOW) and 150×10^{-6} (\sim SMOW), respectively

reduction of water to hydrogen by iron-bearing silicates during hydrothermal activity could have significantly contributed to the D/H increase of the Martian's atmosphere, especially if the mean temperature of crust alteration was low enough. Estimates of primordial amounts of water that are based on the present-day D/H ratio of atmospheric water vapor could have been overestimated if Mars has undergone an extensive hydrothermal activity.

Concluding remarks

At high temperatures, oxidation of the FeO component of biotite by water results in a production of H₂. The hydrogen isotope apparent fractionation factor α between H₂O and H₂ was measured in the temperature range 600–1200 °C. The linear dependency of α vs. T⁻² resembles both experimental and theoretical fractionation lines that were determined for equilibrium hydrogen isotope exchange between water and hydrogen gas. This result suggests that H₂O and H₂ could be in isotopic equilibrium during the dehydration reaction. If we admit the net flux of Fe³⁺ toward the mantle as a plausible estimate during the Archean (Lécuyer and Ricard 1999), a flux of hydrogen escape of 10¹⁰ atom H.cm⁻².s⁻¹ in an oxygen-free atmosphere may produce a δ D increase of Earth's oceans up to 50‰. In a similar way, if Mars has undergone an extensive hydrothermal activity, water loss by oxidation of iron-bearing silicates could also have contributed to the present-day high D/H ratio of Martian's atmosphere.

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