# Revision 1

# Chemical reactions in the $Fe_2SiO_4$-$D_2$ system with a variable

# deuterium content at 7.5 GPa

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# Abstract

Hydrogen-induced decomposition of fayalite ($Fe_2SiO_4$) at high pressure is of considerable interest

for a better understanding of the chemical processes occurring in the cores and mantles of icy satellites.

At pressures up to 10 GPa and temperatures 250−300 °C typical of the cores and mantles of Jupiter's

and Saturn's satellites a variable amount of hydrogen can react with fayalite contained in their rocks.

Volatile compounds that can form via these reactions are usually identified by mass spectroscopy. In

our experiments, we used compressed deuterium gas instead of hydrogen to ensure that the volatiles

analyzed by mass spectroscopy could only result from decomposition of fayalite. To study the effect

of the amount of deuterium present in the system, the fayalite (Fa) samples were deuterated at P = 7.5

GPa and T = 280 °C with the preset molar ratios $D_2$/Fa = 1, 1.5, 2.2, and 5 in the reaction cell. The

deuterated samples were further quenched to the liquid $N_2$ temperature and, after releasing the

pressure, removed from the reaction cell and studied by quadrupole mass-spectroscopy, X-ray

diffraction and Raman spectroscopy. Our results showed that the high-pressure deuteration invariably

led to the chemical decomposition of fayalite. The solid products of the reaction varied from a mixture

of ferrosilite ($FeSiO_3$) and iron at $D_2$/Fa = 1 to a mixture of silica and iron at $D_2$/Fa = 2.2. The

decomposition occurred via breaking the Fe-O bonds and was always accompanied by the formation

of water. Applying the observed reactions to the natural conditions of, e.g., the center of Titan or

Ganymede, one may infer that fayalite can be dissolved in the hydrogen fluid or replaced by iron,

ferrosilite or silica depending on the molar ratio $H_2$/Fa.


Keywords: fayalite, hydrogen, ferrosilite, high pressure, decomposition reaction, silica, iron

# Introduction

The recent discovery of considerable amounts of molecular hydrogen in the Enceladus plumes (Waite et al. 2017) suggests its presence in the interiors of other icy moons of Saturn and those of Jupiter. Most hydrogen on Enceladus is assumed to be produced by the reaction of the waters of its mantle ocean with a silicate core (Waite et al. 2017), and mantle oceans and silicate cores are typical of many icy moons. Under natural conditions, the hydrogen thus produced can form a pure fluid (Bali et al. 2013), which will react with the silicates, too. It is expected that the silicate cores of such icy moons as Enceladus and, for example, Titan are largely composed of olivines, solid solutions $Mg_{2-x}Fe_xSiO_4$, and water ice (Fortes, 2012). Consequently, our understanding of the processes occurring in the inner parts of icy satellites will be incomplete in the absence of physico-chemical data on the interaction of olivines with hydrogen at high pressures. Previous X-ray diffraction and Raman spectroscopy studies revealed a partial decomposition of the magnesium end-member of olivines, forsterite ($Mg_2SiO_4$), to MgO and $SiO_2$ at hydrogen pressures 2–10 GPa and T > 1000 °C (Shinozaki et al. 2012 and Shinozaki et al. 2013). Recently (Efimchenko et al. 2019), we observed the hydrogen-induced decomposition of another end-member olivine compound, fayalite ($Fe_2SiO_4$), at much lower temperatures ranging from ~375 °C at P = 1.4 GPa to ~175 °C at P = 7.5 GPa. Fayalite was shown to completely decompose to a mixture of silica, water and metallic Fe or FeH, when it was surrounded with a large amount of molecular hydrogen ($H_2/Fa \geq 5$).

However, fayalite can be in contact with a smaller amount of hydrogen ($H_2/Fa < 5$) in the natural conditions. As is known, a deficiency of one component can lead to an interruption in the chemical reaction or to a change in the composition of the reaction products. The standard reaction of hydrogen-induced fayalite decomposition at P = 7.5 GPa:
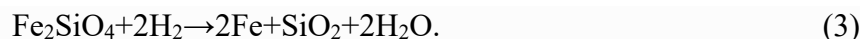
$$Fe_2SiO_4 + 3H_2 = 2FeH + SiO_2 + 2H_2O, (1)$$

requires $H_2/Fa = 3$ (Efimchenko et al. 2019). If the amount of hydrogen is less than $H_2/Fa = 3$, two

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different reaction paths are possible. First, fayalite may simply not decompose on contact with less

hydrogen ($H_2$/Fa < 3). The second way is the decomposition of fayalite into a mixture of compounds

different from that observed at $H_2$/Fa $\geq$ 5. In particular, hydrogen can form only one hydrogen-rich

compound, iron hydride or water. The formation of iron hydride can occur by the following reaction:

$$Fe_2SiO_4 + H_2 \rightarrow 2FeH + SiO_2 + O_2. \tag{2}$$

Water can be formed by the reaction:

$$Fe_2SiO_4 + 2H_2 \rightarrow 2Fe + SiO_2 + 2H_2O. \tag{3}$$

Reaction (2) requires $H_2$/Fa = 1. Reaction (3) can occur at $H_2$/Fa = 2.

In the present paper, we studied the reaction of fayalite with a $D_2$ gas using a quenching technique.

After the deuteration was complete, the sample was rapidly cooled (quenched) to the boiling

temperature of $N_2$; the pressure was reduced to atmospheric; the sample was removed from the

reaction cell and studied by quadrupole mass-spectroscopy, X-ray diffraction and Raman

spectroscopy. As seen from reactions 2 and 3, the quenched samples could contain water and iron

hydride; the latter is unstable under ambient conditions and decomposes with the release of $H_2$

(Antonov 2002). We used deuterated samples to ensure that the volatile reaction products analyzed

by quadrupole mass-spectroscopy could only be formed in the reaction of fayalite with the $D_2$ gas.

## Methods

The initial sample of fayalite powder was synthesized by a solid-state reaction of silica, carbonyl

iron and hematite at 1000 °C in a reduced atmosphere. The as-prepared sample contained a certain

amount of particles of unreacted iron, which were further removed by a permanent magnet. X-ray

diffraction showed that this sample is single-phase fayalite with an orthorhombic Pnma structure and

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lattice parameters a = 10.471(6) Å, b = 6.087(4) Å, c = 4.817(4) Å, in agreement with Anthony et al. (2001).

The deuteration of fayalite was carried out in a Toroid-type high-pressure apparatus (Khvostantsev, 2004) with a squirrel-type heater made of Nichrome wire 0.5 mm in diameter. Aluminum deuteride ($AlD_3$) was used as an internal deuterium source. The fayalite sample and $AlD_3$ were placed together in a high-pressure cell made of Teflon and separated from each other by a Pd foil and boron nitride layer. To evolve deuterium, aluminum deuteride was decomposed at P = 1.5 GPa by heating to T = 280 °C. The pressure of the $D_2$ gas thus produced was then increased until reaching P = 7.5 GPa. The temperature was measured with an accuracy of ±10 °C with a Chromel-Alumel thermocouple. The pressure was estimated with an accuracy of ±0.3 GPa using the pressure / ram load dependence determined in separate experiments. The quantities of $AlD_3$ were selected so as to release molecular deuterium in an amounts corresponding to the molar ratios $D_2$ / $Fe_2SiO_4$ =1, 1.5, 2.2 and 5. A more detailed description of the hydrogenation procedure can be found elsewhere (Antonov, 2017). The powder sample of $Fe_2SiO_4$ was exposed to the pre-selected conditions for 24 hours. Then the high-pressure apparatus with the sample inside was quenched to the liquid $N_2$ temperature and the pressure was released. The high-pressure apparatus was disassembled under liquid nitrogen and the sample was retrieved from the cell and stored in liquid $N_2$ until the measurements.

The types and contents of volatile products of the fayalite decomposition were determined on the quenched samples using a quadrupole mass-spectrometer XT100M Extorr with the electron beam ionization. To study the chemical compositions of volatile compounds released at temperatures below 25 °C, the quenched sample was placed on the bottom of a quartz ampule cooled with liquid nitrogen, the ampule was pumped out to P = $10^{-9}$ Torr, connected to the mass spectrometer, and then its lower end together with the sample was heated from T = -196 °C to room temperature. While deuterated

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samples were used, we could ignore water ice condensed on the inner wall of the pre-cooled quartz ampule when loading the quenched sample. To analyze the gas released during heating from T = 25 to 730 °C, the sample was loaded in the quartz ampule at room temperature. The heating rate was about 20 °C/min. The temperature was measured using a Chromel-Alumel thermocouple attached to the bottom of the quartz ampule from outside. Pumping the ampoule and the mass-spectrometer chamber continued throughout the experiment. The compounds vaporized from the sample were ionized in the chamber by an electron beam with an electron energy E=70 eV. Collisions of the evaporated molecules with electrons led to the formation of positively charged ions as a result of the $M + e^- = M^+ + 2e^-$ reaction.

The ions thus formed entered a quadrupole mass analyzer consisting of four metal rods, to which an alternating voltage $U = U_0 + V\cos(\omega t)$ was applied. By changing the parameters $U_0$ and $V$, only ions of a certain mass could pass through the analyzer. After passing through the quadrupole mass analyzer, the ions came into the Faraday cup, a device for determining the intensity of a particle beam. The Faraday cup was made of a conductor thick enough to absorb all incoming ions. The resulting current was assumed to be proportional to the partial pressure of the ions of a pre-selected mass.

To analyze the chemical composition of the releasing gas, we used two operating modes of the mass spectrometer: mass sweep and trend. In the first mode, we recorded the pressures for all masses from 1 to 50 m/z. The acquisition time of each record in the mass-sweep regime was about 14 sec. This mode allowed detecting peaks corresponding to the volatile decomposition products of fayalite. The recorded spectra were analyzed and compared with the spectra of possible individual compounds available in the NIST database. In the second mode, we recorded the time dependence of the pressures for some masses detected in the first mode. Both modes were used at the regime of continuous heating of the deuterated samples.

Raman spectra from the deuterated and initial samples were recorded in a back-scattering

geometry using a micro-Raman setup comprised of an Acton SpectraPro-2500i spectrograph and a CCD Pixis2K detector system cooled down to $-70\ °C$. The measurements were performed near the liquid nitrogen temperature in the spectral range from 140 to 4500 $cm^{-1}$. The 532 nm line of a single-mode YAG CW diode pumped laser was focused on the sample by an Olympus 50× objective in a ~2 μm diameter spot that was slightly defocused due to the light refraction in the nitrogen vapors. The spatial resolution was also ~2 μm and the spectral resolution varied between 2.3 and 4.1 $cm^{-1}$. The laser line in the scattered beam was suppressed by a super-notch filter with the optical density OD = 6 and bandwidth ~160 $cm^{-1}$, while the beam intensity before the sample was ~5 mW. The data acquisition time was 120 sec.

The quenched samples heated to room temperature were also studied by powder X-ray diffraction under ambient conditions with a Siemens D500 diffractometer using Cu Kα radiation selected by a diffracted beam monochromator. The obtained diffraction patterns were analyzed by the Rietveld method using the POWDERCELL2.4 software with an uncertainty in the phase composition of about ±1 mol.%.

## Results

### Faylite -2.2D$_2$ and Fayalite-5D$_2$ samples

The sample deuterated at P = 7.5 GPa, T = 280 °C with the starting molar ratio $D_2/Fa = 2.2$ was studied by Raman spectroscopy, X-ray diffraction and quadrupole mass-spectroscopy.

Figure 1 shows the Raman spectra collected at ambient pressure on the quenched Fayalite-2.2D$_2$ sample submerged in liquid nitrogen. As seen from Fig. 1, lines of the initial *Pnma* fayalite disappeared after deuteration and new peaks at 517 $cm^{-1}$ and 655 $cm^{-1}$ arose in the Raman spectra. The peak at 517 $cm^{-1}$ can definitely be attributed to coesite, $SiO_2$, while the peak at 655 $cm^{-1}$ may correspond to both fayalite with a spinel-type structure and to magnetite $Fe_3O_4$. To resolve the

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uncertainty and determine phase composition of the Fayalite-2.2$D_2$ sample, it was studied by X-ray diffraction.. As shown in Figure 2, there are no diffraction peaks from the initial *Pnma* fayalite structure. Instead, the pattern contains peaks of a fayalite phase with the $Fd\overline{3}m$ spinel structure and lattice parameter a=8.2425 Å, which is slightly larger than the that of (a=8.237 Å) of magnetite $Fe_3O_4$. A more detailed analysis of the diffraction pattern showed that the sample contained 38.8 mol. % of fayalite with the spinel structure; 23.6 mol% of coesite; 21.8 mol% of α-quartz $SiO_2$; 23.2 mol% of bcc iron and a small amount (2.52 mol%) of hematite $Fe_2O_3$.

The chemical compositions of volatile compounds formed during the fayalite decomposition were obtained by quadrupole mass-spectroscopy. The mass-spectrum of the Fayalite-2.2$D_2$ sample recorded in the mass sweep regime is shown in Fig. 3. In addition to the lines of $H_2O$, CO, and $CO_2$, which were frozen in the mass-spectra cell while loading the sample, we observed peaks at 3 and 4 m/z corresponding to DH and $D_2$ molecules, and peaks at 19 and 20 m/z, which could be attributed to DHO and $D_2O$ molecules.

Figures 4a and 4b show the mass-spectra recorded in the trend regime for the samples Fayalite-2.2$D_2$ and Fayalite-5$D_2$, respectively. On both spectra, we observed the release of deuterium at temperatures near –10 °C and evaporation of heavy water near the room temperature. However, the maximal pressures for these gases evaporated from the Fayalite-2.2$D_2$ sample were lower than those for the Fayalite-5$D_2$ sample. The maximal deuterium pressure for the Fayalite-2.2$D_2$ sample ($P_{D2}$ = $10^{-8}$ Torr) is one and a half orders of magnitude less than for the Fayalite-5$D_2$ sample. The difference is due to the decomposition of iron deuteride FeD formed in the sample prepared using a higher molar ratio of $D_2/Fa$ = 5. In the Fayalite-2.2$D_2$ sample, iron deuteride did not form and the much smaller amount of deuterium was only released from its solid solutions in silica and bcc iron.

The $D_2O$ pressure for the Fayalite-2.2$D_2$ sample is also an order of magnitude lower than that for the Fayalite-5$D_2$ sample. We hypothesized that heavy water in the Fayalite-2.2$D_2$ sample could react

with other substances formed after the fayalite decomposition. In this case, $SiO_2$, bcc iron, and fayalite with the spinel structure should be enriched in heavy water and lose it in the mass-spectra cell at $T > 25$ ºC. To verify this assumption, we heated Fayalite-2.2D$_2$ and Fayalite-5D$_2$ samples from room temperature to 650 ºC and recorded their mass spectra in the trend mode. The obtained time dependencies are shown in Fig. 5. The maximal value of the $D_2O$ pressure in the mass-spectrum of the Fayalite-5D$_2$ sample does not exceed $10^{-11}$ Torr in the entire studied temperature range (Fig. 4b). In the spectrum of the Fayalite-2.2D$_2$ sample, the $D_2O$ pressure begins to increase at $T = 142$ ºC and reaches a maximum value of $P_{D2O} = 2 \cdot 10^{-10}$ Torr at $T = 526$ ºC (Fig. 4a). This means that the amount of heavy water leaving this sample is at least an order of magnitude higher than that of the Fayalite-5D$_2$ sample. In addition, a significant portion of the heavy water decomposed upon heating the Fayalite-2.2D$_2$ sample and also formed a $D_2$ gas. This is indicated by the simultaneous change in the pressures of the $D_2$, DH, DHO and $D_2O$ gases at temperatures above 267 ºC.

The results obtained with X-ray diffraction, Raman spectroscopy and mass spectroscopy demonstrate that fayalite deuterated at the starting molar ratio of $D_2/Fa = 2.2$, was partly decomposed via the reaction:

$$Fe_2SiO_4 + 2D_2 \rightarrow 2Fe + SiO_2 + 2D_2O, \tag{4}$$

while its unreacted portion acquired a cubic spinel structure. It should be noted that pathway (4) of fayalite decomposition at $T = 280$ ºC was previously observed at pressures of 2.8-3.3 GPa and initial molar ratios of $H_2/Fa > 5$ (Efimchenko et al. 2019). Presumably, the decomposition of fayalite at $D_2/Fa = 2.2$ should occur within the pressure range 2.8-7.5 GPa, and the deuterium fluid should be completely replaced by $D_2O$ when the pressure is increased to $P = 7.5$ GPa. In this case, heavy water may dissolve in the unreacted fayalite and/or silica. Some portion of the heavy water may also react with iron and produce 2.5 mol% hematite by the reaction:

$$2Fe + 3D_2O \rightarrow Fe_2O_3 + 3D_2. \tag{5}$$

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### Fayalite-1D$_2$ and Fayalite-1.5D$_2$ samples

One may expect that at the initial molar ratios D$_2$/Fa < 2, reaction (3) will not occur since the amount of deuterium is insufficient for the formation of D$_2$O. To verify this assumption, two samples of fayalite were deuterated at P = 7.5 and T = 280 °C with initial molar ratios of D$_2$/Fa = 1 and 1.5, and then studied by X-ray diffraction at ambient pressure and temperature and by mass-spectroscopy in the course of heating from T = –196 to 700 °C. Raman spectra were not obtained due to the large luminescent background from both samples. The collected X-ray diffraction patterns are shown in Fig. 6. A profile analysis of these diffraction patterns showed that both samples were partially decomposed and the residual fayalite (39.3 mol%  in the Fayalite-1.5D$_2$ sample and 42.8 mol% in the Fayalite-1D$_2$ sample) acquired a spinel-type structure with the lattice parameters a= 8.2415 and 8.2365 Å, respectively. Both samples also contained bcc iron (10.01 and 7.3 mol%) and P2$_1$/c ferrosilite (49.9 mol% and 16.49 mol%). The Fayalite-1.5D$_2$ sample additionally contained 34.2 mol% coesite. The presence of elemental iron in the sample Fayalite-1D$_2$ was further proved by EDX. Some areas of the sample were shown to contain up to 78.5 at% of iron. The obtained SEM images and EDX data for this sample can be found in the Supplementary materials.

Figure 7 shows mass spectra of the quenched samples Fayalite-1.5D$_2$ (Fig. 7a) and Fayalite-1D$_2$ (Fig. 7b) recorded in the mass sweep regime during heating from –196 to 25 °C. As in the spectrum of the Fayalite-2.2D$_2$ sample, there are peaks with the masses corresponding to HD, D$_2$, DHO, and D$_2$O molecules. In addition, both spectra have small peaks at m/z = 30, 32, and 34. Mass-spectra of the Fayalite-1.5D$_2$ and Fayalite-1D$_2$ samples recorded in the trend regime when heated from –196 to 25 °C are shown in Figure 8. In both spectra, we observed evaporation of deuterium at temperatures around –40 to –20 °C and evaporation of heavy water near the room temperature. In addition, we recorded time dependences of pressures for the molecules with masses 30, 32 and 34 previously

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detected in the mass sweep regime. In the process of heating, the pressures of these gases changed simultaneously, therefore indicating their origin from one compound. This compound was likely to be silane $SiD_4$. However, the maximal pressure values for the gases with masses 30, 32 and 34 were smaller by one or two orders of magnitude compared to those for $D_2O$ and $D_2$. Consequently, silane was probably an impurity in heavy water and molecular deuterium.

Figure 9 shows time dependences of pressures for the detected masses recorded in the trend regime in the course of heating the samples Fayalite-1.5$D_2$ (Fig 9a) and Fayalite-1$D_2$ (Fig 9b) from room temperature to 730 °C. The dependences demonstrate the evaporation of $D_2O$, DHO, and $D_2$ molecules in approximately the same temperatures range up to T ~ 500 °C as for the sample Faylite-2.2$D_2$. However, the maximal gas pressures of these molecules in the mass-spectra of Fayalite-1.5$D_2$ and Fayalite-1$D_2$ samples were an order of magnitude lower than those for the sample Fayalite-2.2$D_2$. This suggests that the heavy water formed at the fayalite decomposition did not react with other decomposition products to the same extent as in the sample Fayalite-2.2$D_2$.

Based on our X-ray diffraction and mass-spectroscopy data, the decomposition reaction of fayalite in the Fayalite-1$D_2$ sample should be:

$$Fe_2SiO_4+D_2 \rightarrow FeSiO_3+Fe+D_2O \qquad (6).$$

Together with iron, ferrosilite and $D_2O$, the sample Fayalite-1.5$D_2$ also contained a coesite phase of $SiO_2$. Therefore, the assemblage of the sample after the fayalite decomposition reaction can be written as:

$$2Fe_2SiO_4+3D_2 \rightarrow FeSiO_3+3Fe+SiO_2+3D_2O \qquad (7).$$

Note that the coefficients on the left side of Eqs. (6) and (7) correspond to the initial molar ratios for the studied samples. The lower concentration of ferrosilite in the Fayalite-1.5D$_2$ sample compared to Fayalite-1D$_2$ is likely to be a result of its decomposition via the reaction:
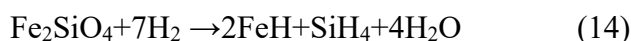
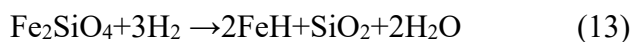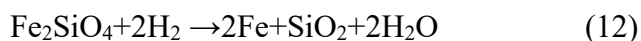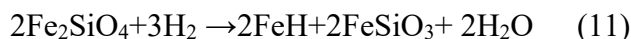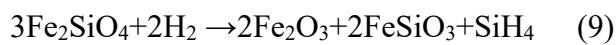$$FeSiO_3 + D_2 \rightarrow Fe + SiO_2 + D_2O \tag{8}.$$

As follows from this equation, the decomposition of ferrosilite can take place when $D_2/FeSiO_3 > 1$. This condition was fulfilled in the sample Fayalite-1.5D$_2$, so reaction (7) can be considered as the sum of reactions (6) and (8).

## Discussion

According to our mass-spectroscopy data, all four deuterated samples contained D$_2$O, which could only be formed upon the decomposition of fayalite. This fact may indicate the formation of D$_2$O as a driving force for the fayalite decomposition in the deuterium atmosphere. The formation of D$_2$O can only occur when a sufficient amount of deuterium is contained in the sample. The formation of D$_2$O during the decomposition of fayalite precludes the formation of FeD and SiO$_2$ via reaction (1) at a molar ratio of $D_2/Fa = 1$. Instead, ferrosilite and iron are formed.

The formation of Fe, SiO$_2$, FeSiO$_3$, and D$_2$O in the deuterated samples shows that fayalite-deuterium reactions can be considered in the four-component Fe-Si-D$_2$-O$_2$ system. Most likely, the fayalite-hydrogen system can be considered as a four-component system as well. Using the CSpace program (Torres-Roldán et al. 2000), we calculated all possible reactions in the Fe-Si-H$_2$-O$_2$ system. The number of these reactions is 126, if their products are limited to the 9 phases observed in the present work (FeH, Fe, FeSiO$_3$, Fe$_2$SiO$_4$, Fe$_2$O$_3$, SiO$_2$, H$_2$, H$_2$O, SiH$_4$). However, only 6 of the calculated 126 reactions include the interaction between hydrogen and fayalite. These 6 reactions are

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listed below in increasing order of the starting $H_2/Fa$ molar ratio:

$$3Fe_2SiO_4+2H_2 \rightarrow 2Fe_2O_3+2FeSiO_3+SiH_4 \quad (9)$$

$$Fe_2SiO_4+H_2 \rightarrow Fe+FeSiO_3+H_2O \quad (10)$$

$$2Fe_2SiO_4+3H_2 \rightarrow 2FeH+2FeSiO_3+ 2H_2O \quad (11)$$

$$Fe_2SiO_4+2H_2 \rightarrow 2Fe+SiO_2+2H_2O \quad (12)$$

$$Fe_2SiO_4+3H_2 \rightarrow 2FeH+SiO_2+2H_2O \quad (13)$$

$$Fe_2SiO_4+7H_2 \rightarrow 2FeH+SiH_4+4H_2O \quad (14)$$

The calculated reactions (10) and (12) coincide with reactions (6) and (4) described earlier. Reactions (13) and (14) were predicted by Efimchenko et al. (2019) for fayalite decomposition at the starting molar ratios $H_2/Fa \geq 3$. However, the system with $H_2/Fa = 1.5$ did not behave as predicted by reaction (11). As described in the previous section (Eq. (7)), the quenched sample contained Fe instead of the expected FeD and a considerable amount of $SiO_2$, which should not be formed at all according to Eq. (11). In addition, the sample also contained some unreacted fayalite. These suggest that the sample did not reach the equilibrium state during the high-pressure experiment. The unusual behavior of the Fayalite-1.5$D_2$ system needs further investigation.

Reaction (9) should occur at the starting molar ratio $H_2/Fa = 0.67$ and give silane without water. Previous studies (Shinozaki et al. 2013; Shinozaki et al. 2014) on reactions and phase transitions in the other end-member of olivine, forsterite ($Mg_2SiO_4$), revealed the abundant breaking of the Si-O bonds with the formation of MgO, $H_2O$ and $SiH_4$ at pressures 2–11 GPa and T > 1000 °C. The breaking of these bonds in the $SiO_4$ tetrahedra during the reaction of quartz and hydrogen was also confirmed by theoretical studies (Futera et al., 2017). At the same time, no breaking of the Mg-O bonds was observed at these pressures and temperatures. Thus, it should be concluded that reaction (9) and the formation of silane can only occur by breaking the Si-O bonds at T > 1000 °C. In contrast, the data obtained here and in the study of Efimchenko et al. (2019) led us to conclude that the decomposition

of fayalite in the Fayalite-Hydrogen system proceeds mainly by breaking the Fe-O bonds, whereas only a small part of the Si-O bonds breaks, which is manifested in the formation of small amounts of silane.

## Implications

The fundamental difference between the decomposition mechanisms of fayalite and forsterite can also lead to different interactions of hydrogen with iron- and magnesium-rich olivine in geological systems. Figure 10 shows the melting curves of the iron-containing phases, the decomposition curve of fayalite in a hydrogen atmosphere, the average geotherm for slabs in the Earth's mantle and the estimated pressures and temperatures in the cores of Titan, Ganymede, Europa, and Callisto. Among the all icy satellites, the expected temperatures ~220‑620 °C in the Titan's core are closest to that of the present study. According to exiting models, the estimated pressure in the center of Titan should depend on the core composition and can vary from 4.8 GPa (partly dehydrated silicates and water ice) to 5.9 GPa (troilite) (Fortes, 2012). Taking into account the moment of inertia, the most likely substances of Titan's core are the partly dehydrated silicates and water ice, so the pressure in its center should be close to 4.8 GPa (Fortes, 2012; Castillo-Rogez and Lunine, 2010). Serpentinization reactions probably occurring under these conditions can lead to the generation of hydrogen and, therefore, to the interaction of $H_2$ with fayalite-containing rocks.

If fayalite in the Titan's core rocks interacts with large amounts of molecular hydrogen ($H_2$/Fa > 3) at pressures of $P \geq 4$ GPa, it should decompose and produce $SiO_2$ and $FeH_x$ (Efimchenko et al. 2019). On the other hand, our results suggest that the reaction of fayalite-containing rocks with less hydrogen ($H_2$/Fa <3) should lead to the formation of iron, ferrosilite or silica. Since all these substances have melting curves lying above the temperatures of Titan's core, they must remain solid

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and cannot migrate from the hydrogenation zone. The same assumptions may apply to slabs in the Earth's mantle if they produce a significant amount of molecular hydrogen (Sokol et al. 2009)

Current temperatures of ~1400 °C in the centers of Europa and Ganymede (Kronrod and Kuskov, 2006; Jin S and Ji J H., 2012) far exceed the temperature of the present study. Besides, the cores of theses satellites do not contain silicates and consist of compounds of iron, sulfur and hydrogen (Kronrod and Kuskov, 2006; Schubert et al. 2004; Sohl et al. 2002). However, both satellites were much colder in the early stages after their formation (Bhatia and Sahijpal, 2017) and the pressure and temperature in their centers were close to those in the center of Callisto at the present time (P ~ 3.5 GPa, T~ 20-25 °C) (Nagel et al. 2004). Callisto is currently a partially differentiated body and consists of a mixture of iron, FeS, silicates and ice (O.L. Kuskov and V.A. Kronrod, 2005). It is reasonable to assume that after the formation, both Europa and Ganymede had a similar interior structure. With the subsequent heating of their interiors, iron and water could react with each other and produce hydrogen by reaction (6). Further heating and differentiation increased the pressure and temperatures in the centers of these satellites to values above the curve of fayalite decomposition in a hydrogen atmosphere, thereby initiating the formation of the compounds observed (this study and Efimchenko et al. 2019). When the interior temperature rose to its current level, while the amount of hydrogen was $H_2$/Fa ~ 7, silica had to decompose into $H_2O$ and $SiH_4$ fluids (Shinozaki et al. 2014). Iron hydride $FeH_x$ should also melt under these conditions (Fig. 10); the resulting fluids of $FeH_x$, $H_2O$ and $SiH_4$ will further migrate up or down depending on their densities until fayalite completely disappears from the hydrogenation zone (Efimchenko et al. 2019).

According to Shinozaki et al. (2013), the decomposition of forsterite ($Mg_2SiO_4$) under high hydrogen pressures can only occur in the presence of a large amount of hydrogen ($H_2$/Fo > 4), which is necessary for breaking the Si-O bonds. The periclase (MgO) formed in this reaction remains solid in the silicate rocks because its melting curve is much higher than the pressures and temperatures

characteristic of the satellites cores.

Similar processes of decomposition of fayalite and forsterite may hypothetically occur at the core-mantle interface of Ganymede, since its $FeSH_x$ core should release hydrogen, which diffuses upward and reacts with the silicate mantle (Shibazaki et al., 2011).

## Acknowledgments

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## Figure captions

**Figure 1**. Raman spectra of the Fayalite–$2.2D_2$ sample synthesized at 7.5 GPa and 280 °C (black solid

line) and the initial fayalite sample (red dashed line). Both spectra were collected at ambient pressure

and –196°C.

**Figure 2**. X-ray diffraction pattern of the Fayalite – $2.2D_2$ sample deuterated at 280 °C and 7.5 GPa

(CuKα radiation, room temperature and ambient pressure).

**Figure 3**. Quadrupole mass-spectra measured in the regime of heating the Fayalite – $2.2D_2$ quenched

sample from -196 to +20 °C in a pre-evacuated quartz tube.

**Figure 4**. Time dependences of the pressures for masses 4, 20, 32, 30, 34 on heating the samples

Fayalite-$5D_2$ (**a**) and Fayalite-$2.2D_2$ (**b**) from -196 to +25 °C.

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**Figure 5**. Time dependences of the pressures for masses 3, 4, 19, 20 on heating the Fayalite-2.2D$_2$ sample from 25 to 650 °C (**a**) and the Fayalite-5D$_2$ sample from 25 to 600 °C (**b**).

**Figure 6**. X-ray diffraction patterns of the Fayalite-1.5D$_2$ (**a**) and Fayalite-1D$_2$ (**b**) samples deuterated at 280 ºC and 7.5 GPa. The patterns were collected on the quenched samples at ambient pressure and temperature using CuKα radiation.

**Figure 7**. Quadrupole mass-spectra measured in the mass-sweep regime of heating the Fayalite-1.5D$_2$ (**a**) and Fayalite-1D$_2$ (**b**) quenched samples from –196 to +25 °C in a pre-evacuated quartz tube.

**Figure 8**. Time dependences of the pressures for masses 4, 20, 32, 30, 34 on heating the samples Fayalite-1.5D$_2$ (**a**) and Fayalite-1D$_2$ (**b**) from –196 to +25 °C.

**Figure 9**. Time dependences of the pressures for masses 3, 4, 19, 20 on heating the sample Fayalite-1.5D$_2$ from 25 to 650 °C (**a**) and the sample Fayalite-1D$_2$ from 25 to 730 °C (**b**).

**Figure 10**. Melting curves of iron (Shen et. al., 1998; solid green line), iron hydride (Hiroi et al., 2005; solid blue line) and ferrosilite (Kato et al., 1984; solid black line and solid squares). The curve of decomposition of fayalite in a hydrogen atmosphere (Efimchenko et al., 2019; solid red line). The P-T profile of the Earth's average subduction geotherm (Syracuse et al., 2010; dashed red line). Shaded areas show the supposed P,T conditions in the centre of the icy satellites Callisto (1), Titan (2), Ganymede (3), and Europe (4). The black asterisk shows the temperature and pressure of deuteration.
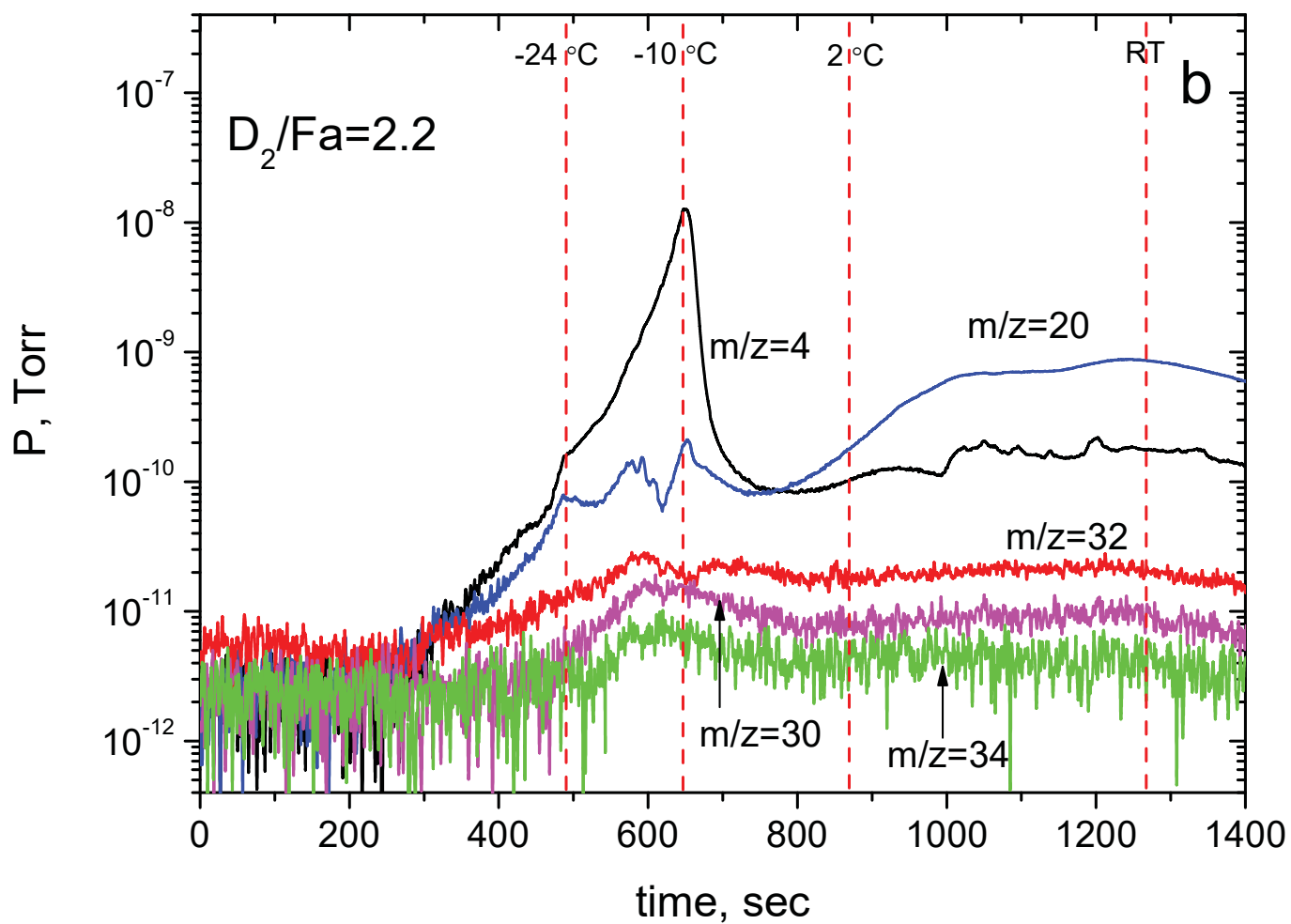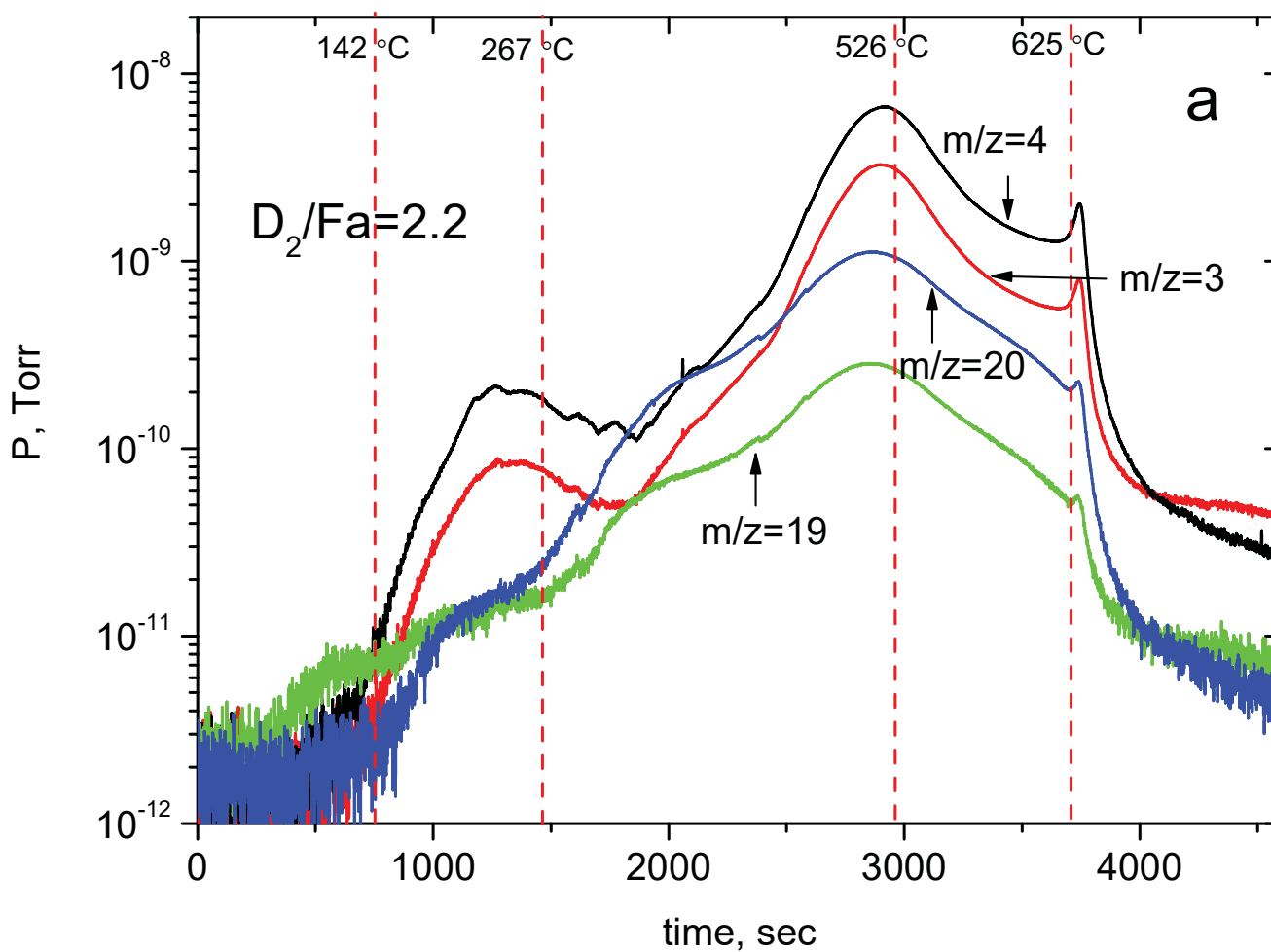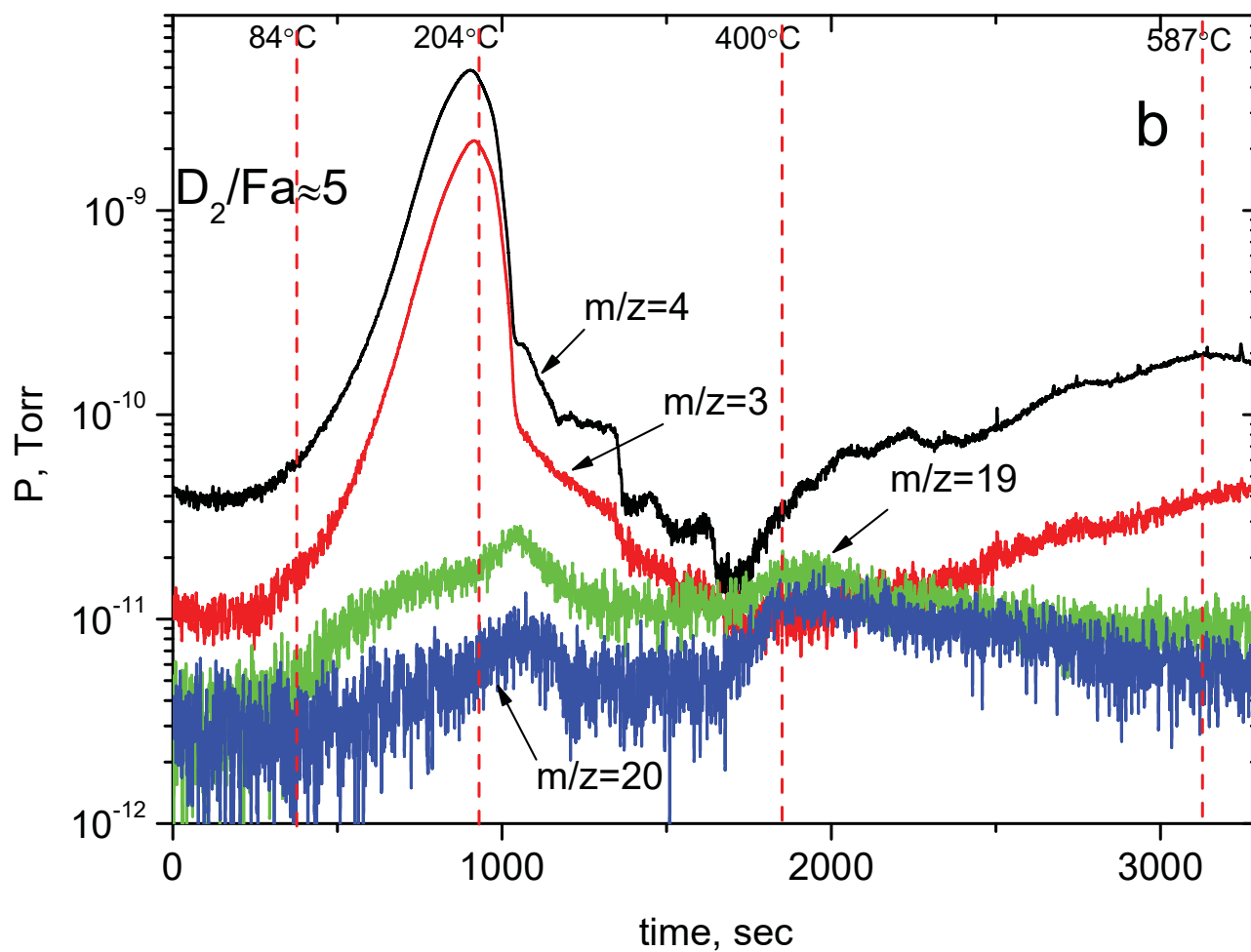
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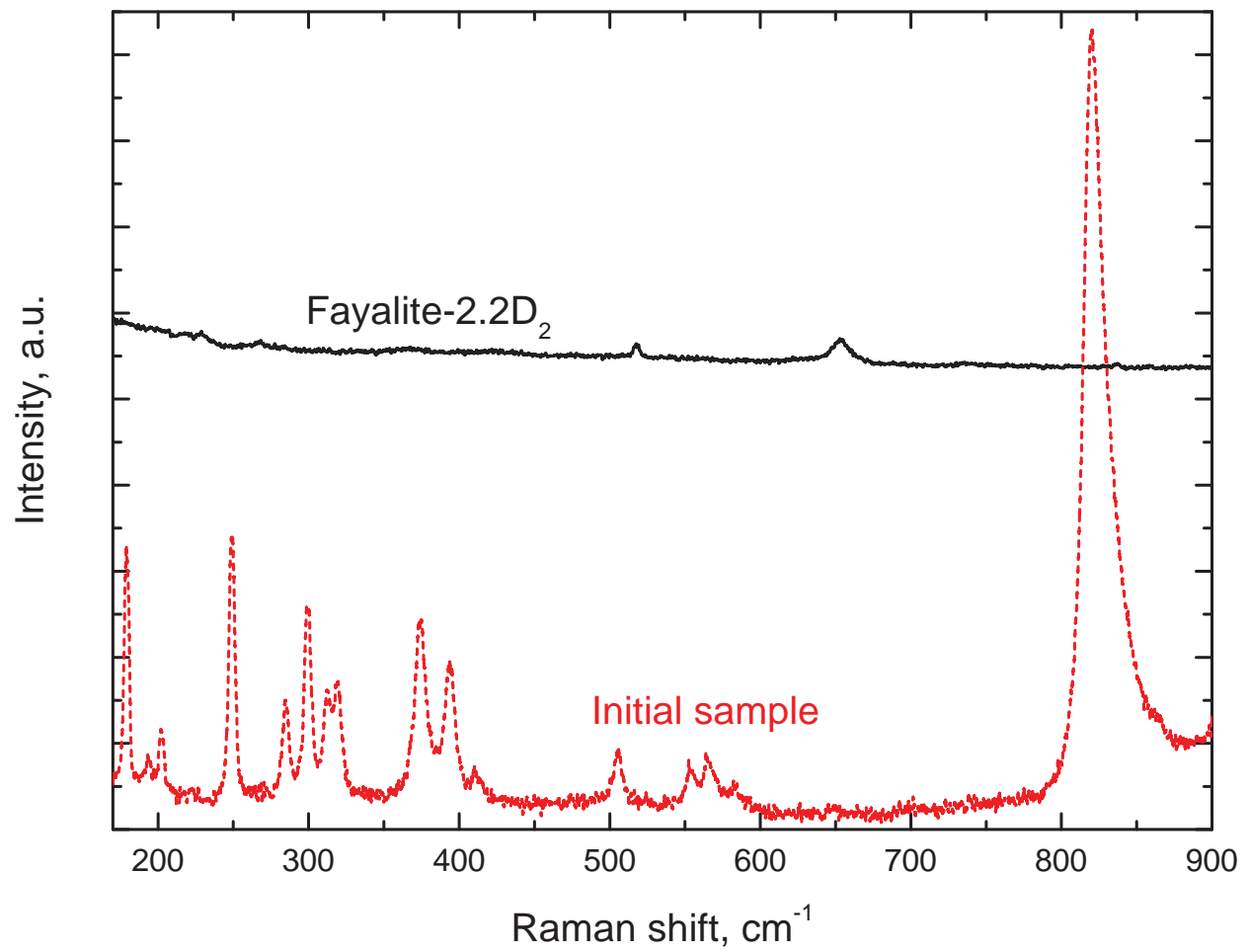
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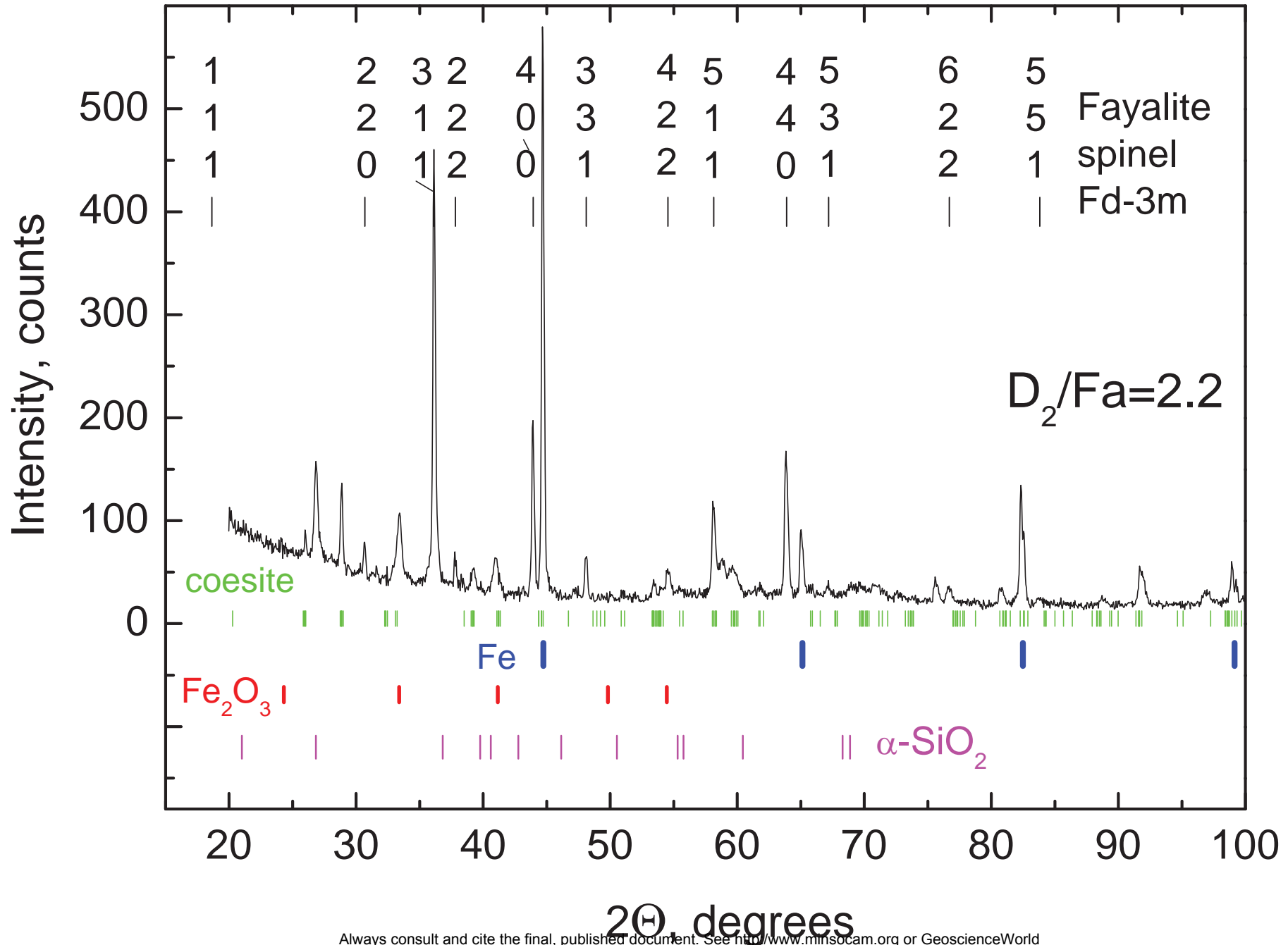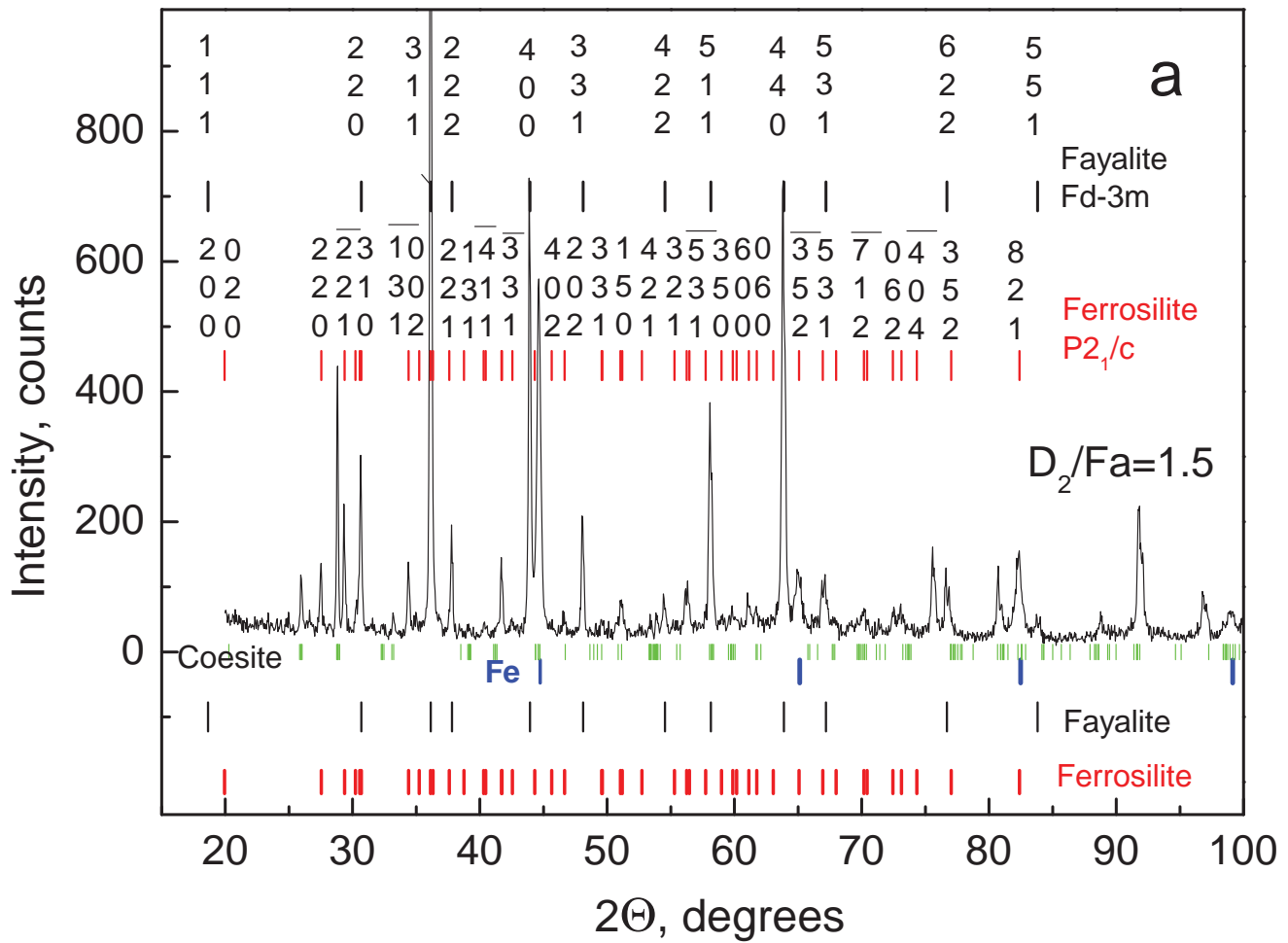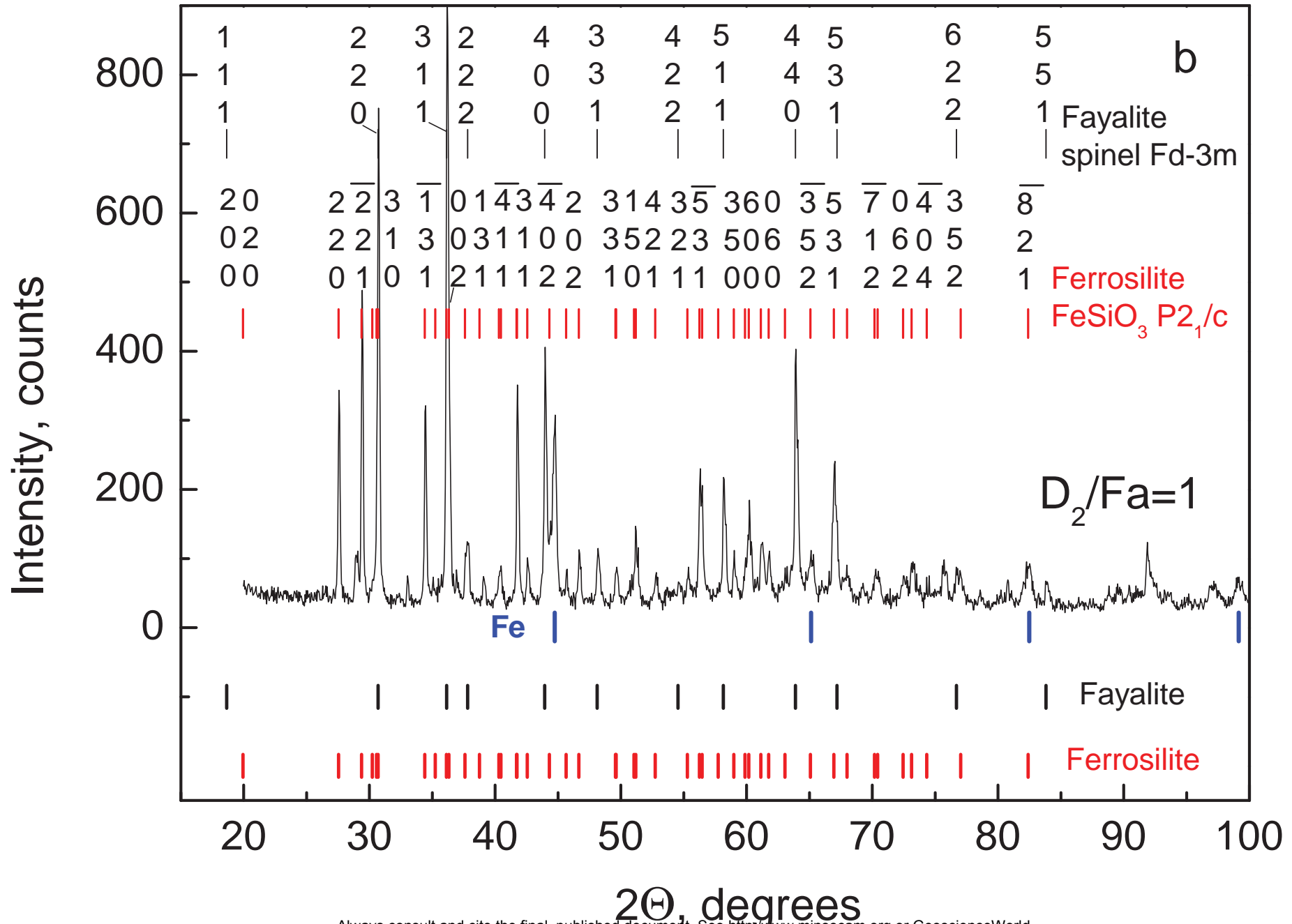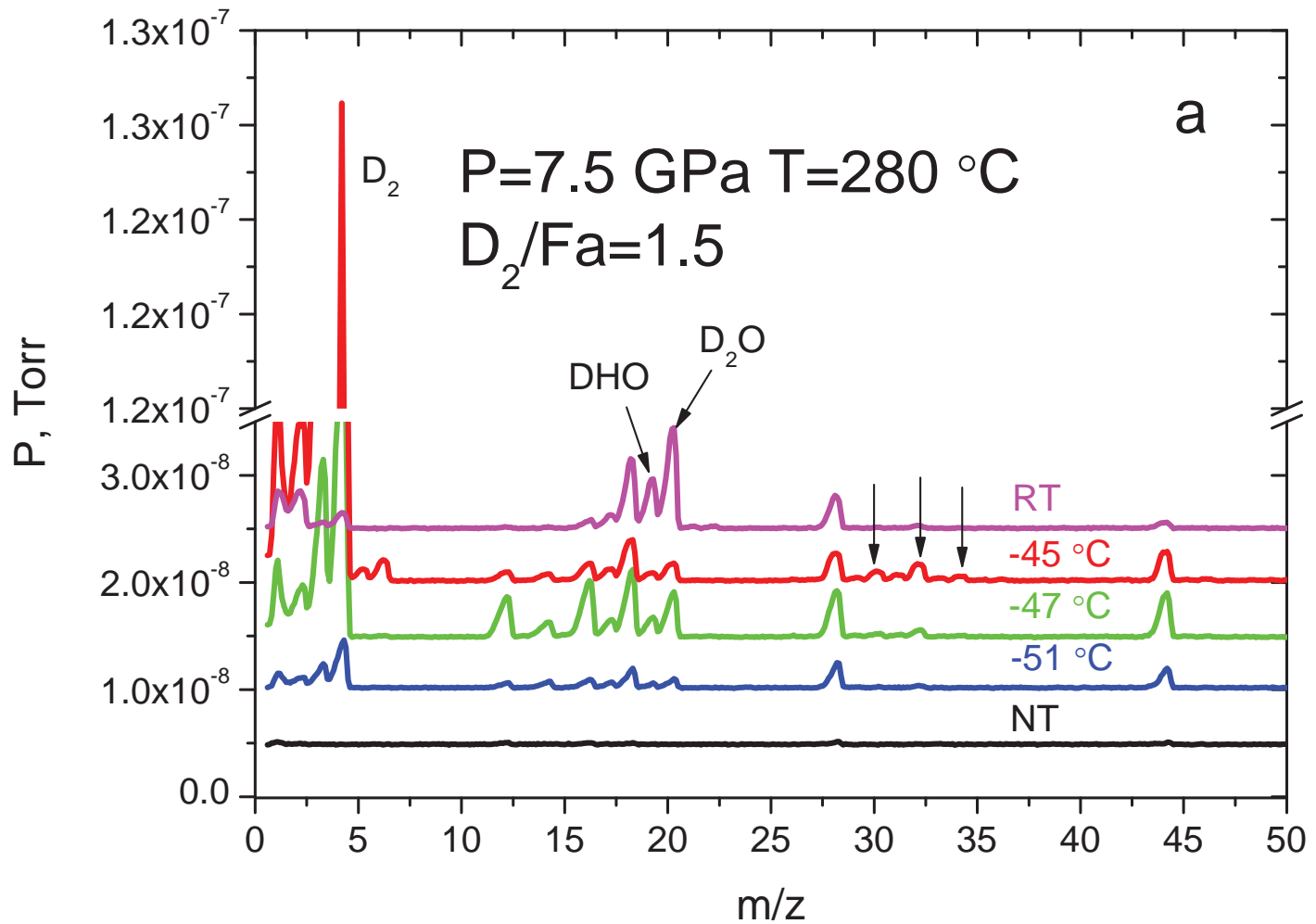
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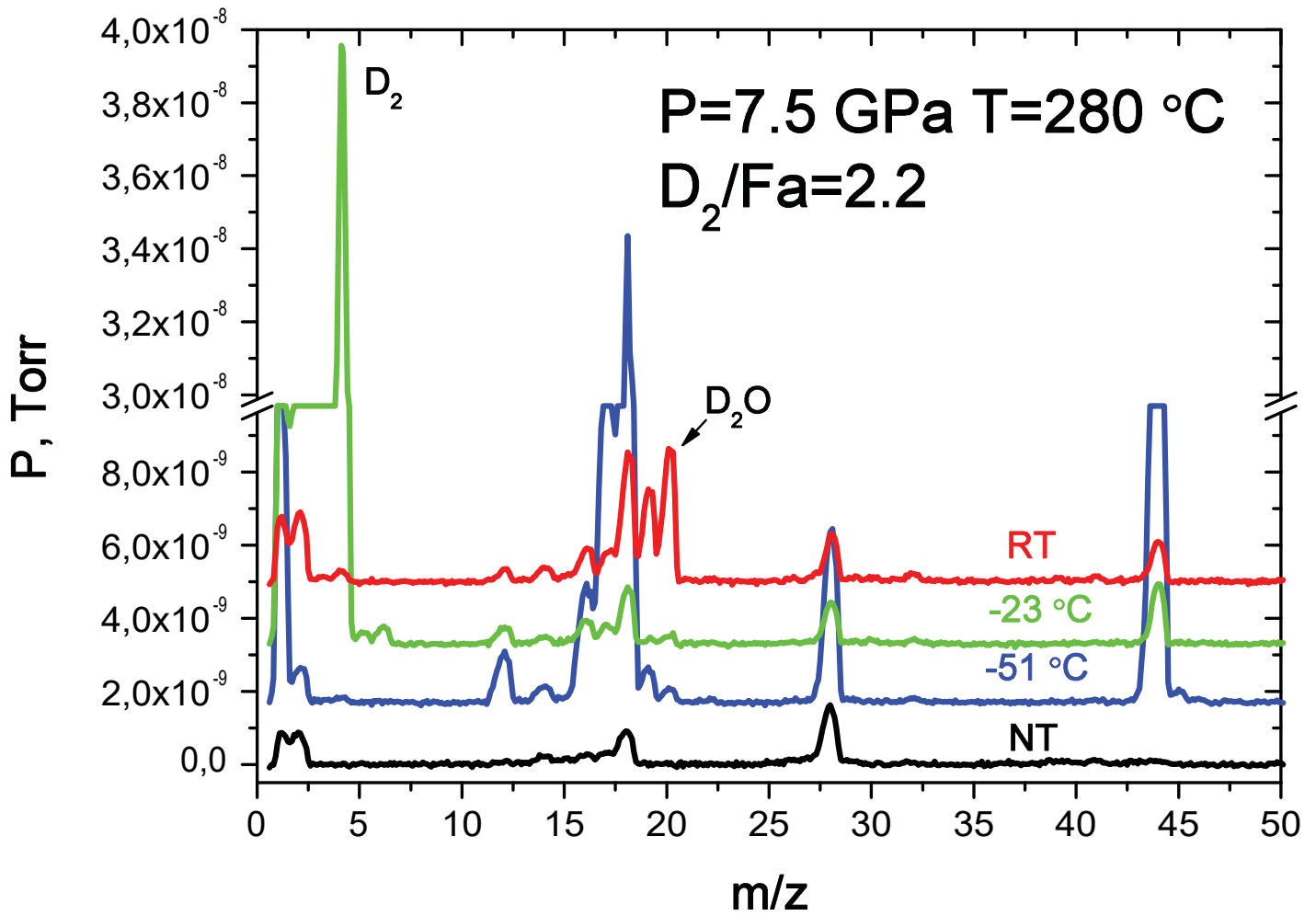
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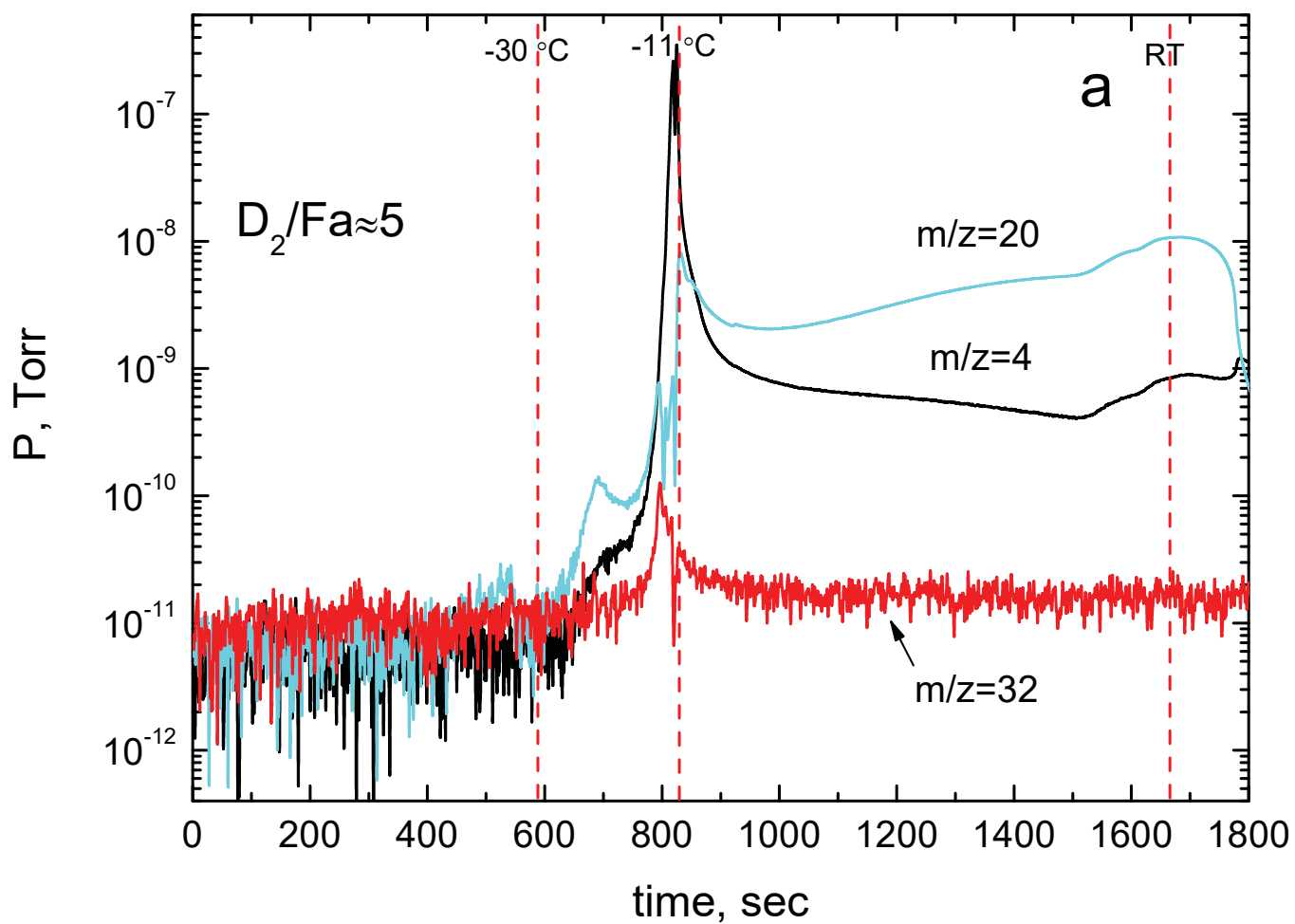
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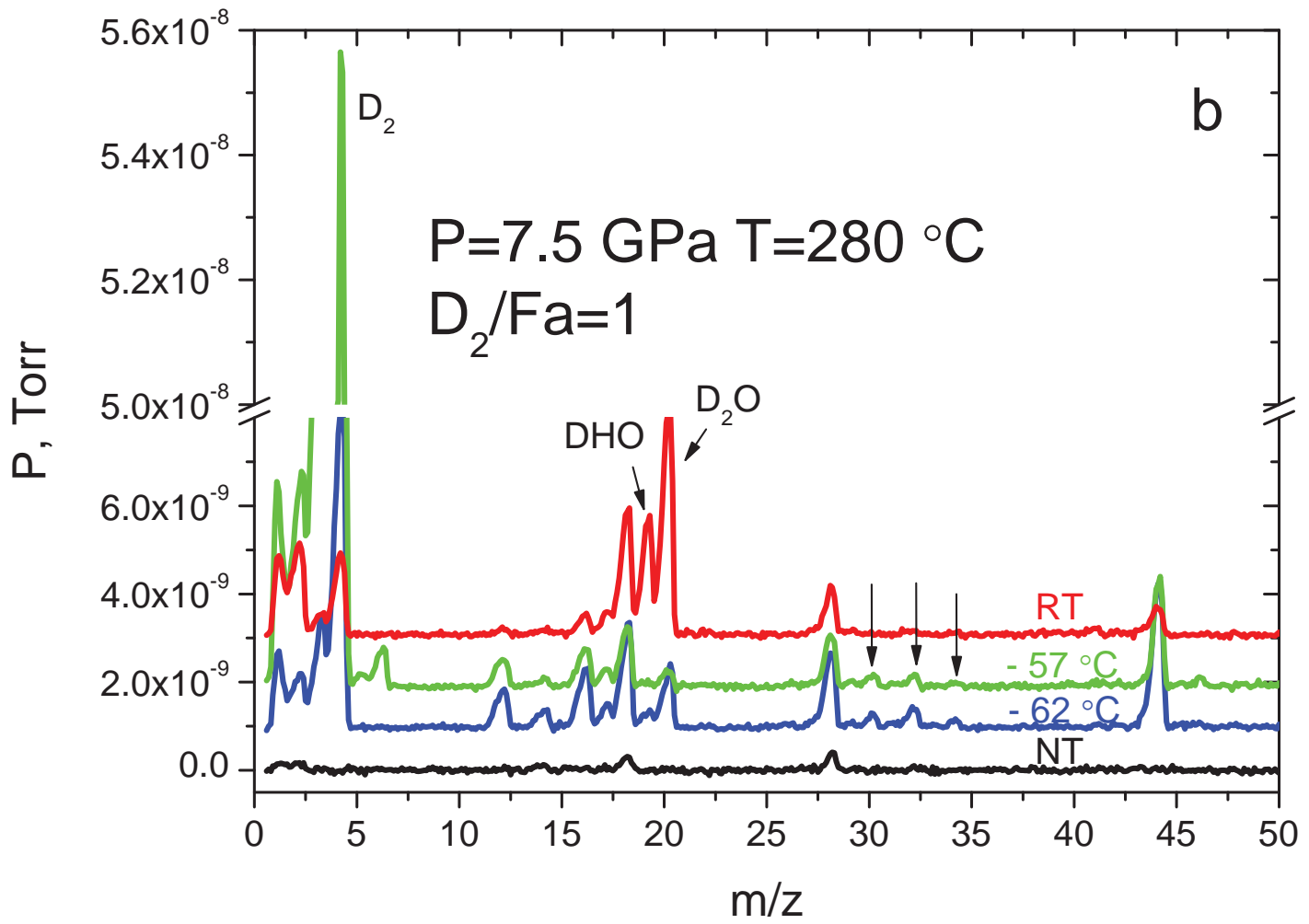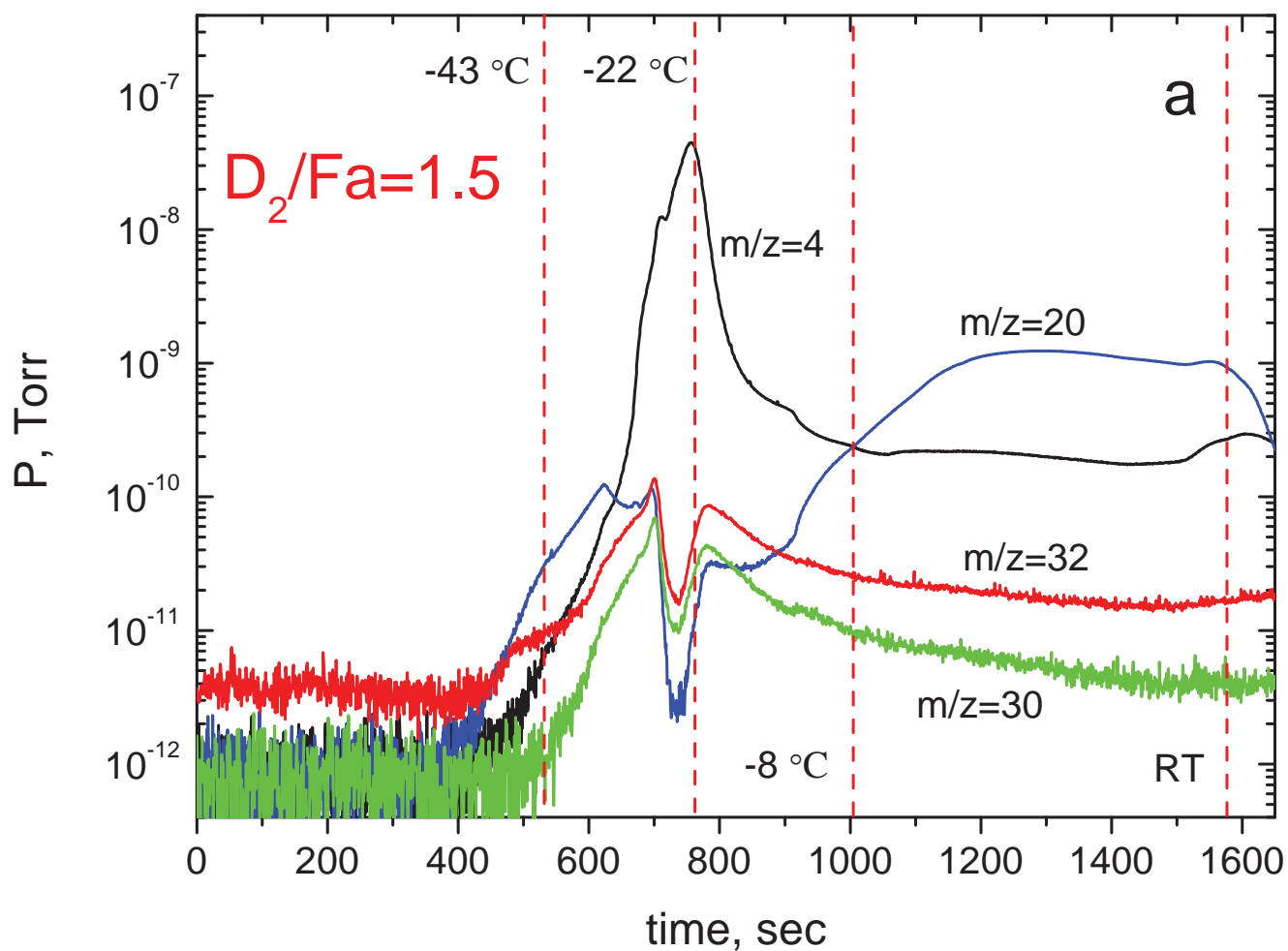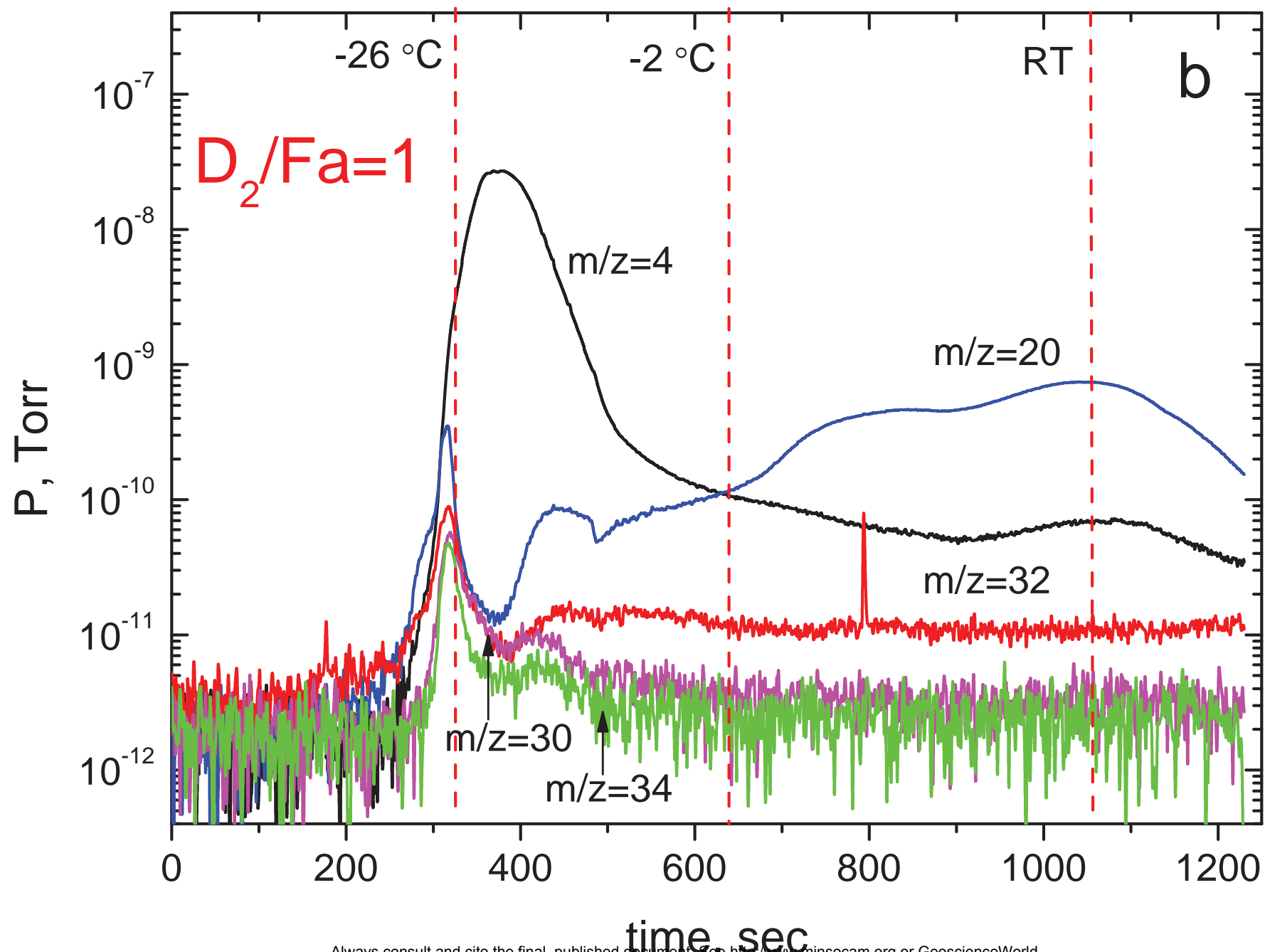
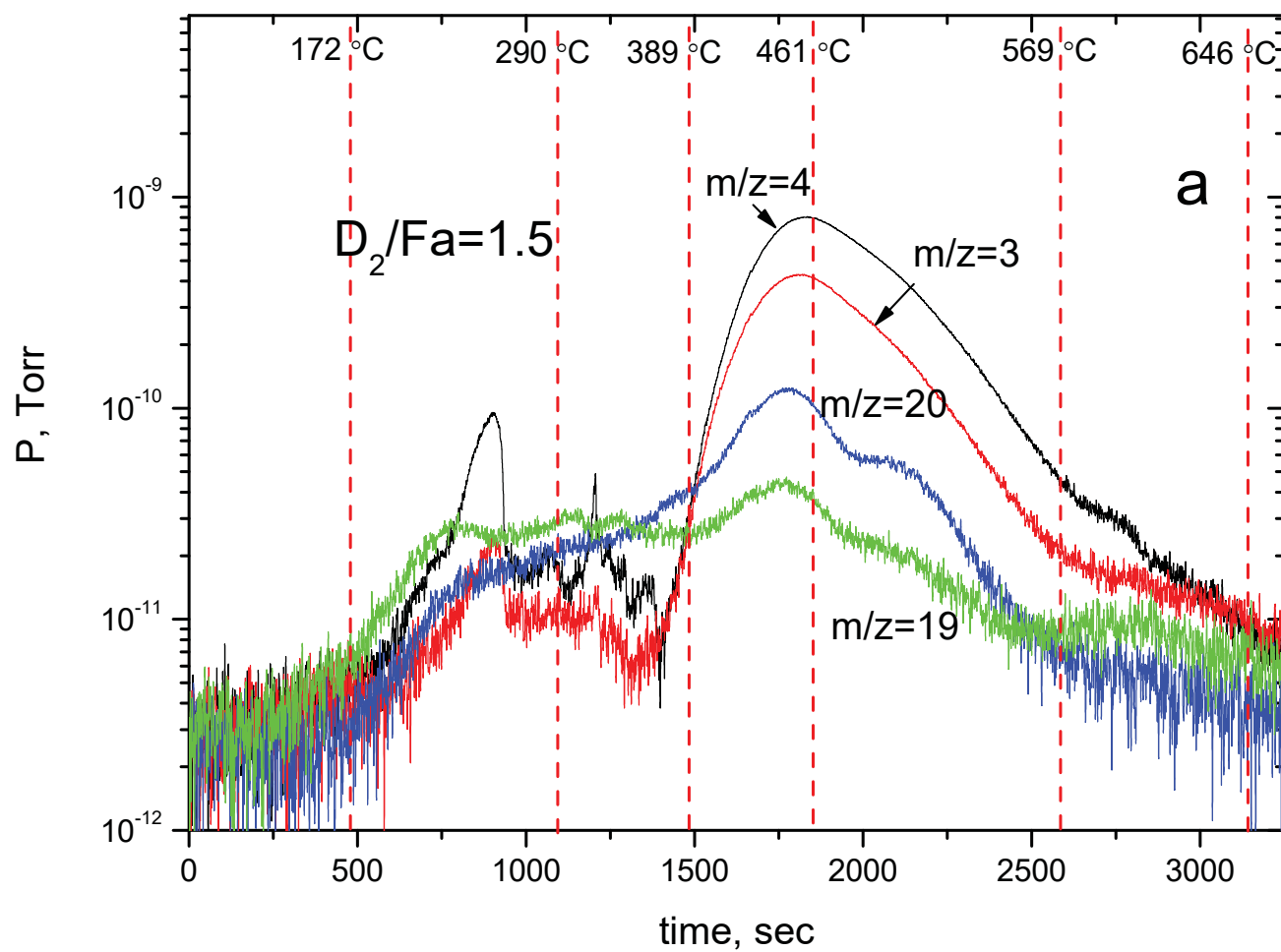Figure 5a

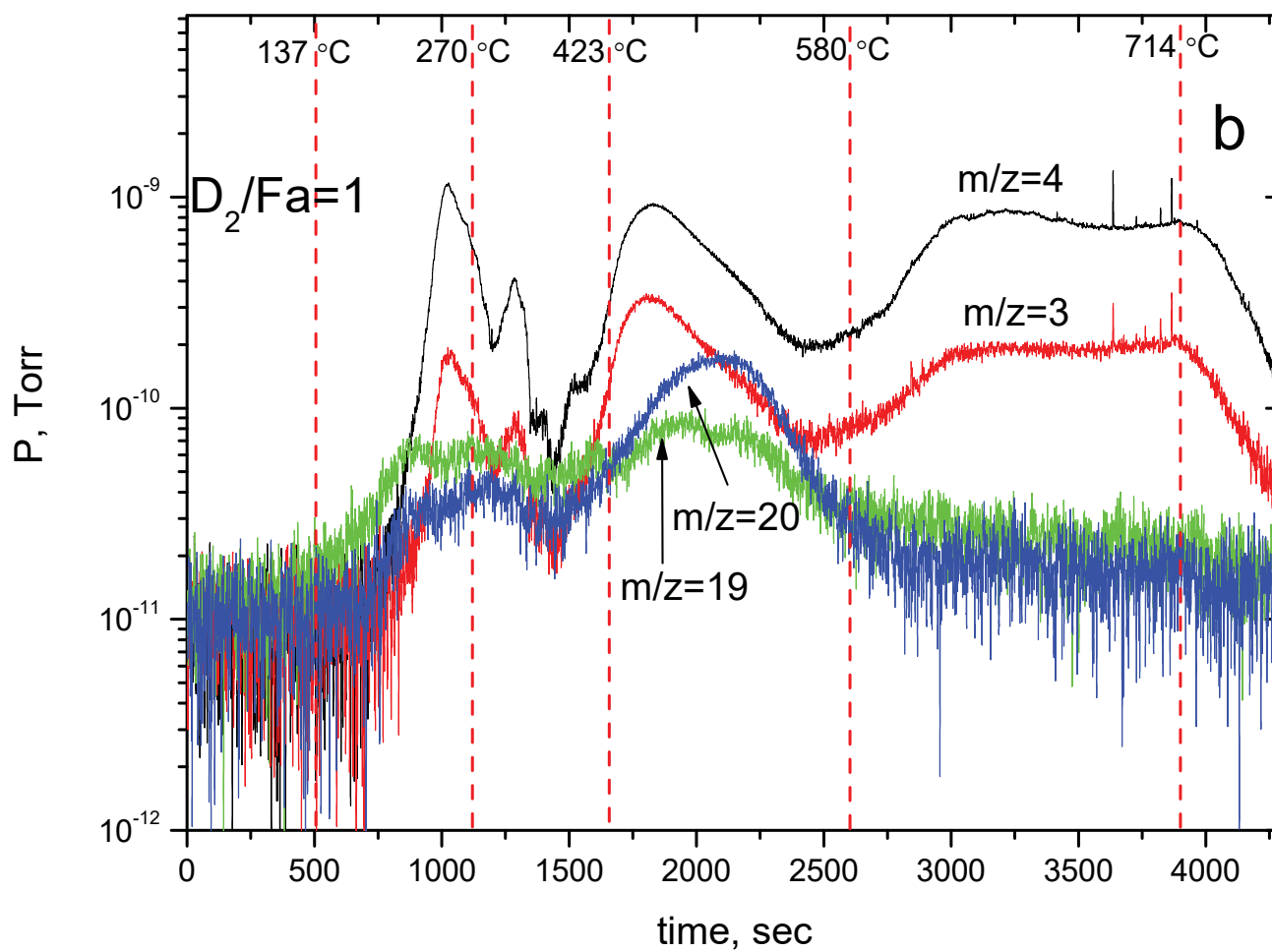Figure 5b

Figure 6a

Figure 6b

Figure 7a

Figure 7b

Figure 8a

Figure 8b

Figure 9a

Figure 9b

Figure 10