Cryogenic SIMS preserving elemental distributions formed under extreme conditions: Hydrogen distribution measurement in iron

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ABSTRACT

We established a cryogenic secondary ion mass spectrometry (Cryo-SIMS) system, in which all procedures—sample recovery, transport, and analysis—are performed under cryogenic temperatures. Using this system, we determined hydrogen concentrations in Fe-H alloys, which form only under high pressure and lose hydrogen upon decompression at ambient temperature. The hydrogen contents obtained were in good agreement with the X-ray diffraction (XRD) measurements conducted under high pressure. The present cryogenic SIMS techniques can be applied to the determination of hydrogen isotopic composition of iron alloys, which is not possible with XRD analysis, but is important for understanding the origin of water on Earth.

1 | Introduction

Secondary ion mass spectrometry (SIMS) is among the few techniques capable of highly sensitive analyses of trace light elements including hydrogen [1]. Early efforts to analyze liquids, such as fluid inclusions, employed a cryogenic sample stage to suppress volatilization under the ultra-high vacuum conditions required for SIMS analyses [2]. However, elemental distributions established under extreme pressure and temperature (*P*-*T*) conditions are sometimes not preserved during decompression to ambient pressure for sample recovery. A typical example is an iron-hydrogen alloy: hydrogen escapes from the iron lattice during decompression when the crystal structure changes to body-centered cubic (bcc) at room temperature [3, 4]. The study of metal hydrides is important because hydrogen in metals is known to cause their embrittlement [5–7]. In addition, hydrogen is considered likely to be a major light element impurity of the Earth's core [4, 8, 9], but its exact composition remains uncertain [10]. The hydrogen isotopic ratio in the core is also unknown.

Here, we established a workflow to execute all processes after sample synthesis under cryogenic temperatures by developing a Cryo-SIMS system that enables the introduction and analysis of frozen samples in ultra-high vacuum [11–15]. We used this system to examine Fe-H alloys originally synthesized under high *P-T* conditions in a diamond-anvil cell (DAC). The sample was decompressed and recovered from the DAC in liquid N_2, then transferred to a SIMS instrument for analysis. The hydrogen contents in iron determined by the SIMS measurements were in good agreement with those estimated by XRD analyses performed under high pressures. The present technique enables three-dimensional quantification of element concentrations and isotopic ratios in a small sample synthesized under extreme *P-T* conditions relevant to the core and will thus be helpful for understanding the origin and distribution of Earth's water (hydrogen).

2 | Experimental Procedures

Iron-hydrogen alloys were synthesized under high *P-T* in a laser-heated DAC combined with synchrotron XRD measurements [16, 17]. We used a circular Re gasket (3 mm in diameter), preindented it to ~40 μm in thickness, and drilled a ~100 μm diameter hole at its center to form a sample chamber. A ~7 μm thick Fe foil (5N, Mairon-UHP, Toho Zinc Co. Ltd.) was placed between the ~10 μm thick KCl layers, which served as both a pressure medium and a thermal insulator, while leaving room for hydrogen. The entire DAC was then dried in a vacuum oven at 400 K for at least 2 hours to eliminate moisture in the sample chamber. Subsequently, supercritical hydrogen fluid was introduced into the sample chamber using a 200 MPa high-pressure gas apparatus (PRETECH Co., Ltd.) at SPring-8 [16, 17]. After compression under room temperature, it was heated from both sides with a pair of 100 W single-mode Yb fiber lasers (IPG Photonics) at the beamline BL10XU, SPring-8. The entire sample was hydrogenated upon heating to <1000 K for about 30 minutes. Furthermore, we melted the central portion of the Fe-H sample by heating to 2440(±120) K at 48(±5) GPa for 3 seconds. Temperature was measured using a spectro-radiometric method [18]. Pressure was determined based on the thermal EoS of KCl [19].

We collected XRD patterns of the sample on a flat panel X-ray detector (Perkin Elmer, XRD0822 CP23) with an incident X-ray beam that was monochromatized to ~30 keV and focused to 6 μm in diameter (full-width at half maximum) [18] (Figure 1). Given that the lattice volume of Fe expands proportionally with the hydrogen content [20], the hydrogen concentration, x, in FeH_x was estimated from the XRD data collected at 300 K [4, 16, 17] as:

$$x = \frac{V_{FeH_x} - V_{Fe}}{\Delta V_H} \quad (1)$$

where V_{FeH_x} and V_{Fe} are the volumes per Fe atom for FeH_x determined from the present XRD measurements and for pure Fe from earlier experiments [21], respectively, and ΔV_H represents the increase in the lattice volume of Fe caused by the incorporation of an H atom [22]. Upon annealing at <1000 K, the hydrogen content of the sample increased to x = 0.25 (Figure 1). After heating to 2440 K, we found x = 0.30(±0.05) at the center of the laser-heated hot spot, corresponding to the melted portion consisting of quench crystals with the face-centered cubic (fcc) structure that formed from the liquid upon temperature quenching. The XRD analyses also showed an fcc phase with x = 0.87(±0.08), corresponding to the surrounding unmelted area, where the hydrogen concentration increased due to the higher temperature, which further enhanced hydrogenation.

The sample was then decompressed in liquid nitrogen to avoid hydrogen loss from the iron. Earlier experiments [23] demonstrated that hydrogen remains in the iron lattice below approximately -70 °C under vacuum. To do this, we first submerged the DAC in liquid nitrogen and waited for several minutes for the temperature to equilibrate. We then fully released pressure, retrieved the rhenium gasket containing the Fe-H sample and KCl, and placed the gasket in an in-house cryo-holder, all while ensuring the sample remained in the liquid nitrogen. It was then placed in a sample carrier also filled with liquid nitrogen and transported to the SIMS instrument at Hokkaido University. The sample temperature was maintained at liquid nitrogen temperature throughout these processes. A valved environmental control airlock was attached to the sample carrier to introduce the sample into the SIMS system. While the carrier was being evacuated, the sample holder was lifted from the liquid nitrogen and stored in the airlock that was filled with evaporated nitrogen gas and sealed off from the outside air. The airlock was then immediately attached to the SIMS system, and the sample was transferred via a storage chamber to a liquid nitrogen-cooled freezing stage (Techno I.S.), where a thermocouple located directly underneath the sample holder monitored the temperature and ensured it stayed below -180 °C. It took approximately 50 seconds to remove the sample from the carrier filled with liquid nitrogen and place it on the freezing stage.

The Fe-H sample, mounted on a freezing stage, was examined with an isotope microscope system consisting of a stigmatic SIMS instrument (CAMECA ims-1270e7) and a stacked CMOS-type active pixel sensor (SCAPS), which provides quantitative projection images of secondary ions emitted from the sample surface and thus enables quantification of the abundance of each element from the intensity map [24]. The sample surface was irradiated with a 13 keV O^- beam, defocused to approximately 50 μm in diameter (the projection image exhibits submicron lateral spatial resolution, see Figures 2 and 3), at a probe current of 100 nA and a sweep electrode setting of 150 × 150 μm on the sample surface. Secondary ions sputtered from the sample surface were extracted at 10 keV while preserving their positional information

and projected onto the SCAPS detector through an energy offset, contrast aperture, energy slit, and exit slit. Pre-sputtering was conducted until the KCl pressure medium on top of the Fe foil was removed, and analysis was performed once the entire Fe foil was exposed. The isotopes analyzed were $^{1}H^{+}$ and $^{56}Fe^{+}$, with net signal acquisition times of 2000 and 5 seconds, respectively. The quantitative images obtained were processed using ImageJ software. The isotope images were appropriately noise-reduced by multi-frame averaging [25], and the line profiles were averaged over 10 pixels.

3 | Results

Figure 2a shows a hydrogen image obtained using the developed Cryo-SIMS method. Hydrogen was detected throughout the entire Fe foil (see Figure 3 for the outline of the Fe foil). The gray scale represents the total number of ions detected over the entire acquisition time. The dark (melted) area at the center of the Fe foil corresponds to the portion heated to 2440 K by laser irradiation while the DAC was pressurized to 48 GPa. The XRD peaks from the hexagonal close-packed (hcp) structure disappeared during heating, indicating that this region melted (Figure 1). The KCl pressure medium remained between the Fe foil and the Re gasket, as well as in the area that was not completely removed by pre-sputtering (Figure 2a). Figure 2c shows the line profile of $^{1}H^{+}$ counts, indicating that the hydrogen signal from the melted portion is weak, approximately one-fifth of that for the surrounding area. Hydrogen was also detected from the region of the gasket that was in contact with H_2, where rhenium was also hydrogenated. We note, however, that such hydrogenation of the gasket was limited to its rim, precluding a remarkable hydrogen loss to the outside of a sample chamber during heating.

After performing these cryogenic analyses, the sample holder was transferred from the freezing stage to a room-temperature, vacuum storage chamber and left overnight to allow the sample temperature to increase to 300 K. The sample was then returned to the freezing stage, and similar analyses were performed again under cryogenic temperatures. While traces of hydrogen were detected from the hydrogenated Re and water-adsorbed KCl, no hydrogen signal was observed from the Fe foil (Figure 2b). According to the line profile in Figure 2d (note that the vertical axis is a linear scale), the hydrogen signal in the Fe foil area was below the noise level, indicating that the hydrogen in the Fe had almost completely been lost upon increasing temperature to room temperature.

Figure 3 provides the Cryo-SIMS images for Fe before and after raising sample temperature to 300 K, and their respective line profiles. Under cryogenic conditions, the Fe signal from the melted area was lower than in the surrounding area, just like the H signal, but the difference was minor compared to H. We also note that the Fe signal was reduced after increasing the

temperature to room temperature, particularly in the surrounding unmelted portion. There was almost no difference in signal between the central melted area and its surroundings at room temperature.

Finally, we compare the H/Fe count ratios obtained by Cryo-SIMS with the H/Fe molar ratios (equivalent to x in FeH_x) determined from the XRD data in Figure 4. When considering their uncertainties, the correlation line between the data for H-poor melted and H-rich surrounding areas (x = 0.30±0.05 and 0.87±0.08, respectively, from the XRD data) goes to the origin of the coordinate system, indicating that these SIMS and XRD measurements are in good agreement with each other.

4 | Discussion

Hydrogen was detected from an Fe foil that was hydrogenated at high pressure and kept at low temperatures throughout the subsequent procedures, from decompression in liquid nitrogen to analyses on a cryo-stage in the SIMS instrument (Figure 2a). In contrast, hydrogen was no longer observed once the temperature of the Fe foil was increased to room temperature overnight in a vacuum and then analyzed again under the same cryogenic conditions (Figure 2b). This clearly demonstrates that temperature is related to the behavior of hydrogen. Indeed, it has been shown that FeH rapidly loses hydrogen when it reaches about -70 °C in a vacuum [23], indicating that the loss of the hydrogen signal in SIMS was certainly due to hydrogen escape when the sample temperature was increased. This dictates that successful SIMS analysis of hydrogen in iron requires maintaining the sample temperature below -70 °C [23] throughout the entire process, from sample recovery to ion beam irradiation. The detection of hydrogen in iron in this study demonstrates that the developed Cryo-SIMS system enables cryogenic analysis by maintaining temperatures below -70 °C.

While SIMS is a highly sensitive in-situ analytical method, a matrix effect is known, in which the signal intensity obtained varies depending on the crystal structure and composition of the target [26]. We note that both the H and Fe signal intensities obtained by Cryo-SIMS were lower in the melted area at the center of the Fe-H sample than in the surrounding unmelted portion (Figures 2a, 3a). It indicates a compositionally derived matrix effect, since Fe-H alloys in both melted and unmelted areas should have adopted the fcc crystal structure until hydrogen was released from iron (the fcc structure observed by high-pressure XRD data for both melted and unmelted parts should have been preserved after pressure release under cryogenic temperatures). Moreover, the Fe intensity from hydrogen-lost pure Fe foil acquired after the sample temperature was raised to room temperature was overall lower (Figure 3b) than that from Fe-H alloys (Figure 3a). It is consistent with the observation described above—the lower

the hydrogen counts, the lower the iron counts (Figures 2a, 3a)—although it may be due to a slight difference in the primary ion beam intensity or a difference in crystal structure (bcc is the stable structure at 300 K). Because of such a matrix effect, the three-fold difference in the H/Fe molar ratio (Figure 4) caused the five-fold difference in hydrogen counts from iron between the melted and surrounding unmelted portions (Figure 2a). While these H and Fe analyses were performed after the KCl layer on top of the Fe foil was removed by pre-sputtering, we obtained only the background level of potassium in the secondary ion image of $^{39}K^{+}$ for the Fe-H sample, indicating that the effect of potassium contamination was negligible.

The H/Fe ratios of the molten and unmolten regions obtained by XRD and SIMS analyses are plotted on a single straight line passing through the origin of the coordinate system (Figure 4), indicating the potential for use as a calibration curve for the SIMS determinations of hydrogen in iron without XRD data. The Cryo-SIMS techniques developed in this study enable highly sensitive quantification of the hydrogen isotope ratio and concentration with submicron-scale lateral spatial resolution and nanometer-scale depth resolution, while maintaining its distributions formed in extreme high-pressure and -temperature environments relevant to planetary interiors. The presence of a large amount of hydrogen in the Earth's core has been supported by various aspects, such as its siderophile (iron-loving) nature [4] and compatibility of the density and velocity of liquid Fe-H with seismological observations of the outer core [27]. A combination of high-pressure melting experiments and Cryo-SIMS measurements is expected to reveal hydrogen isotopic fractionation between the silicate mantle and the metallic iron core, which gives the bulk Earth hydrogen isotopic ratio constraining the origins of Earth's water (hydrogen).

Samples retrieved from high pressures are usually handled at ambient pressure and temperature under atmospheric air. However, samples synthesized under high *P-T* often change their crystal structure when the pressure is released at room temperature, and, as demonstrated here, sometimes change their chemical composition (e.g., lose hydrogen). We applied our newly developed Cryo-SIMS techniques to the high *P-T* sample and successfully determined hydrogen concentrations in Fe-H alloys before hydrogen escapes from iron above -70 °C [23]. This Cryo-SIMS method will also contribute to the characterization of living organisms, which are mostly composed of water that evaporates in the ultra-high vacuum of a SIMS instrument and therefore cannot be analyzed unless at cryogenic temperatures. This new method enables isotope analysis of water in the brain or vacuoles in plants. Samples from space may also require the present techniques, which involve sample recovery and transfer in liquid N_2 and high vacuum environments under cryogenic temperatures, thereby helping to avoid contamination and alteration by air.

5 | Conclusion

We established a fully cryogenic SIMS workflow (Cryo-SIMS), in which all processes, including sample preparation, transfer, and analysis, are performed under cryogenic conditions using liquid nitrogen. This suppresses atomic and molecular mobility and therefore effectively prevents elemental redistribution, preserving the original elemental and isotopic distributions. Here, we applied such Cryo-SIMS techniques to the quantification of hydrogen concentration in Fe-H alloys, which form only under high *P*-*T* conditions and lose hydrogen when samples are recovered at ambient temperature. The Cryo-SIMS analyses showed the hydrogen contents in iron, in good agreement with synchrotron XRD measurements performed under high pressure. The method developed in this study will also be useful for investigating biological samples and those retrieved from space by sample return missions.

Author Contributions

Naoya Sakamoto: conceptualization (equal), methodology (equal), investigation (equal), formal analysis (equal), resources (equal), funding acquisition (equal), writing – original draft (equal). **Nagi Ikuta**: investigation (equal), formal analysis (equal), writing – original draft (equal). **Kei Hirose**: methodology (equal), funding acquisition (equal), writing – original draft (equal). **Shoh Tagawa**: investigation (equal). **Koutaro Hikosaka**: investigation (equal). **Shuhei Mita**: investigation (equal).

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this work will be available upon reasonable requests.

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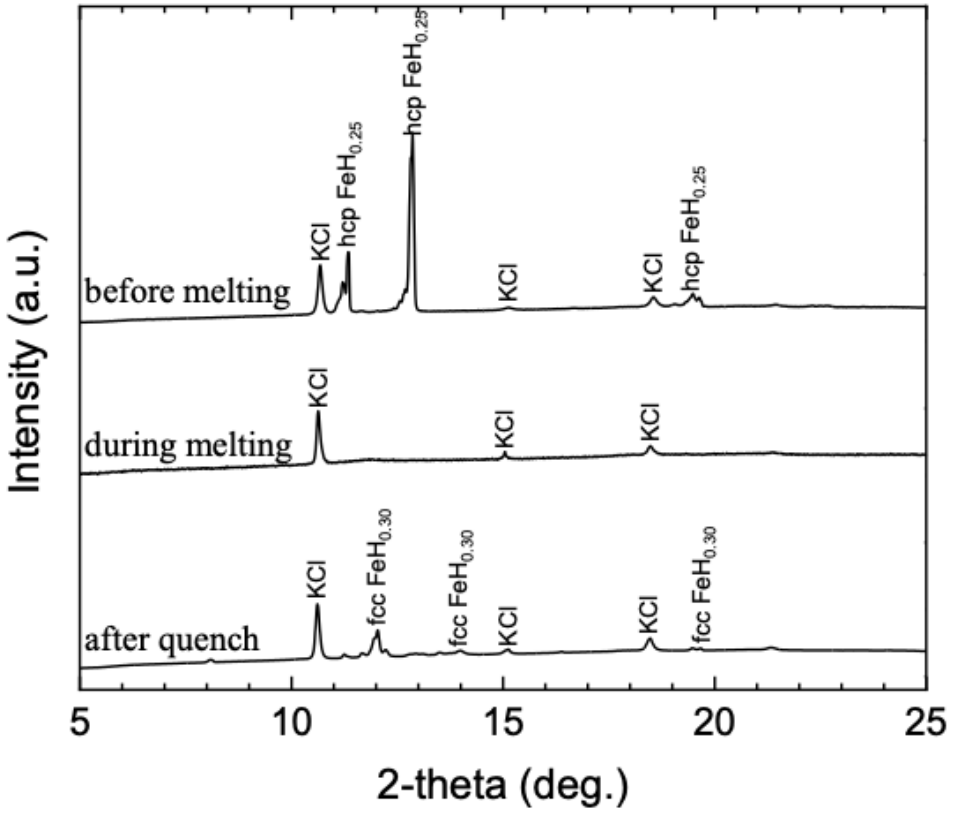

FIGURE 1 | XRD patterns obtained at 48 GPa before/during/after melting the Fe + H_2 sample. Loss of the peaks from hcp $FeH_{0.25}$ indicates melting. Fcc $FeH_{0.30}$ formed from liquid upon quenching the temperature.

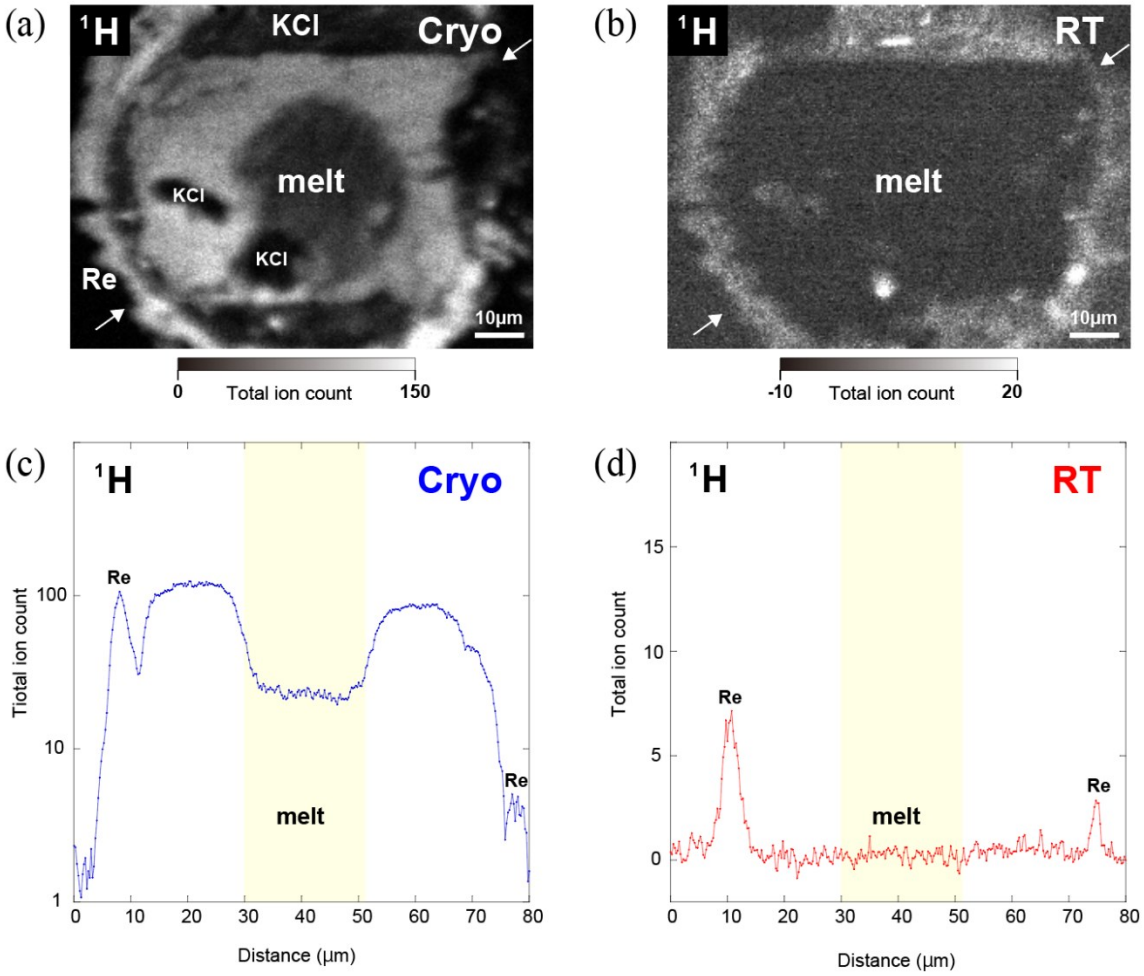

FIGURE 2 | (a) Hydrogen image of an Fe foil analyzed using Cryo-SIMS, and (c) its line profile between the arrows. Hydrogen signals were detected from the center of the laser-heated hot spot (quenched melt) and from the rest of the Fe foil (unmelted). Hydrogen was also emitted from the edge of a Re gasket holding the sample. It shows the extent to which rhenium has hydrogenated, indicating that a limited amount of hydrogen was lost from a sample chamber to the gasket. The ratio of hydrogen signals from the unmelted Fe-H to liquid is approximately 5:1. (b) After cryo-analysis, the sample temperature was temporarily raised to room temperature in a vacuum overnight, and Cryo-SIMS analysis was then performed again on the cryo-stage. A small amount of hydrogen was still emitted from the edge of the Re gasket and from the remaining KCl pressure medium, while the hydrogen signal from the Fe foil was below the noise level (negative counts resulted from dark frame subtraction) (d). The counts in (c) and (d) were obtained by subtracting the counts in a dark frame from those in a sample measurement.

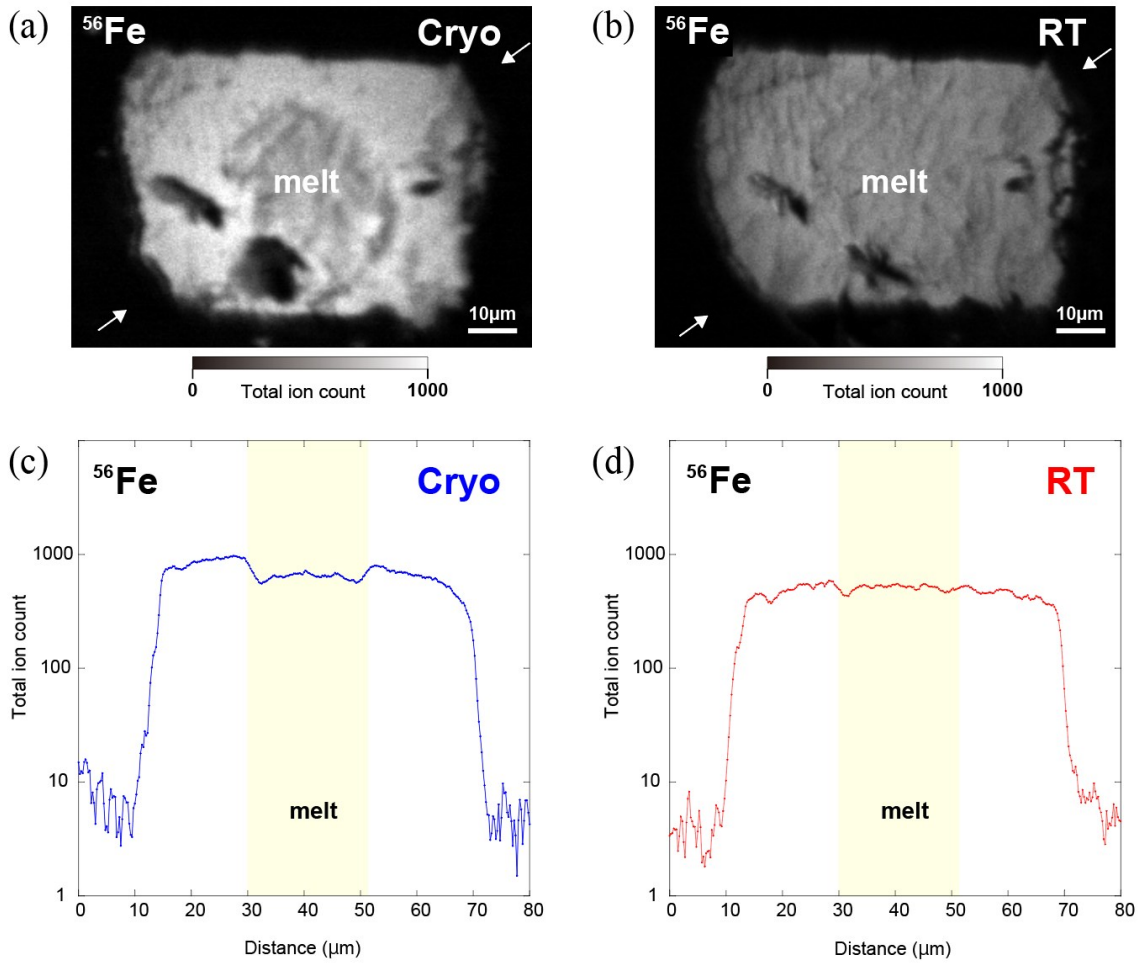

FIGURE 3 | Iron maps collected with Cryo-SIMS before (a, c) and after the sample temperature was increased to room temperature temporarily and hydrogen was lost from iron (b, d). Similar to the hydrogen maps in Figure 2. The iron intensity in the melted area where hydrogen concentration has been reduced is lower than the surrounding area (a) and is further lowered after all hydrogen has been lost from the Fe foil (b). The iron intensity is thus positively correlated with the impurity (hydrogen) concentration, showing a matrix effect (the effect of the difference in crystal structure between before and after increasing the temperature to room temperature may be minor).

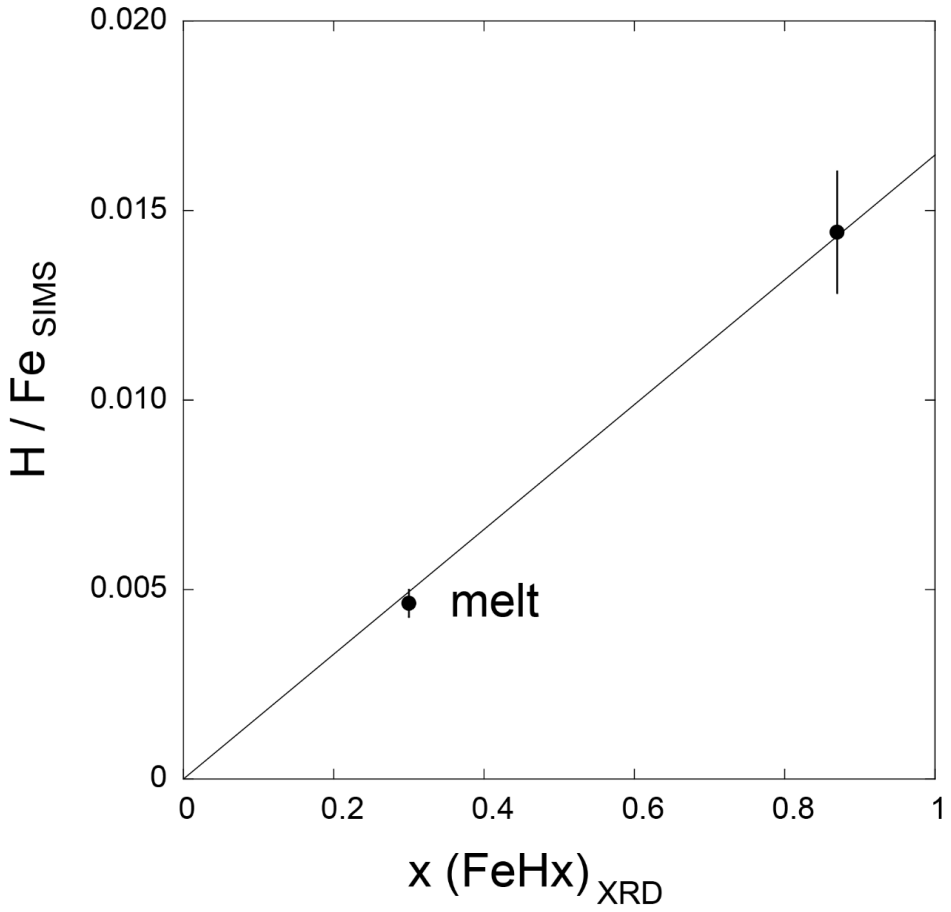

FIGURE 4 | Comparison between the H/Fe count ratio obtained by Cryo-SIMS and hydrogen concentration, x in FeH_x (equivalent to the H/Fe molar ratio) from XRD data for the melted and unmelted areas in a sample. These data are plotted nearly on a straight line going to the origin of the coordinate system, indicating that both measurements are consistent with each other. This line may be used as a calibration curve for the SIMS determination of hydrogen in iron.