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**Measurement of Iron Self-Diffusion in Hematite Single Crystals by SIMS
and Comparison of Cation Self-Diffusion in Corundum-Structure Oxides**

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Abstract

Iron bulk self-diffusion coefficients were measured in Fe₂O₃ single crystals using an original methodology based on the utilization of ⁵⁷Fe stable isotope as iron tracer, and depth profiling by secondary ion mass spectrometry (SIMS). The iron self-diffusion coefficients were measured along and perpendicular to c-axis direction, between 900 and 1100° C, in oxygen atmosphere. Along c-axis they can be described by $D_{//c}$ (cm²/s)= $5.2 \times 10^6 \exp [-510 \text{ (kJ/mol)/RT}]$, and are close to reliable data available in the literature, obtained by means of radioactive techniques. Perpendicular to c-axis, $D_{\perp c}$ (cm²/s)= $83 \exp [-430 \text{ (kJ/mol)/RT}]$, and the coefficients are smaller than coefficients along c-axis. The results are compared with previously obtained results of cation bulk self-diffusion in Cr₂O₃ and in Al₂O₃ single crystals.

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Introduction

Alumina (Al₂O₃), chromia (Cr₂O₃) and even hematite (Fe₂O₃) films are of great importance as the protection ensured by such films against oxidizing and aggressive atmospheres is efficient for long times at high temperatures. Moreover, these oxides have the same crystal structure of corundum and it is interesting to know how bulk cation self-diffusion differ in them and to try to understand the role of these diffusivities on their respective growth by oxidation of metallic alloys.

Previous studies allowed to determine the cation bulk self-diffusion coefficients in these oxides either using a radioactive solution [1-6] or by SIMS [7] and it is important to compare results obtained by different methods. Indeed, two of the most accurate techniques to measure diffusion coefficients in solids are the radioactive techniques, using a radioactive isotope as tracer with depth profiling by sectioning and counting, and the secondary ion mass spectrometry (SIMS) used for depth profiling of stable tracers.

When adequately employed, both techniques should present the same performance, in spite of, due to its specificity, the radioactive techniques to be less susceptible to interpretation errors. On the other hand, SIMS is very attractive because there is not necessity to manipulate radioactive materials. It also offers the possibility of measuring very short depth profiles (from a few nanometers) and thus, it allows to use short annealing times and/or low temperatures, on very small samples, when compared to those used by radioactive techniques. Moreover, it may be applied to the depth profiling of all isotopes of the natural elements.

In fact, SIMS has shown to be a powerful technique to study diffusion in solids and has been extensively applied by a few authors of this work to determine self-diffusion and impurity diffusion coefficients in a wide variety of oxides used in different technological fields, such as UO_2 (nuclear fuel) [8, 9], ZnO (electroceramic) [10], $(\text{Gd}_{0.9964}\text{Ca}_{0.0036})\text{Sn}_2\text{O}_7$ (solid electrolyte) [11], $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ (glass) [12], Cr_2O_3 (used to simulate oxide layer grown on Cr-alloys) [7, 13-15].

In order to make comparison between the performance of radioactive techniques and SIMS to measure diffusion coefficients in ceramic oxides, measurements of iron self-diffusion in hematite present a great interest as earlier works [1-5] determined self-diffusion coefficients by means of radioactive techniques and, though performed on samples from different sources, they show reasonable agreement above 900°C .

In this study, iron self-diffusion in hematite single crystals has been determined for the first time by SIMS, using the ^{57}Fe stable isotope as iron tracer. To check the results obtained by SIMS, only the data previously determined by Atkinson and Taylor [5], and by Hoshino and Peterson [6] will be taken into account, because they are the most recent and show excellent agreement.

Afterwards, a comparison of the present results for iron self-diffusion in Fe_2O_3 with the more recent data of cation bulk self-diffusion in Cr_2O_3 [7] and in Al_2O_3 [1] will be presented.

Experimental

Materials and Sample Preparation

The Fe_2O_3 natural single crystals were supplied by the Department of Geology of the Federal University of Ouro Preto, Brazil. Mössbauer spectroscopy and X-ray diffraction analyses showed

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hematite to be the only phase in these crystals. A JXA-8900RL Jeol microprobe analyzer with EDS and WDS (PET, LiF, TAP and LDE crystals) detectors was employed in order to detect the presence of minor elements in the Fe_2O_3 crystal. The detection limit of such a technique for the most common elements in iron oxide is about 100 ppm (~ 0.01 at %). In the present case, the photon detection statistics was improved by counting for 10 minutes on the peak positions and background positions. In these conditions, only Al was detected with a content of Al_2O_3 equal to 0.16 ± 0.02 wt%.

The isotope ^{57}Fe was used as iron tracer. The natural iron has the following isotopic composition (atomic %): ^{54}Fe (5.8), ^{56}Fe (91.72), ^{57}Fe (2.2) and ^{58}Fe (0.28). The source of tracer used in this work was iron powder, which was enriched (95.8%) with the isotope ^{57}Fe . This iron was supplied by Chemotrade GmbH (Germany). The impurities in this iron were: C ($<0.044\%$), and less than 0.01% for each of the following elements Mg, Al, Si, Cr, Ni, Cu and Zn.

The diffusion specimens have been used with the dimensions 4mm x 4mm x 1mm. These samples were polished with diamond suspensions of 9, 6, 3, 1 and $0.25\mu\text{m}$ using an automatic polisher Phoenix of Buhler. The polished surface was parallel or perpendicular to the basal plane of the crystal. After the polishing, the samples were cleaned in acetone under ultrasound, and then submitted to a pre-annealing to equilibrate them with the temperature and oxygen pressure to be used in the diffusion annealings.

After the pre-annealings, a ^{57}Fe film was deposited on the polished surface of the samples. The deposition of the ^{57}Fe film on Fe_2O_3 was performed by molecular beam epitaxy, under a vacuum of 2×10^{-9} mbar, with a deposition rate of 0.11 nm/min. The thickness of the film was about 10 nm as shown by figures 1 a and b.

Diffusion Experiments and Depth Profiling

The samples with the ^{57}Fe film were submitted to the diffusion annealings at 951° , 1000° , 1052° , and 1100° C for diffusion perpendicular to c-axis, and at 900° , 1000° , and 1100° C for diffusion parallel to c-axis. A dynamic oxygen atmosphere of 10^5Pa was used. These annealings were performed in a tubular furnace, with the samples in a Pt crucible placed inside a silica tube. At 1000° and 1100° C, a couple of samples were placed in the crucible, for simultaneous diffusion along and perpendicular to c-axis, exactly in the same experimental conditions. The ^{57}Fe depth profiles were established by secondary ion mass spectrometry (SIMS). These SIMS analyses were performed using a 4F-CAMECA apparatus at Laboratoire de Physiques des Solides et Cristallogénèse – CNRS/Meudon-Bellevue, France. The ^{57}Fe depth profiles were established by using a 10 keV Cs^+ primary beam. The analysis were performed at an area of $150\mu\text{m} \times 150\mu\text{m}$, and the signals of the ions $^{54}\text{Fe}^-$, $^{56}\text{Fe}^-$, $^{57}\text{Fe}^-$ and $^{58}\text{Fe}^-$ were taken from a central zone of $33\mu\text{m}$ in diameter. The ^{57}Fe concentration, $[^{57}\text{Fe}]$, as function of the sputtering time, was determined from

the intensities (I) of the signals of the secondary negative ions $^{54}\text{Fe}^-$, $^{56}\text{Fe}^-$, $^{57}\text{Fe}^-$ and $^{58}\text{Fe}^-$ by means of the following relationship:

$$[^{57}\text{Fe}] = [I(^{57}\text{Fe}^-)/(I(^{54}\text{Fe}^-) + I(^{56}\text{Fe}^-) + I(^{57}\text{Fe}^-) + I(^{58}\text{Fe}^-))] \quad (1)$$

The penetration depths were obtained assuming a constant sputtering rate and measuring the depth of the crater by means of a Talystep profilometer. The diffusion profiles were determined parallel or perpendicular to the c-axis direction in Fe_2O_3 crystal.

Results

Figure 2 shows a typical SIMS spectra of the iron isotopes in hematite after a diffusion annealing at 1000°C . The ^{57}Fe depth concentrations profiles were deduced from the SIMS spectra using the methodology previously described.

Figures 3 shows the ^{57}Fe diffusion profile measured along c-axis at 900 and 1100°C (Fig.3a and b, respectively), and perpendicular to c-axis after diffusion annealing at 1100°C (Fig.3c), under oxygen atmosphere, in hematite crystal.

For the conditions used in the diffusion experiments, i.e., diffusion from a thin film in a semi-infinite medium, the tracer concentration, $C(x)$, as a function of the depth (x) is given by a Fick's second law solution as follows [16]:

$$C = [Q/(\pi Dt)^{1/2}] \exp(-x^2/4Dt), \quad (2)$$

where Q is the amount of tracer deposited on the surface per unit area, D is the diffusion coefficient, and t is the diffusion-annealing time. In this case, the experimental points of the diffusion profile must present a linear behaviour in a plot of $\ln [^{57}\text{Fe}]$ versus x^2 , as shown in Figures 4, which are related to the diffusion profiles of Figures 3.

The slope (p) of the straight line in the plot of $\ln [^{57}\text{Fe}]$ versus x^2 is equal to $-1/4Dt$, which allows the determination of the bulk diffusion coefficient through the expression: $D = -1/4p t$.

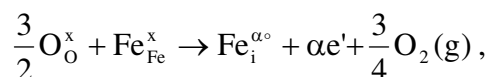
The results obtained for iron self-diffusion coefficients measured in hematite by SIMS are listed in Table 1. For the iron diffusion parallel to c-axis direction in Fe_2O_3 crystals, the diffusion coefficients can be described by the following Arrhenius equation: $D_{//c} (\text{cm}^2/\text{s}) = 5.2 \times 10^6 \exp [-510 (\text{kJ/mol})/RT]$, while for the iron diffusion perpendicular to c-axis, the diffusion coefficients are given by the relationship: $D_{\perp c} (\text{cm}^2/\text{s}) = 83 \exp [-430 (\text{kJ/mol})/RT]$.

Figures 5a-b compares iron diffusion profiles determined parallel and perpendicular to c axis, at 1000°C and 1100°C , in the same experimental conditions. The diffusion along c-axis is greater than that perpendicular to c-axis, which shows that there is iron diffusion anisotropy in hematite.

Discussion

Iron self-diffusion in Fe_2O_3

Fe_2O_3 has the corundum structure, and is oxygen deficient, with a small non stoichiometry [17]. The most important atomic point defect in Fe_2O_3 should be oxygen vacancies and iron interstitial irons. The formation of interstitial iron ion and of oxygen vacancies can be described by the following reactions:



and

$$O_O^x = V_O^{\gamma\circ} + \frac{1}{2} O_2(g) + \gamma e',$$

where O_O^x and Fe_{Fe}^x are oxygen ion and iron ion in their regular sites, respectively, $Fe_i^{\alpha\circ}$ ($Fe_i^x, Fe_i^\circ, Fe_i^{\circ\circ}$ or $Fe_i^{\circ\circ\circ}$) is an interstitial iron, and $V_O^{\gamma\circ}$ (V_O^x, V_O° or $V_O^{\circ\circ}$) is an oxygen vacancy. Therefore, there are four possible charge states ($\alpha = 4$) for interstitial iron and three possible charge states ($\gamma = 3$) for oxygen vacancy.

In the literature, it is assumed that the iron self-diffusion mechanism in hematite takes place by means of iron interstitial [4-6], but the charge state of this defect is not clear yet.

Himmel et al. [3] have determined iron diffusion coefficients in natural hematite crystals. The impurity content was not informed. The radioactive isotope ^{55}Fe was used as iron tracer. The diffusion experiments were performed at two different temperatures: 1000° and 1217° C, in pure oxygen at 1 atm pressure, parallel and perpendicular to c-axis of the crystal. The iron diffusion coefficient was determined by means of the Decrease of Surface Activity Method [16]. This is an indirect method without depth profiling. In these experimental conditions, they found an activation energy of 381 kJ/mol, and the iron diffusion was independent of the crystallographic direction.

Chang and Wagner [4] have determined iron diffusion coefficients, along c-axis, in Fe_2O_3 neutral single crystals as a function of oxygen partial pressure at 1200° and 1300° C. Chemical analysis of the crystals revealed at least 200 ppm (by wt) of impurities, being the most abundant the Ti (68), V(47), Mn (22), Mg(18), and Si(12). The radioactive isotope ^{55}Fe was used as iron tracer, and the diffusion coefficient was determined by the Gruzin' method [16], but apparently without depth profiling. The oxygen pressure dependence of the iron diffusion coefficient indicated that iron migrates interstitially in hematite crystals as triply-charged interstitial ($Fe_i^{\circ\circ\circ}$), and the activation energy determined from the two temperatures, in 1 atm oxygen atmosphere, was 360 kJ/mol.

Atkinson & Taylor [5] have measured iron diffusion in synthetic crystals of hematite along c-axis direction. Chemical analysis of the crystals revealed 3% Pb and a total of 500 ppm for the transition metals Cr, Mn and Ni combined. The diffusion experiments were performed between 708 and 1303°C using the radioactive isotope ^{59}Fe as iron tracer. The diffusion profiles were established by

mechanical sectioning, above 900° C, or argon ion sputtering at lower temperatures. Above 900° C, Atkinson and Taylor obtained the following Arrhenius equation: $D(\text{cm}^2/\text{s}) = 1.6 \times 10^9 \exp [-577 (\text{kJ/mol})/RT]$, while below 900° C, they obtained the expression: $D (\text{cm}^2/\text{s}) = 2.8 \times 10^9 \exp [-173(\text{kJ/mol})/RT]$. These authors proposed that in high-temperature region (above 900° C), the iron diffusion behaviour is characteristic of pure Fe_2O_3 , while at temperatures below 900° C, the behaviour may have been influenced by impurities. Atkinson and Taylor [5] have reviewed and discussed the iron diffusion atomic mechanisms in hematite, without a conclusion about the charge state of the interstitial iron.

Hoshino & Peterson [6] measured the iron diffusion in natural hematite single crystals along c-axis, with Ti, V, Mn and Ni being the major impurities, each about 30ppm by weight, Cl (10 ppm), As (7 ppm), Cr (3 ppm), Na (2 ppm) and Mg (2 ppm). The experiments were performed using the isotope ^{59}Fe as iron tracer and depth profiling by mechanical sectioning and counting. Between 1100° C and 1300° C, in an oxygen pressure of 10^5Pa , they proposed the following Arrhenius equation for the iron volume diffusion in hematite: $D(\text{cm}^2/\text{s}) = 8.7 \times 10^7 \exp [-539 (\text{kJ/mol})/RT]$, and suggested that interstitial iron ions diffuse in Fe_2O_3 as doubly-charged interstitial ($\text{Fe}_i^{\circ\circ}$).

Figure 6 shows a comparison of our results with those of the literature [3-6], only taking into account data about iron diffusion along c-axis of the Fe_2O_3 crystals, and above 900° C. In general, in spite of the differences among the impurity contents of the samples, of the different techniques, and of the different temperature ranges used, the data about iron self-diffusion in hematite show reasonable agreement. In particular, the more reliable diffusion coefficients, obtained by using depth profiling, of Hoshino and Peterson [6], and Atkinson and Taylor [5], show very good agreement with our results, obtained by SIMS, which indicates that the iron self-diffusion coefficient is a well-defined property for hematite, along c-axis direction, above 900° C, under oxygen atmosphere.]

Iron diffusion anisotropy

It was shown above that the iron diffusion along c-axis is greater than that perpendicular to c-axis and the diffusion coefficients are plotted in figure 7 as an Arrhenius graph. These results showing iron diffusion anisotropy are unequivocal due to the fact that the diffusion experiments for the two directions were performed exactly in the same experimental conditions. It is the first time that iron diffusion anisotropy in hematite is reported.

One way to understand the iron diffusion anisotropy, is to take into account the general expression for solid-state diffusion coefficients: $D = \gamma \lambda^2 \Gamma$, where γ is a geometric factor, λ is the jump distance, and Γ is the jump frequency [16]. Usually, the geometric factor is given by $\gamma = 1/N$, where N is the number of neighbouring sites into which the ion can jump, while λ is the jump distance between these sites. In our experimental conditions (fig.7), the ratio $D_{//c} / D_{\perp c}$ is greater than 20, at 1000° C,

and greater than 50 at 1100°C. As iron only occupies octahedral sites in corundum structure, the γ value is the same for diffusion in both directions considered in this work. On the other hand, there is no conclusive model describing the migration pathways for interstitial iron in hematite, which could give the λ values. Atomistic simulation of iron transport in hematite by means of interstitial migration was performed by Catlow et al [18]. They have investigated direct interstitial migration in which the interstitial iron ($\text{Fe}_i^{\circ\circ}$) diffuses through an anion triangle between nearest-neighbour interstitial sites. They found a unusual very high activation energy of more than 970 kJ/mol. They have also discussed several possible indirect interstitial pathways, i.e., interstitially mechanisms for iron diffusion in hematite, and have found activation energies ranging from 193 kJ/mol to 1024 kJ/mol. Each calculated activation energy was found to be different of the experimental values given above. The calculated activation energy nearest the experimental data shown above is 657 kJ/mol corresponding to a mechanism in which the interstitial iron moves in the ab plane to displace a lattice cation to the nearest interstitial site within that plane. No calculation was made for the migration of doubly-charged interstitial iron ($\text{Fe}_i^{\circ\circ}$). Whatever the mechanism investigated by Catlow et al., the difference between the λ values both along and perpendicular to c- axis is not enough to justify the ratio $D_{//c} / D_{\perp c}$ observed in this work. Therefore, values of γ or λ cannot explain the difference between the iron diffusion coefficients measured parallel or perpendicular to c-axis in Fe_2O_3 crystals, and the interstitial iron diffusion anisotropy should be principally related to different jump frequencies (Γ) for the two different crystallographic directions used in this work, which is not surprising for an hexagonal structure like the corundum structure of hematite. It is worth noting that, the ratio $D_{\perp c} / D_{//c}$, in the hexagonal structure, is found, experimentally, to be less than 1 as the ratio c/a is greater than $\sqrt{8/3}$ [16]. It is in good agreement with our results for which $D_{\perp c} / D_{//c} < 1$, and $c/a \approx 2.7 > \sqrt{8/3}$.

Other two important technological oxides, $\alpha\text{-Al}_2\text{O}_3$ and Cr_2O_3 , have the same structure as Fe_2O_3 . Diffusion anisotropy for the chromium self-diffusion in Cr_2O_3 crystals was observed by Hoshino and Peterson [19] between 1490° and 1570° C, in different partial oxygen pressures. According to these authors, the value of the ratio $D_{//c} / D_{\perp c}$ for chromium self-diffusion in Cr_2O_3 is ca. 1.7. They suggested that the chromium diffusion both parallel to and perpendicular to the c-axis takes place by means of triply-charged vacancies ($\text{V}_{\text{Cr}}^{\circ\circ\circ}$), with different jump frequencies of chromium ions for the two directions. Thus, the difference between $D_{//c}$ and $D_{\perp c}$ is small for chromium diffusion in Cr_2O_3 crystals.

As far as we know, there are no data available in the literature about aluminium diffusion anisotropy in Al_2O_3 crystals.

Cation self-diffusion in hematite, chromia and alumina

The results concerning cation bulk self-diffusion in Al_2O_3 , Cr_2O_3 and Fe_2O_3 are gathered in figure 8a. Concerning alumina, the more recent results [1] were taken and they correspond to self-diffusion along c-axis in alumina single crystals under air. Concerning chromia, it also concerns single crystals, but the surface plane was not a $|0001|$ plane, but a $|01\bar{1}2|$ plane (i.e. at 57.7° from $|0001|$ plane). The diffusion treatment was performed in 10^{-5} atm oxygen, but Sabioni et al. found that diffusion in chromia did not depend on the oxygen pressure [7, 13-14]. According to figure 8a, it looks like diffusion is much faster in hematite than in chromia and alumina. This could be due, at least for a part, to the differences in non-stoichiometry for the three oxides, but it is necessary also to consider that these oxides have different melting temperature and the representation of Fig.8a is not satisfying. The comparison of self-diffusion in oxides having the same crystal structure and different melting temperature is more adequate in a normalized Arrhenius diagram ($\log D$ versus T_m/T , where T_m = melting temperature in Kelvin) [8]. This was done in figure 8b and, then, it appears that the differences between the three oxides are not so marked: alumina, which is the most stoichiometric of the three oxides, is characterised by smaller self-diffusion coefficients, while chromia and hematite are very close each other. Such results agree also with oxidation rates of materials developing one of these oxides as a protective film. The oxidation rate of alumina former alloys is smaller than the oxidation rate of chromia former alloys, while the growth rate of hematite is not far from that of chromia [17]. It is just important to note that such bulk diffusion rates given in figures 8 cannot justify the oxidation rates of materials forming one of these three oxides as a protective film. Indeed, it indicates that the oxide growth is controlled by grain boundary diffusion [20-21]. The differences between the various activation energies found for diffusion in these oxides will not be discussed for several reasons. First there is a great uncertainty in the determination of such activation energies especially when the number of experimental points is limited, and it is the case for most of the works mentioned here due to the difficulties encountered in these studies. Moreover, amongst the various results in the literature, it can be remarked that the temperature range and the oxygen pressure are often varying from one study to another. So, the comparison of the activation energies does not seem satisfying.

Conclusions

For the first time iron diffusion has been simultaneously measured along and perpendicular to c-axis in hematite crystals. The measurements were performed using an original methodology based on the utilization of ^{57}Fe stable isotope as iron tracer, and depth profiling by secondary ion mass spectrometry (SIMS). The results obtained for the diffusion along c-axis show very good agreement

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with the more reliable diffusion coefficients previously determined by using radioactive techniques. In the experimental conditions used in the present study, there is iron diffusion anisotropy in hematite crystals, the diffusion along c-axis being greater than that perpendicular to c: along c-axis, self-diffusion can be described by $D_{//c} \text{ (cm}^2\text{/s)} = 5.2 \times 10^6 \exp [-510 \text{ (kJ/mol)/RT}]$, and, perpendicularly to c-axis, $D_{\perp c} \text{ (cm}^2\text{/s)} = 83 \exp [-430 \text{ (kJ/mol)/RT}]$. Comparison of self-diffusion in Al_2O_3 , Cr_2O_3 and Fe_2O_3 , in a normalized Arrhenius diagram, shows that cation self-diffusion in alumina, which is the most stoichiometric of these oxides, is smaller than in chromia and hematite.

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Figure Captions

1. Iron profile as a function of the depth after an heat-treatment at 800°C, a) ^{57}Fe counts and b) ^{57}Fe concentration, showing that the thickness of the deposit was 10 nm maximum.
2. Evolution of the intensity of iron isotopes as a function of the sputtering time after a diffusion annealing at 1000°C.
3. Iron concentration profile versus penetration depth in Fe_2O_3 single crystals, a) and b) along c-axis after diffusion at 900 and 1100°C respectively, c) perpendicular to c-axis after diffusion at 1100°C.
4. Evolution of the logarithm of the iron concentration as a function of x^2 obtained from figure 3, a) and b) along c-axis after diffusion at 900 and 1100°C respectively, c) perpendicular to c-axis after diffusion at 1100°C.
5. Comparison of iron concentration profile versus penetration for diffusion along to and perpendicular to c-axis at a) 1000°C, b) 1100°C. The smaller the slope, the greater the diffusion coefficient.
6. Arrhenius plot of the diffusion coefficients obtained for iron diffusion along c-axis of hematite single crystals. Comparison with Atkinson et al. [5], Hoshino et al. [6], Himmel et al. [3] and Chang et al. [4] works.
7. Arrhenius plot of the diffusion coefficients obtained for iron diffusion in hematite single crystals along to and perpendicular to c-axis.
8. Comparison of cation self-diffusion in Fe_2O_3 , Cr_2O_3 and Al_2O_3 single crystals, a) Arrhenius plot, b) plot of the diffusion coefficients versus T_m/T , T being the melting point of the oxide.

Table I : Iron self-diffusion coefficients measured in hematite single crystals

Table 1 – Bulk diffusion coefficients of iron in Fe₂O₃ single crystals

Temperature (° C)	Time (s)	D _⊥ (cm ² /s)	D _∥ (cm ² /s)	D _∥ / D _⊥
900	1.677x10 ⁵		1.1x10 ⁻¹⁶	
900	1.677x10 ⁵		1.1x10 ⁻¹⁶	
951	6.090x10 ⁴	6.1x10 ⁻¹⁷		
951	6.090x10 ⁴	2.6x10 ⁻¹⁷		
1000	1,800x10 ⁴	1.8x10 ⁻¹⁶	4.6x10 ⁻¹⁵	25.6
1000	1.800x10 ⁴	2.2x10 ⁻¹⁶	4.6x10 ⁻¹⁵	20.9
1052	5.640x10 ³	7.9x10 ⁻¹⁶		
1052	5.640x10 ³	8.1x10 ⁻¹⁶		
1100	1.020x10 ⁴	4.1x10 ⁻¹⁵	2.4x10 ⁻¹³	58.5
1100	1.020x10 ⁴	4.1x10 ⁻¹⁵	2.2x10 ⁻¹³	53.4

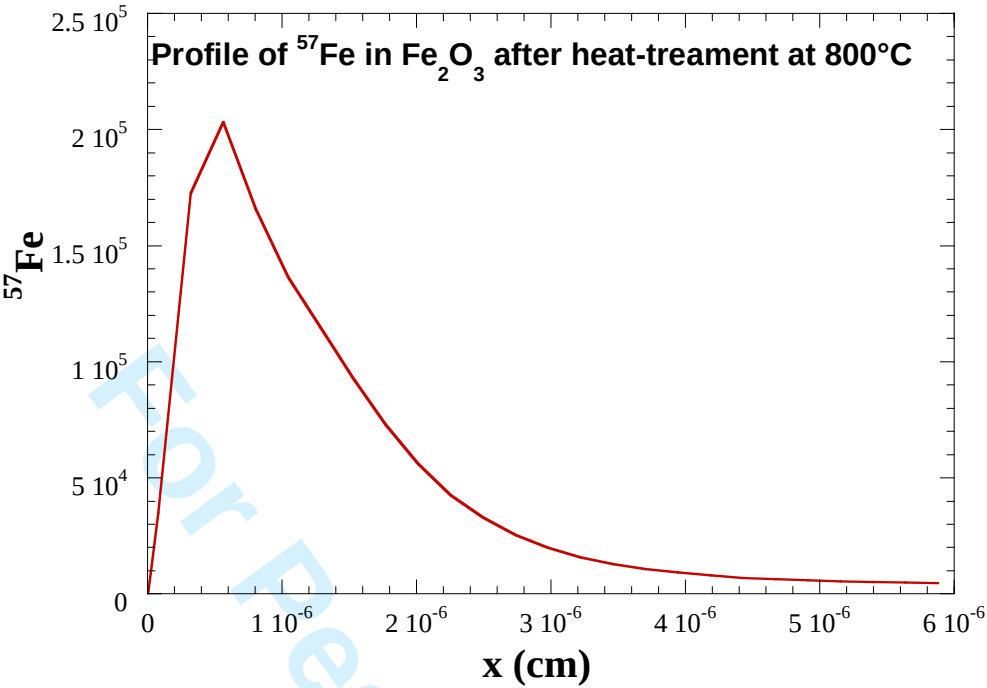


Fig.1a

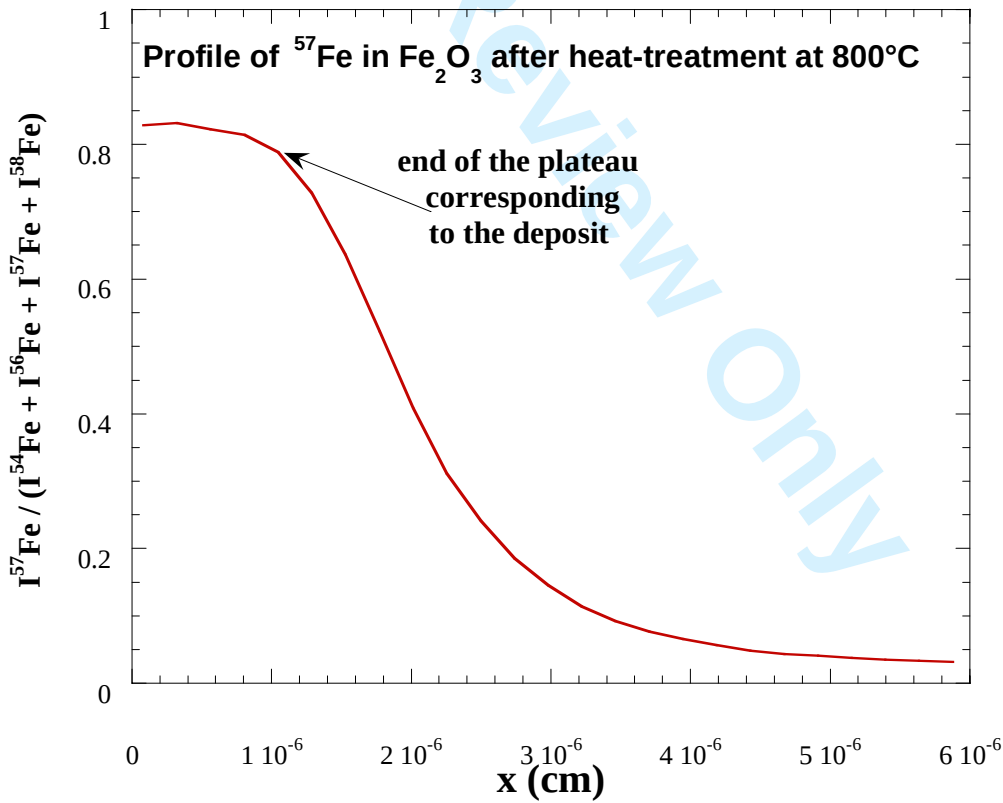


Fig.1b

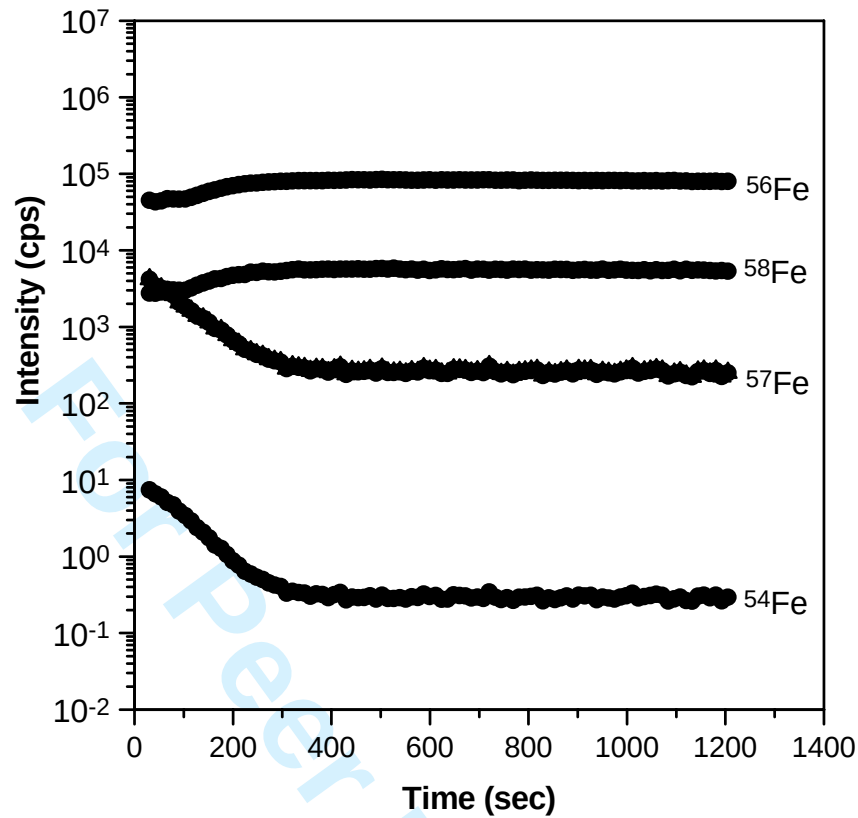


Fig.2

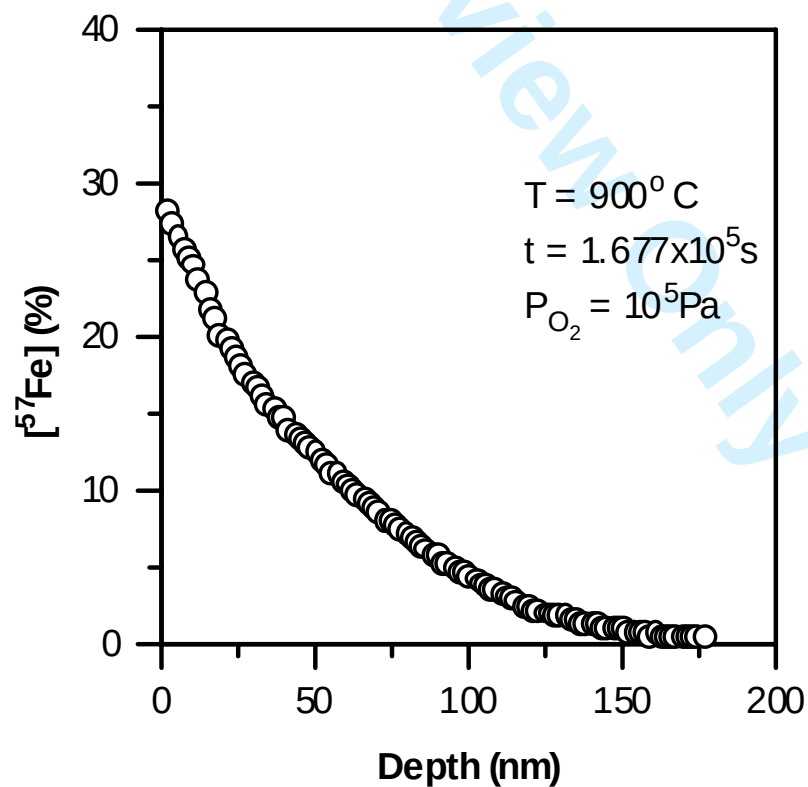


Fig.3a

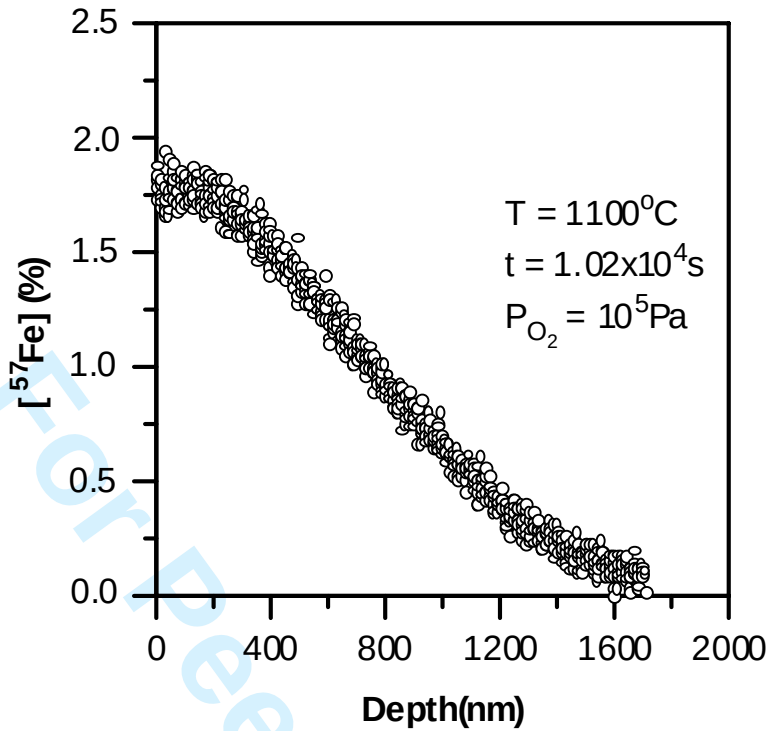


Fig.3b

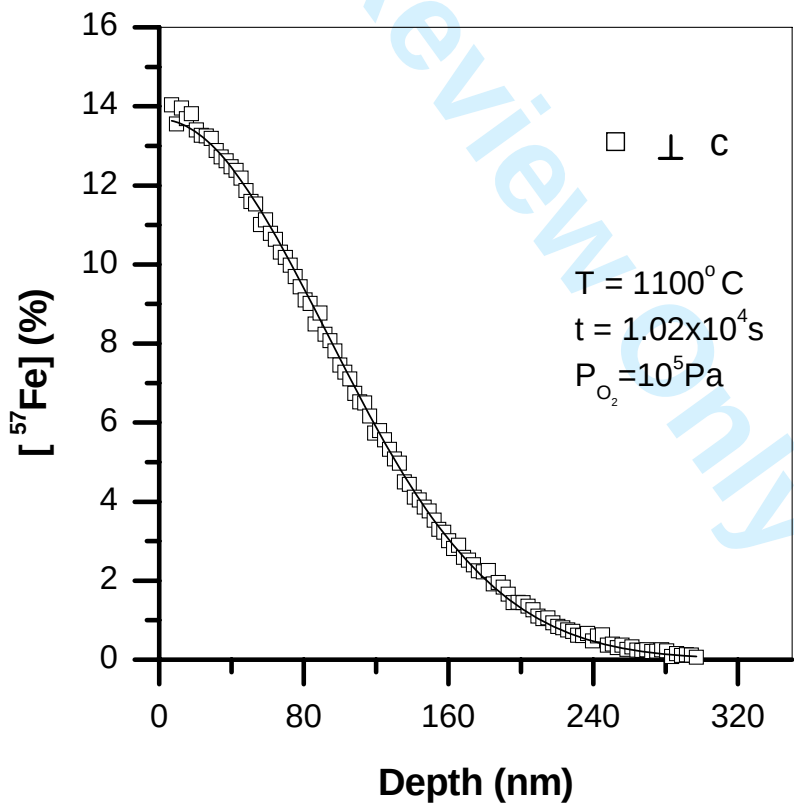


Fig.3c

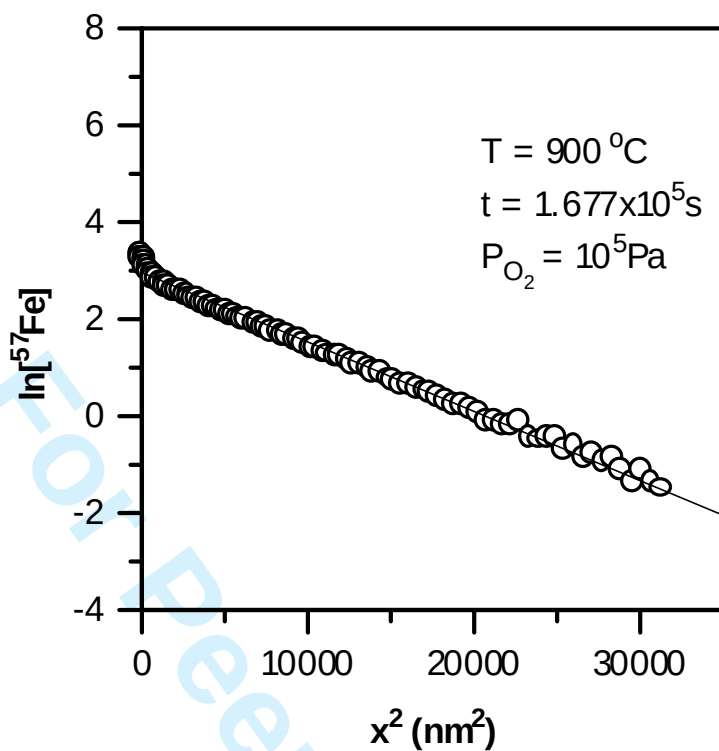


Fig.4a

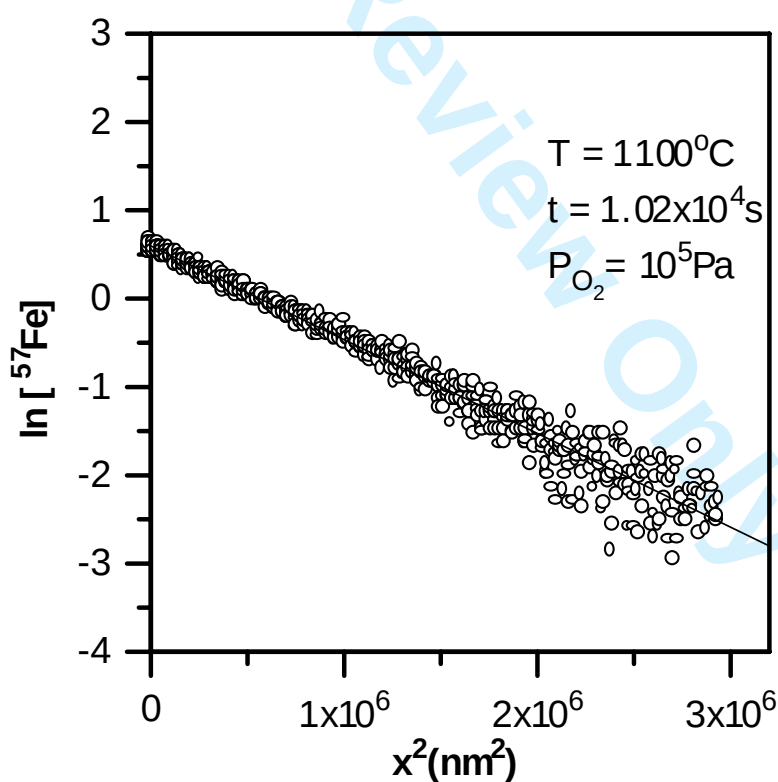


Fig.4b

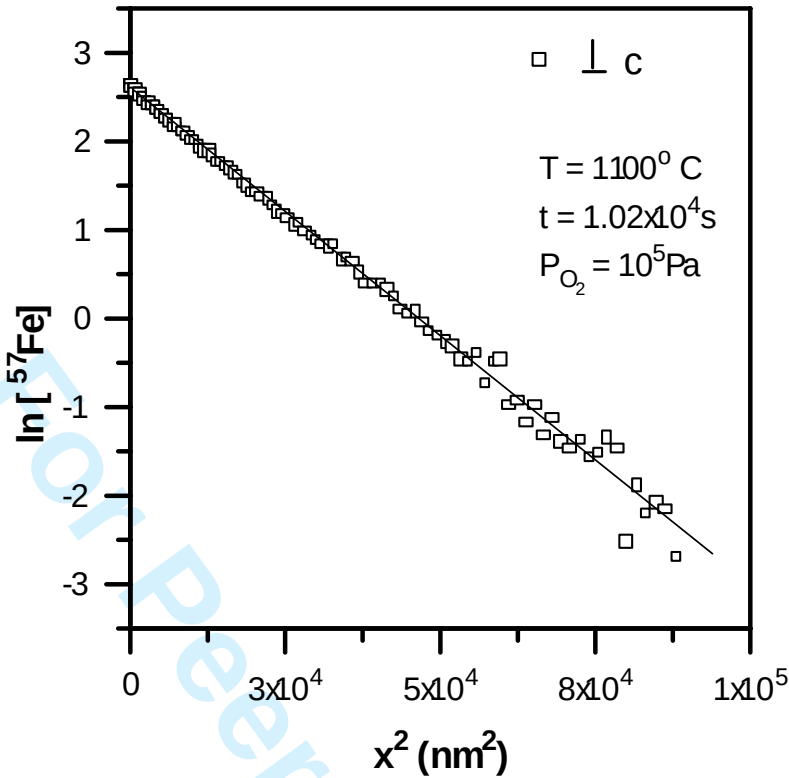


Fig.4c

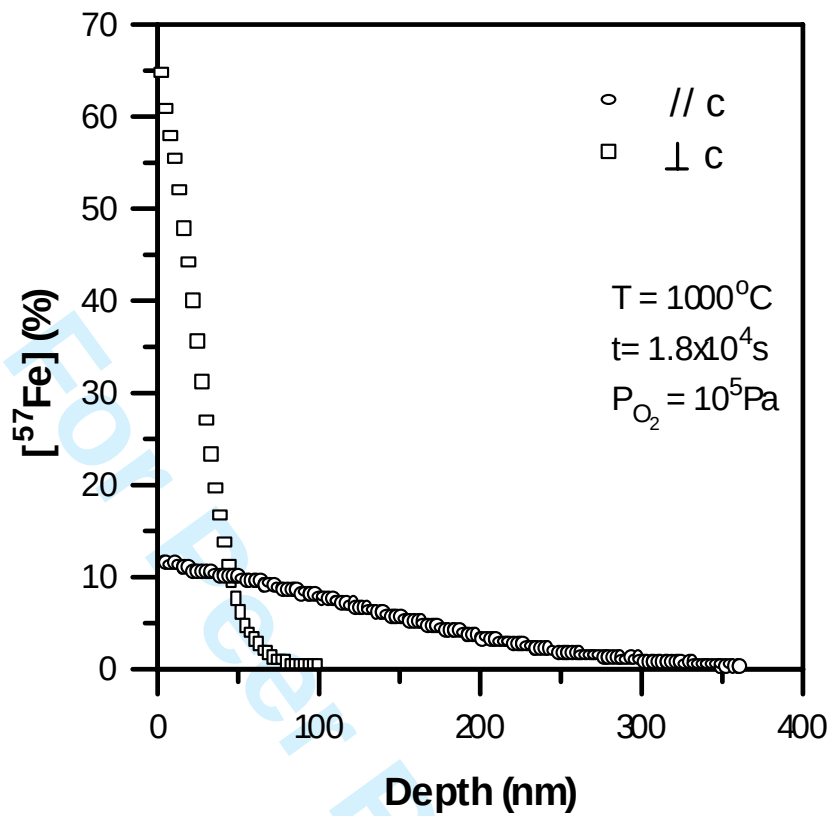


Fig.5a

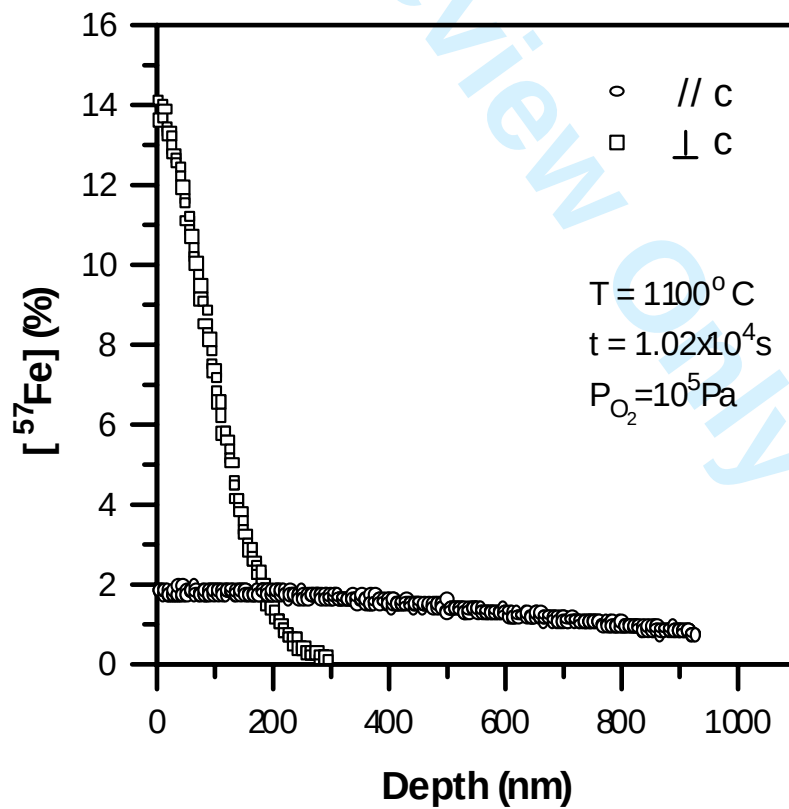


Fig.5b

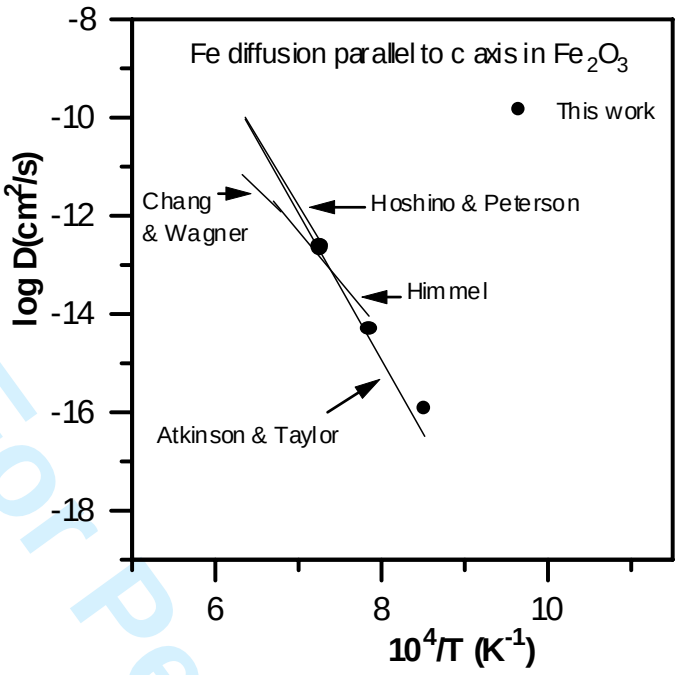


Fig.6

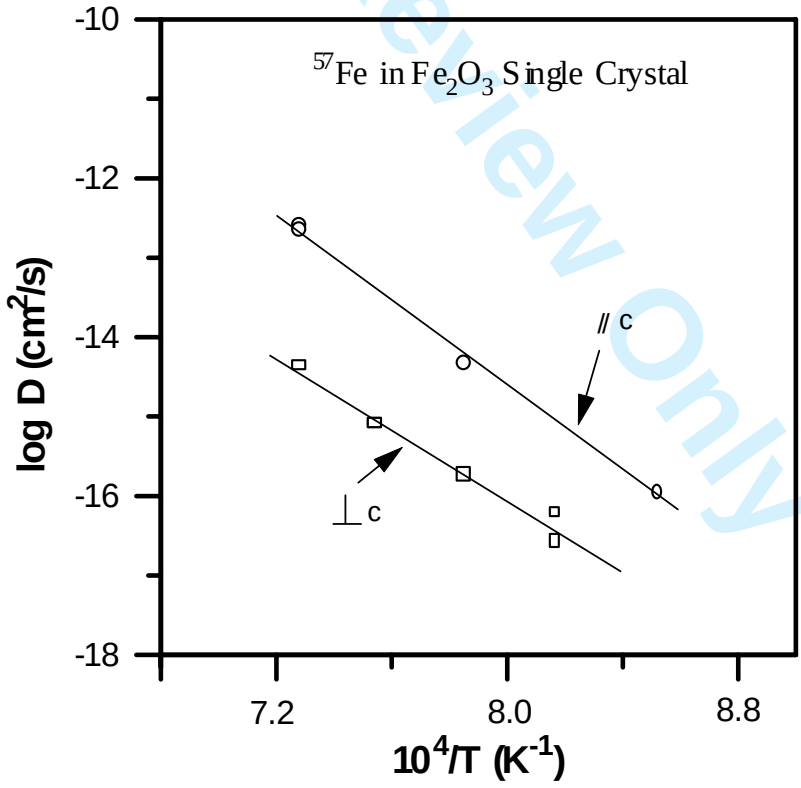


Fig.7

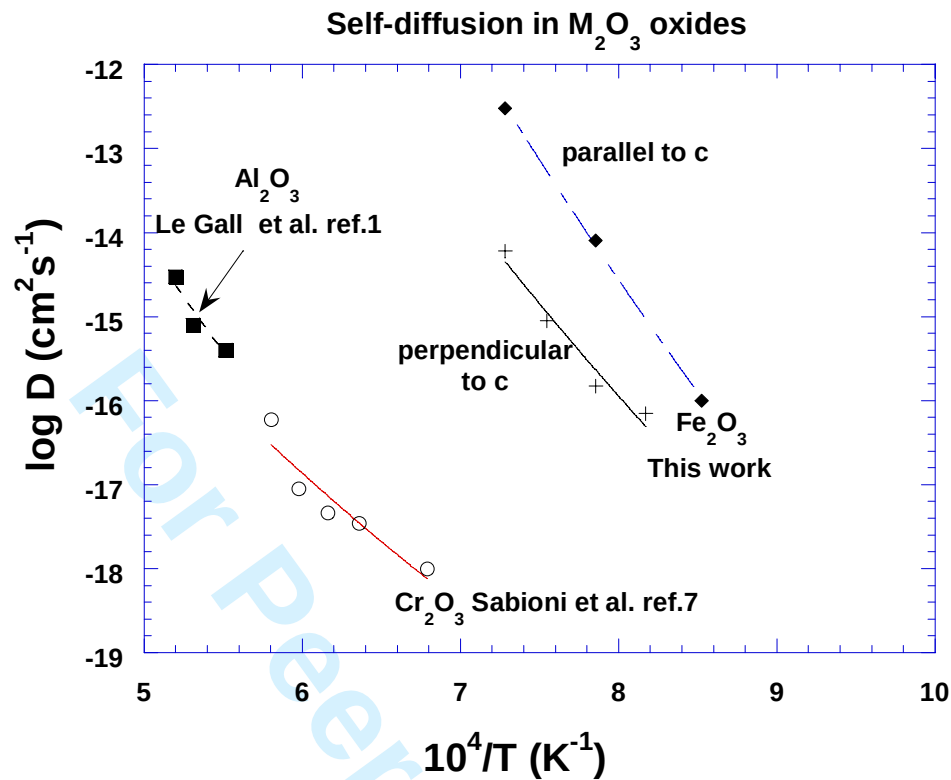


Fig.8a

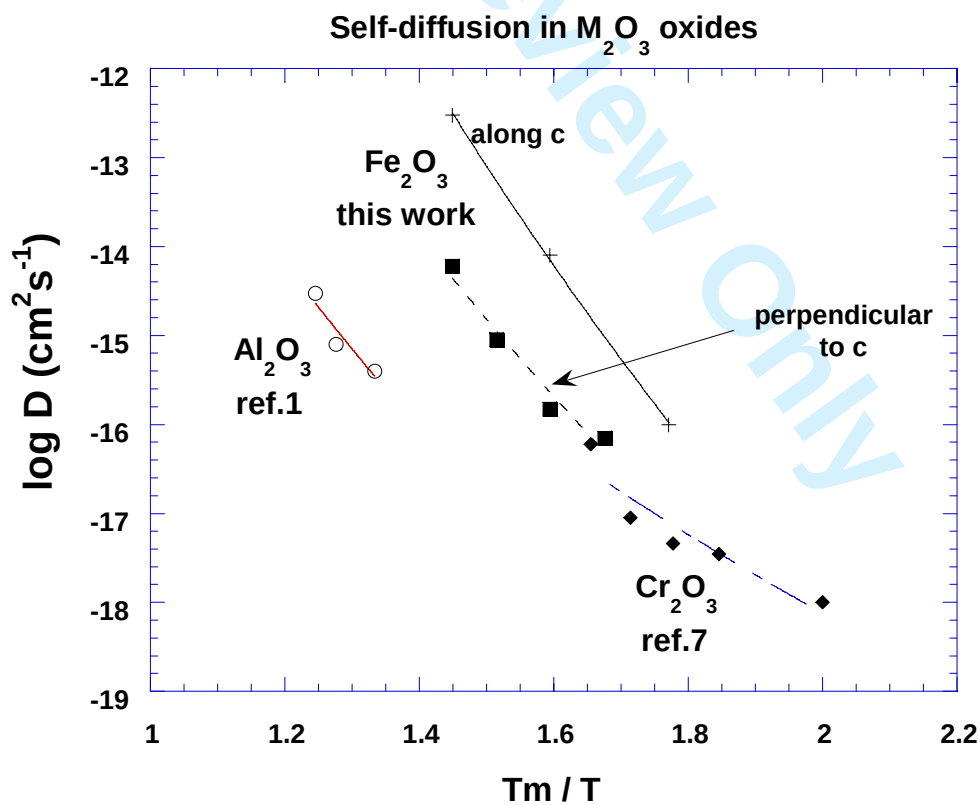


Fig.8b

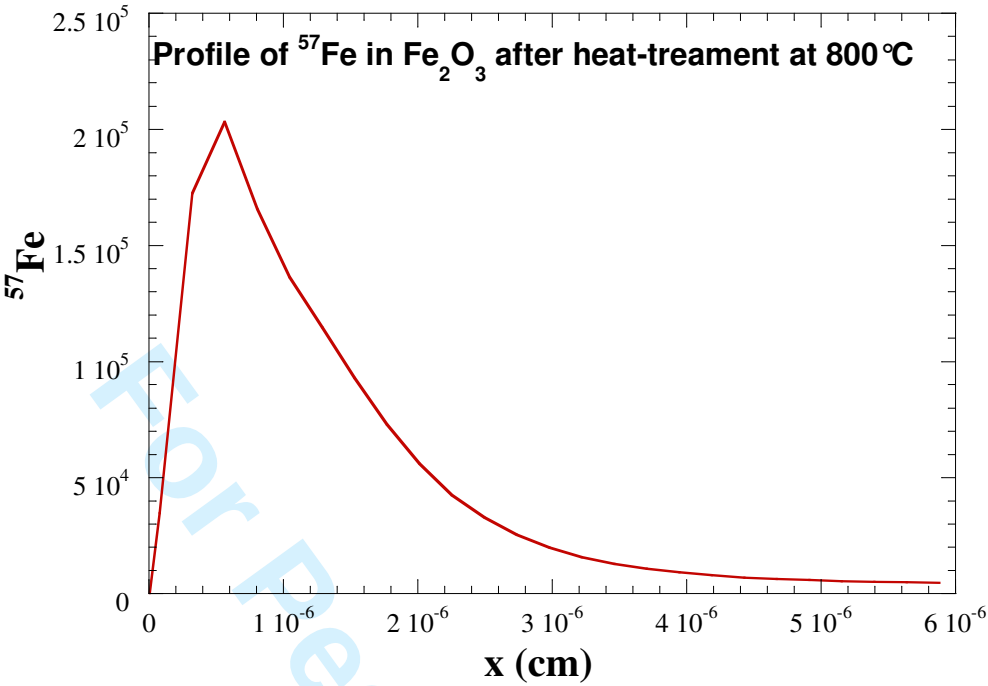


Fig.1a

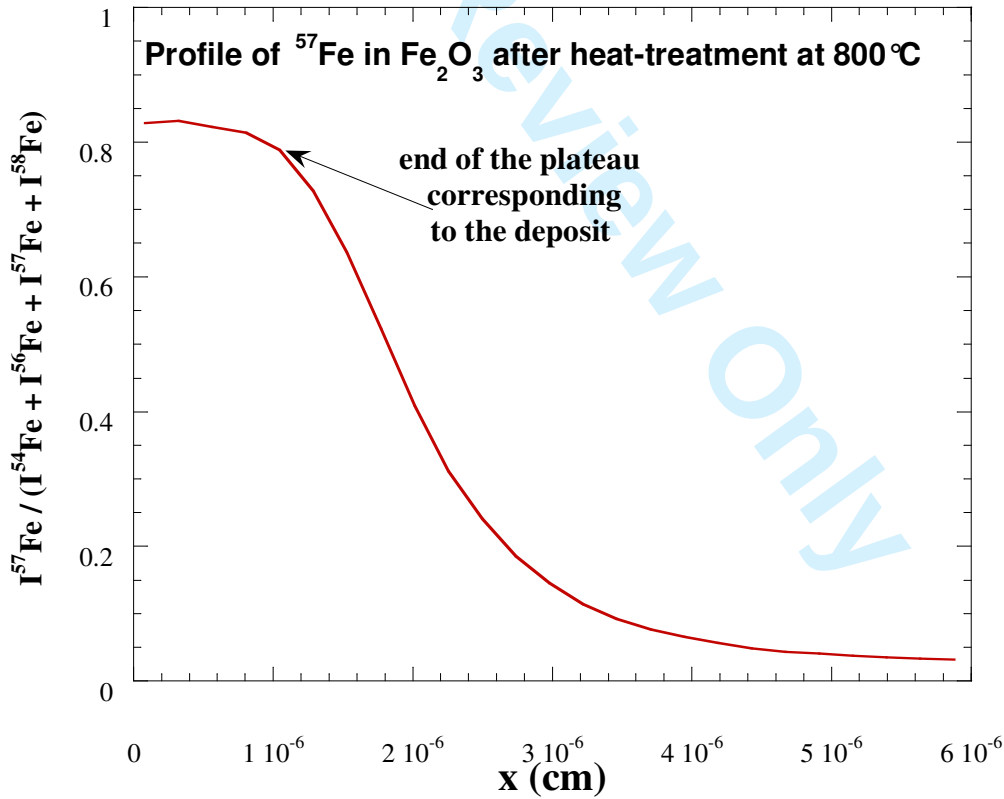


Fig.1b

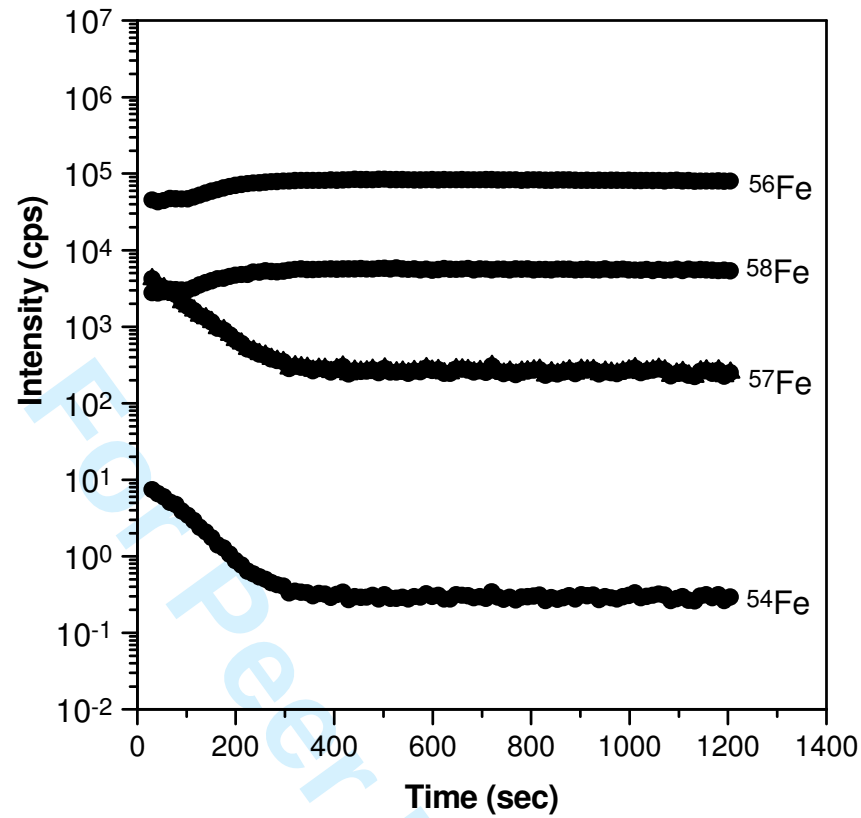


Fig.2

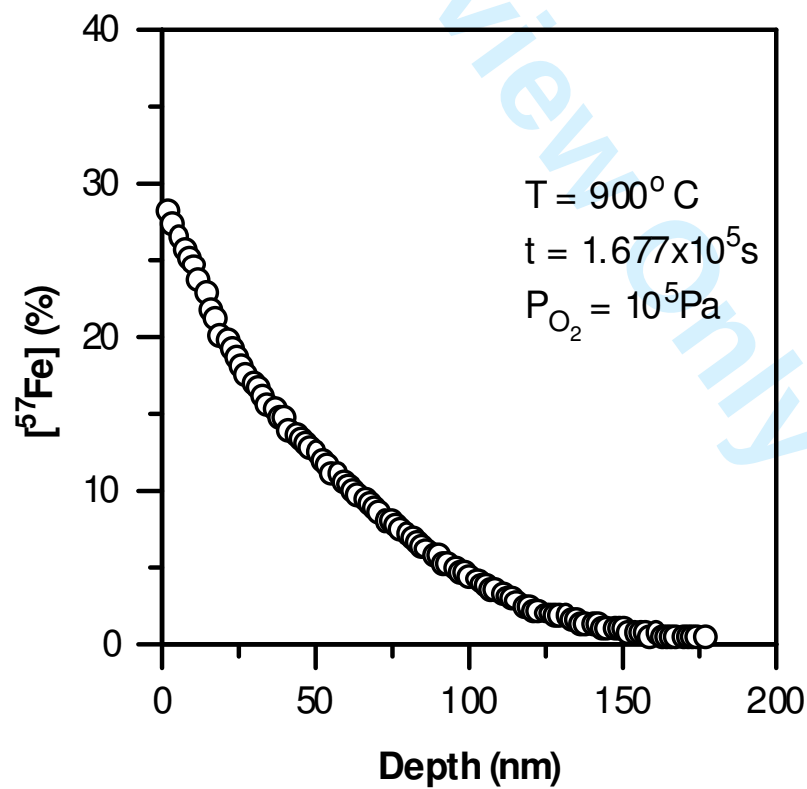


Fig.3a

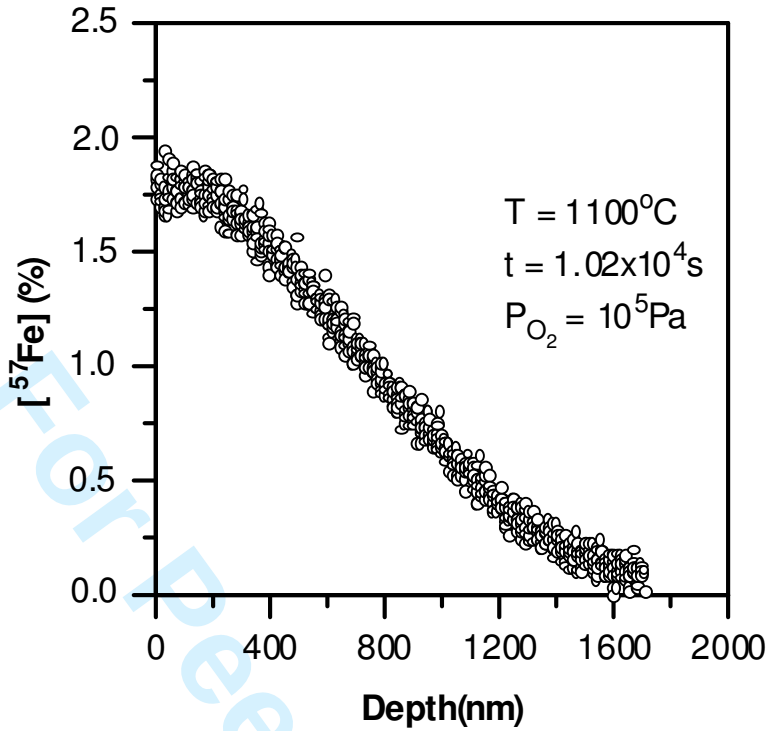


Fig.3b

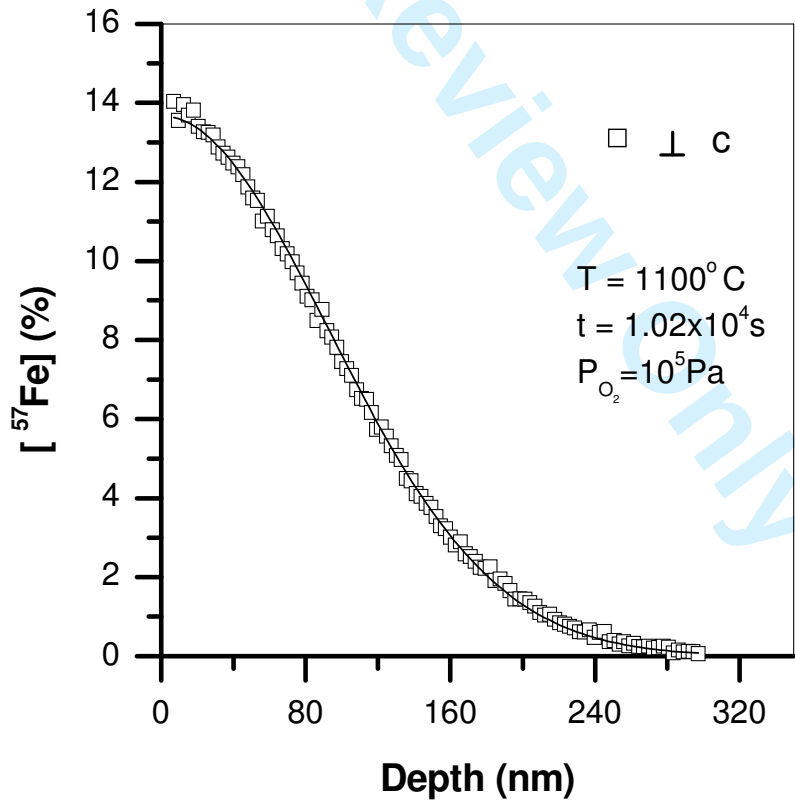


Fig.3c

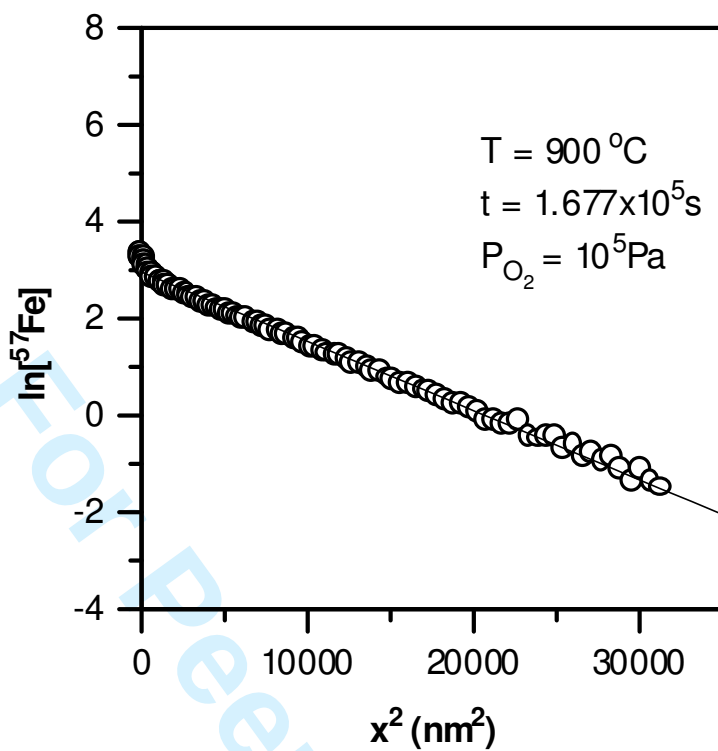


Fig.4a

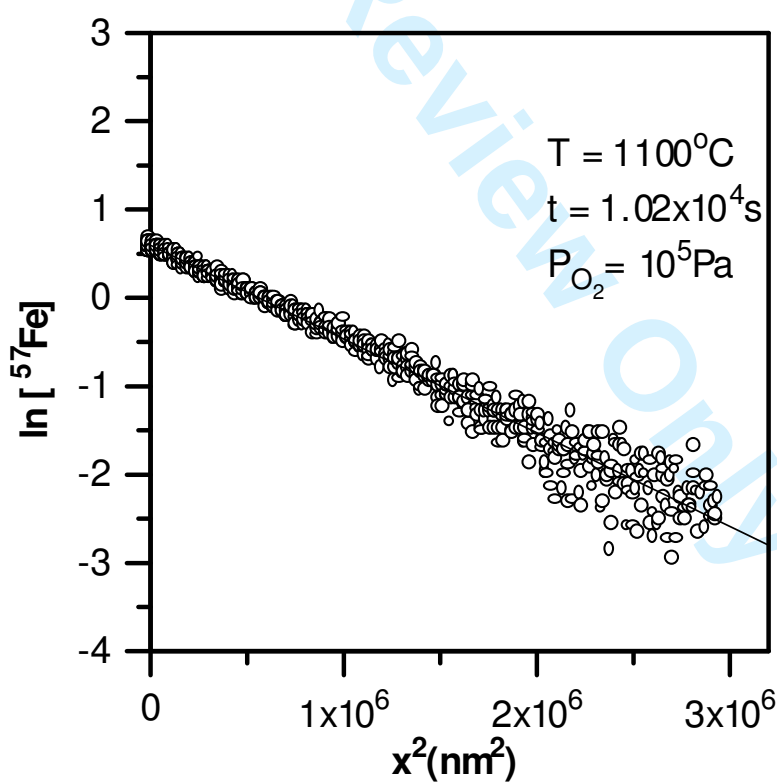


Fig.4b

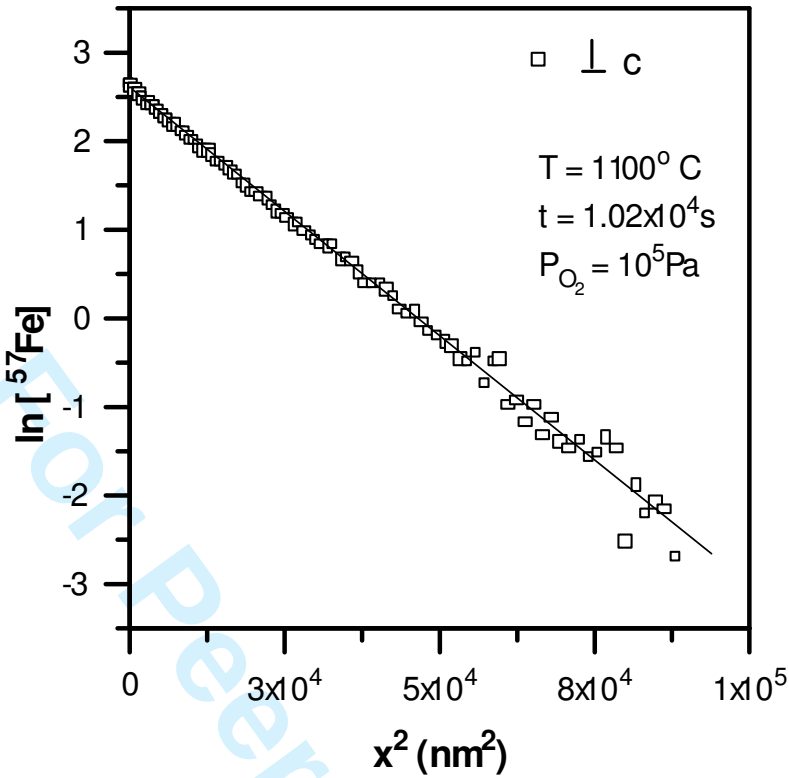


Fig.4c

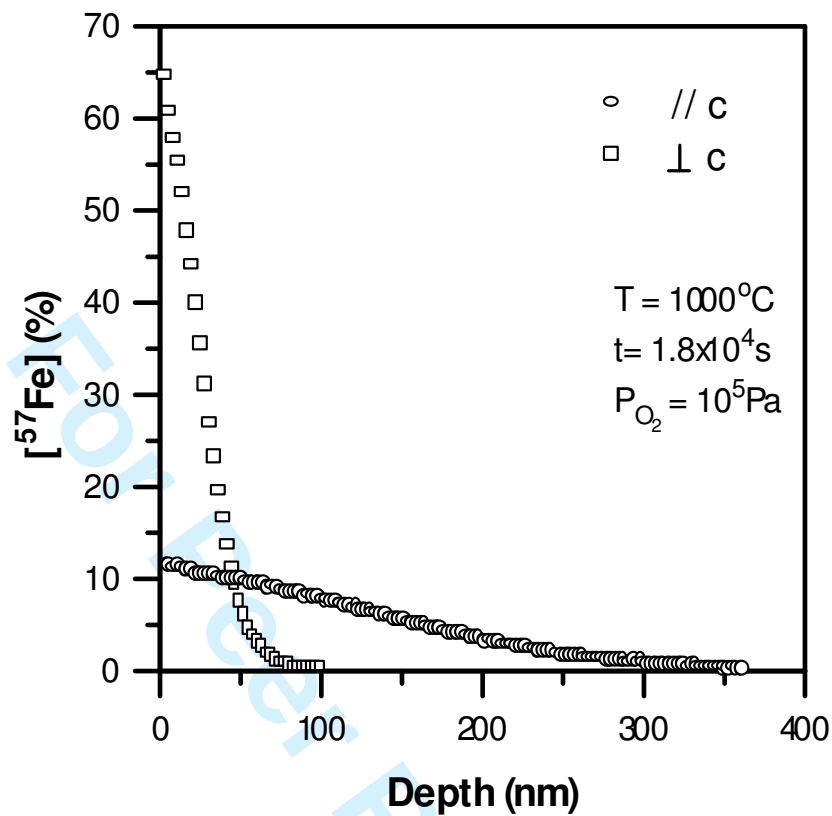


Fig.5a

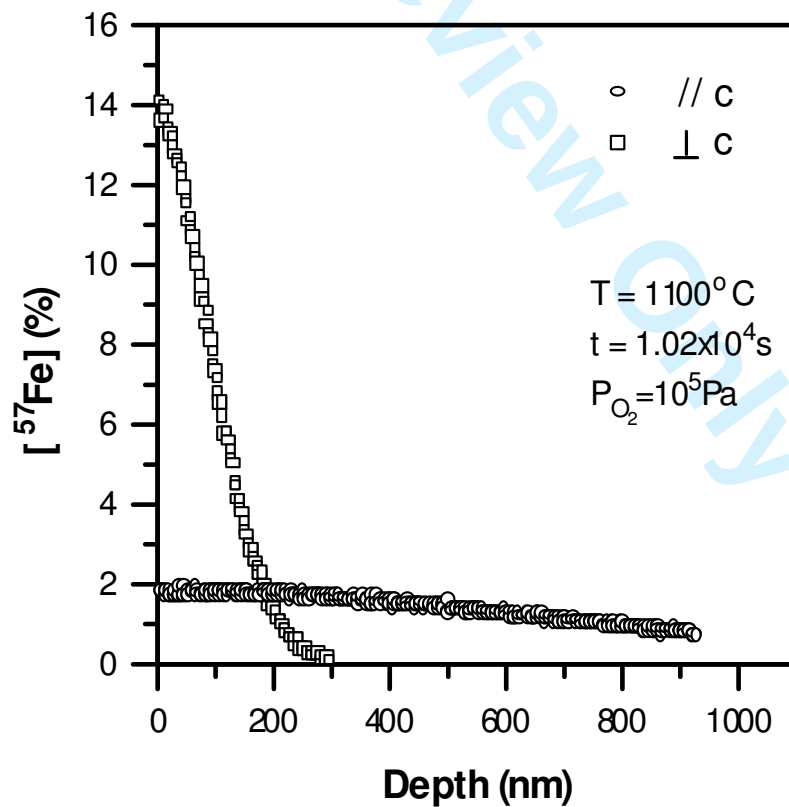


Fig.5b

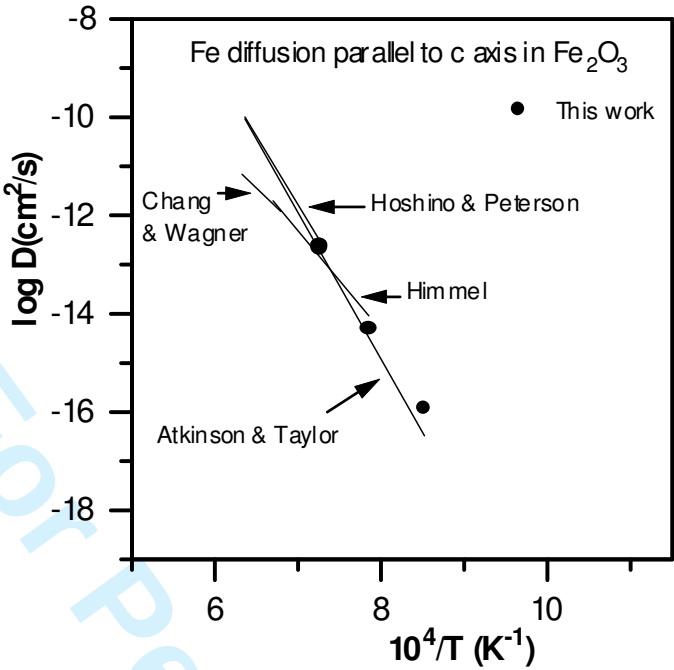


Fig.6

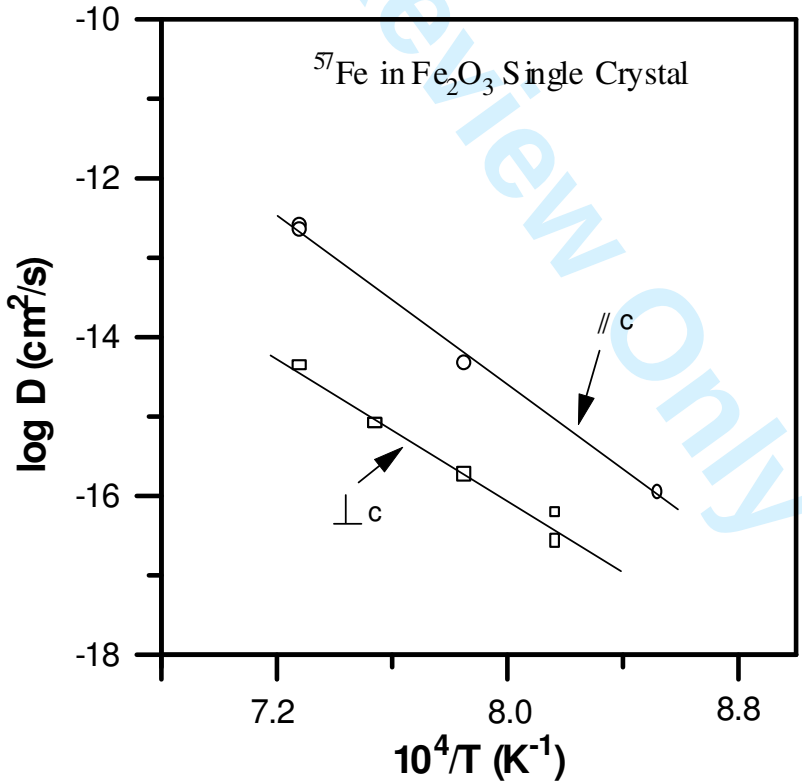


Fig.7

