

An Explicit Solution to Extract Self-Diffusion and Surface Exchange Coefficients from Isotope Back-exchange Experiments

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ABSTRACT

In this contribution, we provide an analytical solution to the one-dimensional transient diffusion equation to estimate oxygen self diffusion and effective surface exchange coefficients of fast oxygen ion conducting materials exposed to multi-step ^{18}O isotope exchange procedures. The isotope exchange procedure and subsequent analytical techniques such as the Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) provide an effective means to analyse diffusion characteristics of labeled isotopic species in such materials. Although an analytical solution exists for representing the diffusion profiles of labeled species obtained from a single-step exchange procedure, it is not applicable to the diffusion profiles resulted from consecutive procedures with dynamically altered initial and surface boundary conditions. Hence, a new analytical solution composed of integral transform equations is found for the transient diffusion problem representing the isotope back-exchange procedure in a semi-infinite spatial domain. The analytical solution is then used to determine the self-diffusion and surface exchange coefficients as fitting parameters for tracer gas diffusion profiles obtained from multi-step isotope exchange experiments. It is demonstrated that our solution provides a flexible means to analyse the effects of ambient gas compositions on transport properties of oxygen ion conducting materials.

Keywords

Isotope exchange, mixed ionic electronic conductors, Laplace transform, diffusion in semi-infinite media.

1. INTRODUCTION

Understanding the effect of in situ gas composition on the transport properties of fast oxygen ion conducting materials has a paramount importance in successfully designing robust and efficient electrochemical conversion devices such as solid oxide fuel cells (SOFCs), solid oxide electrolyser cells (SOECs) and gas sensors. Often those properties, namely the oxygen self-diffusion coefficient (D^*) and the effective surface exchange coefficient (k^*), are determined from experiments conducted in controlled atmospheres which may not be representative of the actual device operating conditions.

The isotope exchange depth profiling method, initially developed by Kilner, provides a means to extract D^* and k^* values by analysing the tracer gas diffusion profiles in samples annealed under high purity isotope enriched oxygen [1,2]. While it is widely accepted and used, the method

inherently requires the use of high concentration of labeled oxygen species in the ambient gas which could be costly and restrictive for investigating the effects of multicomponent gas mixtures of typical operating environments on the transport properties.

Recently, Cooper *et.al.* [3] have developed the back-exchange technique to remedy this and to investigate the influence of oxygen containing species on the surface and bulk transport properties of mixed electronic and ionic conducting ceramics. The technique involves a two-stage procedure starting with a standard isotope exchange in ^{18}O enriched environment followed by a back-exchange in isotope unenriched environment. In addition to the novel experimental technique, Cooper *et.al.* [3] provided an analytical solution for the back-exchange diffusion problem for a special case where D^* and k^* values were assumed to be constant for all stages of the isotope exchange procedure. Acknowledging the limited applicability of the analytical solution, a finite difference method was used by Cooper *et.al.* [3] to numerically solve the diffusion problem for fitting the experimental back-exchange depth profile data with multiple D^* and k^* values. In this contribution, however, the authors provide an analytical solution that can be used to extract multiple D^* and k^* values for the isotope back-exchange procedure.

2. ANALYTICAL SOLUTION

The two step isotope exchange procedure involves a protocol of utilising separate gas compositions for each step while keeping the rest of the thermodynamic variants, such as the annealing temperature and the oxygen partial pressure, constant. During the first step of the procedure, the isotope exchange is carried out in a gas composition of high isotopic ^{18}O concentration. In the consequent step of the procedure, the isotope back-exchange is carried out under a gas composition of lower or no labeled isotopic species. Comparing the physical dimensions of the substrate exposed to the exchange procedure and the characteristic diffusion length of the isotopic tracer species from the exchange surface, the problem can be described as a transient one-dimensional diffusion in a semi-infinite medium. Here, the authors will construct a model for each step by introducing appropriate boundary and initial conditions describing the corresponding step of the exchange procedure. The aim is to obtain an analytical solution to the diffusion problem for each step and utilise those solutions to extract D^* and k^* values from experimentally measured data for isotopic ^{18}O diffusion depth profiles.

2.1 Isotope Exchange:

Although a well known analytical solution [4,5] exists for the transient one-dimensional diffusion problem in semi-infinite domain describing the tracer gas diffusion depth profiles that result in

from the isotope exchange procedure, we will revisit the solution procedure and reconstruct the solution using integral transform methods. The solution will then be employed not only for extracting D^* and k^* values from experimentally measured data but also for expressing the initial condition for the diffusion problem arising from the subsequent stage (*i.e.* the back-exchange step) of the isotope exchange procedure.

The time dependent diffusion problem in semi-infinite spatial dimension with a surface exchange type boundary condition and a uniform initial isotopic tracer gas concentration can be described as

$$\begin{aligned}
\frac{\partial C'_1}{\partial t} &= D_1^* \frac{\partial^2 C'_1}{\partial x^2}, & \forall (x, t) \in [0, \infty), (0, \infty), \\
C'_1|_{t=0} &= 0, & \forall x \geq 0, \\
C'_1|_{x=0} &= 1 + \frac{D_1^*}{k_1^*} \frac{\partial C'_1}{\partial x} \Big|_{x=0}, & \forall t > 0, \\
C'_1|_{x \rightarrow \infty} &= 0, & \forall t > 0.
\end{aligned} \tag{1}$$

where C'_1 is the normalised isotopic tracer gas fraction defined by

$$C'_1 = \frac{C_1(x, t) - C_{\text{bg}}}{C_{\text{gas}} - C_{\text{bg}}}, \quad \forall (x, t) \in [0, \infty), (0, \infty) \tag{2}$$

$C_1(x, t)$ is the isotope gas concentration, C_{bg} and C_{gas} are the background isotope and the enriched gas concentrations for the isotope exchange procedure. D_1^* and k_1^* are the self-diffusion coefficient and the effective surface exchange coefficient respectively. By defining the following dimensionless spatial and temporal coordinates

$$x_1 = \frac{k_1^*}{D_1^*} x, \quad \forall x \geq 0, \tag{3}$$

and

$$t_1 = \frac{k_1^{*2}}{D_1^*} t, \quad \forall t \geq 0. \tag{4}$$

the equation set (1) can be rewritten in the new coordinate system as

$$\begin{aligned}
\frac{\partial C'_1}{\partial t_1} &= \frac{\partial^2 C'_1}{\partial x_1^2}, & \forall (x_1, t_1) \in [0, \infty), (0, \infty), \\
C'_1|_{t_1=0} &= 0, & \forall x_1 \geq 0,
\end{aligned} \tag{5}$$

$$C_1'|_{x_1=0} = 1 + \left. \frac{\partial C_1'}{\partial x_1} \right|_{x_1=0}, \quad \forall t_1 > 0,$$

$$C_1'|_{x_1 \rightarrow \infty} = 0, \quad \forall t_1 > 0.$$

Now the solution of the initial value problem defined in (5) can be constructed by using the Laplace transforms. With this, the scaled time dependent diffusion equation (5)₁ will be transformed to an ordinary differential equation with corresponding boundary conditions given by

$$\frac{d^2 \bar{C}_1'}{dx_1^2} - p_1 \bar{C}_1' = 0, \quad \forall x_1 \in [0, \infty), p_1 \in \mathbb{C},$$

$$\bar{C}_1'|_{x_1=0} = \frac{1}{p_1} + \left. \frac{d\bar{C}_1'}{dx_1} \right|_{x_1=0}, \quad (6)$$

$$\bar{C}_1'|_{x_1 \rightarrow \infty} = 0.$$

where \bar{C}_1' is the Laplace transform of the normalised isotopic tracer gas fraction. The coefficients of the general solution to the ordinary differential equation (6)₁ can be determined by applying the surface and far-end boundary conditions (6)₂ and (6)₃ respectively. Hence, the Laplace transform of the isotopic tracer gas fraction, as the solution of the system (6), can be obtained as

$$\bar{C}_1' = \frac{e^{-\sqrt{p_1} x_1}}{p_1(1 + \sqrt{p_1})}, \quad \forall x_1 \in [0, \infty), p_1 \in \mathbb{C}. \quad (7)$$

The inverse Laplace transform of the equation (7) will involve evaluating the following complex valued line integral;

$$\mathcal{L}^{-1}\{\bar{C}_1'\} = C_1' = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \bar{C}_1' e^{p_1 t_1} dp_1 \quad (8)$$

The Cauchy integral theorem can be applied to evaluate the above integral by constructing a contour path that closes in the left hand of the complex plane. Since the integrand is multivalued along the negative real axis and has a pole at the origin, a branch cut, as shown in figure 1, is required to exclude those singularities.

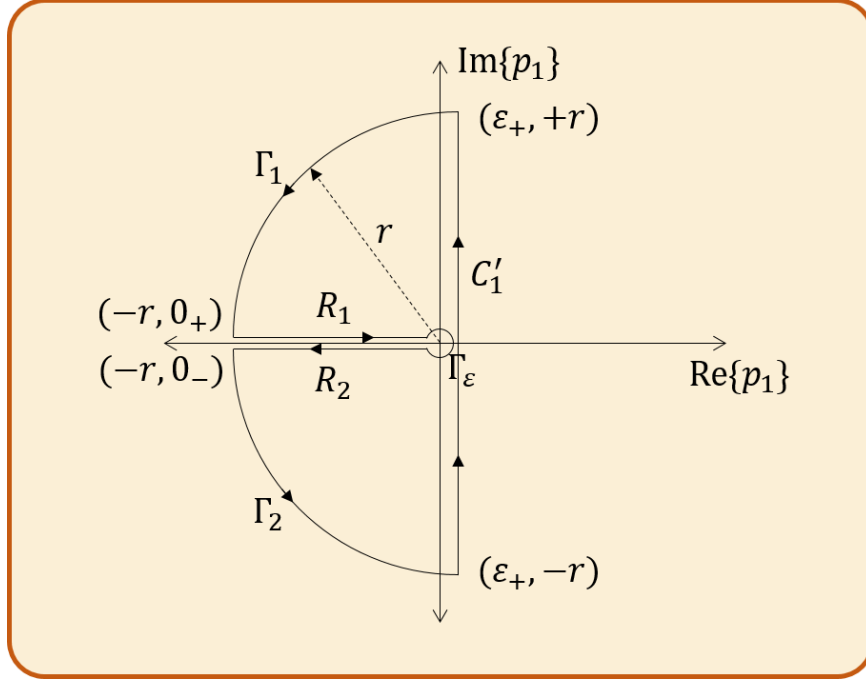


Fig. 1. The branch cut and contour paths, parametrised by $p_1 = r e^{i\theta}$, to close in the left half of the complex plane $(\text{Re}\{p_1\}, \text{Im}\{p_1\}) = (r \cos(\theta), r \sin(\theta))$, $0 < r < \infty$, $-\pi < \theta \leq \pi$. The radius of the pole is ε .

As the singularities are now excluded by the branch cut and the integrand is analytic everywhere inside the enclosed domain, the sum of the integrals over the labelled paths of the closed contour will become zero. Therefore, the integral defining the isotopic tracer gas concentration can be evaluated by using the following sum of the path integrals.

$$C'_1 = -(\Gamma_1 + R_1 + \Gamma_\varepsilon + R_2 + \Gamma_2) \quad (9)$$

Issuing the appropriate parametrisation over the individual paths and taking limits as $r \rightarrow \infty$ and $\varepsilon \rightarrow 0$, the inverse Laplace transform of the isotopic tracer gas fraction can be evaluated as

$$C'_1 = 1 - \frac{1}{\pi} \int_0^\infty \frac{e^{-rt_1}}{(1+r)} \left\{ \frac{\sin(\sqrt{r}x_1)}{r} + \frac{\cos(\sqrt{r}x_1)}{\sqrt{r}} \right\} dr \quad (10)$$

Substituting $r = u^2$ into the equation (10), the solution can be written in the following form

$$C'_1 = 1 - \frac{2}{\pi} \int_0^\infty \frac{e^{-u^2 t_1}}{(1+u^2)} \left\{ \frac{\sin(ux_1)}{u} + \cos(ux_1) \right\} du. \quad (11)$$

Note that the equation (11) is identical to Crank's solution [5] in our new coordinate system defined by x_1 and t_1 . The solution can be plugged in to the equation system (5) to verify that the differential equation together with its initial and boundary conditions are satisfied.

2.2 Isotope Back-exchange:

The initial value problem to describe the diffusion process of the isotopic tracer gas during the back-exchange procedure can be described as

$$\begin{aligned}
 \frac{\partial C'_2}{\partial t} &= D_2^* \frac{\partial^2 C'_2}{\partial x^2}, & \forall (x, t) \in [0, \infty), (\phi, \infty), \\
 C'_2|_{t=\phi} &= C'_1(x, \phi), & \forall x \geq 0, \\
 C'_2|_{x=0} &= \frac{D_2^*}{k_2^*} \frac{\partial C'_2}{\partial x} \Big|_{x=0}, & \forall t > \phi, \\
 C'_2|_{x \rightarrow \infty} &= 0, & \forall t > \phi.
 \end{aligned} \tag{12}$$

where D_2^* and k_2^* are the self-diffusion coefficient and the effective surface exchange coefficient respectively. ϕ is the duration of the isotope exchange procedure. $C'_1(x, \phi)$ is the initial isotope fraction distribution given by the solution of the isotope exchange problem at time $t = \phi$. As in the previous case, C'_2 is defined as the normalised isotopic tracer gas fraction by using

$$C'_2 = \frac{C_2(x, t) - C_{\text{bg}}}{C_{\text{gas}} - C_{\text{bg}}}, \quad \forall (x, t) \in [0, \infty), (0, \infty) \tag{13}$$

By defining a new dimensionless temporal coordinate as

$$t_2 = \frac{D_2^* k_1^{*2}}{D_1^{*2}} (t - \phi), \quad \forall t \geq 0. \tag{14}$$

and recalling the dimensionless spatial coordinate defined earlier, we can then rewrite the equation system (12) as

$$\begin{aligned}
 \frac{\partial C'_2}{\partial t_2} &= \frac{\partial^2 C'_2}{\partial x_1^2}, & \forall (x_1, t_2) \in [0, \infty), (\phi_1, \infty), \\
 C'_2|_{t_2=\phi_1} &= C'_1(x_1, \phi_1), & \forall x_1 \geq 0, \\
 C'_2|_{x_1=0} &= k^* \frac{\partial C'_2}{\partial x_1} \Big|_{x_1=0}, & \forall t_1 > \phi_1, \\
 C'_2|_{x_1 \rightarrow \infty} &= 0, & \forall t_1 > \phi_1.
 \end{aligned} \tag{15}$$

where ϕ_1 is the duration of the previous isotope exchange procedure in the dimensionless temporal coordinates given by the equation (4) and k^* is the dimensionless surface exchange coefficient defined by

$$k^* = \frac{D_2^* k_1}{k_2^* D_1^*} \quad (16)$$

Once again, we will construct the solution of the initial value problem given in system (15) by using Laplace transforms to obtain the following ordinary differential equation and its boundary conditions.

$$\begin{aligned} \frac{d^2 \bar{C}'_2}{dx_1^2} - p_2 \bar{C}'_2 + C'_1(x_1) &= 0, & \forall x_1 \in [0, \infty), p_2 \in \mathbb{C}, \\ \bar{C}'_2|_{x_1=0} &= k^* \left. \frac{d\bar{C}'_2}{dx_1} \right|_{x_1=0}, & (17) \\ \bar{C}'_2|_{x_1 \rightarrow \infty} &= 0. \end{aligned}$$

After determining the coefficients of the general solution of the differential equation (17)₁ by using the surface and far-end boundary conditions, the Laplace transform of the isotopic tracer gas fraction for the back-exchange problem can be written as

$$\begin{aligned} \bar{C}'_2 &= -\frac{e^{-\sqrt{p_2}x_1}}{p_2(1+k^*\sqrt{p_2})} + \frac{2}{\pi} \frac{(1-k^*)}{(1+k^*\sqrt{p_2})} \int_0^\infty \frac{e^{-u^2\phi_1} e^{-\sqrt{p_2}x_1}}{(1+u^2)(u^2+p_2)} du \\ &+ \frac{1}{p_2} - \frac{2}{\pi} \int_0^\infty \frac{e^{-u^2\phi_1}}{(1+u^2)(u^2+p_2)} \left\{ \frac{\sin(ux_1)}{u} + \cos(ux_1) \right\} du. \end{aligned} \quad (18)$$

The inverse Laplace transform of the equation (18) can then be obtained by evaluating the following complex valued integral

$$\mathcal{L}^{-1}\{\bar{C}'_2\} = C'_2 = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \bar{C}'_2 e^{p_2 t_2} dp_2 \quad (19)$$

Similar to the previous case, in order to evaluate the above integral, we will construct a closed contour as depicted in figure 2.

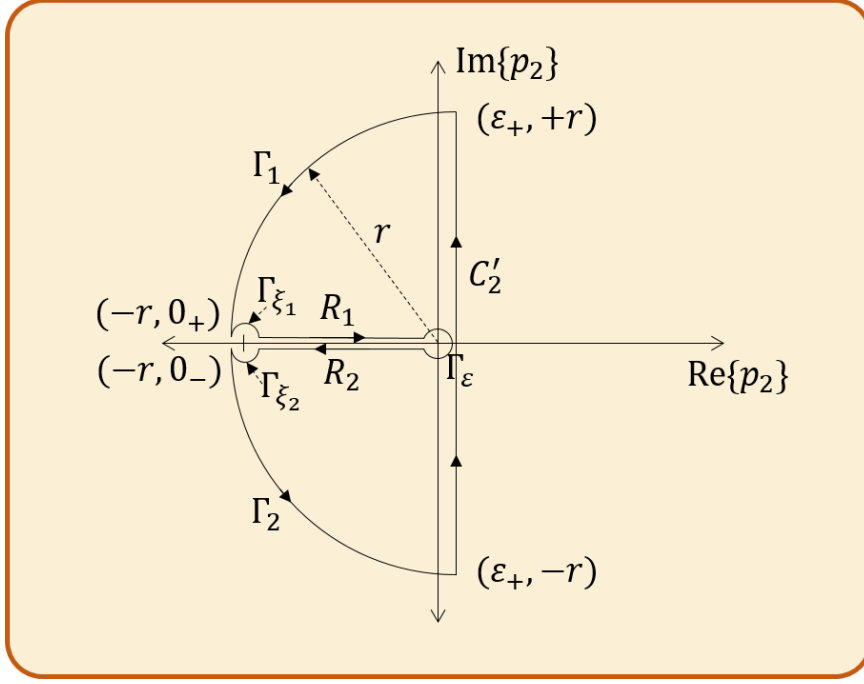


Fig. 2. The branch cut and contour paths, parametrised by $p_2 = r e^{i\theta}$, to close in the left half of the complex plane $(\text{Re}\{p_2\}, \text{Im}\{p_2\}) = (r \cos(\theta), r \sin(\theta))$, $0 < r < \infty$, $-\pi < \theta \leq \pi$. The radii of both poles are ε .

This time, in addition to the pole at $p_2 = 0$, we have an additional pole at values of $p_2 = -u^2 = -r$. Since the integrand is multivalued over the negative real axis, we should exclude that portion of the domain by introducing a branch cut similar to the previous case. Therefore, the complex valued line integral given by the equation (19) can be evaluated by using the Cauchy integral theorem over the closed contour shown in figure 2. Hence, we have the following expression to evaluate the inverse Laplace transform of the normalised isotopic tracer gas fraction during the back-exchange procedure.

$$C'_2 = -(\Gamma_1 + \Gamma_{\xi_1} + R_1 + \Gamma_\varepsilon + R_2 + \Gamma_{\xi_2} + \Gamma_2) \quad (20)$$

Utilising the appropriate parametrisation over the individual paths and taking the limits when $r \rightarrow \infty$, and $\varepsilon \rightarrow 0$, the solution to the equation set (15) can be found as

$$C'_2 = -\frac{2}{\pi} \int_0^\infty \frac{e^{-u^2(\phi_1+t_2)}}{(1+u^2)} \left\{ \frac{\sin(ux_1)}{u} + \cos(ux_1) \right\} du \\ + \frac{2}{\pi} \int_0^\infty \frac{e^{-u^2 t_2}}{(1+k^*u^2)} \left\{ \frac{\sin(ux_1)}{u} + k^* \cos(ux_1) \right\} du$$

$$\begin{aligned}
& + \frac{2}{\pi} (1 - k^*) \int_0^\infty \frac{e^{-u^2 (\phi_1 + t_2)} \{\cos(ux_1) - k^* u \sin(ux_1)\}}{(1 + u^2)(1 + k^{*2}u^2)} du \\
& - \frac{2}{\pi} (1 - k^*) e^{\phi_1} \operatorname{erfc}(\sqrt{\phi_1}) \int_0^\infty \frac{e^{-u^2 t_2} u \{\sin(ux_1) + k^* u \cos(ux_1)\}}{(1 + u^2)(1 + k^{*2}u^2)} du \\
& - \frac{4}{\pi^2} (1 - k^*) \int_0^\infty \frac{e^{-u^2 t_2} \{\sin(ux_1) + k^* u \cos(ux_1)\}}{(1 + u^2)(1 + k^{*2}u^2)} \{\sqrt{\pi} D_-(u \sqrt{\phi_1})\} du. \quad (21)
\end{aligned}$$

where $D_-(x)$ is the Dawson function given by

$$D_-(x) = e^{-x^2} \int_0^x e^{t^2} dt \quad (22)$$

Note that when $t_2 = 0$, the equation (21) collapses to the solution provided in the previous section as the initial condition for the back-exchange problem. On the other hand, our solution satisfies the surface and far-end boundary conditions. Hence, we have a unique solution to the back-exchange problem formulated in system (15).

For a given concentration distribution data obtained from the isotope back-exchange procedure, our solution can be used to extract all four values of $D_1^*, k_1^*, D_2^*, k_2^*$ as fitting parameters regardless of any constraints (*i.e.* there is no requirement for any of the coefficients to be the same for consecutive exchange procedures). In the following section, we will demonstrate how the self diffusion and surface exchange coefficients can be extracted from the depth profiles obtained in multi-step isotope exchange procedures.

3. RESULTS & DISCUSSION

Experimentally measured isotope depth profile data can be modelled by using the solutions provided in this contribution. The D^* and k^* values may be used as model fitting parameters to minimise the residuals between the measured and calculated profiles in, for instance, the non-linear least-squares formalism. For example, a depth profile obtained from the isotope exchange procedure can be modelled by using D_1^* and k_1^* as a pair of fitting parameters of the equation (11). Similarly, the equation (21) can be fitted to a measured isotope back-exchange depth profile data (after normalisation) by using D_1^*, k_1^*, D_2^* , and k_2^* as four independent fitting parameters.

In addition to the standard mathematical verification, solutions found in this work were utilised to reproduce the experimentally measured isotope depth profiles for $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ reported by Cooper *et.al.* [3]. Although, the intended use of the solutions is to extract transport properties rather than regenerate data in an opposite fashion, the authors thought that the data regeneration

would be a good way to cross validate the solutions. Therefore, D^* and k^* values as best fit variables together with the accompanying experimental parameters listed in Table 1 were taken from the publication by Cooper *et.al.* [3] and employed in our solutions to reproduce the normalised isotope fraction depth profiles.

Sample	D_1^*, D_2^* [cm^2/s]	k_1^* [cm/s]	k_2^* [cm/s]	ϕ [h]
A	1.6e-08	1.1e-06	-	1.4
B	1.7e-08	1.4e-06	1.6e-06	0.66
C	1.7e-08	1.3e-06	3.3e-06	0.66

Table 1. Parameters used in the solutions (11) and (21) to reproduce the isotope depth profile data measured by Cooper *et.al.* [3]. In addition, C_{bg} , and C_g are taken as 0.2% and 99.999% respectively.

Figure 3 depicts the reproduced normalised isotope fraction depth profiles for three different exchange experiments reported by Cooper *et.al.* [3]. The profile shown in red colour for the sample A was generated by using the equation (11), and the green as well as the blue coloured profiles for samples B, and C were generated by using the equation (21). For all evaluations, the spatial variable was varied up to the depth value of 450 μm from the surface.

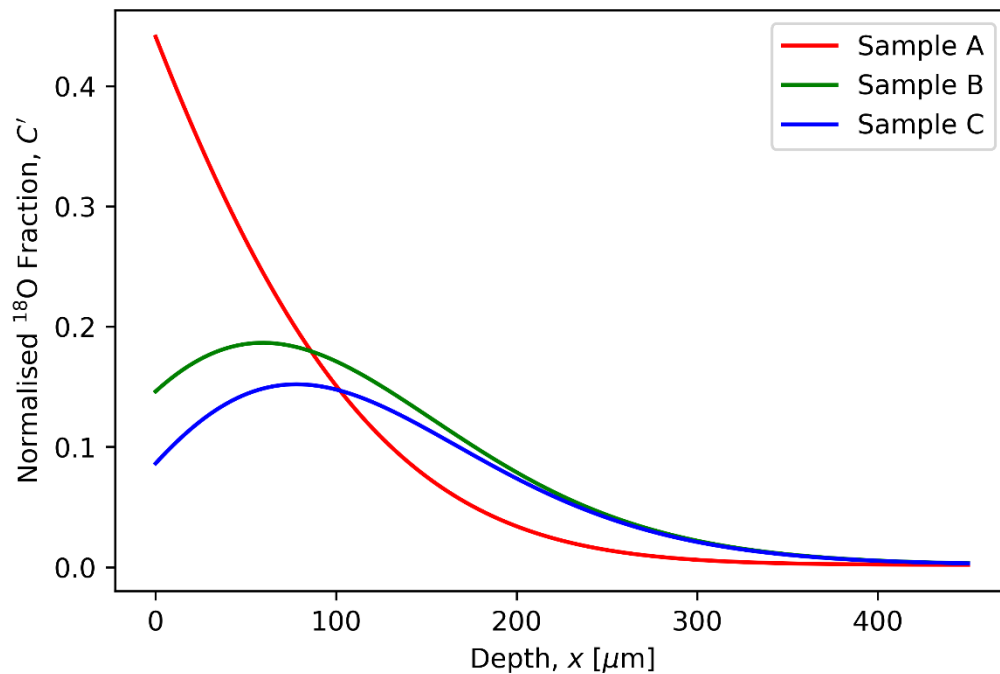
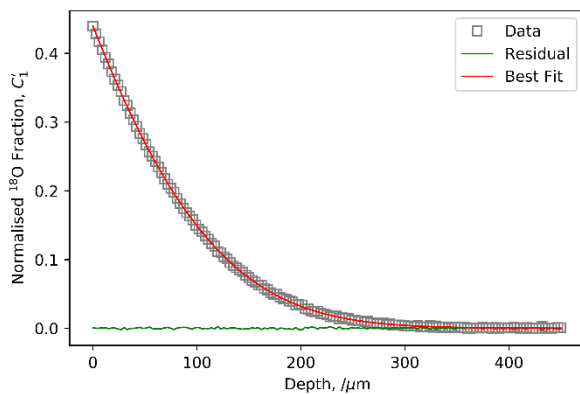


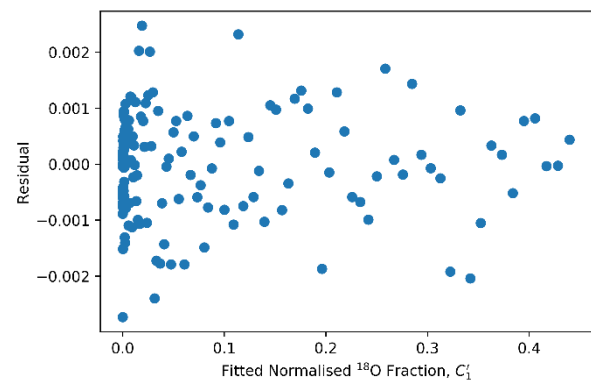
Figure 3. Regenerated isotopic depth profile data reported by Cooper *et.al.* as experimental measurements of samples A, B, and C [3].

Prior to proceeding with the estimation of D^* and k^* values, a small random noise with normal distribution (mean= 0, standard deviation=1%) was added to the regenerated data. With this small perturbation, it was aimed that the extracted transport properties would be slightly different than those used for regenerating data reported by Cooper *et.al.* [3]. As for the estimation procedure, the solutions provided here were utilised for calculating the residuals as objective functions of a non-linear optimisation method, as implemented in the LMFIT [6] module for Python and the Optimisation Toolbox for MATLAB (Release 2017b) [7]. In both implementations, the D^* and k^* values were chosen as variable parameters for minimising the residuals between the regenerated data and the calculated profiles in the least-squares formalism. The fifth-order approximation [8] for the Dawson function as described in the Supporting Information was utilised in the MATLAB implementation to speed up the improper integral evaluations. A graphical user interface for the isotope depth profile curve fitting (DPFit) was developed by using MATLAB's App Designer. The DPFit MATLAB package can be freely obtained from the authors.

Figure 4a shows the randomly perturbed data for the sample A together with the residuals and the best fit curve obtained by varying D_1^* and k_1^* as fitting parameters of the equation (11). As a result of the non-linear least squares minimisation procedure, the oxygen self-diffusion coefficient and the effective surface exchange coefficient were obtained as $1.60\text{e-}08\text{ cm}^2/\text{s}$ and $1.10\text{e-}06\text{ cm/s}$ respectively. The corresponding uncertainty values were estimated as $\pm 0.20\%$ and $\pm 0.09\%$. Figure 4b depicts the residual values plotted against the calculated isotope depth profile. The random pattern of residuals that form a uniform band around the mean value of zero indicates how well the regenerated data has been represented by the best-fit curve.



(a)



(b)

Figure 4. a) Best fit (red line) obtained by using the equation (11) to model the normalised isotope fraction depth profile measurement data (gray squares) for sample A. Residuals (green line) of the non-linear least squares fit. b) Spread plot for the residuals vs. best fit.

Figure 5a shows the perturbed data for the sample B and the best fit curve obtained by varying D_1^* , k_1^* , D_2^* , and k_2^* as fitting parameters of the equation (21). For this case, the two pairs of the self diffusion and effective surface exchange coefficients were listed in Table 2. The uncertainty for all the coefficients were found to be less than $\pm 2.7\%$.

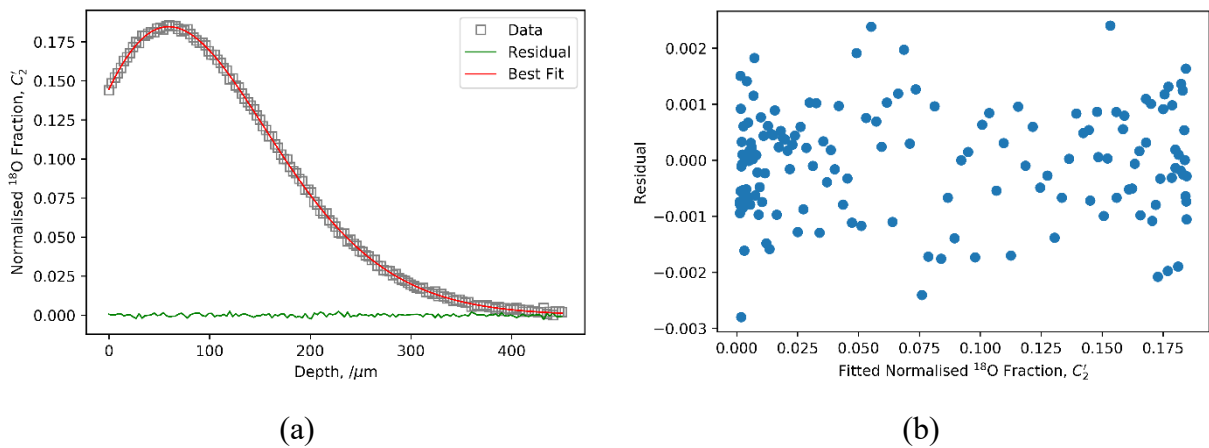


Figure 5. a) Best fit (red line) obtained by using the equation (21) to model the isotope depth profile measurement data (gray squares) for sample B. Residuals (green line) of the non-linear least squares fit. b) Spread plot for the residuals vs. best fit.

As for the sample C, the perturbed data and the best fit curve obtained by varying the two pairs of the fitting parameters are shown in figure 6a. The extracted values for the two pairs of the transport coefficients are listed in table 2 with a maximum uncertainty of $\pm 2.4\%$. The distribution of the residual is shown in figure 6b.

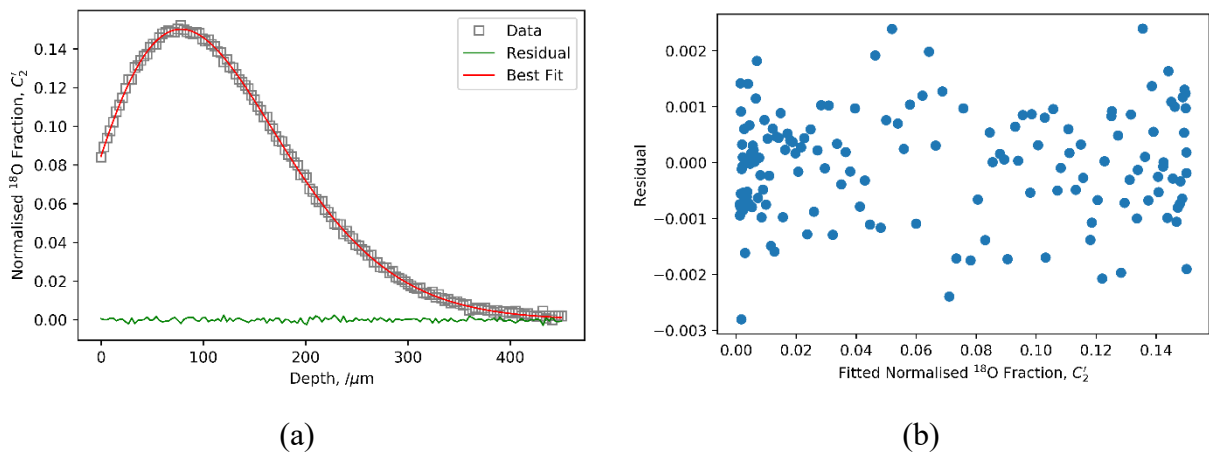


Figure 6. a) Best fit (red line) obtained by using the equation (21) to model the isotope depth profile measurement data (gray squares) for sample C. Residuals (green line) of the non-linear least squares fit. b) Spread plot for the residuals vs. best fit.

Sample	D_1^* [cm ² /s]	k_1^* [cm/s]	D_2^* [cm ² /s]	k_2^* [cm/s]
A	1.60e-08	1.10e-06	-	-
B	1.65e-08	1.42e-06	1.73e-08	1.62e-06
C	1.65 -08	1.32e-06	1.73e-08	3.34e-06

Table 2. Parameters extracted from the isotope depth profile data (with added random noise) reported by Cooper *et.al.* [3].

As listed in table 2, the self diffusion coefficients (D_1^* and D_2^*) extracted from the isotope back-exchange depth profile data, for samples C and D, were calculated as slightly different from each other. Although those values may be considered as identical within the limits of experimental accuracy, the analytical solution provided in this work has no prior assumption to consider them identical. Therefore, our solution can be used to accurately extract those transport properties for cases where they might differ from each other due primarily to the effect of other oxygen containing species' diffusion into to the sample (*i.e.* multi-component diffusion).

4. CONCLUSION

An analytical solution to the one-dimensional transient diffusion equation with a surface exchange type boundary condition and a specified initial diffusion profile was constructed. The solution composed of integral equations was then utilised to extract the self-diffusion (D^*) and the effective surface exchange (k^*) coefficients from a set of isotope back-exchange depth profile data obtained from literature. The non-linear least-squares method was utilised to solve the minimisation problem defined by the residual between data and our solution as an objective function parametrized by the D^* and k^* values. It was shown that all D^* and k^* values (*i.e.* before and after the procedure) can be accurately extracted from a depth profile data obtained from the isotope back-exchange procedure.

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