Available online at www.sciencedirect.com

ScienceDirect

Geochimica et Cosmochimica Acta 126 (2014) 70–77

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

Rayleigh equation for evolution of stable isotope ratios in contaminant decay chains

Patrick Höhener [a,*], Olivier Atteia [b,1]

[a] Aix-Marseille Université, Laboratoire Chimie Environnement, FRE 3416 – CNRS, Marseille, France
[b] ENSEGID, 1 allée Daguin, 33607 Pessac, France

Received 4 March 2013; accepted in revised form 22 October 2013; available online 7 November 2013

Abstract

In isotope geochemistry, the Rayleigh equation describes the evolution of isotope ratios in a parent compound as a function of reaction progress, and associated equations describe isotope ratios in an instantaneous product and an accumulated product. The Rayleigh equation is commonly used for fitting fractionation factors of processes undergoing kinetic isotope fractionation such as biochemical reactions. This work extends the equations associated with the Rayleigh equation for describing the isotope ratios in intermediate products in a chain of reacting species degrading with first-order kinetics. A general solution is presented for decay chains of any length, and explicit examples are presented for the biodegradation of a substrate or a mixture of substrates through 3 intermediate products to a final product. Applications of these analytical solutions for the fitting of enrichment factors for intermediate compounds in laboratory experiments are demonstrated with a spreadsheet. This avoids separate experiments to measure each intermediate product. The utility of the equations for the assessment of slopes in dual isotope plots is furthermore illustrated, and limitations of its use are critically discussed.

1. INTRODUCTION

In 1981, Mariotti and co-workers measured stable nitrogen isotope ratios in substrates and products during the biochemical conversion of nitrate to nitrous oxide by denitrifying bacteria and of ammonia to nitrite by nitrifying bacteria. The authors presented a detailed derivation of equations and approximations that can be used for the mathematical description of isotope ratios in a degrading substrate and a product formed from the substrate. Mariotti and co-workers (1981) referred to Lord Rayleigh, who derived similar equations for the case of fractional distillation of mixed liquid, and to Jacob Bigeleisen who studied the effect of isotopic substitution on the rate of chemical reactions (Bigeleisen, 1952). Nevertheless, Mariotti et al. (1981) is most often cited today in geochemistry when credit is given to the Rayleigh equation applied for kinetic isotope fractionation through transformation processes. The approximation for the evolution of the reacting substrate is used in every laboratory study that quantifies a fractionation or enrichment factor from a series of measured stable isotope data of common stable isotopes such as ^{13}C, ^{2}H, ^{15}N, ^{18}O or ^{34}S. Recommendations for the best statistical procedures for fitting of the Rayleigh equation have been made (Scott et al., 2004). The Rayleigh equation has also been extended to competing degradation pathways (Van Breukelen, 2007). It has furthermore been pointed out that for isotopes which are not rare in nature such as deuterium when studying deuterated compounds, the approximations are not valid, and the exact and somewhat extended Rayleigh equation must be used (Hunkeler et al., 2002b).

Although Mariotti and co-workers (1981) studied a contaminant decay chain, namely the transformation of nitrogen from NO_3^- to NO_2^- and to N_2O and finally to N_2, their derivation did not treat the isotope evolution of intermediate products. Other authors did calculate the

---

[*] Corresponding author. Tel.: +33 4 13 55 10 34; fax: +33 4 13 55 10 60.

E-mail addresses: patrick.hohener@univ-amu.fr (P. Höhener), Olivier.ATTEIA@ipb.fr (O. Atteia).

[1] Tel.: +33 (0) 557 12 10 12; fax: +33 (0) 557 12 10 10.

0016-7037/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.gca.2013.10.036

isotope evolution of intermediate products, but did not present analytical equations for that. Hunkeler and co-workers (2002a) presented the evolutions of ^{12}C in the decay chains of *cis*- and *trans*-dichloroethene through vinyl chloride to ethene studied in laboratory microcosms and described in words how these equations could be written for ^{13}C degradation and how δ^{13}C could subsequently be determined.

However, they did not report how exactly the fitting of isotope ratios was performed. Enrichment factors for the degradation of the intermediate product were also obtained by separate experiments with the intermediate product as substrate (Hunkeler et al., 2002a). Parameter estimation in contaminant decay chains with or without including isotope data were attempted with numerical models: Morrill et al. (2006) presented a numerical parameter estimation model for enrichment factors in the decay chain of chloroethenes in laboratory microcosms, which was based on the Levenberg–Marquardt minimization technique. The model is appropriate for any set of isotopically fractionating, sequential, linear (non-branching) reactions during which mass balance is maintained. Beranger et al. (2005) applied such numerical estimation methods to data of chloroethenes in laboratory columns with advective–dispersive transport, but this needed even more sophisticated genetic algorithms and sometimes more than 7000 iterations.

The elucidation of degradation processes in lab and field studies is nowadays often based on the measurement of two stable isotope ratios in the degrading contaminant (Zwank et al., 2005; Rosell et al., 2007; Van Breukelen, 2007; Hofstetter et al., 2008; Elsner, 2010; Hunkeler et al., 2011; Rosell et al., 2012). This two-dimensional isotope application is also called dual isotope assessment. To predict slopes in dual isotope plots, a forward calculation of the changes of the isotope ratios in the two elements under consideration is needed. This has been done with the Rayleigh equation for the substrate, but for intermediates, only numerical model approaches were used (Hunkeler et al., 2009).

An analytical solution for concentrations in contaminant decay chains with infinite members has been derived by Sun et al. (1999a). This analytical solution has also been applied to the decay chain of chloroethenes, and was then implemented in a reactive transport model and is promoted by the US EPA as the BIOCHLOR model (EPA, 2000). In a further study, Sun et al. (1999b) presented how also decay chains with reactions to several parallel daughter products can be treated in analytical solutions. But, although analytical models are available for contaminant decay chains, there has been so far to our knowledge no solution for the evolution of isotope ratios in these contaminant decay chains. We are not aware of any Rayleigh-type equation for decay chains.

The main objective of this work was therefore to derive analytical equations for the isotope evolution of intermediate products and a final product in a sequential linear decay chain of reacting species. These equations were validated and their validity with respect to the governing assumptions is discussed. The second objective was to create a simple tool with analytical Rayleigh equations for fitting isotope data of a decay chain in a spreadsheet. A further aim was to show the application of these equations for constructing dual isotope plots.

2. THEORETICAL DEVELOPMENT

For the description of a contaminant decay chain, we will number the species in this study in the following way:

$$\underset{C_1}{\textbf{Substrate}} \xrightarrow{k_1} \underset{C_2}{\textbf{Intermediate Product 1}}$$

$$\xrightarrow{k_2} \underset{C_3}{\textbf{Intermediate Product 2}} \ldots \xrightarrow{k_n} . \underset{C_{n,\mathrm{fin}}}{\textbf{Final Product}}$$

The conversion of each species is complete (1:1 stoichiometry) and follows first-order kinetics. The final product does not undergo any further transformation.

2.1. Historical background

Let us recall first the classical Rayleigh equation and its associated equations, using our numbering for substrate and final product. The evolution of the isotope ratio in the substrate, R_1 is a function of the fraction remaining f_1 and the fractionation factor α_1 for the transformation of substrate to product, and is given by the classical Rayleigh Eq. (1).

$$R_1 \approx R_{1,0} f_1^{(\alpha_1 - 1)} \tag{1}$$

R_1 is the ratio of the concentration of heavy isotopes $^{\mathrm{H}}C_i$ divided by the concentration of light isotopes $^{\mathrm{L}}C_i$ in the substrate. $R_{1,0}$ is the initial isotope ratio in the substrate obtained from the measured initial isotopic ratio of the compound which is usually given in the delta notation (here δ^{13}C) and relates to $R_{1,0}$ via Eq. (2)

$$R_{i,0} = R_{\mathrm{standard}} \left(\frac{\delta^{13} C_{i,0}}{1000} + 1 \right) \tag{2}$$

with R_{standard} is $^{\mathrm{H}}C/^{\mathrm{L}}C$ in the international standard (0.011237 for ^{13}C (Coplen et al., 2006)).

In the delta notation, and using the enrichment factor $\varepsilon = 1000 * (\alpha - 1)$, a further approximation can be made as explained in Mariotti et al. (1981), and Eq. (1) can be written more simply as Eq. (3).

$$\delta^{13}\mathrm{C}_1 \approx \delta^{13}\mathrm{C}_{1,0} + \varepsilon_1 \ln(f_1) \tag{3}$$

Eqs. (1) and (3) are only approximations, but they are sufficiently accurate for isotope pairs with one isotope being much rarer than the other (this is the case for ^{13}C, ^{2}H, ^{15}N, ^{18}O or ^{34}S). A priori, the simplified relations hold for $|\varepsilon|$ values $< 20‰$ and for δ^{13}C values not too different from zero (Mariotti et al., 1981).

The accumulation of the final product in a simple 2-member substrate-product chain is noted as (Eq. (4), Mariotti et al., 1981).

$$\delta^{13} C_{2,\mathrm{fin}} \approx \delta^{13} C_{1,0} - \varepsilon_1 \frac{f_1 \ln f_1}{1 - f_1} \tag{4}$$

2.2. Degradation chains

For degradation chains with intermediate products which undergo first-order kinetic degradation with 1:1 stoichiometric yields in batch, we derive hereafter a new general Rayleigh equation, starting from the analytical solution for