Rayleigh fractionation of stable isotopes from a multicomponent source

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Abstract—A formulation of the Rayleigh equation for the stable isotopic evolution of a multicomponent source reservoir is presented. Its applicability to the carbon and oxygen isotopic evolution of a fluid-rich carbonate magma and the crystallizing calcite carbonatite is demonstrated using data from the Amba Dongar carbonatite complex, Deccan province, India. The initial \( \delta^{13}C \) of the parent magma for this complex has been estimated to be \(-5.3 \pm 0.2\%\) relative to V-PDB.

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1. INTRODUCTION

The Rayleigh equation, which depicts the stable isotopic evolution of a homogeneous reservoir from which a phase is continuously extracted, is well known (Rayleigh, 1896; Broecker and Oversby, 1971):

\[
\delta - \delta_o \approx 10^3((a - 1) \ln f) \tag{1}
\]

where \( \delta \) and \( \delta_o \), respectively, are the stable isotopic compositions of an element in the reservoir to start with and when a fraction \( f \) of the original amount of the element is left, \( a \) the isotopic fractionation factor between the phase separating out and the reservoir. There are instances where a reservoir has many discrete components, with different isotopic ratios, each contributing isotopes of an element to a compound/phase forming and separating out. For example, in the formation of hydrothermal graphite, \( \text{CO}_2 + \text{CH}_4 \rightarrow 2\text{C} + 2\text{H}_2\text{O} \) (Deines, 1980), \( \text{CO}_2 \) and \( \text{CH}_4 \) each contribute one atom of carbon to the graphite. Similarly, the oxygen isotopic composition of the rain water condensing from a cloud mass will be controlled by that of the relative amounts of liquid and vapor phases present in the cloud (Craig and Gordon, 1965). Other important natural examples are the calcite precipitation at the expense of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) from fluid/magma, metamorphic decarbonation, and serpentinitization processes. An approximate treatment for a two-component source has already been reported by Pineau et al. (1973). Here we treat the general problem of Rayleigh isotopic fractionation from a multicomponent source and derive a precise equation for the stable isotopic evolution of the parent reservoir. We illustrate this model by the example of calcite precipitation from a magma, using the stable carbon and oxygen isotope data from Amba Dongar carbonatite complex, Deccan flood basalt province, India.

2. RAYLEIGH ISOTOPIC FRACTIONATION FROM A MULTICOMPONENT SOURCE (RIFMS)

We assume that: (1) the different components of the source are always in stable isotopic equilibrium with each other (i.e., the stable isotopic composition of the source reservoir at any time can be expressed as a product of isotopic composition of the most abundant component of the source and a linear combination of the fractionation factors between the other components and the former component, see Appendix); (2) the compound that forms is in instantaneous isotopic equilibrium with the source before being removed; (3) the process is isothermal; and (4) the abundance of the heavier isotope is much smaller than that of the lighter isotope of the element under consideration (e.g., \( [^{13}\text{C}] \ll [^{12}\text{C}] \)). Assumption (3) may not be required for high temperature processes, where the temperature dependence of the isotopic fractionation factor is small.

The equation that describes the stable isotopic evolution of the multicomponent reservoir, in \( \delta \) notation, is:

\[
(\delta - \delta_o) \approx 10^3(\frac{\alpha_{c-1}}{a} \ln (\frac{af - b}{a - b})) - \ln f \tag{2}
\]

where \( \delta \) and \( \delta_o \) denote the isotopic composition of the source at any time \( t > 0 \), and at \( t = 0 \), respectively and \( f \) is the fraction of remaining atoms of the element under consideration left in the source. \( \alpha_{c-1} \) is the temperature-dependent equilibrium fractionation factor of the element, between the product \( c \) and the first (major) source component \( 1 \). The constants \( a \) and \( b \) are weighted mean values of the equilibrium fractionation factors between the different source components and the major component. In the case of \( a \), the weights are the numbers of atoms of the element under consideration contributed by various source components. In the case of \( b \), besides this, the weight factor includes the critical values of \( f \) (i.e., the values of \( f \) corresponding to the steps at which different source components exhaust). The detailed derivation of the above equation and the definitions of \( a \) and \( b \) are given in the Appendix. The stable isotope ratios of the product \( c \) and the multicomponent source \( s \) can be related by a fractionation factor \( A \):

\[
A = R_c/R_s = \frac{R_c / R_1}{(a - b) / (a - b)} = \frac{\alpha_{c-1}}{(a - b) / (a - b)} \tag{3}
\]

where \( R_c \), \( R_s \), and \( R_1 \) denote the stable isotope ratios of the product, the multicomponent source and the first source component, respectively. Therefore, the stable isotopic composition of the product as a function of \( f \) will be:

\[
(\delta - \delta_o)_{\text{product}} = (\frac{\alpha_{c-1}}{a - b}) (\delta_{\text{source}} - (\frac{\alpha_{c-1}}{a - b}) (\delta_{\text{source}}) + 10^3 ((\frac{\alpha_{c-1}}{a - b}) - (\frac{\alpha_{c-1}}{a - b})) \tag{4}
\]

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