Earth and Planetary Science Letters 468 (2017) 38–50

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

www.elsevier.com/locate/epsl

Triple oxygen isotope composition of leaf waters in Mpala, central Kenya

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ARTICLE INFO

Article history:
Received 18 August 2016
Received in revised form 6 February 2017
Accepted 8 February 2017
Available online xxxx
Editor: H. Stoll

Keywords:
triple oxygen isotopes
d-excess
plant waters
transpiration

ABSTRACT

Variations in triple oxygen isotopes have been used in studies of atmospheric photochemistry, global productivity and increasingly in studies of hydroclimate. Understanding the distribution of triple oxygen isotopes in plant waters is critical to studying the fluxes of oxygen isotopes between the atmosphere and hydrosphere, in which plants play an important role. In this paper we report triple oxygen isotope data for stem and leaf waters from Mpala, Kenya and explore how $\Delta^{17}O$, the deviation from an expected relationship between $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios, in plant waters vary with respect to relative humidity and deuterium excess (*d-excess*). We observe significant variation in $\Delta^{17}O$ among waters in leaves and stems from a single plant (up to 0.16‰ range in $\Delta^{17}O$ in leaf water in a plant over the course of a signal day), which correlates to changes in relative humidity. A steady state model for evaporation in leaf water reproduces the majority of variation in $\Delta^{17}O$ and *d-excess* we observed in leaf waters, except for samples that were collected in the morning, when relative humidity is high and the degree of fractionation in the system is minimal. The data and the steady state model indicate that the slope, λ_{transp}, that links $\delta^{17}O$ and $\delta^{18}O$ values of stem and leaf waters and characterizes the fractionation during transpiration, is strongly influenced by the isotopic composition of ambient vapor when relative humidity is high. We observe a strong, positive relationship between *d-excess* and $\Delta^{17}O$, with a slope 2.2 ± 0.2 per meg $‰^{-1}$, which is consistent with the observed relationship in tropical rainfall and in water in an evaporating open pan. The strong linear relationship between *d-excess* and $\Delta^{17}O$ should be typical for any process involving evaporation or any other fractionation that is governed by kinetic effects.

1. Introduction

Small deviations from the expected relationship between $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios are increasingly being used in studies of atmospheric chemistry, global productivity, seawater evolution, paleoclimate, and hydrology. These deviations are sensitive both to processes that involve mass-independent isotopic fractionation, such as photochemical reactions in the stratosphere (*e.g.*, Luz et al., 1999), and mass-dependent fractionation that includes kinetic fractionation of water as it moves through the hydrologic cycle (*e.g.*, Li et al., 2015) and transpiration (Landais et al., 2006). As such, triple oxygen isotopes have been used to reconstruct global productivity (*e.g.*, Luz et al., 1999), respiration rates (Angert et al., 2003), past atmospheric CO_2 levels (Bao et al., 2009; Pack et al., 2013) water–rock interactions (Pack and Herwartz, 2014) and glacial–interglacial hydrologic conditions at the ocean surface (*e.g.*, Landais et al., 2008). Many of these studies depend on knowing the effects of photosynthesis and transpiration on the triple oxygen isotopes in atmospheric O_2 and water vapor, but the field is limited as there has only been one empirical study on triple oxygen isotopes in leaf waters (Landais et al., 2006).

The triple oxygen isotope composition of a material is typically expressed as the deviation from an expected trend line:

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http://dx.doi.org/10.1016/j.epsl.2017.02.015
0012-821X/

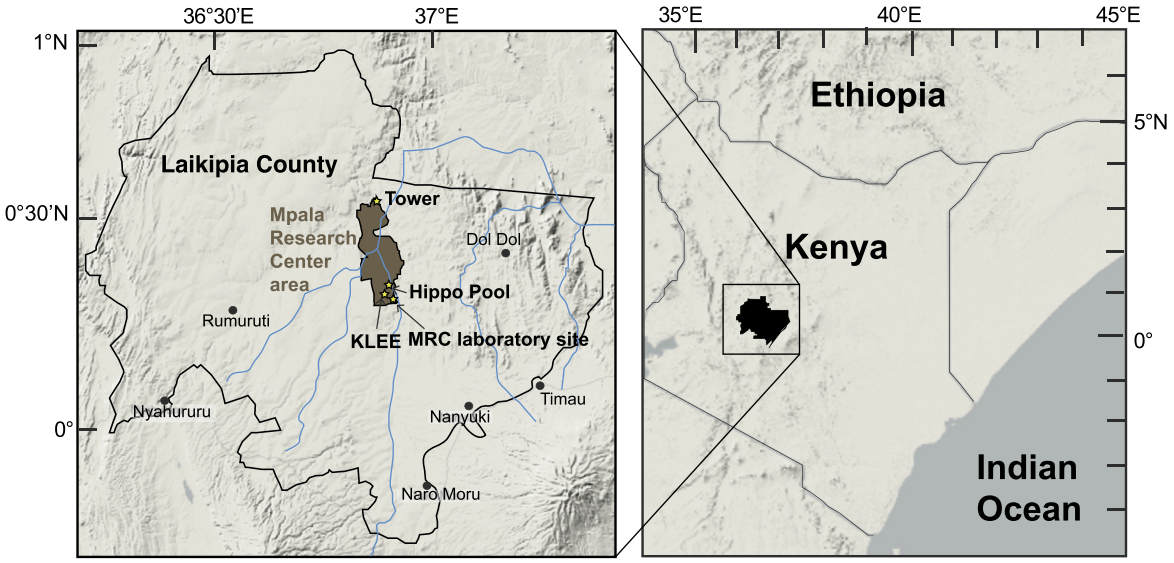

Fig. 1. The study area in central Kenya with the location of the Mpala Research Center marked in brown and the four sampling sites discussed in the text marked with stars. The political boundary of Laikipia county is marked in black and nearby towns are indicated with black circles (based on Fig. 1 in Riginose et al., 2012). The major rivers are outlined with blue lines, based on Fig. 1 in Franz et al. (2010). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

$$\Delta^{17}O = \delta'^{17}O - \lambda_{ref}\delta'^{18}O \quad (1)$$

where λ_{ref} represents the slope of the reference line, and

$$\delta'^{x}O = \ln(\delta^{x}O + 1) \quad (2)$$

where $x = 17$ or 18 and $\delta^{x}O = ({}^{x}O/{}^{16}O)_{sample}/({}^{x}O/{}^{16}O)_{standard} - 1$ (Hulston and Thode, 1965; Miller, 2002). The definition of "$\Delta^{17}O$" is equivalent to that of "^{17}O-excess" which is used in some hydrologic studies (*e.g.*, Luz and Barkan, 2010). Here we define λ_{ref} as 0.528, because meteoric waters plot in $\delta'^{18}O$–$\delta'^{17}O$ space along a slope of 0.528 ± 0.0001 (Luz and Barkan, 2010).

The λ term that we use for this slope is similar to the fractionation exponent, θ, as they both describe the relationship between $^{17}O/^{16}O$ and $^{18}O/^{16}O$ ratios. However, they are distinct in that λ is an empirically derived relationship among a suite of samples, whereas θ is a constant that defines the relationship between $\delta^{18}O$ and $\delta^{17}O$ during a single fractionation process (Barkan and Luz, 2005, 2007). Values for θ can be derived from the mass law theory where $^{17}\alpha_{A-B} = {}^{18}\alpha^{\theta}_{A-B}$ and the fractionation factors for the two materials A and B are defined as $\alpha_{A-B} = (\delta_A + 1)/(\delta_B + 1)$ (Criss, 1999; Young et al., 2002).

The fractionation exponent, θ, is generally larger for equilibrium processes than for kinetic processes involving the same materials (Matsuhisa et al., 1978; Young et al., 2002). For example, the exponent (θ_{eq}) is 0.529 ± 0.001 for equilibrium between liquid water and water vapor (Barkan and Luz, 2005), whereas the exponent associated with kinetic fractionation (θ_k) of water vapor in air is 0.5185 ± 0.0003 (Barkan and Luz, 2007). The similarity in slope λ observed for meteoric waters (0.528 ± 0.0001), to θ_{eq} for water (0.529 ± 0.001), justifies its use as a reference slope (λ_{ref}) for the definition of $\Delta^{17}O$ in hydrologic or paleoclimate studies. Given this, the use of 0.528 as λ_{ref} means that $\Delta^{17}O$ values (the deviation in $\delta'^{17}O$ values from the reference line, see eq. (1)) can be used as an indication of the degree of kinetic fractionation during evaporation and transpiration (Barkan and Luz, 2007; Landais et al., 2006).

In order to use the triple oxygen isotope composition of geologic materials to deduce meaningful information about hydroclimate, atmospheric pCO_2, or global productivity (*e.g.*, Luz et al., 1999; Landais et al., 2008; Passey et al., 2014), we must first understand the distribution of $\Delta^{17}O$ in plant waters today. In the single published dataset on triple oxygen isotopes in leaf waters, Landais et al. (2006) described a relationship between $\delta^{17}O$ and $\delta^{18}O$ associated with transpiration and proposed that λ_{transp}, the slope of line linking stem and leaf water in $\delta'^{17}O$–$\delta'^{18}O$ space, has a negative correlation with relative humidity (Rh) and is insensitive to plant species, geography, or the portion of the leaf that is sampled (Landais et al., 2006). The λ_{transp}–Rh relationship proposed by Landais et al. (2006) is important because if it accurately describes fractionation during global transpiration then it can be used widely in interpretations of triple oxygen isotope data used to understand the global carbon cycle and O_2 budgets and in geologic materials that record the isotopic composition of leaf water (*e.g.*, Pack et al., 2013; Passey et al., 2014).

The objective of this paper is to develop a better understanding of the controls on λ_{transp}, the extent of variation in $\Delta^{17}O$ of leaf waters, and the relationships between $\Delta^{17}O$ and *d-excess* in leaf waters. We focused our study on stem and leaf water samples that would build on the study by Landais et al. (2006) and expand the collective dataset of $\Delta^{17}O$ in leaf waters ($\Delta^{17}O_{LW}$) to include additional species and to extend the work to the semi-arid tropics by sampling waters in the Mpala Research Center in central Kenya.

2. Materials and methods

2.1. Research sites and sample collection

All sample collections were made in the Mpala Research Center (MRC), which encompasses 190 km^2 of semi-arid savanna on the Laikipia Plateau of the central Kenya highlands (0°17′35″ N, 36°53′55″ E, elevation 1600–1800 m.a.s.l., Fig. 1). Mean annual rainfall at the MRC is ca. 500–550 mm (Okello et al., 2008; Franz et al., 2010) and is distributed primarily between two rainy seasons in March–May and October–December (Camberlin and Philippon, 2002), brought by the easterly and southeasterly winds from the Indian Ocean (Nicholson, 1996). Mean monthly temperatures range between 17 and 23 °C (Okello et al., 2008). There is some variation in temperature, elevation, soil composition, and rainfall amount within the MRC area that results in complex mosaic of vegetation (Franz et al., 2010). There are mainly two kinds of soils in this area: poorly-drained vertisols on which the dominant woody