



Experimental determination and theoretical framework of kinetic fractionation at the water vapour–ice interface at low temperature

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Abstract

Water isotopes are commonly used for climate reconstruction from ice cores. The different heavy isotopes of water such as H_2^{18}O , H_2^{17}O or HDO give information about local temperature but also temperature and humidity of water vapour sources. Quantification of these parameters relies on the good knowledge of equilibrium and kinetic isotopic fractionation at each step of the water cycle. One of the strongest limitations when interpreting water isotopes in remote Antarctic ice cores is the formulation of the isotopic fractionation at solid condensation (vapour to ice). This classical formulation also implies a good knowledge of coefficients for equilibrium fractionation and water vapour diffusion in air as well as supersaturation in clouds. The uncertainties associated with these different parameters make the formulation of isotopic fractionation at solid condensation only empirical.

Here, we make use (1) of recent development in the measurements of water isotopes in the water vapour through infra-red spectroscopy and (2) of the possibility to measure accurately ^{17}O -excess of water to test the classical formulation and parameterization of isotopic fractionation at solid condensation. A first experiment involving very strong supersaturation evidences a strong kinetic effect on ^{17}O -excess at solid condensation, similar to d-excess. It also shows the limits of the classical formulation of water isotopic fractionation during solid condensation estimation at very low temperature. A second experiment performed in a cloud chamber under controlled conditions uses cavity ring down spectrometers (CRDS) to determine the spatial variability of water vapour isotopic composition due to diffusion (kinetic effect) during solid condensation. The spatial variability of water vapour isotopic composition can be relatively well reproduced by the resolution of diffusion toward a cold plate. This preliminary study opens new perspectives to revisit the classical formulation of water isotopic fractionation during solid condensation at very low temperature.

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1. INTRODUCTION

As the cold trap of the global water cycle, Antarctica is a unique archive of Earth's past climate and water cycle. On long timescales (up to 800,000 years), climate changes are retrieved from the water isotopic records of deep ice cores (Petit et al., 1999; EPICA, 2004; Jouzel et al., 2007). Indeed, water isotopic records ($\delta^{18}\text{O}$ or δD) are linked to condensation temperature through the Rayleigh distillation effect (the cooler the air, the less water it can hold).

Still, important limitations prevent us from obtaining a quantitative temperature record from $\delta^{18}\text{O}$ and δD profiles in polar ice cores. In Greenland, variations in the moisture source (Charles et al., 1994), seasonality of the precipitation (Fawcett et al., 1997; Krinner et al., 1997), and the link between condensation and surface temperature (existence of an inversion layer) (Loewe, 1936) can bias by a factor of two the temperature reconstructions from ice cores. In Antarctica, the same effects are at play (Sime et al., 2009; Laepple et al., 2011) but other factors should be considered too because the mean annual temperature is lower than in Greenland (less than $-55\text{ }^{\circ}\text{C}$ today on the East Antarctic plateau). Indeed, reconstructing polar temperature from isotopic composition of the snow is generally based on models describing the physics of isotope fractionation (either simple isotopic models describing water fractionation following Rayleigh distillation (Ciais and Jouzel, 1994), or Atmospheric General Circulation Models – AGCM – including the description of the water isotopes (Hoffmann et al., 1998; Schmidt et al., 2005; Risi et al., 2010; Werner et al., 2011)). These models, developed over the last decades, rely on the knowledge of the fractionation coefficients associated with each phase transition and on simple assumptions concerning cloud microphysics. Indeed, all mass dependent and symmetry dependent physical processes involve fractionation: the different isotopes do not have the same saturated vapour pressure or diffusivity in air. At low temperature, both vapour–solid equilibrium fractionation and the different diffusivities of water isotopes in air should be considered (Jouzel and Merlivat, 1984). A recent effort was made to determine the temperature dependence of the fractionation coefficients associated with δD and $\delta^{18}\text{O}$ (Ellehöj, 2011). The results turned out to be significantly different from the previous determination (Majoube, 1971a,b). Moreover, the evolution of diffusivities of water isotopes in air has never been studied at temperatures lower than $10\text{ }^{\circ}\text{C}$ (Merlivat, 1978; Cappa et al., 2003; Luz et al., 2009). Using diffusivity values measured at $20\text{ }^{\circ}\text{C}$, as is commonly done, limits the quantitative interpretation of water isotopes in remote Polar Regions. In the classical formulation of the fractionation during ice/snow condensation, the ratio between kinetic (diffusivity) and equilibrium fractionation is only controlled by the degree of supersaturation of water vapour over ice. From available observations, it is expected that supersaturation increases with decreasing temperature and thus has a very strong influence at the very low temperatures encountered in central Antarctica. Even if recent studies have shown high supersaturation levels near the ground level, in the lower atmospheric boundary layer (Style and Worster, 2009;

Genthon et al., 2013; Gallet et al., 2014) and in the higher atmosphere (Gettelman et al., 2006), the supersaturation in Antarctica remains poorly documented, and is thus very crudely tuned in isotopic models (Ciais and Jouzel, 1994). This further limits the models' ability to provide a quantitative link between water isotopic ratios and temperature. To progress on these issues, controlled laboratory experiments are needed to test the values of the fractionation coefficients, as well as the models describing water fractionation at snow formation.

In addition to the primary temperature information provided by δD and $\delta^{18}\text{O}$, the combination of δD and $\delta^{18}\text{O}$ in the form of the deuterium excess ($d\text{-excess} = \delta\text{D} - 8 \times \delta^{18}\text{O}$ (Dansgaard, 1964)) has been used over the last decades and provides information related to relative humidity during evaporation over the ocean (Gat, 1996) and re-evaporation in the convective zones (Risi et al., 2008). It also has an important added value in polar regions since $d\text{-excess}$ has been shown (1) to help tuning the supersaturation spatial evolution (Ciais and Jouzel, 1994; Werner et al., 2011) and (2) to provide information on past changes of moisture source temperature. Vimeux et al. (1999) have indeed first used this tracer in the remote East Antarctica Vostok ice core over a timespan from present to 150 kiloyears before present (kyrs BP) to evidence a change in the moisture source temperature associated with Earth's obliquity. Unfortunately, this second order parameter of isotopic composition is not yet used widely in Polar Regions. One reason for the relatively little use that has been made of this tracer is probably that $d\text{-excess}$ in polar ice cores is not as simple to interpret as previously thought since it also varies with relative humidity of the source, local temperature in polar regions (Jouzel et al., 2007), and the precise trajectory of the water masses (Bonne et al., 2015).

Recently, the increased precision provided by new analytical approaches has permitted the measurements of a new complementary tracer of the hydrological cycle: ^{17}O -excess, defined as $^{17}\text{O}\text{-excess} = \ln(\delta^{17}\text{O} + 1) - 0.528 \times \ln(\delta^{18}\text{O} + 1)$ (Barkan and Luz, 2005; Landais et al., 2008). Like $d\text{-excess}$, ^{17}O -excess shows variations in the hydrological cycle because the different fractionation processes, equilibrium and kinetic (diffusion), modify $\delta^{18}\text{O}$ and $\delta^{17}\text{O}$ in different ways. At low latitudes, ^{17}O -excess, like $d\text{-excess}$, is controlled by relative humidity that imposes the relative importance of equilibrium to kinetic fractionation during evaporation and re-evaporation. Consequently, both ^{17}O -excess and $d\text{-excess}$ increase when relative humidity decreases. At higher latitudes, ^{17}O -excess and $d\text{-excess}$ show different evolutions. $d\text{-excess}$ is affected by local temperature, because the relationship between the fractionation coefficients associated with δD and $\delta^{18}\text{O}$ is temperature dependent (Luz et al., 2009; Majoube, 1971a,b). ^{17}O -excess is much less affected by changes in local temperature and keeps the signature of relative humidity acquired at low latitudes (this is so because the relationship between the fractionation coefficients associated with $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ is independent of temperature). Still, this does not seem to hold true in very isolated regions of East Antarctica where ^{17}O -excess is also influenced by condensation temperature through the increasing influence of kinetic fractionation

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