Chemical Geology 266 (2009) 194–204

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

A new procedure for separating and measuring radiogenic isotopes (U, Th, Pa, Ra, Sr, Nd, Hf) in ice cores

Sarah M. Aciego [a,*], Bernard Bourdon [a], Maarten Lupker [b], Joerg Rickli [a]

[a] *Institute of Isotope Geochemistry and Mineral Resources, Clausiusstrasse 25, NW, ETH-Zurich, Zurich, Switzerland*
[b] *Centre de Recherches Pétrographiques et Géochimiques, CNRS, BP20, Vandoeuvre-les-Nancy, France*

ARTICLE INFO

Article history:
Received 14 January 2009
Received in revised form 29 May 2009
Accepted 2 June 2009

Editor: J. Fein

Keywords:
U-series
Hf
Nd
Sr
Ice cores
Sea salt

ABSTRACT

A new method for the radiogenic isotope (U–Th–Pa–Ra, Sr, Nd, Hf) analysis of the soluble and insoluble components found within ice cores is presented. Melting experiments with rock standards in the presence of EDTA indicate that carbonates, as well as silicates, can be buffered sufficiently to preclude dissolution. The use of EDTA allows adsorbing species, such as Th and Hf, to remain in solution during melting thus fully separating the dust (insoluble) and sea salt (soluble) components of the ice after filtration. A new elemental separation scheme for low sample masses, less than 5 mg solid material, utilizes 4 primary ion exchange columns and two "clean-up" columns to fully isolate U, Th, Pa, Ra, Sr, Nd, and Hf while maintaining high yields. Elution schemes measured for USGS rock standards and a Chinese loess are presented to provide a comparison for variable matrix compositions. Mass spectrometer techniques were modified to measure small aliquots of the standards, equivalent to the amounts found in ice core samples, 10 ng and less. A MC-ICPMS was employed for the measurement of U, Th, Pa, Ra, and Hf; results of the experiments show that with ion yields up to 1%, rock standards have errors for $^{234}U/^{238}U$ of 1%, $^{230}Th/^{232}Th$ of 1.5%, $[^{228}Ra]$ of 9%, and $^{176}Hf/^{177}Hf$ of 100 ppm. MC-TIMS measurements of Sr and Nd show similar errors for small sample sizes: $^{87}Sr/^{86}Sr$ of 50 ppm and $^{143}Nd/^{144}Nd$ of 80 ppm. This new analytical method increases the number of possible tracers measured from a single sample, reducing separation times and sample consumption, as well as providing the addition of a radiometric clock, U-series, to the traditional suite of isotopic tracers, Sr, Nd, and Hf.

1. Introduction

The isotopic compositions of the hydrosphere and cryosphere are primarily controlled by rocks exposed at the Earth's surface. Analyzing and interpreting the isotopic compositions of uranium-series isotopes (U, Th, Pa, Ra), strontium (Sr), neodymium (Nd), and hafnium (Hf) has become a powerful tool to trace surface processes (e.g. climate change, ocean circulation and chemical weathering) both in terms of fluxes and timescales. One of the more powerful tools for studying these processes is the ice core record; ice sheets record temperature, humidity, atmosphere composition, sea ice extent and dustiness all as a function of time. The Sr, Nd and Pb isotopic composition of dust within ice can provide information about source area, transport pathways and source area climate (Biscaye et al., 1997; Delmonte et al., 2004; Fischer et al., 2007). Work by Pettke (2002) and Van De Flierdt et al. (2004) indicate that Hf may be an additional useful tracer for the provenance of dust, although its concentrations are low. Furthermore, Fireman (1986) and Goldstein et al. (2004) have hypothesized that U-series disequilibria can develop in ice due to recoil of daughter products from particulate solids trapped within the ice. The methodology for separating and measuring each of these elements depends on the amount of sample available and the matrix material. In the case of ice cores, the amount of material is so low (<1 mg dust/kg ice) that pre-existing methodologies are insufficient to measure Sr, Nd, Hf, and U-series in a single sample.

The purpose of this work is threefold. First, provide a method for clean separation of the soluble (precipitation, sea salt, and adsorbed elements) and insoluble components (carbonate and silicate dust) for ice samples. Second, provide a chromatographic method that allows quantitative separation and recovery of each element of interest (U–Th–Pa–Ra, Sr, Nd, Hf). Third, show that the former procedures allow for accurate and precise measurements of the isotopic compositions. These techniques should be applicable to ice cores, as well as to other studies of sub-milligram samples such as pore and river waters, micro-milled speleothems and evaporation rinds.

2. Experimental procedures

2.1. Reagents, lab ware, and spikes

All chemical separation and sample handling were performed under class 10 laminar flow hoods within a class 10,000 clean laboratory. Ultra-pure reagents were used throughout the chemistry steps: HCl, HNO_3 and HF were double distilled in a PicoTrace cupola

---

[*] Corresponding author.
E-mail address: aciego@erdw.ethz.ch (S.M. Aciego).

0009-2541/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemgeo.2009.06.003

distillation apparatus and ammonia purchased from Seastar Chemicals. Water was purified using the milli-Q Element Millipore purification system, resulting in 18.2 MΩ grade water. Ethylenediaminetetraacetic acid (EDTA) was purchased as an ultra-pure grade diammonium salt and dissolved with water to form a 0.5 M solution. Purification of the EDTA solution can be accomplished by cation exchange at 0.01 M (Volpe et al., 1991) to a baseline value of 100 ppt U and Th, and <0.05 fg/g Ra. Purification for Ra using cation exchange is much more efficient than for U and Th. These elements are retained on the column resin by adjusting the pH: Ra is retained at pH<9 while U and Th are retained at pH<4 with complete separation at pH<2 (Fritz and Umbreit, 1958; Nelson, 1964). However, EDTA must be buffered above pH 2 otherwise it precipitates within the column; acceptable Th and U blanks are hard to achieve which may explain why Goldstein et al. (2004) reported ~100 pg blanks with this methodology. In order to attain better blank levels, we used additional cleaning steps. After one pass through the cation column at pH 4, to remove the radium and strontium, further purification was accomplished by repeated precipitation–dissolution steps. Following the work of Mitchell et al. (1984), we found that precipitating with clean concentrated HCl, decanting the supernatant, rinsing with clean 1 M HCl, then re-dissolving in H_2O buffered with ammonia resulted in halving the blanks. Repeated precipitation–dilution steps result in 0.5 M EDTA with <10 ppt U, Th, Sr, and Nd, <0.05 fg/g ppt Ra, Pa, and Hf. The pH of EDTA solutions was adjusted by adding ultra-pure ammonia.

In order to avoid contamination, either from manufacturing or previous samples, an aggressive cleaning procedure was adopted for all PFA and PTFE lab ware. Materials were first rinsed in ethanol, then boiled sequentially in reagent grade fresh aqua-regia, 25% HCl, and 18 MΩ water. Finally, the lab ware was cleaned with a mixture of hot double distilled HNO_3 and HF before rinsing with milli-Q Element water.

We used a range of rock standards and elemental solutions to evaluate the success of the melting, filtration, and chemical procedures, as well as mass spectrometer techniques. Three rock powders are certified USGS standards (AGV-2, BHVO-2, and BCR-2), which have been characterized for elemental and Sr, Nd, and Hf isotopic measurements. Two other rock powders are U-series standards (TML and AThO) that are well characterized for both concentrations and isotopic compositions. We also used a loess sample (CDL) from Central China as an internal lab standard with similar characteristics to dust found within ice cores: diverse mineralogy including clay minerals and carbonate, a size distribution varying from 0.2 to 10 µm, and an isotopic composition more suitable for comparison to ice core dust or source area samples. Dilute Alpha Aesar standards (certified 3% concentration accuracy) were used to test the melting, filtration and elution procedures. Spikes were calibrated either with our in-house gravimetric standards (made from Hf, Th, Sr, and Nd solids) or with international reference standards (^{226}Ra NIST SRM4966, ^{238}U NIST SRM 3164).

Single element spikes of ^{229}Th, ^{233}U, and ^{236}U were prepared at dilute concentrations, less than 0.12 ppb, such that weighing errors could be minimized for ultra-low level samples. The ^{228}Ra spike was prepared using standard techniques: a ~50 year old 50 mg aliquot of a $Th(NO_3)_4$ salt was dissolved and the radium was separated by cation exchange (Volpe et al., 1991). The initial $^{228}Ra/^{226}Ra$ ratio of the tracer was 1.309 ± 0.011, and this ratio was corrected for decay of ^{226}Ra and ^{228}Ra using $\lambda_{226} = 0.1205\ \mathrm{yr}^{-1}$ and $\lambda_{228} = 4.332 \times 10^{-4}\ \mathrm{yr}^{-1}$. The ^{233}Pa spike was prepared regularly every 4–6 months by neutron irradiation of ^{232}Th in the Paul Scherrer Institut reactor in Villigen, Switzerland. Solutions of Th metal were dried in pre-cleaned quartz glass ampoules 4 mm in diameter and 10 cm long, resulting in 1 mg of Th in nitrate salt form at the bottom of each ampoule. The ampoules are evacuated to less than 0.01 mbar, then sealed by melting the glass. After irradiation, the tops of the tubes were cut off with a diamond saw, the salt dissolved in a concentrated HNO_3–dilute HF mixture and removed by pipette. The ^{233}Pa spike was separated from Th and other elements using the procedures of Bourdon et al. (1999). Spikes of ^{84}Sr, ^{179}Hf, and ^{150}Nd were used to determine total procedural blanks and yields.

2.2. Separation of dust from ice core samples

2.2.1. Principles

The components we are attempting to separate from ice cores consist of three main parts: carbonate and silicate solids, soluble materials, including elements dissolved in precipitation and sea salt, and adsorbed materials. The behavior of these components initially during transport to the ice sheets and finally during sample processing determines the laboratory procedures we have used to separate them.

Silicates are primarily clays—illite, kaolinite and chlorite (Biscaye et al., 1997)—with some quartz, minor pyroxenes and olivine (Sala et al., 2008). The source of the carbonate within the dust fraction is difficult to determine, as both dust and marine solids could be sources. However, there is some indication that the marine influence can dominate the carbonate budget. Banta et al. (2008) found that silicate dust deposition on Greenland at coastal ice core sites was fairly equal to the deposition at inland ice core sites, but coastal sites had three times more carbonate load. Similarly, Sala et al. (2008) showed that ice from Talos Dome, close to the Ross Sea, had both hydrous and anhydrous carbonates with the hydrous form dominating the total abundance, indicating a near marine source. More importantly, while the hydrous carbonate dissolves rapidly during ice melting (Sala et al., 2008), the anhydrous form can be buffered and remain insoluble.

The soluble fraction will be some mixture of sea salt, which contains seawater trace elements, and precipitation. Precipitation in the form of rain will dissolve some fraction of dust traveling in the same air mass. Dissolution of dust by snow should be limited in high-altitude inland ice core locations because of the drying of the air masses. Conversely, lower altitude, near ocean ice core locations will have a mix of wet and dry air masses (Fischer et al., 2007), which could produce precipitation with higher trace element concentrations.

The fraction adsorbed onto the dust grains will contain the particle reactive U-series daughters, such as ^{230}Th and ^{231}Pa that are ejected from dust grains during uranium decay, as well as some easily scavenged trace metals such as Pb. Ideally, in order to extract as much information as possible about dust and sea salt, we would like to be able to fully separate these three components. During melting of the ice core, dissolution must be minimized for both anhydrous carbonates and silicates while preventing adsorption of elements present in the soluble fraction or ejected from dust grains. Filtering should fully separate the soluble and insoluble fraction. This procedure is different from other ice core procedures designed for mineral dust analyses, which use a decanting method (Delmonte et al., 2004) or remove all carbonates (Biscaye et al., 1997).

The biggest hurdle in this procedure is not dissolving the solid dust grains which would mix the isotopic compositions of the seawater and continental sources of material. For pure isotopic tracing (e.g. Sr isotopes) this effect is secondary, but is of the highest importance for the U-series dating technique. If congruent dissolution occurs, the outer surface will be affected first, and since this domain in the dust grains is responsible for the excess of daughter nuclides in the ice, dissolution will push both the liquid and the solid fractions toward secular equilibrium and an incorrect, young age. The second source of uncertainty created by dissolution is that carbonates will dissolve at a faster rate given the slightly acidic conditions of polar ice (Sala et al., 2008). Dust-derived carbonate will have an isotopic composition that could differ from the local marine carbonates and sea salt, thereby affecting isotopic tracers of sea salt and surface seawater as well as the initial conditions for U-series dating.

Previous work on U-series dating of ice focused primarily on adsorption (Fireman, 1986) and minimizing dissolution of silicate