



Research paper

Experimental investigation of the effects of mineral dust on the reproducibility and accuracy of ice core trace element analyses

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ABSTRACT

Determination of trace element concentrations by inductively coupled plasma mass spectrometry (ICP-MS) can yield valuable information about paleoclimate from ice core records. Typically, ICP-MS analyses are performed on melted and acidified ice core samples which contain particulate material i.e., mineral dust. This particulate material is usually enriched in trace elements relative to ice core samples. Consequently, it is important to constrain the effect of acidification on mineral dust present in ice core samples and to assess the contribution of dust leaching to the trace element budget of ice cores.

We have conducted a systematic experimental investigation designed to replicate the conditions of conventional ice core trace element analyses. Powdered rock standards of various lithologies were leached in 1 wt.% HNO₃ and the leachates were sampled at regular time intervals. Oxides and sheet silicate minerals, in the ferromanganese nodule (Nod-P-1) and granite (JG-2) leachates respectively, released available trace elements into solution relatively quickly; trace element recovery reached 57% for Mg and 42% for Mn in the granite leachate and recoveries between 60 and 80% were reached for most elements in the ferromanganese nodule leachate after only 12 h of leaching. In contrast, mafic minerals in the basalt (BHVO-2) and dolerite (W-2) released trace elements slowly, achieving recoveries of <20% for elements from Li to Mn after 12 h of leaching. The mafic minerals continued to release trace elements into solution over several weeks causing Al and Ti concentration increases to >4000%. These results demonstrate that acidification of ice core samples containing mineral dust will cause time- and mineral-dependent leaching of trace elements. Leaching behaviour of trace elements remained constant with varying mineral dust concentration but freezing pre-acidified samples was found to promote leaching of some trace elements. Ideally, all ice core samples would be fully digested or filtered to eliminate the error introduced by partial dissolution of dust but this is time-consuming and impractical. We therefore recommend acidifying samples for as long as practical to reach a maximum leachable concentration. For datasets obtained by conventional methods, Al is identified as the most suitable element to use as a terrestrial tracer because it is leached to a uniform extent across all lithologies. Fundamental flaws are identified in the calculation of crustal enrichment factors which are likely to cause some elements to appear enriched as a result of incongruent leaching. Ratios of trace elements, in particular rare earth elements (REEs), leached from mineral dust will not reflect those of the dust and are not suitable as tracers of dust provenance.

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1. Introduction

Ice cores provide continuous, high-resolution records of past atmospheric and environmental conditions (e.g. Fischer et al., 2007).

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Increasingly, conventional stable isotope and major ion analyses of ice cores are being complemented by determination of trace elements by inductively coupled plasma mass spectrometry (ICP-MS) (Barbante et al., 1997; Planchon et al., 2001; Gabrielli et al., 2006; Purdie et al., 2010). The typical method of ICP-MS analysis involves analysing melted, acidified, ice core samples that have not been filtered or centrifuged to remove particulates (e.g. Barbante et al., 1997).

Sample acidification is a prerequisite for ICP-MS analysis of solutions but when particulates are present in the sample solution, acidification can cause particulate dissolution. The principal inorganic constituents of ice core samples are marine salts and mineral dusts and, whilst marine salts are readily soluble, mineral dusts are relatively insoluble. However, once the sample is acidified, typically to 1 wt.% HNO₃, trace elements can

be leached, at least partially, from the mineral dust particles into solution. ICP-MS determinations of trace elements in ice core samples therefore do not solely measure the soluble chemical constituents but also an additional component resulting from the partial dissolution of mineral dust.

This has implications for understanding the trace element budget of ice cores because the contribution of mineral dust leaching to measured trace element concentrations in ice core samples has not been quantified previously and very little is known about how the leaching process varies for different trace elements, minerals or lithologies (Snäll and Liljefors, 2000). Silicate minerals such as feldspars, clays and pyroxenes, which are commonly found in ice cores (Gaudichet et al., 1988; Ayling and McGowan, 2006), will only undergo partial dissolution because silicate mineral lattices can withstand 1 wt.% HNO₃ solutions (Günzler and Williams, 2001). Therefore, interpretation of ICP-MS data would be aided by an understanding of incongruent leaching i.e., which elements are leached in preference to others and whether the pattern is consistent between dusts with different mineralogies.

There are several further factors which may affect the extent and rate of mineral dust dissolution in an acidified ice core sample, thereby introducing uncertainty concerning the reproducibility and accuracy of trace element concentrations determined by ICP-MS. The most important of these factors is the length of time that samples are acidified prior to analysis. Previous ICP-MS analysis of snow pit samples has shown that replicate analyses of the same sample measured at different time intervals can lead to trace element concentration increases of greater than 100% (Bull, 2009).

A further source of uncertainty in ice core trace element determinations lies in the uptake and incomplete ionisation of dust particles from within unfiltered ice core samples (Vallelonga et al., 2004; Bull, 2009). The extent to which this occurs and its effect on signal intensity (Hobbs and Olesik, 1993) requires further investigation that is beyond the scope of this paper.

This study presents a systematic experimental investigation into the influence of partial dissolution of mineral dust particles on the reproducibility of trace element determinations in ice core samples. Leaching experiments were carried out on geochemically well-characterised, powdered international rock standards in 1 wt.% HNO₃ to examine how trace element measurements vary depending on the length of the acidification time, whether samples were frozen after acidification or not, and variable dust lithologies and concentrations. These findings allow us to make several recommendations for future ice core ICP-MS trace element studies and interpretation of ice core trace element data.

2. ICP-MS trace element analysis of ice cores

The length of time that ice core samples are acidified prior to analysis varies widely between published studies of conventional ICP-MS trace element analyses (Table 1). It is typically 24 h, but in many cases the length of time is not stated by the authors. The effects that resulting variable levels of mineral dust dissolution may have on the reproducibility of ICP-MS measurements ultimately limits the comparability of trace element records from different ice cores. Even if one specific acidification time is chosen, implemented and reported, the nature of ICP-MS analysis requires samples to be analysed in runs that can be > 12 h in length, causing the first sample to have experienced a considerably shorter acidification time than the final sample. An acidification time of > 3 months was adopted by Townsend and Edwards (1998) because unpublished tests on ice core samples found the maximum leachable concentration of Fe was reached at this time, allowing all samples measured to be free of time-dependent leaching effects.

Trace element concentrations in ice cores can also be determined using coupled ice core melter and ICP-MS analysis systems where acidification occurs directly prior to analysis (McConnell et al., 2002; Knusel et al., 2003). Many lithophile elements (e.g. Al and REEs)

record significantly lower concentrations when analysed in this way compared to conventional methods (Knusel et al., 2003). This is presumably because any mineral dust present in the sample is only exposed to acid for a short length of time, thereby minimising trace element leaching.

The type and molarity of acid used to acidify samples is also likely to affect the rate of which leaching occurs and also varies between published studies (Table 1). In some cases, samples from the same location were acidified to different strengths (Tao et al., 2001; Krachler et al., 2004; Krachler et al., 2005), creating a source of uncertainty for comparison of trace element records.

The studies listed in Table 1 also vary widely in their approach to sample storage. It is generally accepted that ice core samples should be stored frozen prior to analysis, however samples were acidified before being refrozen in several studies. This could cause increased leaching of the mineral dust because when freezing takes place, dense acid sinks to the bottom of the vial where mineral dust is also located, causing the mineral dust to be exposed to more concentrated acid whilst freezing takes place.

3. Experiment design

3.1. Overview

In order to replicate the partial dissolution of mineral dust in acidified ice core samples, small amounts of powdered international rock standards were leached in 1 wt.% HNO₃. Leachates were removed at selected times, and are considered to be analogous to ice core samples containing mineral dust which are acidified for different lengths of time prior to analysis. The use of rock standards for which bulk trace element concentrations are well characterised facilitates accurate measurement of the degree to which elements are leached from these standards as analogues of mineral dust.

Two experiments were conducted. The first tested how leachate composition changed with acidification time, dust lithology (rock standard type) and dust concentration. The second examined whether freezing samples after acidification affected leachate compositions.

3.2. Rock standards

The following four rock standards were selected to compare the leaching behaviour of different lithologies: BHVO-2 (Hawaiian Basalt, USGS); W-2 (Centerville Diabase, USGS); Nod-P-1 (Manganese Nodule, USGS) and JG-2 (Granite, Geological Survey of Japan). BHVO-2 is basalt comprised of clinopyroxene and plagioclase feldspar with minor amounts of magnetite. W-2 is a diabase or a dolerite, comprised of plagioclase feldspar, clinopyroxene with minor amounts of muscovite mica, quartz, and opaque minerals (S. A. Wilson, USGS, Personal communication). JG-2 is a biotite-rich granite (Ando et al., 1989) and Nod-P-1 is a Pacific Ocean ferromanganese nodule which is ~70% Fe–Mn oxyhydroxide mineral phases and ~30% quartz and plagioclase feldspar (S. A. Wilson, USGS, Personal communication).

These rock standards encompass a range of textures and mineralogies and contain minerals commonly found in ice core dust (Gaudichet et al., 1988; Ayling and McGowan, 2006). The rock standard lithologies are also comparable to those exposed in the McMurdo Dry Valleys, Antarctica, where the New Zealand contribution to the International Trans-Antarctic Scientific Expedition focuses its snow pit and ice core sampling (Mayewski et al., 2005). Nod-P-1 was selected because its predominantly Fe–Mn oxyhydroxide mineralogy is similar to Fe–Mn oxides coatings on many aeolian particles (Post, 1999) and to desert varnish (Bauman, 1976), which coats the surface of a significant proportion of exposed rocks in the McMurdo Dry Valleys region (Bockheim, 2010).

The grain size distributions of the four rock standards, measured by laser particle counter (Beckman Coulter LS13 320), encompass the grain size range between <1 µm and >80 µm measured on ice core dust

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