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Air handling in clean laboratory environments: the reason for anomalously high boron background levels

Abstract The isotopic analysis of boron from material that carries only trace amounts of boron requires low boron blank levels. Large efforts are taken to keep blank levels low by purifying reagents. We performed exposure experiments and determined procedure blanks before and after the air-handling system was modified from silicate glass filters to polyethylene/polystyrole and active carbon filters. Our investigations demonstrate that the air-handling system may be the major source of boron blank in many laboratories, as the widely used silicate glass filters, which contain boron as a major component, in the form of borax and boric acid, release significant amounts of boron to the air.

Keywords Boron contamination · Boron blank · Volatile boron · Filter materials · Clean laboratory facilities · Air-handling systems

Introduction

The determination of boron concentrations and the characterization of boron isotopic compositions of synthetic and natural materials provide a wide range of applications in industrial processes (e.g., glass or micro wafers) and various disciplines of natural sciences (e.g., geochemistry). Boron is a highly volatile element that shows significant coordination, temperature, and pH-dependent fractionation during phase transition. These properties make boron a suitable tracer for all kinds of fluid–rock interaction and pH-dependent processes in low-temperature and high-temperature hydrothermal systems, magmatic systems, material flux in subduction zones, or in palaeo-ocenaography [1]. Moreover, boron is used for various industrial applications and processes,

for instance in the glass and electronic industry [2]. It is therefore not surprising that the number of laboratories that have started to analyze boron has increased significantly over the last decade.

Clean laboratories are commonly characterized in terms of particles < 0.5 μm m^{-3} air. This characterization has proven to be useful for laboratories working with radiogenic isotopes (e.g., Pb, Hf, Nd, and Sr) and for the electronics industry. Boron, however, may occur as volatile components, in which case the clean-room classification in terms of particle flux is poorly representative for boron. Leeman et al. [3] have suggested that a significant portion of the total blank boron may originate from the ambient laboratory air.

Borax and boric acid are widely used as flame retardant [4]. Legislative regulations concerning fire-protective measures, especially preventing flames from spreading in buildings via air-handling systems, have resulted in the impregnation of most kinds of filter material with borax or boric acid. Laboratories that were designed for the analysis of Pb, Nd, or Sr isotopes (i.e., that were optimized to have a low particle-flux) are likely to use boron-bearing filter material, as boron does not disturb the analysis of these elements. Similarly, commercially commissioned air-handling systems for clean laboratories are likely to use boron-bearing filters—unless the use of boron-free filter material has been specifically requested—as such material (i) can meet the particle-flux requirements, (ii) fulfills requests from legislation towards fire safety, and (iii) keeps the costs low. A later set-up of the analytical procedures to determine boron in trace amounts in such laboratories may result in markedly higher blanks than in laboratories specially designed for the analysis of boron.

In the following, we demonstrate that most of the boron blank originates from the air released by air-handling systems using filters based on silicate glass fibers and that the boron blank may be drastically reduced by replacing the silicate glass fiber filters with low-boron bearing filter material, such as polycarbons and active carbon.

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Sources of blank boron

Boron has a wide range of applications that are relevant to clean laboratories, for instance in bleaching agents, washing and disinfecting agents, and in laboratory glassware (e.g., Duran, Pyrex). However, more than 4% of the annual consumption of boron minerals and compounds in the USA in 1997 [2], was used for the impregnation of fiber and paper as flame retardant. Filter material used for air-treatment in buildings and laboratories typically contains 10–30 wt.% boron in the form of borax or boric acid [4].

Boron contamination performing wet-chemical preparation may occur during sample decomposition, ion-exchange chromatography, and sample drying. Furthermore, there are possible boron contributions from reagents, laboratory equipment, ambient air, and the analyst. Commonly, extraordinary efforts are taken to minimize contamination added from reagents by performing boron-specific cleaning procedures (e.g., see refs. [5, 6]). Boron contamination can be minimized by using clothes cleaned with boron-free washing powders and laboratory equipment made of Teflon and polyethylene. Nonetheless, in laboratories using technologies off-the-shelf or being designed for Pb, Nd, and Sr, the air-handling system may represent the most important boron reservoir.

Experimental

Air handling in clean laboratory facilities

Typically, clean laboratory facilities are specified in terms of particles per volume. For instance, a class 100 laboratory has less than 100 particles > 0.5 μm m^{-3} air (US Federal Standard 209). Because the commercially built laboratory at the GeoForschungsZentrum Potsdam was originally designed for the analysis of the radiogenic isotopes Sr, Nd, and Pb, and not especially for boron chemistry, no efforts were undertaken to provide a boron-free, clean laboratory environment.

The incoming air is purified in a battery of three, increasingly finer pocket filters (pre-cleaning; Fig. 1a). With respect to costs, legal constraints, and the initially planned use of the laboratory, the optimal solution

included silicate glass filters. In August 2001, these filters were replaced by a battery of two polyethylene/polystyrole filters and one active carbon filter (Fig. 1a). After the pre-cleaning, the air passes through a high efficiency particulate (HEPA) filter at the ceilings (Fig. 1b). Acid-charged air is removed completely from the laboratory. In total, 30% of the air volume is replaced from the system and 70% is recycled by passing the air over the last pre-cleaning step and the HEPA filters (Fig.1).

Analytical methods

ICP-OES

Boron concentration analysis for the silicate glass filters was carried out on a VARIAN Liberty 200 ICP-OES using the emission line at 249.773 nm. The solid glassy filter material was decomposed with HF in the presence of mannitol. Boron was chemically separated by cation exchange chromatography using AG 50W-X8 (200–400 mesh) [7]. Calibration was typically made using a 1 μg g^{-1} boron-standard solution diluted in 0.05 M HCl. To obtain precise and reproducible analytical results the boron concentrations in the sample solution were capped between 0.1 and 1 μg g^{-1}. The internal precision and external reproducibility of ICP-OES-measurements are typically better than 2 and 5% [8], respectively.

TIMS

For the determination of boron isotope compositions and the isotope dilution measurements, both the BO_2^- and the $Cs_2BO_2^+$ -graphite method were used.

Samples derived from the exposure experiments and the reagent blanks were measured by NTIMS, collecting BO_2^- ions on masses 42 and 43 on a VG SECTOR 54–30 mass spectrometer by static multi-collection [7]. Samples were loaded without further purification on recently out-gassed rhenium filaments that were coated with a layer of boron-free seawater. After introducing the samples into the mass spectrometer, the filament temperature was automatically increased to 850°C at a rate of 120 mA min^{-1} The filament temperature was then manually raised and the ion beam was focused until

Fig. 1 Schematic representation of the air flow in the clean laboratory facility at the GFZ Potsdam. **a** General filter sequence and air flow and **b** schematic air flow and positions of air filters in a single clean room. *EU5*, *EU8*, and *EU9* refer to EU-filter classes. Air handling is set to exchange 30% of the total air flux
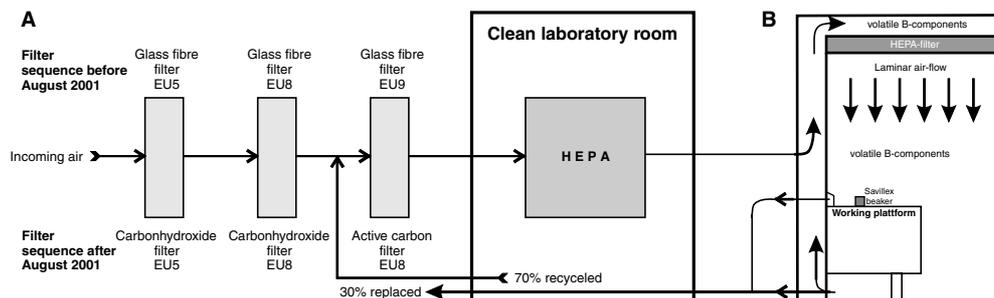
the signal on mass 43 reached 1×10^{-11} A ($\sim$950°C). For the purpose of blank determinations by isotope dilution, data were collected in three blocks of 12 scans each.

The $Cs_2BO_2^+$-graphite method was used to determine the boron concentration of the filter material and procedure blanks for a wet chemical method used to separate boron from other elements after a K_2CO_3fusion [5, 8]. The boron isotope composition was measured on a Finnigan MAT 262 mass spectrometer by static multi-collection on masses 308 and 309 [8]. Silicate glass filters were dissolved in concentrated HF in the presence of mannitol at < 65°C in closed Savillex beakers. The sample solution was then centrifuged and the boron-bearing supernatant evaporated at < 65°C. The dried sample was redissolved in 1 mL of 0.02 M HCl and loaded on a preconditioned polypropylene column filled with 1 mL AG50W X8 (200–400 mesh). To avoid boron loss, the resin was rinsed with another 3 mL of 0.02 M HCl after the sample solution had passed through. The entire solution was collected and evaporated to dryness at < 65°C. For the $Cs_2BO_2^+$-graphite method, samples were loaded onto single tantalum filaments. Degassed filaments were coated with a graphite/ethanol/water suspension (40 mg graphite mL^{-1}) that served as an emitter to enhance ionization efficiency.

After introducing the samples into the mass spectrometer, the filament current was automatically raised to 1.1 A at a rate of 50 mA min^{-1} and then manually at a rate of 20–25 mA min^{-1} until the Cs^+ signal on mass 133 started to appear. The cesium was used to focus the ion beam. The filament current was further raised at a rate of 10–15 mA min^{-1} with permanent focusing until the ion current of $Cs_2^{11}BO_2^+$ reached 1–2×10^{-13} A. Data collection was started between ion beam intensities of 1 and 5×10^{-12} A on mass 309. The ratio of $Cs_2^{11}BO_2^+$ to $Cs_2^{10}BO_2^+$ was measured in blocks of 20 individual scans each with an integration time of 4 s. All scans were checked with a 2SD error criteria for outliers, based on the block averages.

Replicate measurements of NISTSRM 951 gave a mean $^{11}B/^{10}B$ ratio of 4.05416 ± 0.00077 (1SD) for the $Cs_2BO_2^+$-graphite method ($N=83$) and 4.01476 ± 0.00222 (1SD) for the BO_2^- method ($N=12$), respectively [8]. Three $Cs_2BO_2^+$-graphite analyses of NISTSRM 952 gave a $^{11}B/^{10}B$ mean ratio of 0.05413 ± 0.00016 (1SD) [9]. Boron isotope ratios are reported as $\delta^{11}B$ values in ‰ ($\delta^{11}B = [\{^{11}B/^{10}B\}_{sample}/ \{^{11}B/^{10}B\}_{NISTSRM951} - 1] \times 1000$), i.e., normalized to the mean of concurrently measured NISTSRM 951 standards.

Reagents

Water was purified to a conductivity of 18.2 MΩ cm^{-1} with an Academic Milli-Q purification system. Concentrated HCl (Merck, Darmstadt, Germany, analytical grade) was purified by sub-boiling point distillation in the presence of mannitol at 65°C. Concentrated HF (Baker, Ultrex) and ammonia solution (Merck,

Suprapure) were used in commercial high-purity qualities without further purification. Mannitol (Merck, D(−)-Mannit) was used as a complexing agent to prevent boron loss during preparation. Ion exchange chromatography was performed using the cation resin AG 50W-X8 200–400 mesh (Bio Rad, Hercules, CA, USA). Seawater, serving as emitter for BO_2^- measurements, was cleaned for boron by several passes over anion resin AMBERLIT 743 (Fluka, Buchs, Switzerland). Cesium, as cesium carbonate (Aldrich, 99.995%), was used to promote the formation of $Cs_2BO_2^+$ ions on the filament during positive TIMS measurements. NIST graphite, serving as emitter for $Cs_2BO_2^+$ measurements, was suspended in a 3:7 mixture of ethanol and water to a suspension with 40 mg graphite mL^{-1}. NIST boric acids SRM 951 and SRM 952 [10] were used as standard and spike solutions for boron isotope analyses.

Procedures

The boron contamination derived from the ambient laboratory air was investigated by a series of exposure experiments. Open 15-mL Savillex beakers (25-mm inner diameter) filled with 2 mL water, 20–40 mg spike solution (NISTSRM 952), and 10–20 μL 0.02% mannitol solution were placed on the working benches (Fig. 1b) of two clean laboratory rooms for different time intervals. The accumulated amount of boron was determined by using isotope dilution mass spectrometry (ID-MS). The exposure experiment was conducted before and 25 days after the filter change (Fig. 2), respectively. To monitor the level of total boron blanks for a wet chemical procedure to separate boron from silicate rocks prior
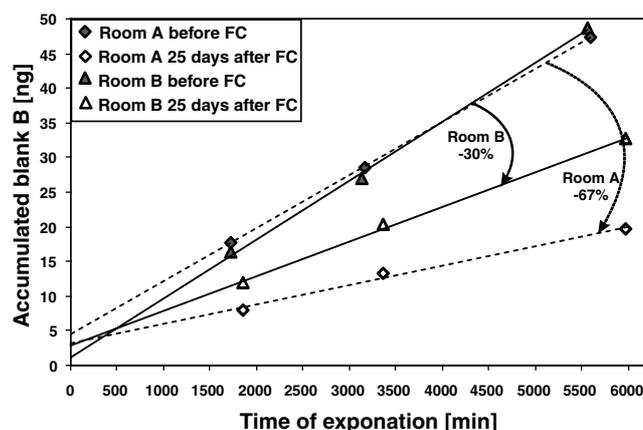
Fig. 2 Exposure experiments: boron accumulation of air-derived boron in open Savillex beakers on the working platforms as a function of time prior to and 25 days after the change of filter material (FC). *Dashed* and *solid lines* show results for rooms A and B, respectively. Equations for the correlation lines are: room A before FC ($y=0.0077\ x + 4.4$); room A 25 days after FC ($y=0.0085\ x + 1.2$); room B before FC ($y=0.0028\ x + 3.2$); room A 25 days after FC ($y=0.0050\ x + 3.0$). All correlation coefficients (R^2) are greater than 0.989

TIMS analysis, we conducted systematic boron procedure blank determinations over a period of 8 months.

Results and discussion

Exposure experiments

All exposure experiments show a linear accumulation of boron with time for both investigated clean laboratory rooms (Fig. 2). Prior to the replacement of the boron-bearing glass pocket filters the accumulation rates show high values between 0.0085 (room A) and 0.0077 (room B) ng boron min^{-1} in the Savillex beakers during exposure of the sample solution. Twenty-five days after the replacement of the boron-bearing filters with poly-carbon and active carbon filters, the accumulation rates decreased systematically to 0.0028 (room A) and 0.0050 (room B) ng boron min^{-1}, which is 30 and 67% of the initial rates (Fig. 2), respectively. The linear pattern of boron accumulation in the Savillex beakers as a function of time ($R^2 > 0.9896$ for all experiments) cannot be explained by blank boron from the reagents. Instead, the temporal variation of boron blank (Fig. 2) demands air-derived contamination of boron. The level of boron contamination decreased rapidly after the change of filter material (Fig. 3). The nearly identical accumulation rates for both investigated clean rooms prior to the filter change reflect an essentially constant boron flux in the entire clean laboratory, suggesting that the boron blank originates from air-handling and that the filters are the main source of contamination. The intersection of the correlations lines with the ordinate indicate a total blank of the used reagents between 4.4 and 1.2 ng boron (Fig. 2), which is consistent with measured reagent blanks after the filter change (Table 1).
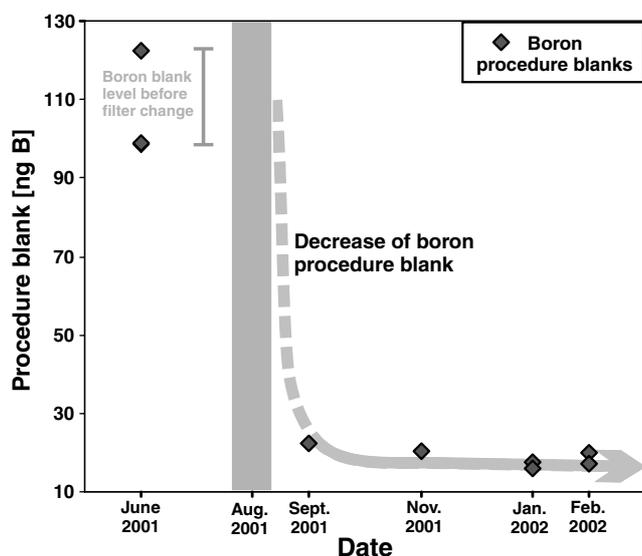
Boron was introduced into the air-handling system and the laboratory for a period of several years and may have accumulated there and has been continuously redistributed. The difference in the decrease of air-derived boron blank between the two investigated clean rooms may be due to different memory effects in the air-handling system (tubings and HEPA filters). There seems to be no difference in the boron flux depending on the position on the working platforms or even between different rooms in the clean laboratory, as the calculated accumulation rates for the two clean rooms are similar (Fig. 2). However, differences like those observed for the exposure experiments after the filter change between room A and B could be due to differences in the air management between days, nights, and weekends.

Procedure blank

The procedure blanks for the wet chemical boron separation showed reproducible blank values of 122.5, 98.7, and 98.9 ng boron before the filter type was changed (Fig. 3). Procedure blanks were continuously determined over a period of 6 months after the change of filter type. The boron procedure blank shows a rapid decrease within the first 2 months after filter change (-80%) and a slower decrease thereafter. From the second to seventh month, the blank level decreased slowly to values below 20 ng boron (Fig. 3), which is the procedure blank after modification of the air-handling system.

The rapid decrease of the overall procedure-blank after change of filter type (Fig. 3) clearly demonstrates that boron derived from the air was the main reason for the elevated boron blanks. It should be noted that a relatively high boron blank in the order of 100 ng boron does not preclude the reliable and correct analysis of boron-rich materials as tourmalines or boron salts, but is not adequate for the analysis of low-boron materials ($< 10\ \mu g\ g^{-1}$), like silicate rocks. The present boron procedure blank of < 20 ng boron for the entire wet chemical preparation is well within the range reported from some other laboratories ([5] 11.6 ng B; [6] 3–4 ng B; [11] 35–40 ng B).

Reagent blanks

Reagent blanks of water and HCl, the main analytical materials, were determined repeatedly, before and after

Fig. 3 Boron procedure-blank evolution before, to, and after the replacement of the boron-containing silicate glass pocket filters

Table 1 Measured reagent blanks before and after the filter change (FC)

Reagents	B (ng mL^{-1}) before FC	B (ng mL^{-1}) after FC	Tonarini et al. [5]
H$_2$O (sub-boiled with mannitol)	4.30–0.62	0.29–0.26	0.26
HCl (twice sub-boiled)	8.50–1.10	0.80–0.37	0.16

Table 2 Boron composition of clean air pocket filters

Pocket filter types	B ($\mu g\ g^{-1}$)	$\delta^{11}B\text{‰}$
New silicate glass filters	179,000	–
Used silicate glass filters	118,000	0.4 and 2.1
Polycarbon filters	0.8 and 1.1	–

Typical analytical uncertainties (2SD) are < 10% for concentration and < 0.7‰ for δ^{11} B measurements [8]

the change of the filter material (Table 1). Before this change, the blank values were much higher than after the change. Apparently, the high reagent blanks before change to polycarbon and active carbon filter materials reflect air-derived boron contamination that were acquired during the evaporation of 5–70 mL reagent, which was necessary to reliably determine blank levels, or that was acquired when the reagents were purified during distillation. In either case, the reagents were exposed to laboratory air.

Filter materials

Commonly used silicate glass pocket air filters consist of a glass-wool-like matrix of glass fibers. For new and used silicate glass filters, we determined boron concentrations of 17.9 and 11.8%, respectively (Table 2). The boron isotope composition of the used material has 0.4 and 2.1‰ δ^{11}B. The 30% lower concentration for used filters relative to new filters suggests loss of boron from the filters during use, which is consistent with the high boron flux in the clean laboratory before August 2001.

Due to fire protection measures, most of the filter boron occurs as impregnation of crystalline H_3BO_3 on the surface of the glass fiber matrix. We speculate that the mobilized boron exists mainly as gaseous or, in humidity, dissolved $B(OH)_3$ in the laboratory air, as the transfer as particles is restricted by the HEPA filters. If a phase transition of boron from solid in the filters to gaseous or liquid in the air occur during mobilization boron-isotope fractionation is likely. Therefore, the boron isotope composition of the mobilized boron should be different to that of the original filters.

The newly installed synthetic polycarbon filter material made of polyethylene and polystyrol contains very low boron concentrations between 0.8 and 1.1 $\mu g\ g^{-1}$

boron (Table 2) and, therefore, the risk of significant boron mobilization from this filter material is minimal.

Conclusions

Boron is widely used as flame-retardant agent in fire-protection measures in air-handling systems. As shown here, some air filters contain more than 15 wt.% boron. This boron is readily mobilized and distributed by the air-handling system. Volatile boron is not removed by HEPA particle filters and, therefore, may cause a blank problem in laboratories that investigate samples with low boron levels. Exposure experiments and reagent blank determinations before and after the change of filter material demonstrate that the change from boron-rich fibrous silicate glass filters to polyethylene/polystyrole and/or active carbon filters reduces the boron blank by more than an order of magnitude.

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