Europlanet TNA Report (078-TNA3)

PROJECT LEADER

Name: Karen Van Hoecke
Address: Department of Analytical Chemistry (UGent) **Krijgslaan 281 – S12** **B9000 Gent, Belgium** **E-mail: karen.vanhoecke@ugent.be**

COLLABORATORS

Name:	**Affiliation:**
Veerle Devulder	Department of Analytical Chemistry (UGent and KULeuven)
Wim van Westrenen	Faculteit der aard- en levenswetenschappen (VUA)
Pieter Vroon	Faculteit der aard- en levenswetenschappen (VUA)
Date of TNA visit:	November 25th – November 28th 2012
No. of access days:	3
No. of days stay:	3
Host laboratory:	Isotope chemistry laboratory – VUA The Netherlands
Reimbursed	Yes/~~No~~

Project Title – **Determination of boron isotope ratios in ancient glass and calcareous materials using multi-collector ICP-MS coupled to a laser ablation for the purpose of archaeometry and paleoclimatic reconstruction.**

Scientific Report Summary.
(plain text, no figures, maximum 250 words, to be included in database)

In the three day visit, standards were prepared for calibration of boron isotope ratio measurements with laser ablation multi-collector ICP - mass spectrometry. Both glass and calcium carbonate standards, spiked with boron, were prepared.
We chose to prepare HIMT glass (high iron manganese and titanium glass), to which the boron source, either boric acid or borax, was added before a second melting procedure. To evaluate the potential loss of boron during the glass melting procedure, different time periods for the second melting were adopted and boron contents in the final glasses were determined.
The $CaCO_3$ standards were prepared by spiking $CaCO_3$ with NIST 951 boric acid solutions and addition of Milli-Q water before homogenization of the powder. The moisture was evaporated at 40 °C and 5 % (w/w) of PTFE-modified PE wax was added as a binder. Pellets were produced by adopting a 5 ton pressure on each mixture for 1 minute.
Boron recoveries determined in glasses were ≤ 33 %.
The final standards will be used for calibration of laser ablation MC-ICP-MS analyses of

ancient glasses and of calcareous materials within the framework of archaeological and palaeoclimatic reconstruction projects. In addition, mass fractionation processes of B isotopes during glass melting will be studied in a follow-up project.

Full Scientific Report on the outcome of your TNA visit

Approx. 1 page

Goals:
Production of HIMT glass spiked with boron. The extent and kinetics of boron loss from samples during high-temperature melting are unknown. To assess the outcome in terms of boron concentrations remaining in the glass after melting we used two sources of boron and a range of experimental procedures. A selection of these standards will be used as calibration standards for LA-MC-ICP-MS analysis of boron isotopes in glasses from archaeological excavations and will be used to elucidate mass fractionation behaviour of boron isotopes as a function of glass manufacturing procedure.
Production of $CaCO_3$ pellets spiked with boron, to be used as calibration standards for LA-MC-ICP-MS analysis of boron isotopes of biogenic and geogenic calcareous materials.

Experimental procedures and results:
1. HIMT glass spiked with boron
1.1 Production of HIMT glass
Appropriate masses of a selection of powders (SiO_2, $CaCO_3$, Al_2O_3, Fe_2O_3, TiO_2, MnO, Na_2CO_3, MgO, K_2CO_3) were weighed and mixed in a mortar under ethanol. After drying in air, the homogeneous powder mix was transferred into a platinum crucible and melted in a box furnace. In a first heating step, the powder was gently outgassed for 7h30min at 650 °C. Subsequently, over a 10 h period, temperature was raised to 1580 °C and was left at this temperature for another 30 minutes. After rapid cooling of the crucible in water, a clear glass was produced.
The glass was crushed to a fine powder in a mortar and divided into 10 fractions. To 9 of these fractions, a source of boron was added and all fractions underwent a second melting step at 1580 °C for a period of 5 to 60 minutes. An overview of all treatments is given in Table 1.

1.2 Boron analysis in HIMT glass
The HIMT glasses spiked with boron were again crushed in a mortar to a fine powder. Each sample underwent a multi-step closed beaker hot plate acid digestion procedure with two evaporation steps at 70 °C in the presence of mannitol to limit B evaporation. Finally, all samples were redissolved in 0.02 M HCl and diluted in 0.5 % (w/w) HF. Boron concentrations were determined using an Element XR ICP-MS instrument at medium mass resolution setting. An overview of B concentrations and recoveries in all glass samples is given in Table 1. From Table 1, it is clear that boric acid was almost completely lost during the second melting procedure at 1580 °C. When borax was used as a source of B, recoveries were ≤ 33 %, indicating that B easily evaporates during the melting at 1580 °C. After 1 h at this temperature, only 5 % of the B added was recovered.

Table 1 - Overview of glass samples: boron source, melting time, B concentrations

N.	B source	Melting time	B conc. added	B conc. found[a]	B recovery[b]
		Min	µg/g	µg/g	%
1	Borax	10	9814	1502	15.3
2	Borax	10	9814	1553	15.8
3	Borax	60	9814	506	5.1
4	Boric acid	10	21700	221	1.0
5	Boric acid	10	21700	339	1.6
6	Borax	5	313	104	32.6
7	Borax	10	214	63	28.7
8	Borax	10	313	80	24.9
9	Borax	30	214	66	30.0
10	/	10	0	2	n.a.

a: determined concentrations were multiplied with a factor of 1.3, as in previous work we experienced an average loss of B of 30 % during sample digestion.

b: recoveries calculated after correction of concentrations for procedural blank (no. 10)

2. $CaCO_3$ pellets spiked with B

Eight fractions of $CaCO_3$ were spiked with either 50 µg/g or 500 µg/g of NIST 951 B isotopic standard and were homogenized by stirring after addition of 1 ml Milli-Q water per g of $CaCO_3$. After drying at 40 °C, the spiked powders were mixed with a chemical binder, Ceridust 3610 PE wax or Ceridust 3920 F PTFE-modified PE wax, with relative binder to $CaCO_3$ weights of 0.05, 0.10, 0.25 and 0.50.
Of each mixture, 0.75 g was pressed into a pellet applying a 5 ton pressure for 1 minute.
According to visual evaluation, all pellets were suitable for further analysis with laser ablation, although the Ceridust 3920 F pellets appeared to have a smoother surface.
However, as for concentration quantification purposes the pellets are dissolved in 10 % HNO_3 and given the fact that pellets containing the Ceridust 3610 dissolved more easily, it was decided to select the pellets containing 5 % (w/w) of Ceridust 3610 for further experimental work.

Final conclusions and outlook:
During the three day research visit, we succeeded in producing both boron-spiked HIMT glasses and boron-spiked $CaCO_3$ pellets. Due to the volatile nature of B, the fractionation between ^{10}B and ^{11}B as a function of time during glass melting will be the subject of a follow-up study. Both glass and $CaCO_3$ pellets will be used as calibration standards in analyses with LA-MC-ICP-MS.

Please include:

- Publications arising/planned (include conference abstracts etc)

No specific publications and/or conference abstracts in preparation. The three day research visit delivered excellent starting material for further studies, but the results – at the current stage – are of a preliminary nature and cannot be published yet.

- Host approval

The host is required to approve the report agreeing it is an accurate account of the research performed.

This report is an accurate account of the research performed, and we look forward to continuing this project.
-- Dr. Wim van Westrenen (local contact) and Prof. Dr. Gareth Davies (Europlanet coordinator)