Design, Performance tests and Application of Melting System for Trace Element Analysis in a Shallow Firn Cores

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1. Abstract

The melting system of ice core samples has been a useful decontamination device. However, it should be very cautious to remove some pollutants caused by ice core drilling in the outer surface of firn cores with typical melting system due to percolation effect of melted samples. In this study, as a major improvement, the melting head of the melting system was constructed with fluorinated ethylene propylene (FEP) coated Cu divided into two zones due to the physical characteristics of firn core and performance tests such as decontamination efficiency and procedural blanks were systematically conducted with the artificial ice core samples (a cross section of 3.2 cm x 3.2 cm, ~10 cm long). Quality of the measurement data was confirmed by analyzing a certified reference material (SLRS5, 1643e for elements) and - 52.3 ~ 27.5 % of relative errors. Ice core samples were efficiently decontaminated by the melting system, which was verified by the signal intensity ratio (S.I.R.) of melting samples from two zones of melting head. Especially, procedural blank tests indicated that the concentrations of elements in melted samples from inner zone of melting head were very comparable with those of system blanks except for Cu. The melting system was rinsed with 0.1% HNO_3 (total 10 ml) in order to remove memory effects of elements between ice core samples melted in series. The inter-comparisons of conventional mechanical chiseling method and melting system using NEEM firn core (#144, #155) agreed well with experimental results except for Cu. Finally, this technique was applied for the measurement of elements in firn core samples (68.675 ~ 71.425 m) drilled at the NEEM site located at the north-western part in Greenland (77.45° N, 51.06° W, surface elevation 2450 m, mean annual temperature 29 °C, accumulation 0.22m ice equivalent per year).

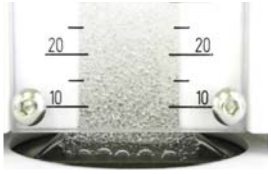

Figure 1. Photo of showing NEEM Firn Core melting processing.

Key words: Melting system, Decontamination, NEEM firn core, Trace element

2. Experimental Method

Melting Method of Ice Core

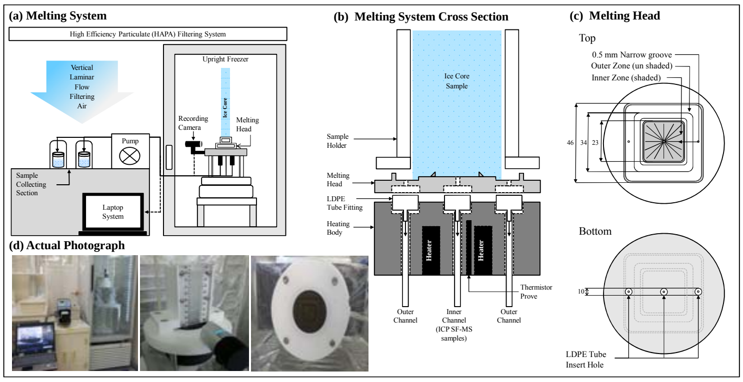

Figure 2. Schematic diagram of the melting system .(a) Melting system in upright freezer of clean booth (sample collecting section class - 10 and upright freezer class - 100); (b) Melting system cross section of the melting head assembly units; (c) Melting head; (d) Actual photograph of melting system.

Details of Melting System

Table 1. Specifications of Melting System

Components	Specifications
Melting Head	
- Material	Fluorinated ethylene propylene (FEP, 50 μm) coated Cu
- Zone	Two (inner and outer zone)
- Type	Rounded square type (inner - 23 mm, outer - 46 mm) Inner zone - Flat surface with narrow groove (0.5 mm) Outer zone - Layered flat surface (34 mm, height - 0.5 mm)
- Surface temp.	38 ± 2℃
- Ice core section	(3.4 ±0.2) × (3.4 ±0.2) cm^2, 10 cm long
- Melting rate (10 cm, RPM 15 to 20)	Inner fraction; 2.56 to 3.42 ml min^{-1} Outer fraction; 1.56 to 2.08ml min^{-1} Melting rate; 0.83 to 0.89cm min^{-1}
- Sample holder	Holder: fluorinated ethylene propylene (PTFE) Frame Scale: Transparent Polypropylene (PP)
- Fitting tubes	Tygon E-Lab tube (Cole-Parmer, CP95608-44 and CP95608-36) Polytetrafluoroethylene (PTEF, Cole-Parmer, #06417-21) Fluorinated ethylene propylene (PFA, Cole-Parmer, #96005-06)
Heating Body	
- Material	Polytetrafluoroethylene (PTFE) coated Al alloy 6106
- Heat source of heating body	200 W Cu rod
Sampling Bottle	
- Material	LEPE wide mouth bottle (NALGENE, 30ml and 60ml)
- Cleaning Method	Nitric acid cleaning method (Hong et al., 2000)
- Distilled water	Milli Q-Academic system (Millipore, Milford, > 18.2MΩ)

Chiseling Method of Ice Core

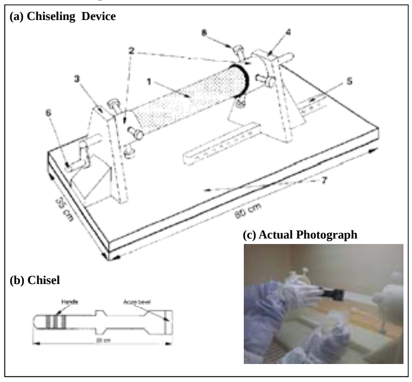

Figure 3. Schematic diagram of (a) the decontamination system, (b) stainless steel chisel used for the chiseling (Candelone et al., 1994) and (c) Actual photograph of decontamination process by chiseling.

3. Results and Discussion

Data Accuracy

Table 2. Concentration of CRM in SLRS5 solution (10 times sample) and melting system procedural blank.

Element	IDL	MSPDL	MSPB	Measured	Certified	RE(%)
^{85}Rb	0.030	0.055	< IDL	1282.7	1300*	1.3
^{88}Sr	0.114	0.117	0.340±0.235	57591.1	53600±1300	-7.4
^{95}Mo	0.041	0.082	0.527±0.082	224.7	270±40	16.8
^{111}Cd	0.028	0.015	0.096±0.030	9.1	6±1.4	-52.3
^{121}Sb	0.028	0.005	0.240±0.005	275.1	300	14.3
^{138}Ba	0.127	0.369	0.208±0.739	15602.0	14000±500	-11.4
^{205}Tl	0.021	0.039	< IDL	4.3	4*	-8.3
^{208}Pb	0.064	0.497	0.935±0.995	75.7	81±6	6.6
^{232}Th	0.129	0.102	< IDL	15.0	13-14*	-10.8
^{238}U	0.018	0.125	< IDL	92.3	93±6	0.8
^{51}V	0.087	0.142	< IDL	404.2	317±33	27.5
^{52}Cr	0.824	0.402	1.139±0.805	239.9	208±23	-15.4
^{55}Mn	0.250	0.218	1.467±0.435	4433.4	4330±180	-2.4
^{56}Fe	4.673	65.629	152.511±131.257	92980.0	91200±5800	-2.0
^{59}Co	0.075	0.256	0.383±0.512	57.4	50	-14.8
^{63}Cu	0.660	26.515	38.808±53.029	18954.7	17400±1300	-8.9
^{66}Zn	1.718	3.704	7.791±7.408	964.8	845±95	-14.2

Note - unit: ng/L; * reference values of reported in 'GeoRem' website;
IDL (Instrumental detection limits, 3σ of 12 times measurement); MSPB (Melting system procedural blanks), MSPDL(Melting system procedural detection limits, 3 σ of 6 times of measurement); RE (Relative errors)

Decontamination Efficiency

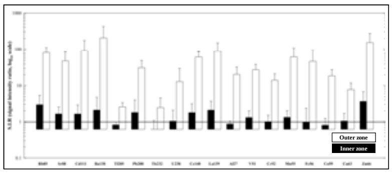

Figure 4. Decontamination efficiencies of trace elements by the melting system. The efficiency was evaluated by the ratios of instrumental intensities between system blank and artificial ice core.

Application for NEEM firn core

The North Greenland Eemian Ice Drilling **"NEEM"** is an international ice core research project aimed at retrieving an ice core from North-West Greenland (camp position 77.45°N 51.06°W) reaching back through the previous interglacial, the Eemian.

source -(image; http://www.wikimedia.com)
(information; http://neem.dk)

Table 3. Comparison of trace elements concentrations recovered from Arctic ice core (unit: ng/L)

	This study			Ref. [1]	Ref. [2]	Ref. [3]	Ref. [4]	Ref. [5]
Elements	Min.	Max.	Avg.					
^{85}Rb	3.8	48.4	13.0		3.7			
^{88}Sr	6.0	131.6	60.2		6.7			120
^{95}Mo	0.5	2.6	1.3					
^{111}Cd	0.4	21.1	2.4	0.3	0.7	0.771		0.2
^{118}Sn	1.2	6.2	3.1					
^{121}Sb	0.12	4.2	1.3		0.5			
^{138}Ba	8.6	174.9	57.9					93.1
^{208}Pb	10.8	58.7	28.5	7.6	4.3	10.2	up to 50	0.5
^{209}Bi	0.48	3.6	1.3					0.1
^{232}Th	0.13	4.3	1.3					
^{238}U	0.04	1.8	0.5		0.01			0.2
^{45}Sc	0.18	1.2	0.5		0.06			
^{51}V	0.19	17.5	6.1		6.7			9.9
^{52}Cr	2.1	26.2	9.4		44.0			3.4
^{55}Mn	11.9	575.8	130.8		10.0			211
^{56}Fe	424.5	6086.2	2377.1		290.0			1250
^{59}Co	0.12	102.5	7.3		2.7			0.65
^{63}Cu	13.5	240.2	93.8	2.8	8.0			2.0
^{66}Zn	51.6	1499.3	373.3	16.0	103.0			
^{27}Al	299.5	6224.4	2028.7	4300.0				200
^{75}As	0.91	25.6	9.4					

Note -
This study (NEEM, Greenland, 1776~1886AD when formal age applied)
Ref. [1] Candelone et al., 1994 (Summit, central Greenland, 1773AD)
Ref. [2] Krachler et al., 2005 (Canadian High Arctic, minimum value since 1845AD)
Ref. [3] McConell and Edwards, 2008 (ACT2, Greenland, annual average during 1772~1860AD)
Ref. [4] McConell et al., 2002 (Summit, Greenland, 1750~1800AD, deduced from Figure 1)
Ref [5] Osterberg et al., 2006 (min values of compiled Greenland ice concentrations since 1491 BP)

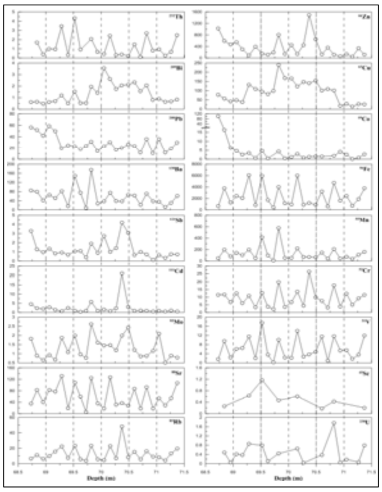

Figure 5. The concentrations of trace elements in the NEEM firn core (68.675 ~ 71.425 m).

Inter-comparisons of Chiseling Method and Melting System

Figure 6. Inter-comparisons of the trace elements concentrations of NEEM firn core samples treated by chiseling (white bar) and melting (black bar). (a) 78.585 ~ 79.135 m; (b) 84.545 ~ 85.195 m

4. References

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