Improvement and performance testing of melting system for measurement of trace elements in firn core drilled at NEEM site, Greenland

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SUPPLEMENTARY MATERIAL

Operating procedures of the melting system

The operating procedures of the firn core melting system were similar to those reported by Hong and others (2015) [1] with modifications to the cleaning method of the melting system between melting procedures to reduce the system BLs of elements.

The PFA and PTFE connection tubes and peristaltic pumping tubes were connected to the melting head and were rinsed with UPW, 1% HNO_3 (ultra grade), and 0.1% HNO_3 (ultra grade) for 10 min each, and then again with UPW for 20 min. After the melting head had been assembled into the melting system inside the freezer, the temperature of the heating body was controlled at ~38 ± 2ºC (type A melting head) or ~ 33 ± 2ºC (type B melting head). Then, the surface temperature of the melting head was consistently checked, especially when the temperature inside the freezer fell below 0ºC.

Before the firn core samples were melted using the melting system, the melting processes were tested with AIC sections to confirm that the system was properly operating. Key parameters, including the melting rate and the volumes of the melted samples from the inner and outer zones of the melting head, were also continuously examined during melting of the firn cores. It is important to periodically exchange the peristaltic pumping tubes because their elasticity can affect the draining rate of the melted samples

through the inner and outer zones. In addition, when the tubes were not in use, they were disconnected to maintain their flexibility.

After the AICs had been melted, the melting system was cleaned with ~ 25 ± 5 mL UPW (~ 40 ± 5 mL 0.1% HNO_3 (ultra grade), and then ~ 40 ± 5 mL UPW for the type B-head melter) through the type A melting head, and ~ 20 mL UPW (~ 10 mL UPW for the type B-head melter) through just the inner zone of the melting head. Then, ~ 10 mL UPW that had flowed out from the inner zone was collected as a system blank to examine the cleanliness of the melting system. The firn core section was placed on the melting head after chiseling the bottom of the core with a clean ceramic knife (FK-110WH, Japan) in case the temperature inside the freezer again fell below 0ºC. It is crucial that the temperature inside the freezer should remain below 0ºC during melting procedures to prevent any melting of the firn core due to the ambient temperature. The melted samples flowed out from the freezer through PFA connection tubes capped with insulating tubes and were collected discretely in sample collection bottles with a depth resolution of ~11±2 cm. The depth resolution was determined based on the accumulation rate of the drilling site and research objectives. The sample collection bottles used for trace elements were thoroughly cleaned using a well established method [2]. After the firn core samples had been melted, the system blanks (~10 mL UPW drained through just the inner zone) were also continuously collected to examine the levels of elements that remained in parts of the melting system.

After the melting processes was complete each day, the melting system was cleaned again by passing ~40 ± 5 mL UPW through the melting head, and the bottom of melting head in direct contact with the heating body was also thoroughly cleaned with UPW. Then, 0.1% HNO_3 (ultra grade) was circulated slowly overnight through the melting head attached to the connection tubes (PFA, PTFE, and peristaltic pumping tubes).

Cleanliness of laminar flow hood

The concentrations of dust with diameter larger than 0.5-μm were consistently measured near the sample collection bottles and the melting head during the preparation period. The dust concentrations measured in the air around the melting system indicated suitable cleanliness during firn core melting procedures. Although the dust concentrations near the sample collection bottles sometimes reached ~1060 particles m^{-3}, they were generally close to zero, which verifies the clean conditions of the air surrounding the bottles. Near the melting head, dust concentration levels were ~10600–14100 particles m^{-3} in the early stage of the preparation period but mostly less than ~3500 particles m^{-3}. These results indicate that the concentrations of dust around the melting head were generally higher than those near the sample collection bottles. This is primarily due to the dispersed dust from the floor by the opening and closing of the refrigerator door and also the cooling fan operating in the bottom of the freezer, despite the fact that an adhesive mat had been placed on the floor in front of the refrigerator.

Table S1. Analytical conditions of inductively coupled plasma sector field mass spectrometry (ICP-SFMS) for the analysis of trace elements in melted sample of firn cores

	Description
System	HR ICP-MS (Element 2)
Plasma power	1250 W
Cool gas	16 L min^{-1}
Aux gas	0.73 L min^{-1}
Sample gas	0.93 L min^{-1}
Guard Electrode	Yes
Sample introduction	Apex with Actively Cooled Membrane (ACM)
Instrumental sensitivity	daily optimized (~1000000 cps for ^{115}In/ ~1500000 cps for ^{238}U)
Double charged ion level	<9 % ($^{137}Ba^{2+}/^{137}Ba$)
Oxide level	<0.1 % ($^{137}BaO/^{137}Ba$)
Stability	<1 %

Table S2. Instrumental detection limits and accuracy tests of inductively coupled plasma sector field mass spectrometry (unit: ng L^{-1})

Element	IDL[a]	Measured conc.	Certified conc.[b]	RE(%)[c]
V(MR)	0.087	404.2	317±33	-27.5
Cr(MR)	0.824	239.9	208±23	-15.4
Mn(MR)	0.250	4433.4	4330±180	-2.4
Co(MR)	0.075	57.4	50[d]	-14.8
Rb(LR)	0.030	1282.7	1240±370[e]	-3.4
Sr(LR)	0.114	57591.1	53600±1300	-7.4
Cd(LR)	0.028	7.7	6±1.4	-28.1
Ba(LR)	0.127	15602.0	14000±500	-11.4
Tl(LR)	0.021	4.3	3.9±2.4[e]	-11.1
Pb(LR)	0.064	75.7	81±6	6.6
Th(LR)	0.129	15.0	13.6±3.3[e]	-10.0
U(LR)	0.018	92.3	93±6	0.8

[a] Instrumental detection limit (IDL) was calculated by 3σ of 12 distilled water samples

[b] Certified values of CRM (SLRS5) [3], [c] Relative error, [d] Information values [3], [e] Reference values [4]

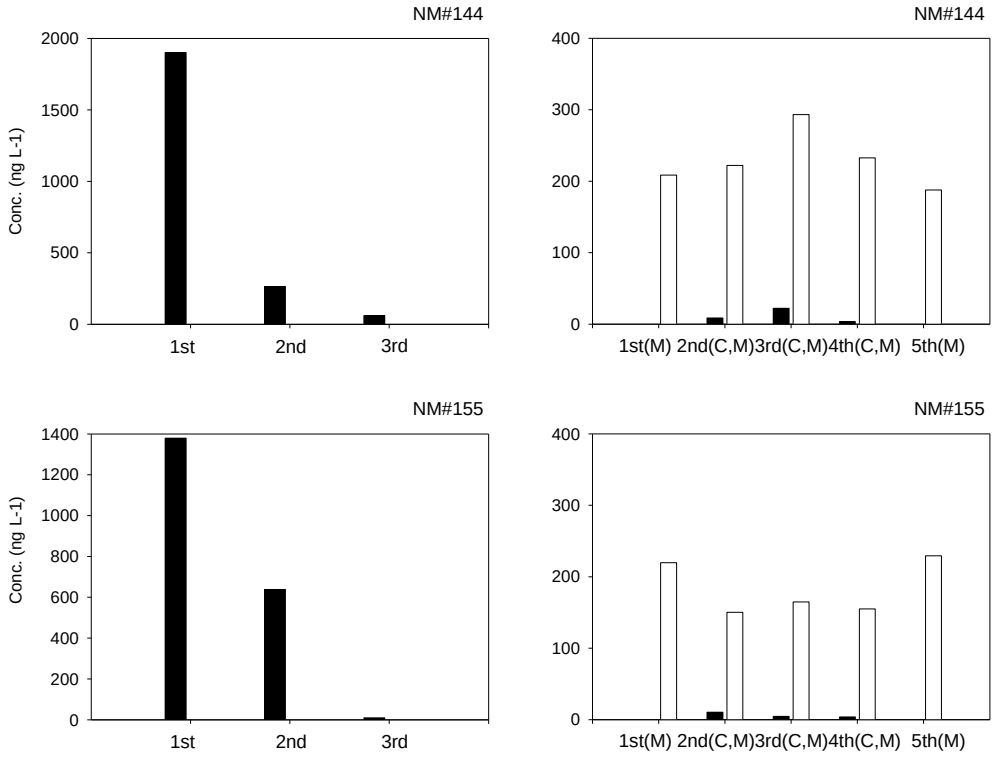

Figure S1. Comparison of concentrations of Cu in firn core samples (NEEM #144, NEEM #155) from conventional chiseling and melting method with FEP coated Cu melting head (black bar: chiseling technique, white bar: melting method, 1st, 2nd, and 3rd layers indicates sliced samples in series from the outer most surface and 2nd(C,M), 3rd(C,M), and 4th(C,M) indicates 2nd, 3rd, and 4th decontaminated samples with depth resolution of ~10cm in the inner part using chiseling and melting method, respectively)

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