Si and S isotopic ratios in environmental and biological samples using MC-ICP-MS

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INTRODUCTION

	Si	S
Importance	7^{th} most abundant element in the universe; Essential for terrestrial life: SiO_2 is a dietary requirement for various organisms; Found in silica form and in uncountable variations from the natural silicates (e.g. talc, mica etc)	10^{th} most abundant element in the universe; Essential for terrestrial life: one of the components that make up proteins and vitamins; Found in a variety of different forms in nature because it can possess a +6 to -2 oxidation state
Isotopic fractionation	Important to address different aspects of global aquatic cycles of Si; Fractionation can occur either due to biological processes or due to inorganic processes.	Used in hydrology to trace natural and anthropogenic sources of S. Fractionation occurs by two processes in nature: 1) equilibrium fractionation during inorganic reactions between sulfur bearing ions, molecules and solids; 2) fractionation due to the reduction of sulphate ions (by either inorganic process or biogenic processes).

Stable isotopes, (abundance, %)	^{28}Si (92.18)		^{29}Si (4.71)			^{30}Si (3.12)	^{32}S (94.93)	^{33}S (0.76)		^{34}S (4.29)	^{36}S (0.02)		
MC-ICP-MS detection	Yes		Yes			Yes	Yes	Yes		Yes	No		
Main interferences (resolution)	$^{12}C^{16}O$ (1557)	$^{14}N^{14}N$ (958)	$^{12}C^{16}O^{1}H$ (1104)	$^{14}N^{14}N^{1}H$ (774)	$^{28}Si^{1}H$ (3504)	$^{14}N^{16}O$ (1239)	$^{16}O^{16}O$ (1801)	$^{16}O^{16}O^{1}H$ (1259)	$^{32}S^{1}H$ (3908)	$^{16}O^{18}O$ (1297)	^{36}Ar (77366)	$^{35}Cl^{1}H$ (3748)	$^{18}O^{18}O$ (1152)
Desolvation	+	–	+	+	+	+	+	+	+	+	–	+	+

INSTRUMENTATION AND MATERIALS

MW sample preparation: **Microwave sample preparation workstation (Ethos, Milestone, Monroe, CT, USA);**

Sample introduction: **Apex-Q (Elemental Scientific Inc., Omaha, NE, USA); Aridus (CETAC Technologies, Omaha, NE, USA);**

Reference materials for bracketing: **NIST-8546 (NBS-28, Silica Sand, SiO_2) and NIST-8554 (NZ1, Silver Sulfide, Ag_2S) ;**

Detection: **NEPTUNE (Thermo Scientific, Bremen, Germany).**

RESULTS AND DISCUSSIONS

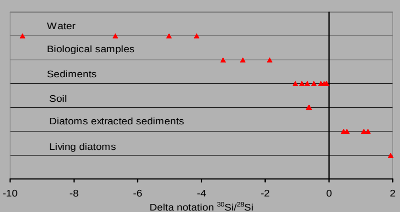
Si using MC-ICP-MS

Cups configuration:

Analytical performances:

		Original	APEX	Aridus
Average sensitivity measured at m/z=28 for 10ppm of Si, V		0.162	1.13	1.45
% of interferences from the total signal	m/z = 28	~ 70%	~ 30%	‹ 3%
	m/z = 29	‹ 5%	low	low
	m/z = 30	low	low	low
Internal precision, RSD, %	$^{29}Si/^{28}Si$	0.040	0.347	0.004
	$^{30}Si/^{28}Si$	0.046	0.58	0.005
	$^{30}Si/^{29}Si$	0.98	4.8	0.009
Potential monitored area, amu		0.008	0.012	0.017

$\delta^{30}Si$:



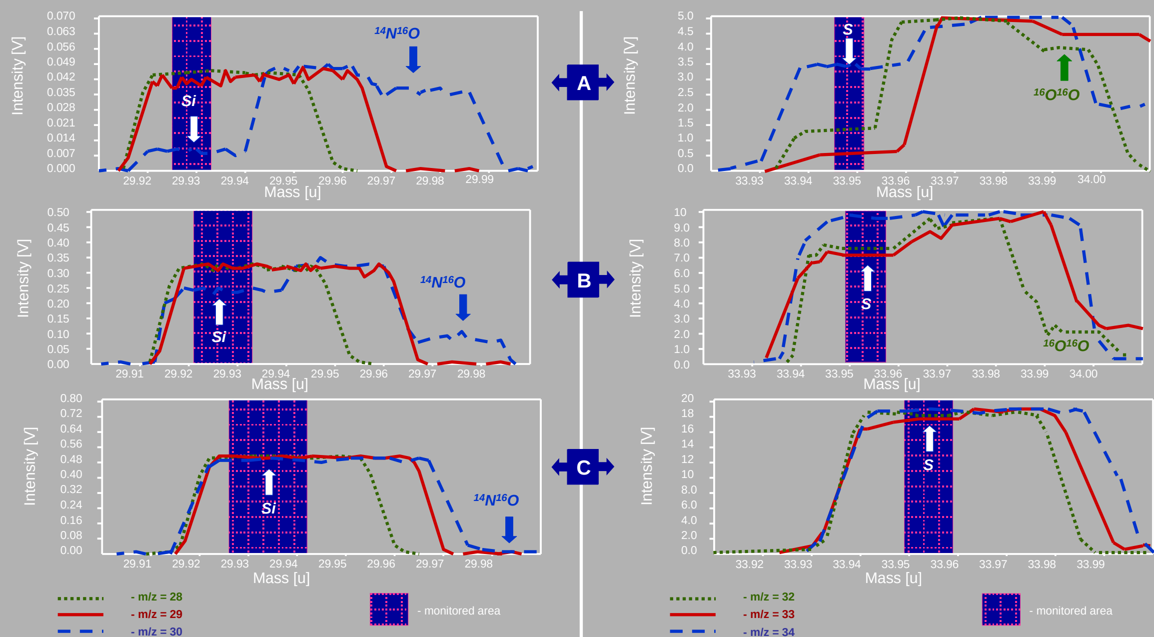


Figure 1. Comparison of different sample introduction systems for the measurement of silicon isotopic ratios:
A – original NEPTUNE nebulizer; B – APEX high sensitivity desolvating unit; C – ARIDUS desolvating sample introduction system

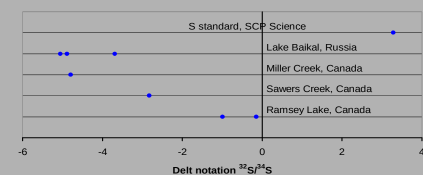
S using MC-ICP-MS

Cups configuration:

Analytical performances:

		Original	APEX	Aridus
Average sensitivity measured at m/z=32 for 10ppm of S, V		1.65	6.96	19.4
% of interferences from the total signal	m/z = 32	~ 85%	~ 15%	low
	m/z = 33	~ 97%	~ 20%	‹ 3%
	m/z = 34	~ 33%	‹ 3%	low
Internal precision (n = 100), RSD, %	$^{33}S/^{32}S$	0.022	0.0090	0.046
	$^{34}S/^{32}S$	0.0054	0.0019	0.0037
	$^{33}S/^{34}S$	0.019	0.0095	0.049
Potential monitored area, amu		0.006	0.009	0.011

$\delta^{32}S$:



*S isotopic composition for NIST-8554: 94.8871 atom % ^{32}S; 0.7563 atom % ^{33}S; 4.3463 atom % ^{34}S; 0.0103 atom % ^{36}S

CONCLUSIONS

- MC-ICP-MS in medium resolution mode allows precise measurement of Si isotopic ratios for all 3 stable Si isotopes;
- Desolvating unit ARIDUS gives the best analytical characteristics and removes all major interferences;
- Preliminary results demonstrate clear fractionation of Si isotopes between different type of samples.

- MC-ICP-MS in medium resolution mode allows precise measurement of Si isotopic ratios for 3 out of 4 stable S isotopes;
- Desolvating unit ARIDUS gives the best analytical characteristics and removes all major interferences for ^{34}S and ^{32}S;
- Preliminary results demonstrate that filtrated water samples enriched with heavier ^{34}S isotope.