Evaluation of the Mg doping approach for Si mass fractionation correction on Nu Plasma II MC-ICP-MS

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Introduction

The high ionization efficiency and high sample throughput of MC-ICP-MS, make it an obvious choice for precise and accurate Si isotope measurements. There are, however, a few analytical challenges:
- polyatomic interferences
- significant mass fractionation drift
- potential matrix effects due to the high ionization efficiency of the ICP source for most elements

The Pseudo-High Resolution capability of the Nu Plasma II MC-ICP-MS allows simultaneous measurements on the interference-free shoulders of Si isotopes. Matrix effects can be reduced via rigorous chemical purification and sample-standard bracketing (SSB) is used to correct for the instrumental mass fractionation. This correction, however, may not always be sufficient, as the instrumental fractionation drift between two analyses may be significant (Cardinal et al., 2003).

As an alternative, Mg may be added to the Si solutions to be used as an external standard. There have been debates in the literature regarding the benefit of using Mg for Si mass fractionation correction (De La Rocha et al., 2002; Cardinal et al., 2003; Zambardi et al., 2010). It is argued that adding Mg may worsen matrix effects leading to mass fractionation instability with larger drift in Mg than Si (Georg et al., 2006).

Experiments

Experiments were performed in both 'wet plasma' and 'dry plasma' modes on the Nu Plasma II (Fig. 1). Both SSB and Mg doping were adopted for the Si mass fractionation correction for comparison. Effects of various Si to Mg ratios as well as the presence of different cation matrices were also investigated.

Fig 1. Nu Plasma II MC-ICP-MS

Solution was introduced in 2% HNO_3 acid, using an Aridus-II Desolvating Nebuliser System (dry plasma) or a PFA cyclonic spray chamber (wet plasma), with a 90 μL/min PFA concentric nebuliser (dry plasma) or a 140 μL/min PFA concentric nebuliser (wet plasma), and the Enhanced Sensitivity interface. A sapphire injector was attached to a Si-free fully ceramic demountable torch (D-Torch, Glass Expansion). The sapphire injector produces lower interferences and Si background for a comparable sensitivity. After plasma ignition, a 3h period of stabilisation was allowed prior to the measurements to minimise plasma instability period caused by Si introduction (Cardinal et al., 2003).

Data was collected using dynamic analysis. Each analysis consisted of 2 blocks of 25 integrations of 5 s on-peak measurements of Si in cycle 1 and 2 blocks of 25 integrations of 5 s on-peak measurements of Mg in cycle 2, following an 'on peak' blank measurement of a 2% HNO_3 solution with an integration time of 60 s. A 150 s wash was performed after each analysis. No tuning of the instrument or nebuliser was made once the measurement sequence had started. Measurements were carried out on the interference-free shoulders of the ^{28}Si, ^{29}Si and ^{30}Si peaks, in the Pseudo-High Resolution mode (50 μm source defining slit, medium resolution) with a resolving power of approximately 8,100 (5, 95% Edge Resolving Power) at 10% transmission.

Si isotopes partially resolved from their respective interferences in Pseudo-High Resolution mode are shown in Fig. 2. The potential doubly charged ion interference from $^{58}Ni^{2+}$ was negligible as singly charged $^{58}Ni^+$ was not observed in a previous magnet scan.
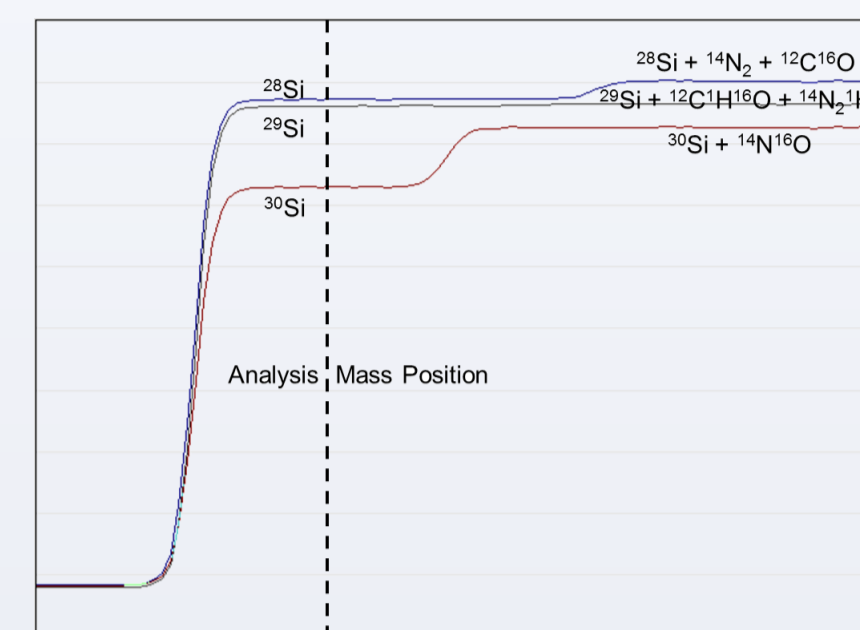

Fig 2. Si isotopes ^{28}Si, ^{29}Si and ^{30}Si partially resolved from their respective interferences in the Pseudo-High Resolution mode using the 50 μm source defining slit.

Si sensitivity achieved in the Pseudo-High Resolution mode was approx. 20 volts/ppm on 'dry plasma', and 1.8 volts/ppm on 'wet plasma', at 10% transmission. The Si blank after a 150 s wash was observed to be below 1 ppb. As reported by Georg et al. (2006), it was observed that the background increased over the first few hours due to the accumulation of Si in the introduction system and remained stable afterwards. Although dilute HF may help reduce the Si blank, it may also cause instrumental fractionation instability, and suppress the Si signals by a factor of 20% - 30% (Georg et al., 2006), therefore only 2% HNO_3 was used for wash. Typical internal precision of the measured $^{29}Si/^{28}Si$ was better than 0.025‰ (2SE).

Results & Discussion

For 'dry plasma', a 500 ppb Si Alfa Aesar ICP standard solution doped with Mg SRM 980 standard solution with [Si]/[Mg] ratio of 1:1 was used for repeat analyses over 24 hours. The measurement sequence was repeated for the same Si solution doped with [Si]/[Mg] ratio of 2:1. Similar experiments were conducted in the 'wet plasma' mode, using 5 ppm Si Alfa Aesar + Mg SRM 980. In Fig. 3, $\log(^{30}Si/^{28}Si)$ is plotted against $\log(^{29}Si/^{28}Si)$ for all raw ratios analysed in wet and dry plasma modes. The two display a linear correlation ($R^2 = 0.9999$) and the slope of the fractionation line is within errors to the theoretical mass dependent kinetic fractionation value of 2.0, indicating strictly exponential mass dependent fractionation throughout the period of measurement with the presence of Mg matrix at different levels.
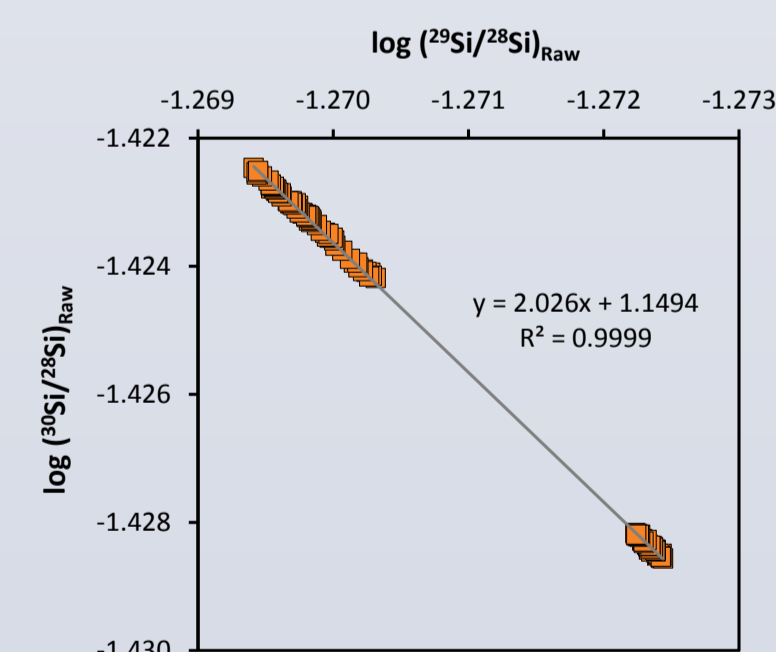

Fig 3. Linear correlation between $\log(^{29}Si/^{28}Si)$ and $\log(^{30}Si/^{28}Si)$ of ratios measured in wet and dry plasma modes. The slope of the fractionation line is within errors of the theoretical value of 2.0.

The Mg doping approach assumes identical β_{Si} and β_{Mg}. However, various studies suggested that the relationship of the two may vary between different analytical sessions (De La Rocha, 2002; Cardinal et al., 2003). Fig. 4 plots $\log(^{29}Si/^{28}Si)$ against $\log(^{25}Mg/^{24}Mg)$ for measurements performed in the a) 'wet plasma' mode, and b) 'dry plasma' mode. Although the β_{Si}/β_{Mg} ratios are slightly different between the two plasma modes, the difference is, quite small and may be mainly due to the shifting mass fractionation between the two different plasma modes. All β_{Si}/β_{Mg} ratios fall within the empirical range of 0.95 - 1.27 reported by Cardinal et al. (2003). The two 16 h analytical sessions measured in 'wet plasma' mode, as well as the two 24 h sessions measured in 'dry plasma' mode, both yielded consistent β_{Si}/β_{Mg} ratios, respectively, suggesting a satisfyingly small day-to-day variation in the relationship between the mass fractionation coefficients of Si and Mg in the operating plasma mode. These small variations may be monitored and corrected for by using the experimental slope obtained on a daily basis (Cardinal et al., 2003).
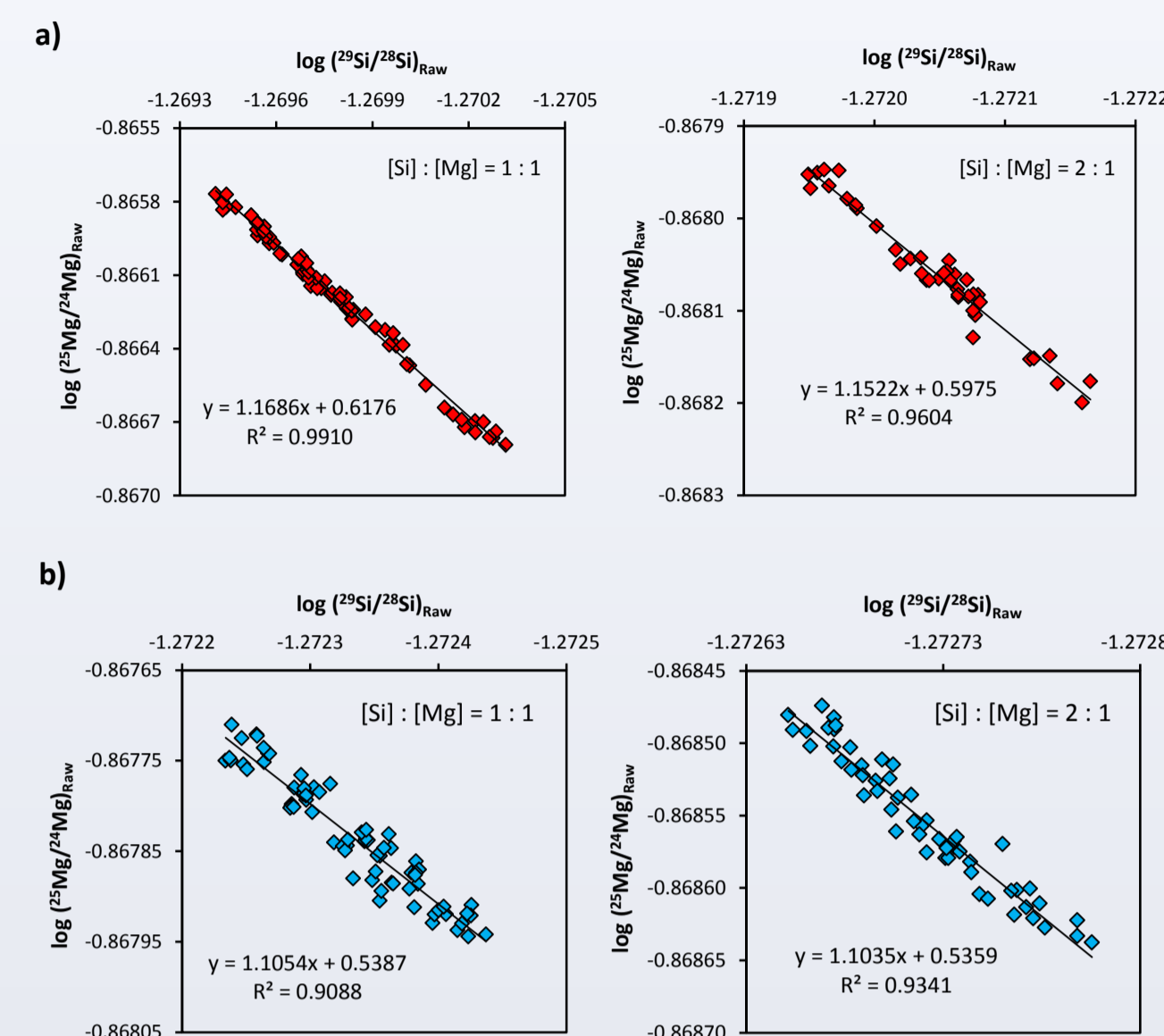

Fig 4. $\log(^{29}Si/^{28}Si)$ versus $\log(^{25}Mg/^{24}Mg)$ measured during the two a) 'wet plasma' analytical sessions and two b) 'dry plasma' analytical sessions. The slopes of the trend lines define the β_{Si}/β_{Mg} ratios.

Measured Si ratios are compared with the Mg corrected Si ratios (for the sequence of [Si]/[Mg] ratio = 1:1) in Fig. 5. It is noticed that the Mg correction has greatly reduced the Si raw ratio drift in both 'wet' and 'dry' plasma modes.
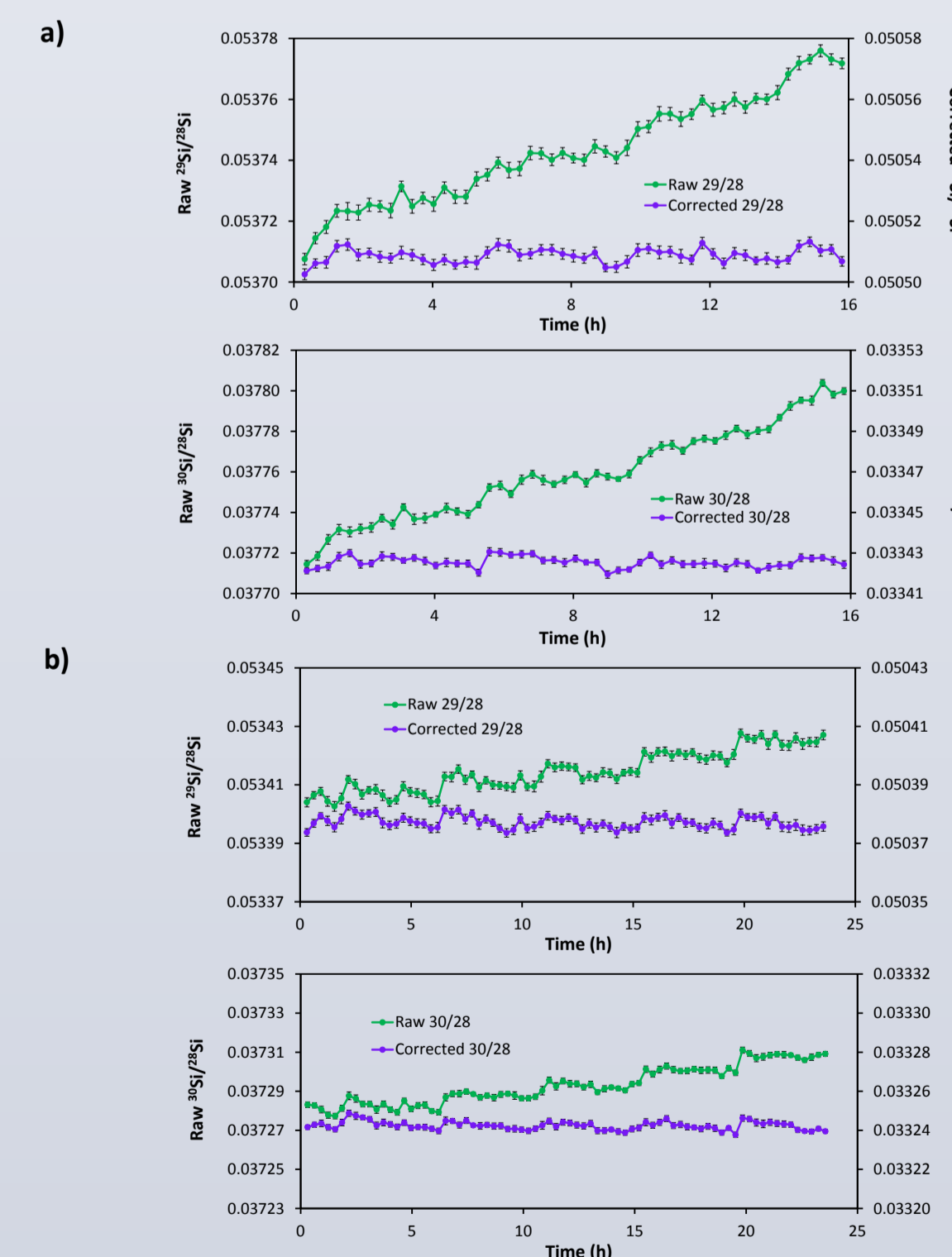

Fig 5. a) Raw Si ratios versus Mg corrected Si ratios measured on 'wet plasma' during an analytical session of 16 h. b) Raw Si ratios versus Mg corrected Si ratios measured on 'dry plasma' during an analytical session of 24 h. Error bars are 2SE.

The external reproducibility of the Si raw ratios, SSB corrected ratios, Mg corrected ratios, and ratios corrected using the combination of the two approaches are compared in Table. 1, for both wet and dry experiments. The SSB correction yielded δ values within errors of 0‰ as expected.

Table 1. Comparison of the external reproducibility (2σ) of the Si raw ratios with Si ratios corrected using different approaches.

Plasma modes	Ratios	Raw (‰)	SSB Correction (‰)	Mg Correction (‰)	SSB + Mg Correction (‰)
Wet	29/28	0.64	0.10	0.09	0.06
Wet	30/28	1.19	0.16	0.16	0.11
Dry	29/28	0.26	0.08	0.08	0.06
Dry	30/28	0.52	0.12	0.12	0.09

From Table 1, both SSB and Mg correction produce similar external precisions, ranging from 3 - 7 fold improvement comparing with the raw ratios. The combination of SSB and Mg correction produces the best external precisions. This suggests Mg normalisation in the short 5 s cycles can sufficiently correct for the short term Si ratio drift as a quasi-instantaneous correction, while daily variations between the fractionation coefficients of Si and Mg can be adequately corrected for with the SSB approach being used in combination (Cardinal et al., 2003).

Natural samples may contain variable matrices, the presence of which can affect the reproducibility of the isotope measurement (Zambardi et al., 2010). Cationic species that are not separated from Si could cause potential matrix effects (Georg et al., 2006) as is demonstrated in Table 2. For this work, the above Si-Mg solutions have all been doped with a 20 fold concentration of either Na matrix or Ca matrix, respectively.

Table 2. Comparison of the external reproducibility (2σ) of the $^{29}Si/^{28}Si$ raw ratios with the ratios corrected using different approaches. Same solutions as used in Table 1 were spiked with Ca or Na to reach a [matrix]/[analyte] ratio of 20:1.

Plasma modes	Matrix	Raw (‰)	SSB Correction (‰)	Mg Correction (‰)	SSB + Mg Correction (‰)
Wet	Ca^{2+}	0.32	0.18	0.56	0.48
Wet	Na^+	0.14	0.13	0.47	0.43
Dry	Ca^{2+}	2.45	0.37	1.57	0.37
Dry	Na^+	0.67	0.19	0.49	0.20

As is shown in Table 2, significant matrix effects were observed even after the SSB correction. Albarède and Beard (2004) concluded that, non-silicic species may modify the ionization of the analyte and lead to non-spectral matrix effects that cannot be corrected by simple SSB correction. Mg can not then be used for the correction of Si fractionation since the mass fractionation behaviour of Mg and Si no longer correlate.

Conclusions

- The β_{Si}/β_{Mg} ratios are consistent and only show small day-to-day variations on the Nu Plasma II in both wet and dry plasma modes, enabling effective Mg external normalization of Si isotope ratios.
- Although it is argued that the presence of Mg may cause a matrix effect, the combination of the Mg doping and SSB appears to provide the most effective correction for Si on the Nu Plasma II regardless of the sample introduction systems.
- Mg doping cannot effectively correct for Si instrumental mass fractionation in the presence of certain matrix (e.g. Na, Ca) elements.

References

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