Characteristic Performance of Guard Electrode in LA–SF–ICP–MS for Multi-Element Quantification

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ABSTRACT: The performance characteristics of the use of a guard electrode in laser ablation–sector field–inductively coupled plasma–mass spectrometry for multiple element quantification were investigated in this study. The guard electrode (GE) shapes and increases the ion density of the plasma prior to injection into the sample cone. The results illustrate that the GE shifts the ionization zone back to the sample cone which requires a larger carrier gas flow rate for compensation. The signal intensity of 55 elements was enhanced by a factor of 3–20 with the use of GE (hereafter denoted “GE-on mode”) compared to that without using GE (hereafter denoted “GE-off mode”), however, at the cost of higher oxide and doubly charged ion yields. The enhancement capability was negatively correlated with elemental mass number. Elements with low mass number showed a large sensitivity improvement. The limits of detections were not improved in the GE-on mode due to the enhanced background intensity. Ion transmission efficiency was improved by a factor of 3–20 and the linear relationship between mass number and transmission efficiency in GE-off mode is changed to the quadratic relationship in GE-on mode. Mass discrimination may be limited to lower mass elements with no further increase at >100 a.m.u. The ion profile in ICP illustrated that the GE increases the ion density of the plasma, which is probably related to the reduced ion kinetic energy distribution. The analyses of seven MPI-DING and one USGS glass reference materials show that the analytical precision in the GE-on mode is improved by a factor of 2–4 in comparison to the GE-off mode, and accuracy is almost identical in both modes.

INTRODUCTION

Laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS) as a prominent micro-analysis technique has been widely used in the geosciences,^{1,2} such as in situ quantitative analysis of multi-elements in glasses and minerals,^{3,4} zircon U–Pb geochronology,^{5,6} and isotope ratio determination.^{7–11} To improve the precision and accuracy of in situ trace-element and isotope analysis and to apply LA–ICP–MS to small or isotopically heterogeneous samples, greater analytical sensitivity is required.^{12,13} Approaches for signal enhancement mainly involves four aspects: (a) flushing a small amount of diatomic molecular gas (e.g. H₂, N₂ and O₂) or H₂O into the carrier gas,^{12,14–16} (b) modification of sample and/or skimmer cones,^{8,17–19} (c)

improvement of vacuum system^{19,20} and (d) using the guard electrode (GE) (or called “shielded torch”). Studies of the first three aspects have been carried out in recent years. Previous studies^{12,15,16,22} reported that adding a small amount of H₂, N₂ or O₂ into the carrier gas could achieve a signal enhancement and improve the ICP ionization efficiency, while hydrogen-, nitrogen- or oxygen-based polyatomic interferences increase. Hu *et al.*⁸ showed that instrument sensitivity of hafnium can be increased effectively using the X skimmer and Jet sample cones, but at the cost of a larger non-linear mass fractionation. Yuan *et al.*²¹ and Kimura *et al.*²⁰ documented that an improved interface vacuum can achieve several-fold greater sensitivity without sacrificing measurement accuracy.

Compared to the addition of a small amount of diatomic molecular or H₂O and/or improvement (or reconstruction) of the vacuum system, application of the guard electrode is convenient and does not introduce any extra matrix, but it may be related to stronger polyatomic interferences²³ and higher oxide formation.²⁴ Appelblad *et al.*²⁴ systematically investigated the performance of the guard electrode with a solution ICP–MS method and reported that using the guard electrode could lead to a signal enhancement, but also with high oxide formation and severe non-spectral interferences. Becker *et al.*²⁵ reported that application of the guard electrode yielded greater sensitivity with a factor of up to 5 using the Meinhard, MicroMist microconcentric and ultrasonic nebulizers. Chen *et al.*²⁶ documented that the sensitivity of 39 investigated elements was increased by a factor of 17–58 using the guard electrode, and both the CeO⁺/Ce⁺ and Ce²⁺/Ce⁺ ratios were suppressed with the addition of 4% ethanol. A shielded torch has merits, including diminished plasma offset potentials, reduced kinetic energy distribution and improved ion transmission efficiency. Xu *et al.*¹⁰ documented that influence of the guard electrode on the sensitivity of LA–MC–ICP–MS was minimal for dry plasma, but it became significant in the presence of N₂. Tong *et al.*²³ showed that using the guard electrode led to a two-fold sensitivity enhancement for Sr, but it significantly increased the yield of polyatomic ion interferences (Ca-related ions and TiAr⁺). These previous studies mainly focused either on solution (or called “wet plasma”) ICP–MS or on a single-element analysis (e.g. Sr²³ or Nd¹⁰) with LA–ICP–MS. However, few studies were focused on the performance characteristics of the guard electrode for multiple element quantification using LA–ICP–MS. Liu *et al.*²⁷ systematically investigated the impact of guard electrode on the LA–quadrupole (Q)–ICP–MS.

In this study, we carried out a systematical study related to the enhancement effect of guard electrode for a LA–sector field (SF)–ICP–MS with respect to carrier gas flow optimization, yields of oxide and doubly charged ions, as well as the ion profile in ICP. The limits of detection (LODs) in both modes were compared. The signal enhancement effects were investigated from the perspectives of elemental mass numbers, the 1st ionization potential, and transmission efficiency. Precision and accuracy in the GE-on and GE-off modes were evaluated by the measurement of MPI-DING and USGS glass reference materials.

EXPERIMENTAL

Instrumentation. All experiments were carried out on an ELEMENT 2 sector field ICP–MS (Thermo Fisher Scientific, USA) in combination with a 193 nm ArF-Excimer laser ablation system (RESOLUTION M-50, Australian Scientific Instruments, Australia) at the LA–ICP–MS laboratory at the Geowissenschaftliches Zentrum (GZG), University of Göttingen, Germany. Details of instrumental configuration are summarized in Table 1.

Table 1. Typical Operating Conditions of LA–SF–ICP–MS System

<i>Laser ablation system</i>	
Type & mode	ArF-Excimer & RESOLUTION M-50
Wavelength, nm	193
Pulse length, ns	20
Energy density, J cm ⁻²	~3.0
Laser frequency, Hz	5
Ablation cell	Laurin Technic S-155
Spot sizes, μm	23, 50
Ablation gas (He), mL min ⁻¹	250–1000
Ablation time, s	35
<i>ICP–MS</i>	
Type & mode	Element 2 & magnetic sector-field
RF power, W	1500
GE modes	On and Off
Plasma gas (Ar), L min ⁻¹	15
Auxiliary gas (Ar), L min ⁻¹	1.0
Carrier gas (Ar), mL min ⁻¹	600–1000
Dwelling time, ms	10
Sample cone	Standard sample cone (Ni)
Skimmer cone	H skimmer cone (Ni)
Detector	Dual (Counting and Analog)
Resolution	~300

Helium (He) as the carrier gas was merged with argon (Ar) in the inner cell of a Laurin S-155 ablation cell. We used standard sample cone (Ni) and H skimmer cone (Ni) in this study. A ‘squid’ signal smoothing device was used to improve the signal stability.²⁸

Materials and experimental setup. Two NIST glass reference materials (NIST SRM 610 and NIST SRM 612), seven MPI-DING glass reference materials (StHs6/80-G, ATHO-G, T1-G, ML3B-G, KL2-G, GOR132-G and GOR128-G) and one USGS glass reference material (BCR-2G) were used in this study. The reference values were collected from the GeoReM database (<http://georem.mpch-mainz.gwdg.de/>).

The experiments for carrier gas flow optimization in the GE-off and GE-on modes were carried out using the line scanning ablation mode (spot size: 23 μm, scanning speed: 3 μm s⁻¹) and NIST SRM 612 as the ablation material. The He and Ar flow rates were optimized in the range of 250–1000 mL min⁻¹ and 600–1000 mL min⁻¹, respectively. The ion distribution profiles were acquired by scanning the ICP torch horizontally from -1.4 to +0.2 across the sampler profiles at 10 different sampling depths (e.g. -5.0, -4.5, -3.0, and +2.5).

Measurements of the glass reference materials were performed using the discrete spot mode (spot size: 50 μm). Each measurement consisted of measuring the background signal (10 seconds), followed by 50 s ablation of a glass reference material. NIST SRM 610 was used as the primary calibration material and Ca as the internal standard. All other glasses were treated as “unknown”. Data reduction was made in Iolite 3.0 software.²⁹

Guard electrode. The guard electrode is made of platinum and is inserted between the torch and load coil to diminish the plasma offset potential (Fig. 1).²⁴ The offset potential existing between

Fig. 1 Configuration diagram of plasma interface with a guard electrode (modified after Petra *et al.*²³).

plasma and sample cone may lead to serious secondary ion discharge effects and increase kinetic energy spread.^{24,25} The secondary ion discharge effect is one of the main reasons producing doubly charged ions. A large ion kinetic energy spread results in low ion transmission efficiency.

RESULTS AND DISCUSSION

Carrier gas flow optimization. Eggins *et al.*³⁰ and Günther *et al.*³¹ reported that the sensitivity was improved by a factor of 2–3 using He as the carrier gas. Helium has advantages over Ar; for example, it has a higher thermal conductivity, lower density and viscosity. These characteristics could improve the carrier efficiency of ablated particles. Here, we conducted the carrier gas tuning experiment with respect to the He and Ar gas flow rates in the GE-off and GE-on modes. ⁸⁸Sr was used for signal monitoring. The results illustrate that the sum of the He and Ar gas flow rates is an important factor influencing signal intensity (Fig. 2). A sufficient gas flow rate needs to push the ionization zone to the optimum position towards the sample cone. The Ar flow rate seems to be more crucial compared to He, especially when He exceeds 600 mL min⁻¹ in the GE-off mode. This may relate to the reduced ion density and cooling effect of the plasma due to the higher ionization potential of He. The larger gas flow rate in the GE-on mode illustrates that the guard electrode shifted the ionization zone back to the sample cone.

To further understand the guard electrode on different elements, three isotopes, ⁸⁸Sr, ¹³⁹La and ²³²Th, were monitored with the

Fig. 2 Influence of He and Ar gas flow rate on the ⁸⁸Sr signal intensity in GE-off and GE-on modes.

Fig. 3 (a) Signal intensities of ⁸⁸Sr, ¹³⁹La and ²³²Th at GE-on and -off modes as a function of Ar + He gas flow rate. (b) Oxide production (ThO^+/Th^+) and (c) doubly charged ion production ($\text{Ca}^{2+}/\text{Ca}^+$) as a function of Ar gas flow rate in GE-on and GE-off modes. Helium carrier gas flow rate is fixed at 600 mL min⁻¹. The dashed lines indicate the optimal gas flow rate, which is defined on the instrument conditions of optimal sensitivity with the ThO^+/Th^+ ratio of <2%.

change of carrier gas flow rate. The He flow rate was changed ranging from of 250–1000 mL min⁻¹ on the condition that the Ar flow was fixed at 950 mL min⁻¹ in the GE-off and GE-on modes. The results are shown in Fig. 3a where the dashed lines illustrate the optimal gas flow rate.

Fig. 3a illustrates that at the GE-off mode, the signal intensities of the three isotopes increased at a gas flow rate from 1200 mL min⁻¹ to 1500 mL min⁻¹ and declined in the range from 1500–1950 mL min⁻¹. A lower carrier gas flow rate may lead to less ablated particles being carried into the ICP. Higher carrier gas flow rates can result in shorter residence time in the ICP meaning that particles cannot be ionized completely, and a higher gas flow could cause a shift of the optimal position of the plasma ionization zone away from the sample cone.²⁴ At the GE-on mode, the signal intensities of the three isotopes increased with an increase in the gas flow rate, and did not reach a peak in the investigated carrier gas flow range. These results illustrate that the required gas flow rate for the GE-on mode is larger than that of the GE-off mode. The physical principle behind this observation of shifting the ionization zone backward to the sample cone is unclear, but it is probably related to a reducing kinetic energy distribution.

Effects on oxide and doubly charged ions. The spectral interferences caused by oxides (such as ¹³⁷Ba¹⁶O > ¹⁵³Eu) and doubly charged ions (such as ¹³⁸Ba²⁺ > ⁶⁹Ga⁺) are of particular importance for LA-ICP-MS analysis and frequently affects measurement accuracy. In this study, the ThO⁺/Th⁺ ratio was monitored to study the oxide formation rate as there is no naturally occurring isotope at 248, and the Th-O bond is among the strongest known for oxides (878.9 kJ mol⁻¹). Thus, the ThO⁺/Th⁺ yield represents a maximum oxide production rate expected for the given plasma conditions. The Ca²⁺/Ca⁺ ratio represents the doubly charged ion productions. The results are shown in Fig. 3b and Fig. 3c. The ratios are calculated from the background-subtracted signal intensities.

As shown in Fig. 3b, the oxide production rate increases with an increase in Ar gas flow rate in both the GE-on and GE-off modes, which is consistent with previous observations.^{27,32–33} The oxide production rate grew slower with an Ar gas flow rate of less than 1000 mL min⁻¹, while it grew rapidly when the carrier gas flow rate increased to more than 1000 mL min⁻¹. This phenomenon could be explained by the cooling effects of the plasma with an increase in the gas flow rate. Oxide yields in the GE-on mode are larger than of the GE-off mode, indicating that the oxide formation in the GE-on mode may be enhanced at the plasma-interface.²⁷ Further studies need to be carried out to understand the oxide formation in the GE-on mode. Oxide yields should be observed with more attention when using the GE-on mode for LA-ICP-MS analysis.

As demonstrated in Fig. 3c, the Ca²⁺/Ca⁺ ratio increases until it reaches a plateau with an increase in the Ar gas flow rate in both the GE-off and GE-on modes, while the Ca²⁺/Ca⁺ ratio was larger

in GE-on compared with GE-off. Doubly charged ions are mostly formed by secondary discharge (e.g. Skata *et al.*³⁴). A shielded torch could reduce such secondary discharge effects. For example, as described in Chen *et al.*²⁶, compared to GE-off mode, the doubly charged ions (Ce²⁺/Ce⁺) at the optimum nebulizer gas flow rate was reduced by factor of 1.5 for the 2% HNO₃ in the GE-on mode using “wet plasma” SF-ICP-MS. However, our results illustrate that the formation of doubly charged ions may not be only caused by the secondary discharge, at least not for a sector field ICP-MS instrument in the “dry plasma” mode. It is not clearly understood this discrepancy in “wet plasma” and “dry plasma”, but it is probably related to the impact of “water” during ionization process in plasma. Meanwhile, the larger enhancement effect at low mass compared to high mass might also be partly attributed to this phenomenon. As shown in Fig. 4, the estimated enhancement factor at mass number of 20 is approximately two times larger than

Fig. 4 (a) Sensitivity and enhancement factors of 55 investigated elements at GE-on and GE-off modes. The sensitivity is given as the ratio of elemental intensity to their concentrations and corrected by their isotopic abundance. The enhancement factor is given as the ratio of the sensitivity factors in GE-on versus GE-off mode. (b) Limits of detection of 49 investigated elements in GE-on and GE-off modes. (c) Ion transmission efficiency as a function of mass number in GE-on and GE-off modes.

that of mass numbers of 40. Nevertheless, the doubly charged ions should be paid more attention when using the GE-on mode for LA-ICP-MS analysis.

Effects on sensitivity and limits of detection. Fig. 4a shows the sensitivity and enhancement factors of the 55 investigated elements in the GE-off and GE-on modes. The sensitivity factors of all elements are larger in the GE-on mode than that of GE-off mode. The profiles of the sensitivity factor across all elements for both modes are similar, indicating that the guard electrode does not substantially affect ICP ionization. The signal intensities of elements with lower mass numbers have a larger enhancement factor (Fig. 4a). The sensitivity of elements with a low mass number, such as Li, Be and B, were enhanced by a factor of 20, while elements with a high mass number, such as Hf, Th, and U, were enhanced by a factor of only 3. The enhancement factor of P and As with higher 1st ionization potentials (10.49 eV and 9.81 eV, respectively) was much higher than that of their neighbors. Liu *et al.*²⁷ reported that the effect of the guard electrode was negligible for 60 investigated elements in LA-ICP-MS. It is suggested that the difference of mass spectrometry (quadrupole vs. sector field ICP-MS) or the operating parameters may result in variable enhancement effects. The reduced kinetic energy distribution and potential high ionization efficiency in the GE-on mode could explain the enhancement effect observed in this study. The enhanced sensitivity could significantly improve the analytical precision, especially for elements at low concentrations.

Instrument sensitivity is not the only factor influencing the limits of detection (LODs). The background signal also plays a very important role.³⁵ Fig. S1 plots the gas background intensity of 55 investigated isotopes in the GE-on and GE-off modes. The background intensity is substantially higher in the GE-on mode (Fig. S1). For instance, the gas background intensity of REEs increased more than 10-fold. The stronger background signal may be due to the reduced ion kinetic energy distribution with the guard electrode. The LODs are calculated following the protocol proposed by Longerich *et al.*³⁵ using NIST SRM 610 for the GE-on and GE-off modes (Fig. 4b). The results illustrate that the LODs were not improved in the GE-on mode compared to the GE-off mode. For elements with a high mass number, the LODs even became worse. Both the improved sensitivity and background intensity in the GE-on mode are attributed to this phenomenon.

Effects on ion transmission. For the investigation of ion transmission efficiency, elements with similar 1st ionization potential (5.5–7.5 eV) were selected for this study. This test is using the optimized parameters in the GE-off and GE-on modes. Fig. 4c illustrates the sensitivity as a function of mass number for elements with a 1st ionization potential in the range of 5.5–7.5 eV.

A quadratic relationship between sensitivity and mass number was observed in the GE-on mode, while a linear relationship was seen in the GE-off mode (Fig. 4c). The change of ion transmission efficiency from the linear to the quadratic relationship may be related to the reduced ion energy distribution with a shielded torch.

Fig. 5 Radial and axial ion distributions of ^{88}Sr , ^{139}La and ^{232}Th in GE-off mode (Ar gas flow rate: 1000 ml min⁻¹ and 1250 ml min⁻¹) and in GE-on mode (Ar gas flow rate: 1250 ml min⁻¹). The box indicates the sampling areas.

Our results are consistent with Appelblad *et al.*²⁴ These authors investigated the ion transmission efficiency using the guard electrode in solution–ICP–MS. The results clearly illustrate that the observed change in ion transmission efficiency from the GE-off to the GE-on mode is not caused by “dry” versus “wet” plasma conditions. Instead, it is probably related to the effect of the guard electrode. The transmission efficiency in the GE-on mode has a quadratic relationship with mass number, which may reduce the mass discrimination effects for elements with mass number >100 a.m.u. (Fig. 4c).

Effects on spatial profile of ion distribution. The ion distribution in the ICP provides useful information on the reaction of aerosol particles inside the ion source¹¹ and gives valuable inside information on the predominant ionization mechanism³⁵. Our results illustrate that at the GE-off mode, the increase in Ar gas flow rate (from 1000 to 1200 mL min^{−1}) leads a narrow ion spatial distribution. The axial widths of all three elements decrease significantly with an increase in Ar gas flow rate (Fig. 5). The cooling effect along with the large Ar gas flow rate may contribute to this phenomenon. Aghaei *et al.*³⁷ computationally investigated the occurrence of rotational motion of the auxiliary and carrier gas flows. Their studies indicate that a strong rotational motion occurs in the auxiliary gas flow when the Ar carrier gas rate is in a small range, which may also explain our observations. The guard electrode shapes and increases the ion density in the plasma (Fig. 5), which is probably related to the reduced kinetic ion energy distribution. The dependence of ion distributions on atomic mass was found in the GE-off mode at two different Ar gas flow rates, while it is reduced at the GE-on mode. Lower dependence on the atomic mass may partially reduce the mass discrimination effects.

Precision and accuracy. Precision is a particularly important factor for the quality of analytical data. At the optimized parameters in the GE-off and GE-on modes, we assessed the improvement of analytical precision by the signal enhancement. NIST SRM 610 is used as calibration reference material and Ca is applied as internal standard. Multiple analyses (n=12) of 28 elements (including REEs) in seven MPI-DING reference materials (StHs6/80-G, ATHO-G, T1-G, ML3B-G, KL2-G, GOR132-G and GOR128-G) were carried out. Analytical precision is expressed as one time the relative standard deviation (%RSD, n=12). Fig. 6 illustrates the relationship between analytical precision and concentration in logarithmic scale in the GE-off and GE-on modes.

As shown in Fig. 6, the trends of RSD and mass fractions follow a negatively linear relationship in both modes, indicating that the analytical precision is dominated by the Poisson counting statistics instead of the chemical heterogeneity of the samples.³⁸ The analytical precisions for 28 elements are improved by a factor of 2–4 in the GE-on mode. Elements with low mass fractions show better improvement compared to that with high mass fractions. This could be explained by the enhanced signal intensity, which

Fig. 6 Mass fractions versus relative standard deviation (RSD) for selected elements on logarithmic scale in GE-off and GE-on and modes. Elements plotted here include Sc, V, Co, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Th and U.

reduces the uncertainty derived from the Poisson counting statistics, in particular for elements with weak signals. Fig. 6 shows that the analytical precision for the investigated elements in the GE-on mode are less than 10% when the concentration is higher than 0.1 μg g^{−1}.

The accuracy of the GE-on and GE-off modes was evaluated by analysis of ML3B-G, StHs6/80-G and BCR-2G. The results were calculated using NIST SRM 610 as calibration reference material and Ca as internal standard (Fig. 7). The complete data are summarized in Table S1 and plotted in Fig. 7. The accuracy is expressed by the relative deviation (RD, %) and given as [(mass fractions)_{el} - (reference value)_{el}] / (reference value)_{el} × 100). Fig. 7 illustrates that the accuracy of the GE-off and GE-on modes are substantially identical. The analytical results of most elements are within 10% relative deviation to the reference values in both modes. Tong *et al.*²³ reported that the interferences of Ca-related ions and TiAr⁺ on Sr isotopes are enhanced in the GE-on mode, and may seriously impact the accuracy of ⁸⁷Sr/⁸⁶Sr ratios. Fig. 7 shows that the results of Sr in ML3B-G, StHs6/80-G and BCR-2G in the GE-on mode are similar to the GE-off mode and well match the reference values, indicating that the enhanced interference of the Ca-related ions and TiAr⁺ have a limited effect on the quantitative analysis of Sr. It is worth noting that the results of several major elements including TiO₂, MgO and K₂O have a system deviation using NIST SRM 610 as the calibration material. This suggests that matrix effects of these major elements may exist between NIST SRM 610 and geological glasses.

CONCLUSIONS

We investigated the optimization of the carrier gas flow rate and yields of the oxides, doubly charged ions in the GE-on and GE-off modes in LA–SF–ICP–MS. The results illustrate that the guard electrode shifts the ionization zone backward to the sample cone, in which a larger gas flow rate is required to compensate.

Fig. 7 Results of 52 elements in ML3B, StHs6/80-G and BCR-2G in GE-on and GE-off modes. The relative deviation (RD, %) and given as $[(\text{mass fractions})_{el} - (\text{reference value})_{el}] / (\text{reference value})_{el} \times 100$.

Yields of oxide and doubly charged ions were enhanced in the GE-on mode in comparison to the GE-off mode. These interference ions ascend with an increase in carrier gas flow rate in both modes. An increase in oxide in the GE-on mode indicates that there might be an enhanced oxide formation at plasma interference. Doubly charged ions may not be derived from the secondary discharge of the plasma. The enhancement capability is element-specific and is largely related to the mass number and the 1st ionization potential. Elements with a low mass number and a high 1st ionization potential (>8 eV) show a large improvement in signal intensity. The limit of detection in the GE-on mode is not improved due to the enhanced gas background intensity. The ion transmission efficiency changed from linear correlation in the GE-off mode to quadratic correlation in the GE-on mode, which may reduce the mass discrimination effects. The analysis of MPI-DING reference materials illustrates that the analytical precision of the GE-on mode was better by a factor of 2–4 than that of the GE-off mode, and the accuracy was identical for both modes.

ASSOCIATED CONTENT

Please contact the corresponding author for Supporting Information. **Table S1:** Dataset of major and trace elements in ML3B, StHs6/80-G and BCR-2G in GE-on and GE-off modes. The relative deviation (RD, %) and given as $[(\text{mass fractions})_{el} - (\text{reference value})_{el}] / (\text{reference value})_{el} \times 100$. **Fig. S1:** Intensities of gas background of 55 investigated elements in GE-on and GE-off modes.

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Notes

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