

## RESEARCH ARTICLE



# Accurate measurement of K/Ca in low-[K] carbonate samples using laser-ablation sector-field inductively coupled plasma mass spectrometry

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## Funding information

Hessisches Ministerium für Wissenschaft und Kunst (LOEWE program; VeWA consortium); Wilhelm and Else Heraeus Foundation; Deutsche Forschungsgemeinschaft

**Rationale:** Potassium (K) is a major component of several silicate minerals and seawater, and, therefore, constraining past changes in the potassium cycle is a promising way of tracing large-scale geological processes on Earth. However, [K] measurement using inductively coupled plasma mass spectrometry (ICP-MS) is challenging due to an ArH<sup>+</sup> interference, which may be of a similar magnitude to the K<sup>+</sup> ion beam in samples with <0.1% m/m [K].

**Methods:** In this work, we investigated the effect of the ArH<sup>+</sup> interference on K/Ca data quality by comparing results from laser-ablation (LA)-ICP-MS measured in medium and high mass resolution modes and validating our LA results via solution ICP-optical emission spectroscopy (OES) and solution ICP-MS measurements. To do so, we used a wide range of geological reference materials, with a particular focus on marine carbonates, which are potential archives of past changes in the K cycle but are typically characterised by [K] < 200 µg/g. In addition, we examine the degree to which trace-element data quality is driven by downhole fractionation during LA-ICP-MS measurements.

**Results:** Our results show that medium mass resolution (MR) mode is sufficiently capable of minimising the effect of the ArH<sup>+</sup> interference on K<sup>+</sup>. However, the rate of downhole fractionation for Na and K varies between different samples as a result of their differing bulk composition, resulting in matrix-specific inaccuracy. We show how this can be accounted for via downhole fractionation corrections, resulting in an accuracy of better than 1% and a long-term reproducibility (intermediate precision) of <6% (relative standard deviation) in JCP-1NP using LA-ICP-MS in MR mode.

**Conclusion:** Our [K] measurement protocol is demonstrably precise and accurate and applicable to a wide range of materials. The measurement of K/Ca in relatively low-[K] marine carbonates is presented here as a key example of a new application opened up by these advances.

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## 1 | INTRODUCTION

Since the first trace element measurements using laser ablation (LA) as a sample introduction technique for inductively coupled plasma (ICP)-based analytical approaches in the mid- to late 1980s,<sup>1</sup> there has been both a steady and rapid advance in both LA and ICP-mass spectrometry (MS) instrumentation and methodologies. For example, LA-ICP-MS has been widely used to investigate the elemental and isotopic composition of various geological samples at a high spatial resolution, including fluid inclusions in minerals,<sup>2–4</sup> speleothems,<sup>5,6</sup> ostracod shells,<sup>7</sup> and foraminifera.<sup>8,9</sup> In addition, the high spatial resolution capability of LA-ICP-MS, especially in the vertical direction when conducting spot analysis via depth profiling, has facilitated the investigation of compositional heterogeneity at sub-micrometre resolution,<sup>8,10,11</sup> providing insights into (e.g.) biomineralisation processes.

Although LA-ICP-MS has become increasingly common, interferences by atomic or molecular (polyatomic) ions with the same mass-to-charge ratio ( $m/z$ ) as the analyte of interest remain a source of inaccuracy and/or imprecision. The molecular/polyatomic ion interferences are produced from the interaction of ions with Ar or other common ions present in the sample matrix or carrier gases, such as H, N, O and Cl. For instance, interferences such as  $^{40}\text{Ar}^1\text{H}^+$  on  $^{41}\text{K}^+$ ,  $^{38}\text{Ar}^1\text{H}^+$  on  $^{39}\text{K}^+$ ,  $^{40}\text{Ar}^{16}\text{O}^+$  on  $^{56}\text{Fe}^+$ ,  $^{40}\text{Ar}^{16}\text{O}^1\text{H}^+$  on  $^{57}\text{Fe}^+$ ,  $^{40}\text{Ar}^{14}\text{N}^+$  on  $^{54}\text{Fe}^+$  and  $^{40}\text{Ar}^{35}\text{Cl}^+$  on  $^{75}\text{As}^+$  are an issue.<sup>12–15</sup> In addition, interferences can be caused by spectral overlapping that often results when the abundance of an interference is significantly larger than the peak of adjacent mass, with the magnitude of the issue dependent on the mass-resolving power of the instrument. Conventional quadrupole (Q) mass analysers are capable of a mass resolution ( $R$ ) of  $\sim 300$ ,<sup>14</sup> whereas magnetic sector-field (SF)-ICP-MS instruments, such as the Thermo Fisher Scientific Element XR (utilised here), offer different mass resolution modes, that is, low ( $R = \sim 300$ ; LR), medium ( $R = \sim 4000$ ; MR) and high ( $R = \sim 10\,000$ ; HR), with the separation of polyatomic interferences from analytes of interest requiring medium or high resolution. The issue of both polyatomic interference and abundance sensitivity is important for the measurement of K/Ca, the principal focus of this contribution.

Potassium is a major component of the solid Earth, with an average mass fraction of 260  $\mu\text{g/g}$  in the Earth's mantle, 2.8% m/m in the upper continental crust and  $\sim 1350\ \mu\text{g/g}$  in mid-ocean ridge basalt.<sup>16–18</sup> Potassium is also a major ion in seawater ( $\sim 10.2\ \text{mmol/kg}$ ;  $\sim 380\ \mu\text{g/g}$ ) and is incorporated to a substantial degree in authigenic clay minerals and marine  $\text{CaCO}_3$ .<sup>19</sup> Because it is present at a relatively high concentration in a wide range of materials, it has been identified as a potential indicator for global-scale geochemical processes.<sup>20–23</sup>

Trace element incorporation into marine carbonates is an important tool for palaeoclimate and palaeoenvironmental reconstruction.<sup>24–31</sup> However, despite the potential for reconstructions of the K cycle for determining past changes in, for example, Earth surface processes, only a few studies have measured K/Ca in marine carbonates, which are typically characterised by K/Ca of 0.17–0.23 mmol/mol, equivalent to 63–85  $\mu\text{g/g}$  of [K] (measured by air-acetylene flame atomic absorption spectrophotometry [AAF-AAS]<sup>32</sup>

and ICP-optical emission spectroscopy [OES]<sup>33,34</sup>). However, to our knowledge, even fewer studies have determined [K] using in situ microanalysis at low ( $<1000\ \mu\text{g/g}$ ) concentrations,<sup>35,36</sup> presumably because of the analytical difficulties associated with this measurement described earlier. In addition to these, the lack of well-characterised carbonate reference materials has meant that determining the accuracy of LA-ICP-MS measurements is not currently straightforward (to our knowledge, only one previous study has reported the K mass fraction of a commonly used carbonate reference material, JCP-1, using atomic absorption spectrometry; Okai et al.<sup>37</sup>). Likewise, most previous K measurements in marine samples reported earlier were determined using techniques other than ICP-MS, such as AAS,<sup>32,38</sup> ICP-OES<sup>34</sup> or nanoSIMS.<sup>36</sup>

Although there are only limited studies of potassium in marine carbonates, materials with higher [K] have been widely investigated using both solution-based techniques and in situ microanalysis.<sup>39–43</sup> Various approaches have been proposed to reduce the magnitude of the  $\text{ArH}^+$  interference on ICP-MS measurements: (1) measurement in MR or HR modes is capable of resolving polyatomic molecular interferences (e.g.  $^{23}\text{Na}^{16}\text{O}$  and  $^{38}\text{Ar}^1\text{H}^+$  on  $^{39}\text{K}$ )<sup>15</sup>. The required mass resolution ( $R$ ) to separate  $^{39}\text{K}^+$  and  $^{38}\text{Ar}^1\text{H}^+$  is  $\sim 5600$ , and HR measurements on SF instruments are thus capable of fully separating the interference, albeit with an associated reduction in sensitivity. (2) The use of reaction cell instruments, if available, with  $\text{H}_2$  as the cell gas decreases the  $\text{ArH}^+$  interference by forming Ar plus  $\text{H}_2$  or  $\text{H}_3^+$ .<sup>44,45</sup> (3) Working in 'cool plasma' conditions, achieved by reducing the plasma radio frequency (RF) power, resulted in a substantial reduction of most severe polyatomic interferences derived from Ar complexes.<sup>46,47</sup> However, cold plasma conditions increase the risk of matrix-dependent fractionation occurring in the plasma.<sup>46</sup>

Here, we evaluate the quality of K/Ca measurements using LA-SF-ICP-MS and establish a methodology for K/Ca measurement for low-K marine carbonate samples, including a comparison of LA-ICP-MS measurements made in MR mode (partially resolving the  $\text{ArH}$  interference) to solution ICP-MS measurements in HR mode (full resolving the interference). Given the lack of carbonate reference materials with well-characterised [K], we also report the long-term data quality of K/Ca in several carbonate reference materials (JCP-1NP, JCT-1NP and MACS-3NP) determined using LA and compare the results to new solution-SF-ICP-MS (HR mode) and ICP-OES measurements.

## 2 | MATERIALS AND METHODS

To establish a methodology suitable for the determination of K/Ca in relatively low-[K] carbonate samples ( $<200\ \mu\text{g/g}$ ), we performed experiments using LA-SF-ICP-MS in both MR and HR modes. The principal aim of doing so was to investigate the extent of the  $\text{ArH}^+$  interference on K/Ca measured in geological reference materials with a wide range of K mass fractions. Given that the measurement of alkali elements is of widespread interest in the Earth sciences but is known to be potentially characterised by strong methodologically induced fractionations during LA measurement,<sup>48,49</sup> we extend this analysis to include other (alkali) elements, including sodium. In

addition, we report solution-based ICP-OES measurements of carbonate reference materials to determine the accuracy of our LA K/Ca results. We also investigated a range of low-[K] marine carbonate samples using LA-ICP-MS (MR and HR modes) as well as solution-based ICP-MS (HR mode) to demonstrate that our LA methodology produces accurate results.

## 2.1 | Laser-ablation sector-field inductively coupled plasma mass spectrometry

A RESOLUTION 193 nm ArF LA system (now: Applied Spectra, California, US), equipped with a Laurin Technic (Canberra, Australia) S-155 two-volume LA cell,<sup>50</sup> connected to a magnetic SF-ICP-MS (Element XR; Thermo Fisher Scientific, Bremen, Germany) at the Frankfurt Isotope and Element Research Center (FIERCE), Goethe University Frankfurt, was used for all LA-ICP-MS measurements. Ablation was carried out in a helium atmosphere with argon added to the top of the smaller-volume inner cell, and an additional diatomic gas, N<sub>2</sub>, was added downstream of the ablation cell. The LA-ICP-MS operating parameters used in this study are described in Table 1 and Table S1 (supporting information). The instrument was tuned daily by measuring NIST SRM612 (60 µm; 6 Hz) to maximise sensitivity, that is, >4.5 million cps on <sup>238</sup>U, while maintaining the oxide production rate <1% (ThO/Th; *m/z* 248/232) and the doubly charged production rate <2% (*m/z* 22/44) in LR mode, achieved using the laser and ICP-MS parameters given in Table 1. A range of reference materials were analysed, including the National Institute of Standards and Technology (NIST) glasses (NIST SRM610, NIST SRM612, NIST SRM614 and NIST SRM616), which were used for primary standardisation; the MPI-DING glasses (GOR 128-G, GOR 132-G, ATHO-G, KL2-G and StHs 6/80-G); as well as the carbonate reference materials (JcP-1, JcT-1 and MACS-3). Monitored masses (*m/z*) were <sup>11</sup>B, <sup>23</sup>Na, <sup>24</sup>Mg, <sup>25</sup>Mg, <sup>27</sup>Al, <sup>39</sup>K, <sup>43</sup>Ca and <sup>88</sup>Sr. In the case of our LA measurements, we used the nano-pellet versions of the original carbonate reference materials (JcP-1NP, JcT-1NP and MACS-3NP),<sup>51</sup> which are more homogeneous than the original carbonate reference materials.<sup>52</sup> The nano-pellets of the carbonate reference materials used in this study were provided to Wolfgang Müller/David Evans by Dr. Dieter Garbe-Schönberg in 2014–2015 and have been stored in the presence of moisture-absorbing granules and later in a designated low-humidity chamber.

In addition, we investigated a range of marine CaCO<sub>3</sub> samples including corals, foraminifera and molluscs using LA-ICP-MS in both HR and MR modes (see the Supporting Information for a sample list). All marine carbonates were treated with 1% NaOCl in an ultrasonic bath for 5 min to oxidise any organic material. Samples were then rinsed twice or thrice with 18.2 MΩ cm deionised water (milli-Q, MERCK, Germany), followed by a final cleaning step with methanol in an ultrasonication bath.

Data reduction followed established protocols (e.g. Heinrich et al.<sup>43</sup>) and was performed using an in-house Matlab script,<sup>49</sup> which subtracts blank values from sample data and calibrates trace element ratios using a depth-dependent measured/reported element/<sup>43</sup>Ca

**TABLE 1** Summary of the laser-ablation system and ICP-MS operating parameters.

Laser ablation (RESOLUTION M-50)		
Sampling mode	Spot; line	
Wavelength	193 nm	
Fluence	~6.3 J cm <sup>-2</sup>	
Repetition rate	3 Hz	
Spot size	50 µm	
He	300–400 mL min <sup>-1</sup>	
N <sub>2</sub>	3.5–4.0 mL min <sup>-1</sup>	
SF-ICP-MS (ThermoFisher Scientific Element XR)		
	Laser ablation	Solution
Resolution mode	Medium (R = ~4000) and high mass (R = ~8000) resolution	High mass resolution (R = ~8000)
Torch RF power (W)	1330–1380 W	1350–1400 W
Sample cone	Ni jet cone	Ni jet cone
Skimmer cone	Ni H cone	Ni H cone
Sample gas flow (L min <sup>-1</sup> )	0.80–1.00 L min <sup>-1</sup>	1.10–1.15 L min <sup>-1</sup>
Auxiliary gas flow (L min <sup>-1</sup> )	0.60–0.90 L min <sup>-1</sup>	0.70 L min <sup>-1</sup>
Sensitivity	4–7 million cps of <sup>238</sup> U (NIST SRM612, 60 µm, 6 Hz) in low mass resolution mode	6–8 million cps of <sup>238</sup> U at ~1 ppb in low mass resolution mode

Abbreviations: ICP, inductively coupled plasma; MS, mass spectrometry; SF, sector field.

ratio derived from repeat analysis of the NIST SRM61X glasses (<sup>43</sup>Ca was used as the internal standard in all cases). The elemental mass fractions of the NIST glasses were taken from Jochum et al.,<sup>53</sup> with the exception of Mg in NIST SRM610, for which we use that of Pearce et al.,<sup>54</sup> following the recommendation of Evans and Müller.<sup>49</sup> To determine the accuracy of the measurements when treating the secondary reference materials as unknowns, the elemental values of the MPI-DING glasses were taken from Jochum et al.,<sup>41</sup> and we initially used the JcP-1 values of Okai et al.<sup>37</sup> but revisit these in light of our own data in the discussion section.

## 2.2 | Solution-based measurement of carbonate reference materials and a suite of marine carbonate samples

Carbonate reference materials were measured with solution-based analysis with both SF-ICP-MS in HR mode and ICP-OES to compare bulk values determined with the LA-ICP-MS method described in Section 2.1. A range of marine carbonates samples including corals,

foraminifera and molluscs were also investigated with solution-based analysis using ICP-MS in the HR mode. While the nano-pellets of carbonate reference materials (JCp-1NP, JCT-1NP and MACS-3NP) were measured using LA-ICP-MS, the solution measurements were performed on original carbonate powder reference materials (referred to here as JCp-1, JCT-1 and MACS-3). In the case of MACS-3, we used fragments of the United States Geological Survey (USGS) pressed powder pellets because, to our knowledge, a MACS-3 powder reference material is unavailable.

For solution ICP-MS analysis, ~0.8 mg of JCp-1 and a range of marine carbonate samples were treated with different cleaning methods (Table 2) and finally dissolved in 2 mL of 0.5N HNO<sub>3</sub> (resulting in a [Ca] of ~160 µg/g) for analysis. Three aliquots of ~0.8 mg of each sample were divided into three groups. The first group was not subjected to any pretreatment. The second group was treated with 500 µL of 1% alkali buffered H<sub>2</sub>O<sub>2</sub> (freshly prepared solution of 100 µL of H<sub>2</sub>O<sub>2</sub> in 10 mL of 0.1N NH<sub>4</sub>OH). The third group was treated with 500 µL of 1% alkali buffered H<sub>2</sub>O<sub>2</sub>, followed by 300 µL of 0.0005N HNO<sub>3</sub>. The treatments with 1% alkali buffered H<sub>2</sub>O<sub>2</sub> and 0.0005N HNO<sub>3</sub> were carried out for 8 and 2 min, respectively, in an ultrasonic bath. Both treatments were followed by rinsing with 18.2 MΩ cm deionised water (milli-Q). After each step, samples were centrifuged for 10 min at 5000 rpm, after which the supernatant was carefully removed. Finally, samples were dissolved in 0.5N HNO<sub>3</sub>. The K/Ca of the carbonate reference material JCp-1 and the marine carbonate samples was determined using a Thermo Fisher Scientific Element XR in the HR mode. ICP-MS operating conditions are given in Table 1. Standardisation was performed using a set of standards with K concentrations of 2.5, 5, 10, 20, 35, 50, 75 and 100 µg/g and a constant Ca concentration of 160 µg/g (the Ca concentration was set to be identical to all unknowns). This ratio calibration approach has been shown to improve the precision of carbonate samples during ICP-OES measurements.<sup>55</sup> All calibration standards were prepared with double-distilled 0.5 M HNO<sub>3</sub>. Sample K/Ca was determined by normalising <sup>39</sup>K count rates to the internal standard <sup>43</sup>Ca.

For ICP-OES analysis, powder of the reference materials JCp-1 and JCT-1 and fragments of a MACS-3 pellet were directly dissolved in ~0.5N HNO<sub>3</sub> (Table 2). These solutions were then used to prepare five aliquots of each reference material by mixing with a yttrium solution and adjusting the Ca concentration to 100 mg/L (JCp-1, JCT-1) or 300 mg/L (MACS-3). The Y concentration was set to 1 mg/L for each aliquot, which was used for internal standardisation. In this

approach, yttrium is utilised as an internal standard to correct for potential non-spectral interference introduced by, for example, carbon or the acids used, as well as the difference in view mode (axial or radial).<sup>56–58</sup> For external calibration, four multi-element solutions were prepared by mixing single-element ICP standard solutions. The concentrations of Mg, Na, Sr and K in these calibration standards were adjusted to cover the typical range of element/Ca ratios of the reference materials.<sup>37,52</sup> ICP-OES measurements were performed with a dual viewing iCap 6300 (Thermo Fisher Scientific, Bremen, Germany) at Goethe University Frankfurt. Intensities for K, Mg and Sr were measured in axial mode using lines 766.4, 279.5 and 421.5 nm, whereas Na and Ca were measured radially at 589.5 and 315.8 nm, respectively. The background-subtracted intensities of all elements of interest were normalised internally using the Y values obtained from the nearest spectral line out of the three selected for Y measurements. Following the Y normalisation, elements are ratioed to calcium, and the calibration is performed using the intensity ratio method as suggested by de Villiers et al.<sup>55</sup>

### 3 | RESULTS AND DISCUSSION

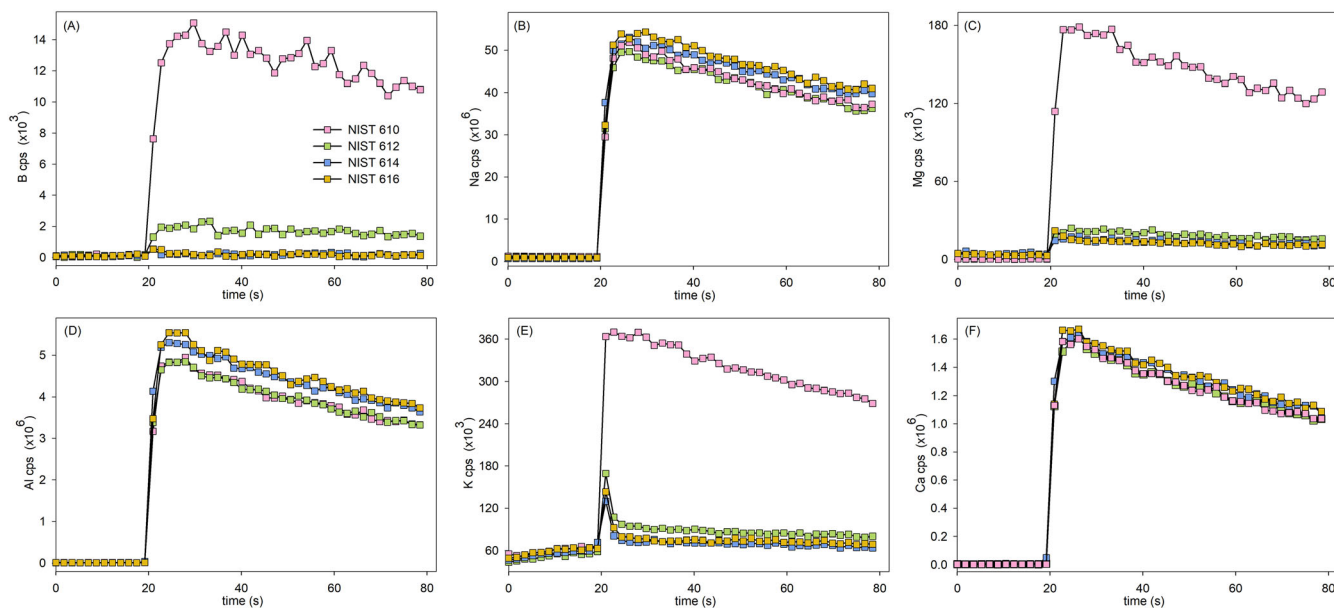
#### 3.1 | The effect of surface contamination on LA-ICP-MS K/Ca measurements

In our laboratory, the NIST glass reference materials are routinely cleaned with ethanol before analysis to remove the bulk of any previous ablation blanket and other possible surface contamination. To test whether this is an effective procedure for minimising surface K contamination, we compared <sup>39</sup>K LA depth profiles through four NIST glasses to other common analytes. No initial spike in count rates indicative of surface contamination was observed for any major element, including Ca, Na, or Al (Figure 1), and, although boron is well known for being contamination prone,<sup>59–61</sup> no initial B spike was observed (Figure 1A). Similarly, no initial spike was observed for Mg. However, an initial K spike was regularly observed in NIST SRM612/4/6, having K mass fractions of ~62, 30, and 29 µg/g (Figure 1E). A similar phenomenon has been reported for other low-mass fraction contamination-prone analytes. For example, Russo et al.<sup>62</sup> reported high initial peaks for Pb/Ca in the NIST SRM61x glass reference materials using a 266 nm laser, whereas Evans and Müller<sup>9</sup> demonstrated substantial degrees of Zn contamination in the absence of pre-ablation cleaning. This is the case whether or not

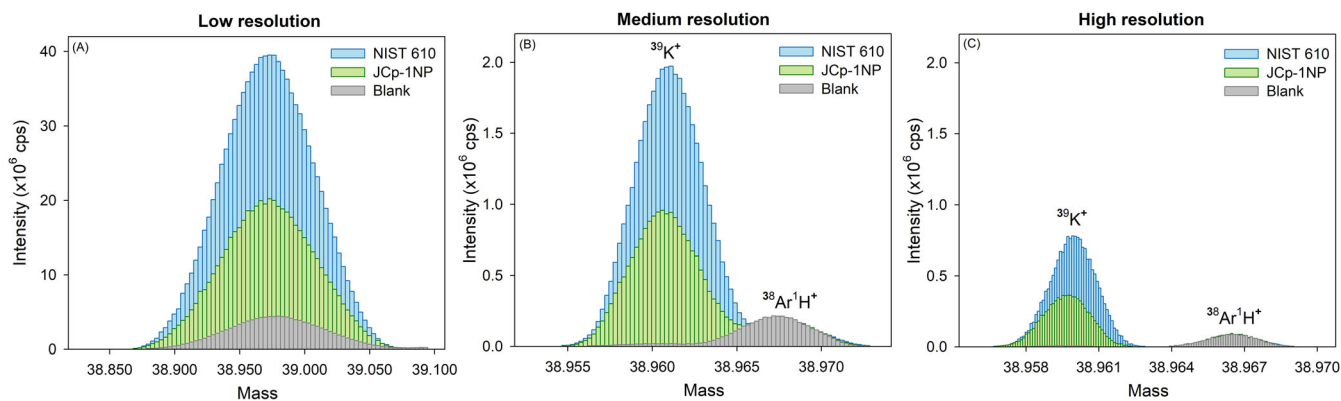
**TABLE 2** Sample treatment procedures for solution ICP-MS/ICP-OES.

Analytical method	Treatment no.	Treatment	Dissolution
Solution ICP-MS	1	Untreated	Dissolution in 0.5 M HNO <sub>3</sub>
	2	1% H <sub>2</sub> O <sub>2</sub> (in 0.1N NH <sub>4</sub> OH)	
	3	1% H <sub>2</sub> O <sub>2</sub> (in 0.1N NH <sub>4</sub> OH) + 0.0005N HNO <sub>3</sub>	
Solution ICP-OES	...	Untreated	Dissolution in 0.5 M HNO <sub>3</sub>

Abbreviations: ICP, inductively coupled plasma; MS, mass spectrometry; OES, optical emission spectroscopy.



**FIGURE 1** Representative element count rate responses during ablation of the National Institute of Standards and Technology (NIST) SRM61x glasses: A, boron; B, sodium; C, magnesium; D, aluminium; E, potassium; and F, calcium. For an equivalent plot displayed as  $\text{El}/\text{Ca}$  ratios, see Figure S1 (supporting information). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]



**FIGURE 2** Representative spectral interference of  $^{38}\text{Ar}^1\text{H}^+$  on  $^{39}\text{K}^+$  in A, low; B, medium; and C, high mass resolution measurement modes. The y-axis scale is the same as in panels B and C, showing the degree of sensitivity decrease between these modes. Ablation was carried out by line scan analysis with a beam size of  $60\ \mu\text{m}$  and a repetition rate of 6 Hz. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

the data are ratioed to Ca (Figure S1 [supporting information]). Given that we observe only surface K spikes for the NIST glasses with lower K mass fractions, which implies that the observation is unlikely to be driven by laser-sample surface coupling effects,<sup>63</sup> we identify remnant surface contamination as a likely cause for the initial K spikes. Modifying our cleaning procedure for the NIST glasses to involve a step with a few drops of 0.01 M  $\text{HNO}_3$ , followed by sonication in ultrapure ethanol and Milli-Q rinsing, removed the initial peaks for K, confirming this hypothesis. Therefore, to measure K/Ca in low-[K] samples, it is necessary to follow an effective cleaning procedure with either chemical cleaning or pre-ablation or, at the very least, to ensure that these portions of the dataset are not considered when processing the data.

### 3.2 | K/Ca measurements using LA-SF-ICP-MS in MR and HR modes

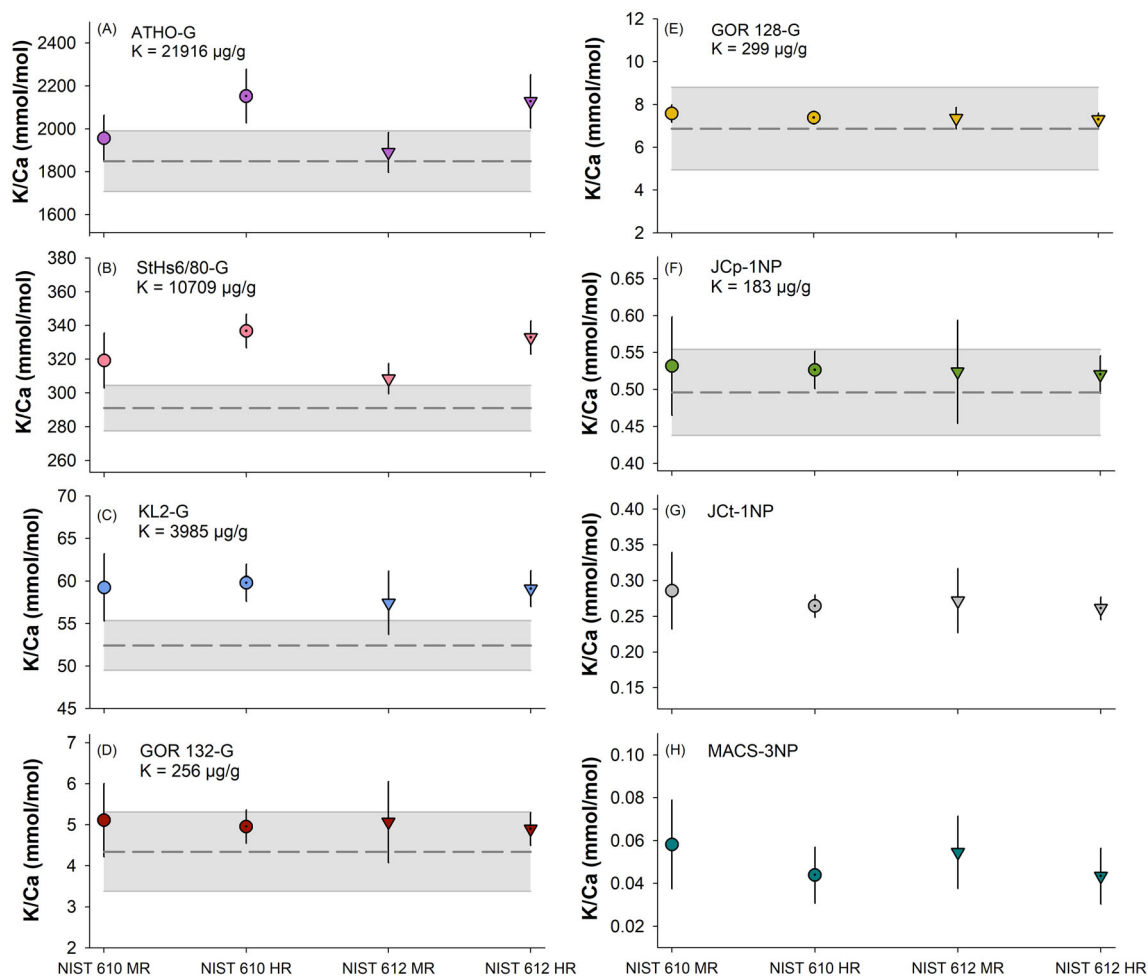
The degree of separation of  $^{38}\text{Ar}^1\text{H}^+$  and  $^{39}\text{K}^+$  during the analysis of NIST SRM610 and JcP-1NP measured using LA-ICP-MS in LR, MR and HR modes is shown in Figure 2. The measurement in LR is incapable of resolving the spectral interference. In MR, the tail of the  $^{38}\text{Ar}^1\text{H}^+$  peak interferes with the  $^{39}\text{K}^+$  peak, whereas the  $^{38}\text{Ar}^1\text{H}^+$  and  $^{39}\text{K}^+$  peaks are fully separated in HR. However, sensitivity is reduced by a factor of 2–3 at HR relative to the MR mode, such that the decrease in sensitivity may become the limiting factor in the trade-off between mass resolution and limit of detection. For instance, the limit of detection for the measurement in MR mode is

7.3  $\mu\text{g/g}$  (K/Ca: 0.02 mmol/mol), whereas in HR mode it is 13.0  $\mu\text{g/g}$  (K/Ca: 0.04 mmol/mol). Thus, the signal-to-background ratio is maximised in MR, which is therefore likely to be the optimum resolution for low-K marine carbonate measurements (e.g. foraminifera, corals and bivalves with  $[\text{K}] < 200 \mu\text{g/g}$ ), provided the  $\text{ArH}^+$  contribution remains sufficiently stable that it can be accurately quantified and corrected for.

We initially investigated whether the degree of  $\text{ArH}^+$  and  $\text{K}^+$  peak separation offered by MR is sufficient to produce accurate and precise data using geological reference materials with K mass fractions ranging from  $\sim 90$  to 22000  $\mu\text{g/g}$ . Because MR does not entirely resolve the polyatomic interference from  $\text{ArH}^+$ , K/Ca was determined in two ways. In our method, 40 channels were selected for the K mass window, with the interference of the  $\text{ArH}^+$  peak tail dominantly impacting the right side of the  $^{39}\text{K}$  peak (Figure 2). Using these data, we included (1) all 40 channels when calculating K/Ca, and (2) only the first 25 channels (left side of the peak), for which the

$\text{ArH}^+$  interference is much lower (background less than  $2 \times 10^4$  cps compared to  $94 \times 10^4$  cps [NIST 610] and  $49 \times 10^4$  cps [JCp-1], when averaging all channels). Although reducing the number of channels resulted in a decrease in precision, we observed that the mean values fall within uncertainty of each other (Figure S2 [supporting information]). The difference in the mean value calibrated with the same standard (NIST SRM610/2) was less than 2% for all reference materials except MACS-3NP (3%) (Figure S2 [supporting information]).

Given that half-peak measurements resulted in no improvement in data quality, we next compared measurements of all of these reference materials in MR to HR mode in which the  $\text{K}^+$  and  $\text{ArH}^+$  peaks are well resolved (Figure 2), using all available channels. We observed overall very similar accuracies between the two resolutions (Figure 3; Table S2 [supporting information]). Specifically, the mean K/Ca values of reference materials measured in HR are within 5% of those measured in MR, demonstrating that full separation of the



**FIGURE 3** Comparing K/Ca values measured using Laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) in high mass resolution (HR) and medium mass resolution (MR) modes. The dashed lines and grey-shaded regions represent the reported K/Ca values and associated 2SD uncertainty, respectively (MPI-DING reference materials<sup>41</sup>; JCp-1<sup>37</sup>). The standard used for calibration is shown on the x-axis. The K/Ca data are derived from one session, with the exception of GOR 128-G, GOR 132-G, JCp-1NP, JCt-1NP and MACS-3NP measured in MR. In these cases, the K/Ca data represent the long-term average values of seven different sessions. Error bars are 2SD. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

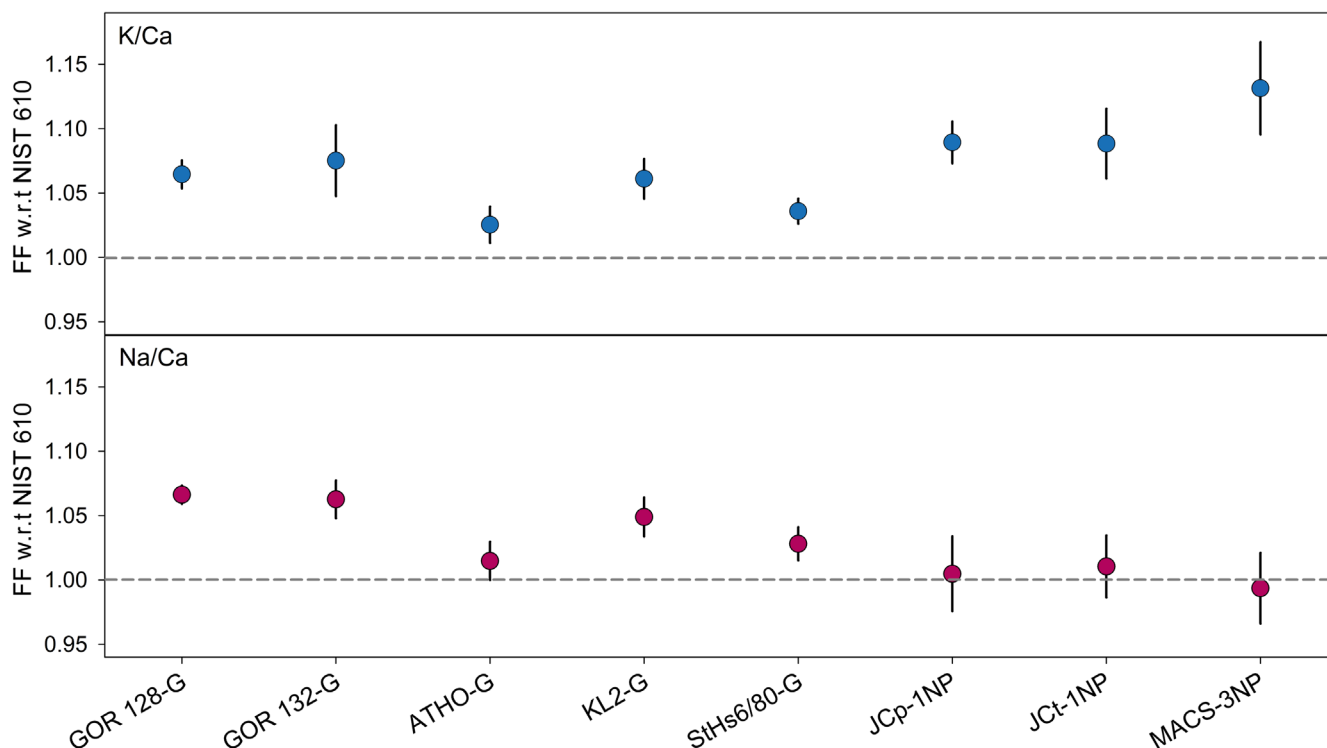
interference is counterbalanced by the loss in sensitivity. Moreover, comparing the measurements of individual sessions demonstrates that the standard deviation of K/Ca measurements of low-K carbonate reference material is similar in MR and HR modes (Figure S5 [supporting information]). An exception was observed for reference materials with a very high [K], that is, ATHO-G and StHs/80-G, which were characterised by a difference in mean K/Ca of 10% and 5%, respectively (Figure 3). This exercise also demonstrates that NIST SRM610/612-standardised data are of broadly similar quality, although we use NIST SRM610 as the calibration standard for all sample K/Ca measurements as we found that this results in an improved long-term reproducibility (see Supporting Information Section 3 and Figure S3 for rationale/demonstration of this).

### 3.3 | Matrix-dependent fractionation of alkali metals during Laser Ablation

Spot analysis in LA-ICP-MS often results in downhole inter-element/isotope fractionation, which is an additional potential source of inaccuracy when non-matrix-matched standardisation is used or if sub-percentage level accuracy and precision are required.<sup>64,65</sup> Downhole fractionation depends on the sample matrix, ablation pit aspect ratio and laser beam power density.<sup>66</sup> We assess whether this

is an issue for K/Ca measurements, using the definition of the downhole 'fractionation factor' (FF) of Fryer et al.<sup>67</sup>; i.e., it is equal to the analyte/internal standard ratio of the second half of the analysis relative to the first half of a single analysis. In the case of analytes with similar behaviour to the internal standard (<sup>43</sup>Ca), such as the alkali earth metals, no significant differences in FFs between the NIST glasses and carbonates were observed when using a 193 nm laser.<sup>49</sup> However, the alkali elements have been observed to be characterised by matrix-dependent downhole fractionation,<sup>48,49,68</sup> which means that this is a possible source of inaccuracy in the measurements performed here. Indeed, Evans and Müller<sup>49</sup> reported an accuracy offset in Na, Li and Rb over a range of ablation and tuning conditions, likely resulting from the differential downhole fractionation between the NIST glasses and CaCO<sub>3</sub> reference materials.

The analyses presented here demonstrate that different reference materials are characterised by different downhole FFs (Figure 4; Figure S4 [supporting information]). These results are displayed as the downhole fractionation of K/Ca and Na/Ca relative to NIST SRM610 in Figure 4 (Table S3 [supporting information]). Here, the FFs were estimated for each session and then averaged over all analytical sessions. The K/Ca and Na/Ca FFs (relative to the mean FF measured in the primary calibration standard NIST SRM610) appear to be strongly matrix dependent. In the case of the MPI-DING glasses, these range between 1.01 and 1.08, with a close correspondence between the Na and K FFs ( $r^2 = 0.93$ ) but no clear



**FIGURE 4** Fractionation factors relative to NIST SRM610 averaged across seven analytical sessions except for ATHO-G, KL2-G and StHs6/80-G (one session). Number of replicates (n): n (GOR 128-G): 50, n (GOR 132-G): 49, n (ATHO-G): 5, n (KL2-G): 7, n (StHs6/80-G): 8, n (MACS-3NP): 46, n (JCP-1NP): 47, n (JCT-1NP): 45. Error bars represent the 2SE of all measurements. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

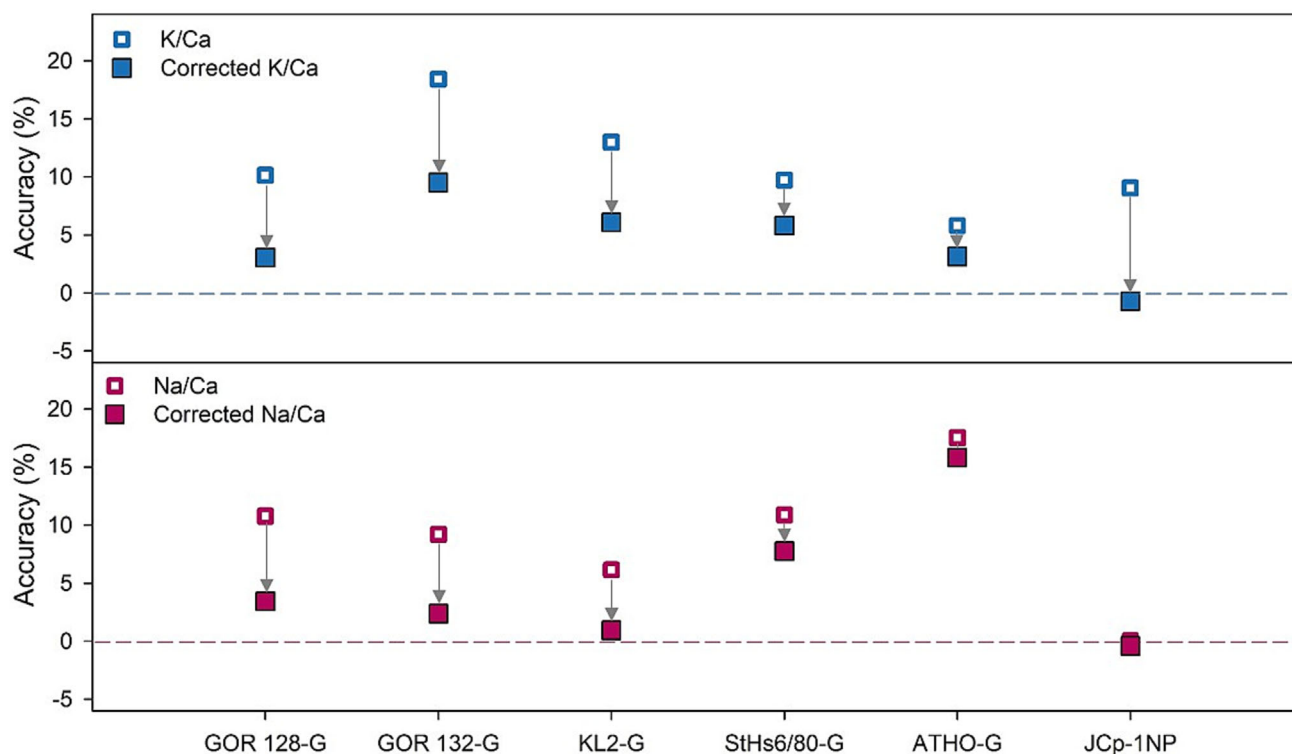
relationship to the bulk composition of the glass. In contrast, the K/Ca FF in the carbonate reference materials were higher than those of Na/Ca.

Given the consistency of the measured FFs between analyses/sessions, we explore whether accuracy can be improved by applying a correction based directly on these measured FFs. Correcting for downhole fractionation in this way, that is, adjusting the measured element/Ca values by a percentage equal to the fraction factor, we demonstrate an improvement in the accuracy of K and Na in all reference materials considered here of 2%–10% (Figure 5). Although there are other possible sources of inaccuracy,<sup>15</sup> we suggest that this is a simple method by which accuracy can be substantially improved in the case of elements characterised by significant matrix-dependent downhole fractionation in future studies.

### 3.4 | Comparison of K/Ca values of different marine carbonate samples measured using LA and solution ICP-MS

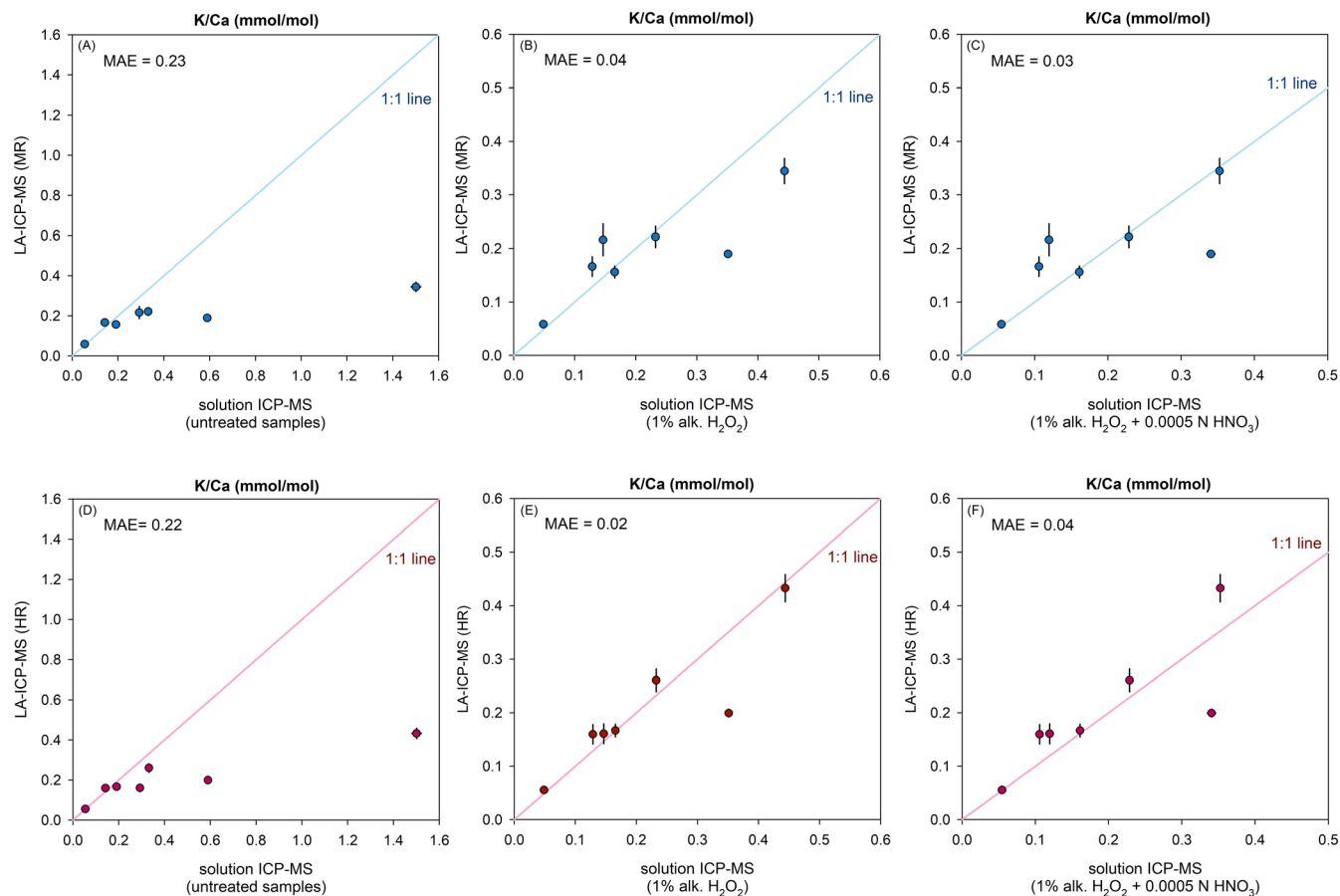
To validate the LA-ICP-MS methodological recommendations outlined above, we determined the K/Ca of a range of marine carbonates including corals, foraminifera and molluscs using both LA and solution ICP-MS (see Section 2.2; Table S4 [supporting information]; Figure 6). For the K/Ca measurements using solution-SF-ICP-MS in HR, each

sample was crushed using an acid-cleaned agate mortar and pestle and subjected to different treatment methods (see Section 2.2; Table 2) before dissolution using 0.5N HNO<sub>3</sub>. The solution K/Ca values after each treatment were compared to data from the same samples measured using LA-ICP-MS in Figure 6. All samples showed a decrease in K/Ca when treated with H<sub>2</sub>O<sub>2</sub> compared to no treatment when measured using solution ICP-MS, which is likely the result of a substantial portion of the K being present in an organic or readily leached fraction (as may also be the case for Na; see Gray et al.<sup>69</sup>). The H<sub>2</sub>O<sub>2</sub>-treated samples measured using solution ICP-MS are characterised by K/Ca within the uncertainty of both the MR and HR LA-ICP-MS results (Figure 6). The only exception is a modern larger benthic foraminifera sample (*Operculina ammonoides*), which is characterised by a lower K/Ca value when measured using LA-ICP-MS. These foraminifera have a complex microstructure and are characterised by substantial inter- and intra-individual heterogeneity such that this may represent real sample variability rather than an analytical issue, given the good agreement obvious in the remainder of the dataset. The same is true when comparing the LA-ICP-MS data to the solution analyses including a further weak acid leach (Figure 6), suggesting that a single oxidative step is sufficient to remove organic-bound and/or readily leached/surface-adsorbed K in these samples. Furthermore, the results demonstrate that both our MR and HR LA-ICP-MS data are accurate compared to solution ICP-MS analyses. Although we do observe a minor improvement in data quality



**FIGURE 5** NIST SRM610-standardised Na/Ca and K/Ca accuracy of the MPI-DING glass reference materials and a carbonate reference material (JcP-1NP) before and after correction for downhole fractionation using the fractionation factors from Figure 4. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]





**FIGURE 6** K/Ca values measured in a range of marine carbonate samples by solution inductively coupled plasma mass spectrometry (ICP-MS) (high mass resolution [HR]) and laser ablation (LA)-ICP-MS (medium mass resolution mode [MR], top row, and high mass resolution mode [HR], bottom row). The x-axis labels describe the cleaning procedures applied before the solution ICP-MS measurements (samples were cleaned in the same way before all LA measurements). Error bars are 2SE. The K/Ca data measured using LA-ICP-MS are corrected for downhole fractionation as described in Section 3.3. MEA is the mean absolute error. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/rcm.9921)]

between MR and HR, for example, the mean absolute error (MAE) decreases from 0.04 to 0.02 mmol/mol when comparing to the solution results with an H<sub>2</sub>O<sub>2</sub> step only (Figures 6B and 6E), it may be that an improvement of this magnitude is not sufficient to offset the sensitivity reduction of other simultaneously collected analytes.

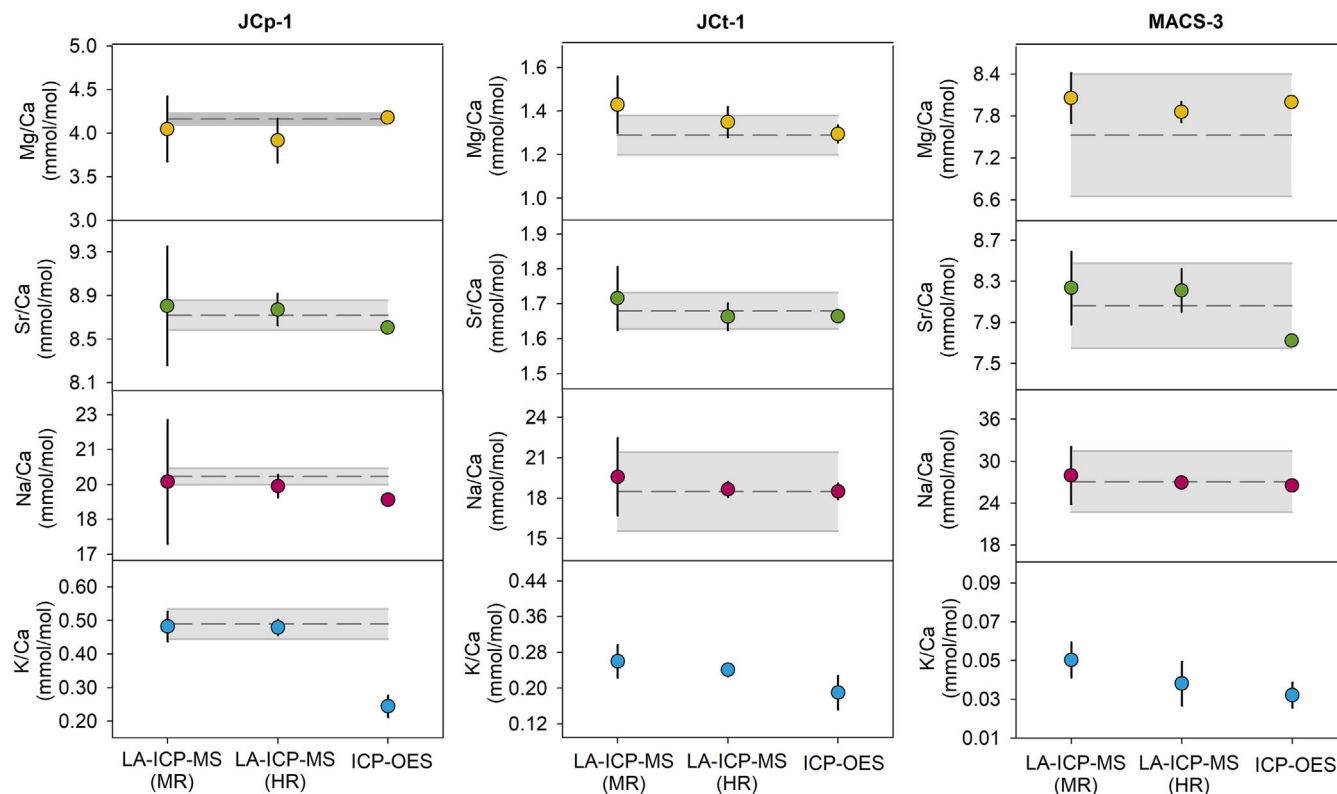
### 3.5 | Long-term LA-ICP-MS carbonate reference material K/Ca data compared with solution ICP-OES and solution ICP-MS measurements

Given the sparsity of carbonate reference material [K] data, we performed both long-term LA-ICP-MS and solution ICP-MS/OES measurements of three commonly used reference materials, including seven different sessions of JcP-1NP, JcT-1NP and MACS-3NP, measured in MR using <sup>43</sup>Ca as the internal standard and NIST SRM610 as the primary calibration standard.

All Mg/Ca, Sr/Ca and Na/Ca LA-ICP-MS data fall within the uncertainty of the reported values for the three carbonate reference materials. Specifically, Mg/Ca accuracy of JcP-1NP, JcT-1NP, and

MACS-3NP measured using LA-ICP-MS in MR was  $-3\%$ ,  $+11\%$  and  $+7\%$ , respectively, relative to the reported values. Sr/Ca accuracy in the same three reference materials was  $+1\%$ ,  $3\%$  and  $+2\%$ , respectively, whereas the Na/Ca accuracy was  $-1\%$ ,  $+6\%$  and  $+4\%$ , respectively. Likewise, our ICP-OES data agree within uncertainty with the reported values in all cases except JcP-1 Na/Ca, which showed an offset of  $-5\%$ .

In contrast, in the case of K/Ca, we find poor agreement between the two techniques. The long-term measured K/Ca in JcP-1NP using LA-ICP-MS in MR ( $0.48 \pm 0.04$  mmol/mol) is statistically identical to the K/Ca result from HR ( $0.48 \pm 0.02$  mmol/mol). These LA-ICP-MS values are with 2% of the K/Ca value ( $0.49$  mmol/mol) in JcP-1 reported by Okai et al.<sup>37</sup> However, the K/Ca in JcP-1 measured using ICP-OES is  $\sim 50\%$  lower than that using LA-ICP-MS. This cannot simply represent an analytical bias between the two techniques given that we find good agreement between our LA-ICP-MS and solution ICP-OES data for JcT-1 and MACS-3 (Figure 7; Table S5 [supporting information]). In addition, we note that we find poor agreement between our MACS-3 data and previously reported values, which range from 0.74 to 1.5  $\mu\text{g/g}$  (excluding one extreme outlier), with a



**FIGURE 7** El/Ca ratios in three carbonate reference materials measured using laser-ablation sector-field inductively coupled plasma mass spectrometry (LA-SF-ICP-MS) (JCp-1NP, Jct-1NP and MACS-3NP) in high mass resolution (HR) and medium mass resolution (MR) modes and solution ICP-optical emission spectroscopy (OES) (JCp-1, Jct-1 and MACS-3). Error bars are 2SD. The dashed line and grey-shaded area represent the mean  $\pm$  2SD reported values for JCp-1,<sup>37</sup> Jct-1,<sup>52,70</sup> and MACS-3.<sup>71</sup> The number of replicate measurements for ICP-OES = 5, LA-ICP-MS (MR) = 48 and LA-ICP-MS (HR) = 30. The K/Ca data measured using LA-ICP-MS are corrected for downhole fractionation (Section 3.3). [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

suggested compiled value of 1.1  $\mu\text{g/g}$  (GEOREM database version 34<sup>71</sup>); however, good agreement between our LA and ICP-OES results indicates that this value should be revised.

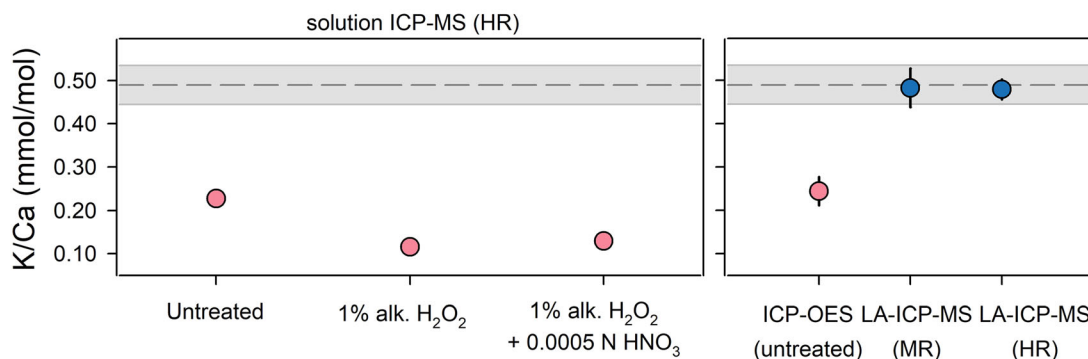
We further investigate the cause of the difference in measured JCp-1 K/Ca between LA-ICP-MS and solution-ICP-OES, by comparing the latter data to measurements made by solution-SF-ICP-MS in HR, following the different treatment procedures outlined in Section 2.2 (see Table 2 and Figure 8).

This exercise demonstrates that although the K/Ca values in JCp-1NP measured using LA-ICP-MS in MR and HR agree well, the K/Ca value in JCp-1 measured using solution-ICP-MS in HR is  $\sim$ 50% lower (Figure 8; Table S6 [supporting information]), similar to the K/Ca results from ICP-OES (Figure 7). Although we observe a decrease in K/Ca values after  $\text{H}_2\text{O}_2$  treatment, suggesting the presence of K in an easily leachable phase such as remnant organics in JCp-1 (Figure 8), the solution ICP-MS measurement of the untreated powder is substantially lower than our LA data or the reported value of Okai et al.<sup>37</sup> The further conundrum in these conflicting results is that although our LA-ICP-MS data agree well with the information value of Okai et al.,<sup>37</sup> the K/Ca ratio of 0.49 mmol/mol is far higher than that expected for *Porites* coral, from which this reference material is derived (see Mitsuguchi and Kawakami, 2012,<sup>32</sup> and compare to

sample J1 in Table S4 [supporting information]). One possible explanation for this is that both our LA data and the original analysis by Okai et al.<sup>37</sup> target a contaminant phase that is not present in our solution (ICP-OES/MS data).

The overall elemental composition of JCp-1 has been previously well characterised.<sup>37,52,72</sup> However, the K concentration in JCp-1 is reported in only one article (i.e. Okai et al.<sup>37</sup>). The lower K/Ca in JCp-1 measured using solution ICP-MS (HR) and ICP-OES compared to LA-ICP-MS may be due to the presence of more than one K-bearing phase as reported in the case of Na in planktonic foraminifera,<sup>69</sup> which is differentially sampled by different techniques or cleaning procedures or that the powder of this carbonate standard (and, therefore, the LA pellets) gained K during the initial preparation of the original JCp-1 powder.

JCp-1 was prepared from a *Porites* sp. coral colony, which was crushed and cleaned with pure water in an ultrasonic bath before a final milling process using balls made of 'high alumina' for about 4 days.<sup>37</sup> Previous work on K incorporation into corals has shown that the expected K/Ca should fall between 0.16 and 0.22 mmol/mol,<sup>32,34</sup> as we also measure here using solution ICP-MS/OES. Therefore, it is more likely that the higher K/Ca value measured using LA-ICP-MS in this study and the AAS measurement following strong acid digestion



**FIGURE 8** K/Ca measured in JCp-1 using solution-sector-field inductively coupled plasma mass spectrometry (SF-ICP-MS) in high mass resolution mode (HR), following different treatment procedures before dissolution in 0.5N HNO<sub>3</sub>. The data shown in pink circles are measurements of the JCp-1 reference material powder, whereas blue circles are the nano-pellet form of the reference material. Error bars are 2SD. The dashed line and the grey-shaded regions represent the originally reported value and 2SD uncertainty, respectively.<sup>37</sup> The K/Ca results from laser ablation (LA)-ICP-MS measurement in medium mass resolution mode (MR) represent values averaged from seven analytical sessions, whereas the K/Ca in HR represents one measurement session. The K/Ca data measured using LA-ICP-MS are corrected for downhole fractionation. [Color figure can be viewed at [wileyonlinelibrary.com](http://wileyonlinelibrary.com)]

of JCp-1 with HF/HNO<sub>3</sub>/HClO<sub>4</sub> reported by Okai et al.<sup>37</sup> is due to K contamination during the sample preparation, which is not present in our solution analyses. One possible source of contamination could be from the alumina balls, which is also evidenced by the higher-than-expected Al content of this reference material (Al: ~480 µg/g; Al/Ca: ~1.90 mmol/mol)<sup>37</sup> compared to pristine coral aragonite (Al/Ca: <0.01 mmol/mol; see sample J1 in Table S4 [supporting information]). In contrast to our LA analysis, which potentially samples contaminant phases in the powder, and the AAS analysis of Okai et al.,<sup>37</sup> which used an extremely aggressive dissolution procedure, the solution measurements that we report use a much milder dissolution step (0.5N HNO<sub>3</sub>), which may not dissolve the K fraction contributed during milling or via another method of contamination. As such, we suggest careful consideration of the dissolution process during solution-based analysis for the purposes of reference material characterisation for microanalysis, and overall our results serve to highlight the potential large offsets that may exist between different analytical techniques that are related more to the characteristics of the material than any potential analytical bias.

## 4 | CONCLUSION

Determining the K/Ca of marine carbonates provides a potential method of reconstructing the oceanic potassium cycle, as well as offering constraints on the biomineralisation of important CaCO<sub>3</sub>-producing organisms.<sup>73</sup> However, the relatively low K concentration typical of CaCO<sub>3</sub>, along with the ArH<sup>+</sup> interference on K<sup>+</sup> when performing these measurements using ICP-MS, means that accurately and precisely determining K/Ca is challenging. To address this, we overcome these and other issues via a number of methodological improvements using LA as a sampling technique that is demonstrably accurate and usefully precise, summarised as follows:

1. When analysing the lower [K] NIST 61x glasses, we observed that an initial K spike could bias the standardisation procedure, suggesting easy surface contamination of K. To overcome this, careful data processing and the elimination of potential contamination by either a precleaning procedure or pre-ablation should be undertaken.
2. Previous work has shown that the NIST SRM61x glasses are suitable reference materials for investigating lithophile elements in carbonates using 193 nm LA systems.<sup>7,49</sup> We observe no difference in K/Ca accuracy when standardising with NIST SRM610/612 but a much higher standard deviation in the raw K/Ca count ratio of the NIST SRM612 glasses, likely as a result of its lower K mass fraction. As such, we recommend the use of NIST SRM610 as the primary calibration standard.
3. Although ArH<sup>+</sup> and K<sup>+</sup> are not fully resolved in MR mode, the mean value of K/Ca measured in a number of silicate and carbonate reference materials was statistically indistinguishable from the K/Ca value in HR mode (which fully resolves the analyte and ArH<sup>+</sup> interference). Therefore, K/Ca measurement in MR likely provides the optimal trade-off between peak separation and sensitivity for most applications.
4. We show that downhole fractionation of K/Ca and Na/Ca with respect to NIST SRM610 varied to a large degree between different reference materials, with Na and K FFs following a similar matrix-dependent trend within the MPI-DING reference materials. Correcting K/Ca data based on simultaneously measured FFs improves the accuracy of the measurement.
5. We provide new HR solution ICP-MS measurements of three commonly used carbonate reference materials and highlight a possible Al and K contamination of JCp-1 reference material. Although well homogenised, the choice of dissolution process during solution-based measurement may lead to the very different values that we measure using different analytical techniques and

note that both our LA results and the original reported [K] are difficult to reconcile with several studies that have characterised the K/Ca of coral aragonite. This highlights the need to carefully consider the effect of different cleaning procedures on reference material reported values, particularly when more than one phase may be present.

Overall, our measurements, conducted over multiple sessions spanning 6 months, demonstrate that MR is sufficiently capable of minimising the effect of ArH<sup>+</sup> interference on the K<sup>+</sup> peak, yielding accurate results (<1%) with a long-term precision (intermediate reproducibility) of <6% (relative standard deviation) in JCp-1NP. Reproducible results of K/Ca in a range of marine carbonate measured by LA-ICP-MS in MR and solution-SF-ICP-MS in HR further confirm that K/Ca measurements made using LA-ICP-MS in MR have the potential to provide accurate and precise datasets and are an advantageous method, in particular, for samples with low [K].

#### AUTHORS CONTRIBUTIONS

**Romi Nambiar:** Conceptualization; methodology; formal analysis; investigation; writing—original draft; writing—review and editing. **Jorit F. Kniest and Alexander Schmidt:** Investigation; writing—review and editing. **Jacek Raddatz:** Resources; writing—review and editing. **Wolfgang Müller and David Evans:** Conceptualization; methodology; resources; writing—review and editing.

#### ACKNOWLEDGEMENTS

This work is part of the VeWA consortium funded by the Hessen State Ministry for Higher Education, Research and the Arts through the LOEWE programme. We thank Jonathan Erez for providing us with samples for this study. FIERCE is financially supported by the Wilhelm and Else Heraeus Foundation and by the Deutsche Forschungsgemeinschaft (DFG: INST 161/921-1 FUGG, INST 161/923-1 FUGG and INST 161/1073-1 FUGG), which is gratefully acknowledged. This is FIERCE contribution No. 150. We gratefully acknowledge the thoughtful comments of two reviewers, which improved the clarity of this contribution. Open Access funding enabled and organized by Projekt DEAL.

#### PEER REVIEW

The peer review history for this article is available at <https://www.webofscience.com/api/gateway/wos/peer-review/10.1002/rcm.9692>.

#### DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available in the supplementary material of this article

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## SUPPORTING INFORMATION

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**How to cite this article:** Nambiar R, Kniest JF, Schmidt A, Raddatz J, Müller W, Evans D. Accurate measurement of K/Ca in low-[K] carbonate samples using laser-ablation sector-field inductively coupled plasma mass spectrometry. *Rapid Commun Mass Spectrom.* 2024;38(5):e9692. doi:[10.1002/rcm.9692](https://doi.org/10.1002/rcm.9692).