

Supplementary Information

**All-Solid-State Fluorine Mapping by BaF⁺ Formation from Surface-Coated Barium
in Femtosecond LA-ICP-MS/MS**

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Table S1. Operating conditions for CIC.

Combustion (AQF-2100H)	□
Furnace temperature	1100 °C
Combustion gas	O ₂
Combustion gas flow	400 mL·min ⁻¹
Carrier gas	Ar
Carrier gas flow	200 mL·min ⁻¹
Absorbent	NaOH
Absorbent volume	20 mL
Absorbent concentration	15 mM
Combustion time	11 min
Ion chromatography (ICS-2100)	□
Column	Dionex™ IonPac™ AG11-HC (4 mm i.d. × 50 mm) and Dionex™ IonPac™ AS11-HC (4 mm i.d. × 250 mm)
Eluent	KOH, Gradient mode, 26 mM from 0 to 10.0 min, 60 mM from 10.1 to 15.0 min, and 26 mM from 15.1 to 20.0 min
Column temperature	35 °C
Eluent flow	1.0 mL·min ⁻¹
Injection volume	200 µL
Suppression current	149 mA
Detection mode	Electric conductivity
Monitored ions	F ⁻ PO ₄ ³⁻ (as internal standard)

SI 1. Estimation of Ba mass-loading on the sample surface

Microscope glass slides (nominal size 76×26 mm; area ≈ 19.8 cm²) were mechanically polished using Al₂O₃ abrasive with a grit size of #1000. The Ba-containing PVA solution (PVA, Ba, and Sc concentrations of 30000, 2000, and 200 mg·L⁻¹, respectively) was then manually applied to the polished glass surface using a silicone spatula. The mass of each glass slide was measured before and after coating, and the coating load (mg·cm⁻²) was calculated from the mass difference and the coated area of the slide.

In a representative gravimetric experiment with five glass slides, the average mass of deposited solution per coating step was 11 mg·cm⁻², corresponding to an average Ba loading of 21 µg·cm⁻² per coating step, with a relative standard deviation (RSD) of 39 % across the five slides. Because the coating and drying procedure in the LA-ICP-MS experiments was repeated three times, the cumulative Ba mass loading on the sample surface was estimated to be ~ 60 µg·cm⁻². As a practical note, each coating layer was dried for 3 min on a pre-heated hot plate at 80 °C. Prolonged heating caused visible yellowing of the PVA film. Although its direct analytical impact was not separately evaluated, such conditions were avoided as a precaution to minimize possible film deterioration. As the coating was applied manually, the average loading and spatial uniformity inevitably vary; however, the resulting variability in Ba coating thickness is corrected for in the main text using ⁴⁵Sc¹⁶O⁺ or ¹³⁴Ba⁺ as coating internal standards.

Given the PVA concentration of 30000 mg·L⁻¹ in the coating solution, an average deposited solution mass of 11 mg·cm⁻² per coating step corresponds to a dry PVA mass of approximately 0.33 mg·cm⁻² per coating, i.e. about 1.0 mg·cm⁻² after three consecutive coat-and-dry cycles. Assuming a density of 1.25 g·cm⁻³ for solid PVA, this total PVA mass corresponds to an average dry coating thickness of $t \approx (1.0 \text{ mg}\cdot\text{cm}^{-2}) / (1.25 \text{ g}\cdot\text{cm}^{-3}) \approx 8 \times 10^{-4} \text{ cm} \approx 8 \text{ }\mu\text{m}$ after three coating cycles.

Table S2. LA-ICP-MS/MS parameters used for the optimization experiments and auxiliary raster measurements.

ICP-MS	
Dwell time	100 ms
Laser ablation system	
Repetition rate	10000 Hz
Raster speed	4 mm·s ⁻¹
Pitch	5 μm

These modified parameters were used to increase signal intensity for the optimization experiments and auxiliary raster measurements. Unless otherwise noted, the remaining parameters were identical to those listed in Table 1.

Table S3. Fluorine concentrations (mass%) in F-free (F00) and F-doped (F15) samples determined by combustion ion chromatography (CIC). Four replicate measurements (n=4) are reported together with the average (Avg.), standard deviation (SD), standard error (SE), and 95% confidence interval.

	F00	F15
<i>n</i> = 1	<0.002	1.47
<i>n</i> = 2	<0.002	1.48
<i>n</i> = 3	<0.002	1.50
<i>n</i> = 4	<0.002	1.50
Avg.	<0.002	1.49
SD	-	0.02
SE	-	0.008
95% Confidence Interval	-	0.02

SI 2. Optimization of Measurement Conditions for BaF⁺ Detection

For the optimization experiments described in this section, one measurement corresponded to one independent rectangular raster acquired under the conditions in Table S2. For Table 4 and Figs. S1–S5, one measurement corresponded to one 0.5 × 0.5 mm rectangular raster, and the normalized values were calculated from the averaged net intensities extracted from the stable portion of each scan profile rather than by point-by-point normalization.

For Figs. S1–S5, the BaF⁺ intensities were compared after correction for differences in the coating Sc signal between F00 and F15. Specifically, the F15 BaF⁺ intensity was converted to a Sc-adjusted equivalent intensity according to

$$I_{BaF, adj(F15)} = \frac{I_{BaF(F15)} \times I_{ScO(F00)}}{I_{ScO(F15)}} \quad (S1)$$

where scandium was monitored as ⁴⁵Sc¹⁶O⁺ under O₂ reaction conditions. The right-axis F15/F00 ratio was calculated from these Sc-adjusted F15 intensities and the corresponding F00 BaF⁺ intensities. The left-axis intensities therefore represent the measured BaF⁺ intensity for F00 and the Sc-adjusted equivalent BaF⁺ intensity for F15.

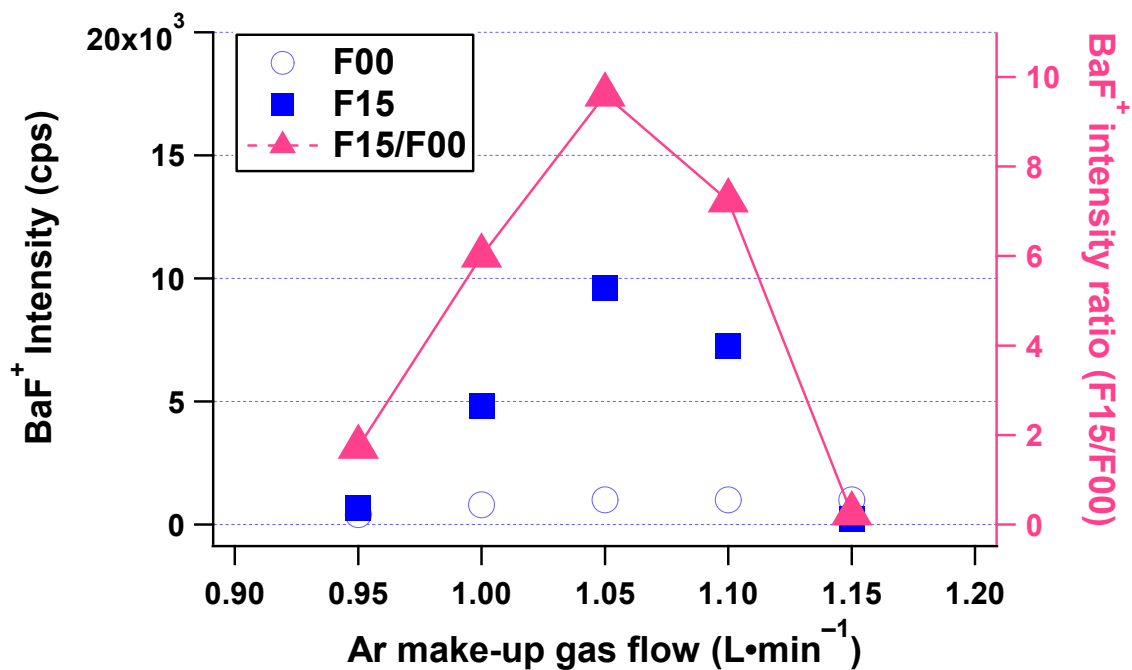


Fig. S1. Effect of Ar make-up gas flow rate on the BaF⁺ signal intensity of F00, the Sc-adjusted equivalent BaF⁺ intensity of F15, and the resulting F15/F00 signal ratio. Pink triangles and the dashed line show the BaF⁺ intensity ratio F15/F00 (right axis).

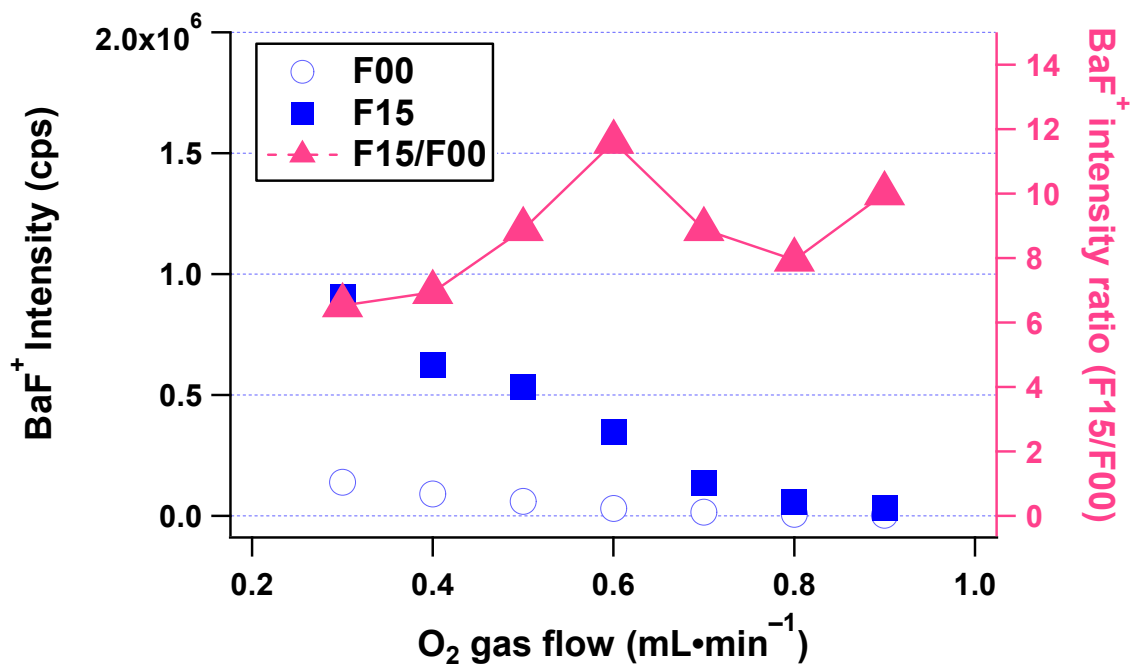


Fig. S2. Effect of O₂ gas flow rate on the BaF⁺ signal intensity of F00, the Sc-adjusted equivalent BaF⁺ intensity of F15, and the resulting F15/F00 signal ratio. Pink triangles and the dashed line show the BaF⁺ intensity ratio F15/F00 (right axis).

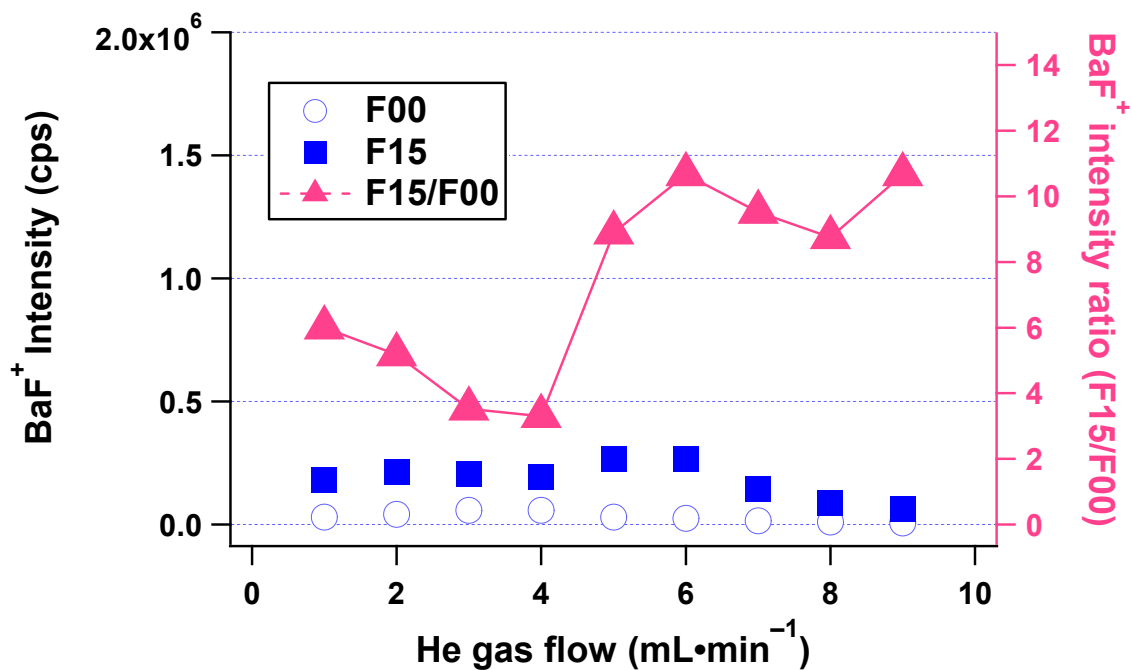


Fig. S3. Effect of He gas flow rate on the BaF⁺ signal intensity of F00, the Sc-adjusted equivalent BaF⁺ intensity of F15, and the resulting F15/F00 signal ratio. Pink triangles and the dashed line show the BaF⁺ intensity ratio F15/F00 (right axis).

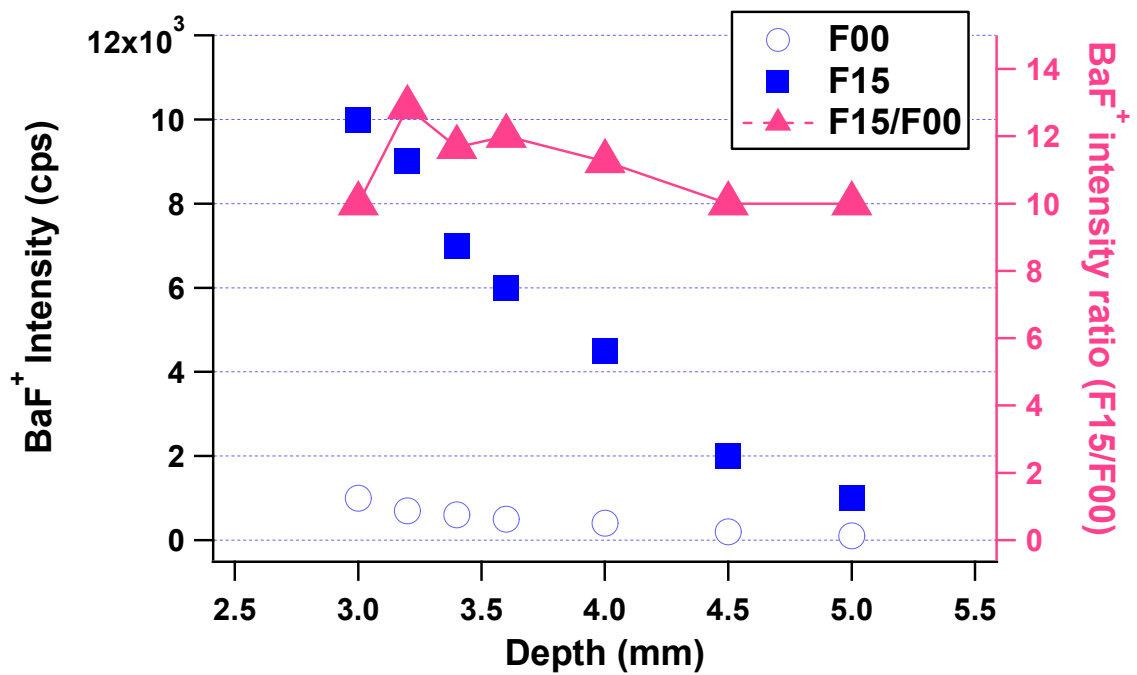


Fig. S4. Effect of sampling depth on the BaF⁺ signal intensity of F00, the Sc-adjusted equivalent BaF⁺ intensity of F15, and the resulting F15/F00 signal ratio. Pink triangles and the dashed line show the BaF⁺ intensity ratio F15/F00 (right axis).

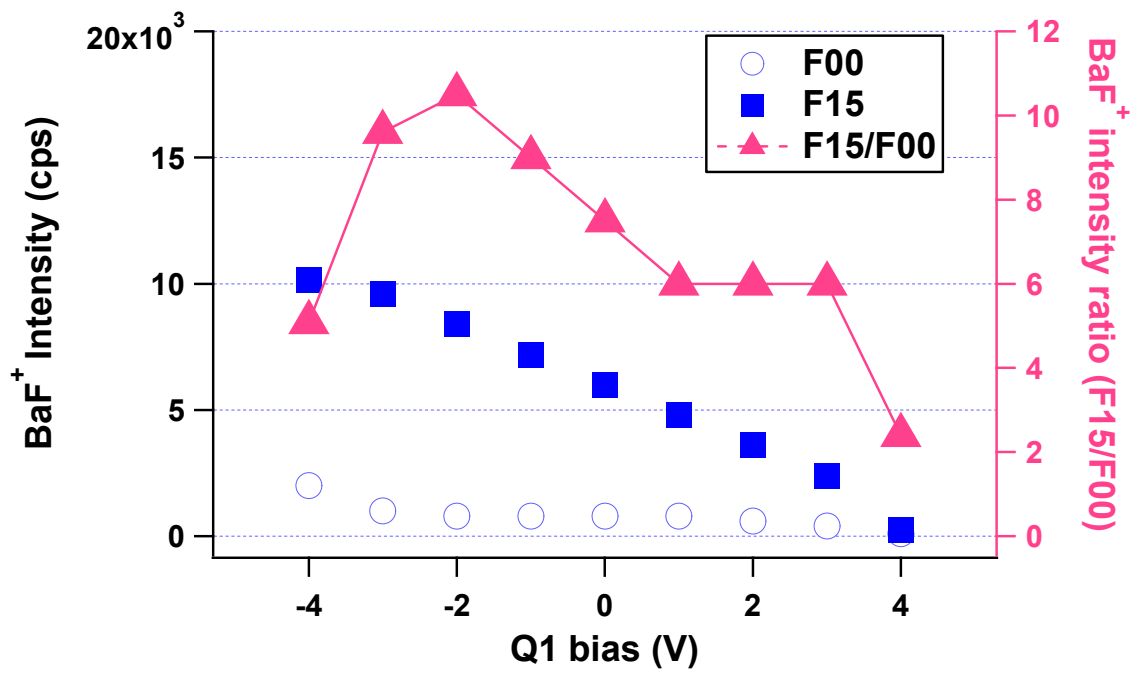


Fig. S5. Effect of Q1 bias on the BaF⁺ signal intensity of F00, the Sc-adjusted equivalent BaF⁺ intensity of F15, and the resulting F15/F00 signal ratio. Pink triangles and the dashed line show the BaF⁺ intensity ratio F15/F00 (right axis).