

Using LA-ICP-MS to analysis elemental composition of statoliths of Scyphozoan jellyfish

Tiezhu Mi^{1, 2*}, Shibin Zhao^{3, 4}, Minzhi Qiu^{3, 4}, Bochao Xu^{2, 3}, Qingzhen Yao^{2, 3}, Yu Zhen^{1, 2}, Zhiqing Lai^{5, 6}, Fang Zhang⁷, Zhigang Yu^{2, 3}

¹ Key Laboratory of Marine Environment and Ecology of Ministry of Education, Ocean University of China, Qingdao 266100, China

² Marine Ecology and Environmental Science Laboratory, Pilot National Laboratory for Marine Science and Technology (Qingdao), Qingdao 266237, China

³ Frontiers Science Center for Deep Ocean Multispheres and Earth System/Key Laboratory of Marine Chemistry Theory and Technology of Ministry of Education, Ocean University of China, Qingdao 266100, China

⁴ College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China

⁵ Key Laboratory of Submarine Geosciences and Prospecting Techniques of Ministry of Education, Ocean University of China, Qingdao 266100, China

⁶ College of Marine Geosciences, Ocean University of China, Qingdao 266100, China

⁷ Key Laboratory of Marine Ecology and Environmental Sciences, Institute of Oceanology, Chinese Academy of Sciences, Qingdao 266071, China

Received 1 November 2021; accepted 14 February 2022

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Abstract

Scyphozoan jellyfish outbreak events are drawing increasing attentions during the past decade. Elemental compositions of statoliths are helpful to understand jellyfish life history and blooming mechanisms, but very rare endeavor has been focused on the Scyphozoan class. In this work, we explored the feasibility of element analysis of *Aurelia aurita* (a representative Scyphozoan jellyfish outbreak species in China) which may be used as proxies of environment parameters during jellyfish living and moving. Statolith crystals of *Aurelia aurita* were found to be a gathering of hexahedron type trigonal needle with size of 10–50 μm long, and 5–10 μm in diameter. By using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) downhole profiling method, elements such as Ca, Sr, Mg, Na and P were found to be above the limit of detection and limit of quantification. The epidermis of statocyst could significantly impact the element analyses, so the real statolith element signal section needs to be selected based on elements and Ca profiles together with care. By laser ablated a signal spot repeatedly, the analytical uncertainty was about 3%–4% for Sr/Ca content ratio and Mg/Ca content ratio, but above 10% for other element/Ca content ratios ($n=3$). Based on the analysis of statolith from temperature-control cultured jellyfish, Sr/Ca content ratios among different statoliths of the same jellyfish were about 6% ($n=14$), demonstrating biological processes/vital effects causing small variations compared with analytical uncertainties. Therefore, Sr/Ca content ratios may be used as a potential proxy to reveal the living environment variations the Scyphozoan jellyfish has experienced, such as temperature history, which is helpful to understand jellyfish bloom mechanisms.

Key words: LA-ICP-MS, statolith, element/Ca content ratios, Scyphozoan jellyfish, *Aurelia aurita*

Citation: Mi Tiezhu, Zhao Shibin, Qiu Minzhi, Xu Bochao, Yao Qingzhen, Zhen Yu, Lai Zhiqing, Zhang Fang, Yu Zhigang. 2022. Using LA-ICP-MS to analysis elemental composition of statoliths of Scyphozoan jellyfish. Acta Oceanologica Sinica, 41(11): 81–87, doi: 10.1007/s13131-022-2034-0

1 Introduction

Under multiple pressures of global climate change and human activities, frequent occurrences of marine ecological disasters has become a notable problem (Purcell, 2005). For example, jellyfish blooms have been increasingly reported with negative impacts on marine human activities that prevail all around the world in last twenty years, such as the Mediterranean Sea, the Gulf of Mexico, the Japan Sea, the Chesapeake Bay (Lotan et al., 1994; Brodeur et al., 1999; Graham, 2001; Uye and Ueta, 2004; Condon and Steinberg, 2008; Richardson et al., 2009;

Sun et al., 2012; Bosch-Belmar et al., 2017). In China, jellyfish bloom events have also started to draw increasing attention since the beginning of the 21st century (Sun et al., 2012). Dong et al. (2010) reported that jellyfish blooms are becoming an annual event in the Bohai Sea, Yellow Sea and northern East China Sea. For example, *Nemopilema nomurai* bloomed in the East China Sea in 2003 (Ding and Cheng, 2007); *Cyanea nozakii* bloomed in the Liaodong Bay, Bohai Sea in 2004 (Wang et al., 2014); *Aurelia aurita* bloomed in Yantan and Weihai coast in 2007, and Qingdao coast in 2009, respectively (Sun, 2019). Offshore industries,

Foundation item: The National Key Research and Development Program of China under contract No. 2017YFC1404402; the National Natural Science Foundation of China under contract Nos U1906210 and 41876075.

*Corresponding author, E-mail: mitiezhu@ouc.edu.cn

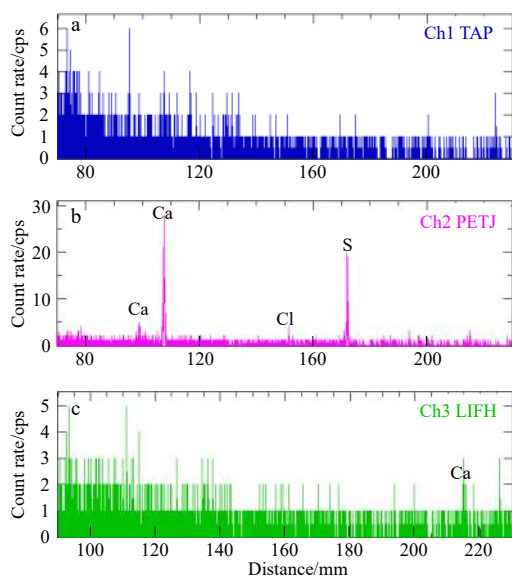


Fig. 2. Major elemental composition results of Electron Microprobe analysis on a single crystal, including the spectrum of Ch1 TAP (a), Ch2 PETJ (b), and Ch3 LIFH (c). The x-axis is the detection position which is the distance between the X-ray source and the diffracting crystal. cps: counts per second.

The influence of epidermis was found to be significant, however, the operation of stripping off the epidermis is very challenging. Based on our own experience during sample preparations, the scyphozoan statolith crystals are very fragile, and not stucked together tightly; it is thus difficult to polish a smooth surface with all statolith crystals staying in their original positions. This is especially harsh for researchers who do not have their

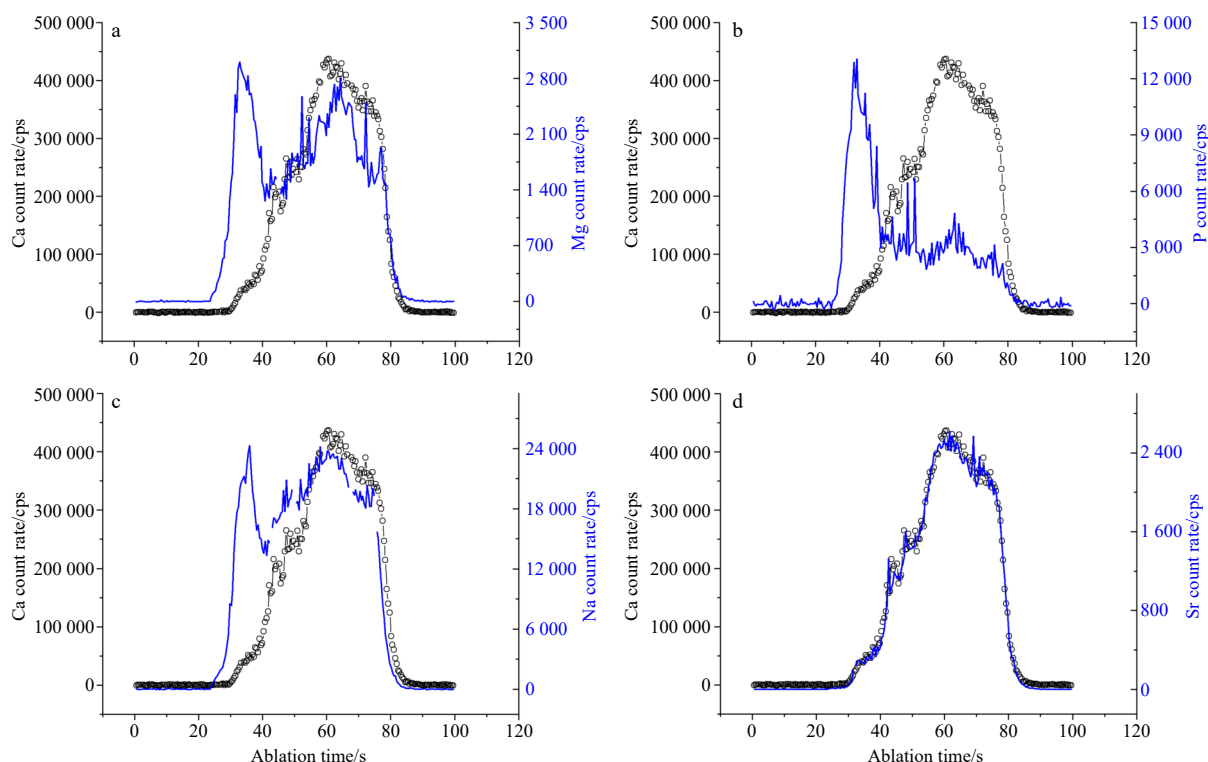


Fig. 3. The downhole profiles of elements (in blue) and Ca (in black) from downhole ablation. Panels a, b, c and d show profiles of elements Mg, P, Na and Sr, respectively. The statocyst epidermis was not polished. cps: counts per second.

Table 2. The limit of detection (LOD) and limit of quantification (LOQ) of each element in statolith by laser ablation downhole profiling analysis ($n=9$)

Elements	Ca	Mg	P	Sr	Na
LOD/cps	75	246	1 493	17	25 883
LOQ/cps	178	480	2 236	46	28 765

Note: cps represents counts per second.

own LA-ICP-MS facilities and need to do analysis in other labs after long distance travelling. When the scyphozoan statoliths are analyzed by LA line-scanning or area-mapping approaches, special care should be taken to make sure the epidermis has been fully removed. Fortunately, one can use the downhole profiling method to get rid of the epidermis influence by choosing the section with significant Ca signals.

4.2 Data quality of element/Ca ratios in statolith as potential aquatic proxies

Convincing proxy should only corresponded with environmental variations, but not analytical or vital effects. We therefore carefully checked the analytical uncertainty by laser ablating one single spot multiple times ($n=3$). The ratios range from 2.6 mmol/mol to 2.8 mmol/mol with an average of (2.7 ± 0.1) mmol/mol for Sr/Ca content ratios, from 5.3 mmol/mol to 6.9 mmol/mol with an average of (6.1 ± 0.8) mmol/mol for P/Ca content ratios, from 22.9 mmol/mol to 24.0 mmol/mol with an average of (23.4 ± 0.6) mmol/mol for Mg/Ca content ratios, and from 79 mmol/mol to 94 mmol/mol with an average of (84 ± 8) mmol/mol for Na/Ca content ratios (Table 3). The ratios of Sr/Ca and Mg/Ca are fairly stable among three repeated ablation analysis, with uncertainties of about 3%–4% (Table 3). The well reproducibility is expected, because Sr, Mg and Ca are all belonged to the alkaline metal group. Similar biogeochemical behaviors may result in homo-

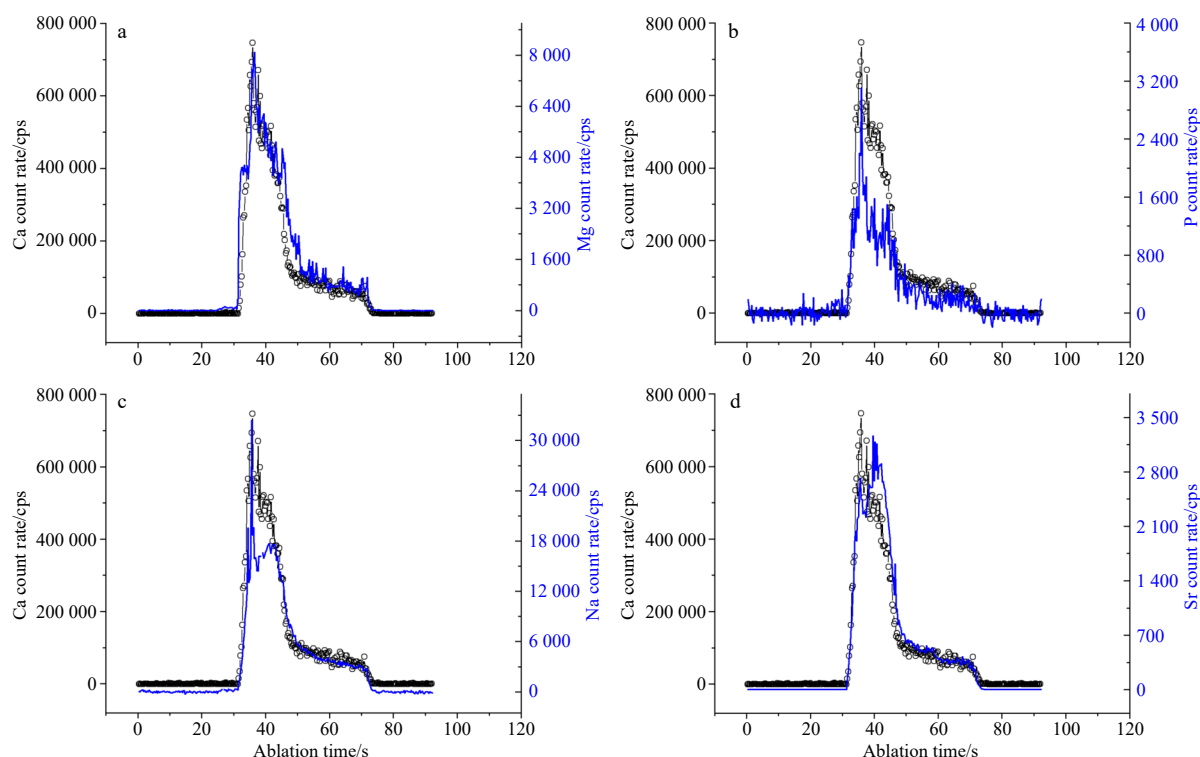


Fig. 4. The downhole profiles of elements (in blue) and Ca (in black) from downhole ablation. Panels a, b, c and d show profiles of elements Mg, P, Na and Sr, respectively. The analyzed statolith was polished to get rid of the epidermis. cps: counts per second.

Table 3. The repeated analysis of element/Ca content ratios in the same spot of the statolith

No.	(Sr/Ca content ratio)/ (mmol·mol ⁻¹)	(P/Ca content ratio)/ (mmol·mol ⁻¹)	(Mg/Ca content ratio)/ (mmol·mol ⁻¹)	(Na/Ca content ratio)/ (mmol·mol ⁻¹)
1	2.8±0.3	6.3±1.3	23.3±3.2	94±9
2	2.7±0.4	5.3±3.0	24.0±27.5	79±15
3	2.6±0.3	6.9±4.0	22.9±15.3	81±26
Average	2.7	6.1	23.4	84
STDEV (%)	0.1 (4%)	0.8 (13%)	0.6 (3%)	8 (10%)

genous distribution of these elements in statolith crystals (Campana, 1999). Other element/Ca content ratios are more variable, with uncertainties of about 10%. Large counting variations are caused by the bump element profile during ablation analysis, which might be influenced by heterogeneously distributed element content in statolith crystals. Similar findings were reported in other marine mineral samples analyzed by laser ablation down-hole profiling approach, such as foraminifera shells (Guo et al., 2019). Therefore, Sr/Ca and Mg/Ca content ratios have higher possibility to be used as potential environment proxy.

Vital effect was further evaluated by analyzing multiple spots on one single statolith, but just focused on Sr/Ca ratio. Fourteen ablation spots were uniformly setup to cover the statolith. The section between 40 s and 70 s of all the fourteen profiles were well overlapped together, demonstrating Sr/Ca ratios in the entire statolith were homogeneously distributed (Fig. 5). Singles on the sections of before 40 s and after 70 s are very bumpy, which might be influenced by the epidermis introduced heterogeneous elemental compositions. The vital effect on Sr/Ca ratios is therefore very trivial. The calculated Sr/Ca ratios were ranged from 2.6 mmol/mol to 3.1 mmol/mol, with an average of (2.9±0.2) mmol/mol ($n=14$). The reproducibility of the 14 analysis was about 6%, which is only 2% above the reproducibility of one single spot analysis. Therefore, variations of Sr/Ca ratios caused by vital effect from one

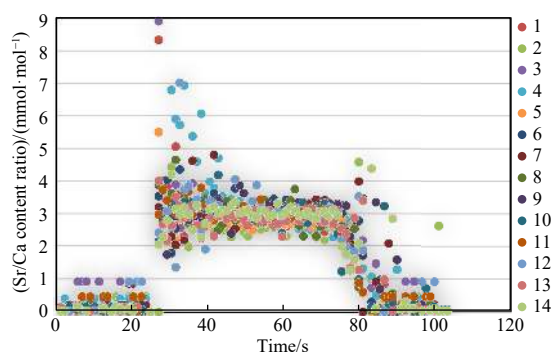


Fig. 5. Fourteen counting profiles of Sr/Ca content ratios uniformly ablated on one single statolith.

single statolith is trivial.

We also compared ablation Sr/Ca content ratios among different statoliths from the same jellyfish, and different individual jellyfishes (Table 4). There was no significant difference of Sr/Ca content ratios among different statoliths of the same jellyfish. Because the analyzed jellyfishes were all cultured under the same temperature and seawater environment, the steady statolith Sr/Ca ratio values were well corresponded with their stable liv-

