Phase-specific isotopic analysis of dissolved selenium in seawater

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Background

Selenium (Se) is both a required micronutrient in marine environments and a toxin at elevated concentrations, with six stable isotopes (74, 76, 77, 78, 80, 82) and multiple oxidation states (Se^{2-}, Se^0, Se^{4+}, Se^{6+}). The isotopes and redox states of Se make it an important trace element to understand, as it has proven to be useful in paleo-redox studies[1,2]. Isotopic compositions of Se in modern seawater have not been well studied[3], but redox reactions knowingly cause isotopic fractionations for Se (Fig. 1). **Here, we show developing methods to successfully separate Se oxyanions (selenite and selenate) from seawater at volumes up to 1L, and we present Se yields and isotopic measurements from these methods.**

Results

- Seawater volumes of 500-1000mL caused incomplete yields and increased $\delta^{82/78}Se$ values, but improved when acidified prior to chemistry (Fig. 2A & 2B)
- Double-spike deconvolution (see M. Kipp's poster!) corrects isotope effects from yields <100% (<30mL of SW) (Fig. 2B)
- Se^{6+} (selenate) has no affinity for resin (Fig. 2C)
- Chemistry effectively removes Na by a factor of ~1700 for a final Na concentration of ~3ppm and Na/Se of 1500. Tests up to 100Na/Se show no isotopic effect on $\delta^{82/78}Se$ (Fig. 2D)

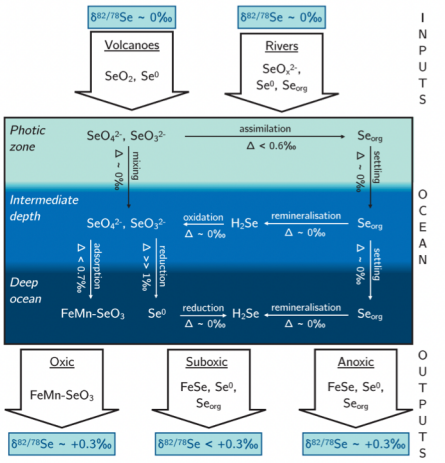

Figure 1. Overview of the marine biogeochemical cycle of selenium with isotopic fractionations associated with each flux or pathway indicated. Figure from Stüeken and Kipp 2020[4].

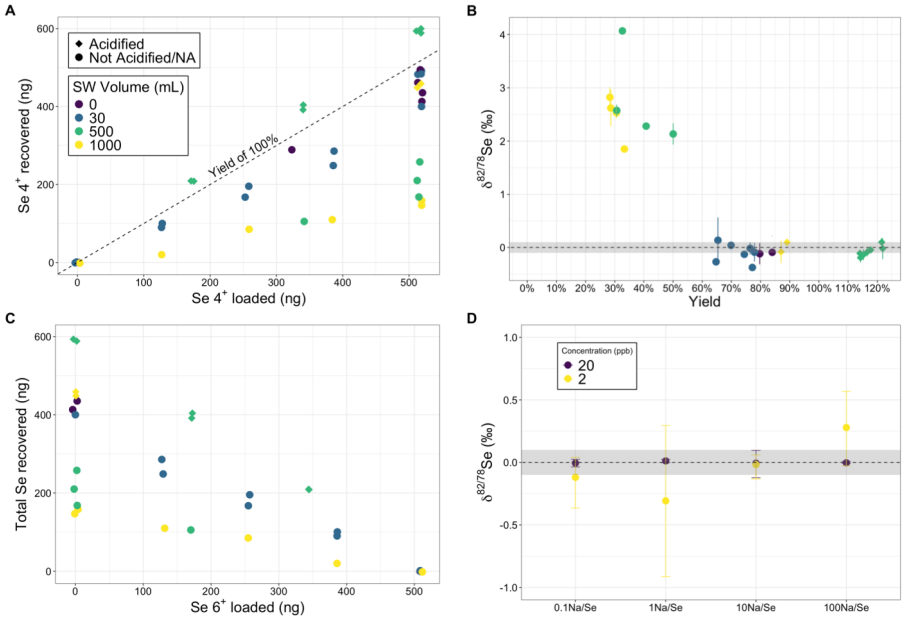

Figure 2. Seawater with 0-500 ng of Se added in varying forms (NIST SRM 3149 or pure selenite/selenate salts). A) Se^{4+} loaded with apparent yield based on Se^{4+} recovered. The volume of seawater and whether they were acidified is shown by color and shape of the points, respectively (*legend applies to B&C*). B) $\delta^{82/78}Se$ ± 2se based on Se^{4+} yield. Seawater samples (>30mL) not acidified had large isotope effects (>1.5 ‰). C) Se^{6+} loaded shows negative correlation with total Se recovered, indicating no affinity of Se^{6+}. D) $\delta^{82/78}Se$ ± 2se values from varying proportions of Na/Se run at different concentrations, showing all within error of 0 ‰.

Methods

- Thiol-silica resin used to separate Se from matrix due to its affinity for Se^{4+} (selenite)
- Pure selenite and selenate salts, and NIST SRM 3149 were added to solutions in varying proportions
- Seawater was filtered with 0.2µm pore size filters before chemistry
- Some seawater was acidified with 6M HCl (twice-distilled) to varying molarities (0.01-0.1M)
- Isotopic analyses conducted in the GAIA Lab (Duke University) using a Nu Sapphire MC-ICP-MS with a collision reaction cell (CRC)

Column & dry-down procedure

Condition with **15mL 0.5M HCl** (twice-distilled)

Load samples at **2-3mL/min**

Wash with > **50mL 0.5M HCl**

Elute with **5mL C. HNO_3** for > 1 hour

Dry to incipient dryness (~4-6 hours, 130 ºC)

Reflux in **1-2mL 5.5M HCl** for 1 hour, 100 ºC

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Phase-specific isotopic analyses of Se & Next Steps

Mixing of isotopically distinct Se phases in analyses can lead to misinterpretation of what biogeochemical reactions are occurring, as this causes a diluted isotopic signature from each respective phase. **COMING SOON**: Implement these methods to seawater samples from **GEOTRACES GP16** cruise through the Eastern Tropical Pacific oxygen deficient zone (Fig. 3).

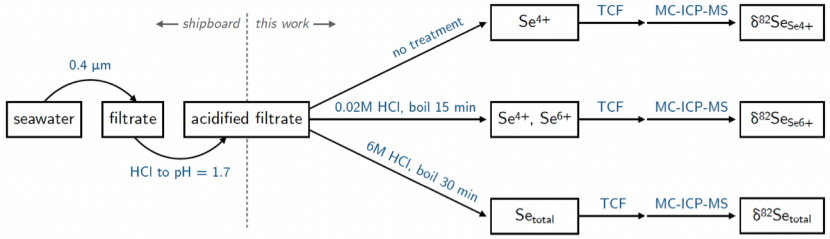

Figure 3. Proposed procedure for phase-specific analyses of Se isotopes (Se^{4+}, Se^{6+} and bulk Se). This procedure will be applied to seawater from GEOTRACES GP16 cruise. Figure generated by MAK.

Acknowledgements

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References

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Abstract link