

Si Natural Abundance Preparation

Silicon stable isotope preparation method is adapted from De La Rocha *et al.*, 1996. Water samples are filtered through 0.6 μ m PCTE filter into clean PP or PC bottles. Samples should be kept tightly capped with caps Parafilmed. Keep bottles at room temperature and in the dark if possible. The amount of dissolved silicic acid (dSi) in the sample must be at least 5 μ moles – determine the volume of sample required using this guideline: i.e. if the dSi concentration is 1 μ M, then you need 4L of water.

Reagents:

TEA-Moly

per 1L Nanopure:
dissolve 8g NH₄ Molybdate
mix in 24ml conc. HCl
dissolve 15.34g TEA Hydrochloride
store in dark for at least one week to let contaminant Si precipitate out

To Clean:

filter reagent using a 0.6 μ m PCTE filter IMMEDIATELY prior to use
clean reagent is stable for 1-2 months if kept in dark

Dilute TEA-Moly (for rinsing)

mix 3 parts clean TEA-Moly with 5 parts Nanopure

Add TEA-MOLY reagent in a 0.6/1 ratio (reagent/sample).

Let the precipitate form for at least 24 hours (yellow precipitate) – leave up to 1 week for less concentrated samples.

Filter on 0.6 μ m (47 mm) PC filter, rinse with ~10ml dilute TEA-Moly 3 times.

Place filter in Platinum crucible and combust using Program 1 (De La Rocha *et al.*, 1996).

Transfer the pure SiO₂ (white powder) to a 1.5 ml microcentrifuge tube for cesium protocol.

CESIUM PROTOCOL

In a 1.5 ml centrifuge tube, put less than 2.4 mg of pure SiO₂.

Add 1 ml of 7.5 μ M HF

Let dissolve overnight

Add 0.5 ml of CsCl 3M

Let precipitate overnight

Centrifuge and discard supernatant, rinse the precipitate with 1 ml of ethanol twice.

Dry in the oven at 60C.

RUNNING ON MAT252

IRMS method as per Brzezinski *et al.*, 2006. Fill 5 μ L wiretrol to 0.5 μ L with cesium fluorosilicate sample and transfer to Kiel vial. Rinse sample down to bottom of vial with ethanol. Dry in oven @ 100C for 2 hours. Grease rim of vials with Krytox and return tray to oven. Heat to >150C for at least 2 hours to burn off HF and completely remove any moisture.

Put tray in N₂ purged Kiel box and let sit for 24hours with N₂ flowing continuously into the box. After 24 hours, turn on chiller and cool box to 3C before starting run.

Multiple runs with standard deviation <0.05 are acceptable, some samples may need to be run more than 3 times. The laboratory standard is Big Batch (BB). BB is run approximately every 8 samples.

For more detailed information, see the papers referenced below.

De La Rocha, C.L., Brzezinski, M.A., DeNiro, M.J., 1996. Purification, Recovery, and Laser Driven Fluorination of Silicon from Dissolved and Particulate Silica for the Measurement of Natural Stable Isotope Abundances. *Anal. Chem.* 68, 3746-3750.

Brzezinski M.A., Jones, J.L., Beucher, C.P., Demarest, M.S., Berg, H.L., 2006. Automated Determination of Silicon Isotope Natural Abundance by the Acid Decomposition of Cesium Hexafluosilicate. *Anal. Chem.* 89, 6109-6114.