SIMS ANALYSIS OF SILICON ISOTOPES : INSTRUMENTAL EFFECTS AND APPLICATION TO A LEOVILLE REFRACTORY INCLUSION.

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Introduction: The silicon isotopic composition of meteorites and lunar samples have been measured by conventional methods for three decades [e.g. 1, 2]. Molini-Velsko *et al.* [3] made a comprehensive study of *bulk* meteorites and did not find large isotopic anomalies. Our goal was to measure the silicon isotopic composition of *individual components* in meteorites to better constrain their fabric and evolution. The ion microprobe is a well suited technique for this purpose, however we found out that large instrumental mass fractionation (IMF) effects occur during the measurement of silicon isotope ratios by this technique. The magnitude of the IMF depends on the mineral analyzed, resulting in the so-called "matrix effect", that has to be corrected in order to recover the true mineral isotopic composition. In order to overcome this issue, we have analyzed series of minerals (olivines, pyroxenes, feldspars, melilites, quartz) and characterized their IMF. Using these calibrations, we could measure the silicon isotopic composition of several phases of the refractory inclusion MRS6 of Leoville.

Methods: Natural (olivines, pyroxenes, feldpars, melilite, quartz) and synthetic (forsterite, and melilite endmembers) minerals were used as silicon isotope standards. Several fragments of each mineral were embedded in epoxy and polished. They were further analyzed with the CAMPARIS Cameca SX50 or SX100 electron microprobes at Université Paris VI. A setup of 15 kV, 10nA was used for the analyses.

The silicon isotopic compositions of these minerals were measured using the IMS-Orsay ion microprobe at CSNSM. A 0.1 to 3nA primary Cs^+ ion beam was accelerated at 14.5 kV and negative silicon secondary ions were analyzed from the sample. The primary beam was shaped into a ~ 50 μm diameter flat bottom spot with a field aperture allowing to select only the central 10 μm of the impacted area for the analysis. The three silicon isotopes were measured by peak jumping mode using electrostatic commutation means at constant magnetic field. Mass resolution was set at 3000 in order to resolve the ^{28}SiH interference from ^{29}Si. The transfer lenses were set to produce a highly demagnified crossover providing enhanced collection efficiency and spectrometer transmission on small analyzed areas. The ^{28}Si, ^{29}Si and ^{30}Si isotopes were counted on an electron multiplier for 1 second for each isotopes and count rates were corrected for a detector dead time of 52.4 ns. San Carlos olivine (Fo_{91}) was used as a primary standard to correct for instrumental mass fractionation. All analyses were later normalized to NBS28 thanks to the measurement of San Carlos olivine and of 5 other natural and synthetic minerals by high-resolution MC-ICPMS on the Nu Plasma 1700 at ETH Zürich [4]. For the other natural samples, their true silicon isotopic compositions are assumed to be zero within analytical uncertainties, according to values measured for mafic silicates by Douthitt [5]. The silicon isotopic composition of the MRS6 refractory inclusion from Leoville was measured using these settings.

The oxygen isotopic composition MRS6 was measured using the ion microprobe Cameca IMS1270 national facility at CRPG Nancy (France). The setup used for these analyses is described in [6].

Instrumental effects : The instrumental mass fractionation (IMF) is calculated from the average of $\delta^{30}Si/2$ and $\delta^{29}Si$ values, as measured delta values fall on the mass fractionation line. The precision of the analyses is 0.35‰/amu (1σ) including reproducibility (Figure 1).
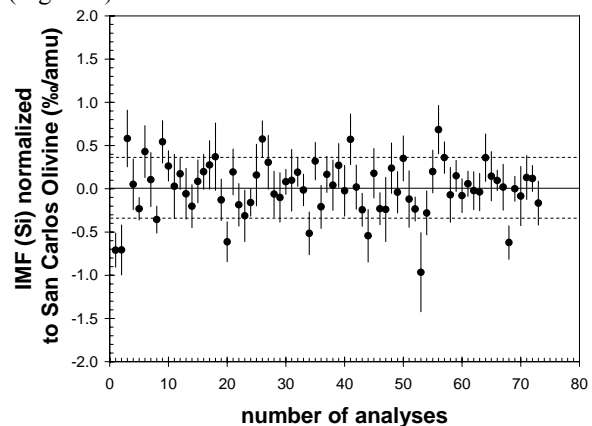

Figure 1: reproducibility of the silicon isotope analyses on our primary standard (San Carlos Olivine). The precision is 0.35‰ (1 σ)

Olivine is the mineral for which matrix effects are the most drastic : there is a 20‰/amu matrix effect between forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). We noted a trend of a complex correlation between the

IMF of olivines and their silicon concentration (Figure 2). On the other hand, one can see that in the range of forsteric olivine (Fo$_{80-100}$), there is no noticeable matrix effect between the olivines. It is interesting to note that the trend of the matrix effect is opposite to what is observed for oxygen isotopes where the IMF is less for Fe-rich olivines than for Mg-rich olivine.
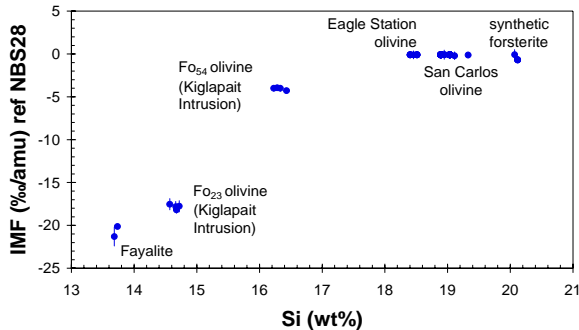

Figure 2 : instrumental mass fractionation (IMF) normalized to San Carlos olivine and NBS28. Error bars are 1σ.

We could only analyze a narrow range of composition for orthopyroxenes (from En$_{70}$ to En$_{98}$) and clinopyroxenes (En$_{39.2}$Wo$_{49.5}$ to En$_{47.8}$Wo$_{50.6}$). For these minerals, the matrix effect is around zero for orthopyroxenes and at most 1.5‰/amu for the analyzed clinopyroxenes for which it follows an inverse linear correlation with the (Si+Al) weight concentration.

Feldspars and melilite also show inverse linear correlations between the IMF and the Si weight content of the mineral, with a maximum of 8‰/amu between the albite and the anorthite endmembers, as well as between the gehlenite and akermanite endmembers.

By measuring the crater depths in different minerals and knowing our experimental conditions, we were able to calculate the probability of secondary ion production (P^{28}Si for ^{28}Si for instance) and the concentration of Cs$^+$ implanted in the sample. It could be modelled, and experimentally observed, that instrumental mass fractionation was negatively linearly correlated with 1/P^{28}Si, whereas P^{28}Si is positively linearly correlated with the concentration of implanted Cs ions, paving the way for IMF matrix effect correction procedures.

Measurement of the Leoville MRS6 refractory inclusion : Earlier ^{10}Be measurements of the Leoville CAI are reported by [7]. The Mg isotopic composition of the inclusion shows the presence of extinct ^{26}Al in the CAI with an initial ^{26}Al/^{27}Al ratio of $4.6 \pm 0.6 \times 10^{-5}$ (unpublished data). The ^{10}Be measurements show a complex heating history of

MRS6 that caused a partial isotopic resetting of the ^{10}Be-B system [7].

We measured the oxygen and silicon isotopic composition in the same phases that were analyzed previously for ^{10}Be. The oxygen isotopic data fall on the CCAM line, with melilite δ^{18}O values ranging from -7.4‰ to +8.3‰, the fassaite δ^{18}O are from -27.6‰ to -31.1‰, δ^{18}O in spinel is at -30.8‰ and -33.1‰ and in anorthite at -33.8‰.

The three silicon isotopes were measured on the same locations as for oxygen isotopes for 4 melilite spots, 3 fassaite grains and 1 anorthite mineral. The silicon isotopic compositions fall on a mass fractionation line. Fassaite minerals have δ^{30}Si ranging from 13.2‰ to 16.9‰ (Figure 3). These elevated values may have to be taken with caution as no terrestrial analogue is available for matrix effect correction of fassaite. The matrix effect corrections (-1.2‰/amu to -3.2‰.amu) used an extrapolation of the clinopyroxene trend mentioned above. Melilite and anorthite do not show large isotopic effects, with δ^{30}Si around zero (Figure 3).
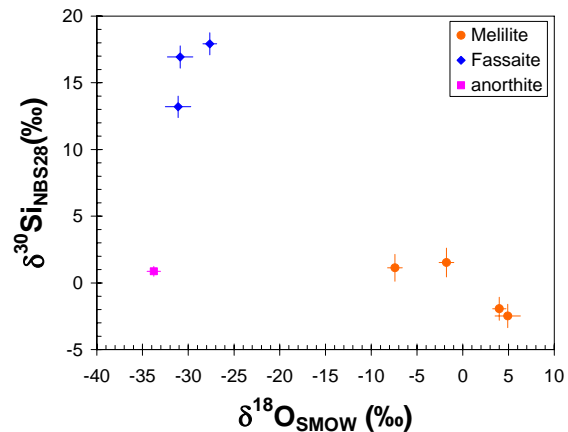

Figure 3 : Silicon vs oxygen isotopic composition for some phases of MRS6 Leoville refractory inclusion.

References:
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