Local FS-IR laser - fluorination CF-IRMS $\delta^{34}S$, $\delta^{33}S$ isotope analyses of sulfides

A. V. IGNATIEV[1] AND T. A. VELIVETSKAYA[1]

[1]Far East Geological Institute FEB RAS, Vladivostok, Russia. (ignatiev@fegi.ru)

The advantages of laser ablation method include direct estimation of sulfur isotope ratio in minerals, no chemical procedures, reduced risk of sample contamination, and determination of spatial isotope variations. Contemporary laser techniques make it possible to analyze $^{34}S/^{32}S$ isotope ratio with good spatial resolution [1] and allow to achieve high precision analysis of four stable isotopes of sulfur at nanomole level [2].

We have developed a method for determination of $^{33}S/^{32}S$ and $^{34}S/^{32}S$ isotope ratios (in SF6) using IR femtosecond laser system (PHAROS, Light Conversion Ltd, Lithuania), repetition rate (up to 1.0 kHz) IR-fs-laser with pulse energy (100 - 200 μJ). Our equipment consisted: cylindrical stainless steel chamber, a nickel reactor, two six-port Valco valves, two cryogenic traps, chromatographic column, and specially designed interface that allowed us to measure the isotope ratio in the high vacuum mode. After ablation of the sample, the aerosol was injected into the reactor by the He-flow. Vapors of BrF_5 were entered into a heated zone of the reactor (350°C) to produce SF_6. Cryogenically purified SF_6 was passed through the chromatographic column to the specially designed interface on the ion source of a MAT-253 mass spectrometer to measure triple isotope ratios of sulfur. The method was tested using international standards IAEA-S-1, IAEA-S-2, and IAEA-S-3, and natural samples of pyrite, sphalerite, galena, arsenopyrite, chalcopyrite, pyrrhotite, and elementary sulfur. The precision of replicate analyses of sulfide minerals with laser ablation is typically 0.1 - 0.2‰ (1σ) for $\delta^{34}S$ and 0.05‰ (1σ) for $\Delta^{33}S$. This method increases the spatial resolution of the laser ablation in situ analysis up to 30 microns and considerably reduces the analysis time (~ 15 minutes). The slope of the line λ is 0.5148 with a correlation coefficient of 0.99999, where $\lambda = \ln(1+ \delta^{33}S/1000)/ \ln(1+ \delta^{34}S/1000)$.this study was supported by the Russian Foundation for Basic Research, grant #15-05-00740.

[1] Crowe D. J. et al. 1990. *Geochimica et Cosmochimica Acta* **54**:2075–2092. [2] Ono S. B. et al. 2006. *Chemical Geology* **225**:30– 39.