

**DEVELOPMENT OF A METHOD FOR ACCURATE DETERMINATION OF TRIPLE SULFUR ISOTOPE RATIOS OF SULFIDE MINERALS IN METEORITES BY LASER ABLATION AND ISOTOPE RATIO MASS SPECTROMETRY.**

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**Introduction:** 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  $^{34}\text{S}/^{32}\text{S}$  isotope ratio with good spatial resolution [1] and allow to achieve high precision analysis of four stable isotopes of sulfur at nanomole level [2]. Here we report a new laser method for local sulfur isotope analyses of sulfides with high precision and accuracy by isotope ratio mass spectrometer running in continuous flow mode.

**Method and results:** The first step was to develop a method for determination of  $^{34}\text{S}/^{32}\text{S}$  isotope ratio (in  $\text{SO}_2$ ) using a nanosecond UV laser (UP-213, New Wave Research) and infrared femtosecond laser (Integra-C-1.0, Quantronix). Our equipment consisted out: cylindrical stainless steel chamber, a quartz reactor, and six-port Valco valve coupled to a cryogenic trap. Helium flow running through the chamber transferred some laser ablation particles into the hot oxidation reactor ( $900^\circ\text{C}$ ) to produce  $\text{SO}_2$ . Total  $\text{SO}_2$  condensed in the trap at liquid nitrogen temperature. Next, the trap was stepwise heating and purified  $\text{SO}_2$  was transferred by the He-flow to the ion source of MAT-253 mass spectrometer to measure the sulfur isotope ratio. This method was tested using international standards and natural samples of pyrite, sphalerite, galena, arsenopyrite, chalcopyrite, pyrrhotite, and elementary sulfur. The results of  $\delta^{34}\text{S}$  analysis of all minerals were in accordance with the  $\delta^{34}\text{S}$  values obtained by recognized classical method. The method allows measuring the  $\delta^{34}\text{S}$  variations with a reproducibility of 0.1–0.2‰ ( $1\sigma$ ) and with a lateral resolution of 80–100 microns, depth ~ 30–50 microns.

The second step, we have developed a method for determination of  $^{33}\text{S}/^{32}\text{S}$  and  $^{34}\text{S}/^{32}\text{S}$  isotope ratios (in  $\text{SF}_6$ ) using nanosecond UV laser (NWR-213, New Wave Research) and UV femtosecond laser (NWR Femto UC, New Wave Research). 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  $\text{BrF}_5$  were entered into a heated zone of the reactor ( $350^\circ\text{C}$ ) to produce  $\text{SF}_6$  which was then condensed into the liquid nitrogen trap. The trap was stepwise heating and purified  $\text{SF}_6$  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 allows to measure the  $\delta^{34}\text{S}$  values with reproducibility of 0.1‰ ( $1\sigma$ ) and  $\Delta^{33}\text{S}$  with a reproducibility of 0.02–0.05‰ ( $1\sigma$ ); lateral resolution of 30–40 microns, depth ~ 30–40 microns. The slope of the triple isotope line was 0.5148, correlation coefficient of 0.99999.

**References:** [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.