Matrix effects in sulfide analyses using nano- and femtosecond lasers

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Trace element analysis of geological samples by LA-ICP-MS is affected by a variety of fractionation effects from the side of the mass spectrometer as well as from fractionation during the ablation process. Several studies in recent years evaluated the impact on isotopic and elemental fractionation for a varity of matrices. With the introduction of femtosecond laser ablation systems, elemental and isotopic fractionation has been reported to be eliminated for a large variety of sample matrices.

Few studies tried to quantify frationation effects of sulfides applying femtosecond laser ablation. From earlier studies utilising nanosecond laser systems a strong melting of sulfides has been reported, leading to evaporation of S and possible fractionation of chalcophile and siderophile elements between the ablated sulfide and the produced sulfide melt. Melting of the sample under the laser beam requires matrix matched standards that expirience the same degree of melting.

We applied three different LA-ICP-MS systems (213 nm solid state, 193 nm excimer, and 200 fs laser) to the analysis of different sulfide minerals (pyrrhotite, chalcopyrite, and sphalerite). Ablation craters were investigated via BSE images to compare the amount of melt produced, and fractionation factors were calculated to determine the degree of fractionation during the drilling of the laser into the sample.

Our results show significant differences in sample melting between 213 nm laser, 193 nm laser, and fs laser. While samples show massive melting applying the 213 and 193 nm systems, no melting has been observed utilizing a femto second laser. Nevertheless fractionation of PGE/S and PGE/Fe with crater dephts has been observed for all three systems, which seems to be independent of sample melting.

Analyses of a synthetic pyrrhotite with known PGE concentrations using the fs laser yielded moderately precise and accurate concentrations (3-4%; 4-14%) utilizing a sulfide as external standard. Application of NIST610 SRM as external standard improved the precision to 1.4-2.4% and the accuracy for Rh and Pt to 5% while Pd is too low by a factor of 3.