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Instrumental development on ultraviolet-femtosecond-laser ablation (UV-Fs-LA) and its elemental analysis application

Jun-Ichi Kimura[1*], Chang Qing[1]

[1]IFREE/JAMSTEC

We have developed a 266/200 nm wavelength ultraviolet-femtosecond-laser ablation (UV-Fs-LA) system using frequency tripled and quadrupuled near infrared (800 nm) Fs Ti-sapphire regenerative amplifier LA source (Spectra Physics, Solstice). Laser focusing optics was optimized using a high-power UV objective lens (ThorLab) for 200 nm and an aspherical objective lens (Edmond Optics) for 266 nm in order to compensate Gaussian energy profile of the laser beam. Maximum crater sizes were 30 um in 200 nm and 90 um in 266 nm depending on laser fluence threshold on silicates (~10J/cm2). Flat bottom crater was not achievable by single spot analysis due to interference of the ultra-short pulse laser. Circular or line raster analysis by moving sample stage improved crater shape and thus signal stability for 60 to 120 sec. Ablation quality becomes comparable to homogenized excimer or Nd-YAG nanosecond lasers. Ultra-short pulse (> 300 fs) combined with UV wavelength minimizes formation of coarse ablation aerosols, thus minimizes aerosol deposition around craters and stabilizes signals detected in mass spectrometer. Combined with a sector field (SF)-ICPMS (Thermo Fischer Scientific, Element XR) with high-sensitivity and wide-dynamic range (up to T(10^12) cps) enabled simultaneous analysis of more than 43 elements including major (SiO2, TiO2, Al2O3, Fe, MnO, MgO, CaO, Na2O, K2O, P2O5) and trace (Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Th, U) elements from craters 20-50 by 20-50 um (diameter vs. depth) in size. Analytical precision is normally better than 3% in wt.% to sub-ppm levels. Accuracy is usually within 5%, when matrix matched standard is used (e.g., BCR-2G analysis using BHVO-2G), if not within 15 % (e.g., BCR-2G analysis using SRM612 glass). Accurate analysis of all major elements enables perfect correction of ablation efficiency different between samples. This realizes stand-alone analysis of UV-Fs-LA-SF-ICPMS without assist of electron probe micro analyzer (EPMA) in determining internal standard composition used for ablation efficiency correction. Furthermore, this internally consistent simultaneous major element correction eliminates errors propagated from different sampling volume between the two analytical methods. This advantage can be extended to metal analysis as ultra-short pulse dramatically improves stoichiometric sampling from metallic samples.

Keywords: fentosecond, laser ablation, elemental analysis