







Femtosecond Laser Ablation-Time of Flight Inductively Coupled Plasma Spectrometry for Elemental Analysis of Fluid Inclusions.

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Introduction

Minerals may incorporate tiny droplets of fluids while they crystallize. These fossil inclusions can provide direct information of the physical and chemical conditions presented during the growth of minerals.

LA-ICP-MS has become a powerful analytical technique to quantify trace elements in these fluid inclusions thanks to excellent analytical capabilities such as spatial resolved analysis, multielement analysis and stable isotope measurements. In most cases reaching precisions below 3 % expressed as RSD and limits of detections below 1 mg/kg.

In this work, Fluid inclusion analysis are carried out by coupling a fs laser with a TOF-ICP-MS. The main benefit of using a femtosecond pulse is that induces a lower heat effect region in the sample and produces a fine aerosol size distribution. The TOF system is a mass analyzer with the capability of collecting entire mass spectrum at a rate of 30KHz, which is ideal for the transient nature of signals produced by the fluid inclusions.

Experimental

The experimental system included a 343nmfs-LA system (J100 Applied Spectra, Inc.) coupled to an ICP- TOF-ICP-MS (GBC Scientific Optimass 9000). The fs-laser (Amplitude Systems, S-Pulse) was an ytterbium diode pumped technology with a fundamental wavelength of 1030 nm.

Figure 1. ASI J100 fs-laser ablation system



Table 1. Experimental Conditions

| TOF-ICP MS GBC | |
|-------------------------------------|-------|
| Forward power, W | 1200 |
| Plasma Ar gas flow rate, Imin-1 | 11.00 |
| Auxiliary Ar gas flow rate, I min-1 | 0.80 |
| Make-up Ar gas flow rate, I min-1 | 0.90 |
| Extraction lens, V | -1500 |
| Skimmer, V | -1400 |
| Z1, V | -1000 |
| Y mean, V | -200 |
| Y deflection, V | -3 |
| Z deflection, V | -30 |
| Laser Ablation System J-100 | |
| Applied Spectra | |
| Wavelength, nm | 343 |
| Pulse energy, µJ | 190 |
| Fluence, J cm ⁻² | x |
| Spot size, µm | 35 |
| Repetition rate, Hz | 5 |
| Carrier He gas flow rate, I min-1 | 0.90 |

Method

Analysis of a N612 glass standard and fluid inclusion hosted in quartz veins from Naxos Metamorphic Complex, Greece (figure 2) were carried out by using raster ablation mode at 500 µm.s⁻¹ speed at repetition rate of 100 Hz. A square crater of 40x 40 μm area was generated. The main goal was to removed layers of the host-mineral without any loss of the components in the fluid inclusion during this sampling process.

Figure 2. Inclusion sample



Results and discussion

Figure 3 shows an example of square craters produced after high repetition rate ablation on NIST 612 glass and quartz. Figure 4 shows the comparison between 44Ca signal after the classical approach of digging a hole until reaching the inclusion, and the raster mode approach. The combination of high repetition rate with the appropriate speed provides a better quality of the aerosol and diffusion of the particles to the ICP. Figure 5 reveals that it is easy to differentiate the signal coming for the inclusion from the signal coming from the host-mineral.

Figure 3. Square craters produced on NIST 612 and quartz

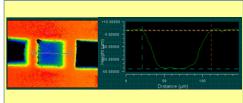


Figure 4. ⁴⁴Ca signal comparison between the ablation

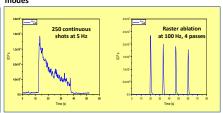
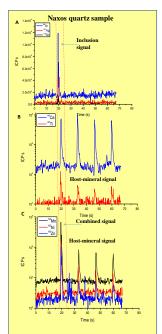


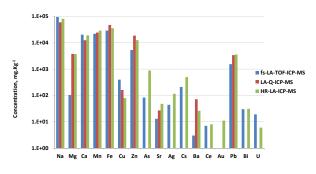
Figure 5. Elemental Characterization



Results and discussion

The results obtained in this study using NIST 612 as standard were compared with previously reported data using a LA-quadrupole ICP-MS and LA-HR-ICPMS with stationary continuous shots (Figure 6). Results compared favorably to those previously reported for Naxos samples considering the significant differences between the experimental setups.

Figure 6. Comparison of fluid inclusions results for Naxos samples



Conclusions

Preliminary results show that high-speed raster ablation mode with the high repetition rate femtosecond laser is a promising sampling technique since allows clear separation between the fluid inclusion signals and the host-mineral. One of the main reasons is that a more effective release of particles from the ablation site is achieved

References

C. A. Heinrich, T. Pettke, W. E. Halter, M. Agner-Torres, A. Audétat, D. Günther, B. Hattendorf, D. Bleiner, M. Guillong, and I. Horn, Geochimica et Cosmochimica Acta 2003 67 3473-3496

M. M. Allan, B. W. D. Yardley, L. J. Forbes, K. I. Shmulovich, D. A. Banks, and T. J. Shepherd, American Mineralogyst, 2005, 90, 1767-1775.