Fluid Inclusions Analysis

Feasibility Study Using 213nm Laser

Analytical Instrumentation

The analysis of fluid inclusions in various host matrices can give vital information about the evolution of hydrothermal fluids in the Earth's crust. It can also provide unique constraints on the conditions of mineral growth. A detailed knowledge of fluid inclusion chemistry can be used to produce much better constrained models for the evolution of important fluid systems, in particular ore deposits. Often, inclusions just contain an aqueous liquid and/or gas phase, but solids, known as daughter minerals, may also be present.

Fluid inclusions are generally small (typically <10µm) and can be located at different depths from the sample surface, thereby presenting a formidable analytical challenge. Techniques such as Electron Probe Micro-Analysis, Proton Induced X-Ray Analysis, Synchrotron X-Ray and Secondary Ion Mass Spectrometry (SIMS) have been used for the analysis of solutes in fluid inclusions. However, these methods encounter difficulties, particularly if the fluid inclusion is not near the sample surface.

Laser-ablation ICP-MS offers the advantage that the laser can drill a deep channel to the fluid inclusion beneath the sample surface. However, as the host matrix for fluid inclusions is often a transparent quartz sample, the 266nm (Nd:YAG 4th harmonic wavelength) laser is not suitable due to its unstable ablation characteristics.

So far, the successful analysis of fluid inclusions using laser-ablation ICP-MS has occurred mostly with ArF excimer lasers with a 193nm wavelength. The analysis of fluid inclusions using this method has been constrained to only a few laboratories worldwide, due to its high operating cost.

The development of the 213nm laser (Nd:YAG 5th harmonic wavelength) represents a breakthrough for this type of analysis using a routine analytical tool. This system significantly improves absorption efficiency for incoming laser light for transparent matrices enabling precise control of the laser ablation process in fluid inclusion hosts, such as quartz.

Analysis of Fluid Inclusions Using Nd:YAG Lasers

As the host matrix for fluid inclusions typically consists of transparent quartz, their analysis presents a particular challenge.

Figure 1 shows optical microscope pictures obtained on the LUV213 laser system. The picture on the left shows several fluid inclusions at diameters from <10µm to approximately 20µm. The spherical vapor bubble seen in these inclusions indicates that a fluid phase is present, in addition to a number of solids—"daughter minerals"—precipitated inside the inclusion subsequent to trapping of the inclusion fluid.

Figure 1: Fluid inclusions in a quartz sample prior to and after the laser ablation.

For the multi-element analysis of such small inclusions, a multi-element time-resolved analysis mode is essential (Figures 2—4). Data are taken from the start of the analysis; while a channel is drilled towards the fluid inclusion, the elemental composition of the host matrix is characterized. These data, as well as gas background data, can later be subtracted from the data obtained once the fluid inclusion is opened. While the data on the y-axis illustrate the signal arising from the ablated material, the x-axis represents elapsed time during the ablation run. Knowing the depth penetration rate of the laser for a given matrix, this time axis can later be converted into a depth axis. Only the data from the period of release of material from the fluid inclusion—from opening until the complete removal of its contents —are integrated for the analysis. The data before and after this event can be used for background correction.

Figure 2 shows the signal obtained from the LUV266. Although Ba and Sr signals can be observed after a 100sec ablation time, this only lasts for around 10sec duration. This is probably due to the poor coupling of 266nm into the quartz sample; the ablation is not controlled and therefore the drilling to the fluid inclusion, as well as the opening of the inclusion, will show erratic behavior. This figure illustrates that the 266nm laser is not suitable for fluid inclusion analysis.

Figure 3 shows the signal obtained from the LUV213 using laser energy of 0.15mJ, a pulse repetition of 5Hz and a crater size of 10µm. After an ablation of 110sec, a

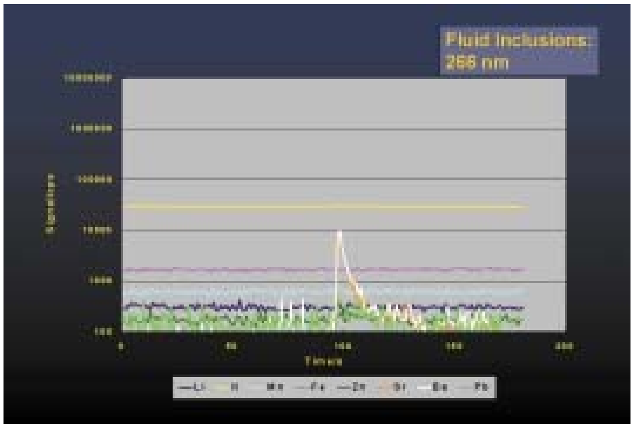

Figure 2: Fluid inclusion signal obtained from LUV266.

channel is drilled to the fluid inclusion and once opened, a clear and stable signal can be observed for around 60sec. All elements monitored, such as Li, K, Mn, Fe, Zn, Sr, Ba and Pb show stable signals at levels, which are several magnitudes higher than the background level. It should be noted that the gas and the matrix background are on similar levels, indicating the purity of the host quartz matrix.

Figure 4 shows the results from the LUV213 using a rapid method. A higher laser energy of 0.25mJ was used and a higher repetition rate of 20Hz. Once the inclusion was approached, the crater size was changed from 10µm to 30µm.

Discussion and Conclusions

Two different approaches have been tested for fluid inclusion analyses, the slow approach as shown in Figure 3 and a rapid approach, as shown in Figure 4.

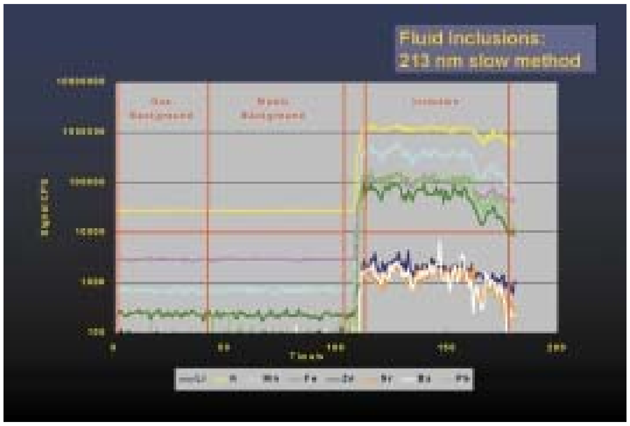

Figure 3: Fluid inclusion signal using the LUV213—slow

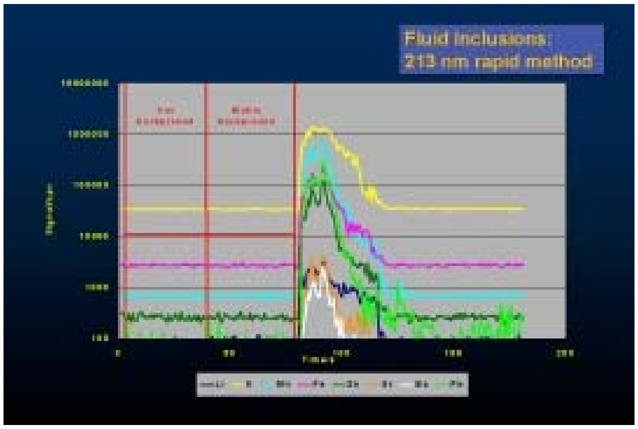

Figure 4: Signal obtained from LUV213.

The slow method incorporates a slow depth penetration (using slow repetition rate) and a small crater in order to release the fluid slowly. This leads to a long and stable signal and should ensure that all of the fluid is released for analysis. This method 'tickles' the fluid out of the inclusion. Arguments against this method are that small parts of solid phases might be left on the inclusion walls, or solids may be precipitated from solution and remain inside the inclusion cavity after ablation.

The rapid method uses a higher energy density and a higher repetition rate of 10 or 20Hz in order to achieve a faster depth penetration to drill a channel to the fluid inclusion. Once this channel is drilled using a small crater, the crater size is changed to a larger diameter after the fluid inclusion has been reached. The aim is to ablate the fluid inclusion contents—both fluid and solid phase—rapidly, so the content is analyzed almost at once. The signal duration is therefore much shorter and the background contribution might be smaller. The argument against this method is that the surrounding matrix might be analyzed, as well as the inclusion contents, and the signal is much shorter which could lead to poorer precision.

Both approaches will have their benefits and Figure 3 and 4 illustrate that either approach can be chosen using the LUV213. The ablation behavior is precisely controlled and the analysis of fluid inclusion can be successfully performed using the 213nm Nd:YAG wavelength.

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