Analytical Methods Applied to Fluid and melt Inclusions

- Most early work to analyze fluid inclusions involved bulk analysis whereby fluids were released from inclusions by either crushing the host mineral (Leeds group) or by heating to decrepitate the inclusions and release of the fluids (Barker)
- Starting in the 1980s, analytical techniques for FI evolved from bulk methods to methods that allowed individual FI to be analyzed
- Today, the two most commonly used methods for FI analysis are Raman spectroscopy and laser ablation ICPMS
- Essentially all analyses of MI have involved individual inclusions
- The most common analytical methods used for MI are electron microprobe, ion microprobe (SIMS), Raman, and FTIR



Various analytical methods are used to identify inclusions to be analyzed, and to place temporal (paragenetic) constraints on FI and MI origin.

# Optical Microscopy















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# Cathodoluminescence (CL) (Cold)



Transmitted light (left) and CL image (right) of dolomite from the Buick MVT deposit, Viburnum trend (from Rowan and Leach, 1989, EG). The CL stratigraphy is fairly consistent throughout the district and can be used as a timeline to constrain spatial variations in fluid properties.



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# Cathodoluminescence (CL) (Hot)

Right: Transmitted light (A) and CL image (B) of quartz from the Bingham Canyon Cu deposit, showing dissolution of Q1 before Cu mineralization and deposition of Q2 (from Landtwing et al., 2005)

Below: Q1 quartz that has been partially resorbed before deposition of Q2 quartz from the Hongniu-Hongshan Cu skarn deposit (from Wang et al., 2022)





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# Cathodoluminescence (CL) (Hot)

Peppard and co-workers developed a CL "stratigraphy" for quartz phenocrysts from the Bishop Tuff and used this to identify temporally-associated MI both within individual crystals and between crystals



From Peppard et al., 2001





Raman spectroscopy can provide both qualitative and quantitative data on fluid and melt inclusions.





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From Frezzotti, 2012, JGE

Raman spectroscopy has been used to detect  $H_2O$  in nominally pure  $CO_2$  FI by heating the FI to ~150°C to evaporate the  $H_2O$ , following the method of Berkesi et al. (2011).



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Fig. 5: (a) A fluid inclusion in pegmatite quartz from Ehrenfriedersdorf containing a large sassolite  $[H_3BO_3]$  and a small beryllonite  $[NaBePO_4]$  daughter crystal. (b) Raman spectrum of beryllonite. The weak band at 880 cm<sup>-1</sup> results from the saturated boric acid solution in the inclusion. The superimposed larger band at 880 cm<sup>-1</sup> is from a region of the inclusion containing the sassolite daughter crystal. Thomas & Davidson (2012) have used Raman to identify relatively uncommon minerals in FI, including beryllonite (NaBePO<sub>4</sub>) and sassolite (H<sub>3</sub>BO<sub>3</sub>) in pegmatitic quartz from Ehrenfriedersdorf (left), and claudetite (As<sub>2</sub>O<sub>3</sub>) and sassolite in a FI in tourmaline from the Muiane pegmatite, Mozambique (right).

> From Thomas and Davidson, Z. dt. Ges. Geowiss., 163: 113–126, 2012





Fig. 4: (a) A secondary fluid inclusion in red tourmaline (rubellite) from the Muiane pegmatite, Mozambique, containing daughter crystals of claudetite  $[As_2O_3]$  and sassolite  $[H_3BO_3]$ . From rough volume estimation the inclusion contains more than 11% (g/g) As<sub>2</sub>O<sub>3</sub>. (b) Raman spectra of sassolite (blue) and claudetite (red) characterised by the very strong bands at 880 cm<sup>-1</sup> and 458 cm<sup>-1</sup>, resp. The band marked Tu is from the tourmaline matrix.

Raman mapping, whereby the Raman spectrum is collected as the sample moves in XY  $\pm$ Z under the laser provides information on the spatial distribution of phases in the inclusion.



Raman map (right) and Raman spectrum of a synthetic fluid inclusion in olivine after interaction of the aqueous fluid with the olivine host to form serpentine, brucite, and hydrogen.

BUBBLES '

From Lamadrid et al., 2017

In more recent years, much effort has been devoted to development of quantitative methods in Raman spectroscopy.



Caumon et al. (2014) used synthetic H<sub>2</sub>O-CH<sub>4</sub> FI with known CH<sub>4</sub> concentrations to develop an empirical calibration curve to estimate methane concentrations in fluid inclusions.

From Caumon et al., 2014; Chem. Geol; modified and published in Bodnar and Frezzotti, 2020



In more recent years, much effort has been devoted to development of quantitative methods in Raman spectroscopy.

Moncada, following on earlier work by Mernagh & Wilde, examined the effect of salinity on the shape of the water band.



Many additional studies are ongoing in various labs around the world to develop new Raman-based approaches to analyzing saline aqueous FI.



From D. Moncada, unpub.; modified and published in Bodnar and Frezzotti, 2020

In more recent years, much effort has been devoted to development of quantitative methods in Raman spectroscopy.

Combining measurement of the  $CO_2$  clathrate melting temperature with pressure determined from Raman analysis of the fermi diad can be used to determine salinity of FI.



Many previouslypublished estimates of fluid salinity based on clathrate melting are likely incorrect because the clathrate did not melt in presence of both liquid and vapor  $CO_2$ . From Fall et al., 2011



Quantitative analysis of major, minor and trace elements in fluid inclusions using laser ablationinductively coupled plasma mass spectrometry

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Calibration Strategies for the Elemental Analysis of Individual Aqueous Fluid Inclusions by Laser Ablation Inductively Coupled Plasma Mass Spectrometry

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## 1998

Journal of

Analytical Atomic

Spectrometry



1996





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Gradually increasing the laser spot size during ablation can minimize loss of material from "splashing".



From Gunther et al., 1998 JAAS



The 193 nm laser appears to be ideal for analyzing inclusions in quartz, and produces near perfect holes with little fracturing and flaking of host material. BUBBLES 'Я'

From Gunther et al., 1998 JAAS





While the spectrum obtained from a fluid inclusion and, to a lesser extent, from a melt inclusion is often "spikey" and irregular, the integrated intensities are usually consistent for FI in the same FIA.



While the spectrum obtained by laser ablation ICPMS analysis of a fluid inclusion and, to a lesser extent, from a melt inclusion is often "spikey" and irregular, the integrated intensities are usually consistent for FI in the same FIA. Gunther et al. (1998) report an accuracy of 5-20% based on analysis of synthetic fluid inclusions of known composition.

From Gunther et al., 1998 JAAS











The first detailed study using LAICPMS to analyze FI from an ore deposit to constrain metal contents and fluid evolution was by Audétat et al. (2000) on the Mole Granite, Australia. They showed a clear relationship between concentration and salinity.

Fluids Research Laboratory



Audétat and Pettke (2003) analyzed coexisting melt, brine and vapor inclusions from the Rito del Medio pluton in New Mexico. The data were then used to determine partitioning behavior of various elements between the melt, brine and vapor phases.





Wenz et al. (2011) analyzed FI in sphalerite from the Viburnum Trend MVT deposits by LAICPMS. Based on the elevated Pb contents, they concluded that Pb and S could not be transported by the same fluid, thus requiring two fluid sources – one for metals and one for sulfur.

Wilkinson et al. (2009) measured 104 Pb concentrations FI in sphalerite  $10^{3}$ (mdd) uZ from MVT deposits by LAICPMS. Using inferred Zn/Pb ratios, they calculated Zn concentrations in the 10° ore forming fluids; values ranged 10 up to 5000 ppm in the Irish Frequency deposits and up to 3000 ppm for 8northern Arkansas deposits. These 6 values have implications 10-1 concerning the amount of time and fluid required to form the deposits.



A destructive analytical technique that provides quantitative to semi-quantitative information on FI compositions is electron probe analysis of evaporate mounds generated by decrepitating FI.



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Images courtesy of Dan Kontak

# Proton Probes (PIXE = Particle Induced X-ray Emission; PIGE = Particle Induced Gamma-ray Emission) particle = proton

While PIXE and PIGE showed early promise for analyzing FI, the method was limited by the fact that the geometry of the FI and host material must be known for quantification. As such these methods are still useful for mapping out elemental distributions within FI and MI, but not for quantitative analysis.



From Kamenetsky et al., 2002, Geology



# Cryo-TOF-SIMS: Cryo-Time of Flight Secondary Ion Mass Spectrometry



# **Future Developments**

- Stable isotopic analysis (C, H, O, S, CI) of fluids in individual FI
- Determination of absolute ages of fluids in individual FI (Rb/Sr)
- Rapid mapping of the distribution of phases and components in individual FI & MI
- Improvements in quantitative analysis by Raman spectroscopy
- Ability to analyze smaller (≤1-2 micron) FI & MI
- LA-ICPMS analysis of very low salinity FI, such as those that occur in low-sulfidation epithermal gold deposits
- Improved methods for determination of volatiles in MI
- ????

