Melt Inclusions: A Window into the Sub-volcanic and Mantle Environment

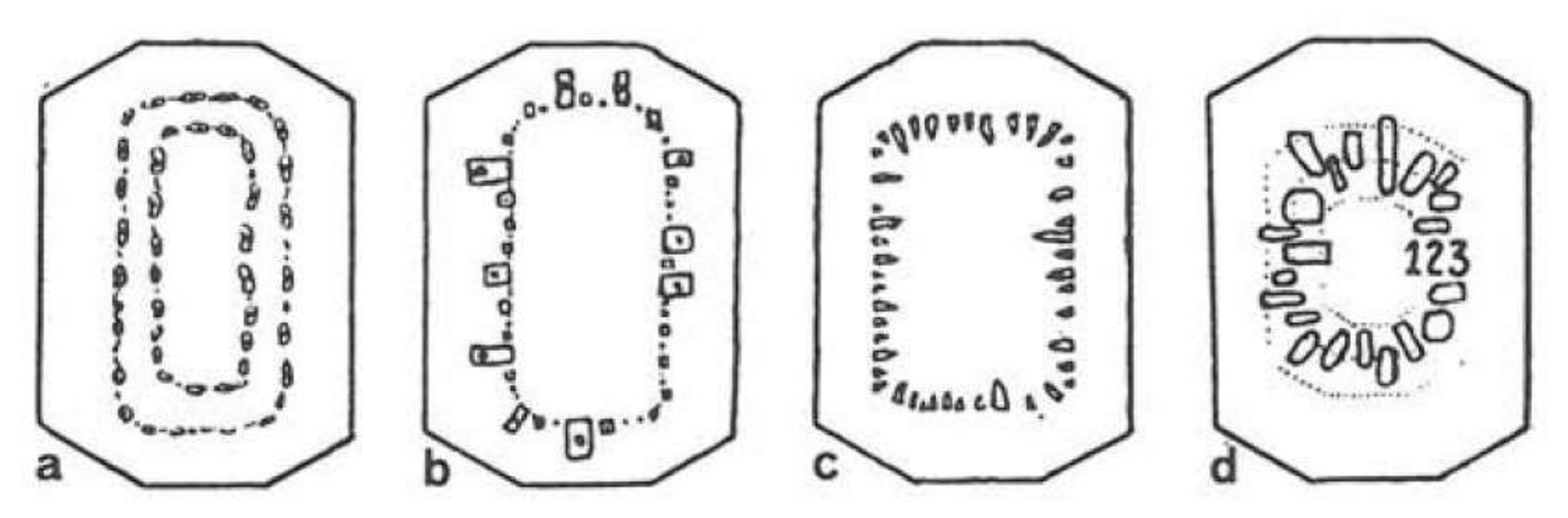
Melt inclusions provide information on the physical and chemical conditions in subvolcanic magma chambers and the mantle. This allows researchers to better understand processes responsible for active volcanism, ore formation, and mantle evolution.

Bingham Canyon, Utah USA

The past 3-4 decades have seen a significant increase in the number of publications reporting data from melt inclusions. This increased activity has been driven by advances in microanalytical methods that have allowed detailed quantitative analysis of individual melt inclusions from diverse geological environments.

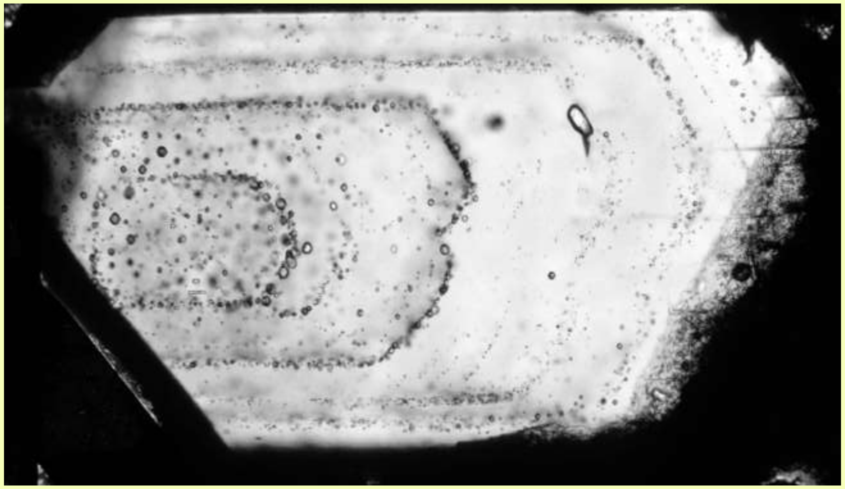
- Mantle petrology & geochemistry: data obtained mostly from electron microprobe (major and minor elements) and ion microprobe (trace elements, especially REE) of MI in mantle xenoliths
- Volcanic processes: data obtained from EPMA and SIMS, combined with FTIR and Raman data on volatile contents of MI in eruption products (tephras)
- Ore-forming systems: data obtained from laser ablation ICPMS analysis to determine metal contents of melts associated with ore formation, supplemented by EMPA, SIMS, Raman and other methods as appropriate

Melt (and fluid) inclusions can be thought of as representing defects in a crystal. If a crystal grows slowly under equilibrium conditions such that temperature, pressure and fluid (melt) composition change gradually (slowly), a “perfect” crystal without melt or fluid inclusions is likely to be produced.

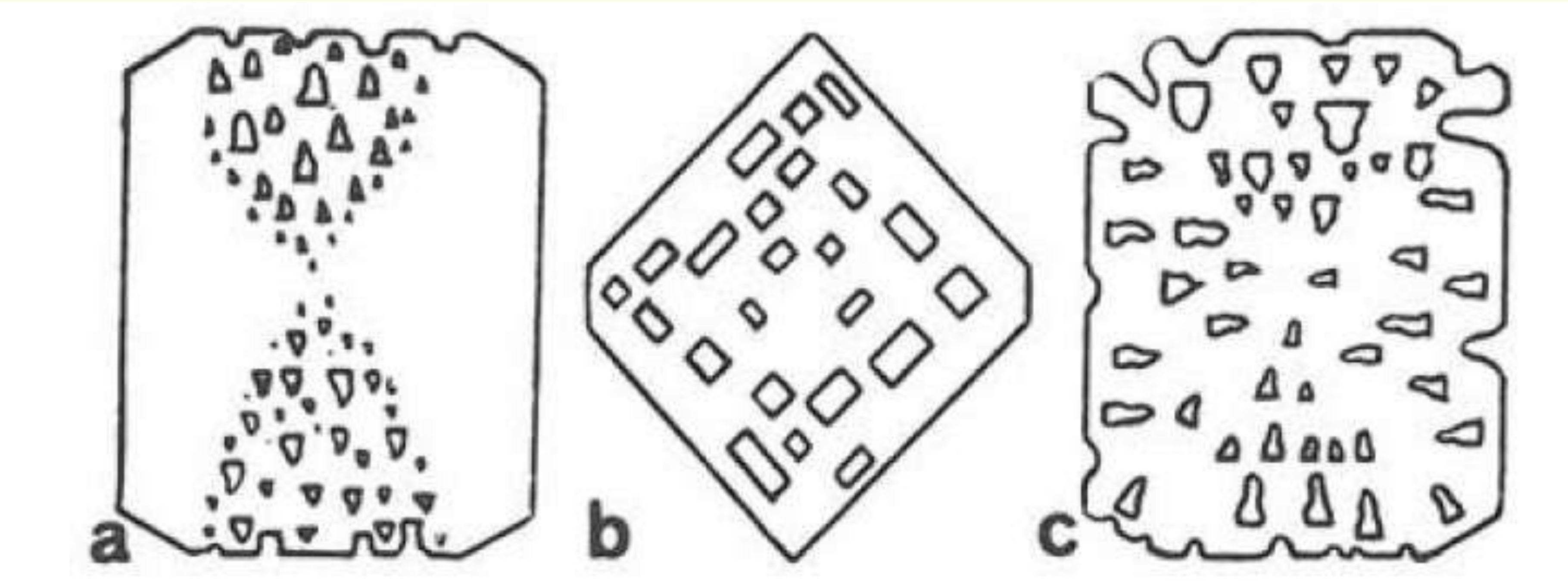


From Roedder, 1984; Fig. 12-3

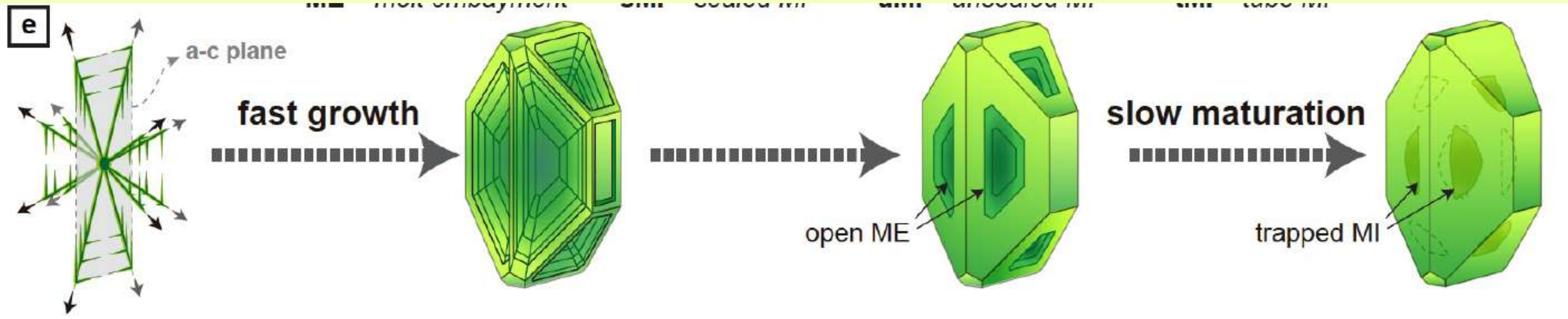
These images show examples of zonal melt inclusions trapped along growth zones in igneous phenocrysts.



If crystals grow rapidly, one face may "grow" more quickly than another face, resulting in formation of reentrants or "holes" in the crystal that later are sealed during further crystal growth, trapping some melt as inclusions in the process.



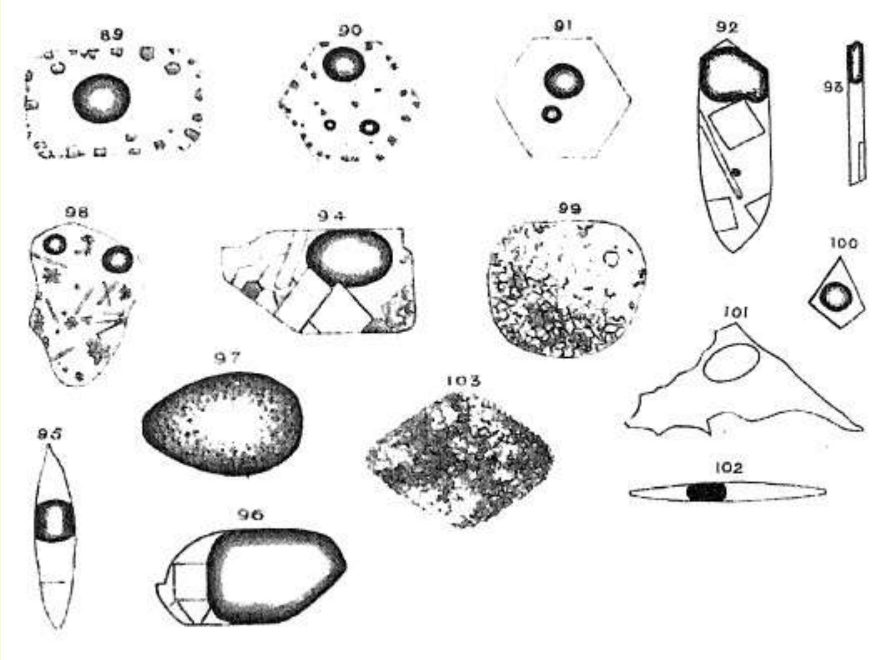
From Roedder, 1984; Fig. 12-3



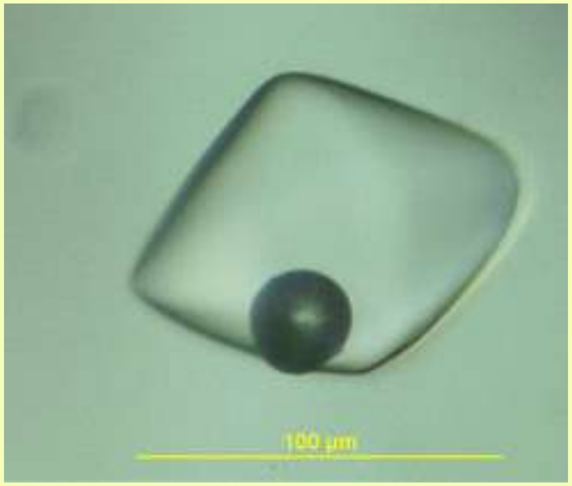
From Wallace et al., 2020; AREPS

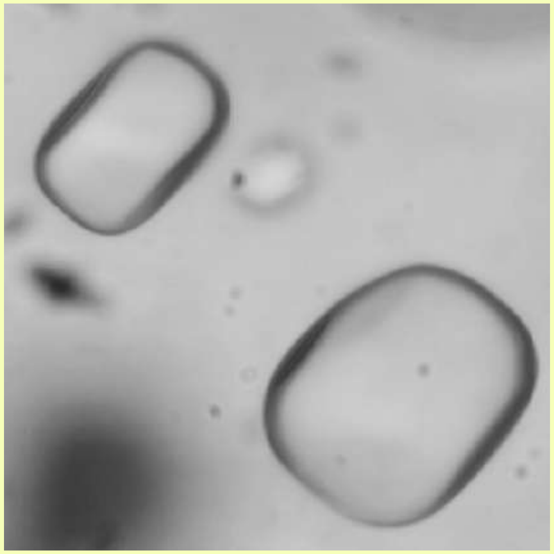
The first detailed scientific description of melt inclusions was the paper *“On the Microscopical Structure of Crystals, Indicating the Origin of Minerals and Rocks”* by Henry Clifton Sorby (1858).

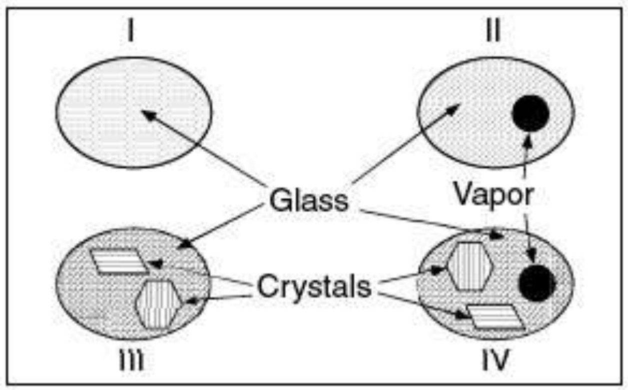
“… still some geologists, only accustomed to examine large masses in the field, may be perhaps disposed to question the value of the facts I have described, and to think the objects so minute as to be quite beneath their notice, … I certainly must protest; and I argue that there is no necessary connexion [sic] between the size of an object and the value of a fact, and that, though the objects I have described are minute, the conclusions to be derived from the facts are great.“

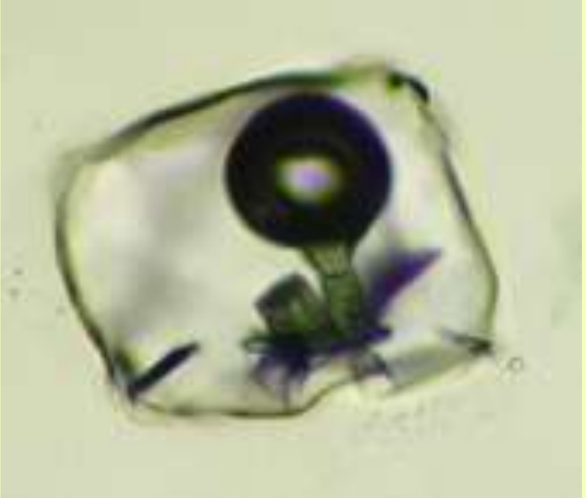


When observed at room temperature, melt inclusions range from being completely glassy (quenched melt), to containing glass + a vapor bubble, to glass + a vapor bubble + 1 or more crystals, to being completely crystallized.



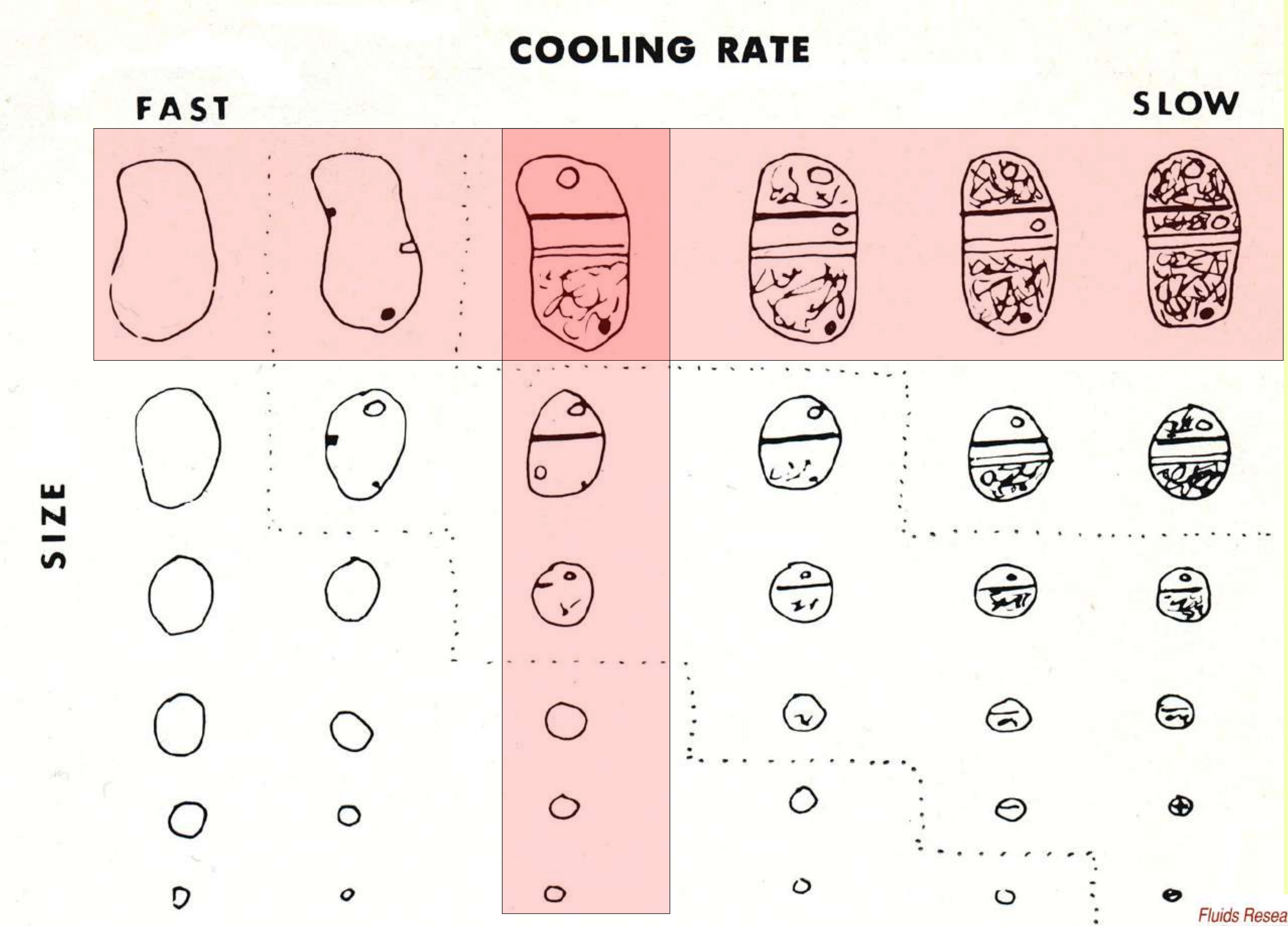






What determines whether a melt inclusion nucleates a vapor bubble, or forms crystals, after trapping?

The phases present in melt inclusions at room temperature is a function of cooling rate, inclusion size, and melt composition, including the volatile content.



From Roedder, 1979

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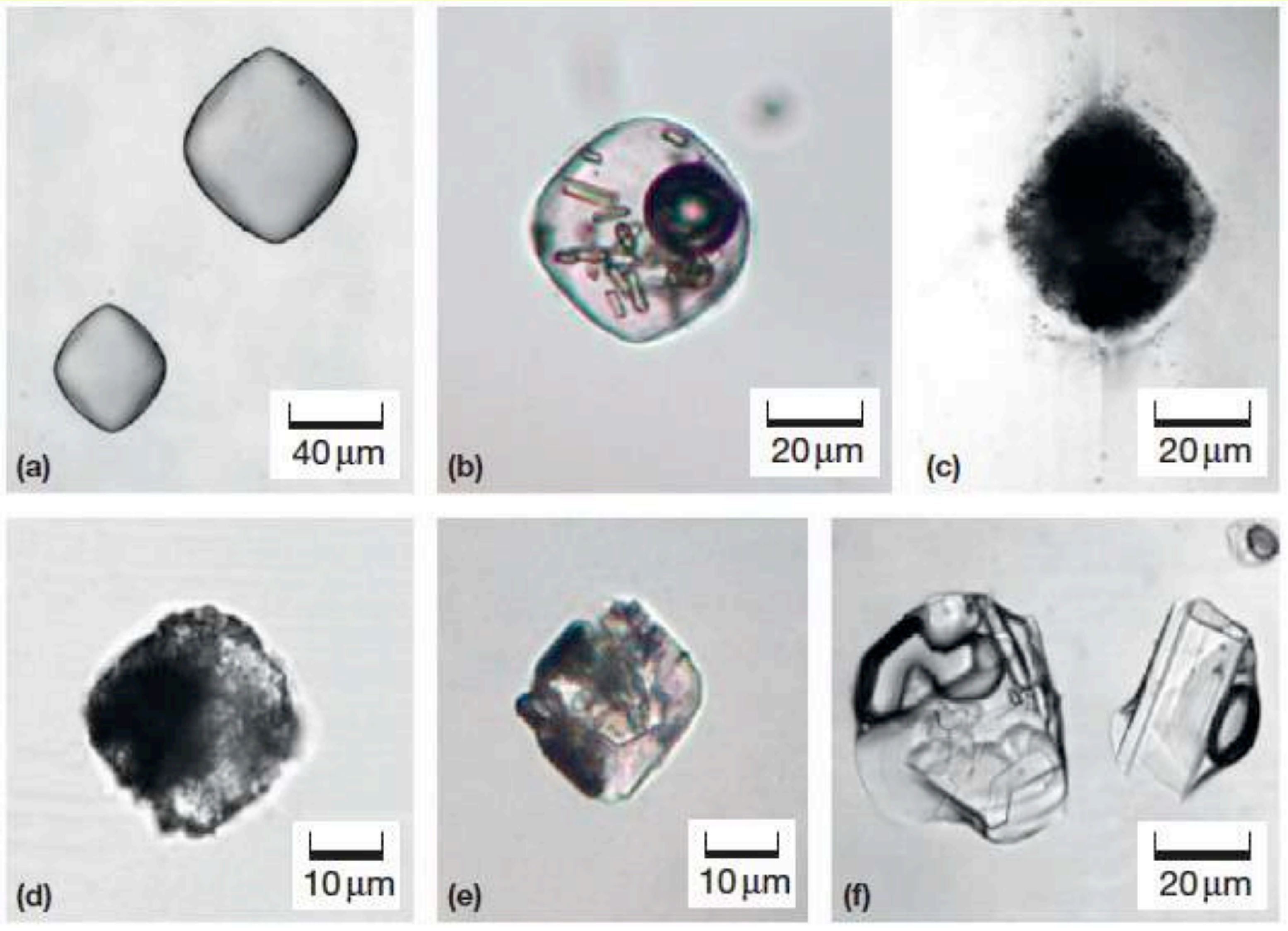
The phases present in melt inclusions at room temperature is a function of cooling rate, inclusion size, and melt composition, including the volatile content.



From Audétat & Lowenstern, 2014, Treatise on Geochemistry

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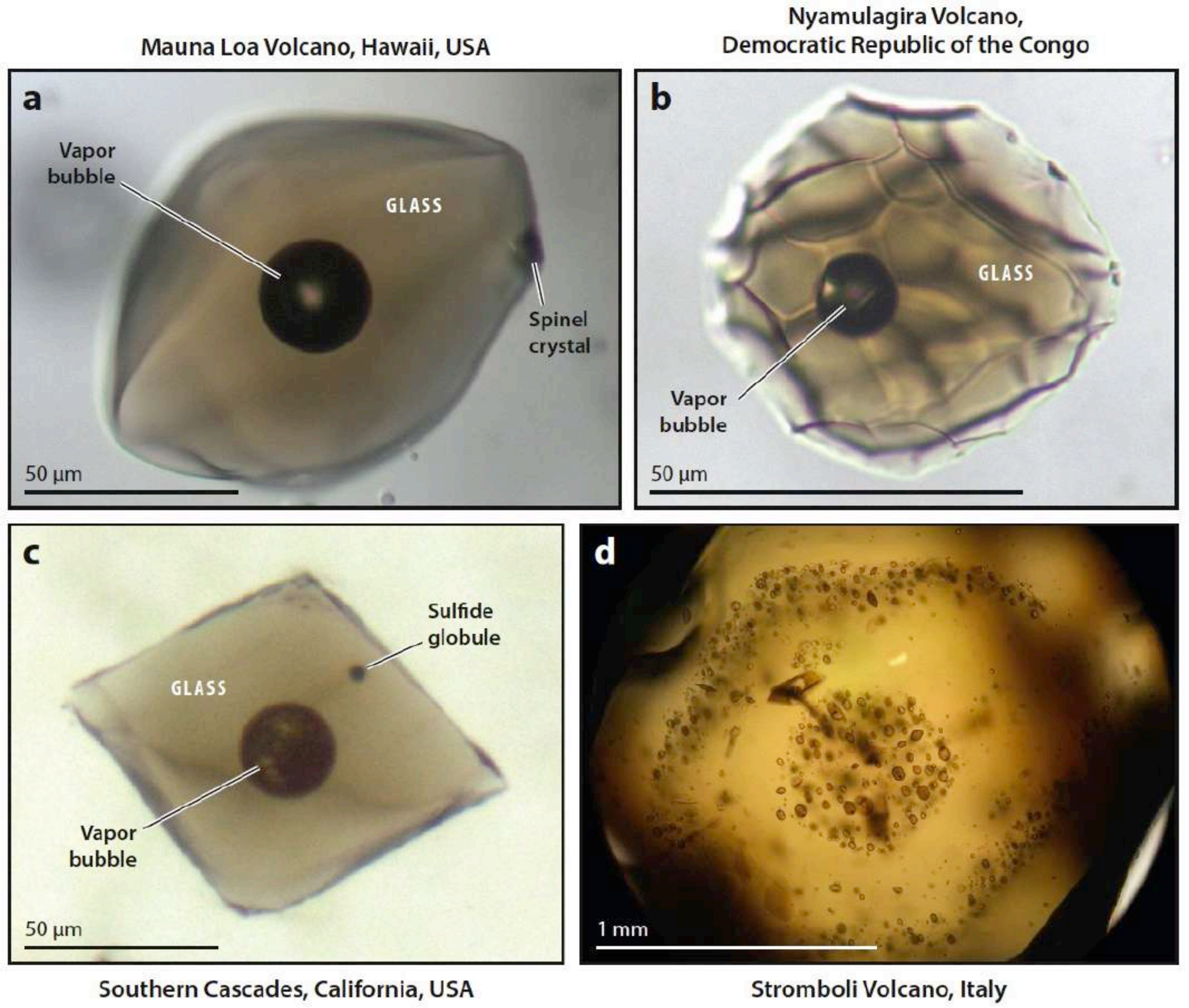
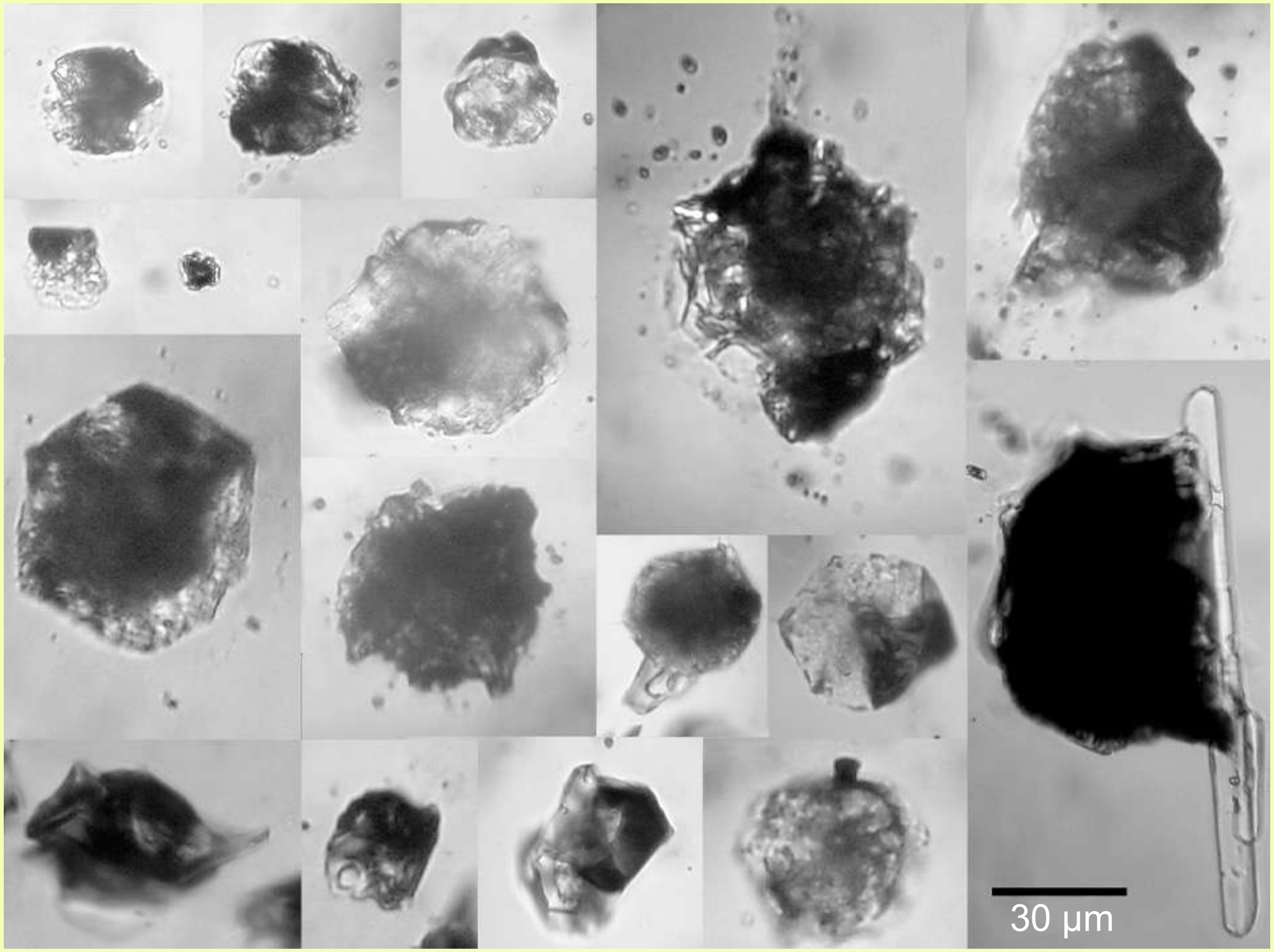
Melt inclusions in volcanic rocks, especially tephras (and less so in lavas), often contain glassy MI, sometimes with vapor bubbles and one or more small crystals (spinels and sulfides) or sulfide globules.

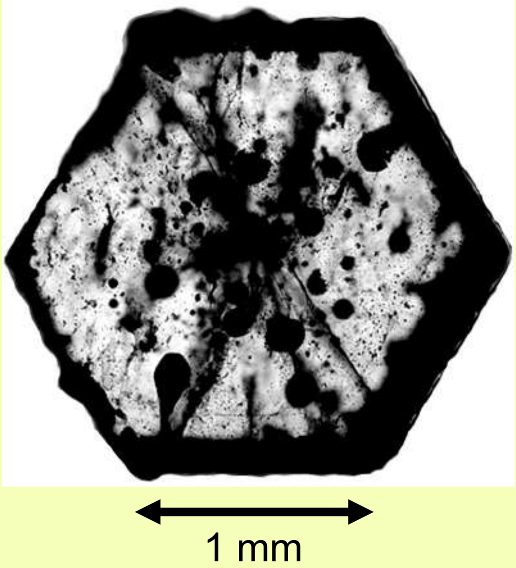
Why, in general, is it better to study MI that are glassy "as found", rather than MI that are partially to completely crystallized?



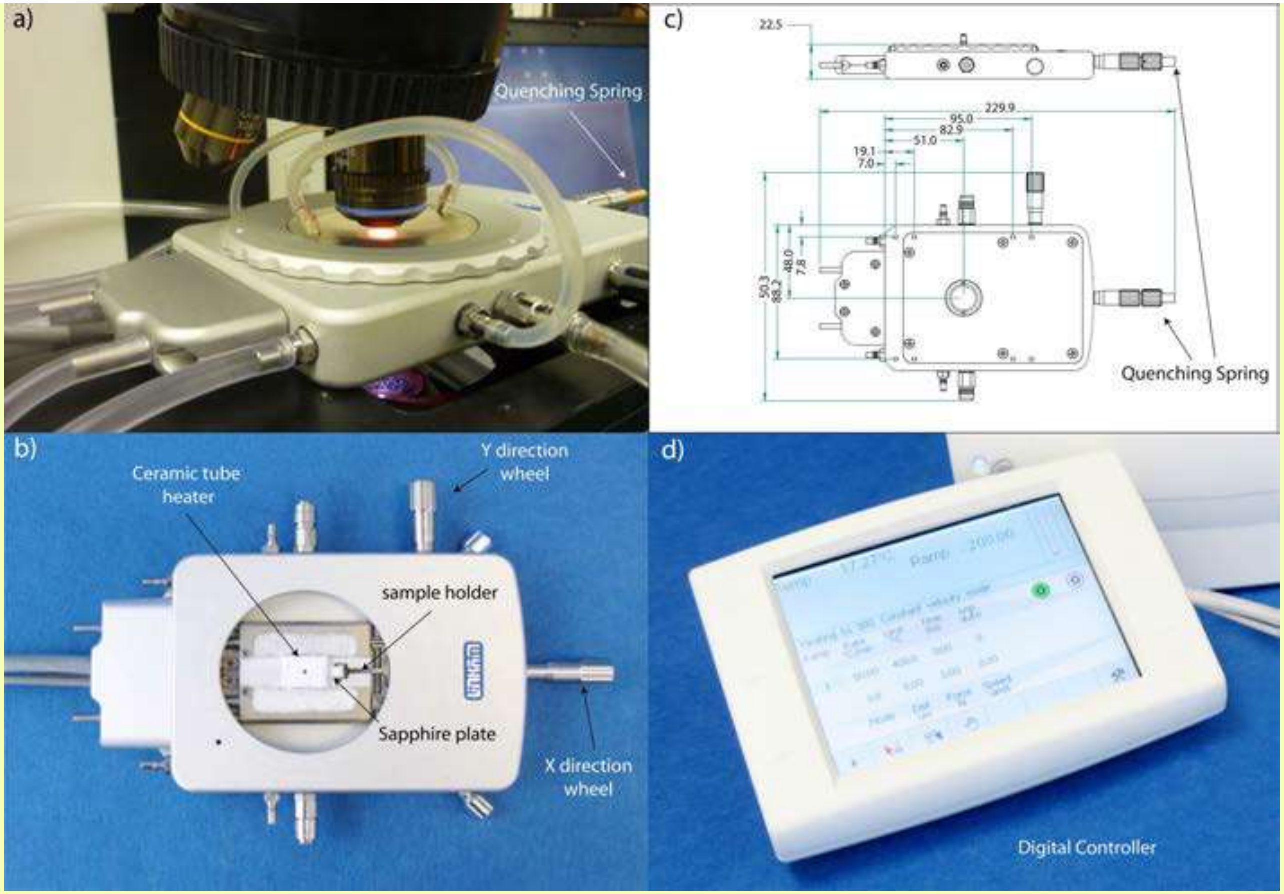
From Wallace et al., 2021, Ann Rev Earth Plan Sci

Melt inclusions in plutonic rocks associated with magmatic-hydrothermal ore deposits are typically completely crystallized and to the inexperienced worker would not be recognized as containing trapped melt.





Quartz phenocryst from the Tyrone, New Mexico, USA, porphyry deposit

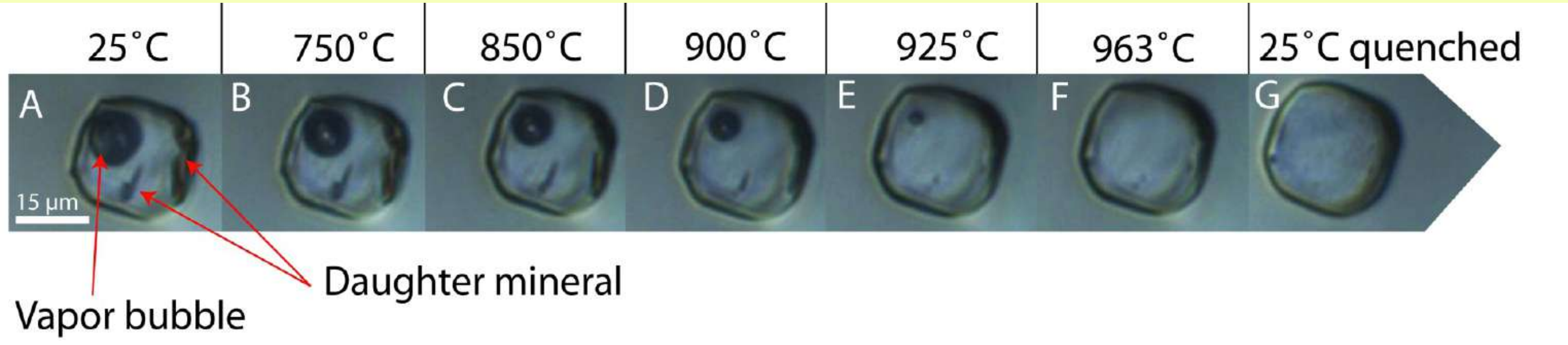


If the MI are partially to completely crystallized can (sometimes) be homogenized to:

(1) produce a glass for later analysis;

(2) obtain an estimate of the trapping T, and;

(3) distinguish between MI and trapped solids.



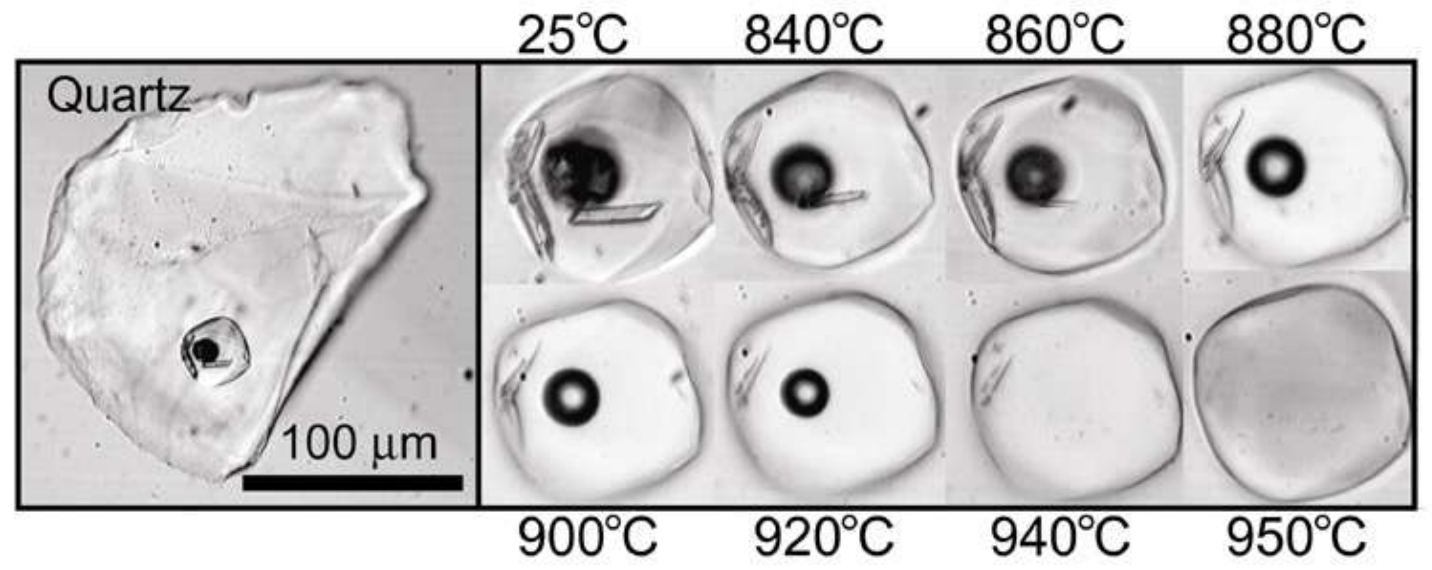
From Esposito et al., 2012

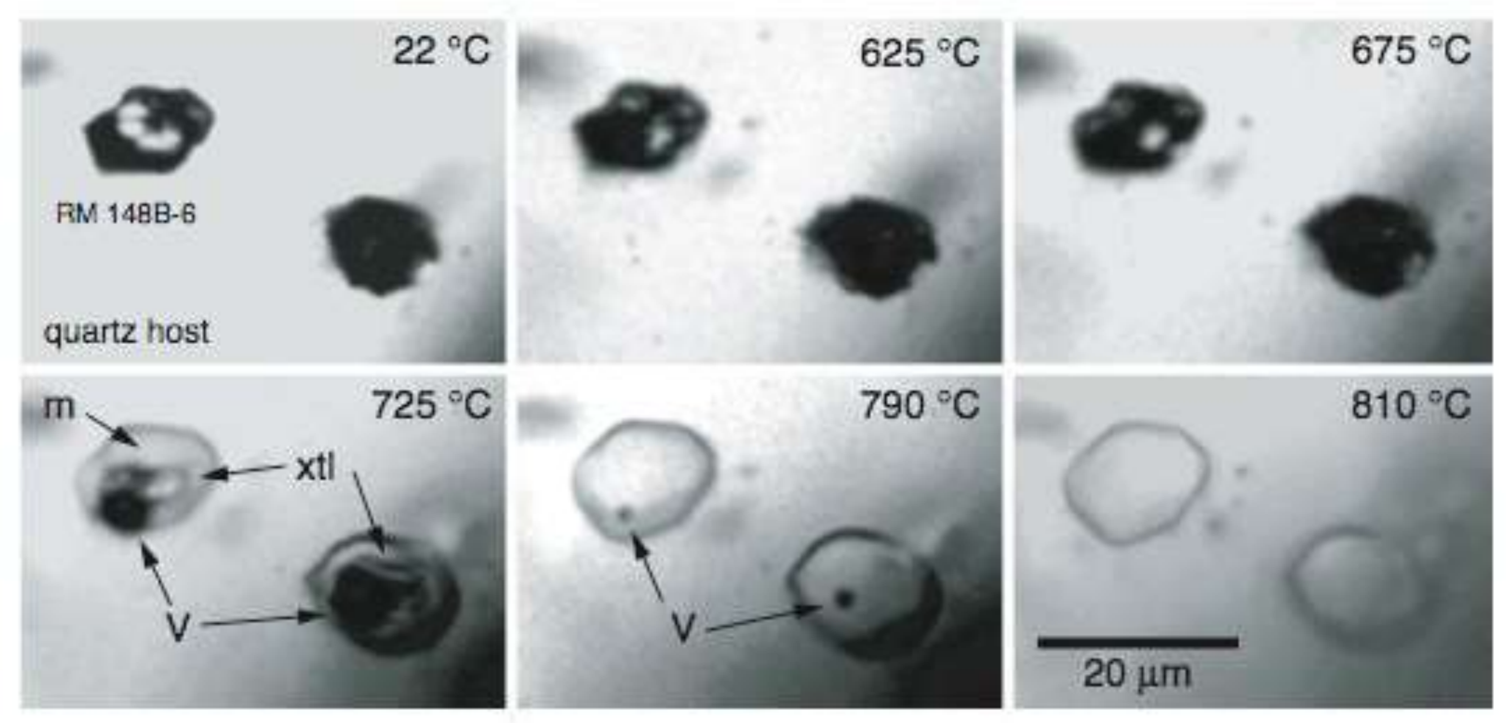
If the melt inclusions are partially to completely crystallized, it might be necessary to first homogenize the MI before analysis.

Yes:
- Electron probe
- SEM
- SIMS

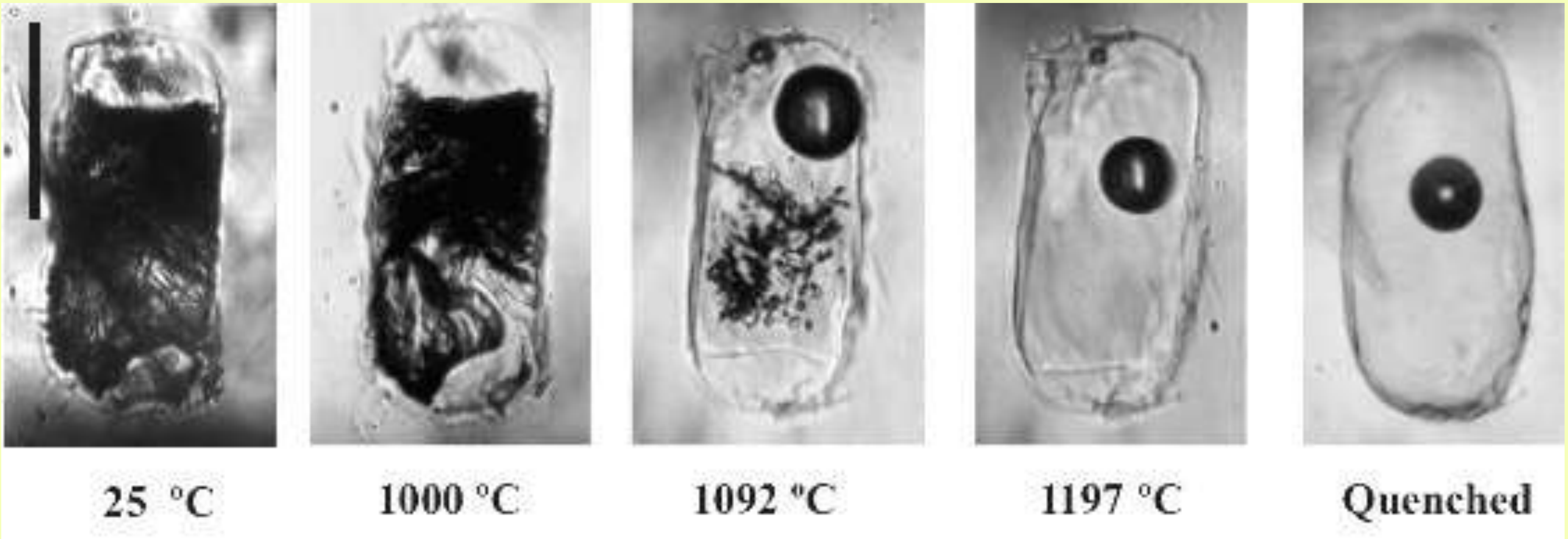
No:
- LAICPMS
- PIXE

Maybe:
- Raman

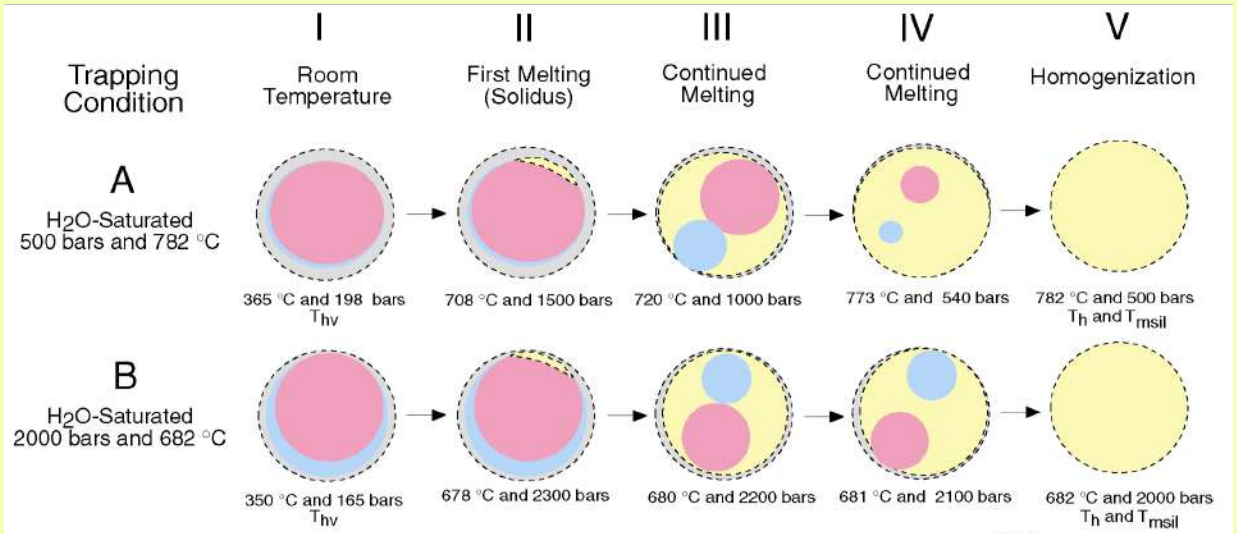




In some cases MI cannot be homogenized when heated at 1 atm pressure. In this case, it may be possible to heat the MI until all solids have melted, or the MI can be heated in a pressure vessel at elevated confining pressure.

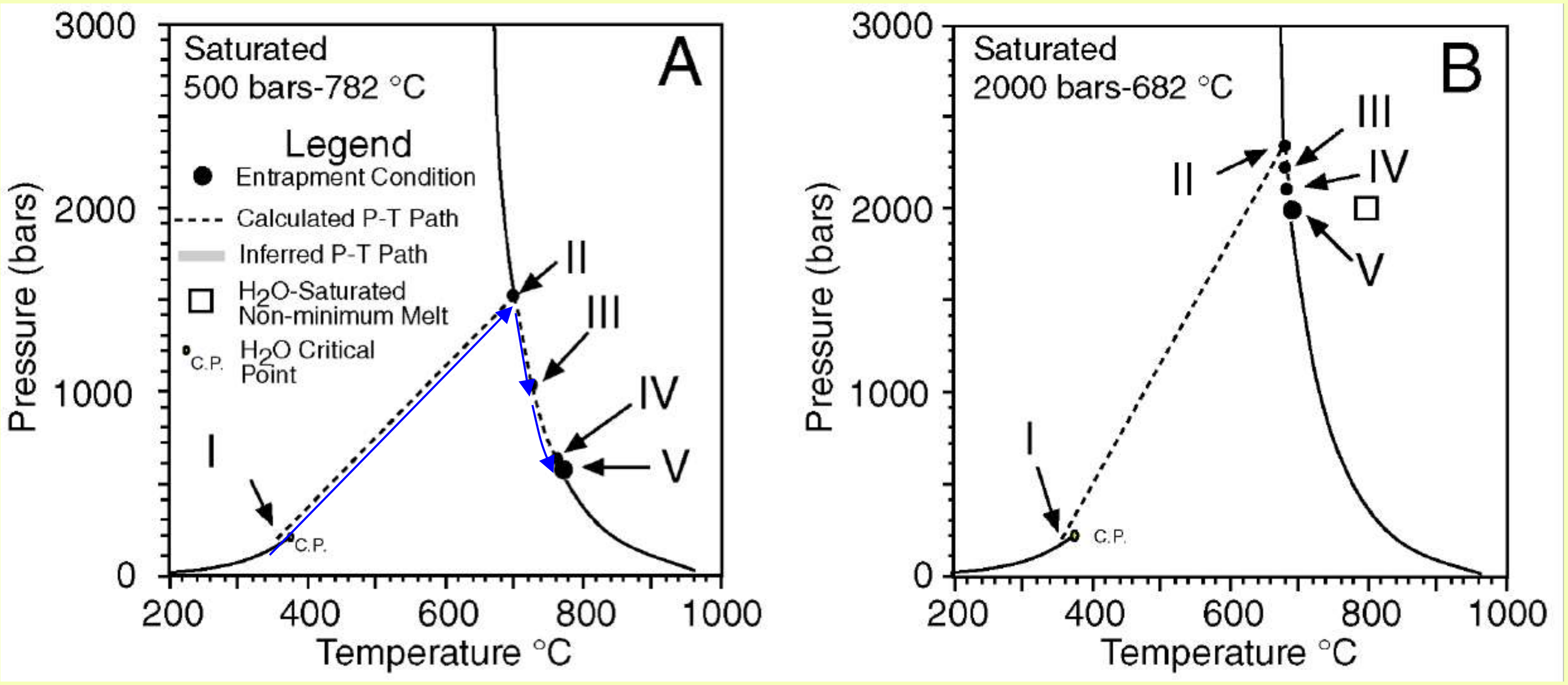


In many instances, H_2O-rich melt inclusions will decrepitate before the homogenization temperature is reached, i.e., before the water vapor bubble completely dissolved into the melt during heating.



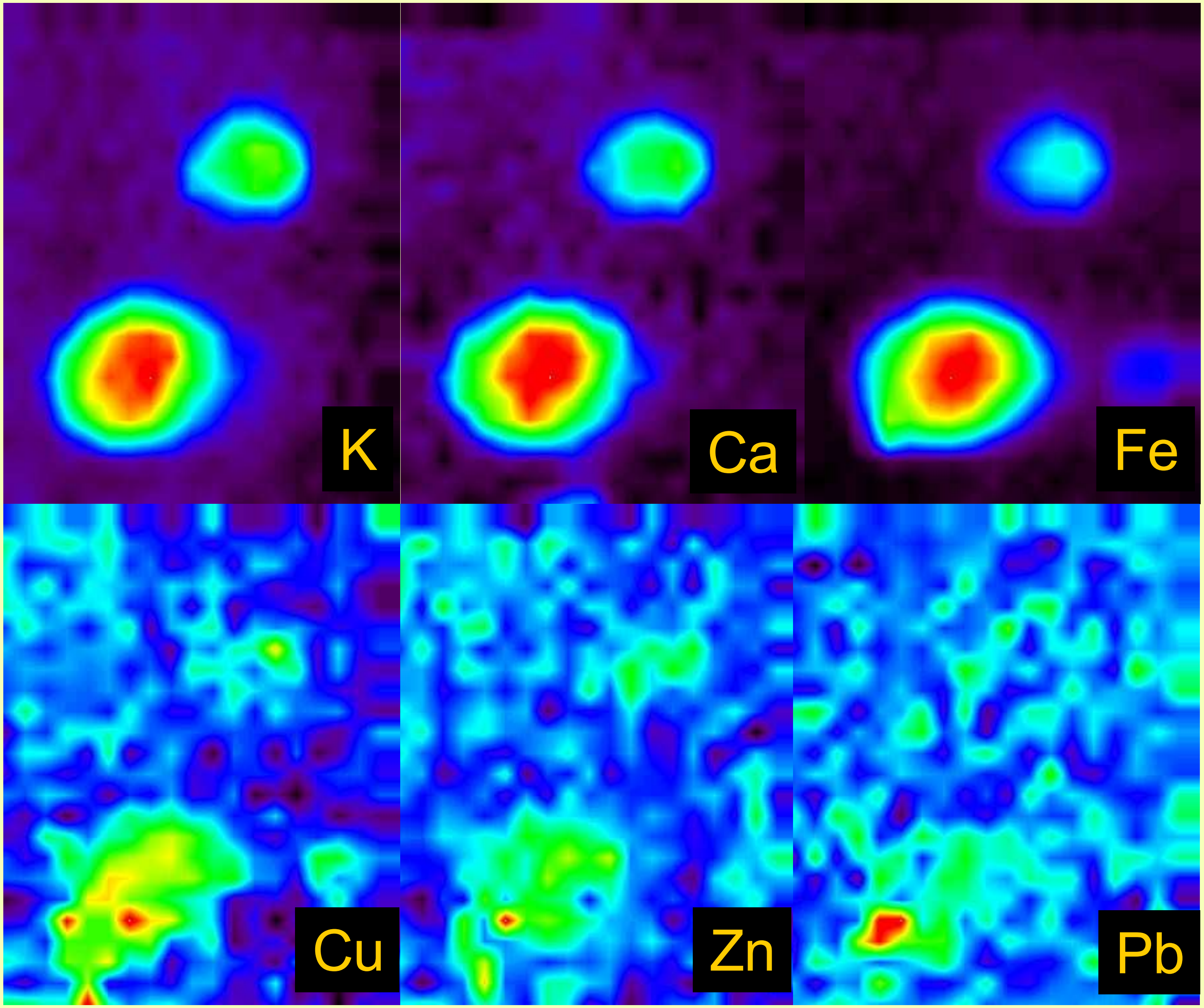
H_2O-rich melt inclusions often decrepitate during natural cooling or during laboratory heating at one atmosphere owing to the large difference between the partial molar volume of H_2O dissolved in the melt compared to the molar volume of the exsolved H_2O phase.

$$\bar{v}_{H2O} < V_{H2O}$$



Student & Bodnar, Petrology, 1996

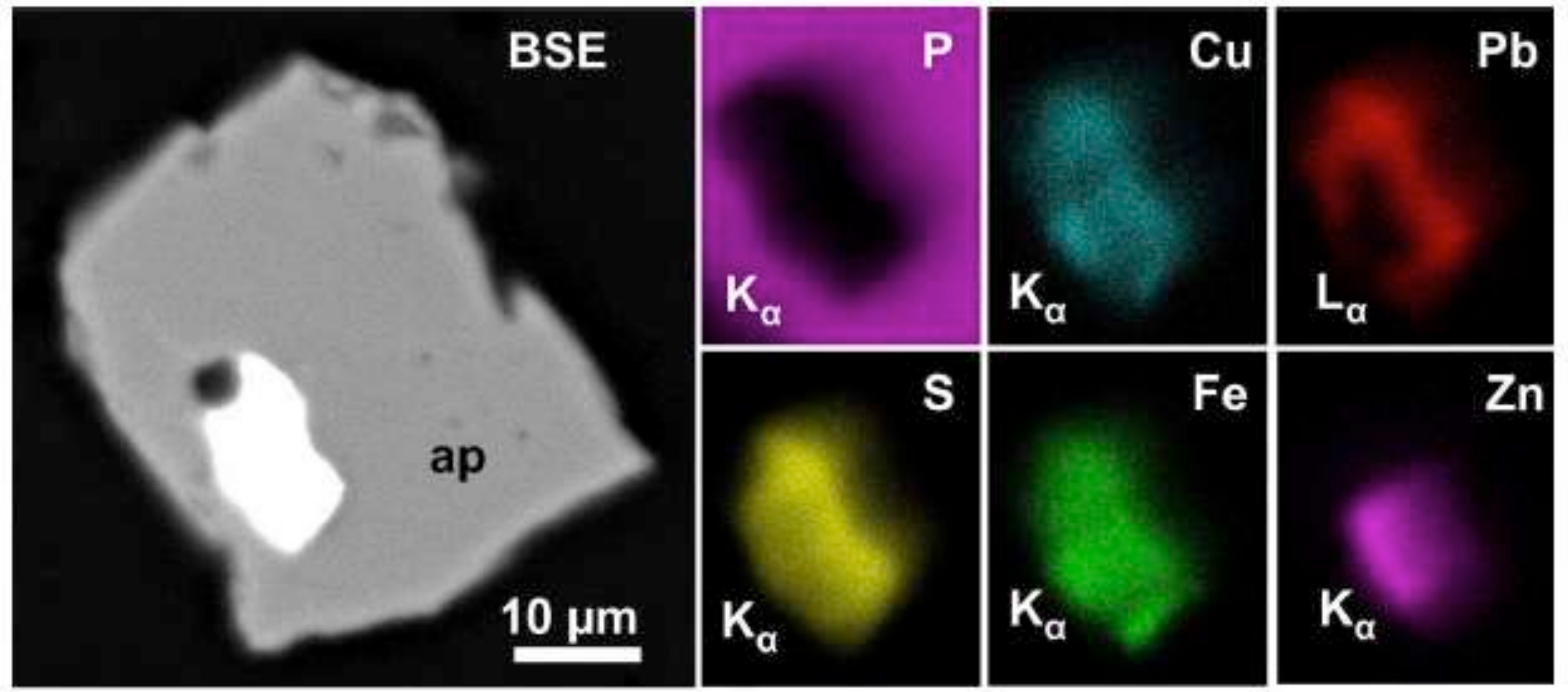
After MI have been homogenized to a glass, the MI may be analyzed using a variety of techniques, depending on the type of information needed.



Synchrotron XRF maps of melt inclusions in quartz

Various techniques may be used to analyze melt inclusions depending on the nature of the MI (glassy, with vapor bubble, crystallized) and the type of information needed.

- Scanning Electron Microscope: BSE images & X-ray mapping to show distribution of phases in crystallized MI or homogeneity of glassy MI.



BSE and elemental maps of a sulfide MI in apatite from the Sudbury Igneous Complex [from Watts, 2014, MS thesis St. Mary's University]

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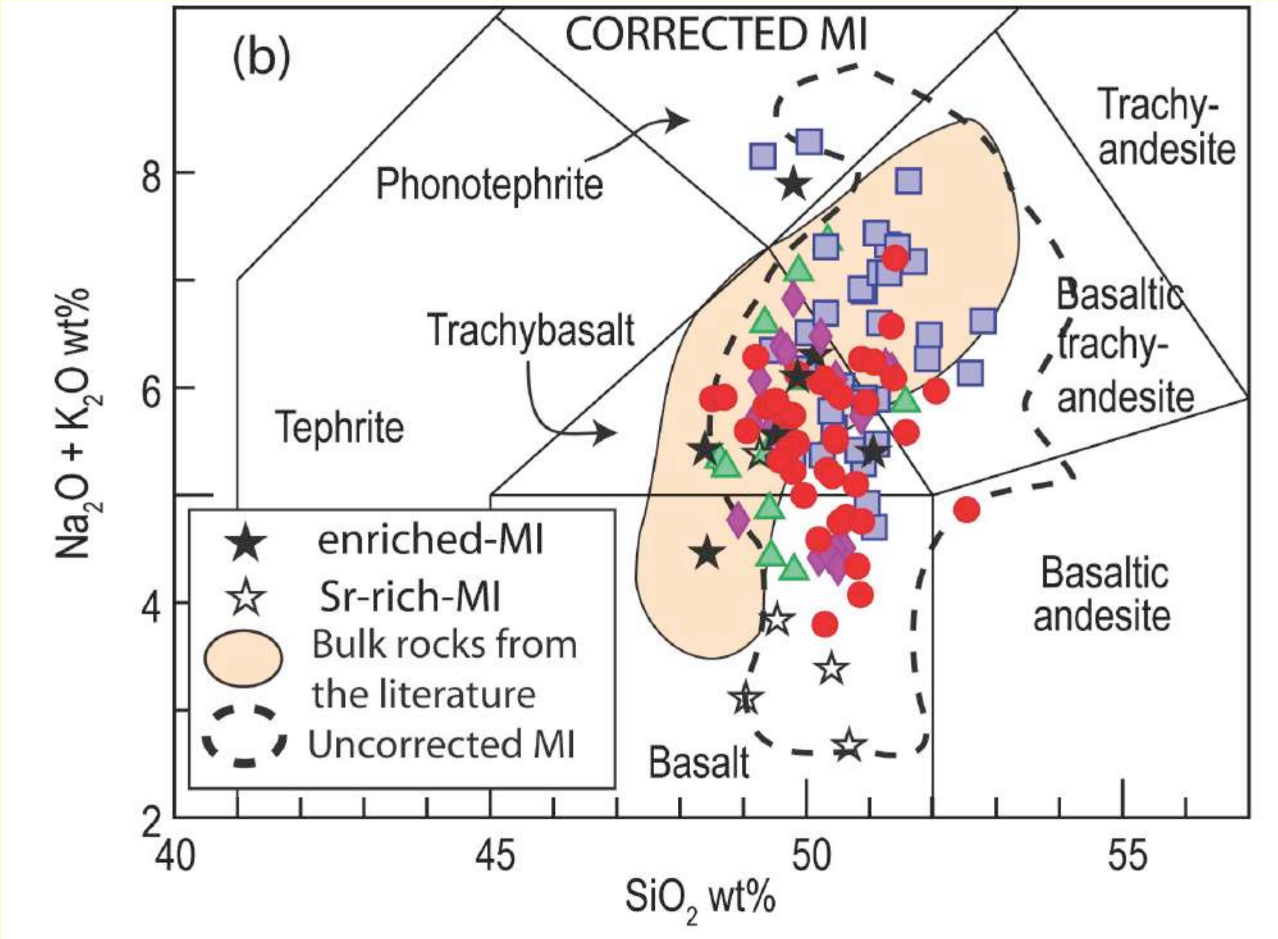
Various techniques may be used to analyze melt inclusions depending on the nature of the MI (glassy, with vapor bubble, crystallized) and the type of information needed.

- Electron Probe Micro Analyzer (EPMA): major and minor element composition of glassy MI.



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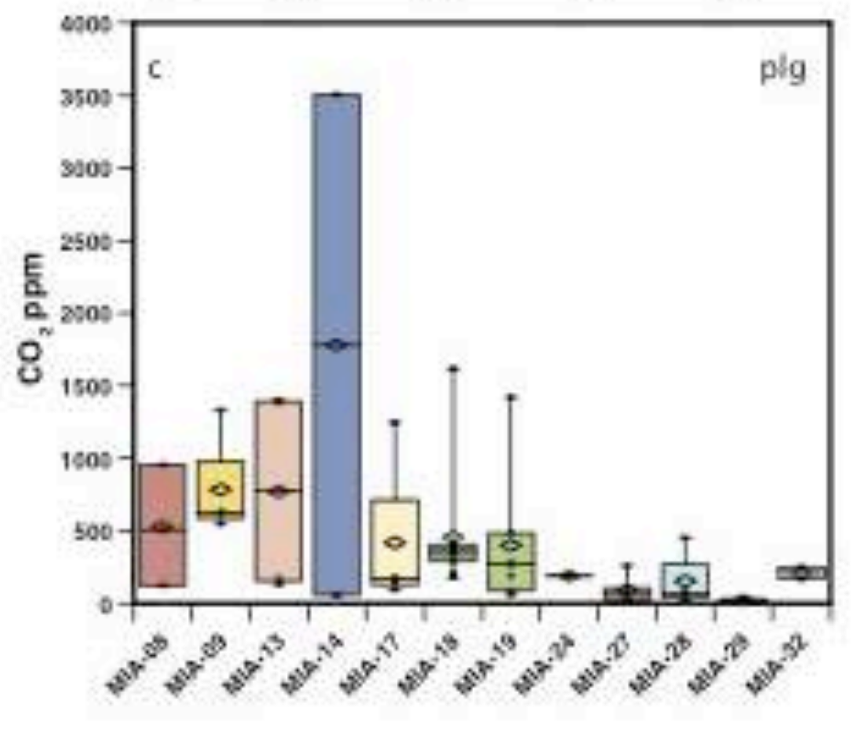
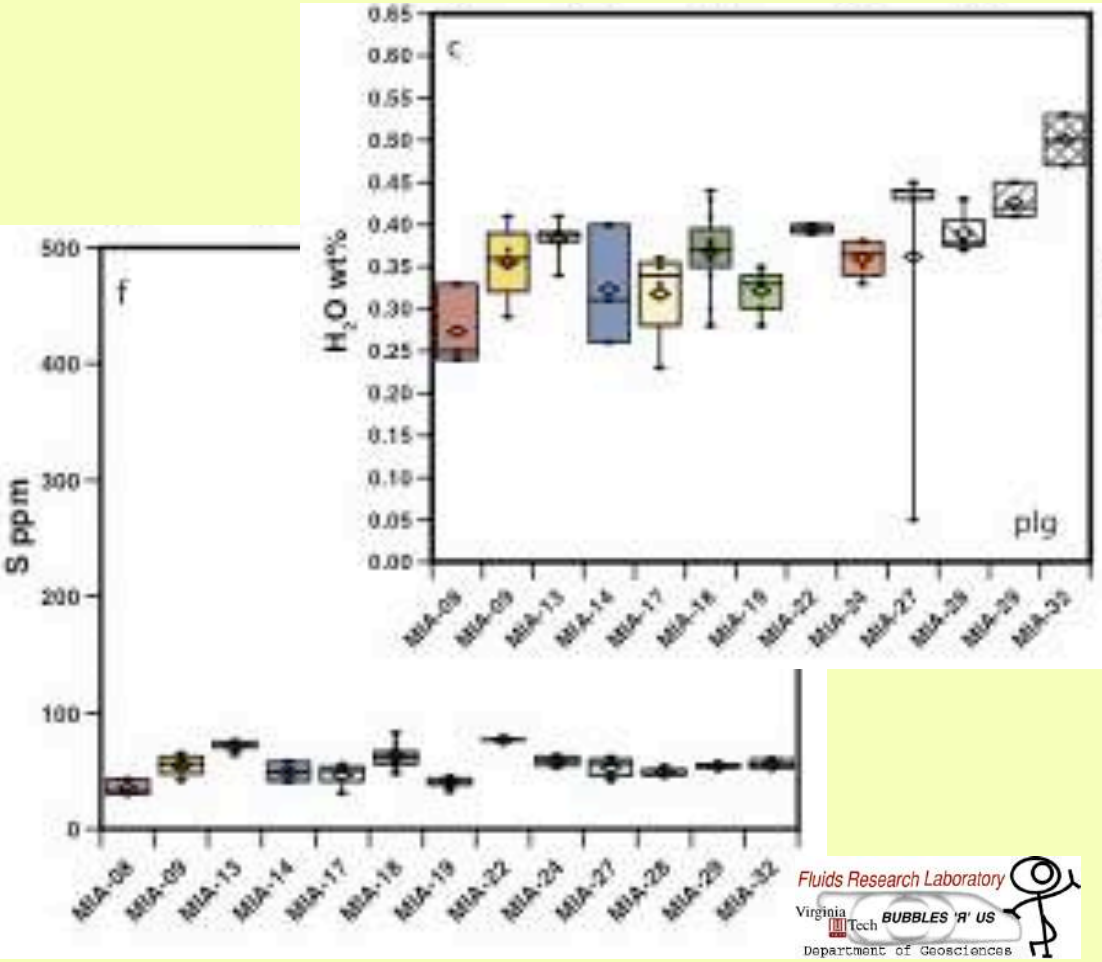
Various techniques may be used to analyze melt inclusions depending on the nature of the MI (glassy, with vapor bubble, crystallized) and the type of information needed.

- Secondary Ion Mass Spectrometry (SIMS): analysis of major, minor and trace elements in glassy MI, including H_2O, CO_2, F, Cl, S





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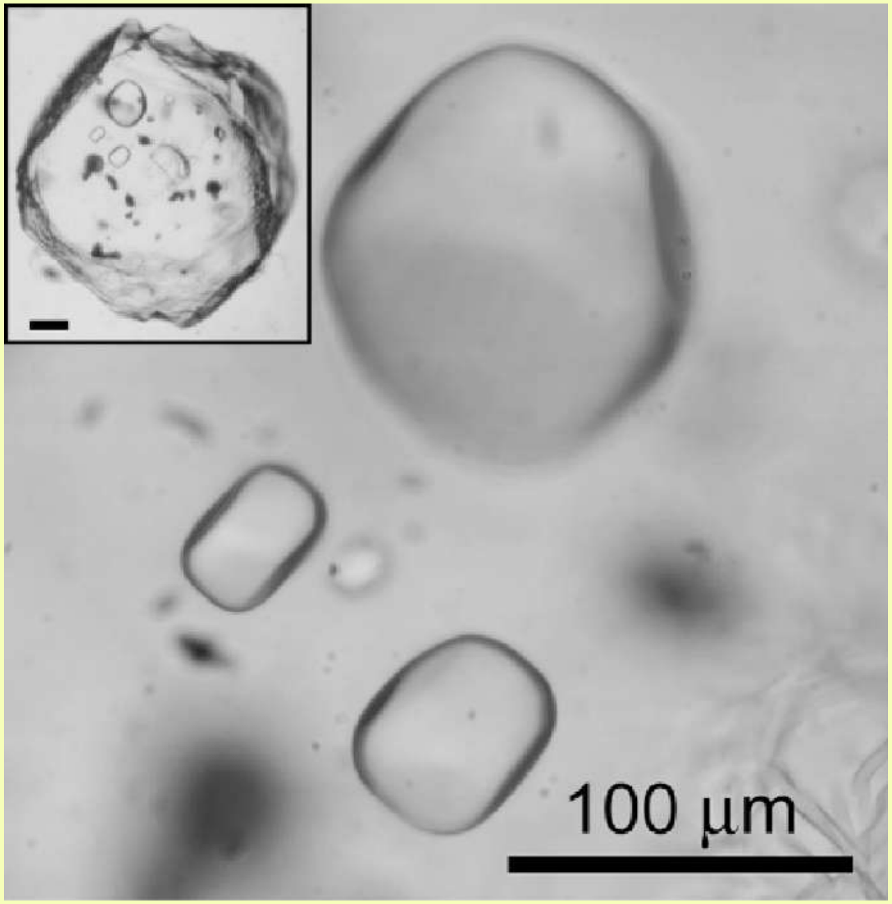
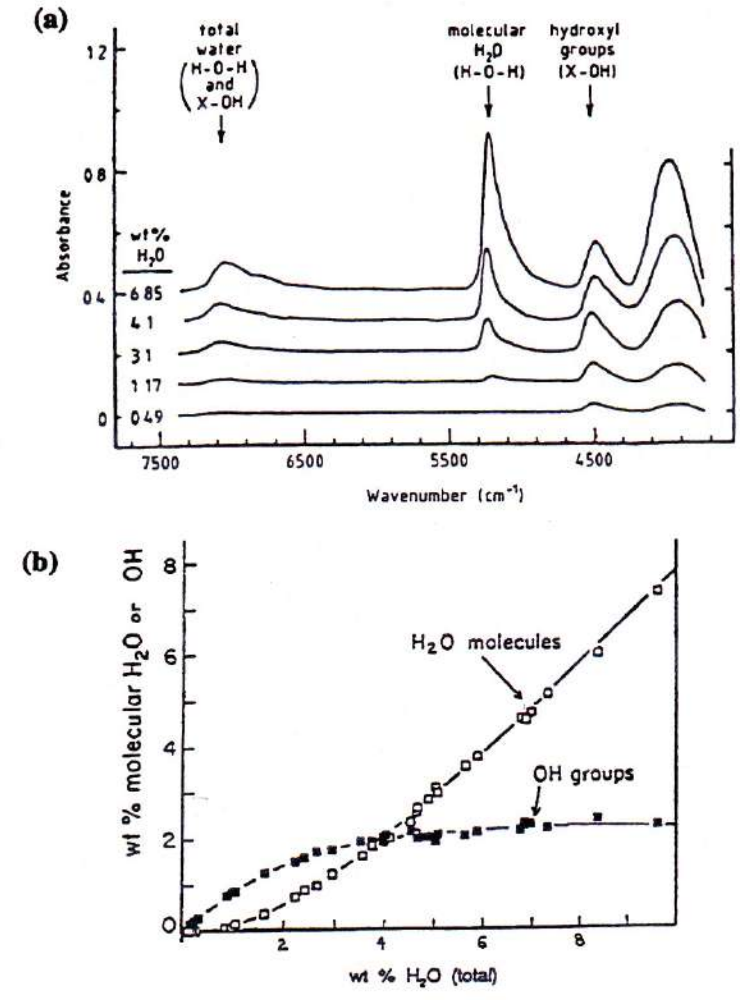
Various techniques may be used to analyze melt inclusions depending on the nature of the MI (glassy, with vapor bubble, crystallized) and the type of information needed.

- Fourier Transform Infrared Spectroscopy (FTIR): H_2O and CO_2 concentrations in glassy MI.

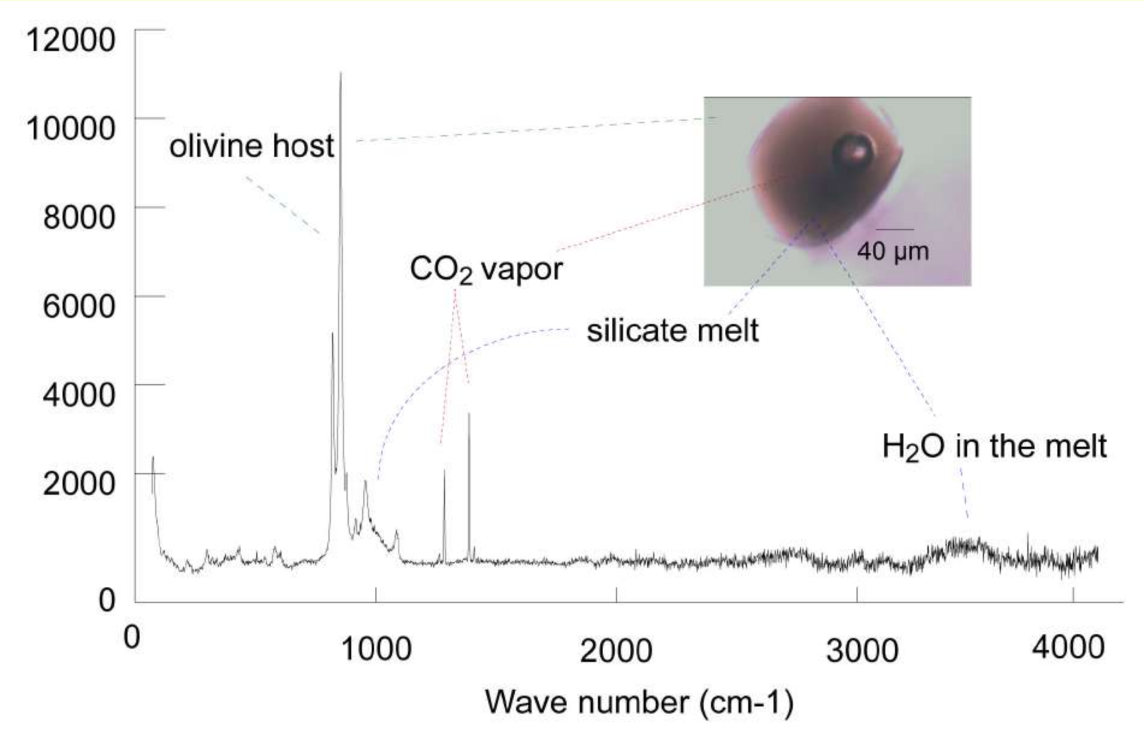


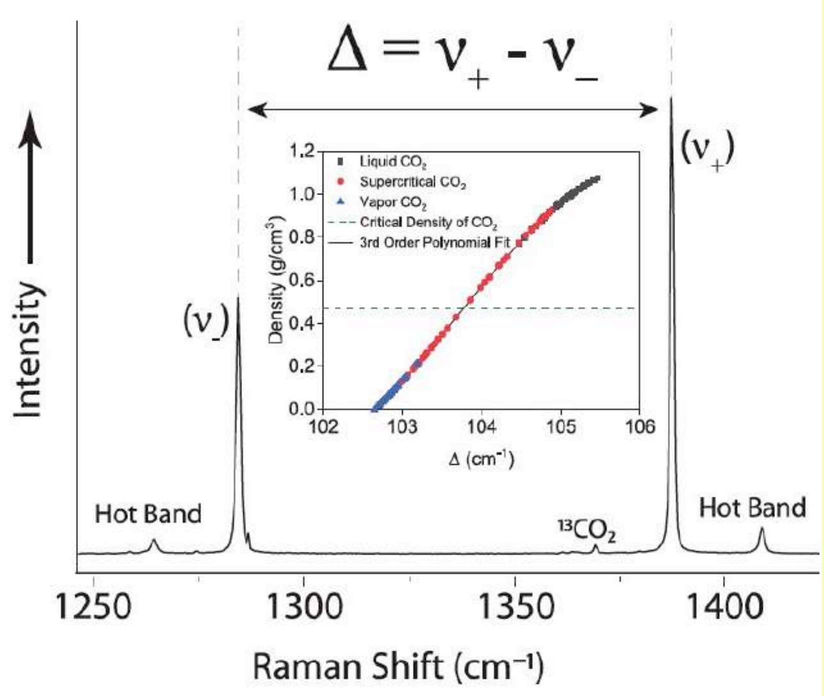


From McMillan, 1994, Reviews in Mineralogy, V 30, Fig 3

Various techniques may be used to analyze melt inclusions depending on the nature of the MI (glassy, with vapor bubble, crystallized) and the type of information needed.

- Raman Spectroscopy: Volatiles in vapor bubbles in MI and H_2O dissolved in the glass (melt) in MI.





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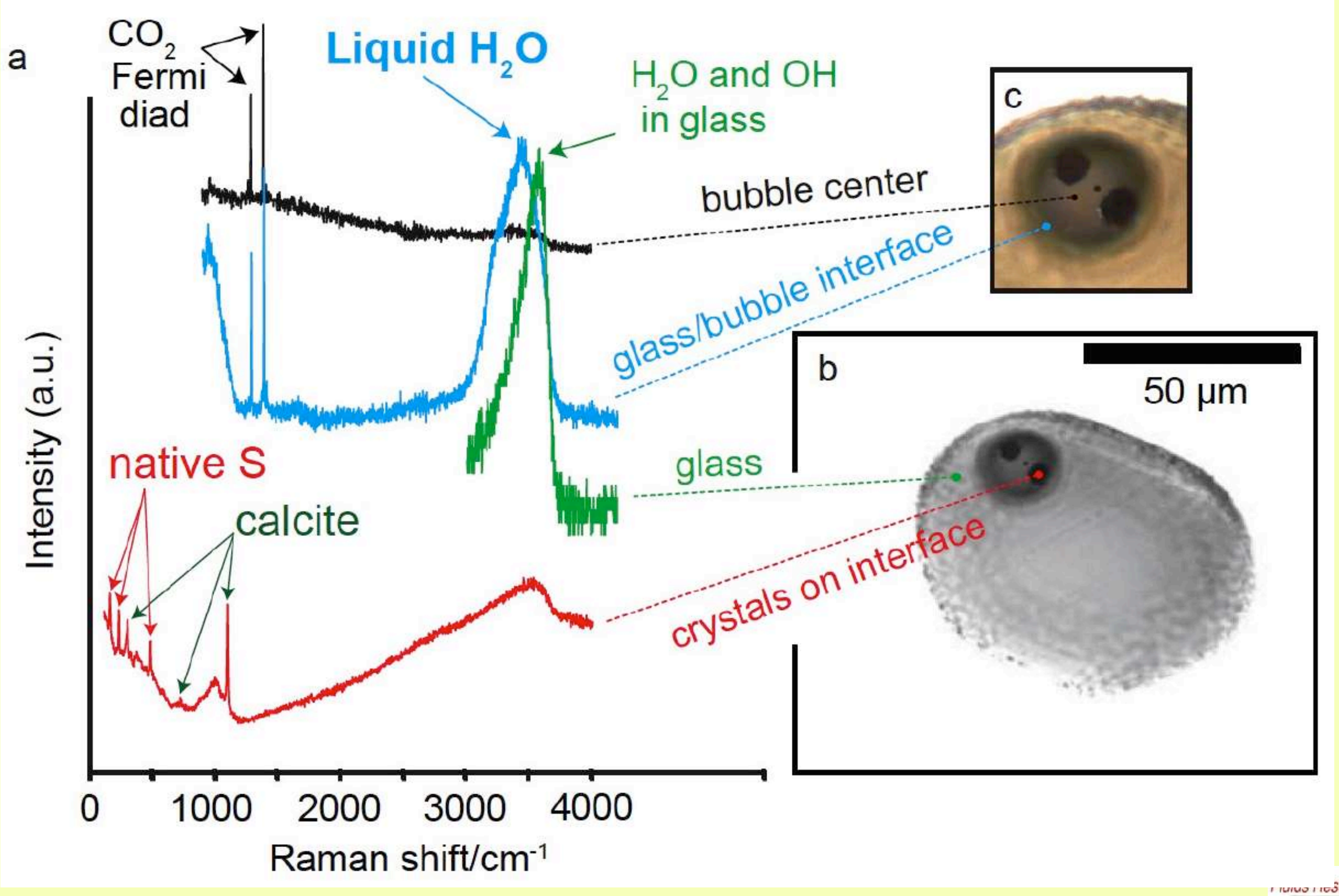
Detailed analyses of the vapor bubbles in MI show that, in addition to H_2O and CO_2, bubbles often contain sulfur, and that the volatile components have interacted with the glass in the MI to form sulfates/sulfides, carbonates, hydrous phases, and other phases.



From Esposito et al., 2016, Amer. Min.

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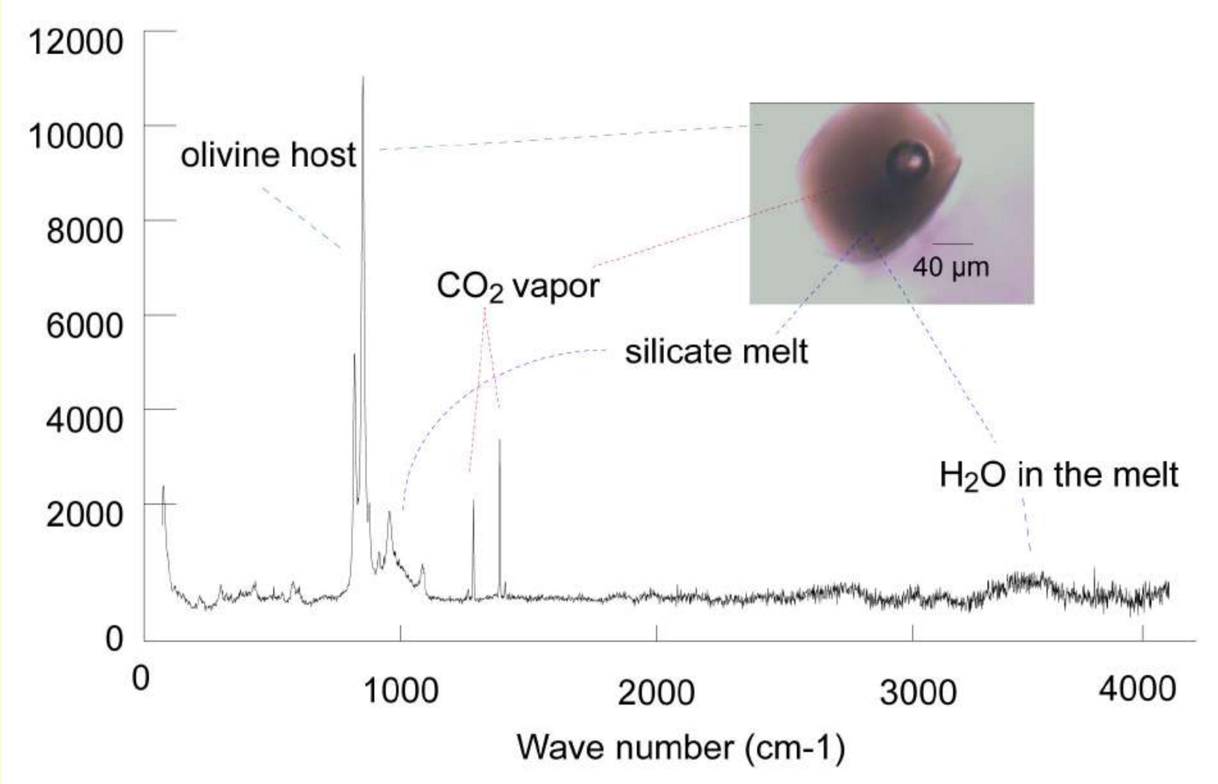
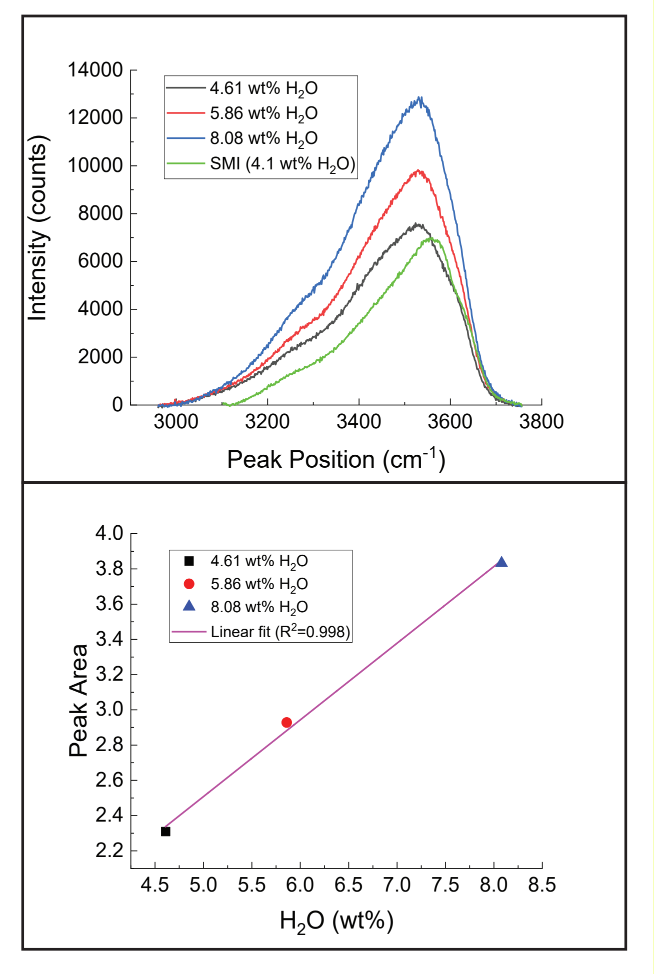
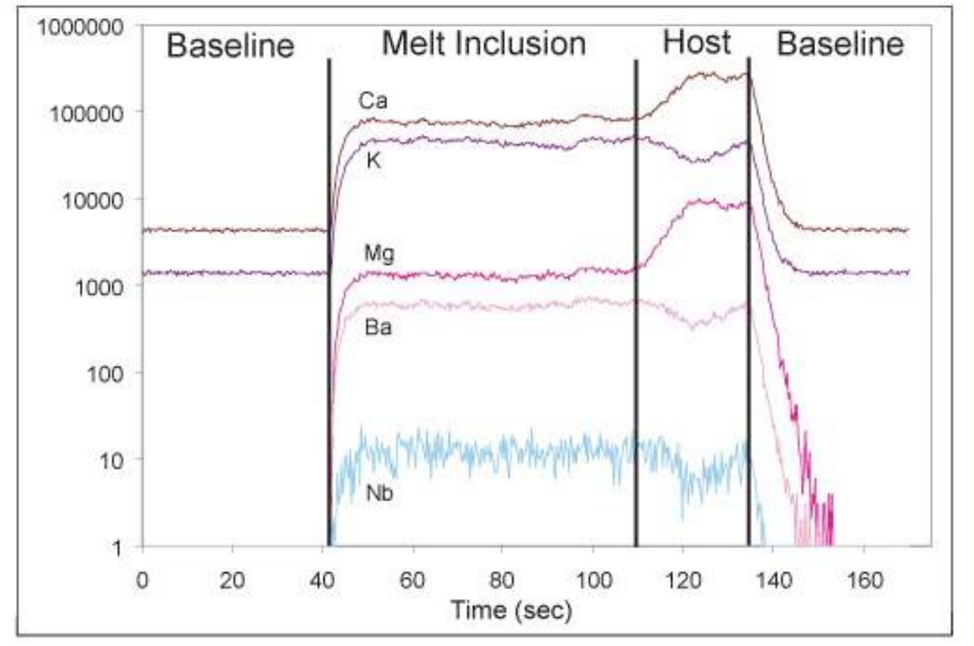


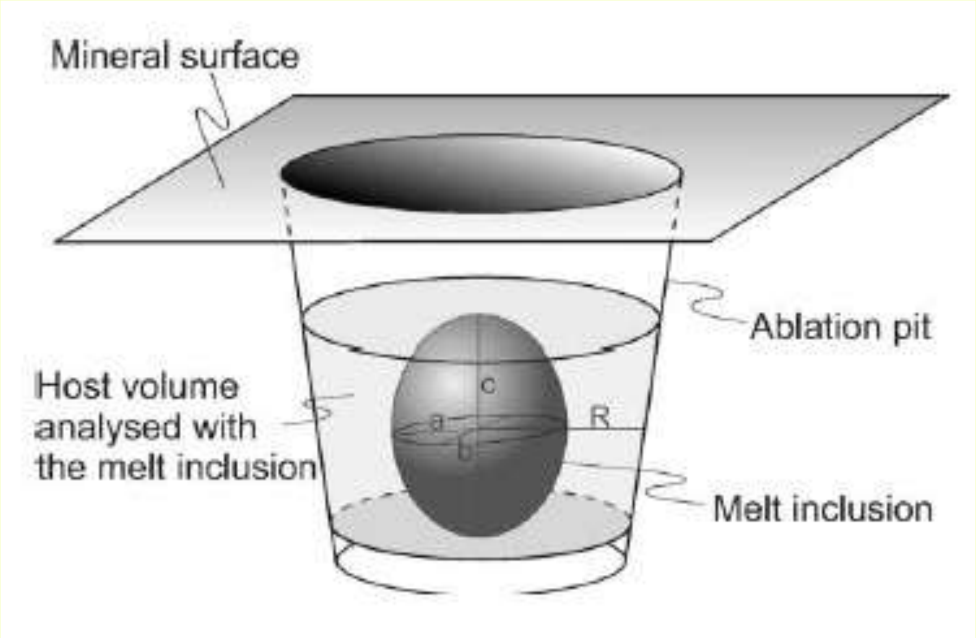


Various techniques may be used to analyze melt inclusions depending on the nature of the MI (glassy, with vapor bubble, crystallized) and the type of information needed.

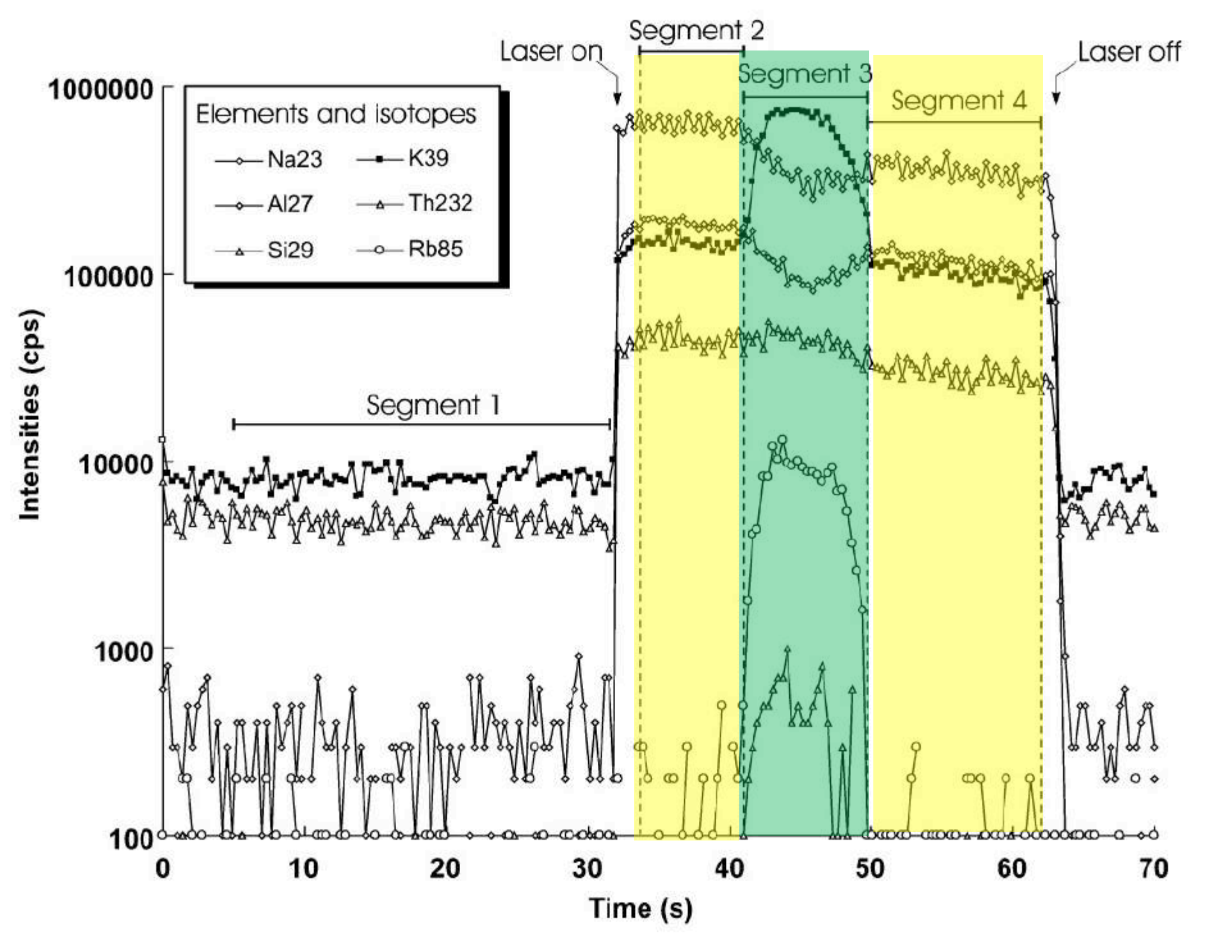
- Laser Ablation Inductively-Coupled Plasma Mass Spectrometry (LA-ICPMS): Analysis of major, minor and trace element abundances in crystallized or glassy MI.

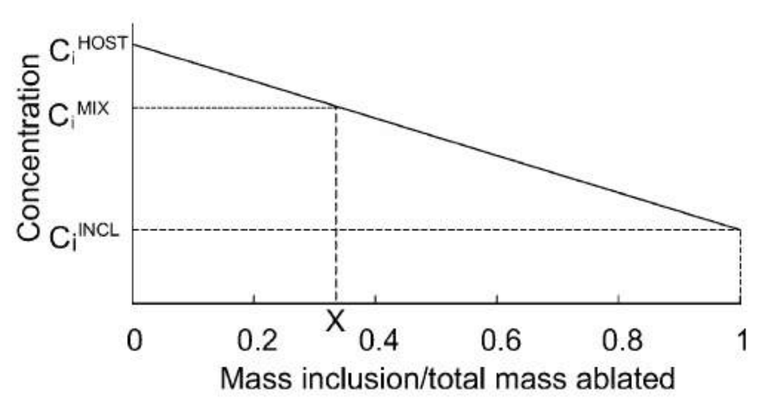


(from Severs et al., GCA, 2009)



From Halter et al., 2002





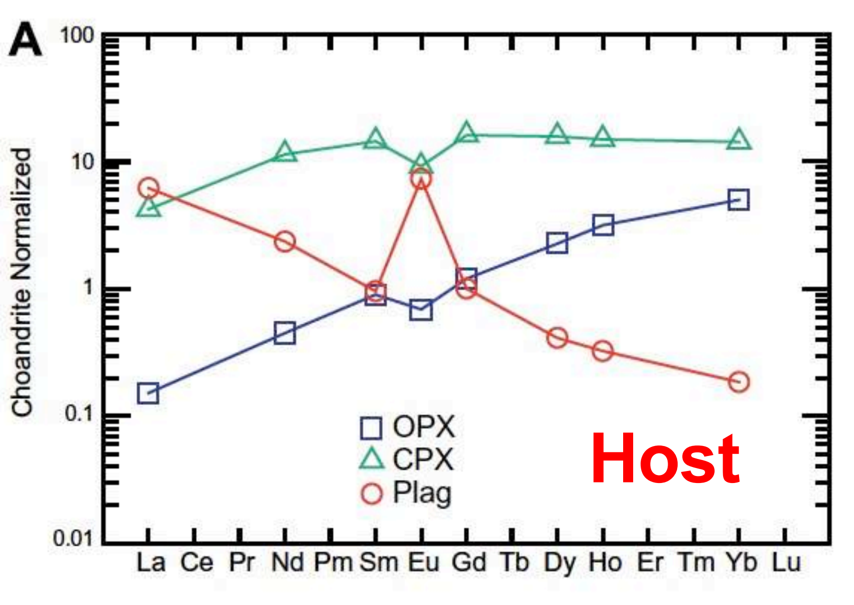
The Halter et al. method requires that the concentration of one element in the melt inclusion is known, and concentrations of other elements are calculated using a mass balance approach. Do we know the concentration of any element in the MI?

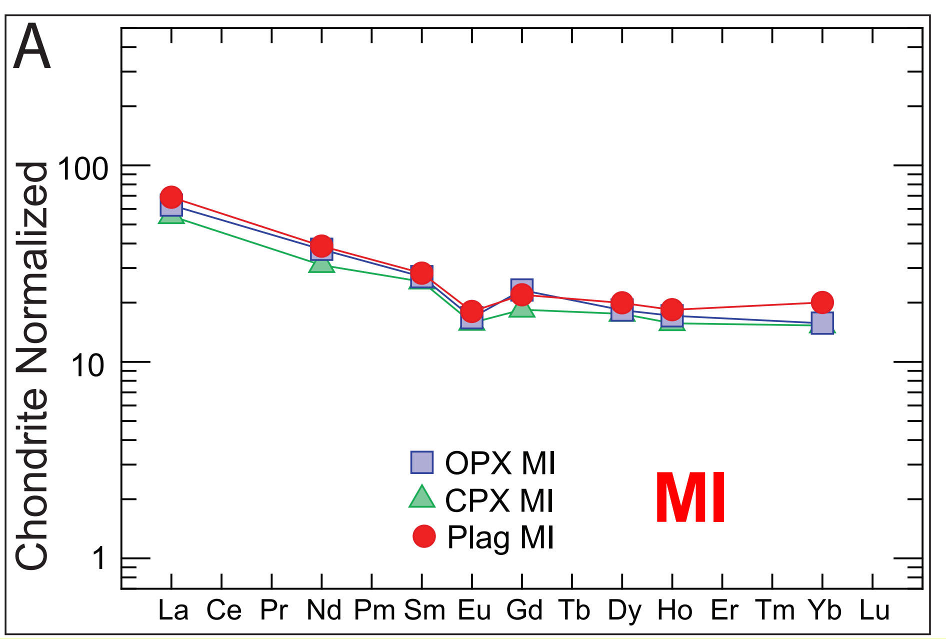
Even if you do not know the concentration of any element in the MI, you could make an “educated guess” and assume that, for example, the SiO_2 concentration is 57 wt.%, or that the Al_2O_3 concentration is 16 wt.% - this would lead to a relatively small error in calculated trace element abundances.

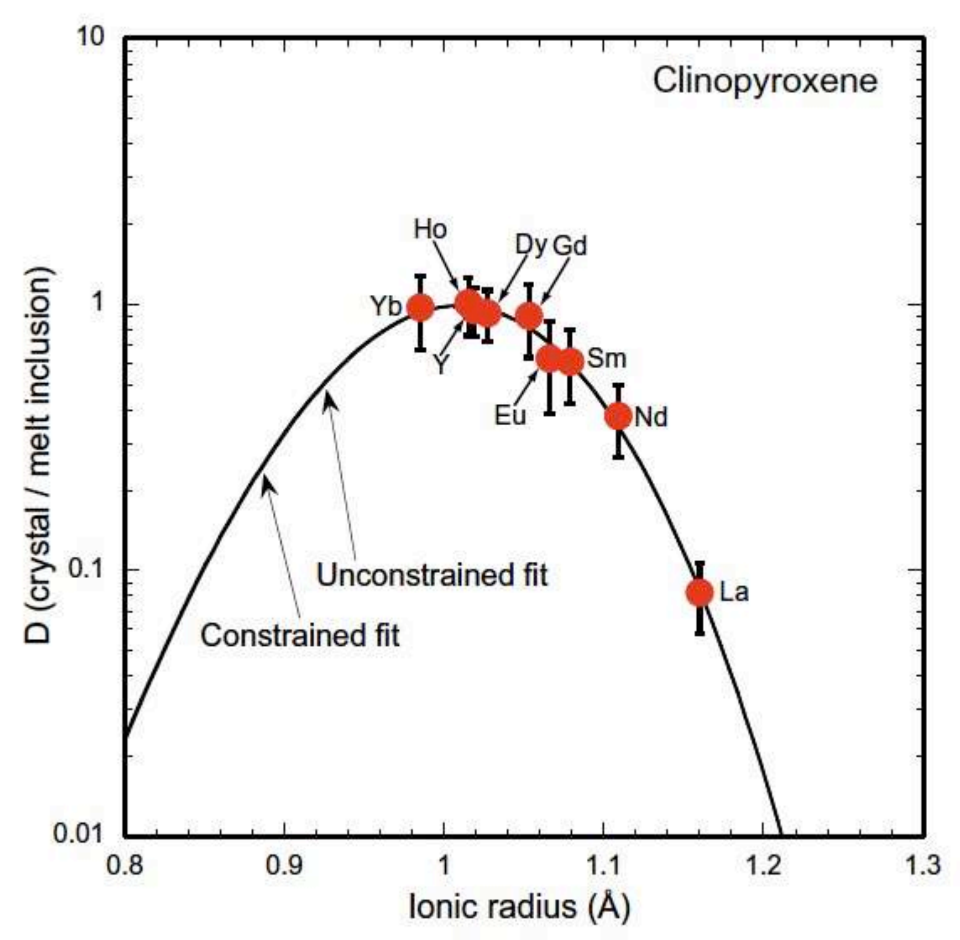
SiO_2 (≈ 5-10% error):
Mafic = 50; Felsic = 65

Rb_{real} = Rb_{meas} *± 10%*
Rb_{real} = *200 ± 20 =*
(~180-220 ppm)

LA-ICPMS analysis of trace element abundances in MI and adjacent host provide a method to estimate partition coefficients.







(from Severs et al., GCA, 2009)

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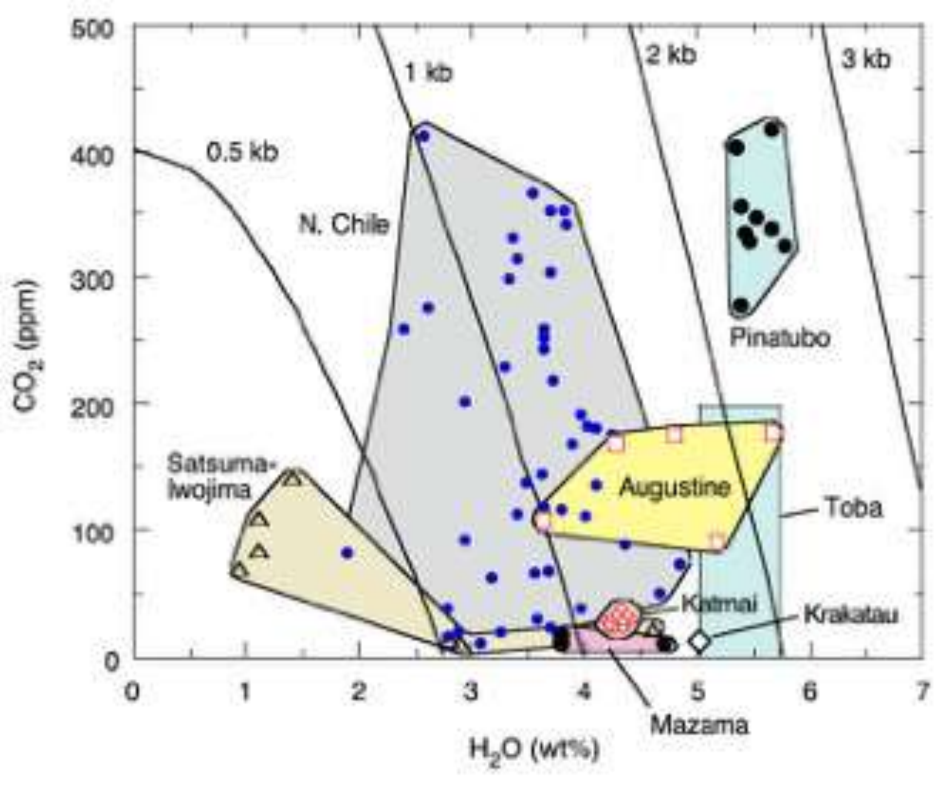
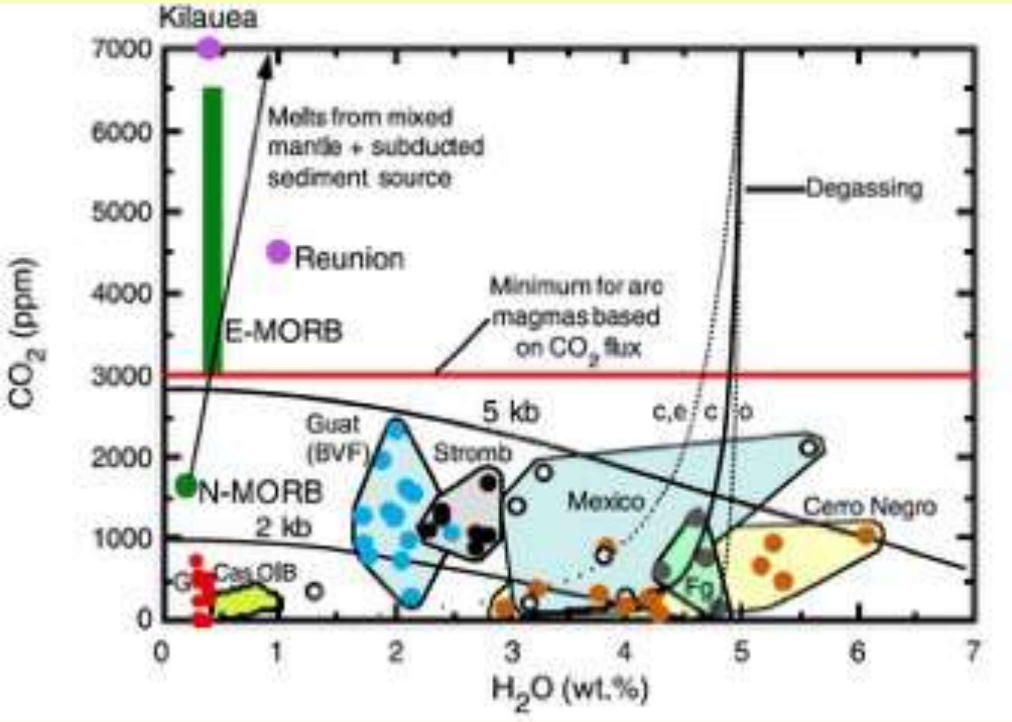
One of the most important contributions of MI is in studies of volcanic systems, where the H_2O-CO_2 contents of MI constrain the pressures (and depths) of MI trapping.





From Wallace, 2005, JVGR

In general, silicic melts (rhyolites and dacites) and mafic (basaltic) melts show similar H_2O contents, but mafic melts have much higher CO_2 compared to silicic melts.

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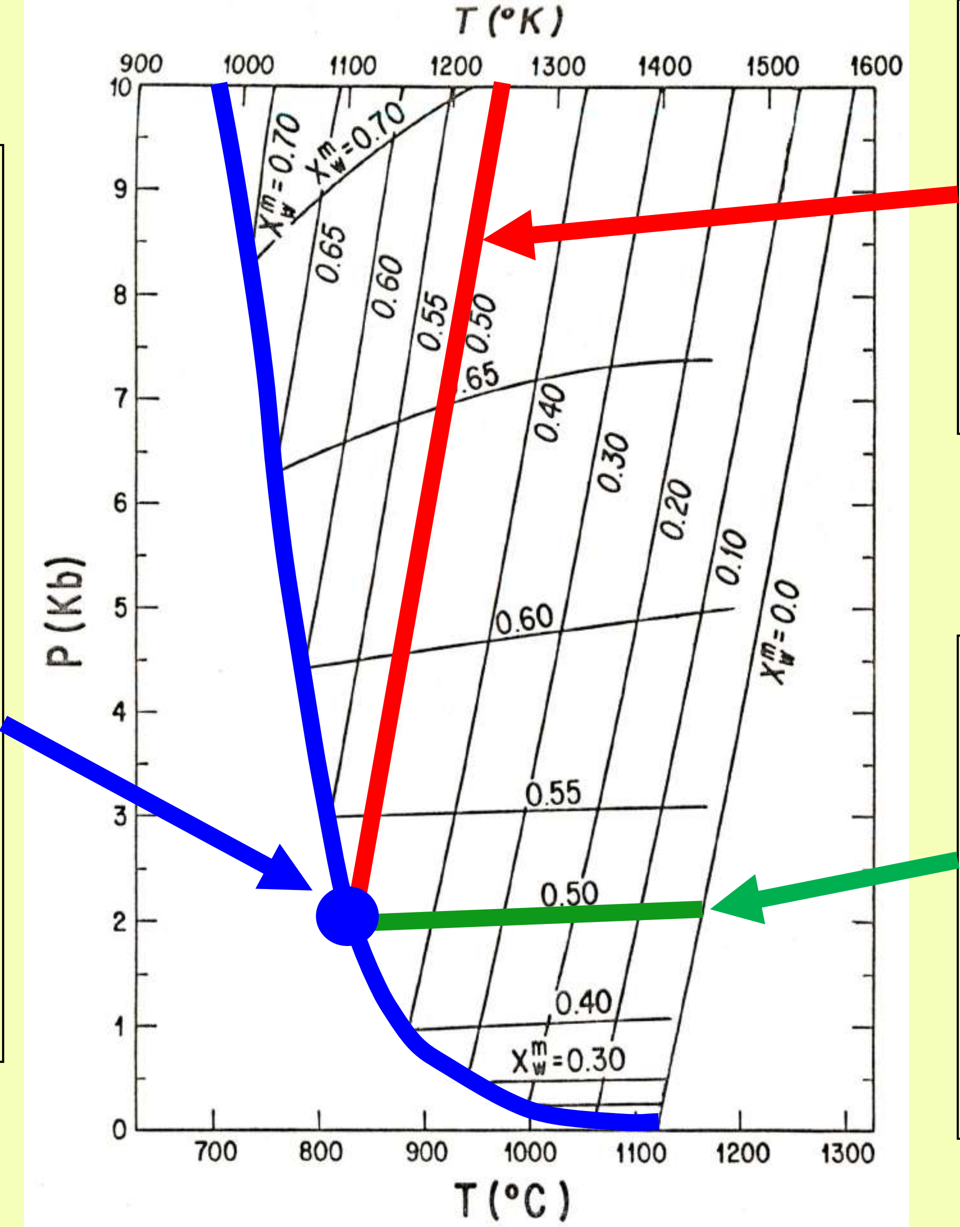
Important questions in MI studies are:

- Where (petrologically) were the MI trapped, or stated differently,
- What phases were in equilibrium with the trapped melt

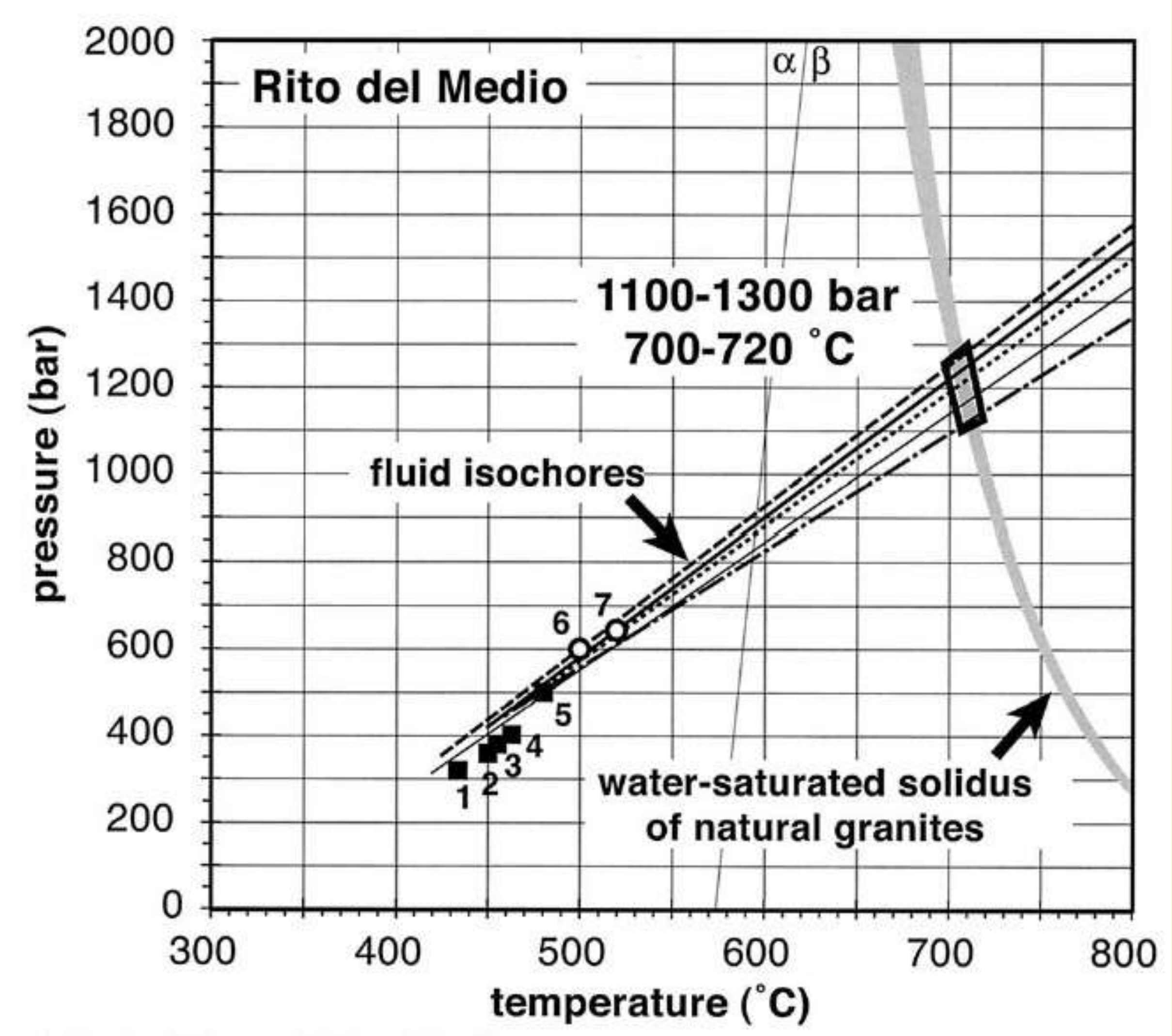
The intersection of an H_2O solubility isopleth with the liquidus corresponding to the same amount of H_2O in the melt defines the H_2O-saturated solidus. Here, melt, crystals and aqueous fluid coexist in equilibrium.

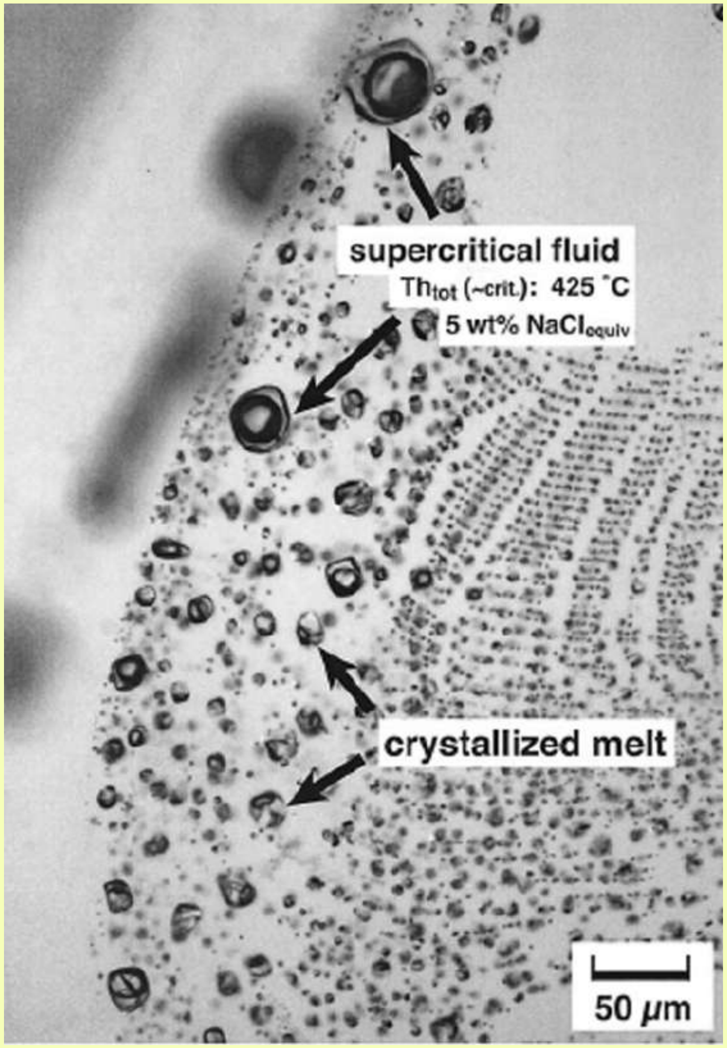


Along each liquidus, a melt containing a fixed amount of H_2O is in equilibrium with solids (crystals).

Along each H_2O solubility isopleth, a melt containing a fixed amount of H_2O is in equilibrium with a fluid (H_2O).

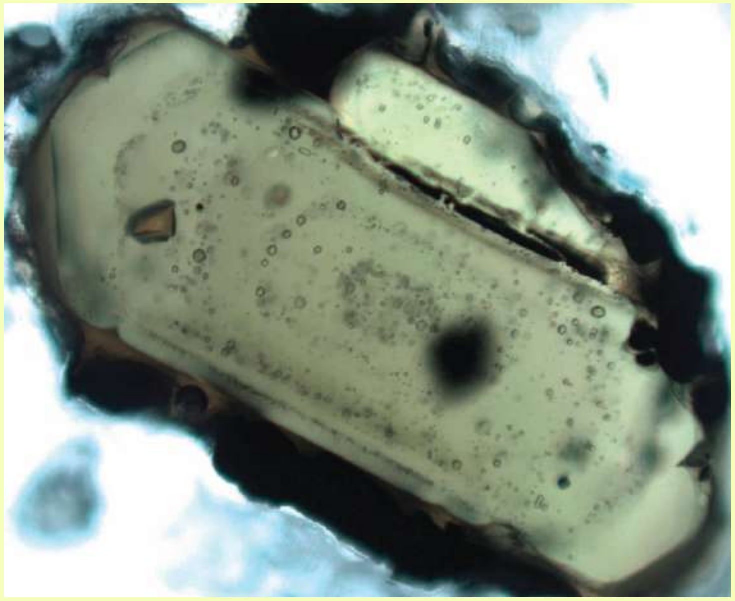
If an inclusion assemblage includes both MI and FI, the inclusions must have been trapped on the volatile-saturated solidus in the granite-H_2O system. Intersection of the FI isochore with the solidus unique defines the P and T trapping conditions.

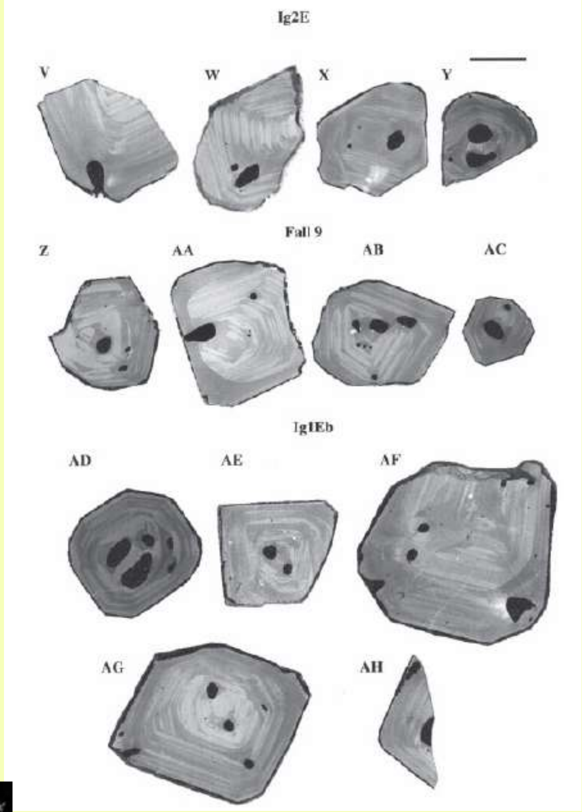




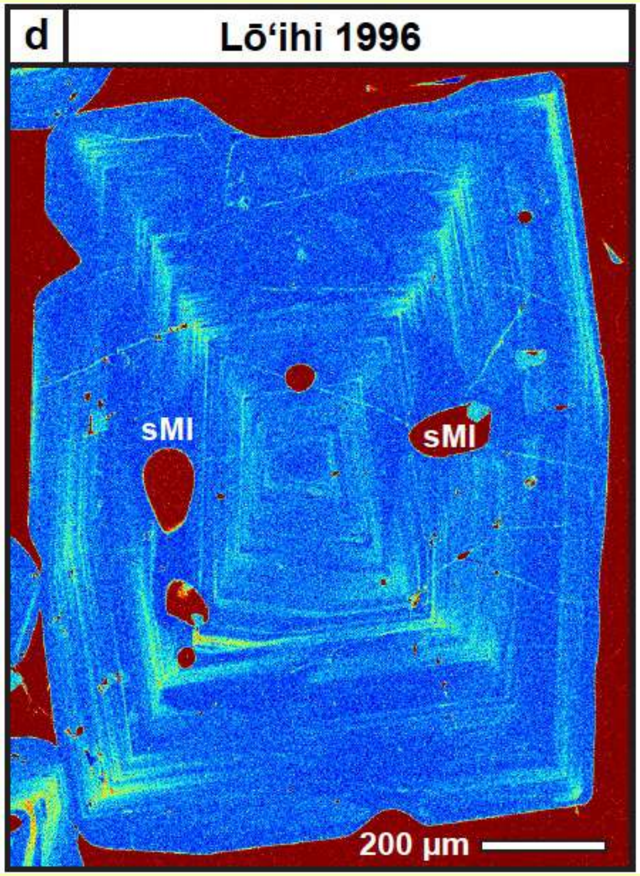
From Audetat and Pettke, 2003, GCA

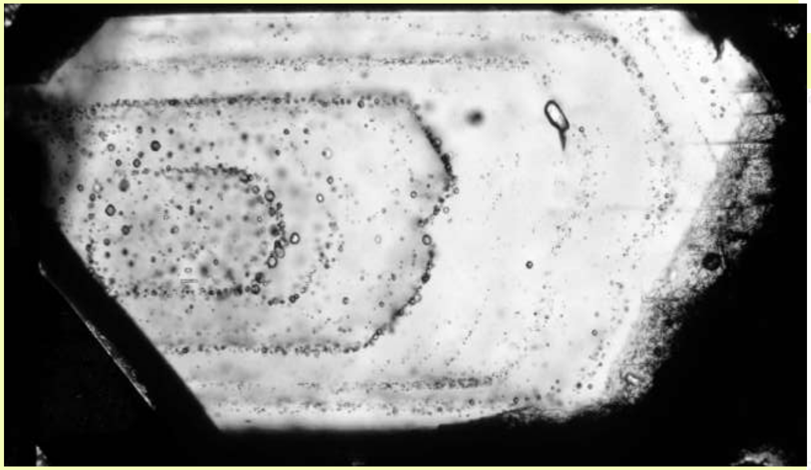
A variety of methods may be used to determine MI paragenesis and to identify MIAs, including normal petrography, CL, and trace element zoning (P shown in Loihi sample).

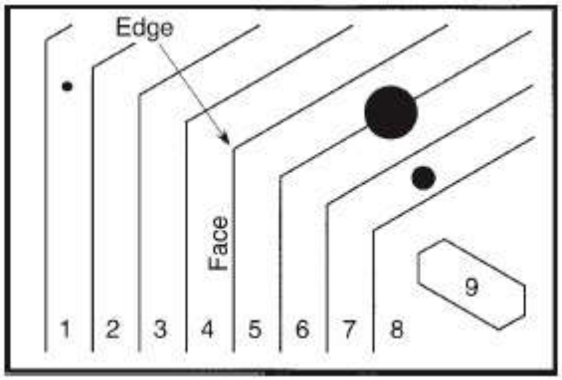




From Peppard et al., 2001

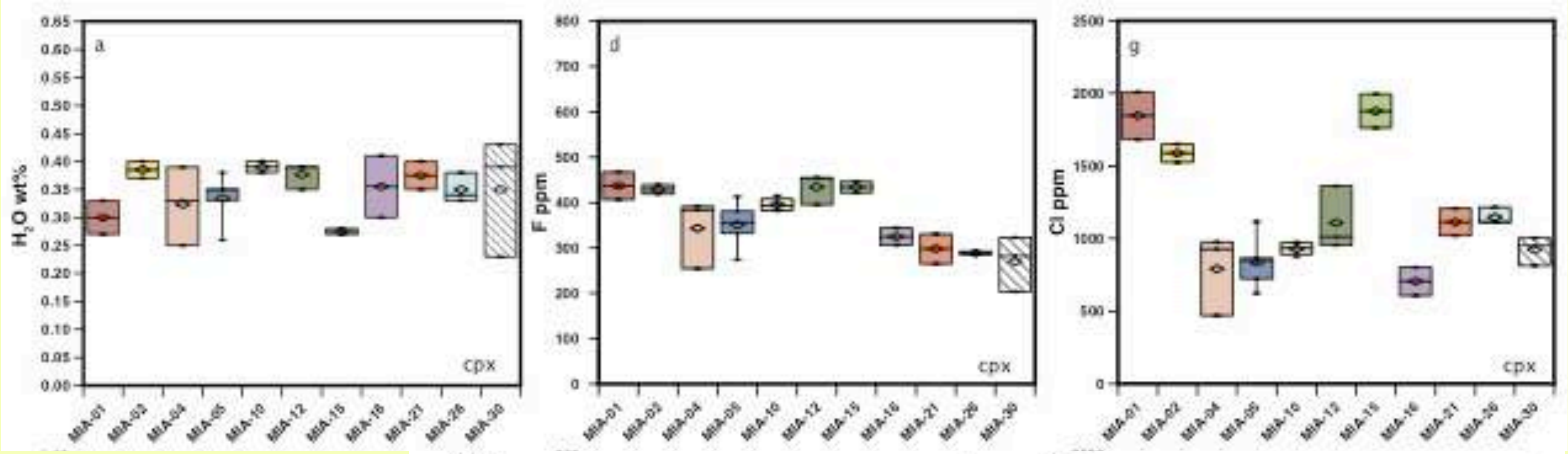


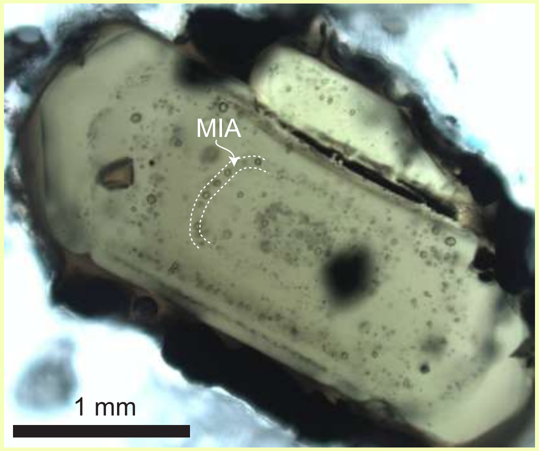


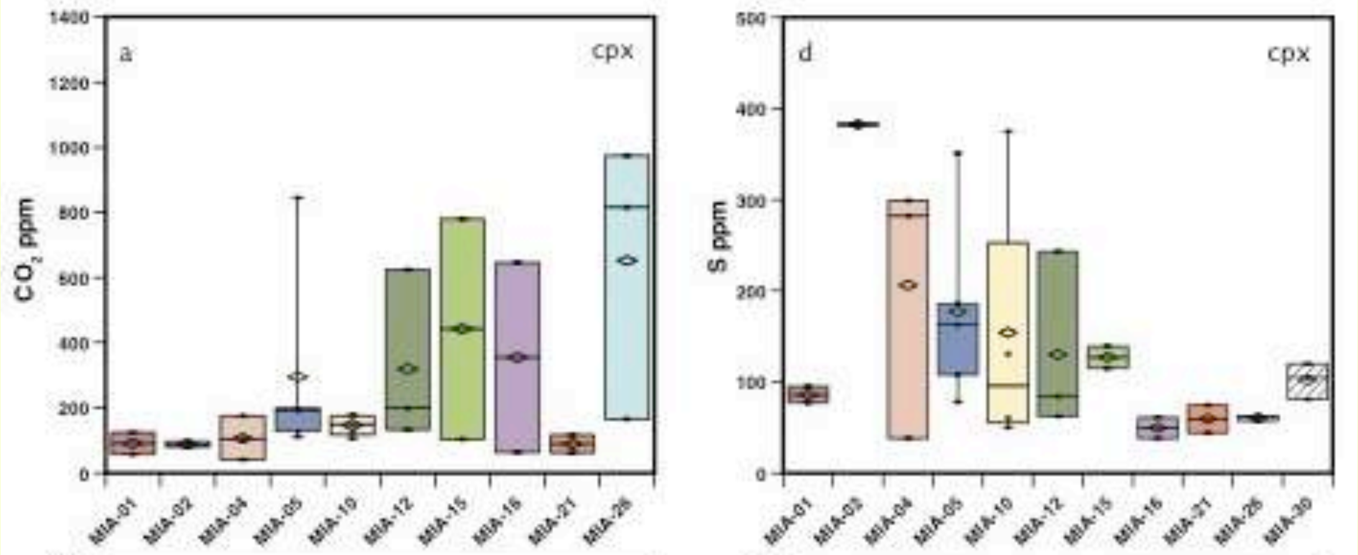


Secondary MI are rare, compared to FI

Analyzing MI within an MIA (group of MI that were all trapped at the same time) allows one to test whether MI represent the composition of the pre-eruptive melt, assuming that all MI in the MIA trapped a melt of the same composition and at the same PT conditions.







From Esposito et al., 2014, Amer. Min.

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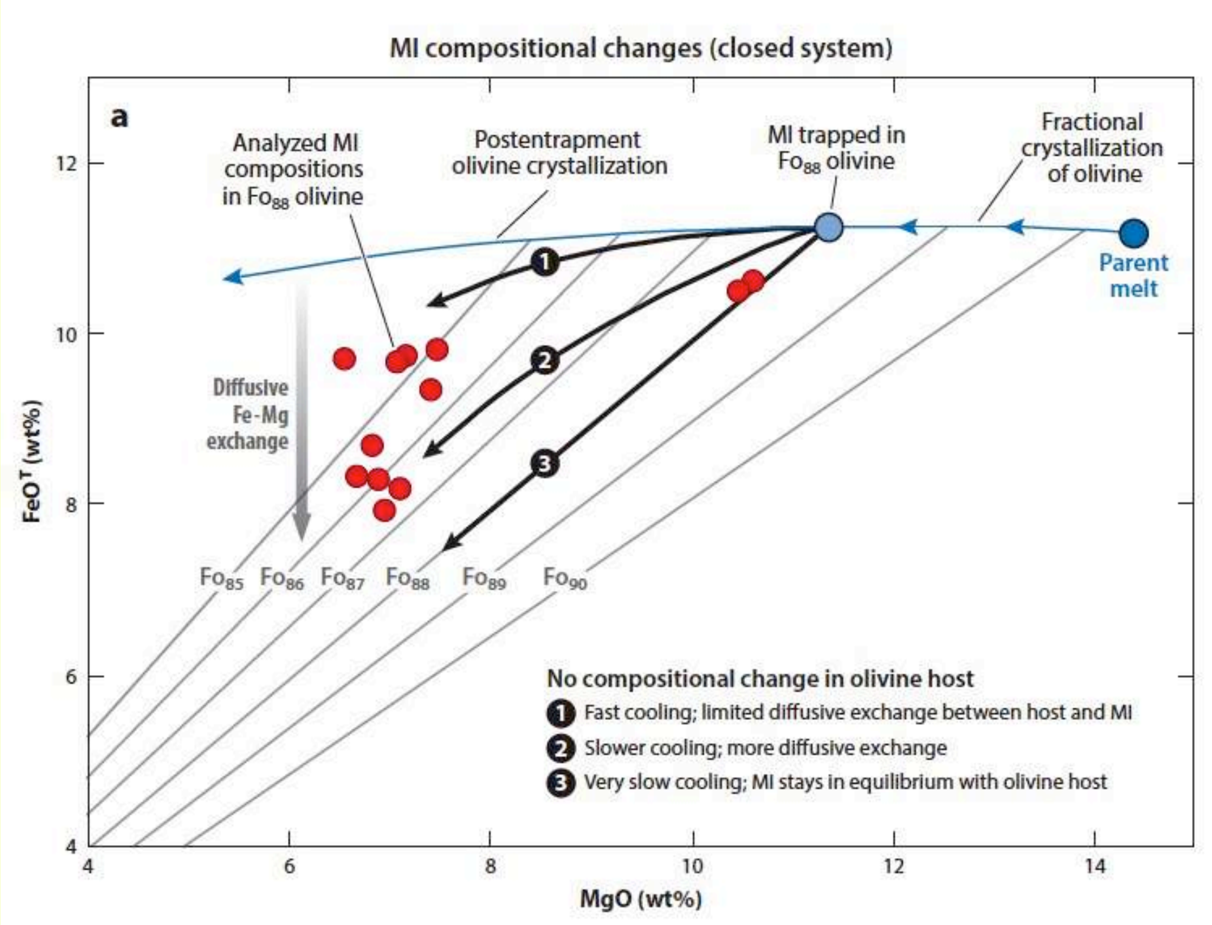
Compared to FI, MI are more likely to experience changes after trapping that could lead to incorrect inferred melt compositions if these changes are not recognized and corrections applied.



From Wallace et al., 2021, AREPS

MI trapped in olivine exchange Mg and Fe with the host olivine during cooling. If the cooling rate is slow, the Mg/Fe ratio in the melt can be changed significantly. Leonid Danyushevsky and colleagues were among the first to recognize this and have developed methods to correct for this post-trapping modification.

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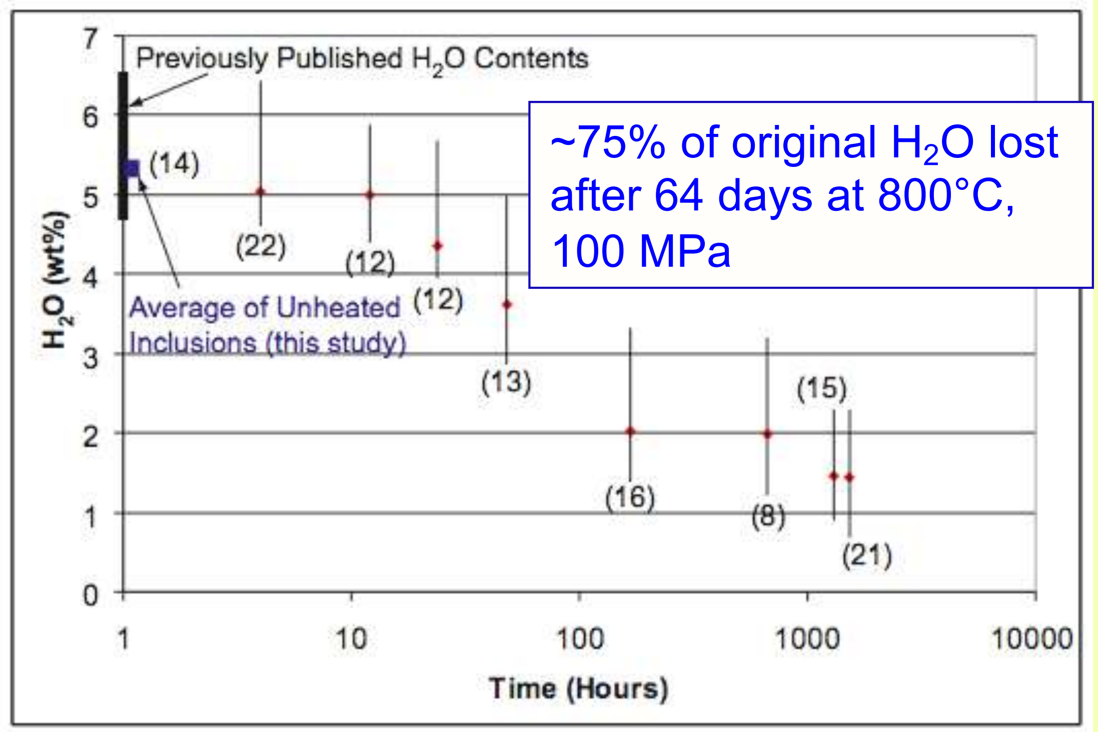
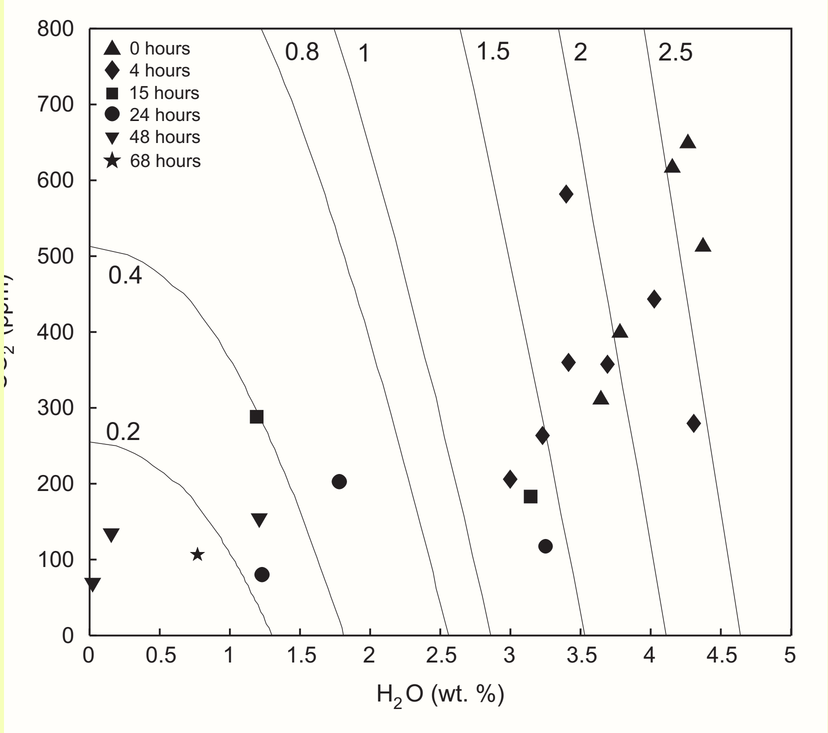
One of the most common types of reequilibration is loss of volatiles, either during cooling in nature or during heating in the laboratory.



~75% of original H_2O lost after 64 days at 800°C, 100 MPa



From Bucholz et al., 2013

Insignificant H_2O loss from MI in quartz from the Bishop Tuff when held at T = 800°C for <12 hr, but significant water loss after ~1 day.

“Our results indicate that measured H_2O, CO_2 and S concentrations and $Fe^{3+}/\Sigma Fe$ ratios of included melts are not necessarily representative of the melt at the time of entrapment and thus are not reliable proxies for upper mantle conditions.” (Bucholz et al., 2013)

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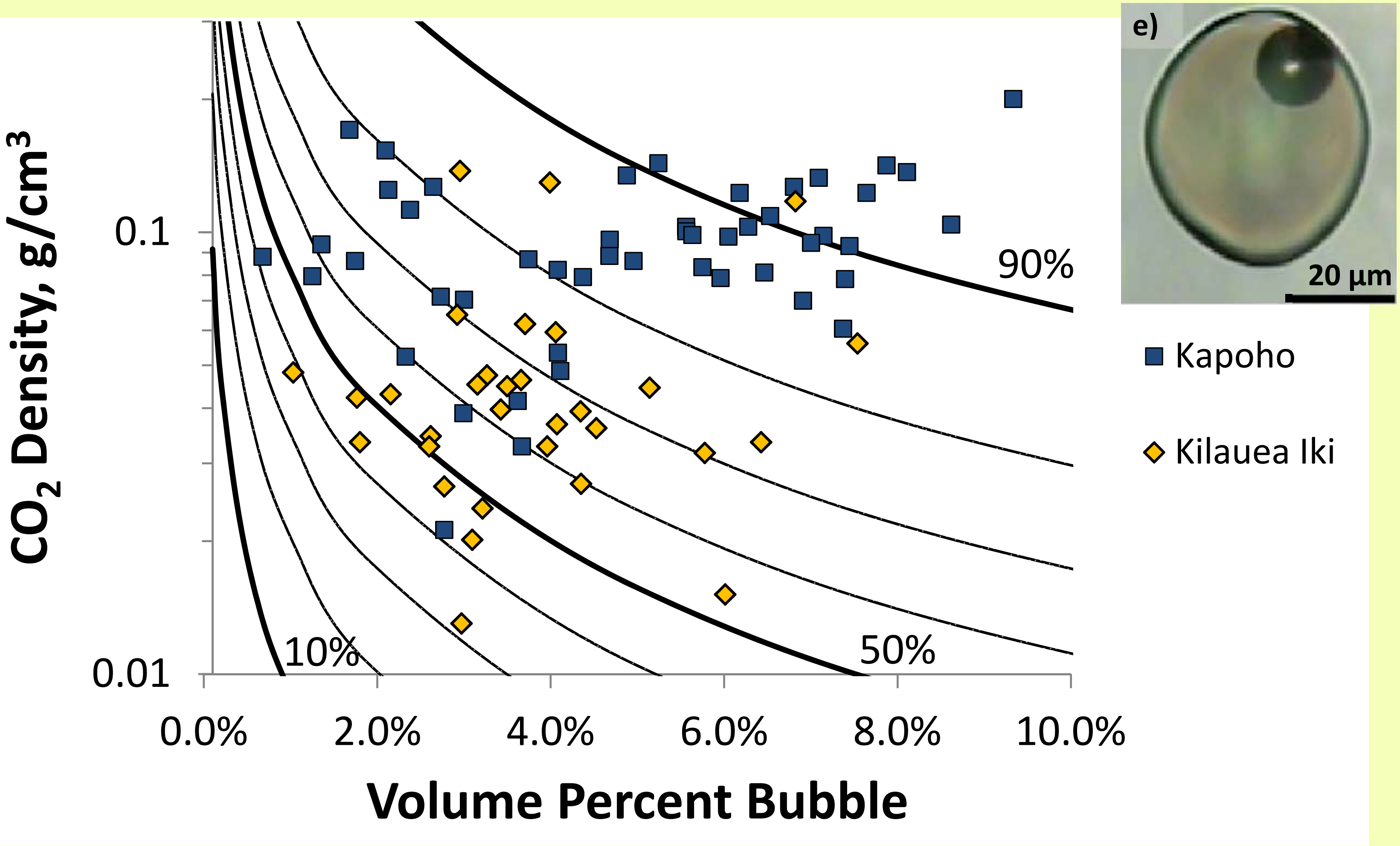
Analysis of bubble-bearing MI in olivine from Kilauea indicates that the majority of the CO_2 in the MI is contained in the bubble. Failure to account for this in analyses of volatiles in the MI leads to false degassing trends.



From Moore et al., 2013

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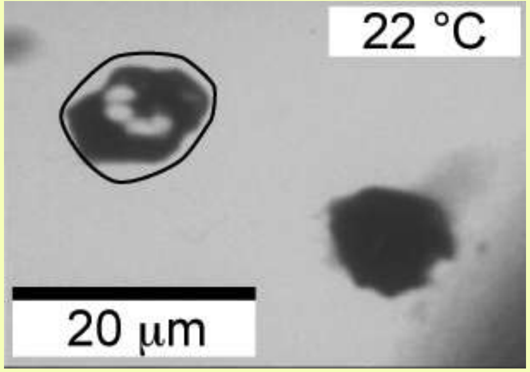
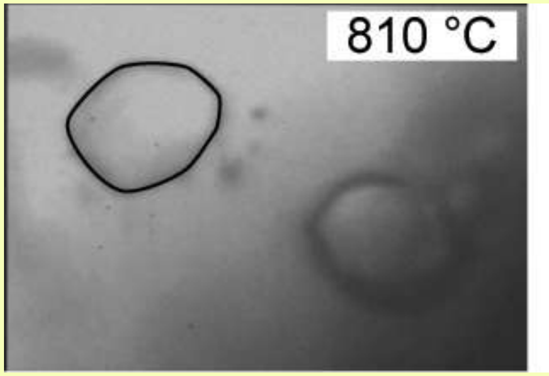
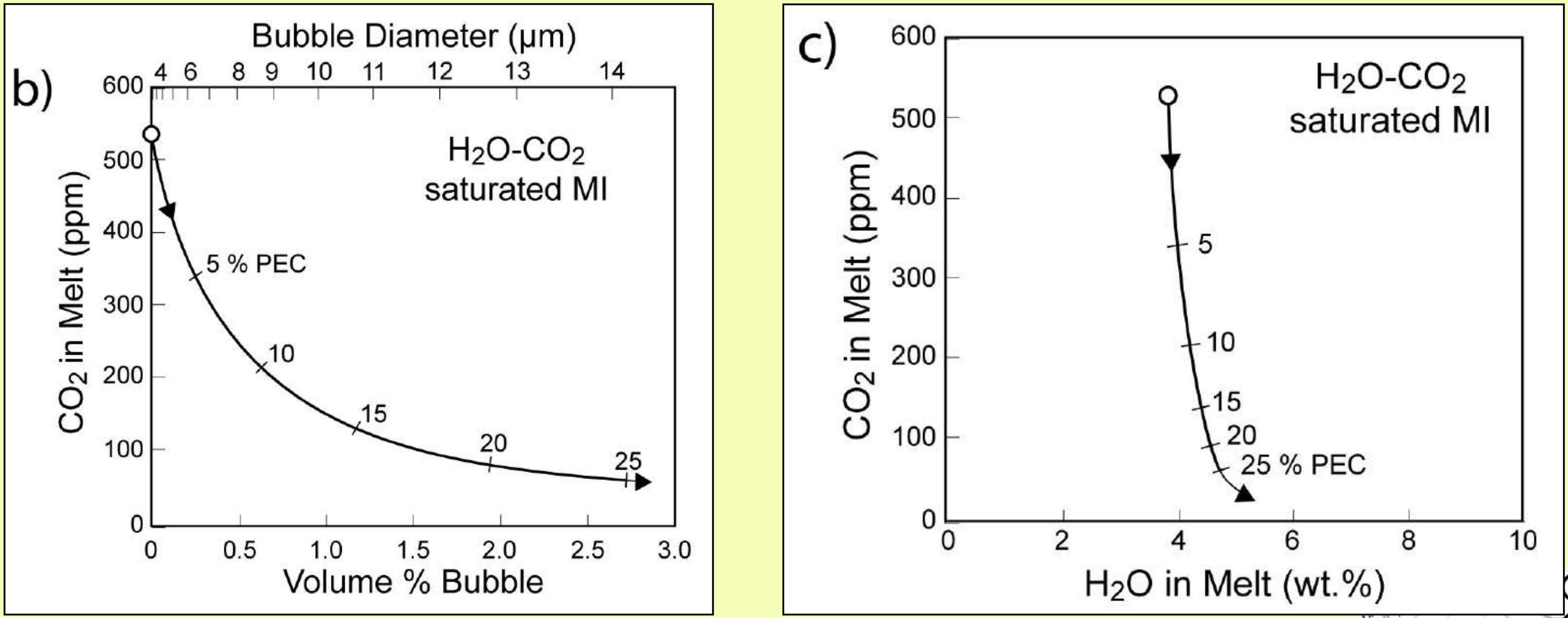
Compared to most FI, post-entrapment crystallization (PEC) on the inclusion walls can be significant and can lead to incorrect melt compositions if not recognized and corrected for.



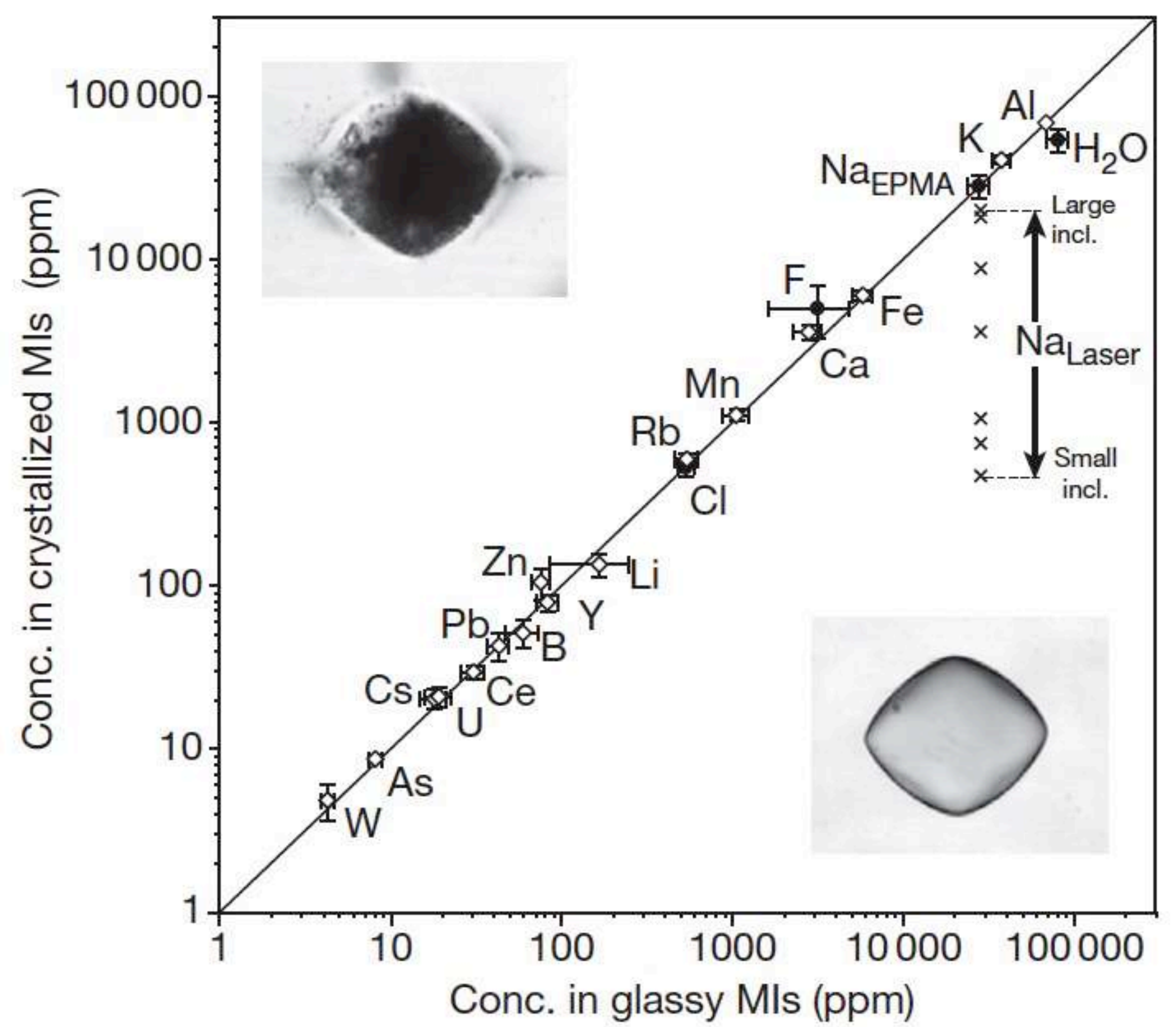
~34 vol% of the melt crystallized on the walls during cooling



- Loss of volatiles from the melt (glass) into the vapor bubble



Steele-MacInnis et al. J. Pet., 2011



In addition to the volatile components, other highly mobile elements such as Na may be lost from MI that cool slowly, as shown by comparison of compositions of crystallized and glassy MI from the Pine Grove system.

From Audétat & Lowenstern, 2014, Treatise on Geochemistry

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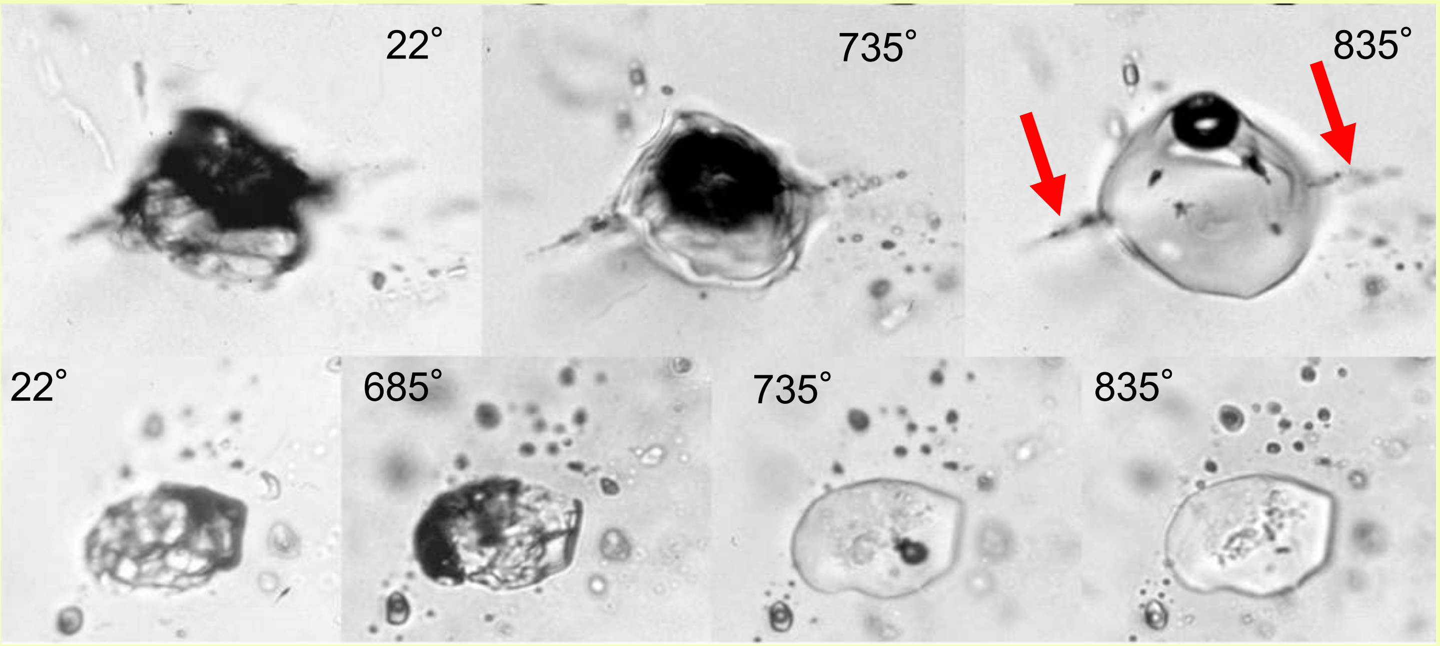
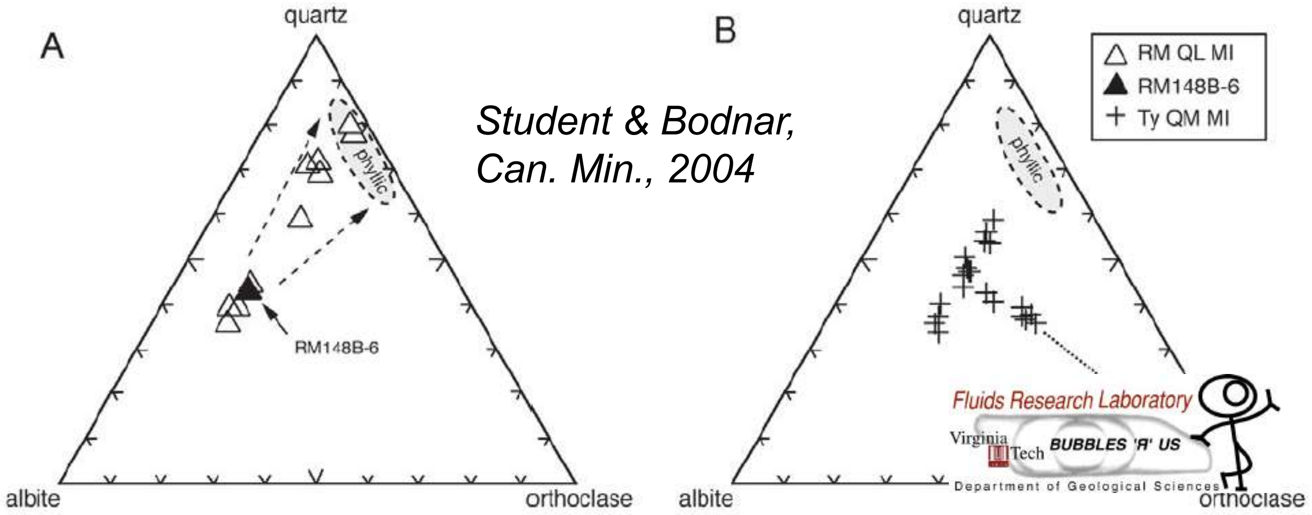
System Administrator Sep 3, 2022 at 8:50:39 AM 88:66:5a:34:95:28

The most destructive irreversible change is when volatile-rich MI decrepitate in nature during cooling, or in the laboratory during heating at one atmosphere. Such changes are identified by petrographic and microthermometric behavior.



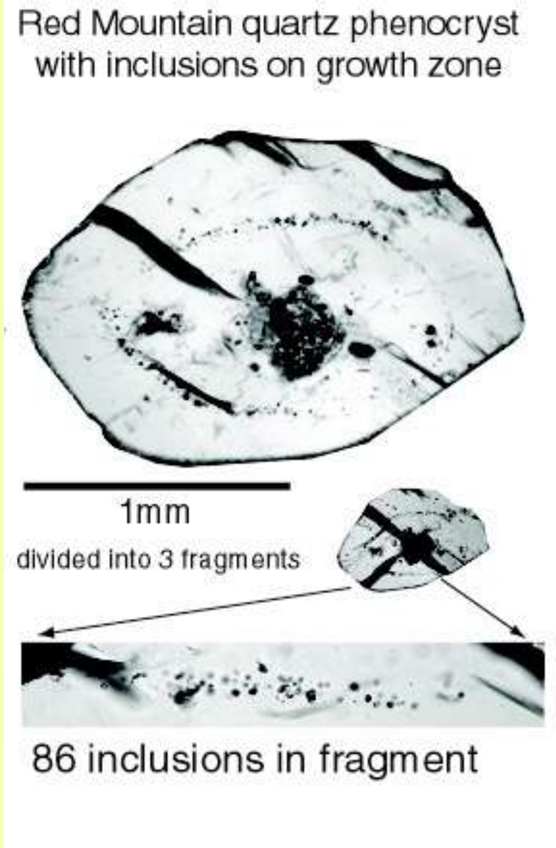
Naturally decrepitated melt inclusions

The modification of MI by sub-solidus fluids was first described by Maria Luce Frezzotti and colleagues.



Student & Bodnar, Can. Min., 2004

Let’s look at one example of using the MIA approach to study MI, and consider the wealth of information that is obtained. We will use a quartz pheno from the Red Mountain, Arizona, porphyry copper deposit to illustrate the approach.

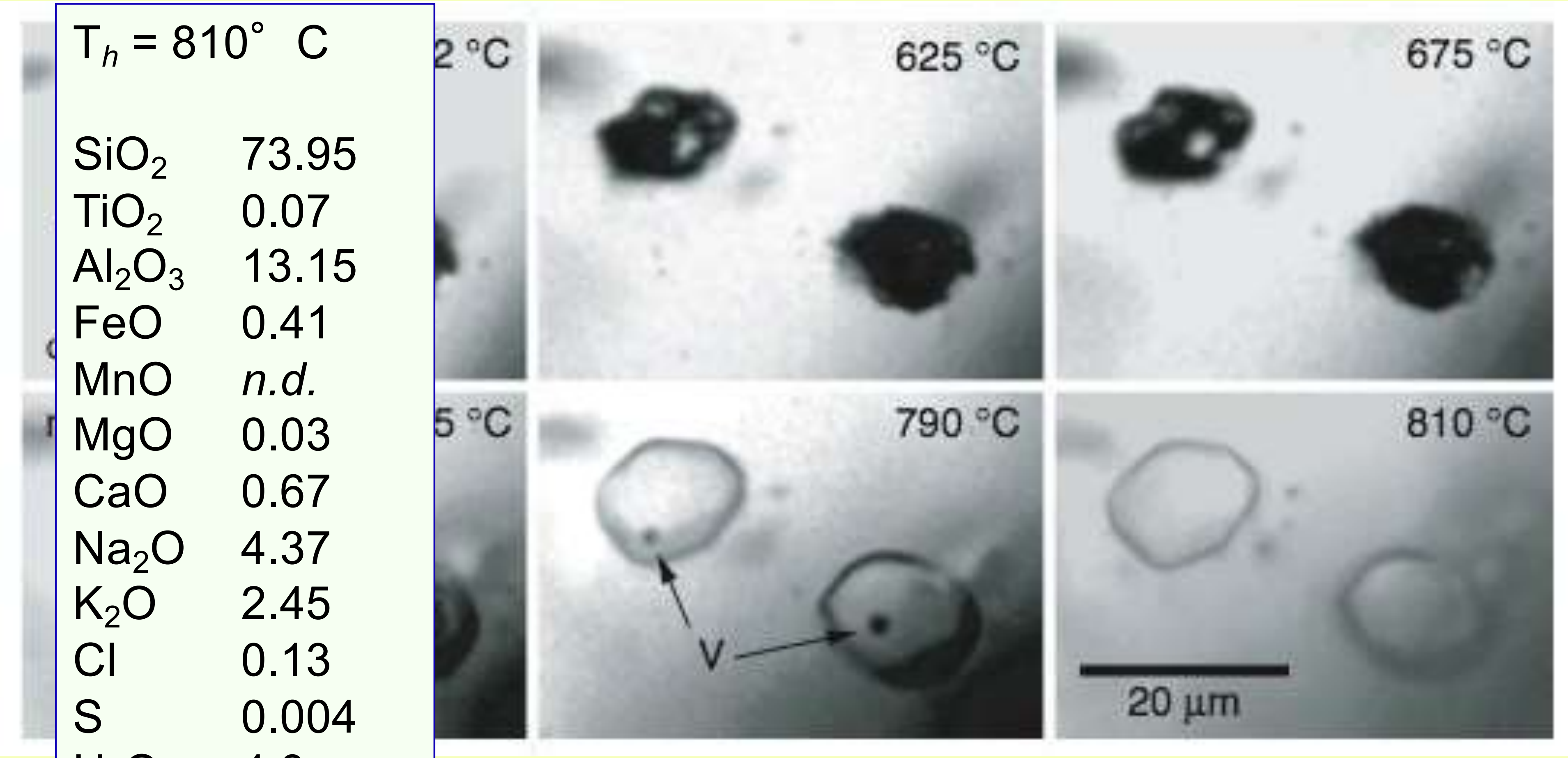


We identified an growth zone/ resorption surface in a quartz pheno that is decorated by a large number of melt inclusions.

The MI were heated in a microscope-mounted heating stage and phase relations were monitored during step heating.

Quartz phenocryst with many melt and fluid inclusions and plagioclase crystals along growth zone (qtz + plag+ H_2O-sat’d cotectic)

At 810° C, 37 out of 86 of the MI homogenized by the simultaneous disappearance of the vapor bubble and the last daughter crystal (plag), indicating that the MI were trapped on the H_2O-saturated solidus and that quartz and plag were crystallizing.



T_h = 810° C

SiO_2	73.95
TiO_2	0.07
Al_2O_3	13.15
FeO	0.41
MnO	*n.d.*
MgO	0.03
CaO	0.67
Na_2O	4.37
K_2O	2.45
Cl	0.13
S	0.004
H_2O	4.8
Cu	13 ppm
Zn	8 ppm

After the MI has been homogenized, it can be analyzed for major, minor, trace elements and volatiles.

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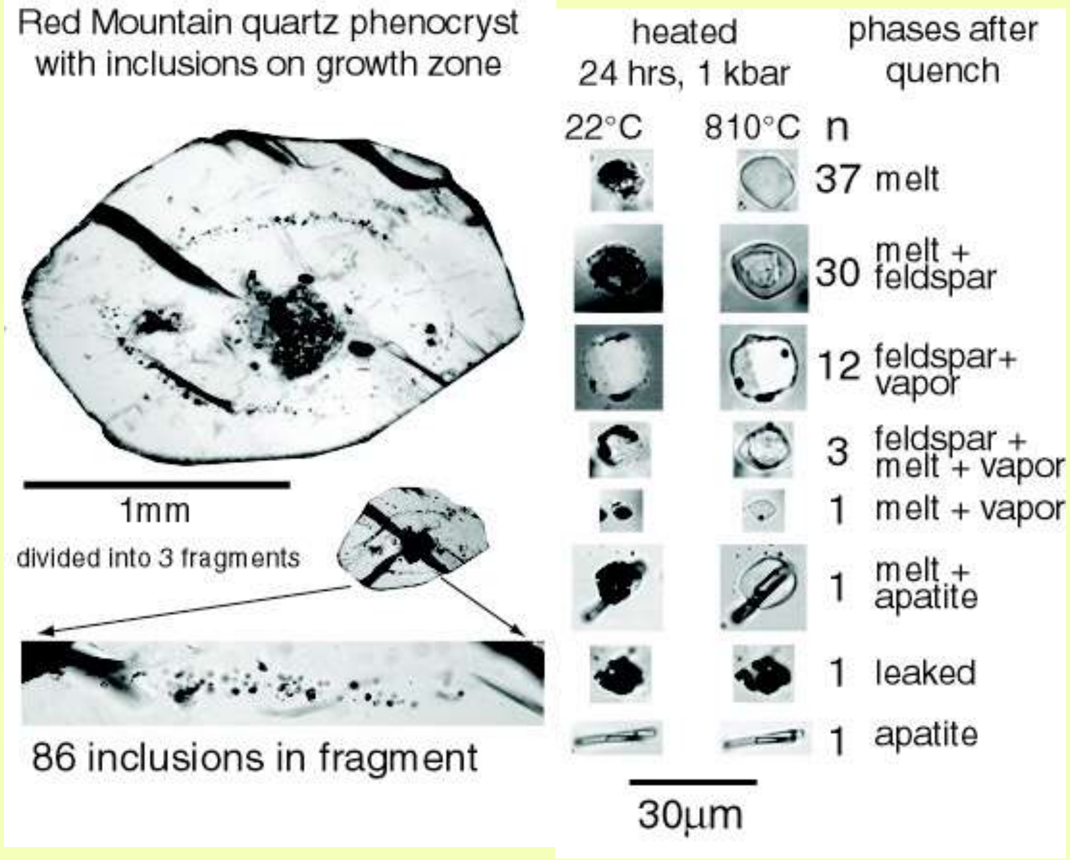

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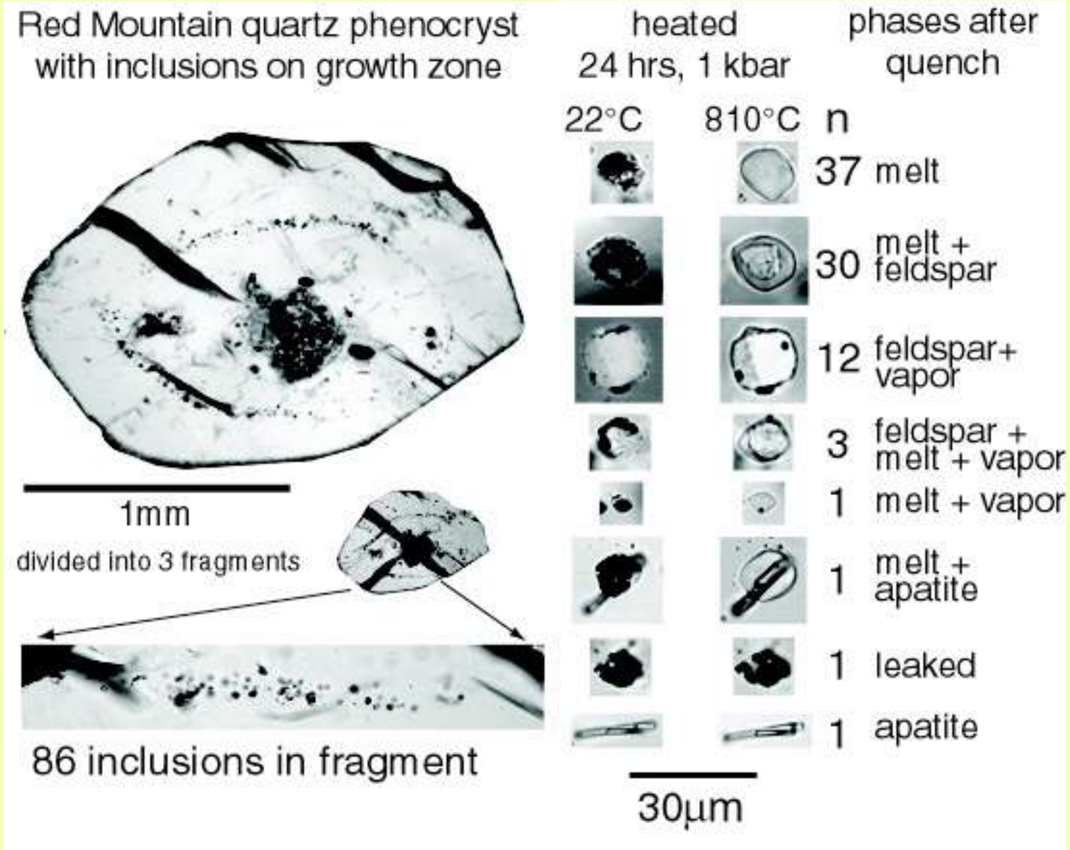
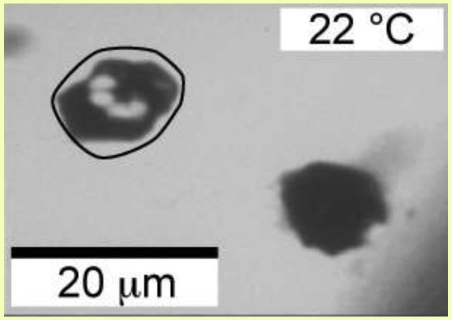
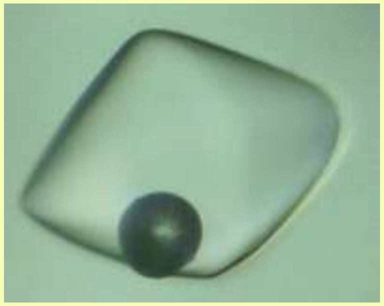
What did we learn from this exercise in which temporally associated MI were studied?



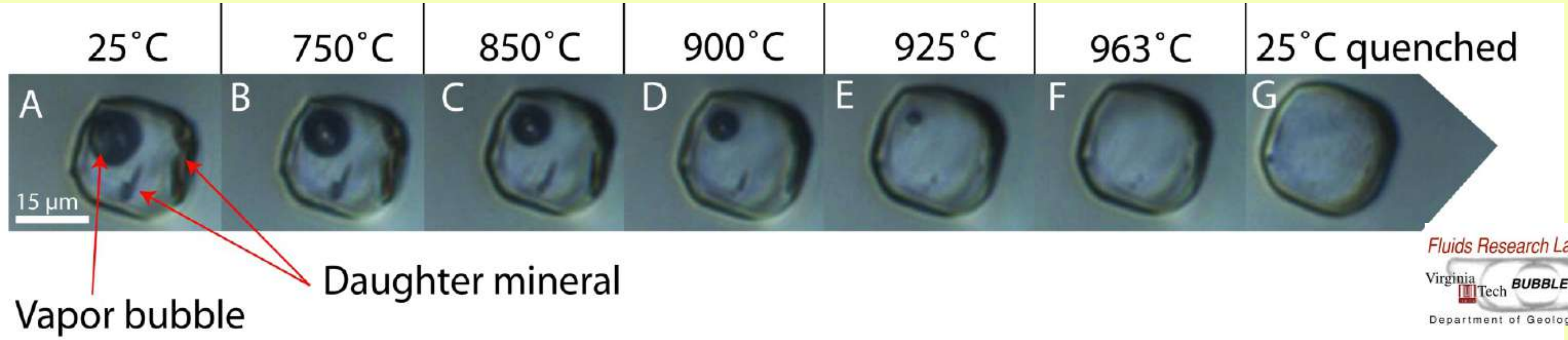
Quartz phenocryst with many melt and fluid inclusions and plagioclase crystals along growth zone (qtz + plag+ H_2O-sat’d cotectic)

- Most of the “MI” in this MIA (49 out of 86) do NOT represent the composition of the melt phase
- If the MI had been analyzed without knowledge of which MI trapped only melt and which trapped melt + crystals, the data would have defined two trends – one from the melt composition to the composition of plagioclase, and one from the melt composition to the composition of apatite
- The MI were trapped on the H_2O-saturated solidus at ~810° C and 1.4 kbars
- The melt was granitic in composition (~74 wt% SiO_2)
- The melt contained 4.8 wt.% H_2O
- Quartz, plag and apatite were stable phases on the solidus
- The melt was depleted in ore metals (this is in agreement with the fact that the host pluton post-dates mineralization)





While our ability to recognize and analyze melt inclusions has developed and matured significantly during the past few decades, the major limitation to use of MI to understand magmatic PROCESSES remains our inability to determine relative ages of MI in a given sample, and to recognize post-entrapment modifications to MI and correct for these changes. Future research efforts should focus on development of innovative methods to constrain MI paragenesis so that we may include "time" in our assessment of melt inclusion contributions.



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