





# A continent entrapped inside a mineral

(nanogranitoid inclusions in metamorphic rocks)

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# Seminar Outline

- How do melt inclusions form?
- Melt inclusions in igneous rocks
- High-temperature metamorphism
- Entrapment of melt inclusions during crustal anatexis
- How are melt inclusions identified ?
- How are melt inclusions microstructurally characterized ?
- How can melt inclusions be analyzed ?
- What can we learn from nanogranitoids inclusions ?
- Problems and pitfalls
- Concluding remarks

#### What are melt inclusions?

#### "Melt inclusions are small droplets of silicate melt that are trapped in minerals during their growth in a magma"

[Audétat & Lowenster, 2014]



Olivine (Mauna Loa volcano, Hawaii)

Small  $\rightarrow$  difficult to recognize Silicate\* melt  $\rightarrow$  containing >50% dissolved silicate Minerals  $\rightarrow$  the host Growth in a magma  $\rightarrow$  magmatic crystallization

\* carbonatitic MI, sulfide MI

### In the beginning ...

The first detailed discussion of melt inclusions within a rigorous geological and petrological context was by





Development and application of microscopy to materials such as thin sections of rocks and metals, pioneering the field of <u>microscopical</u> <u>petrography</u>.

Henry Clifton Sorby (1826-1908)

# In the beginning ...



*"The formation of crystals"* from a state of *igneous <u>fusion</u>* is in every respect analogous to what takes place when crystals are formed in water...There is thus a most perfect analogy between glass- and stonecavities and fluid-cavities in every respect except the nature of the included substances" (Sorby, 1858)

Little attention was given to melt inclusions during the next hundred years

# Progress during the Last 50 Years



Their 20<sup>th</sup> century renaissance was slow. Whereas fluid inclusion studies began to grow in about 1960, the rise in melt inclusion studies did not begin until about 1980

Sobolev & Kostyuk, 1975  $\rightarrow$  application of MI to the study of volcanic rocks

Roedder & Weiblen, 1970  $\rightarrow$  application of MI to lunar samples

Clocchiatti, 1975; Roedder, 1979  $\rightarrow$  origin and methods to investigate MI

LITHC

Sificate-melt inclusions in magmatic rocks: applications to petrology

Primitive mantle magmas recorded as silicate melt inclusions in igneous minerals

SCIENCE DIRECT.

Pierre Schiano\*



Maria-Luce Frezzotti \*

the Last 50 Years

Melt Inclusions Come of Age: Volatiles, Volcanoes, and Sorby's Legacy

CHEMICAL Jacob B. Lowenstern

#### **13.6 Melt Inclusions**

**A Audétat**, Bayerisches Geoinstitut, Bayreuth, Germany **JB Lowenstern**, Volcano Science Center, Menlo Park, CA, USA



ental and petrological studies of men inclusions in ysts from mantle-derived magmas: an overview of techniques, advantages and complications

ELSEVIER

ELSEVIER Danyushevsky<sup>a,\*</sup>, Andrew W. McNeill<sup>a,1</sup>, Alexander V. Sobolev<sup>b,c</sup>

reting H<sub>2</sub>O and CO<sub>2</sub> Contents usions: Constraints from Solubility speriments and Modeling

**Gordon Moore** 

Understanding a volcano through a droplet: A melt inclusion approach

C. Cannatelli <sup>a,b,\*</sup>, A.L. Doherty <sup>a</sup>, R. Esposito <sup>c</sup>, A. Lima <sup>a</sup>, B. De Vivo <sup>a</sup>



1) Entrapment of a melt inclusion not only requires **rapid growth that destabilizes the planar crystal–melt interface and creates embayments** (regions of melt bounded on three sides by a crystal in planar view), but also a period of **slower growth that "seals" the mouth of the embayment** to create a melt inclusion



<sup>[</sup>Baker 2008]



[Audétat & Lowenster, 2014]

Melt inclusions concentrated along growth zones, produced as a result of short pulses of rapid crystal growth

#### [Cannatelli et al., 2016]



2) Another common mechanism is **melt entrapment in response to the presence of surface irregularities** (i.e., adhering mineral grain, vapor bubble, impurities) which act as surfaces to which the melt could cling or adhere







Accidental minerals trapped with the melt commonly show a relative large size (compared with the size of MI) and the presence of indentations within the MI walls





[Cesare et al. 2009]

[Barich et al. 2014]

This process generally creates large, randomly distributed melt inclusions

# 3) Another process is melt entrapment in response to rapid dissolution followed by growth







#### [Blundy & Cashman 2005]



[Audétat & Lowenster, 2014]

Melt inclusions formed in response to crystal dissolution may give rise to the sieve texture commonly observed in plagioclase phenocrysts



#### How do melt inclu

4) Melts may be trapped in cracks de



Typically small, define planar surface



4) Melts may be trapped in cracks developed after crystal growth



PRO HEALKO FRACTIFIES in quarte (magnified 15.4 diameness) contrain connectors retiderly three-phone inclusioners. Phones can be even in the flatmond gale of inclusions at context that recended paper clique liquid (light oblegs grear) and galesses carbon discide time submost light detailed usuals), and adhies states (limb fight wave at lower by).

Typically small, define planar surface



[Roedder, 1962]

# Primary vs. secondary MI

- → **DURING**, and as a direct result of, host growth (**PRIMARY**)
- → AFTER host growth is complete (SECONDARY)



Clearly, the different modes have totally different implications

# Primary vs. secondary MI



- Primary melt inclusions:
  - A, B, C, D, F, G, H, I, J

 $\rightarrow$  formed by various entrapment mechanisms (along surface irregularities, along with an accidental trapped mineral, etc...)

#### - Secondary melt inclusions:

K  $\rightarrow$  formed by healing of fractures in the host

...but E ??

#### - Pseudosecondary melt inclusions:

 $\rightarrow$  formed when fracturing occurs during growth of the crystal. Their formation is followed by additional crystal growth

# Primary vs. secondary MI



gems-inclusions.com





The widespread occurrence of melt inclusions in basaltic rocks shows that their formation is a normal part of the process of **crystallization in igneous rocks** 

"(primary) Melt inclusions are small droplets of silicate melt that are trapped in minerals **during their growth in a magma**"

#### - BINARY EUTECTIC SYSTEM -



Because they contain liquids formed in thermodynamic equilibrium with their host minerals, **primary melt inclusions** produced at different stages of evolution of the melts will **record the** <u>liquid line of descent</u>\* **of magmatic systems**  $\rightarrow$  MI are like time capsules\*\*

 \* series of liquids derived from single parent magma
\*\* assuming they behave as closed systems (isolated from the surrounding environment) after their entrapment



Melt inclusions in igneous rocks may record **the preeruptive volatile content** that usually is lost during degassing and differentiation of magmas



Combining the melt saturation pressures retrieved from the  $CO_2$  and  $H_2O$  contents of melt inclusions is possible to build models of the magmatic plumbing system of volcanoes





Erebus (Antarctica)

[Oppenheimer et al., 2011]

#### Metamorphism

#### Metamorphism means "to change form"



Metamorphism includes all changes that affect rock's mineralogy and texture as a result of changes in pressure, temperature or composition of fluids in the environment

#### Agents of metamorphism

#### Heat



#### Fluids



#### Pressure (stress)



# High-temperature metamorphism



What can we expect when we heat the crust to vey high temperatures (700-1000 °C)?

# High-temperature metamorphism

This question bridges the gap between metamorphic and igneous processes

The temperature may rise enough to cause <u>partial</u> <u>melting</u>



Rocks formed during crustal melting (anatexis) consist of a mixture of melt (silicate liquid) and metamorphic rock (the residue) and are known as **migmatites** (migma  $\rightarrow$  mixture)









"Migmatites are spectacular, complex-looking rocks that can inspire or confuse geologists" (Edward W. Sawyer)

#### Residual granulites $\rightarrow$ melt-depleted, HT metamorphic rocks



#### Determines/affects:

- geochemical differentiation
- rheology of rocks
  - mountain building processes
  - exhumation processes
- igneous activity
  - volcanism
  - plutonism



#### [Sawyer et al., 2011]



Crustal anatexis

#### Leucogranites on Spider Wall, Nuptse, Nepal



#### Rhyolitic provinces in South America



#### Melting reactions

**CONGRUENT MELTING** → solid and liquid have the same compositions

- 1) Qtz + PI + Kfs +  $H_2O$  = liquid
- 3) Ms + PI + Qtz +  $H_2O$  = liquid
- 4) Qtz + Bt + Sil +  $H_2O =$ liquid

**INCONGRUENT MELTING**  $\rightarrow$  the composition of the liquid differs from that of the initial solid

2) Bt + Qtz + PI + Als +  $H_2O = Grt$  + liquid 5) Bt + PI + Qtz +  $H_2O = Grt + Crd$  + liquid 6) Bt + PI + Qtz + Sil = Grt + Opx + liquid Peritectic mineral:

the solid product of incongruent melting reactions

### Incongruent melting

#### - BINARY PERITECTIC SYSTEM -



 $T_{P}$ 

Enstatite melts incongruently to a liquid not of its own composition plus a new solid phase. The growing forsterite may trap droplets of coexisting melt

#### Incongruent melting

Mineral C is produced (grows) together with L (liquid), thereby creating the necessary conditions for primary entrapment of MI

$$A + B = C + L$$

Geological examples of incongruent melting range from the well-known, ideal reaction:

En = Fo + liquid

to the more complex, and of particular relevance to metapelites, reaction

Bt + PI + Qtz + Sil = Grt + liquid
# Entrapment of MI, a twofold process

#### Requirement $\rightarrow$ growth of minerals in the presence of melt



### **1- INCONGRUENT MELTING**

- ✓ little consideration so far
- ✓ in migmatites and granulites
  ✓ during HEATING

#### **2- MAGMA CRYSTALLIZATION**

- $\checkmark$  the most common process
- $\checkmark$  observed in igneous rocks
- ✓ during COOLING

## Entrapment of MI, a twofold process

Requirement  $\rightarrow$  growth of minerals in the presence of melt

### 2- MAGMA CRYSTALLIZATION

 $Liquid_1 = OI + Liquid_2$ 





## Entrapment of MI, a twofold process

#### Requirement $\rightarrow$ growth of minerals in the presence of melt

#### **1- INCONGRUENT MELTING**

Qtz + PI + Bt + Sil = liquid + Grt





# Changing the viewpoint



## What are melt inclusions?

"Melt inclusions are small droplets of silicate melt that are trapped in minerals during their growth in a magma"

"Melt inclusions are small droplets of silicate melt that are trapped in minerals during their growth in a magma in the presence of a melt phase"

# How are melt inclusions identified?

Melt inclusions are very small (< 20  $\mu$ m, often <10  $\mu$ m)

They commonly are polycrystalline and birefringent





[Cesare et al., 2009]

# How are melt inclusions identified?

Melt inclusions can be easily overlooked or considered bad sample preparation or dust

A good optical microscope and well-prepared thin sections are all one needs to make the preliminary, essential observations



# How are melt inclusions identified?







X-ray computed microtomography (XµCT; both synchrotron radiation- and X-ray tube-based) can be applied to investigate in a non-invasive way the **3D** spatial distribution of primary melt inclusions in garnet porphyroblasts

[Parisatto et al., 2018]

The microstructures of MI can be successfully characterized with back-scattered electron (BSE) imaging, using Field Emission Gun (FEG)-based electron microscopes

- Cryptocrystalline
- Negative crystal shape
- Micro- and nano-porosity (volume contraction?)



MI-forming crystals can be identified by acquiring EDS spectra and/or X-ray maps of the major elements



[Cesare et al., 2015]



[Bartoli et al., 2016]

### Granophyric intergrowths: Plagioclase + Quartz



#### Micrographic intergrowths: K-feldspar + Quartz









[Ferrero et al., 2012]

Given the small size of the crystals, Raman microspectroscopy represents a rapid way to identify the phases





Micro Raman spectroscopy mapping has revealed the presence of liquid H<sub>2</sub>O in micro- and nanopores of MI located below the surface of the studied thin section, i.e. entirely enclosed within the host

[Bartoli et al., 2013]



Dual-beam focused ion-beamscanning electron microscop e (FIB-SEM)

#### This technique permits to remove thin foils (250 nm)



## microstructurally characterized?

#### 3D reconstruction of unexposed inclusion



[Cesare et al., 2015]

# Nanogranitoids inclusions

- Cryptocrystalline
- Granitoid phase assemblage
   (Qtz+PI+Kfs+Bt+Ms)



NANOGRANITES (Cesare et al. 2009)

### NANOGRANITOIDS

(Cesare et al. 2015; Bartoli et al., 2016)



1 µm

## The surprise: glassy inclusions

Glass ± trapped phases





# They coexist together in the same cluster

# The surprise: glassy inclusions

Although there is a significant overlap, the two populations are statistically different, → 12.9 vs 8.2 µm

Most of the smaller inclusions remained amorphous (glassy) because of inhibited nucleation



## Does size really matter ?

We need more data...



# Nanogranitoid inclusions



These small data repositories can provide the primary composition of crustal melts at the source

Nanogranitoids, which totally crystallized upon slow cooling, represent the embryos of the upper crustal granitoid magmas

## Fluids in the crust

The phase relations of rocks containing fluids at crustal pressures are well understood. For high water contents the fluid phase is called an "aqueous fluid", whereas for low water and high solute contents, the fluid phase is a "hydrous melt". Supercritical fluids are present above the CP; their water contents are transitional between those of aqueous fluid and hydrous melt



[Hermann et al., 2013]

## Fluids in the crust



In HP-UHP rocks, the term "multiphase solid inclusions" is often used (see Frezzotti & Ferrando, 2015)

**Recovering complete** compositional data, including the volatile contents, requires the heating and remelting of the crystallized melt inclusions to a **homogeneous liquid**, reversing the phase change that occurred along cooling path after their entrapment (i.e. crystallization of daughter phases and fluid exsolution).

#### Experimental reheating



[Cannatelli et al., 2016]

In the case of the microscopemounted heating stage, the heating is usually conducted in an inert atmosphere of He to prevent sample oxidation. Rock wafers containing MI-bearing minerals (e.g. garnet) are separated from double-polished thick (commonly 100–250 µm) sections.







<sup>[</sup>Bartoli et al., 2013]

The obvious disadvantage of the remelting experiments at room pressure is the large overpressure generated in the MI  $P_i >> P_e$ 

Nanogranitoids often decrepitate before remelting, with loss of volatiles (H<sub>2</sub>O)

The rehomogenization occurs at temperature higher than the trapping conditions, favoring melt–host interaction and new minerals

Nanogranitoids experimentally remelted by the heating stage are commonly characterized by

#### i) irregular walls

ii) decrepitation cracks filled with melt

iii) presence of **new crystals** (i.e., not observed in the starting material) iv) the presence of **empty** (vacuum) **bubbles** formed to accommodate the volume lost by  $H_2O$  and melt leaving the inclusion







[Bartoli et al., 2013]

Homogenization <u>under</u> <u>confining pressure</u> using **a piston cylinder apparatus** may overcome the problems described above

MI-bearing minerals are loaded into Au or Pt capsules (external diameter of 3 and 5 mm) together with powdered silica



Because the abundance and the microstructural distribution of nanogranitods vary from sample to sample, <u>different strategies</u> can be adopted







[Cesare et al., 2015]

Despite the <u>trial-and-error nature of this approach</u>, much better quality compositional data can be obtained using a pistoncylinder because several MI-bearing crystals, and in turn a large number of MI, can be rehomogenized simultaneously, once the trapping conditions are determined





Regarding the major elements, approximately 600 nanogranitoids in migmatites and granulites have been analyzed by EMP

Nanogranitoids from each locality show some spread and, at the same time, a distinctive composition with respect to each other





#### LA-ICP-MS (trace elements)





#### NanoSIMS ( $H_2O$ and $CO_2$ )









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- Problems and pitfalls
- Concluding remarks
#### 1) That a rock has melted

There are many microstructural criteria for inferring the former presence of melt in regionally metamorphosed migmatite and granulite terrains which have undergone slow cooling over millions of years

Mineral pseudomorphs after melt films and pools



Crystals with euhedral shapes



[Holness & Sawyer, 2008]

However, recrystallization and deformation in the subsolidus may completely erase most or all evidences of partial melting



#### 1) That a rock has melted



The only evidence that these rocks underwent anatexis at some time in their complex history is represented by the occurrence of nanogranitoid inclusions within relics of Variscan garnet

2) When a rock has melted Because nanogranitoids attest to the growth of a mineral during crustal melting, the geochronology applied on that host mineral allows anatectic events to be dated with unprecedented confidence



2) When a rock has melted Very little evidence of partial melting during prograde metamorphism has been reported until now (Himalayas)



2) When a rock has melted Very little evidence of partial melting during prograde metamorphism has been reported until now (Himalayas)



[Carosi et al., 2015]



In situ U–Th–Pb dating of monazite included in garnets, in the same structural positions as MI, constrains the beginning of partial melting at 41–36 Ma

#### 3) That (part of) a mineral grew in the presence of melt

MI show a systematic distribution in an annulus around garnet core. This distribution matches the concentric chemical zoning of the garnet

These microstructures demonstrate that the MIrich annuli certainly formed during anatexis



[Cesare et al., 2015]

4) The construction of a plausible effective bulk composition for the melting event can take advantage of both i) the reintegration of nanogranitoid composition and ii) the removal of elements fractionated in the subsolidus garnet core



melt inclusions-rich portion of garnet formed during incongruent melting



#### 5) Placing melt in the right phase assemblage



Crystals of kyanite represent the main solid inclusion that favored the entrapment of melt during Grt growth

#### 5) Placing melt in the right phase assemblage



**Before** 

[Barich et al., 2014]



#### 5) Placing melt in the right phase assemblage

Earlier studies proposed that anatexis started in the field of sillimanite during decompression from peak pressures (Platt et al., 2003)

The study of nanogranitoids demonstrated that melt was already present in the system at peak conditions in the kyanite field (Barich et al., 2014)



#### 6) Mechanisms of crustal melting



[Bartoli, 2017]

These enclaves represent a snapshot of anatexis in the mediumto-lower crust, frozen due to the extrusion and rapid cooling of the host lava (frozen migmatites)

6) Mechanisms of crustal melting

MI in plagioclase → earliest granitic melts produced by fluidpresent to fluid-absent muscovite melting

MI in garnet → produced simultaneously to slightly later via fluid-absent melting of muscovite

Matrix melt → formed at higher temperatures by biotite dehydration-melting reactions



#### 7) Melt-fluid immiscibility

Melt-fluid immiscibility in anatectic systems occurs when the quantity of fluid exceeds the amount that is soluble/miscible in the melt at the pressure and temperature of interest



[Tamic et al., 2001]

#### 7) Melt-fluid immiscibility



The zonal distribution of inclusions supports their primary origin i.e., that they have been trapped during the garnet growth

#### 7) Melt-fluid immiscibility



**TYPE I**  $5 < \emptyset < 10 \ \mu m$ Quartz Mg-Fe-Ca carbonates Corundum Gr ± Spl

SEM analysis

TYPE II (nanogranitoids) 10 < Ø < 20 μm Quartz K-feldspar Plagioclase Gr ± Rt ± Bt ± Al-Si



#### 7) Melt-fluid immiscibility





#### 7) Melt-fluid immiscibility

Raman microspectroscopy (Tipe I)



#### 7) Melt-fluid immiscibility



[Tacchetto et al., submitted]

FIB-SEM analyis (Tipe I)

The polycrystalline assemblage is always composed of ferroan magnesite, quartz and graphite. Corundum, Znspinel and a S-Zn bearing phase are also present

#### 7) Melt-fluid immiscibility

	Inclusions						
Solid Phase (%)	1 52%	2 60%	3 31%	4 11%	5 34%	7 40%	8 46%
Magnesite	61.68	68.63	66.36	69.50	81.36	59.77	54.68
Quartz	20.51	19.80	11.46	15.72	6.70	25.50	25.85
Graphite	4.88	1.50	1.65	3.15	6.54	1.43	1.01
Corundum	4.57	8.87	n.p	n.p	n.p	9.88	9.35
Zn-spinel	0.18	0.24	2.09	5.67	4.28	2.12	n.p
Zn-S	n.p	0.03	n.p	0.71	0.63	0.25	0.18
Calcite	n.p	n.p	n.p	0.21	n.p	n.p	n.p
Dolomite	0.02	0.93	n.p	n.p	n.p	n.p	1.52
Pyrophyllite	5.44	n.p	n.p	n.p	n.p	n.p	n.p
Fe-rich phase	2.72	n.p	18.44	5.03	0.49	1.04	7.41
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00



HOMOGENEOUS FLUID

n.p= not present

#### 7) Melt-fluid immiscibility



Coexisting primary Type I and II inclusions → they are related to the same melting event (i.e., trapped at the same P-T conditions; 800-900 °C, 0.6-1.0 GPa)

They represent **different fluids** present in the system during anatexis Type II (nanogranitoids)  $\rightarrow$  anatectic melt Type I  $\rightarrow$  ????

#### 7) Melt-fluid immiscibility



Carbonation reaction:

garnet +  $CO_2$  = carbonate + kyanite

garnet +  $CO_2$  = carbonate + corundum + quartz

This reaction formed the solid assemblage observed in Type I inclusions (Crn + Qtz were able to grow metastably due to the very small size of Type I inclusions)

#### 7) Melt-fluid immiscibility

Type I and II inclusions indicate the **coexistence of a carbon-rich fluid and a silicate melt during anatexis**, in a situation of **melt-fluid immiscibility** 





This finding clearly shows evidence of **carbon mobility during the Neoarchean** (2.5-2.6 Ga) anatexis in a back-arc setting

8) H<sub>2</sub>O contents and fluid regime during melting Constraining the fluid regime during crustal melting is an issue that has received very recently renewed attention



Variable H<sub>2</sub>O contents, but relatively uniform values in nanogranitoids from the same host crystal

#### 8) H<sub>2</sub>O contents and fluid regime during melting



**Metasedimentary** rocks represent heterogeneous materials  $\rightarrow$  granitic melts displaying different H<sub>2</sub>O contents may form in the same rock under conditions of "mosaic equilibrium"

#### 8) H<sub>2</sub>O contents and fluid regime during melting

Conditions of "mosaic" equilibrium can also affect the  $aH_2O$  in the coexisting fluid phase

The first discrete fractions of melt produced in different rock microdomains (graphite-bearing vs. graphite-free) may contain different amounts of water



### Problems and pitfalls

Nanogranitoid inclusions **are not a panacea**; their limitations and challenges must also be understood to fully harness their potential



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Nanogranitoid inclusions **are not a panacea**; their limitations and challenges must also be understood to fully harness their potential

#### Post-entrapment modifications





### **Problems and pitfalls**

Uncovering and polishing the nanogranitoids is a **crucial problem**. The polishing of crystal-bearing MI often results in the complete or partial mechanical removal of the inclusion content



### Concluding remarks

→ A good optical microscope and well-prepared thin sections are all one needs to make the preliminary, essential observations that allow to decide if nanogranitoids are present and suitable for a subsequent, detailed study

→ The characterization of nanogranitoids requires a timeconsuming preparation and use of cutting-edge techniques in addition to more routine ones, but the results so obtained are very satisfactory

→ The small-size of nanogranitoids and of daughter minerals crystallized in them still poses some limitations to a full and fast chemical analysis of these objects. However, in a few years from now, the rapid improvement of analytical techniques will have overcome these problems