

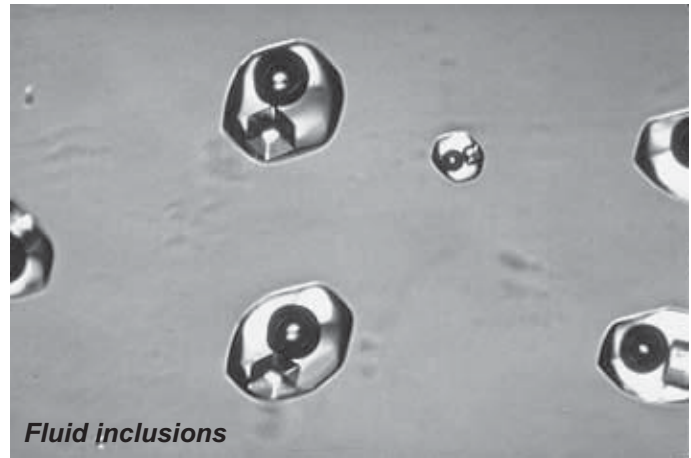
## **Bubbles in Amsterdam** melt and fluid inclusion research at the Vrije Universiteit

*When Jacques Touret, professor of petrology, mineralogy and ore geology, was about to retire from the Vrije Universiteit, my alma mater, I asked around for a contribution about his research. Jacques responded by asking me to drop by. "Why don't you write it?" suggested Jacques and he introduced me to his colleague Igor Nikogosian. Igor then introduced me to melt inclusions.*

On March 29, 2001, the University of Liège in Belgium awarded an honorary doctorate (*Docteur Honoris Causa*) to Jacques Touret. On September 19, 2001, the VU organized a symposium in Jacques's honor: *Fluids at depth*. In addition, the journal *Lithos* dedicated an entire issue to Jacques. Jacques Touret, having reached the Dutch retirement age, was leaving. He has bought a house in France and moved back to his home country, where his wife works as a mineralogist and curator at the Musée de Mines of the École des Mines in Paris. After the recent graduation of Bin Fu, Jacques still has one Ph.D. student left in Amsterdam (Eduardo Campos). Jacques Touret is also a member of the Royal Netherlands Academy of Sciences and as such is currently concerned with documenting the history of the earth sciences. So instead of traveling back and forth to France, he now travels back and forth to The Netherlands, where he will always be very welcome. The Dutch like Jacques, not only because of his scientific contributions but also because of his friendly nature. Jacques is well known for his appreciation of the finer things in life, his enthusiasm, his French charm, and his sense of humor.

### **Fluid inclusion research at the VU**

Jacques Touret joined the Vrije Universiteit in 1980, as a full professor in petrology, mineralogy and ore geology, freshly imported from France. He quickly established a fluid inclusion research lab, which became a reference for this type of research. Jacques's fluid inclusions students came from many countries



*Fluid inclusions*

and have taken their expertise to many countries: Germany (Fons van den Kerkhof), Italy (Maria Luce Frezotti), South Africa (Jan Marten Huizenga), China (Bin Fu and Cong Yuexiang) and soon Chili (Eduardo Campos). Other Ph.D. students have also spread the news about Amsterdam, for instance in Indonesia (Jan Sopaheluwakan) and Zimbabwe (Hielke Jelsma, now in South Africa).

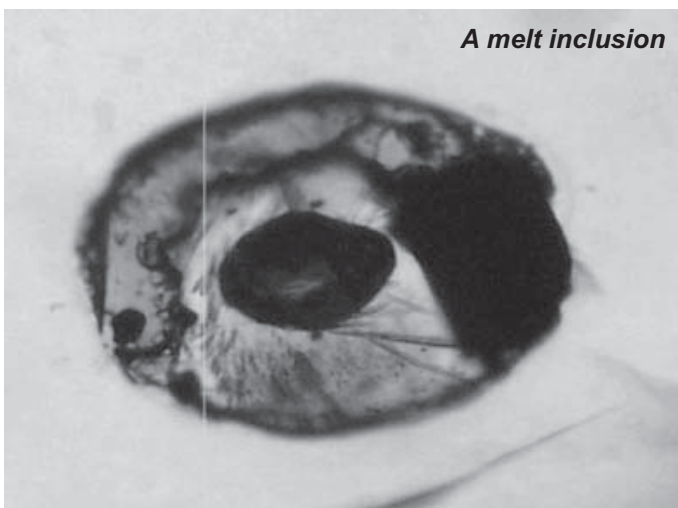
Ernst Burke - the Belgian mineralogist, Raman probe specialist and head of the Microanalysis lab at the VU earth science department - and his coworker Wim Lustenhouwer must be mentioned as well in this respect. Their role was and continues to be essential. Ernst, Wim and their colleagues enable top-notch quality analysis of inclusions.

### **Brief history of fluid inclusion research**

Fluid inclusions were already recognized at the beginning of the eighteenth century and later became a regular part of petrography. H. Vogelsang - professor of petrology at the University of Delft more than a century ago - demonstrated that fluids found in granitic minerals such as beryl, topaz and quartz, were in fact supercritical CO<sub>2</sub>. During the first half of the twentieth century, interest in fluid inclusions waned. Only scientists in the former Soviet Union continued to study them and later became a source of expertise for the west.

Fluid inclusion research initially was largely - but not solely - the domain of metamorphic petrology. Certain high-grade metamorphic rocks that were initially considered rare oddities turned out to be important components of the continental crust. These rocks are called granulites. In the 1970's, granulites were discovered to contain many CO<sub>2</sub>-rich fluid inclusions and this spawned renewed interest in the topic. Granulites are one of Jacques Touret's favorite research topics and that was his angle for studying fluid inclusions.

They are tiny cavities in crystals and can contain three phases (solid, liquid and gas). Fluid inclusions in igneous rocks may represent the volatile phase of a magma. Fluid inclusion research entails the use of a heating-freezing stage with which homogenization temperatures can be determined. The Raman probe is another prominent player in fluid inclusion research: it's an often-used analytical tool. Vital in the work on fluid inclusions is the assumption that the inclusions have not leaked any of their contents. (See also Touret, 2001.) It may come as a surprise to



*A melt inclusion*

earth scientists in other subdisciplines that fluids at depth ( $H_2O$ ,  $CO_2$ ,  $CH_4$ ,  $N_2$ , He) may well exceed by many orders of magnitude the mass of fluids contained in the outer layers of the terrestrial system.

The original fluid inclusion research now appears to be overtaken by one of its categories: melt inclusions. GeoRef turned up 73 results for "melt inclusions" in publications between 1985 and 1970, 52 for publications between 1985 and 1990 and the number has been rapidly increasing since. The 1995 AGU Spring Meeting included a session called "Melt inclusions and petrogenetic indicators in igneous environments". Vol. 4, No. 3 of the journal

*Petrology* contains material that was presented at that symposium.

### Melt inclusion research at the VU

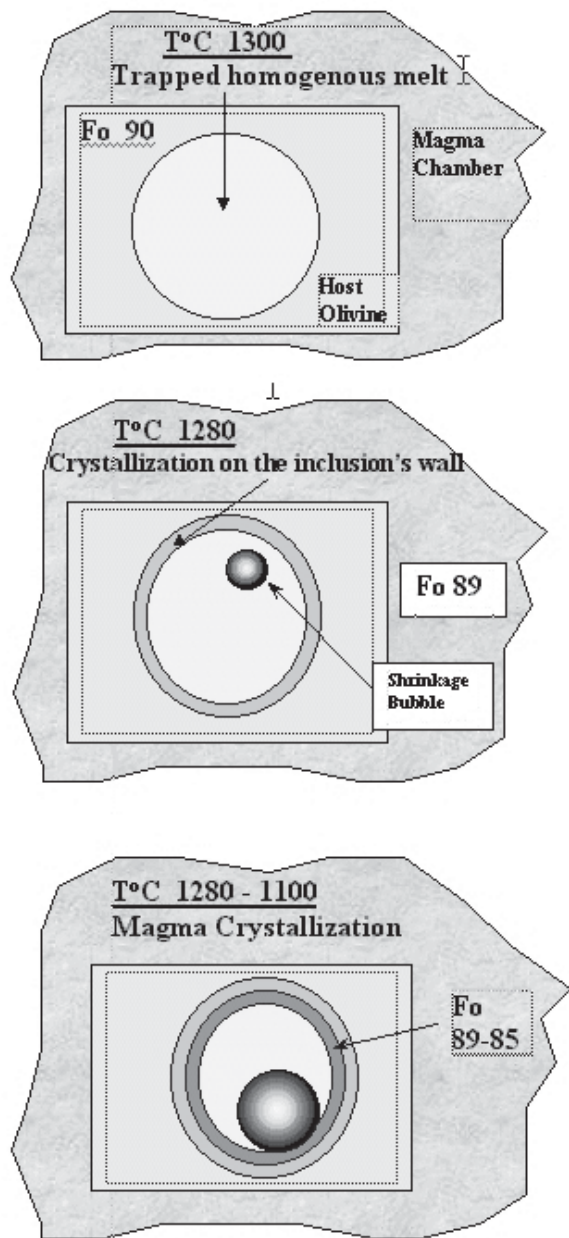
About four years ago, Jacques Touret decided to install melt inclusion facilities at the VU. "Jacques was always telling me that most petrologists were missing half the excitement by not looking at inclusions", writes Tim Elliott who used to work in Amsterdam but is now at Bristol. Jacques then contacted Alex Sobolev who proposed that Igor Nikogosian help him set up the equipment and methods. The VU already had a Linkam stage for melt inclusion work, but it did not allow quenching to glass at equilibrium conditions. Igor came to Amsterdam and set up the stage, with the help of Ernst Burke and particularly his colleague Wim Lustenhouwer. Of course, Igor did not just come to Amsterdam to install the stage. He set up the entire methodology and has been actively boosting melt inclusion research since, particularly by his own contributions to the field.

### Brief history of melt inclusion research

The history of melt inclusion research resembles that of fluid inclusions in general. Melt inclusions had already been noticed in the eighteenth century, but in the 1970's, only Sobolev's group in the Soviet Union and a few other groups (in Japan, China and the DDR) were actually studying them. It was the Russian group that created a crucial breakthrough: the development of the Vernadsky stage. The Vernadsky stage not only enabled heating to high temperatures, but also rapid quenching. Igor Nikogosian was part of Sobolev's group of Ph.D. students in the former Soviet Union. These Russian students have all swarmed out to the west, just as Touret's former fluid inclusion students did. Andrey Gurenko used to work at the GEOMAR research center in Kiel, but has recently moved to Potsdam where he joined Ilya Veksler. Maxim Portnyagin is now in Kiel. Vadim Kamenetsky and Leonid Danyushevsky are both working at the University of Tasmania in Australia. In 2001, the Alexander von Humboldt Foundation gave a Wolfgang Paul Award to Alex Sobolev, then at the Vernadsky Institute of Geochemistry and Analytical Chemistry in the Russian Federation. As a Humboldt awardee, he currently works in Mainz, Germany. While fluid inclusion research appears to have been the domain of metamorphic petrology (not exclusively!), melt inclusions are particularly impacting igneous petrology. Simplified, one could say that petrologists study all aspects of a rock and then try to say what exactly made the rock into what it is now. While this may sound trivial, this kind of information forms the pieces of a puzzle. The assembled puzzle would show the workings and details of the system known as the solid earth, and of part of the hydrosphere and atmosphere as well.

### What are melt inclusions and why are they special?

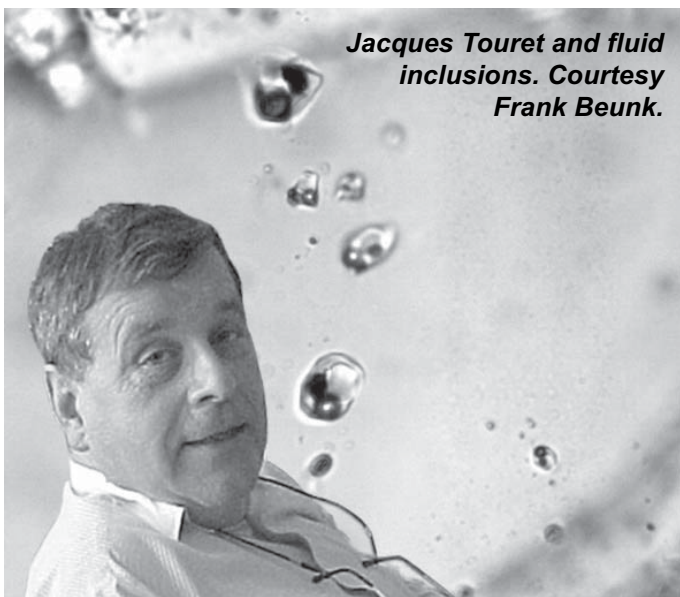
Melt inclusions are tiny blobs of magma trapped within crystals (phenocrysts). At room temperature, they are solid (unlike "regular" fluid inclusions). Their typical size is 1 to 50  $\mu m$  but they can be considerably larger as well. They can be completely glass, partly glass and partly crystalline, or wholly crystalline. Glassy melt inclusions may contain a shrinkage bubble. Primary melt inclusions are the most important as they contain the magma in which the crystal formed. Secondary melt inclusions form after crystallization of the host mineral and are less important, but



*This is what happens to a melt inclusion as it cools. The reverse happens on a heating stage during a microthermometric run. Courtesy Igor Nikogosian.*

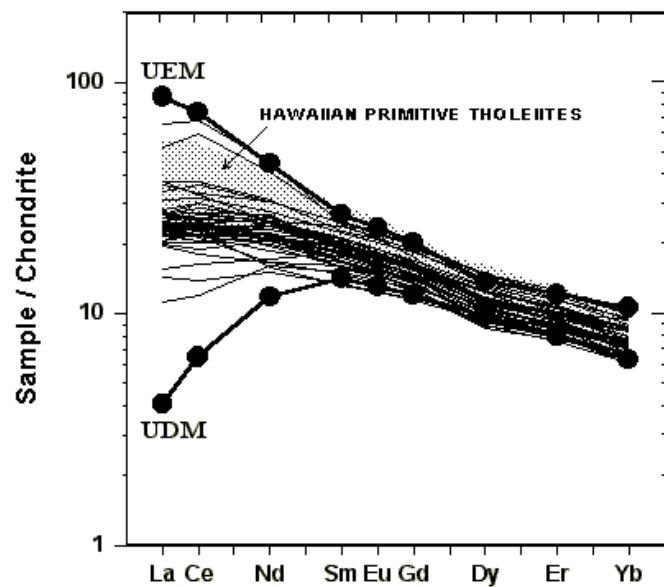
can for instance yield important insights in the nature of metasomatic fluids (see Schiano *et al.*, 1994).

What is so special about melt inclusions is that, ideally, they constitute a time machine. They allow us to look back in time. The processes that (metamorphic and) igneous petrologists study tend to wipe out each other's results. Any rocks we see at the surface of the earth have been subjected to a wide range of processes. All we see is end products. We would like to know how they started out. Were they originally part of one magma in a magma chamber or are they the result of the mixing of several magmas? Did they melt again at some point and assimilate other rocks at that point? Did they assimilate other rocks before they first crystallized? Have they been recycled through the big magma machine and have parts of them been exposed to atmospheric conditions before? Often, we don't know. All we know is that most rocks have come a long way.



Melt inclusions, ideally, are tiny samples taken along that road. They allow petrologists to travel back in time vicariously and take a snapshot of physicochemical conditions of certain points along that path. It won't get any better than that because humans do not live long enough and can't survive high temperatures and high pressures. Humans cannot jump into a subduction zone and witness these processes firsthand, but melt inclusions make good proxies. High-PT experiments are the only other thing that comes close. If you do an 'old-fashioned' whole-rock analysis, you get the chemical result of a series of processes. With supplementation from other data, such as mineral analyses and geothermobarometry, you hope to be able to reconstruct at least some of the rock's history. By using data from melt inclusions in phenocrysts you may end up with a complete PTt (pressure-temperature-time) trajectory and a very good idea of the processes along that trajectory. Melt inclusions are magmatic information agents.

Does it always work this way in practice? Of course not. The ideal scenario is based on the assumption that the melt inclusion is a chemically closed system and has been since the time of entrapment. Melt inclusions tend to become trapped at sites of



Rare earth element compositions of melt inclusions in olivine from Hawaiian tholeiites, including range of whole-rock data. These data are not only normalized to chondrites but also to 10 wt.%  $Al_2O_3$  of primary melt from Sobolev and Nikogosian (1994). These ultra-depleted (UEM) and ultra-enriched (UDM) melt components were completely unknown until they were found in these inclusions trapped in high-Mg olivines. This indicates the co-existence of very different magmas in an efficiently mixing magma conduit.

crystal defects (energetically favorable). These are, of course, also sites of potential diffusion routes. The degree to which a melt inclusion was closed or not is linked to element concentrations, concentration gradients and diffusion coefficients. The larger the chemical contrast between melt and host mineral, the better the isolation (Sobolev, 1996). Danyushevsky *et al.* (2002) recently outlined some of the complications of melt inclusion research. Nielsen and coworkers described earlier how to check the integrity of melt inclusions (1998).

### Methodology

As indicated earlier, the high-temperature heating/quenching stage is paramount in this work. First, phenocrysts with melt inclusions are selected and separated from the rock, mounted in epoxy and polished. Second, if the inclusions are fully vitreous, the composition of the glass can be determined without any problems. If the inclusions are partly of wholly crystalline, the inclusion first needs to be melted and then quenched (to prevent crystal formation), after which the glass can be analyzed. High-temperature microthermometry - the heating/quenching stage - allows the petrologist to determine the equilibrium conditions and crystallization temperatures for the inclusion and its host. Briefly, the inclusion is heated in a pure He atmosphere until it melts. Kinetic experiments - basically consisting of a series of thermometric runs in which the heating rate is varied and the inclusion carefully observed under the microscope - are carried out to determine the best conditions. The run is the reverse of the natural cooling process: the phases in the inclusion disappear

one by one until the contents of the inclusion are completely homogenized. Without visual control, one can only guess what happens in the inclusion and may well end up with false results. It would, for instance, be impossible to quench at the right moment, without visual control.

EPMA, LA-ICP-MS, FTIR spectroscopy, ion probes for trace elements and H<sub>2</sub>O, and SYXRF are some of the analytical tools used in melt inclusion research. The microbeam developments lifted melt inclusion research out of its cradle after the development of the Vernadsky stage. The analytical data can be fed into mathematical models and the results of the microthermometric runs can then be compared to the calculated data.

However, working with melt inclusions is not as easy as it may initially sound. If you heat inclusions too slowly, re-equilibration at conditions not representative of trapping will occur. If you heat inclusions too rapidly, the actual conditions in the inclusion are those of a lower temperature. Overheating (above homogenization) is not necessarily a problem as long as you immediately quench the inclusion. *"But if you overheat a clinopyroxene host by 25 to 50 degrees, you end up with a completely different composition of the melt inclusion"*, warns

Igor Nikogosian. *"Especially for Si, Ca, Al, Ti and Na. It is difficult to make corrections for those."* During these experiments, the host crystal may influence the inclusion, while originally, it was the magma that determined the host mineral. Pressure effects can also play a role: the host mineral is not at its original pressure. That is why it is also very important to rapidly quench a melt inclusion once it has homogenized. See also Danyushevsky *et al.* (2002).

In addition, melt inclusion work can be very painstaking. What you hope to find are so-called exotic inclusions: the ones that have retained very deep parent magmas. No more than about 5% of all the melt inclusions in a rock are exotic. You may end up studying literally hundreds and hundreds of inclusions before you strike pay dirt. The rewards are worth the effort: you may find that the rock you have is not the result of the mixing of three but of five magmas. It is the nature of those magmas that reveals a great deal of information about the processes in the deep earth.

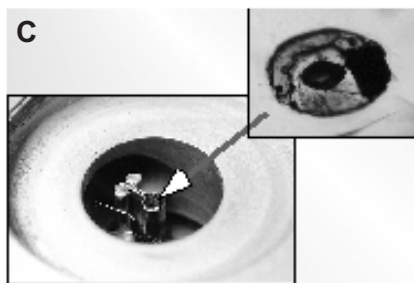
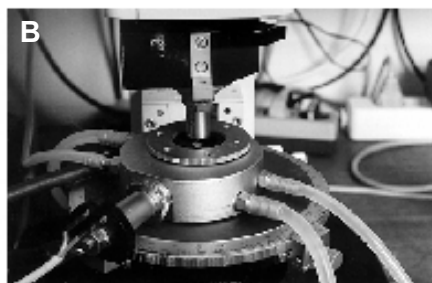
### Examples of melt inclusion work

Melt inclusions enable determination of the oxygen fugacity at the time of magma crystallization, on the basis of the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio in spinel and the composition of the associated olivine (see Danyushevsky and Sobolev, 1996).

Much work has focused on volcanic rocks such as those of Mount Shasta and in Italy and particularly on intraplate magmatism, such as of Hawaii. It is widely accepted that mantle plumes contain recycled oceanic crust. Melt inclusions contain the information to prove this (Sobolev *et al.*, 2000).

A recent development is the determination of the isotope composition in melt inclusions. (See Sobolev, 1996.) Some researchers have, for instance, used <sup>40</sup>Ar/<sup>39</sup>Ar data from melt inclusions in quartz to determine residence time scales of silicic magma chambers, but there are some complications related to the question whether these inclusions can be regarded as a closed system with respect to <sup>40</sup>Ar (Winick *et al.*, 2001). Will isotope work on melt inclusions refute earlier findings? *"While determining isotope compositions of melt inclusions will not dramatically upset earlier findings, I do expect it to reveal new knowledge about the isotope systems"*, replies Igor Nikogosian.

Boron - isotope composition - in melt inclusions is a good tracer for a crustal component diluted with mantle material and indicates that arc magmas also contain an oceanic crust



A. General view of the Vernadsky-Institute type high-temperature set-up with controlled He atmosphere and video display at the VU.

B. Detail of the high-temperature heating stage at the VU (up to 1500 degrees C).

C. General view of the heating/quenching element of the Vernadsky stage at the VU; arrow indicates the position of the melt inclusion. The quenching time is 1-2 seconds.

component (Rose *et al.*, 2001; Gurenko and Chaussidon, 1997).

A spin-off from the work with the Vernadsky stage is that it also enables new fluid inclusion work. Previous fluid inclusion work

*melt inclusions can preserve their original trace element concentrations over time, the same cannot be said of some elements in plagioclase-hosted inclusions.*



*LEFT: Jacques Touret during the ceremony in Liège (front row, third person on the left). Seated on the far right, front row, is His Majesty King Albert II of Belgium. Courtesy Pascale Scarpa. Copyright TILT PHOTOGRAPHY LIÈGE - [www.tilt-photographie.be](http://www.tilt-photographie.be).*

*BELOW: Jacques Touret receives the honorary doctorate from the Université de Liège (March 29, 2001). Courtesy Pascale Scarpa. Copyright TILT PHOTOGRAPHY LIÈGE - [www.tilt-photographie.be](http://www.tilt-photographie.be).*

did not involve heating to over 500 degrees C. Now with the Vernadsky stage, fluid inclusions can also be taken to much higher temperatures that may be much closer to their formation conditions (see Campos *et al.*, 2002).

### Other geoscientists about melt inclusions

Of course, Jacques Touret and Igor Nikogosian are not the only petrologists dedicated to inclusion research. Rumor has it that Dan McKenzie became obsessed with them and that Al Hofmann is also a real convert. So what do you hear if you ask around?

**Liz Cottrell** is a Fulbright Scholar working on her Ph.D. at Lamont, where she now studies core formation as an experimentalist with David Walker. Liz has used melt inclusions in her research and attended a melt inclusion workshop in Grenoble in March of 2000 (cosponsored by Elsevier Science). She writes:

*"While melt inclusions provide one unique tool for understanding petrogenesis, it is easy to misinterpret the data they provide by failing to take into account diffusional processes. Exciting new work focuses on the trace element contents of melt inclusions. However, some trace elements may diffuse rapidly enough to obscure the original information content of the melt inclusions. We tried to quantify this in Cottrell *et al.* (2002) by demonstrating that diffusion will have different but predictable effects in different host phases. For example, while it appears that olivine-hosted*



*Based on the study by Cottrell *et al.* (2002), there are several ways in which the melt inclusion community could improve the quality of both the data and the interpretations of melt inclusions. Every effort should be made to gather data from a variety of phenocryst types from the same location. The partitioning of trace elements varies among crystal hosts, so looking at inclusions in more than one type of phenocryst might unravel any diffusional overprinting of the original concentrations. If only one host type is available, then it is especially important to look at the statistical distribution of trace element concentrations in order to spot the potential effects of diffusion. I believe there is also an untapped wealth of information in the trace element zoning around melt inclusions. With the proper microanalytical work, trace element*

zoning in the crystal surrounding the melt could provide information about the timing and evolution of inclusion compositions.

*The bottom line is that melt inclusion work has an exciting future, but care needs to be taken to unravel the modifications caused by diffusion. This can best be accomplished if high quality trace element data are collected from melt inclusions from multiple hosts from one location and the information compared to model predictions. In this manner, post entrapment diffusion can be quantified and subtracted so that the real information about primary liquids can be elucidated.*

Danyushevsky *et al.* (2002) appear to concur with Liz. They also argue that many articles pay a great deal of attention to interpreting the composition of inclusions, whereas there is little regard for the processes that affect inclusions after trapping.

Roger Nielsen (Oregon State): *"First and foremost - we as petrologists need to get past the prejudice that melt inclusions are "secondary" sources of petrologic information relative to sources we are more familiar with such as bulk rock or lava chemistry. The data obtained from melt inclusions have their own set of interpretive criteria quite apart from "normal" data. However, that does not mean that they are inferior in any way. We will gain our greatest leverage when we can fully integrate all data types. That will require us to abandon hearsay criticism of melt inclusion data and obtain reliable, reproducible experimental constraints on the important processes that can effect the composition of trapped melts."*

Roger agrees that melt inclusions are essentially the only way to obtain data from earlier stages in the differentiation of a volcanic suite. *"This is particularly true with regards to volatiles."* He cautions: *"When interpreting inclusion data, or any small scale geochemical data such as zoning, we must remember that the scale of the features we are measuring are 8-10 orders of magnitude smaller than the environments we are using the data to interpret."*

Tim Elliott (University of Bristol, U.K.) is also highly enthusiastic and emphasizes that he's certainly not the only one. *"The fantastic range in compositions you see in individual olivine crystals (Sobolev *et al.*, 2000) blew everyone's mind. This put some bewildering constraints on melting and mixing processes. I believe that Marc Spiegelman has recently come up with a model that at last can explain some of this in a reasonably physically plausible manner."* According to Tim, melt inclusion research is revolutionizing the understanding of melting and volatile budgets in subduction zones. *"For this, the heating stage does not come into its own as self-quenched inclusions are best. But, such glassy inclusion provide a record of pre-eruptive volatile contents that can't be obtained in any other way."* Tim emphasizes that he admires Igor and considers him a great scientist: working very hard, very skilled and also quite successful at forging international collaborations.

Adam Kent (Dansk Lithosfærecenter, Copenhagen, Denmark) adds: *"I think that the really exciting thing about melt inclusions is that they are making geochemists and petrologists think about the processes that produce igneous rocks in new ways - principally because inclusions provide a record of the tremendous diversity of magma compositions that occur in different igneous*

*environments, such as mid ocean ridges, island arc volcanoes and so on. In many cases our understanding of geochemical processes is largely based on variations between various geochemical components, so something that can help us image these differences in much greater detail is of tremendous value.*

*Although there are still questions regarding the processes that trap and subsequently modify inclusions, advances in analytical techniques promise to provide even more insight in the future. In particular, and in contrast to Igor, I think that development and wide application of techniques for isotopic analyses of melt inclusions will produce important results (and in fact they already have), allowing us to see through melting-related processes and take a fresh look at the nature of the mantle and crustal rocks from which magmas ultimately derive."*

### Future of the inclusion group at the VU

Amsterdam is one of the few places in the world with a fully operational Vernadsky stage. Vernadsky stages are also up and running in Australia (Hobart), Norway (Oslo), and France (Saclay). Vernadsky stages have been, are being, or will be installed shortly in Italy (Siena), the US (Woods Hole and Blacksburg), and Germany (Mainz and Kiel).

The Amsterdam group is involved in many international cooperations and always has been. It is currently rapidly turning out papers based on melt inclusion work. A recent issue of *Chemical Geology* focused completely on melt inclusions and contains the results of the Grenoble workshop. Three papers in that issue are based on work conducted at the VU. A recent issue of *Tectonophysics* also contained a contribution from the VU melt inclusion group. However, these are only a few examples. The group certainly has proved its right to exist and the search for Jacques's successor has started.

A factor that will play a huge role in the future developments at the VU is whether the VU will continue to attract enough earth science students. As in many other countries, this is becoming a problem in The Netherlands. The recent number of applications to the Dutch earth science Master's programs shows a drop of 40 percent (that also happened, for instance, to chemistry). In that light, it is interesting to hear what Liz Cottrell writes about her own career: *"My decision to become an earth scientist stems from the many wonderful mentors I've had in the field. They have offered me guidance, encouragement, and funding."* This demonstrates the importance of individual earth scientists. They can and must inspire students, so that there continue to be opportunities for excellent young scientists - like Liz Cottrell - who can take over in the future. It's not just matters like the number of high-quality publications and the amount of acquired funding, which make a great scientist. It includes the integrity, enthusiasm and power to attract, inspire and keep good people.

Angelina Souren  
Associate Editor for The Geochemical News  
Angie@smarterscience.com