High temperature gas-mixing furnace: experimental set up and applications to Earth Sciences

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Abstract. — The present paper is constituted of two parts. First the set up of a vertical quench furnace is described with special focus on technical details such as the location of the volume in which the temperature reaches its maximum and it is steadier (the hot zone). In the second part some applications in mineralogic and petrologic researches, in which the use of the furnace is crucial are presented; they belong to on-course projects on phase relationships of hawaiitic lava under surface conditions, homogenisation of melt inclusions hosted in olivine and preparation of starting materials for high pressure-temperature experiments.

Riassunto. — Questo lavoro consta di due parti. Nella prima viene descritta la messa a punto di un forno verticale a raffreddamento rapido con particolare riferimento a dettagli tecnici come l'individuazione del volume nel quale la temperatura raggiunge il suo valore massimo ed è più stabile (zona calda). Nella seconda parte vengono presentati esempi di ricerche nel campo della mineralogia e della petrologia sperimentali nelle quali è indispensabile l'utilizzo di un tale forno, come lo studio delle relazioni di fase in una hawaiite a pressione atmosferica, l'omogeneizzazione di inclusioni vetrose in olivina e la preparazione di materiali di partenza per esperimenti in condizioni di alta temperatura e alta pressione.

Key Words: *vertical furnace, quenching, furnace calibration, hot spot, experimental petrology, experimental mineralogy.*

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Introduction

An high temperature vertical gas-mixing furnace is quite an important apparatus in an experimental mineralogy and petrology laboratory. In fact it allows to perform experiments at high temperatures under a controlled atmosphere (thus simulating volcanic systems) and it is indispensable to obtain highly reactive starting materials (i.e. glasses) to be used in high pressure and high temperature experiments. Nonetheless, in order to take advantage of its capabilities, an accurate set up and a careful calibration are required.

Vertical gas-mixing furnace: technical details and calibration

In order to perform effective heating experiments in a controlled atmosphere a commercially available high temperature vertical furnace (Deltech Model DT-31VT-OS2) was modified to enable really fast quenching of the samples and to allow a precise control of the oxygen fugacity under which the runs take place.

The Deltech furnace is designed for use with a 998 grade alumina tube (50 mm outer diameter, and 600 mm length) and is equipped with two B thermocouples (Pt/6%Rh-Pt/30%Rh) positioned mid-height just outside the furnace chamber. One of these is connected to a programmable temperature controller (Eurotherm model 2404), which

regulates the power input to six molydisilicide heating elements via a silicon controlled rectifier (sometimes referred to as a thyristor). The second thermocouple is connected to a protection module that trips off the power if the chamber temperature exceeds a user-defined value (overtemperature protection). Materials used for the chamber and the heating elements ensure a maximum operating temperature of about 1650°C.

In order to profitably use the furnace for research purposes, the knowledge of the following is required:

1) the location and the extension of the hot zone inside the furnace. The hot zone is that volume in the furnace chamber in which the temperature peaks and its value is more stable over time;

2) the actual sample temperature (which must be monitored by an additional thermocouple).

These two parameters can vary with the furnace tuning temperature and their determination can be generically referred to as "furnace calibration".

Furthermore, it is crucial, for a successful experiment, to:

3) achieve a rapid quench of the charge in order to obtain glasses or to preserve the phase(s) stable at high temperature;

4) control the oxygen fugacity during the runs. This is commonly achieved by letting an appropriate mixture of gases flow through the chamber during the experiments.

In order to satisfy these requirements two customized cylindrical brass jackets are mounted on both alumina tube ends (Figure 1): the upper jacket is topped by a cover into which intakes for the quenching electrodes, the monitoring thermocouple and the gas inlet are realized (Figure 1a). A differently-shaped brass cover (Figure 1b) has been manufactured to support the oxygen fugacity probe (see below). A glass quenching pot with a gas outlet is attached to the lower jacket (Figure 1c). In order to avoid gas leaks and thermal damage to the jackets, these are equipped with Viton O-rings and cooled by means of a water flow (approximately 0.2 litres/minute).

The calibration was performed by means of additional monitoring thermocouples; K-type (Ni-Cr/Ni-Al) for T ≤ 1300°C and S (Pt /Pt10%Rh) for T≥ 1300°C. Actual temperature values were measured at different depths inside the furnace; thus the "nominal temperature" (Tn, the set-point of the controller) could be compared to the "real temperature" (Tr) as a function of the distance from the upper end of the alumina tube (Figure 2). Note
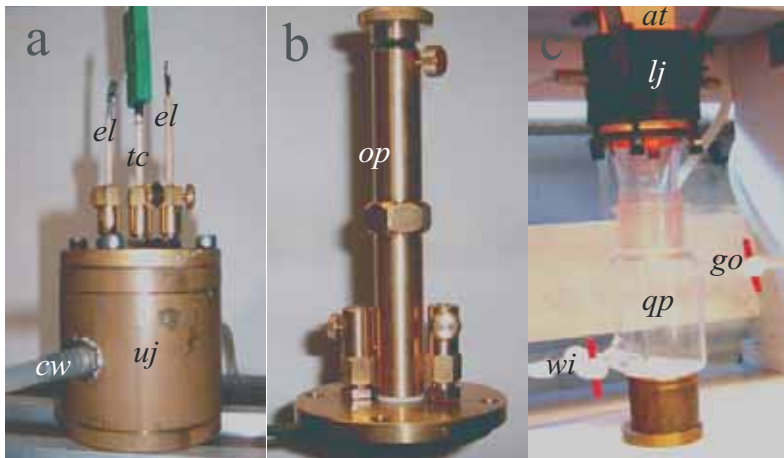

Fig. 1 – Details of jackets and quenching pot. a) and b) show the two different upper jackets (gas inlet not shown), c) refers to the lower jacket. *at*= alumina tube, *cw*= cooling water tube, *el*= electrode, *go*= gas outlet, *lj*= lower jacket, *op*= oxygen probe inlet, *qp*= quenching pot, *tc*= monitoring S thermocouple, *uj*= upper jacket, *wi*= quenching water inlet.
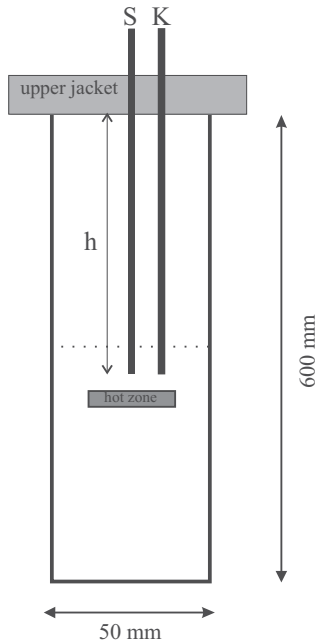
Fig. 2 – Sketch of alumina tube showing the hot zone and the position of S and K thermocouples used in calibration. The dotted segment represents the geometric centre of the tube. The horizontal exaggeration is ~ 4.

that the position of S thermocouple coincides with the alumina tube axis whereas the K one is slightly displaced in a peripheral area of the tube (Figure 2). The calibration was performed in the range 800-1600°C at 100°C steps and the results are reported in Figure 3 where ΔT (Tn-Tr) values are plotted against the thermocouple position inside the tube (h) for different Tn. The heating (and cooling) rate used both for calibration and typical experiments is 5°C/minute. Calibration procedure was started 24 hours after the attainment of set point in order to ensure a complete thermal stabilization of the furnace.

The results of the calibration show that (Figure 3):

a - the hot zone is approximately 2 cm wide, it is located about 6-8 cm below the geometric centre of the alumina tube (h=30) and its position is irrespective of Tn;

b - at T=1300°C the measurements performed by K and S thermocouples give the same results in the hot zone (Figure 3), thus suggesting that the radial T gradients in the tube are negligible;

c - ΔT in the hot zone is always positive and increases with Tn: its values are plotted vs. Tn in Figure 4 and range from 8°C (at Tn=800°C) to 65°C (at Tn=1600°C). Fitting the above data
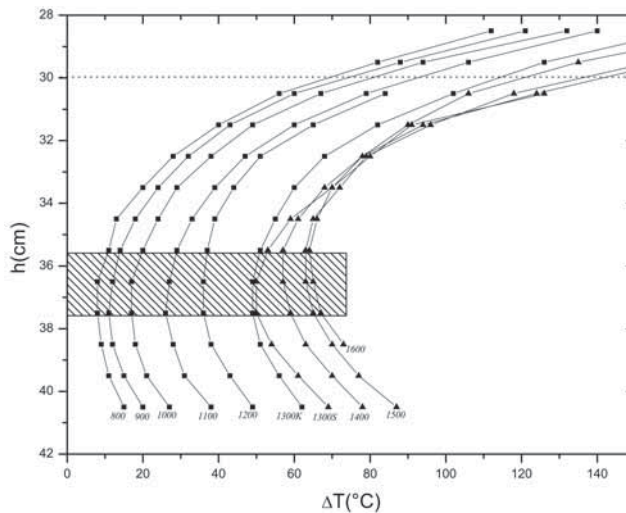

Fig. 3 – Tn-Tr (ΔT) vs thermocouple position inside the tube (h). Curves refer to measures performed at various Tn; 1300K and 1300S refer to measures performed with K and S thermocouples, respectively. The hatched area represents the hot zone. The dotted segment represents the geometric centre of the tube.
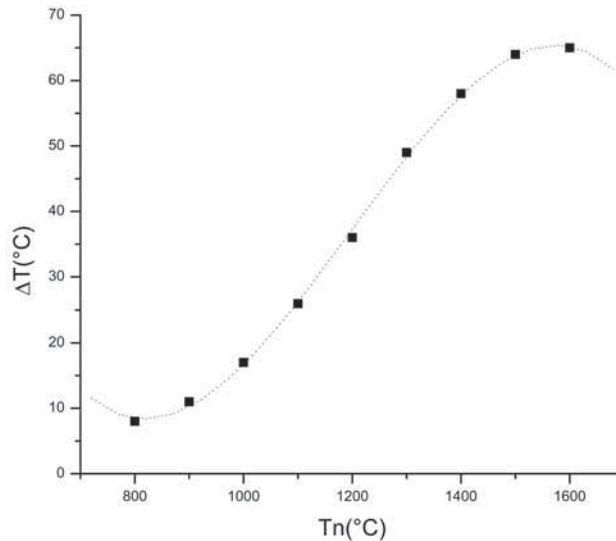
Fig. 4 – Tn vs ΔT. The dotted curve represents the polynomial regression (order=3). The relative equation is reported in the text. Coefficient of determination= 0.99921.

(dotted line in Figure 4) the following expression is obtained:

$$Tr=Tn-352.81-1.02*Tn+9.46*10^{(-4)}*Tn^{(2)}-2.63*10^{(-7)}*Tn^{(3)};$$

d - outside the hot zone T oscillates up to ± 10°C while, in the hot zone T is stable (± 3°C).

The sample can either be contained in a Pt crucible or hosted in a Pt loop (Figure 5) and it is suspended in the hot zone by means of a thin (diameter= 0.2 mm) Pt wire ("quenching wire") connected to two electrodes, constituted by alumina tubes in which two thick (diameter= 0.5 mm) Pt wires are inserted. At the end of the experiment the thin Pt wire is melted via electrical current flow (at about 110 volts) through the electrodes; the sample drops at the bottom of the furnace into a quenching pot filled with cold water. The quenching of the sample takes place in about 0.2 seconds and it is quite effective.

When the oxidation state of elements (such as Fe) has to be fixed, oxygen fugacity values during the experiments may be controlled by means of a mixture of gases (CO and CO_2 in our case) flowing through the furnace chamber. This technique, developed by Darken and Gurry (1945) allows
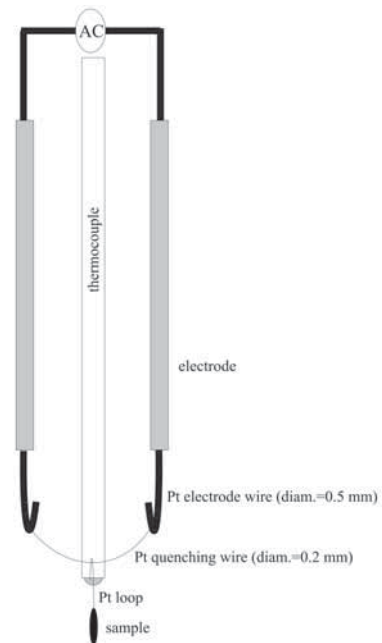

Fig. 5 – Sketch of quenching configuration. In this example (out of scale) the sample is suspended in the hot zone through a Pt loop.

to fix the fO_2 into the tube imposing a CO/CO_2 ratio. From the reaction $CO+0.5O_2=CO_2$, fO_2 can be calculated knowing the equilibrium constant at a given T and assuming that gases behave ideally at high T. Tables where the user may select a fO_2 and T and simply read the required volume percent CO_2 in a CO_2-CO mixture have been compiled by Deines *et al.* (1974). In our set up, the two gases flow into two STEC SEC-E40 mass flow controllers [flow ranges: 0-10 standard cubic centimetres per minute (sccm) for CO, 0-50 sccm for CO_2] prior to be mixed in a mixing chamber. The gas mixture is then allowed into the furnace through the upper brass jacket and the exhaust exits from the lower jacket in order to counterbalance thermal gradients. Oxygen fugacity is monitored by a DS probe (from Australian Oxytrol Systems) consisting of a $SIRO_2$ oxygen sensor with an internal R (Pt /Pt13%Rh) thermocouple suspended into the hot spot (Figure 1b). The sensor is made by a solid zirconia ceramic electrochemical cell (electrolyte) bonded to an alumina tube; the general characteristics of solid electrolytes are discussed in Sato (1971). The obtained signal allows to calculate oxygen concentration according to the Nernst equation which gives the electromotive force developed as a result of changes in oxygen concentrations at each side of an electrolyte; at the top side, oxygen in atmospheric air ($pO_2 = 0.209$) is used as reference.

APPLICATION OF THE VERTICAL GAS-MIXING FURNACE TO EARTH SCIENCES: SOME EXAMPLES

Research studies in which a vertical quench furnace such the one described above can be profitably used span from mineralogy to petrology and material science. Our activity is mainly focused on the investigation of phase relations in natural and synthetic systems at atmospheric pressure, on glass synthesis and on preparation of starting material for high pressure experiments. In the following, some applications, related to on-course projects, will be briefly presented and discussed.

Within a study which is part of an active project aiming to estimate crystal growth rates and their dependence upon lava undercooling with the purpose to interpret crystal size distribution data from Etnean lavas, it was necessary to

synthesise glass from an hawaiite (sample HE-1) representative of the recent activity of Mt. Etna volcano. Two different procedures were followed:

1) about 1 g of powdered rock was inserted in a graphite crucible and suspended in the hot spot by means of the Pt quenching wires. Graphite crucible was chosen since it is known that noble metal containers may lead to iron "loss" from samples in "supra-solidus" conditions. In order to prevent graphite oxidation at high T, the furnace was flushed with an inert gas (Ar) throughout the duration of the experiment. Nominal temperature reached 1455°C (Tr= 1400°C), and the experiment was terminated by quenching in cold water. The glass thus obtained was observed and analysed by a JEOL JXA-8600 electron microprobe at the CNR-Istituto di Geoscienze e Georisorse of Firenze, using an accelerating voltage of 15 kV, a beam current of 10 nA and a 20 μm defocused beam. Data were corrected for the matrix effect using the Bence and Albee (1968) method. The glass does not appear completely homogeneous since metallic Fe droplets were detected. The size of the droplets is 1-2 μm but increases to 100 μm for those in close contact with the graphite crucible. The average of several analyses performed on a glass fragment is reported in Table 1 together with whole rock composition obtained by XRF (Tamponi *et al.* 2002, D'Orazio *personal communication 2005*). The comparison of the data in Table 1 shows that the sample underwent Fe depletion probably caused by unmixing of Fe droplets induced by the extremely reducing conditions (low fO_2) during the experiment. This process was not uniform (note the highest standard deviation relative to FeO) throughout the sample but it was particularly marked close to the graphite crucible. Note the SiO_2 and Al_2O_3 average higher values than the whole rock data which are outside the 95% confidence interval for the glass. This proves the lack of homogeneity of the glass and suggests that a sort of chemical differentiation has occurred in the crucible during the experiment;

2) the rock powder was hosted in several Pt loops (about 100 mg on each loop). In order to avoid Fe "loss" to the loops they were "Fe pre-saturated" before the experiment by annealing them with an aliquot from the same sample under the same T of the experiment. The rock powder was "pelletized" by amalgamating it with some droplets of Moviol

solution. Pt loops were hanged on quenching wire in the hot spot and Tn was set to 1455°C, as in the previous experiment. Quenching in water took place after 2 minutes of annealing. The glass was observed and analysed by using the same electron microprobe (under the same conditions) previously described and it resulted homogeneous (the average of 10 analyses is reported in Table 1). FeO shows the highest standard deviation but its value is comparable with that obtained by XRF. This holds also for SiO_2 and Al_2O_3. Note that in both procedures no loss of alkali, which may tend to volatilize appreciably at T> 900°C (Edgar, 1973) was observed.

The HE-1 glass produced in the latter procedure was subsequently used as a nutrient in crystal growth experiments performed in air at different temperatures using natural plagioclase or clinopyroxene crystals. Phase relations were accurately determined performing several runs at 10°C steps in the interval 1240-1160°C (Orlando *et al.* 2006). In Figure 6 an example of crystals after heat treatment is shown. Figure 6a shows a clinopyroxene crystal not stable at Tr= 1200°C in the partially crystallised lava that tends to be reabsorbed. On the other hand, under the same conditions, plagioclase crystal is stable and tends to grow with a slightly different composition (plr, Figure 6b) due to reactions occurring at the crystal-melt interface, bulk diffusion of components in the melt close to the interface, production and dissipation of latent heat of crystallisation at the interface (e.g. Baronnet 1984).

Experiments in vertical gas-mixing furnace can also be finalised to homogenise melt inclusions: the heating process reverses post-entrapment reactions occurring during cooling history of the rock body and tends to homogenise the inclusion content. We performed several experiments on melt inclusions hosted in olivines from lavas erupted in Sierra Chichinautzin, Mexico. Two different fractions of crystal separates (>250 μm, 180-250 μm) were suspended in Pt crucibles in the hot zone. Experiments were undertaken at temperatures from 1050 to 1200°C at 50°C steps until homogenisation, recognized after SEM observation and EPM analysis on inclusions accurately uncovered and polished (Meriggi 2006), was reached. The accurate temperature control and the capability to quench melt inclusions in less

TABLE 1

	HE-1[1]	graphite[2]		Pt loops[3]		grossular b.c.[4]		ideal[5]
		average	st.dev.	average	st.dev.	average	st.dev.	
N		18		10		7		
SiO_2	47.85	50.73	*1.38*	47.40	0.62	38.24	*0.87*	38.11
TiO_2	1.71	1.81	*0.06*	1.65	0.18			
Al_2O_3	17.10	18.24	*0.45*	17.04	0.26	21.08	*0.60*	21.60
FeO*	10.18	6.50	*2.02*	10.13	0.64			
MnO	0.17	0.20	*0.06*	0.23	0.05			
MgO	5.55	5.75	*0.18*	5.29	0.25			
CaO	10.40	10.74	*0.23*	10.32	0.15	35.54	*0.54*	35.60
Na_2O	3.85	3.99	*0.15*	3.83	0.17			
K_2O	2.01	2.07	*0.11*	2.03	0.07			
Tot	98.82	100.03		97.91		94.86		95.31

[1] D'Orazio, personal communication. Whole rock analysis of HE-1 hawaiite performed by XRF.
[2] Glass synthesised from HE-1 using graphite crucible and Ar flow through the furnace.
[3] Glass synthesised from HE-1 using Fe pre-saturated Pt loops in air.
[4] Glass synthesised from oxides and carbonates and having the grossular bulk composition + 5 wt.% Sc_2O_3 (not analysed).
[5] Theoretical bulk composition on the basis of stoichiometry.

N = number of analyses, st.dev. = standard deviation. Analyses in wt.%.

than 1 second make the utilization of the vertical quench furnace very useful and appropriate for these investigations although it is not possible to observe in situ the phase changes within inclusions on heating.

Experiments in vertical quench (gas mixing) furnace can be particularly useful to synthesise glass to be used as starting material in high P-T experiments. It is well known, in fact, that glasses, besides being homogeneous, are very reactive as starting materials and this can be crucial for success of high P-T experiments, allowing desired reactions to take place in a reasonable length of time. Two examples of this application are hereafter presented:

– in the context of an on-going project aiming to synthesise crystals with a known chemical composition to be utilised as standards in several analytical techniques, a bulk composition of a Pb doped (0.1 wt.%) K-feldspar ($KAlSi_3O_8$) was prepared starting from a mixture of oxides and carbonates. Glass was successfully synthesized annealing 150 mg of the mixture for 1 h at Tr= 1450°C and quenching. The obtained glassy product was used as starting material (with quartz crystallization seeds) in experiments performed at 700°C and 150 MPa (duration= 47 days) in an externally heated pressure vessel (Tem-Press apparatus). In this way Pb doped K-feldspars crystals with size up to 20 μm could be successfully synthesised;

– the understanding of trace-element behaviour in garnets is crucial for geochemical modelling of petrogenetic processes in upper mantle; in this context synthesis of conveniently doped garnets is mandatory. Thus, a multi-technique project for the characterisation of the structural properties of synthetic doped garnets has been undertaken (e.g. Oberti *et al.* 2004). To synthesize Sc doped grossular ($Ca_3Al_2Si_3O_{12}$) a two-step procedure was followed. First, an homogeneous glass was obtained starting from a mixture of oxides and carbonates held on Pt loops at Tr= 1400°C for 1 hour before quenching. This procedure was repeated twice and the product (about 100 mg) was analysed by the electron microprobe. The average and standard deviation of seven analyses performed on different fragments are reported in Table 1 in which theoretical composition is also shown. The close similarity between theoretical and average analysis and the low standard deviations values testify glass homogeneity. In the second stage good quality grossular crystals were synthesised at 2.5GPa and 1200°C in a piston-cylinder apparatus using the glass as starting material.

Conclusions

Calibration of vertical quench (gas mixing) furnace allowed to locate the hot zone into
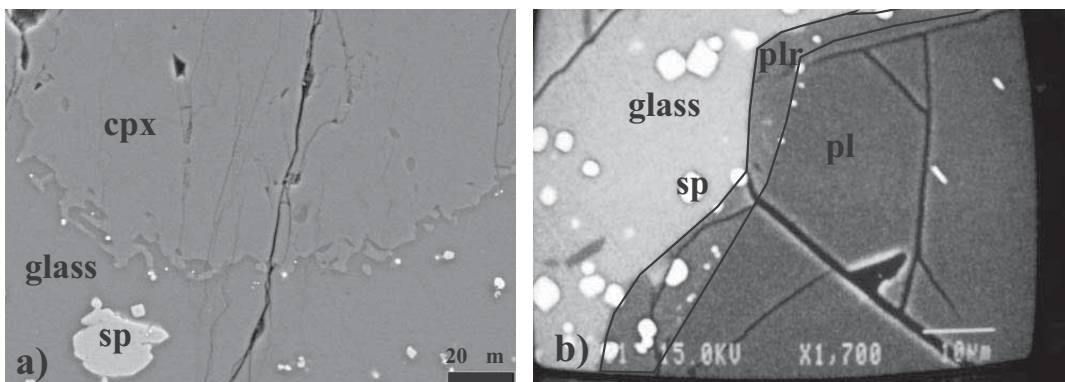

Fig. 6 – Back-scattered images of experimental products: a) At T=1200°C (in air conditions) a clinopyroxene (cpx) crystal is reabsorbed in a glass containing spinel (sp) which composition is that of HE-1 lava. b) At the same T plagioclase (pl) crystal grows; the overgrowth rim (plr) is delimited by the line. Duration of experiments is 15 hours, quenching in deionised water.

the alumina tube about 6-7 cm below the geometric centre and to evaluate its breadth as being about 2 cm wide. Typical T fluctuations in this zone are within ± 3°C. The use of a monitoring thermocouple allowed to estimate the difference between the desired and the actual temperature on the sample. This difference varies with T from 11°C at 800°C to 65°C at 1600°C. Knowledge of this discrepancy allows to run experiments without the need to employ a monitoring thermocouple in the runs. Calibration is mandatory to run experiments in which an accurate T control is required. Glass synthesis from an Etnean lava was performed in air using several pre-saturated Pt loops without suffering Fe- or alkali loss at Tr=1400°C. Phase relationships can thus be determined in effusive volcanic conditions fixing fO_2 by means of a CO-CO_2 mixture and monitoring effective fO_2 values with an apposite solid electrolyte. In the example reported, plagioclase growth and clinopyroxene reabsorption is observed at T=1200°C (in air conditions) in the same lava. Homogenisation of melt inclusions hosted in olivines and their efficient quenching has been successfully accomplished by using this furnace. Finally, two examples of utilization finalised to the production of starting material to be used at high P-T have been presented. Sc-doped garnets and Pb-doped K-feldspars were synthesised (at high P-T) from homogeneous and reactive starting materials obtained by using the vertical quench furnace.

This paper is dedicated to Filippo, our friend and colleague.

REFERENCES

BARONNET A. (1984) – *Growth kinetics of the silicates*. Fortschr. Miner., **62**, 187-232.

BENCE A.E. and ALBEE A.L. (1968) – *Empirical correction factors for the electron microanalysis of silicates and oxides*. J. Geol., **76**, 382-402.

DARKEN L.S. and GURRY R.W. (1945) – *The system iron-oxygen. 1. The wustite field and related equilibria*. J. Am. Chem. Soc., **68**, 798-816.

DEINES P., NAFZIGER R.H, ULMER G.C and WOERMANN E. (1974) – *Temperature - oxygen fugacity tables for selected gas mixtures in the C-H-O system at one atmosphere total pressure*. Bull. of the Earth and Miner. Sci., the Pennsylvania State University, **88**, 32-59.

EDGAR A.D. (1973) – *Experimental Petrology. Basic principles and techniques*. Clarendon Press, Oxford, 217 pp.

HOLLOWAY J.R. and WOOD B.J. (1988) – *Simulating the Earth: experimental geochemistry*. HarperCollinsAcademic, London, 196 pp.

MERIGGI L. (2006) – *Il vulcanismo monogenetico quaternario del Messico Centrale: evidenza di sorgente mantellica eterogenea e modalità evolutive dei magmi*. Ph.D. Thesis, in preparation.

OBERTI R., QUARTIERI S., BOIOCCHI M., BOSCHERINI F., DALCONI C., IEZZI G. and ORLANDO A. (2004) – *A multi-technique in-situ investigation of site preference and local environment of scandium in garnets*. Abstract 32nd International Geological Congress, Firenze, August, 20-28, pag. 1421.

ORLANDO A., PERINELLI C., PIERMATTEI M., CONTE A.M., BORRINI D., D'ORAZIO M., ARMIENTI P., CARROLL M. and LANDI P. (2006) – *Experiments on lavas from Etna and Stromboli, Southern Italy: an invaluable approach to interpret crystal size distribution data*. Abstract, European Geosciences Union General Assembly 2006, Vienna, Austria, 02 – 07 April 2006.

SATO M. (1971) – *Electrochemical measurements and control of oxygen fugacity and other gaseous fugacities with solid electrolyte systems*. In: research techniques for high pressure and high temperature, edited by Ulmer G.C., 43-49 New York, Springer.

TAMPONI M., BERTOLI M., INNOCENTI F. and LEONI L. (2002) – *X-ray fluorescence analysis of major elements in silicate rocks using fused glass discs*. Atti Soc. tosc Sc. Nat., Mem., Serie A, **108**, 73-79.