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The use of graphite for the removal of oxygen from nitrogen purge gas in high temperature microthermometry using the Linkam® TH1500 stage

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Abstract: Gas compositions attained inside the heating chamber of a Linkam® TH1500 heating stage in the temperature interval 400 to 1341 °C were measured with a quadrupole mass analyzer. A small ring of spec. pure carbon was placed inside the chamber, and the system continuously purged with commercial grade nitrogen gas. Effective burning of C, converting trace amounts of O_2 in the purge gas to CO_2 and probably also to CO, occurred at temperatures above 600 °C, where a steady state was approached in less than 2 minutes. Based on measurements of gas compositions and inferences about mass balance, the maximum partial pressure of oxygen at 1300 °C was estimated at 10^{-17} bar. In order to minimize deposition of volatile salts derived from natural samples in the optical pathway of the stage during ordinary microthermometric runs, the gas circulation pattern was slightly modified.

Key-words: high temperature microthermometry, oxygen fugacity.

Introduction

Oxidation of ferromagnesian minerals and ferrous glasses during high temperature microthermometry imposes severe problems which can only be circumvented by maintaining extremely low partial pressures of oxygen within the heating chamber. The use of inert purge gas for removing air and for maintaining thermal equilibrium within the heating chamber is a standard procedure for high temperature measurements. However, the low intrinsic oxygen fugacities of most rock forming ferromagnesian minerals and glasses require that the purge gas does not yield oxygen fugacities higher than those of the rock materials. This corresponds to partial pressures of O_2 in the range of 10^{-20} to 10^{-8} bar for the fayalite-magnetite-quartz oxygen buffer between 600 and 1200 °C. It is evident that many available purge gases will not meet these requirements.

A classical method for removing oxygen from furnaces and heating chambers is to mix a minor amount of hydrogen into the purge gas (e.g. Clocchiatti & Metrich, 1984; Reviews in Sobolev & Kostyuk, 1975; Roedder, 1984). The quantitative oxygen removal from the system is brought about by the formation of steam. This method does, however, require the use of carefully calibrated gas mixtures, and also a sufficient gas circulation within the heating chamber. Another minor drawback of this technique in microthermometry is that hydrogen and the steam formed within the sample chamber favours the volatilization of condensible halogen- and sulphur compounds (pyrohydrolysis). Although of minor importance in most systems, the increased volatile transfer in hydrogen containing systems can cause problems in sulphur and halogen rich samples. Sobolev *et al.* (1980) have constructed a microheater assembly using purified Ar or He as a purge gas. The sophisticated high temperature microthermometry setup of Zapunnyy *et al.* (1989) utilizes a hot zirconium getter and a coulometric solid-electrolyte cell for exact control of oxygen partial pressures in the He purge

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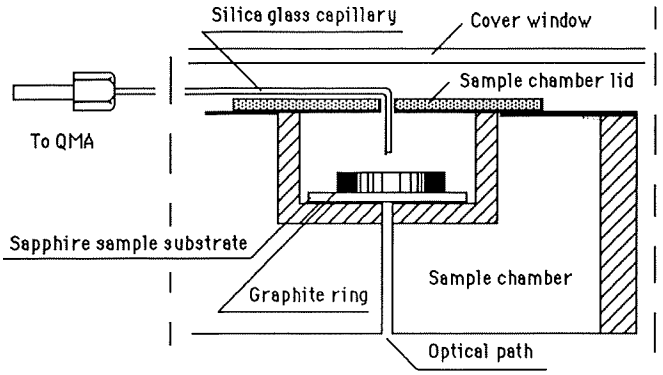

Fig. 1. Schematic cross section of the heating chamber of the Linkam® TH1500 stage. The ruled areas represent sample chamber walls. The graphite ring surrounds the optical path of the stage. Note that the silica glass capillary which is inserted into the central opening of the sample chamber lid is connected directly to the mass spectrometer inlet.

gas. With these two assemblies, the very low levels of impurities in the gas imposes an effective control on undesired reactions in the sample chamber.

The present contribution describes the use of graphite for removal of oxygen from nitrogen purge gas at high temperatures. The technique is based on the presence of solid carbon within the heating chamber. Ideally, a small ring of graphite is placed around the sample and the experiment is then conducted in the usual manner (Hansteen, 1991). Solid carbon is extremely efficient in removing oxygen, and thus the purge gas need not be of superior quality; in fact the present experiment was run with commercial grade nitrogen as purge gas. Also, the burning of graphite produces clean, noncondensible gases and does not favour the volatilization of halogens and sulphur. In order to test the performance of the setup, a heating stage was run at temperatures between 400 and 1341 °C and the gas compositions within the heating chamber were monitored by mass spectrometry. Employing this technique, microthermometric experiments on olivine (Fo_{85-90}) were conducted for more than 10 hours at temperatures above 1000 °C without signs of sample oxidation.

Experimental setup

A Linkam® TH1500 heating stage was used in the experiment; this is intended for use on the (rotating) stage of a petrographic microscope. The heating stage was controlled with a Linkam® TMS90 programmable controller and powered from a PU 1500 power supply. The sample chamber was loaded with a sapphire sample substrate (0.3 mm thickness). A graphite ring (Spec Pure, Ultracarbon) 4.5 mm OD, 3.2 mm ID and 0.9 mm high was placed on the sapphire substrate around the optical path of the stage. Fig. 1, a schematic section of the setup, shows the internal relations of the sample chamber with the graphite ring and the ceramic chamber lid (radiation shield). The gas sampling probe was made of a 0.3 mm ID silica glass tubing which was bent to fit into the central opening of the chamber lid (Fig. 1). The outlet of the silica glass tubing was connected to a 0.8 mm ID teflon tubing outside the sample chamber. The teflon tubing was threaded out through one of the ports of the stage and connected to the inlet valve of a quadroupole mass spectrometer.

The only modification of the stage during the experiment was that its lid was lifted about 1.5 mm by PVC gaskets to give space for the silica glass tubing. The spare gas outlet from the TH1500 housing was connected to a 15 cm long 1 mm ID glass tube. This was done in order to create a slight overpressure in the stage, and to avoid back-diffusion from the external atmosphere.

The stage was purged at slight overpressure (*ca.* 0.05 bar) for about 1 hour before the experiment started, and the inlet to the spectrometer was kept open during this period. The sample consumption of the spectrometer was adjusted to about 50 microliters per minute to assure even diffusion of purge gas into the cell. The mass spectrometric analyses which have been described elsewhere (Jakobsson & Oskarsson, 1990) were performed with a UTI 100C precision mass analyzer.

Reactions within the heating chamber

Reactions within the experimental system can be modelled within the C-O system. The equilibria that might be considered for modelling the gas phase are:

1. $C(s) + O_2 = CO_2$ $K_1 = pCO_2/pO_2$
2. $2C(s) + O_2 = 2CO$ $K_2 = (pCO)^2/pO_2$
3. $CO + 1/2O_2 = CO_2$ $K_3 = pCO_2/pCO \times (pO_2)^{1/2}$

Equations 1 and 2 describe the burning of graphite, and at low temperatures their rates determine the efficiency of oxygen removal. Equation 3 describes the reaction within the gas phase where the buffering action of graphite is no longer dominating. Deviations from thermodynamic equilibrium are most likely to arise from:

a) slow reaction rates at low temperatures, and
b) incomplete equilibration within the mobile gas phase.

It is very doubtful if the gas phase itself can maintain equilibrium within the sample chamber at high temperatures due to the extreme thermal gradients within the stage. Equation 3 will therefore not be considered further, and emphasis will thus be put on the solid/gas reactions (1 and 2; see above).

Analysis of purge gas

The composition of the purge gas was analyzed after about 1 hour of flushing through the Linkam® stage. Carbon monoxide at trace levels in nitrogen can not be analyzed by the Quadrupole mass analyzer due to overlap of the principal masses of both species at 28 AMU. It was confirmed that the purge gas contains oxygen and argon at trace levels (Table 1). The analyzed partial pressure of oxygen in the purge gas is roughly 2×10^{-4} bar which is far more oxidizing than e.g. the hematite/magnetite oxygen buffer.

Standardization of oxygen and argon was made with mixtures of pure nitrogen and carbon dioxide free atmospheric air, and standardization of carbon dioxide was made with mixtures of the purge gas and carbon dioxide. During standardization and heating experiments, the argon impurity (40 AMU) in the purge gas was used as an internal standard for carbon dioxide (44 AMU) analysis. Thus the carbon dioxide analyses are very accurate down to ppm levels.

Table 1. Chemical composition of the nitrogen purge gas used in the experiment (in mol%). Note that the initial oxygen content corresponds to a partial pressure of about 2×10^{-4} bars.

N_2	99.9306
Ar	0.0483
O_2	0.0211
CO_2	0.0000
Total	100.0000

During heating of the Linkam® stage, the oxygen peak at 32 AMU disappeared in the temperature interval 400–550 °C. It is concluded that in this temperature interval, reaction between the graphite and oxygen sets in. However, it is not possible to reproduce the very low analytical values for the carbon dioxide formed until at temperatures above 550 °C.

Two healing experiments were made in the temperature interval 400–1341 °C calibrated at the hottest reaction surface, i.e. the sapphire substrate/carbon ring interface. In the first experiment, the Linkam® stage was programmed to step at about 100 °C intervals towards the maxi-

Table 2. Analysis of CO_2 in purge gas in mol%. The table represents two experiments; programmed heating (column PROGR.) of 90 °C per minute and step heating (column STEP) where analyses were made after about 10-minute equilibration time.

Temp. °C	PROGR.	STEP
400	0.00001	0.00001
580	0.00035	
610		0.00318
610		0.00545
670	0.01013	
700		0.01155
760	0.01215	
818		0.01355
818		0.01305
850	0.01195	
923		0.01076
940		0.01035
1028		0.00915
1030	0.00955	
1120	0.00825	
1210	0.00795	
1237		0.00775
1237		0.00785
1300	0.00760	
1341		0.00735

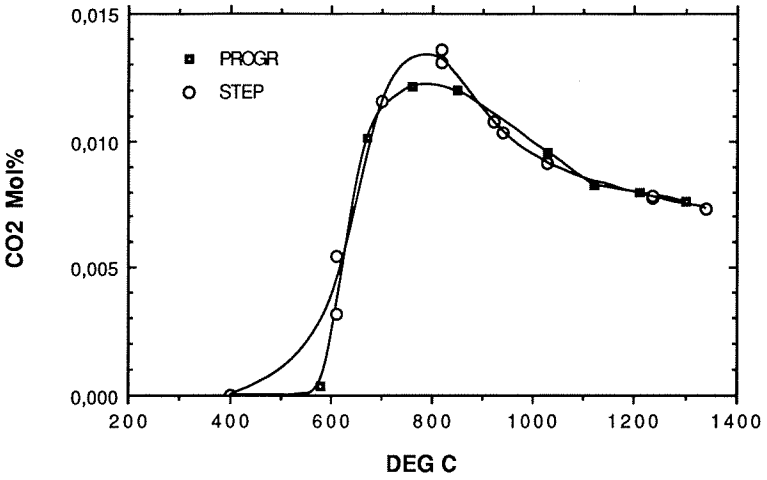

Fig. 2. Analyzed carbon dioxide (mol%) *vs.* temperature inside the heating chamber during experimental runs. Note that at temperatures below 900 °C the step heating (open circles) yields higher abundance than programmed heating (filled squares).

mum temperature. At each step the stage temperature was kept constant while gas analyses were run. In the second experiment, the stage was heated at 90 °C per minute towards the maximum temperature, and the carbon dioxide yield was monitored continuously. The results from the two experiments are listed in Table 2 and shown in Fig. 2. The close resemblance of the results from two experiments can be taken as an indication that the burning of graphite readily consumes the oxygen of the purge gas. At the lower temperatures, the step heating produces slightly higher carbon dioxide levels than the programmed heating. This indicates that the rate of burning is slower at the lower temperatures. Above 900 °C the reaction is fast enough to approach steady state in the sample chamber even during heating rates of 90 °C per minute.

The trend of carbon dioxide formation seen in Fig. 2 indicates that efficient burning of graphite starts slightly below 600 °C, and also that carbon dioxide production is at its maximum at about 800 °C. The quantity of carbon monoxide formed can be calculated from the initial partial pressure of oxygen in the purge gas and mass balance relations. Since it is known that oxygen is consumed above 500 °C, it is concluded that at the onset of burning the reactions are dominated by the formation of CO.

In Fig. 3, the partial pressures of the averaged carbon dioxide and the calculated carbon monoxide are plotted against temperature. The two trends might indicate that the deficiency of oxygen at higher temperatures favours the formation of the monoxide.

Estimated partial pressure of oxygen

It is evident from the experimental setup that equilibrium among the gaseous species within the sample chamber is rather unlikely to attain. The diffusion of fresh purge gas into the sample chamber is inevitably highest at the higher temperatures, when also the reaction rates on the graphite surface is the most rapid. However, the cooling rate of the gas immediately below the sample chamber lid increases markedly at the same time.

It is not possible to confirm equilibrium among the gaseous species based on the present experiment. Therefore no exact value for the partial pressure of oxygen within the sample chamber can be arrived at. However, the apparent steady state of formation of carbon monoxide and carbon dioxide put firm constraints on the possible range of the partial pressure of oxygen.

In Fig. 4 the calculated partial pressure of oxygen within the sample chamber is shown as a function of temperature. The lower trend (open circles) depicts the reaction: $2C + O_2 = 2CO$ based on the calculated carbon monoxide values. The upper trend (filled squares) maps the reaction: $C + O_2 = CO_2$, based on the measured carbon dioxide. It is evident that the maximum partial pressure of oxygen within the system is close to 10^{-17} bar at 1300 °C. Based on the confirmed removal of oxygen and corresponding formation of carbon monoxide (conservation of mass) it is concluded that the actual oxygen pressures are lower than that of the upper curve in Fig. 4, with a limiting value of about 10^{-24} bar at 1300 °C.

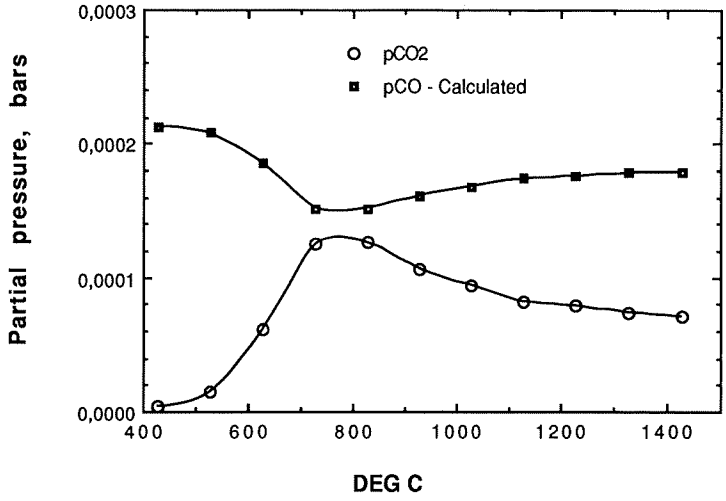

Fig. 3. Analyzed average partial pressure of carbon dioxide and calculated partial pressure of carbon monoxide *vs.* temperature inside the heating chamber. The carbon monoxide is calculated according to the equation: $pCO = (2pO_2 - pCO_2)/2$ which assumes that all available oxygen reacts with graphite (conservation of mass).

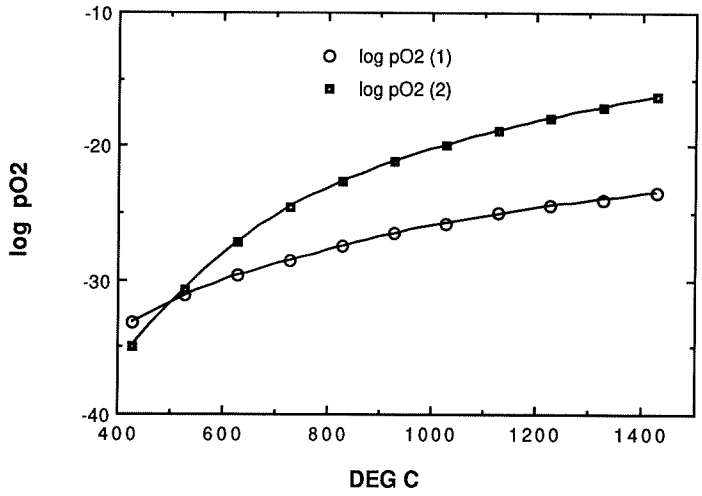

Fig. 4. Partial pressure of oxygen *vs.* temperature inside the heating chamber. The values are calculated based on Robie *et al.* (1979). Open circles (1) represent the graphite/carbon monoxide equilibrium and filled squares (2) represent graphite/carbon dioxide equilibrium. The removal of oxygen in the experiment is effective above about 600 °C and the upper curve is assumed to represent maximum oxygen pressures of the system.

Setup for microthermometric measurements

During prolonged heating runs using natural samples, the portion of the quartz top window placed directly above the opening in the radiation shield gradually loses its transparency. This problem is most severe at temperatures above 1000 °C. We mainly attribute this to partial condensation of volatile species derived from the samples. Deposition occurs in response to cooling of the gas escaping from the sample chamber. Limited reaction resulting in the formation of unidentified crystalline material within the surface of the quartz glass (top window) has also been observed.

In order to partly circumvent this problem during microthermometric runs, we direct the incoming purge gas towards the top window of the stage (Fig. 5). The nitrogen is thus led from one of the gas ports and through a 3 mm OD aluminium tube which has been horizontally flattened at its outlet to obtain an opening 0.7 mm high and 5.0 mm wide. Thus the gas emissions rising from the chamber are partly deflected and cooled, resulting in reduced deposition in the op-

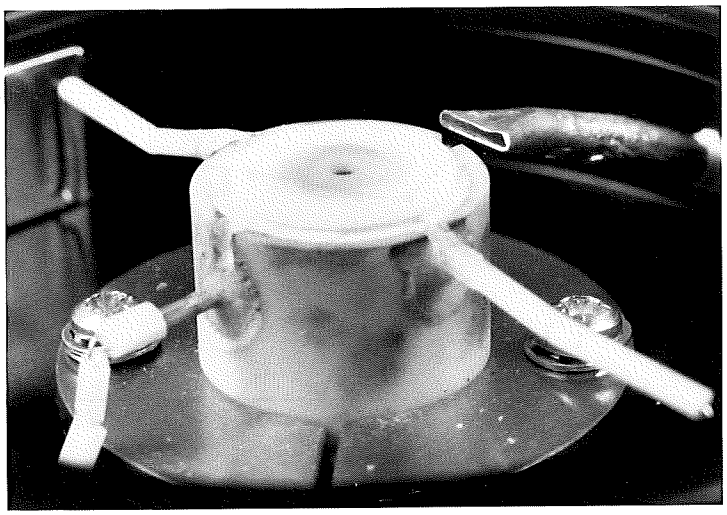

Fig. 5. Photograph of the opened Linkam® TH1500 stage, showing the aluminium tube used for inlet of the purge gas. The tube has been flattened horizontally at its outlet, and is directed towards the top window of the stage when the lid is on.

tical pathway. Flow rates used are 150–200 ml per minute. In this configuration, the two remaining gas ports of the TH1500 are used as outlets, and each outlet is connected to a ca. 20 cm length of thin silicone rubber tubing in order to prevent back-diffusion. The described setup has proven to function reliably (Hansteen, 1991).

Discussion

The principles for maintaining low oxygen partial pressures in the sample chamber during high temperature microthermometry can be subdivided into three groups:

a) Gas-phase reactions within the heating chamber, where fO_2 is adjusted through variations in the relative proportions of two or more gas species (e.g. Ar-H_2, He-H_2, CO_2-H_2) (e.g. Clocchiatti & Metrich, 1984; Reviews in Sobolev & Kostyuk, 1975).

b) Gas-phase reactions within the heating chamber, where fO_2 is adjusted by controlling the purity of an inert purge gas (Sobolev *et al.*, 1980; Zapunnyy *et al.*, 1989).

c) Solid-gas reactions within the heating chamber, where fO_2 is internally controlled (this paper).

A reproducible steady state of oxygen activity can be attained with each of the methods described above. Using the classical method a), the effective fO_2 at the sample surface may be slightly different from the calculative value. This is due to the largely unknown effects of relative differences in diffusion rates for each gas species through the large temperature gradients within the heating chamber. An advantage of methods a) and b) is that fO_2 can be widely adjusted in an unproblematic manner. Method b) has the additional advantage of maintaining relatively low amounts of condensible species in the purge gas, and as developed by Zapunnyy *et al.* (1989), it features an extremely good fO_2 control. The use of a relatively specialized gas purification assembly can in given situations be a minor disadvantage. Method c), as presented here, has the advantage of yielding well reproducible fO_2 levels without the need for any external gas mixing or purification control. However, the oxygen partial pressure can not be adjusted. This might be a minor disadvantage in certain applications.

Conclusions

The presence of graphite within the sample chamber of the Linkam® TH1500 stage maintains very low partial pressures of oxygen at elevated temperatures. The system is apparently not at thermodynamic equilibrium, but attains a reproducible steady state of oxygen activity. The max-

imum partial pressure of oxygen at 1300 °C is estimated at 10^{-17} bar. Oxygen removal from commercial nitrogen by burning on graphite is a simple and clean method that produces low amounts of condensible volatile salts within the sample chamber. The described setup represents a supplement to other high-temperature microthermometric methods.

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