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OXYGEN DIFFUSION IN ORTHOPYROXENE
TG study

M. Zema[1], *P. Ghigna*[2], *M. C. Domeneghetti*[3] *and V. Tazzoli*[3]

[1]Centro Grandi Strumenti, Università di Pavia, Via Bassi 21, 27100 Pavia, Italy
[2]Dipartimento di Chimica Fisica, Università di Pavia, V.le Taramelli 16, 27100 Pavia, Italy
[3]Dipartimento di Scienze della Terra, Università di Pavia, Via Ferrata 1, 27100 Pavia, Italy

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Abstract

Oxygen partial pressure is supposed, by analogy with olivines, to influence the kinetics of the Fe–Mg exchange reaction in orthopyroxene. It has been demonstrated for olivines that the Fe–Mg interdiffusion coefficient is dependent on $P(O_2)$, according to $D_{Fe-Mg} \propto P(O_2)^{-1/6}$ [1–3].

By means of thermogravimetric analyses performed at different $P(O_2)$ on orthopyroxene grains from a volcanic rock it was possible to detect a certain degree of non-stoichiometry which is function of $P(O_2)$. Oxygen moves into or out of the orthopyroxene lattice in response to a compositional gradient. Therefore, in orthopyroxene too, the Fe/Mg interdiffusion and hence the kinetics of the Fe–Mg intracrystalline exchange should be affected by $P(O_2)$. The oxygen chemical diffusion coefficients at $P(O_2)$ ~$5\cdot10^{-19}$ atm were calculated at ~400, 500 and 600°C.

It was also verified on the orthopyroxene from the TPK-30F granulite that, at the operating conditions normally used for single-crystal annealing experiments, oxygen quickly responds to a chemical potential gradient in order to maintain the system in equilibrium conditions.

Keywords: orthopyroxene, oxygen diffusion, thermogravimetry

Introduction

The intracrystalline exchange reaction in orthopyroxene is a well-known process which involves the fractionation of Fe^{2+} and Mg between the two non-equivalent crystallographic sites *M1* and *M2* according to a second-order kinetic law. The temperature dependence of the cation partitioning and the activation energy of the process, under fixed and known operating conditions, have been independently determined by several authors ([4] and references therein). According to the most up-to-date fittings of data available in literature, the equilibrium behaviour of the reaction can be expressed by the relation $\ln K_D = -2557/T(K)+0.547$ [5], where K_D is the cation distribution coefficient expressed as Fe(*M1*)Mg(*M2*)/Fe(*M2*)Mg(*M1*), while the activation energy of the process is ~62 kcal mol^{-1} [6, 7].

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Of course, many factors may influence the kinetics of this reaction and all of them should be taken into account, in particular, when the site distribution in orthopyroxene is used to retrieve information on the thermal history of the host rock ([8] for the explanation of the method and [9] and references therein for its application). Among the factors that are supposed to influence the kinetics of the Fe–Mg exchange in orthopyroxene is the oxygen partial pressure. This assumption is mostly based on the effect of $P(O_2)$ on the Fe–Mg interdiffusion in a very similar system, i.e. olivine solid solution.

Buening and Buseck [1] demonstrated that the Fe–Mg interdiffusion coefficient in olivines varies as $P(O_2)^{-1/6}$ at constant temperature and composition and decreases sharply with increasing forsterite content at constant temperature and $P(O_2)$. They also proposed a defect reaction according to which the entrance of an oxygen atom into the lattice is equilibrated by the oxidation of two Fe^{2+} ions to Fe^{3+} and by the formation of one cation vacancy. By means of thermogravimetric analyses and electrical conductivity measurements, Nakamura and Schmalzried [2, 3] calculated the non-stoichiometry of fayalite and olivine solid solutions as a function of $P(O_2)$ and SiO_2 activity. According to the authors, non-stoichiometry of fayalite is responsible for most of the point defect dependent properties (diffusion, electrical conductivity and optical absorption). They also experimentally determined the $P(O_2)^{-1/6}$-dependence of cation vacancy concentration, which is directly related to the Fe–Mg interdiffusion and should therefore exhibit the same isothermal oxygen potential dependence.

The influence of $P(O_2)$ on the Fe/Mg distribution in olivines was studied by means of single-crystal X-ray diffraction on natural olivine samples equilibrated at high temperatures under controlled $P(O_2)$ conditions [10, 11]. Such experiments showed that varying $P(O_2)$ has a negligible influence on the intracrystalline distribution at equilibrium. However, the $P(O_2)$-dependence of the Fe/Mg interdiffusion coefficient should suggest an influence on the kinetics of the cation exchange even if it cannot be directly related to the equilibrium behaviour. This would have strong implications in the reconstruction of the thermal history of the host rocks.

The most direct way to verify the $P(O_2)$ dependence of the Fe–Mg exchange in orthopyroxene is, of course, the measurement of the kinetic constants from annealing experiments to be performed at different $P(O_2)$ conditions on single-crystals. In order to gain some preliminary information on the non-stoichiometry in orthopyroxene and on the mobility of oxygen in response to a compositional gradient and to assess the experimental conditions for annealing experiments, we carried out some thermogravimetric (TG) analyses on selected orthopyroxene crystals under different oxygen partial pressure conditions.

Experimental

Samples

TG experiments were performed on orthopyroxene grains from the volcanic rock L3 (Aeolian Islands, Italy) and from sample TPK-30F, a granulite of the Central

Gneissic Complex, Complex Mountains, Columbia Britannica [12]. Chemical compositions of the orthopyroxenes from samples L3 [Cámara, pers. comm.] and TPK-30F [5], determined by electron-microprobe analysis (EMPA) operating in the wavelength-dispersive (WDS) mode, are reported in Table 1.

Table 1 Chemical composition of the orthopyroxenes from L3 and TPK-30F

	OPX L3	OPX TPK-30F
Oxide (mass%)		
SiO_2	52.13 (54)	50.96 (25)
Al_2O_3	0.63 (4)	0.92 (2)
FeO	25.35 (31)	30.22 (16)
MgO	19.34 (29)	16.40 (16)
MnO	0.55 (5)	0.43 (6)
TiO_2	0.35 (4)	0.13 (1)
Cr_2O_3	0.09 (2)	0.02 (1)
CaO	1.91 (3)	0.90 (2)
Sum	100.35	99.98
Atoms per formula unit (based on six oxygens)		
Si	1.972 (9)	1.970 (5)
Al	0.028 (1)	0.042 (1)
Fe^{2+}	0.797 (11)	0.979 (8)
Fe^{3+}	0.005 (1)	n.d.
Mg	1.090 (8)	0.947 (6)
Mn	0.018 (1)	0.014 (1)
Ti	0.010 (2)	0.004 (1)
Cr	0.003 (1)	0.001 (1)
Ca	0.077 (2)	0.038 (1)
Sum	4.000	4.000

Standard deviations are in parentheses

For both samples, orthopyroxene crystals with granulometry 125–250 μm were previously separated using a magnetic separator. A further careful selection of the crystals was done by hand at the optical microscope. Due to the limited availability of natural samples and to the difficulty in separating crystals of a pure phase, ~70 mg of orthopyroxene grains from sample L3 (used in two TG measurements in batches of 35 mg) and ~50 mg of orthopyroxene grains from sample TPK-30F were collected and used for TG experiments.

Instruments and methods

Isothermal gravimetric and thermogravimetric measurements were performed with a 951 Thermogravimetric Analyzer attachment of a TA 2000 thermal analysis system, using a platinum sample holder. The measurements were carried out in two different atmospheres: a) an 'oxygen rich' atmosphere, with $P(O_2)=10^{-6}$ atm, which was obtained by flowing a certified mixture of oxygen in nitrogen into the instrument; b) an 'oxygen poor' atmosphere, with $P(O_2)=5\cdot10^{-19}$ atm. To obtain this kind of atmosphere, pure nitrogen was allowed to pass over a mixture of Fe and FeO kept at an appropriate temperature (≅700°C). This gas was then allowed to flow into the thermogravimetric analyzer. This set-up ensures a constant $P(O_2)$ for the duration of the experiment. The partial pressure of oxygen in the flowing gas was measured by putting the gas coming out of the thermogravimetric analyzer through a solid state ZrO_2 potentiometric sensor (J2S Analiseur d'Oxygène D.H.T.V. 800).

In order to retrieve the oxygen (chemical) diffusion coefficient the isothermal gravimetric data were processed according to the Dünwald–Wagner (DW) equation:

$$\alpha=1-\frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-n^2k_{DW}t)$$

which is the solution of Fick second law for spherical geometry [13]. In this equation, α is the degree of advancement of the reaction between a solid sphere of radius r and the external atmosphere. $k_{DW}=\pi^2D/r^2$, where D is the oxygen (chemical) diffusion coefficient, is known as Dünwald–Wagner (DW) constant. The data treatment is somewhat tricky due to the facts that a) DW equation not in closed form and that b) the series converges extremely slowly. However, it can be noticed that α is a unique function of the product $k_{DW}t$: as a matter of fact, a table of α *vs.* $k_{DW}t$ has been calculated as early as 1963 [14]. Therefore, to obtain the diffusion coefficients, for each isothermal step in Fig. 2, the raw thermogravimetric data have been converted into α values, and hence to $k_{DW}t$ products. The slope of the linear plots of $k_{DW}t$ *vs.* t gave k_{DW}.

Results and discussion

In order to verify whether or not oxygen atoms move into or out of the orthopyroxene lattice in response to a compositional gradient or, more precisely, to a chemical potential gradient, we performed two TG experiments in different $P(O_2)$ conditions. Both these experiments were carried out on ~35 mg of orthopyroxene grains from sample L3.

The mass *vs*. time plot obtained at $P(O_2)=10^{-6}$ atm is shown in Fig. 1. The sample was preliminarily heated at ~100°C for 24 h in order to dry it. Subsequently three isotherms of 25 h each at ~400, 500 and 600°C, respectively, were studied. The plot clearly shows that mass increases while sample is heated from ~100 to ~400°C and it reaches equilibrium during the first isotherm. The increase in mass has to be ascribed to the entrance of oxygen into the orthopyroxene lattice, i.e. to a variation of oxygen stoichiometry. The plateau indicates that orthopyroxene equilibrated with the im-

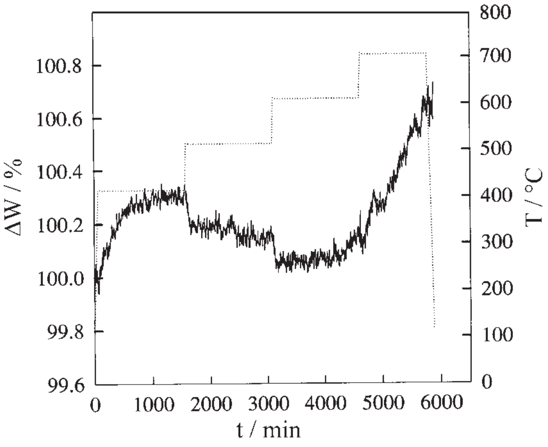

Fig. 1 TG plot at $P(O_2)=10^{-6}$ atm for sample L3. Solid line: mass variation; dotted line: temperature; initial mass: ~35 mg

posed atmosphere. From this point on, increasing temperature gives rise to a loss of mass due to the lower oxygen chemical potential. Equilibria at ~500 and 600°C were reached instantaneously. Towards the end of the isotherm at 600°C, decomposition of orthopyroxene was observed, due to the irreversible assumption of oxygen. This gives an important indication on the stability range of orthopyroxene at $P(O_2)=10^{-6}$ atm. It should be noticed that the mass variations are well above the noise level, which can be assumed to give an estimate of the errors in the TG plots. This is also valid for all the following figures.

The plot shown in Fig. 2 was obtained at $P(O_2)$ ~$5\cdot10^{-19}$ atm. Orthopyroxene quickly loses mass while temperature increases from 100 to 400°C. In this case the

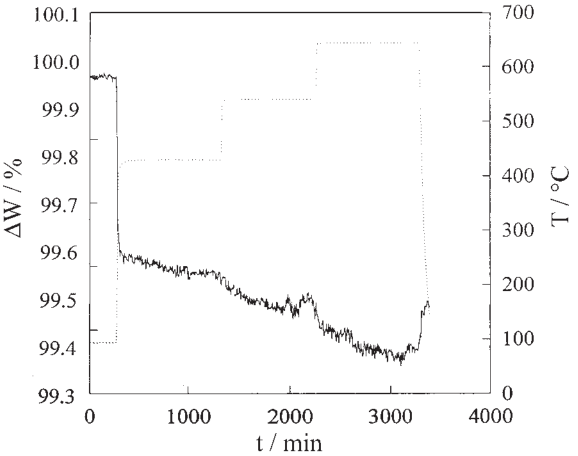

Fig. 2 TG plot at $P(O_2)$ ~$5\cdot10^{-19}$ atm for sample L3. Solid line: mass variation; dotted line: temperature; initial mass: ~35 mg

oxygen goes out of the lattice to equilibrate the structure with the 'O_2-poor' atmosphere. Equilibrium was reached at the three temperatures studied. The total mass loss corresponds to the loss of ~0.07 oxygen atoms per formula unit (a.p.f.u.). It should be noticed that this variation in the oxygen content gives rise to a very small variation in the mass of the sample. This in turn could be safely detected due to the high quality of our data.

The oxygen chemical diffusion coefficients were calculated by the DW equation (Experimental) from the parabolic pattern of the curves obtained during the isotherms, and are reported in Table 2. The values are affected by a very large error due to the wide range of granulometry of the crystals used for the TG experiment and to their irregular forms. The DW equation in fact would imply spherical shaped and homogeneous samples. Unfortunately, oxygen diffusion coefficients at higher temperatures were not measured due to limited range of T of the furnace and therefore it was not possible to calculate a reliable value for the activation energy of the oxygen chemical diffusion.

Table 2 Oxygen chemical diffusion coefficients at $P(O_2)\sim5\cdot10^{-19}$ atm

T/°C	ln$D$/cm^2 s^{-1}	Errors
642	–16.9	1.6
540	–17.0	1.6
430	–17.8	1.8

It is evident from the two plots obtained on sample L3 that oxygen moves into or out of the orthopyroxene lattice in response to an oxygen chemical potential gradient. This means that non-stoichiometry of this silicate can vary as a function of $P(O_2)$. The times we measured to attain the new equilibrium states at the imposed $P(O_2)$ are in perfect agreement with what is reported in literature for similar phases. In fact, both olivine [3] and diopside [15] equilibrate rapidly and reversibly with respect to changes in $P(O_2)$, in a time scale of hours.

As ancillary result, the opposite trends observed at the 'O_2-poor' and 'O_2-rich' atmospheres indicate that the formation of the orthopyroxene from sample L3 occurred at an intermediate value of $P(O_2)$.

The aim of the third thermogravimetric analysis was to determine the time required by the orthopyroxene lattice to equilibrate with atmosphere, under the experimental conditions normally used for single-crystal annealing studies. Therefore, the sample, the size of orthopyroxene grains, temperature and $P(O_2)$ conditions were those which are normally used in the single-crystal annealing studies. The experiment was then carried out at $P(O_2)$ given by IW buffer heated at ~700°C ('oxygen-poor' atmosphere) on ~50 mg of orthopyroxene pure crystals from sample TPK-30F. As before, prior to measuring mass changes, the sample was equilibrated inside the balance at T~100°C for 48 h in order to dry it. The temperature was then increased up to ~750°C at a rate of 50°C min^{-1}. The plot (Fig. 3) shows that the sample started losing

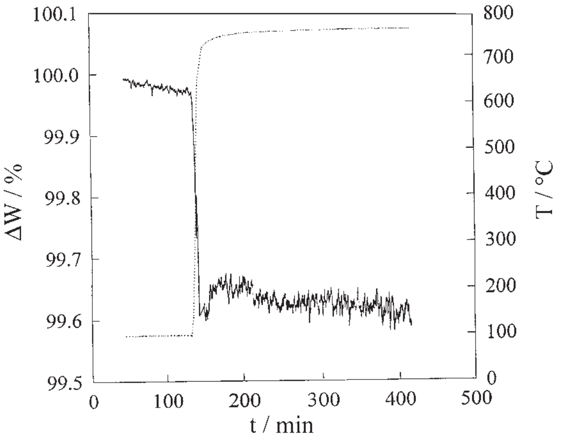

Fig. 3 TG plot at $P(O_2)$ ~$5\cdot10^{-19}$ atm for sample TPK-30F. Solid line: mass variation; dotted line: temperature; initial mass: ~50 mg

mass at T~250°C and reached equilibrium in a few minutes (less than 10 min) when temperature had not yet stabilized at its plateau. No more mass loss was observed during the isotherm. This is an evidence that under these operating conditions the orthopyroxene is always at equilibrium with the atmosphere.

Conclusions

TG experiments described above show that orthopyroxene stoichiometry varies as a function of $P(O_2)$. By analogy with olivines, in orthopyroxene solid solutions too, the Fe/Mg interdiffusion and hence the kinetics of the Fe–Mg intracrystalline exchange may be affected by the $P(O_2)$ at which the sample was equilibrated. The determination of kinetic constants at different $P(O_2)$ conditions by means of single-crystal annealing experiments is then of fundamental importance for a quantitative evaluation of this dependence and all the implications for the reconstruction of the thermal history of the host rocks (work in progress). Experimental conditions for annealing experiments can be easily defined on the basis of this work; in particular, even very short annealing runs can be considered as reliable since the equilibration of orthopyroxene structure with atmosphere was shown to occur instantaneously.

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