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X-ray Determination of Thermal Expansion of Olivines

BY H. P. SINGH

Department of Physics, Punjabi University, Patiala 147002, *India*

AND GENE SIMMONS

Department of Earth and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, *U.S.A.*

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Precise measurement of the thermal expansion of natural olivines at elevated temperatures by X-ray diffraction yields the following equations for the cell volume (V) with temperature (t): $Fo_{92\cdot5}$: $V_t = 291\cdot13 + 83\cdot6 \times 10^{-4}t + 6\cdot5 \times 10^{-7}t^2$, $25 < t < 973\,°C$; $Fo_{90\cdot4}$: $V_t = 291\cdot45 + 80\cdot4 \times 10^{-4}t + 11\cdot3 \times 10^{-7}t^2$, $25 < t < 963\,°C$; $Fo_{53\cdot8}$: $V_t = 298\cdot58 + 76\cdot4 \times 10^{-4}t + 17\cdot2 \times 10^{-7}t^2$, $25 < t < 432\,°C$, where the units are Å^3 and °C. Similar expressions are reported for the individual lattice parameters. Expressions for thermal expansions are derived. Volume thermal expansion varies linearly with temperature. A decrease in the Mg/Fe ratio in olivine decreases the thermal expansion in the observed temperature range.

Introduction

Early studies on linear thermal expansion of olivines were made by Kozu, Uyeda & Tsurumi (1934) and Rigby, Lowell & Green (1946) using dilatometers for their measurements. Recently, Soga & Anderson (1967) measured the average thermal expansion of forsterite with a fused-silica dilatometer using a linear displacement transducer. The only previous X-ray studies on forsterite were done by Skinner (1962). He used an X-ray diffractometer and reported the mean thermal expansion of synthetic forsterite (Mg_2SiO_4) from 20 to 1000 °C. No systematic work has been done to determine the instantaneous thermal expansion in different axes and to see the effect of the Mg/Fe ratio on thermal expansion of olivines. This report presents the detailed measurements of the lattice parameters at elevated temperatures on natural olivines having three different compositions.

Experimental

The experimental details were the same as in our previous work (Singh, Simmons & McFarlin, 1975). The Norelco wide-range goniometer with an MRC high-temperature diffractometer attachment were used. Thin-film sample mounts were found to be most suitable for this work and they were scanned between 16 and 87° 2θ. The temperature of the heating stage was read with a Pt, Pt+13%Rh thermocouple and controlled within ±2 °C. High-purity platinum powder mixed with the sample was used in determining the exact temperature of the sample.

A determinative curve based on analysed natural olivines by Jambor & Smith (1964) was used to determine the compositions of natural olivines. The value of d_{130} for each mineral was measured and the compositions were calculated. We also calculated lattice parameters at 25 °C from our analytical expressions and used them to evaluate d_{130} and d_{174} and to calculate the Fo percentage. The compositions determined by all these methods agreed to within ±1% for each mineral and the mean values are given in Table 1 with some other physical properties.

Table 1. *Characterization of the experimental materials*

Fo percentage	92·5	90·4	53·8
Location	Day Book North Carolina	San Carlos Arizona	Bushveldt S. Africa
Bulk density (g/cm^3)	3·266	3·469	3·765
Refractive indices	$\alpha = 1\cdot642$ $\gamma = 1\cdot678$	$\alpha = 1\cdot653$ $\gamma = 1\cdot691$	$\alpha = 1\cdot729$ $\gamma = 1\cdot771$

Results and discussion

Lattice parameters and cell volumes

In the present study all the measurable peaks lie within $2\theta=16$ to 70°. The extrapolation with the lattice constants calculated from low-angle data to that of $\theta=90°$ may lead to unreliable results. We prefer to use the computer program developed by Evans, Appleman & Handwerker (1963) to calculate the refined lattice parameters from the Bragg equation and an expression for interplanar spacing. All the measurable and sharp non-interfering peaks between 20 and 70° were used for the calculation of the lattice parameters. The observed lattice parameters and cell volumes at different temperatures for three olivines are presented in Tables 2, 3, and 4. Their variation with temperature is given below in the analytical expressions

$Fo_{92\cdot5}Fa_{7\cdot5}$ $25<t<973\,°C$

$$a_t=4\cdot7611+22\cdot6\times10^{-6}t+15\cdot1\times10^{-9}t^2$$
$$b_t=10\cdot2144+122\cdot6\times10^{-6}t$$
$$c_t=5\cdot9875+64\cdot1\times10^{-6}t$$
$$V_t=291\cdot13+83\cdot6\times10^{-4}t+6\cdot5\times10^{-7}t^2$$

$Fo_{90\cdot4}Fa_{9\cdot6}$ $25<t<963\,°C$

$$a_t=4\cdot7618+20\cdot5\times10^{-6}t+20\cdot3\times10^{-9}t^2$$
$$b_t=10\cdot2208+118\cdot9+10^{-6}t$$
$$c_t=5\cdot9896+64\cdot2\times10^{-6}t$$
$$V_t=291\cdot45+80\cdot4\times10^{-4}t+11\cdot3\times10^{-7}t^2$$

$Fo_{53\cdot8}Fa_{46\cdot2}$ $25<t<432\,°C$

$$a_t=4\cdot7897+10\cdot3\times10^{-6}t+36\cdot3\times10^{-9}t^2$$
$$b_t=10\cdot3364+97\cdot0\times10^{-6}t$$
$$c_t=6\cdot0310+80\cdot4\times10^{-6}t$$
$$V_t=298\cdot58+76\cdot4\times10^{-4}t+17\cdot2\times10^{-7}t^2$$

where a_t, b_t, c_t are the lattice parameters of the orthorhombic axes in Å, V_t is the unit-cell volume in Å^3 at t°C, Fo is forsterite (Mg_2SiO_4), and Fa is fayalite (Fe_2SiO_4). The lattice parameters were also calculated by using the above equations and were compared with the observed parameters. The maximum deviations are 0·0017, 0·0024, and 0·0026 Å in the *a*, *b*, and *c* axes respectively. The *b* and *c* lattice parameters vary linearly with temperature. Parabolic equations of the second order fit the *a* lattice parameters and cell volumes better than first and third order in the sense

Table 2. *Lattice parameters and volume thermal expansion coefficients of natural olivine* $Fo_{92\cdot5}Fa_{7\cdot5}$

Temperature (°C)	Lattice parameters (Å) *a*	*b*	*c*	Unit-cell volume (Å^3)	Volume thermal expansion $\times10^6$ (°C^{-1})
25	4·7612	10·2180	5·9878	291·31	28·9
85	4·7634	10·2237	5·9933	291·87	29·1
250	4·7678	10·2457	6·0026	293·22	29·8
395	4·7723	10·2636	6·0150	294·62	30·5
485	4·7752	10·2726	6·0191	295·26	30·9
648	4·7833	10·2948	6·0295	296·91	31·6
842	4·7892	10·3166	6·0406	298·46	32·5
973	4·7982	10·3342	6·0493	299·96	33·1

Table 3. *Lattice parameters and volume thermal expansion coefficients of natural olivine* $Fo_{90\cdot4}Fa_{9\cdot6}$

Temperature (°C)	Lattice parameters (Å) *a*	*b*	*c*	Unit-cell volume (Å^3)	Volume thermal expansion $\times10^6$ (°C^{-1})
25	4·7627	10·2251	5·9908	291·75	27·8
96	4·7644	10·2316	5·9944	292·21	28·3
263	4·7689	10·2510	6·0077	293·69	29·6
355	4·7703	10·2645	6·0122	294·39	30·3
450	4·7742	10·2738	6·0201	295·28	31·1
595	4·7815	10·2903	6·0288	296·71	32·2
690	4·7865	10·3043	6·0343	297·62	32·9
760	4·7883	10·3096	6·0368	297·98	33·5
844	4·7946	10·3197	6·0440	299·05	34·1
963	4·7997	10·3377	6·0510	300·24	35·0

Table 4. *Lattice parameters and volume thermal expansion coefficients of natural olivine* $Fo_{53\cdot8}Fa_{46\cdot2}$

Temperature (°C)	Lattice parameters (Å) *a*	*b*	*c*	Unit-cell volume (Å^3)	Volume thermal expansion $\times10^6$ (°C^{-1})
25	4·7896	10·3383	6·0325	298·71	25·9
103	4·7916	10·3463	6·0403	299·45	26·8
206	4·7939	10·3574	6·0480	300·30	28·0
285	4·7951	10·3647	6·0513	300·75	28·9
339	4·7968	10·3688	6·0600	301·41	29·5
432	4·8013	10·3779	6·0657	302·24	30·6

of a lower variance. Comparison of Tables 2, 3, and 4 shows that a decrease in forsterite concentration in olivines increases the lattice parameters and cell volumes. This suggests that larger Fe^{2+} ions replacing smaller Mg^{2+} ions in olivine increase the lattice parameters and cell volumes.

Thermal expansion

Differentiating the equation for lattice parameter *versus* temperature and evaluating

$$\alpha_t = \frac{1}{a_0}\left(\frac{\mathrm{d}a_t}{\mathrm{d}t}\right)_t$$

where a_t is the lattice parameter in Å at t °C, one can find the instantaneous thermal expansion coefficient α_t in the corresponding axial direction. The instantaneous thermal expansion coefficient of a increases with temperature while those of b and c are constant within experimental error. Instantaneous volume thermal expansion coefficients β_t are represented by the following equations:

$$Fo_{92\cdot5}:\ \beta_t = 28\cdot7\times10^{-6} + 4\cdot5\times10^{-9}t \qquad 25 < t < 973\,°C$$
$$Fo_{90\cdot4}:\ \beta_t = 27\cdot6\times10^{-6} + 7\cdot8\times10^{-9}t \qquad 25 < t < 963\,°C$$
$$Fo_{53\cdot8}:\ \beta_t = 25\cdot6\times10^{-6} + 11\cdot5\times10^{-9}t \qquad 25 < t < 432\,°C$$

where $\beta_t = 1/V_0(\mathrm{d}V_t/\mathrm{d}t)_t$ is volume thermal expansion at t °C.

The mean thermal expansion coefficients for olivines have been calculated from observed data and are presented in Table 5. They have also been calculated in the temperature range of 25 to 400 °C for each olivine for the sake of comparison. The results reveal that the volume thermal expansion coefficient decreases with a decrease of forsterite concentration.

Table 5. *Mean thermal expansion coefficients of olivines*

Specimen	Temperature range	Linear thermal expansion $\alpha_m \times 10^6$ (°C^{-1}) a	b	c	Volume thermal expansion $\beta_m \times 10^6$ (°C^{-1})
$Fo_{92.5}$	25–973	8·2	12·0	10·8	31·3
$Fo_{90.4}$	25–963	8·2	11·7	10·8	31·0
$Fo_{53.8}$	25–432	6·0	9·4	13·5	29·0
$Fo_{92.5}$	25–400	6·1	12·0	10·7	29·6
$Fo_{90.4}$	25–400	6·1	11·6	10·7	29·3
$Fo_{53.8}$	25–400	5·3	9·4	13·3	28·1

A similar conclusion can be drawn from the work of Rigby *et al.* (1946).

Soga & Anderson (1967) measured the linear thermal expansion of forsterite dilatometrically and reported the average value as $11\cdot2\times10^{-6}$/°C from room temperature to 1273 K. Kozu *et al.* (1934) gave a volume expansion $33\cdot1\times10^{-6}$/°C for $Fo_{89\cdot92}$ olivine from room temperature to 1000 °C. These are in fair agreement with our values.

Conclusion

The following conclusions can be drawn from the present study on olivines. (1) Lattice parameters and cell volumes increase with the decrease of forsterite concentrations in the olivines. This could be attributed to the larger size of iron compared with magnesium. (2) Linear thermal expansion in the direction of a and volume thermal expansion increase linearly with temperature while expansion in the directions b and c are constant. (3) The mean volume thermal expansion coefficient increases with the increase of forsterite concentration. This leads to the conclusion that the increase in the Mg/Fe ratio in olivine increases the volume thermal expansion.

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