

Zaoyang chondrite cooling history from Fe^{2+} -Mg intracrystalline ordering in pyroxenes

GIAN MARIO MOLIN

Dipartimento di Mineralogia e Petrologia, Università di Padova, Corso Garibaldi 37, I-35100 Padova, Italy

MARIO TRIBAUDINO

Dipartimento di Scienze Mineralogiche e Petrologiche, Università di Torino, Via Valperga Caluso 37, I-10125 Torino, Italy

AND

ELISABETTA BRIZI

Dipartimento di Scienze della Terra, Università di Perugia, Piazza Università, I-06100 Perugia, Italy

Abstract

The crystal chemistry of clinopyroxene, orthopyroxene and olivine from a crushed fragment of the H5 Zaoyang chondrite has been investigated by X-ray structure refinement and detailed microprobe analysis. The meteoritic pyroxenes have cell and polyhedral volumes which compare well with such data from terrestrial pyroxenes that typically crystallize at low-pressure. Fe^{2+} and Mg are rather disordered in *M1* and *M2* sites of clino- and orthopyroxenes; the closure temperatures of the exchange reaction are 600 and 512°C respectively, which is consistent with a reasonably fast cooling rate, estimated to be of the order of 1°C/day.

The closure temperature for the intercrystalline Ca-Mg exchange reaction for clino- and orthopyroxenes is 900°C, as calculated from clino- and orthopyroxene intergrowth.

The cooling rates obtained from Fe^{2+} -Mg intracrystalline partitioning suggest a cooling of the order of degrees per day at temperatures of 600–500°C due to a strong loss of heat by irradiation.

KEYWORDS: chondrite, pyroxene, crystal-chemistry, cooling rate.

Introduction

THE mineralogical and petrographic features of chondrites can help to elucidate their thermal history and their cooling history constrains the various models relating to their origin (Watanabe *et al.*, 1985); these have therefore been the subject of many previous studies. Cooling rates in chondrites may be calculated in various ways, which give information on the rates through different temperature ranges. Regarding silicate minerals, which are studied in this paper, the cooling rate can be calculated at near liquidus temperature by using the morphologies of crystals in chondrules (Tsuchiyama *et al.*, 1980), while at lower temperatures (down to approximately

1000°C) it may be estimated by using fine textures in minerals, mainly clino- and orthopyroxenes, but also plagioclases, observed by transmission electron microscopy (Kitamura *et al.*, 1983; Müller, 1991). For still lower temperatures, the cooling rate may be calculated from intracrystalline ordering processes, which have closure temperatures varying from 700 to 200°C (Ganguly, 1982). In particular, intracrystalline ordering of Fe and Mg in *M1* and *M2* sites in orthopyroxene has been used in meteorites to estimate the cooling history of the Johnstown diogenite (Molin *et al.*, 1991). Similar information on cooling history may also be obtained from clinopyroxene (Molin and Zanazzi, 1991).

In this work, the Zaoyang chondrite has been examined. The Zaoyang ordinary chondrite fell as a single 14.15 kg mass in a field in Hubey province (China) in October 1984 and was studied petrologically by Wang and Rubin (1987) who classified it as a non-brecciated H5 chondrite, shock facies b. In this paper, X-ray single crystal diffraction data are reported for orthopyroxene, clinopyroxene and olivine. The degree of Fe-Mg order-disorder and structural features of these pyroxene crystals give information on its cooling history and therefore its relations with the parent body.

Experimental

Chemical compositions were obtained on a CAMECA-CAMEBAX electron microprobe operating at 15 kV and 15 nA sample current, using WDS spectrometers. X-ray counts were converted into oxide weight percentages using a PAP correction program provided by CAMECA. Analyses are typically accurate to within 1% for major elements and within 3% for minor ones. Analyses were performed on both isolated single crystals used for X-ray data collection, averaging about ten microprobe spots (Table 1), and on a polished thin-section. From the latter analyses have been made of pyroxenes and olivine from both matrix and chondrules, and of other phases such as kamacite, taenite and troilite. Average analytical results and standard deviations are reported in Table 2. The accessory minerals present were apatite, chromite and pure copper.

A small sample of the chondrite was crushed and single crystals of clinopyroxene, orthopyroxene and olivine (about 100 μm in size) were selected; diffraction data were obtained using a computer-controlled SIEMENS AED four-circle diffractometer with Mo-K α radiation monochromatized by a flat graphite crystal. The equivalent *hkl* and *-hkl* pairs were measured up to $\theta < 30^\circ$ using the ω scan mode. Intensities were corrected for absorption following the semi-empirical method of North *et al.* (1968) and the values of equivalent pairs were averaged. Refinements were carried out in space groups *C2/c*, *Pbca* and *Pbnm*, respectively for clinopyroxene, orthopyroxene and olivine, without chemical constraints, using the STRUCSY program (STOE copyright). No violations of *b*, *c*, *a* glide systematic extinctions were observed in *Pbca* orthopyroxene. The ionization scheme used (Rossi *et al.*, 1983) was 2.5 positive charges for Si, 1.5 negative charges for oxygen, and 2 positive charges for Mg and Fe, with the available atomic scattering factors (Int.

Tab. for X-ray Cryst., 1974; Tokonami, 1965). All structural sites were considered fully occupied. In the first stages of the refinements, isotropic temperature factors were used. The final cycles were performed allowing all parameters (atomic coordinates, anisotropic temperature factors, *M1* and *M2* site occupancies, scale factors and secondary extinction coefficients; Zachariasen, 1963) to vary until the shifts were less than the least-squares difference of the corresponding parameters. Reflections with $I > 3\sigma(I)$ were considered as observed and were given equal weighting when used in the refinement procedure. Table 3 shows other pertinent data.

TABLE 1. Electron microprobe analyses of single crystals used for XREF. Site populations were calculated by microprobe and electron density data on basis of 6 and 4 oxygen atoms respectively for pyroxenes and olivine.

Chemical compositions and site populations			
	Clinopyroxene	Orthopyroxene	Olivine
SiO ₂	53.89	56.99	39.14
TiO ₂	0.21	0.15	
Al ₂ O ₃	0.34	0.53	
FeO	4.00	10.99	17.76
MnO	0.22	0.54	0.46
MgO	18.14	30.76	43.00
CaO	20.58	0.90	0.03
Na ₂ O	0.41		
Cr ₂ O ₃	0.63	0.15	
Total	98.42	101.01	100.39
T site			
Si	1.989	1.987	2.000
Al ^{IV}	0.011	0.013	
M1 site			
Al ^{VI}	0.004	0.003	
Fe ²⁺	0.040	0.022	0.167
Fe ³⁺	0.006	0.002	
Mg	0.926	0.966	0.843
Ti ⁴⁺	0.006	0.004	
Cr	0.018	0.003	
Mn ²⁺			0.010
M2 site			
Ca	0.814	0.027	0.001
Na	0.029		
Fe ²⁺	0.078	0.296	0.207
Mg	0.072	0.654	0.782
Mn ²⁺	0.007	0.015	0.010
K _D	0.040	0.050	0.750

$$K_D = (\text{Fe}^{2+}(\text{M1}) \cdot \text{Mg}(\text{M2})) / (\text{Fe}^{2+}(\text{M2}) \cdot \text{Mg}(\text{M1}))$$

TABLE 2 Average of electron microprobe analyses and estimated standard deviations for pyroxenes, olivine, kamacite and taenite.

	Ca-rich pyroxene	Ca-poor pyroxene	Olivine	Kamacite	Troilite	Taenite
SiO ₂	56.5(1.1)	56.6(1.0)	39.6(0.3)			
TiO ₂	0.3(0.1)	0.1(0.1)				
Al ₂ O ₃	3.9(3.9)	0.1(0.1)				
FeO	3.1(0.3)	11.0(0.3)	17.2(0.3)			
MnO	0.2(0.1)	0.5(0.1)	0.5(0.1)			
MgO	14.4(2.9)	31.2(0.6)	42.6(0.4)			
CaO	20.4(4.5)	0.6(0.1)				
Na ₂ O	1.5(1.4)					
Cr ₂ O ₃	0.5(0.1)	0.1(0.1)				
Fe				94.3(1.1)	63.5(0.3)	57.4(8.0)
Ni				6.5(0.2)		42.3(8.5)
S					37.1(0.1)	
Total	100.8	100.2	99.8	100.8	100.6	99.6

The cation distribution among sites was obtained by the following constraints: (1) balance between atomic fractions and site electron densities from both *M1* and *M2* sites; (2) complete site occupancy of *T*, *M1* and *M2* sites; and (3) bulk valence balance.

As regards pyroxene site partitioning, Ca, Na and Mn²⁺ were assigned to *M2*, and Al^{VI}, Fe³⁺ and Cr³⁺ to *M1*. Following this procedure, the accuracy has about the same order of magnitude

as that discussed in the methodological work of Skogby *et al.* (1992).

Mineral chemistry and classification

A thin polished section of the specimen was used for microprobe analysis to test the homogeneity and composition of minerals in the chondrite fragment from which crystals had been taken for crystal-chemical investigations. Results agree with

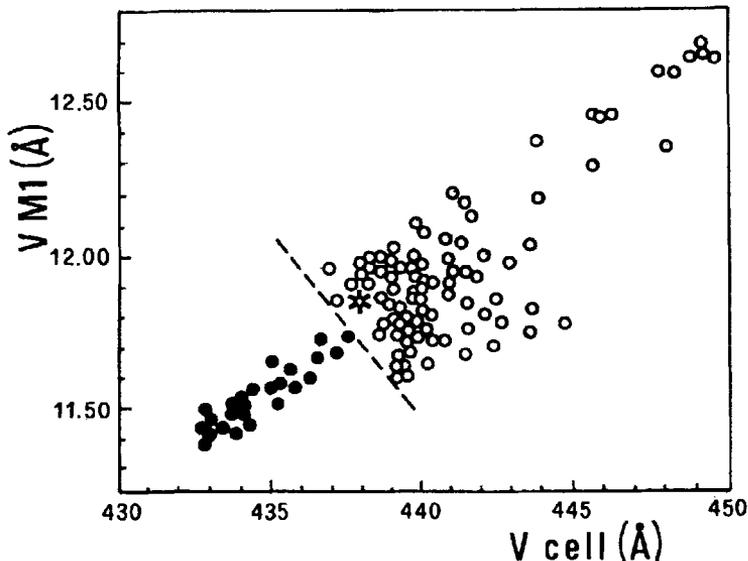


FIG. 1. Clinopyroxene *M1* site volume vs. cell volume plot. Star: Zaoyang clinopyroxene. Filled circles: lherzolite clinopyroxene, open circles: volcanic clinopyroxene (Dal Negro *et al.*, 1989). Dashed line separates crystals from low- and high-pressure terrestrial environments.

TABLE 3. Cell parameters and refinement data of single crystals used for XREF.

Structural parameters (bond lengths in Å, volume (V) in Å ³)							
	Clinopyroxene	Orthopyroxene	Olivine				
a (Å)	9.739(2)	18.286(5)	4.770(1)				
b (Å)	8.908(3)	8.863(2)	10.259(2)				
c (Å)	5.261(1)	5.205(2)	6.003(2)				
β (°)	106.38(2)						
V (Å ³)	437.87	843.69	293.79				
N _{oss}	585	884	466				
R% _{oss}	2.3	3.4	1.8				
Clinopyroxene							
M1 site		M2 site	T site				
M1-O2	2.044(2)	M2-O2	2.277(2)	T-O2	1.594(2)		
M1-O1A2	2.058(1)	M2-O1	2.323(2)	T-O1	1.612(1)		
M1-O1A1	2.134(2)	M2-O3C1	2.600(2)	T-O3A1	1.663(2)		
average	2.078	M2-O3C2	2.751(2)	T-O3A2	1.679(2)		
V(M1)	11.88	average	2.488	T-O _{nbr}	1.603		
		V(M2)	25.31	T-O _{br}	1.671		
				V(T)	2.233		
Orthopyroxene							
M1 site		M2 site	TA site	TB site			
M1-O1A	2.036(2)	M2-O1A	2.134(2)	TA-O1A	1.607(2)	TB-O1B	1.624(2)
M1-O1A'	2.151(2)	M2-O1B	2.091(2)	TA-O2A	1.587(2)	TB-O2B	1.592(3)
M1-O1B	2.172(2)	M2-O2A	2.055(2)	TA-O3A	1.646(3)	TB-O3B	1.673(3)
M1-O1B'	2.065(2)	M2-O2B	2.000(3)	TA-O3A'	1.664(2)	TB-O3B'	1.674(3)
M1-O2A	2.024(3)	M2-O3A	2.320(2)	TA-O _{nbr}	1.597	TB-O _{nbr}	1.608
M2-O2B	2.058(3)	M2-O3B	2.477(2)	TA-O _{br}	1.655	TB-O _{br}	1.674
average	2.084	average	2.180	V(TA)	2.177	V(TB)	2.253
V(M1)	11.94	V(M2)	12.85				
Olivine							
M1 site		M2 site	T site				
M1-O1	2.094(1)	M2-O1	2.187(2)	T-O1	1.617(2)		
M1-O2	2.082(1)	M2-O2	2.061(2)	T-O2	1.657(2)		
M1-O3	2.152(1)	M2-O3	2.232(1)	T-O3	1.634(1)		
average	2.109	M2-O3'	2.066(1)	average	1.635		
V(M1)	12.00	average	2.141	V(T)	2.211		
		V(M2)	12.56				

the data of Wang and Rubin (1987) confirming the high degree of homogeneity of the unbrecciated chondrite.

The $\text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mg})$ ratios of orthopyroxene and olivine are characteristic of H group chondrites. The chemical compositions and standard deviations of the silicate minerals, Fe-Ni alloys and troilite are listed in Table 2. Apatite, chromite and native copper (a plaque a few μm

across in taenite) were found as accessory minerals.

Silicate crystal chemistry

Clinopyroxene (cpx). Due to its scarcity in the chondrite, only one crystal large enough ($100 \times 50 \times 50 \mu\text{m}$) for X-ray diffraction intensity data collection could be found. As may be inferred

from the microprobe analysis (Table 1), the tetrahedral site is mainly occupied by Si (Si = 1.989 a.p.f.u.). This is consistent with the very short mean bond length of the tetrahedron ($\langle \text{Si-O} \rangle = 1.637 \text{ \AA}$, Table 3), one of the lowest observed values in lunar and terrestrial cpx (Dal Negro *et al.*, 1982, 1984, 1989; Takeda, 1972; Manoli and Molin, 1988).

The octahedral $M1$ site is mainly occupied by Mg (Mg = 0.926 a.p.f.u.), while the total content of trivalent ions R^{3+} ($R^{3+} = \text{Al}^{\text{VI}} + \text{Fe}^{3+} + \text{Cr}^{3+} + \text{Ti}^{4+}$) is very low (0.034 a.p.f.u.). The $M1$ site volume (a structural parameter strongly related to the crystallization environment) of 11.88 \AA^3 is a common value in terrestrial cpx from volcanic transitional basalts (Dal Negro *et al.*, 1982) and in alkali basalt to latite lavas (Faraone *et al.*, 1988).

The chemistry and hence the structure of Ca-rich clinopyroxene changes with the pressure of crystallization (Dal Negro *et al.*, 1989). The $M1$ site is particularly sensitive to pressure; it contracts in volume at pressure and hosts small trivalent ions such as Al. At lower pressure the larger divalent Mg and Fe ions enter $M1$. The plot of cell

volume (V_{cell}) vs. volume of the $M1$ site ($VM1$) (Fig. 1) places the Zaoyang cpx in the field of terrestrial low-pressure basaltic cpx.

The relationship between the $M2$ and $M1$ sites is shown by a plot of $M2\text{-O1}$ vs. $M1\text{-O2}$ bond lengths (Fig. 2). The two bond lengths are related (direct and inverse relationship respectively) to the Ca and R^{3+} ion content in terrestrial pyroxenes (Dal Negro *et al.*, 1982). The Zaoyang cpx plot in the field of transitional basalts and is close to the field of some basaltic andesites. This observation is considered later in this paper in the discussion of the Zaoyang cooling history.

Orthopyroxene (opx) is abundant in the Zaoyang chondrite. It is homogeneous ($\text{En}_{82}\text{-Wo}_2\text{-Fs}_{16}$) with sharp extinction. A $100 \mu\text{m}$ single crystal was selected for XREF and EMPA (Tables 2 and 1, respectively).

The SiB site displays a very low content of Al^{VI} , as was also observed for clinopyroxene. The $M1$ site is mainly filled by Mg (0.972 a.p.f.u.) with a very small amount of Fe^{2+} . Trivalent iron is absent from the calculations due to the reducing environment in the parent body. The $M2$ site contains most of the Fe^{2+} (0.296 a.p.f.u.). The

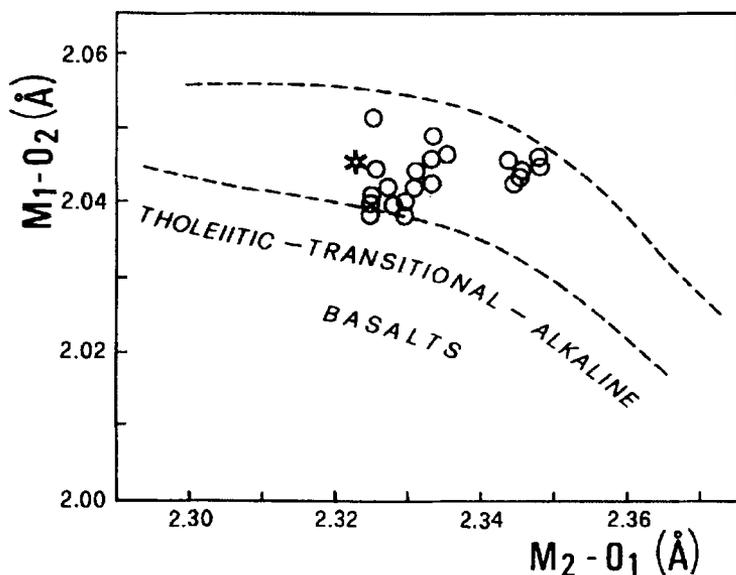


FIG. 2. Clinopyroxene $M1\text{-O2}$ vs. $M2\text{-O1}$ bond length plot. Dashed lines: field of tholeiitic to alkaline basalt clinopyroxene (Dal Negro *et al.*, 1982). Star: Zaoyang clinopyroxene. Open circles: clinopyroxene from calc-alkaline lavas (Molin and Zanazzi, 1991).

crystal-chemical configurations fit all the relationships observed in terrestrial opx (Domeneghetti *et al.*, 1985).

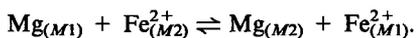
The cell volume and the *M1* and *M2* site volumes for opx vary with the pressure of crystallization. The Zaoyang volumes (cell 834 Å, *M1* 11.88 Å, *M2* 12.85 Å) are all greater than the lherzolitic values of Molin (submitted) which were 835.8–836.6 Å cell, 11.68–11.85 Å *M1*, 12.59–12.64 Å *M2* and instead span those of low-pressure opx (Bertolo and Nimis, 1993).

Olivine is the most abundant silicate mineral in the meteorite, in both chondrules and matrix.

A single optically selected crystal (Fo81) was structurally refined. The crystal-chemical results allow us to compare the Zaoyang olivine to common basic and ultrabasic terrestrial olivines (Princivalle and Secco, 1985). Zaoyang olivine shows a $K_D = 0.75$ [$K_D = \text{Mg}_{(M2)} \text{Fe}_{(M1)}^{2+} / (\text{Mg}_{(M1)} \text{Fe}_{(M2)}^{2+})$] indicative of a high degree of Fe^{2+} ordering in the *M2* site.

Cooling history

Intracrystalline ordering of Fe^{2+} -Mg between the *M1* and *M2* sites in ortho- and clinopyroxenes gives information on their cooling history (Ganguly, 1982). Ordering is measured by the K_D of the reaction



A closure temperature relevant to the observed K_D can be obtained from suitable experimental calibration, as in Molin *et al.* (1991) and Anovitz *et al.* (1988) for orthopyroxenes, or in Molin and Zanazzi (1991) for clinopyroxenes. Data on K_D can be obtained both by single-crystal diffractometry, as in this work, or by Mössbauer spectroscopy. Recently Skogby *et al.* (1992) have shown that significant differences arise between the two analytical methods if Mössbauer thickness corrections are not applied and some systematic differences also occur, especially for Al-rich and Fe-poor samples. In the present work we only use single-crystal X-ray diffraction.

As regards orthopyroxene, a semiquantitative estimate of the cooling rate can be obtained as reported by Ganguly (1982) and by Saxena and Dal Negro (1983) provided that kinetic data, a formulation for the dependence of K_D vs. the closure temperature (T_C), and an estimated crystallization temperature are available. Kinetic data were taken from sample S95 (Saxena *et al.*, 1989) and the K_D vs. T_C equation from (Molin *et al.*, 1991). These calibrations also derive from single-crystal X-ray diffraction.

Crystallization temperature was calculated from the selected clino- and orthopyroxene single crystals at 850°C (Lindsley, 1983). A Ca-rich and Ca-poor pyroxene intergrowth yields a Ca intercrystalline closure temperature of 900°C, confirming the reliability of the chosen temperature calculations which were performed by Saxena and Dal Negro (1983). The cooling rate obtained at a closure temperature of 512°C, using an asymptotic model, was a few degrees per day.

The above cooling rate is close to that estimated from microtextural observations in the Yamato-74191 L3 chondrite (10–100°C/h at 1000°) (Kitamura *et al.*, 1983), the Allende CV3 chondrite (from a few to a few hundred degrees/hour between 1300°C and 1000°C) (Muller, 1991), and in three L chondrites, belonging respectively to groups 3, 3-4 and 4-5 (several degrees/hour to a few dozen from 1000 to 800°C).

However, it should be noted that the above calculation is affected by both experimental and systematic error (Ganguly, 1982; Tribaudino and Talarico, 1992). The cooling rate of few degrees per day must therefore be considered as an order of magnitude figure. Figure 3 shows the closure temperatures of a set of volcanic and metamorphic terrestrial orthopyroxenes, compared with the orthopyroxene of the Zaoyang chondrite and the Johnstown diogenite, according to the calibration of Molin *et al.* (1991). The closure temperature differences reflect different cooling rates of the host rocks, that are roughly estimated to be of the order of °C/hour and of °C/m.y. respectively for volcanic and metamorphic samples. The Zaoyang orthopyroxene falls between the volcanic and metamorphic ranges (closer to the volcanics), while the Johnstown diogenite plots in the metamorphic range, as expected.

Information on the cooling history may also be obtained from intracrystalline ordering in clinopyroxene and the relevant K_D . The Fe^{2+} -Mg ordering in clinopyroxenes is significantly affected by cations other than Fe and Mg, like Ca, Na and trivalent ions which are present in significant quantities (Molin and Zanazzi, 1991): therefore, meaningful comparisons can only be made between samples with similar composition and crystal chemistry. The composition and crystal chemistry of the clinopyroxene of the Zaoyang chondrite are close to those of basaltic andesite clinopyroxenes, as shown by the low Na and trivalent ions and by the closeness to the field of calc-alkaline basaltic clinopyroxenes of the *M1*-O2 vs. *M2*-O1 bond length plot (Fig. 2). Therefore, it seems reasonable to compare the closure temperature of the Zaoyang clinopyroxene with that of the augite of Vulcano Island used for

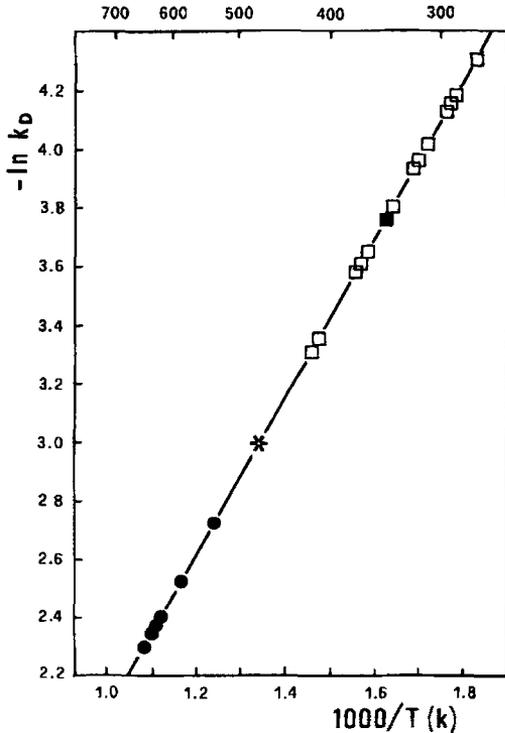


FIG. 3. Orthopyroxene $\ln K_D$ vs. $1/T$ (K) plot (solid line) according to calibration of Molin *et al.*, (1991). Star: Zaoyang orthopyroxene. Filled square: Johnstown diogenite orthopyroxene (Molin *et al.*, 1991). Open squares: metamorphic rock orthopyroxene (Tribaudino and Talarico, 1992). Filled circles: volcanic rock orthopyroxene (Bertolo and Nimis, 1993).

experimental calibration of K_D vs. T_C and applied to the study of the cooling history of a 4 m thick basaltic andesite lava flow (Molin and Zanazzi, 1991). The Zaoyang clinopyroxene closure temperature is 600°C, while those of the lava flow vary from 550–800°C. Applying Jaeger's cooling model for lava flows (Jaeger, 1968), cooling rates from 1–30°C/h were respectively evaluated for central areas and chilled margins, suggesting that the Zaoyang clinopyroxene underwent rather fast cooling probably of the same order of magnitude as a slowly cooled lava flow.

Discussion and conclusions

Crystal-chemical data on clino- and orthopyroxenes for the Zaoyang chondrite suggest low-pressure crystallization conditions and a cooling rate of degrees per day at lower temperatures. This

cooling is consistent with other estimates for chondrites, based on microstructural features observed in chondrules.

In greater detail, the cooling rate estimated from cpx and opx in the Zaoyang chondrite seems lower than other estimates for 3, 3-4 and 4-5 type chondrites at higher temperatures. This may be due to the nature of the Zaoyang chondrite, which belongs to petrographic type 5, for which slower cooling is expected.

The above cooling rate is consistent with a rapid radiative heat-loss at low pressures near the surface or from a small fragment after shock heating due to catastrophic collision which is less probable, because there are no signs of brecciation or strong shock (shock facies b, Wang and Rubin, 1987).

Acknowledgements

We are grateful to R. Hutchison for encouraging this work. G. Biggar and R. Hutchison gave useful comments on the manuscript. Financial support was provided by Italian MURST (60% and 40%) and by CNR Centro di Studio per la Geodinamica Alpina, Padova.

References

- Anovitz, L. M., Essene, E. J., and Dunham, W. R. (1988) Order-disorder experiments on orthopyroxenes: Implications for the orthopyroxene geospeedometer. *Amer. Mineral.*, **73**, 1060–73.
- Bertolo, S. and Nimis, P. (1993) Crystal chemical and structural variations in orthopyroxenes from different petrogenetic environments. *European J. Mineral* **5**, 707–19.
- Dal Negro, A., Carbonin, S., Molin, G. M., Cundari, A. and Piccirillo, E. M. (1982) Intracrystalline cation distribution in natural clinopyroxenes of tholeiitic, transitional and alkaline basaltic rocks. In *Advances in Physical Geochemistry 2* (Saxena S. K. ed). Springer-Verlag, Berlin, Heidelberg, New York, pp.117–150.
- Dal Negro, A., Carbonin, S., Domeneghetti, M. C., Molin, G. M., Cundari, A. and Piccirillo, E. M. (1984) Crystal chemistry and evolution of the clinopyroxene in a suite of high pressure ultramafic nodules from the Newer Volcanics of Victoria, Australia. *Contrib. Mineral. Petrol.*, **86**, 221–9.
- Dal Negro, A., Molin, G. M., Salviulo, G., Secco, L., Cundari, A. and Piccirillo, E. M. (1989) Crystal chemistry of clinopyroxene and its petrogenetic significance: a new approach. *The Lithosphere in Italy* (Boriani, A., Bonafede, M., Piccardo, G. B., and Vai, G. B., eds). Advances in Earth Science

- Research. Accademia Nazionale dei Lincei, Roma.
- Domeneghetti, M. C., Molin, G. M. and Tazzoli, V. (1985) Crystal-Chemical implications of the Mg^{2+} - Fe^{2+} distribution in orthopyroxenes. *Amer. Mineral.*, **70**, 987-95.
- Faraone, D., Molin, G. M., and Zanazzi, P. F. (1988) Clinopyroxenes from Vulcano (Aeolian Islands, Italy): Crystal chemistry and cooling history. *Lithos*, **22**, 113-26.
- Ganguly, J. (1982) Mg-Fe order-disorder in ferromagnesian silicates. II. In *Thermodynamics, kinetics and geological applications. Vol. 2* (Saxena, S. K., ed.). Springer, New York, Berlin Heidelberg, 58-99.
- International Tables for X-ray Crystallography* (1974) Kynoch Press, Birmingham, G. B., Vol. IV, 99-101.
- Jaeger, J. C. (1968) Cooling and solidification of igneous rocks. In *Basalts. Vol. 2* (Hess, H. H. and Poldervaart, A., eds). Interscience Publ., New York, 503-36.
- Kitamura, M., Yasuda, M., Watanabe, S., and Morimoto, N. (1983) Cooling history of pyroxene chondrules in the Yamato-74191 chondrite (L3), an electron microscopic study. *Earth Planet. Sci. Lett.*, **63**, 189-201.
- Lindsley, D. H. (1983) Pyroxene thermometry. *Amer. Mineral.*, **68**, 477-93.
- Manoli, S. and Molin, G. M. (1988) Crystallographic procedures in the study of experimental rocks: X-ray single-crystal structure refinement of $C2/c$ clinopyroxene from lunar 74275 high-pressure experimental basalt. *Mineral. Petrol.*, **39**, 187-200.
- Molin, G. M. (1993) Crystal chemistry and intracrystalline relationships of orthopyroxene in a suite of high pressure ultramafic nodules from the 'Newer Volcanics' of Victoria (Australia). *Mineral. Mag.*, **57**.
- Molin, G. M., Saxena, S. K., and Brizi, E. (1991) Iron-magnesium order-disorder in an orthopyroxene crystal from the Johnstown meteorite. *Earth Planet. Sci. Lett.*, **105**, 260-5.
- Molin, G. and Zanazzi, P. F. (1991) Intracrystalline Fe^{2+} -Mg ordering in augite: Experimental study and geothermometric applications. *European J. Mineral.*, **3**, 863-75.
- Müller, W. F. (1991) Microstructures of minerals in a chondrule from the Allende meteorite. II. Thermal history deduced from clinopyroxenes and other minerals. *Neues Jahrb Mineral., Abh.*, **162**, 237-59.
- North, A. C. T., Phillips, D. C., and Mathews, F. S. (1968) A semi-empirical method of absorption correction. *Acta Crystallogr.*, **A24**, 351-9.
- Principivale, F. and Secco, L. (1985) Crystal structure refinement of 13 olivines in the forsterite-fayalite series from volcanic rocks and ultramafic nodules. *TMPM Tscherm. Mineral. Petrol. Mitt.*, **34**, 105-15.
- Rossi, G., Smith, D. C., Ungaretti, L., and Domeneghetti, M. C. (1983) Crystal-chemistry and cation ordering in the system diopside-jadeite: a detailed study by crystal structure refinement. *Contrib. Mineral. Petrol.*, **83**, 247-58.
- Saxena, S. K. and Dal Negro, A. (1983) Petrogenetic application of Mg- Fe^{2+} order-disorder in orthopyroxene to cooling history of rocks. *Bull. Minéral.*, **106**, 443-9.
- Saxena, S. K., Domeneghetti, M. C., Molin, G. M., and Tazzoli, V. (1989) X-ray diffraction study of Fe^{2+} -Mg order-disorder in orthopyroxene. Some kinetic results. *Phys. Chem. Minerals*, **16**, 421-7.
- Skogby, H., Annersten, H., Domeneghetti, M. C., Molin, G. M., and Tazzoli, V. (1992) Iron distribution in orthopyroxene: A comparison of Mössbauer spectroscopy and X-ray refinement results. *European J. Mineral.*, **4**, 441-52.
- Takeda, H. (1972). Crystallographic studies of coexisting aluminian orthopyroxene and augite of high-pressure origin. *J. Geophys. Res.*, **77**, 5798-811.
- Tokonami, M. (1965) Atomic scattering factors for O^{2-} . *Acta Crystallogr.*, **19**, 486.
- Tribaudino, M. and Talarico, F. (1992) Orthopyroxenes from granulite rocks of the Wilson Terrane (Victoria Land, Antarctica): crystal chemistry and cooling history. *European J. Mineral.*, **4**, 453-63.
- Tsuchiyama, A., Nahagara, H., and Kusciro, I. (1980) Experimental reproduction of textures of chondrules. *Earth Planet. Sci. Lett.*, **48**, 155-65.
- Wang, D. and Rubin A. E. (1987) Petrology of nine ordinary chondrite falls from China. *Meteoritics*, **22**, 97-104.
- Watanabe, S., Kitamura, M., and Morimoto, N. (1985) A transmission electron microscope study of pyroxene chondrules in equilibrated L-group chondrites. *Earth Planet. Sci. Lett.*, **72**, 87-98.
- Zachariasen, W. H. (1963) The secondary extinction correction. *Acta Crystallogr.*, **16**, 1139-44.

[Manuscript received 15 March 1993:
revised 12 May 1993]