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CHEMICAL ZONING OF OLIVINES IN THE YAMATO-791717 CO3 CHONDRITE

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Abstract: The chemical zoning profiles of olivines in the Yamato (Y)-791717 CO3 chondrite have been analyzed in order to explore its thermal history. Two alternative models were applied to distinguish igneous processes from metamorphic features; they are fractional crystallization and diffusive modification of primary composition. It was clarified that chemical zoning of olivines in Y-791717 has been formed by a diffusion process, suggesting that this meteorite has been thermally metamorphosed. Thermal metamorphism of Y-791717 we have shown is consistent with that proposed on the basis of thermoluminescence investigation. A diffusion model also allows us to examine its thermal history in a quantitative way. Using a diffusion model, we have most successfully reproduced measured zoning profiles in isolated and chondrule olivine grains from Y-791717 in the temperature range 800–300°C. The temperature range is broadly consistent with the previously proposed peak metamorphic temperatures for CO3 chondrites.

1. Introduction

It has been demonstrated that the CO3 chondrites form a metamorphic sequence like type 3 ordinary chondrites (*e.g.*, MCSWEEN, 1977; SEARS *et al.*, 1980, 1991; KECK and SEARS, 1987; SCOTT and JONES, 1990). Definitions of the petrologic subtypes for CO3 chondrites have been proposed mainly on the basis of their petrographical properties (MCSWEEN, 1977; SCOTT and JONES, 1990) and thermoluminescence (TL) sensitivity (KECK and SEARS, 1987; SEARS *et al.*, 1991).

Much information on thermal history of chondrites has been derived from intensive studies of compositional zoning in grains of metallic Fe-Ni (*e.g.*, WOOD, 1967) and silicate zoning in chondrules (*e.g.*, MIYAMOTO *et al.*, 1986). Although zoning in metal grains is entirely metamorphic in origin, silicate zoning in chondrules probably resulted from igneous and/or metamorphic processes. Zoning profiles for major and minor elements in the silicate minerals such as olivine and pyroxene in chondrules will provide important data for modelling both crystallization and metamorphism of chondrules and give us information on their thermal histories. MCCOY *et al.* (1991) pointed out that characteristics of chondrule silicates caused by igneous and metamorphic processing must be distinguished carefully before precise models can be developed to explain silicate zoning. Previous studies of thermal histories of chondrites have mostly put emphasis on one of those effects. For example, JONES (1990) has concluded that silicate compositions and zoning profiles of the Semarkona (LL 3.0) chondrules are largely consistent with closed-system fractional crystallization by applying the Rayleigh equation to the zoned olivines. JONES and RUBIE (1991) have developed an Fe-Mg diffusion model to explain silicate zoning of chondrules in several CO3 chondrites.

In the present work, we have analyzed chemical zoning of olivines in the Yamato (Y)-791717 CO3 chondrite in order to study its thermal history. Both crystallization and metamorphic processes have been considered to investigate the cooling history of Y-791717 by applying alternative models, *i.e.* fractional crystallization (JONES, 1990) and diffusive modification (MIYAMOTO *et al.*, 1986; JONES and RUBIE, 1991; MCCOY *et al.*, 1991).

2. Samples and Analytical Techniques

The polished thin section of Y-791717 was supplied by the National Institute of Polar Research. This meteorite is mainly composed of chondrules, mineral fragments, Ca-Al-rich inclusions, and matrix. The main types of chondrules are porphyritic olivine and porphyritic olivine-pyroxene. Small amounts of radial pyroxene and barred-olivine chondrules are also present. Detailed descriptions of Y-791717 are given by KOJIMA *et al.* (1984) and YANAI and KOJIMA (1987).

Electron probe microanalysis was performed on a JEOL JCXA-733 microprobe at the Ocean Research Institute, University of Tokyo. Chemical zoning profiles of olivines from several isolated grains and chondrules in Y-791717 were measured by line analyses at intervals of 1–2 μm. The acceleration voltage was 15 kV and the beam current was 12 nA on a Faraday cage. Thirteen elements were analyzed (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, Cr, V, Ni, and P). Counting times at peak wavelengths were 20 s. The background intensity of each element was counted on both sides of the peak wavelength.

3. Calculation Procedures

Two alternative models were assumed to distinguish igneous and metamorphic features and to constrain thermal history of Y-791717.

3.1. Fractional crystallization

Assuming a closed system, Rayleigh fractionation equation was employed for a fractional crystallization model. According to the equation, during closed-system crystallization

$$\frac{C_L}{C_0} = F^{K_D - 1}, \tag{1}$$

where C_0 is the initial concentration in the bulk liquid, C_L is the concentration in the observed liquid, K_D is the distribution coefficient, and F is fraction of liquid remaining. Equation (1) was applied to the atomic Fe/Mg ratio and CaO wt% in olivines (JONES, 1990). The distribution coefficients (olivine/melt) used in this calculation were 0.35 for Fe/Mg (STOLPER, 1977) and 0.051 for CaO (JONES, 1990). In order to fit the calculated profiles to the observed ones, the least-squares method has been used. The values of F were converted into the corresponding distance from the core.

3.2. Diffusive modification

The equation for a diffusive modification model is

$$\frac{\partial C(x,t)}{\partial t}=\frac{\partial}{\partial x}\left(D\frac{\partial C(x,t)}{\partial x}\right), \tag{2}$$

where C is the Fa component (=Fe/(Mg+Fe), mol%) or CaO content (wt%) in olivine, t is time, x is distance along the diffusion path, and D is the diffusion coefficient. Equation (2) was numerically solved using finite difference approximation in spherical coordinates. It was assumed that the compositional gradients of the Fa components and CaO contents of olivine grains are controlled by atomic diffusion and that initial profiles are uniform (MIYAMOTO *et al.*, 1986). Boundary conditions are

$$\frac{\partial C(0,t)}{\partial x}=0, \tag{3}$$

$$C(r,t)=C_0, \tag{4}$$

where $x=r$ is the interface position between the olivine and the adjacent matrix. It can be a reasonable approximation to determine the value of C_0 that shows the best agreement between the calculated and observed profiles near the rim. According to BUENING and BUSECK (1973), the diffusion coefficient of Fe in olivine parallel to the c axis is expressed by

$$D_{Fe}=10^2(f_{O_2})^{1/6}\exp(-0.045C_{Fe}-3.47)\times\exp[(-61.06+0.2214C_{Fe})/RT],\quad (T\geq 1125°C) \tag{5}$$

$$D_{Fe}=10^2(f_{O_2})^{1/6}\exp(-0.0501C_{Fe}-14.03)\times\exp[(-31.66+0.2191C_{Fe})/RT],\quad (T<1125°C) \tag{6}$$

where D_{Fe} is the Fe-Mg interdiffusion coefficient in cm^2/s, f_{O_2} is the oxygen fugacity, C_{Fe} is the Fa component in mol%, R is the gas constant, and T is the temperature in K. The temperature dependence of the oxygen fugacity was calculated using the f_{O_2}-T relation given by BRETT and SATO (1984) for CO3 chondrites.

$$\log(f_{O_2})=6.4-26900/T. \tag{7}$$

The diffusion coefficient of Ca (D_{Ca}) in olivine parallel to the c axis as a function of temperature is reported by JUREWICZ and WATSON (1988).

$$D_{Ca}=7.0\times10^{-6}\exp(-43/RT).\quad (1220°C\leq T\leq 1350°C) \tag{8}$$

Cooling rates were calculated in four different temperature ranges (1500–1000°C, 1200–500°C, 800–300°C, and 500–100°C).

4. Results

We will focus on one isolated olivine grain and one chondrule olivine grain, which are representative in each grain. The chemical compositions of each olivines are provided in Table 1, showing that these olivines are zoned in Fe and Ca.

4.1. Isolated olivine

The observed zoning profiles for an isolated olivine are shown in Fig. 1. Both the Fa component (Fig. 1a) and CaO content (Fig. 1b) increase from the core to the rim. This olivine also shows a small increase in MnO (0.2–0.4 wt%). No other element shows clear zoning.

4.1.1. Fractional crystallization

The calculated zoning profile for the CaO content agrees with the observed one (Fig. 2b), whereas we obtained poor agreement for the atomic FeO/MgO ratio (Fig. 2a).

4.1.2. Diffusive modification

The calculated zoning profiles are in good agreement with the observed ones for both the Fa component (Fig. 3a) and CaO content (Fig. 3b). Among the four temperature ranges we calculated, the range 800–300°C gives the best fit between the calculated and observed zoning profiles (Fig. 4).

4.2. Chondrule olivine

The observed zoning profiles for a chondrule olivine are given in Fig. 5. The Fa component increases (Fig. 5a), whereas the CaO content decreases (Fig. 5b) from the

Table 1. Representative chemical compositions (wt%) of Y-791717 olivines.

	Isolated olivine		Chondrule olivine	
	Core	Rim	Core	Rim
SiO_2	37.9	36.0	42.1	37.4
TiO_2	0.00	–	0.11	–
Al_2O_3	–	–	0.36	–
FeO	19.26	34.6	0.26	26.2
MnO	0.23	0.36	–	0.21
MgO	41.6	27.8	56.4	35.5
CaO	–	0.24	0.79	0.13
Na_2O	0.00	0.00	–	–
K_2O	0.00	–	–	–
Cr_2O_3	–	–	–	–
V_2O_3	–	0.00	0.00	0.00
NiO	–	–	0.00	0.00
P_2O_5	–	0.00	0.00	0.00
Total	98.99	99.00	100.02	99.44
Fa	20.6	41.1	0.26	29.3

–: below detection limits.

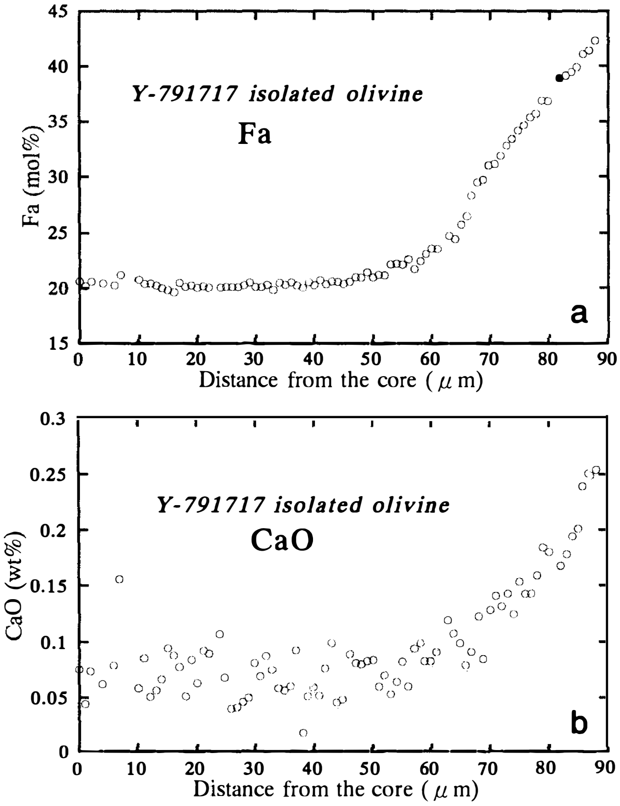

Fig. 1. Observed (open circles) zoning profiles for (a) Fa components (mol%) and (b) CaO contents (wt%) in an isolated olivine of Y-791717. The errors ($\pm 1\sigma$) based on counting statistics for the observed Fa components are within the size of the open circles. Those for Ca contents are approximately 0.02 wt%.

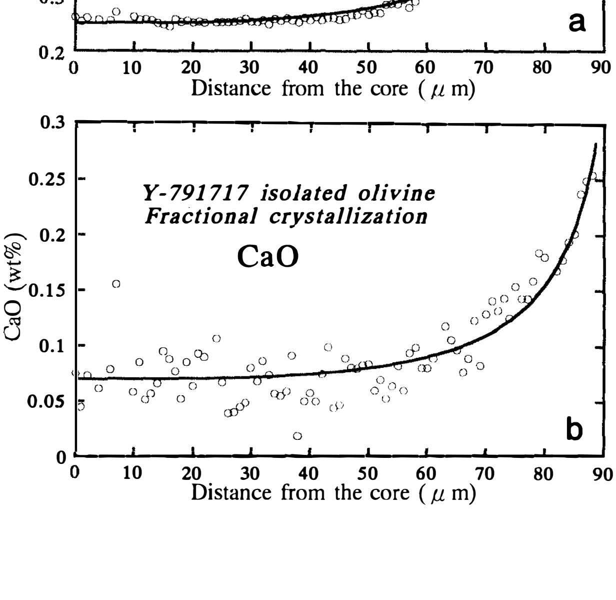

Fig. 2. Calculated (solid curves) and observed (open circles) zoning profiles for (a) atomic FeO/MgO ratio and (b) CaO contents (wt%) in an isolated olivine of Y-791717. Calculated profiles are obtained by a fractional crystallization model using values of $K_D(Fe/Mg) = 0.35$ (STOLPER, 1977) and $K_D(CaO) = 0.051$ (JONES, 1990).

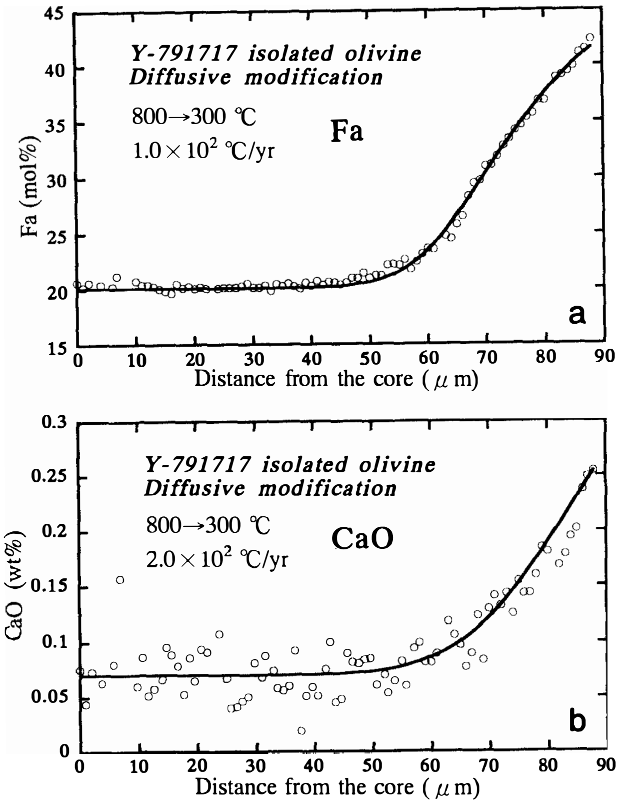

Fig. 3. Calculated (solid curves) and observed (open circles) zoning profiles for (a) Fa components (mol%) and (b) CaO contents (wt%) in an isolated olivine of Y-791717. Calculated profiles are obtained by a diffusive modification model cooling from 800 to 300°C, which gives the best fit (see Fig. 4). Diffusion coefficients are taken from BUENING *and* BUSECK *(1973) for Fe and* JUREWICZ *and* WATSON *(1988) for Ca.*

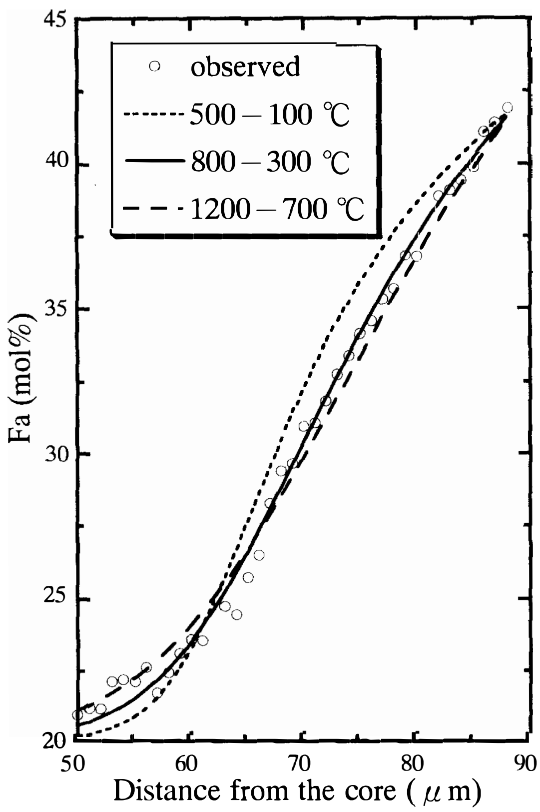

Fig. 4. Comparison among zoning profiles calculated by a diffusion model in different temperature ranges. The temperature range 800–300°C (solid line) shows the best fit.

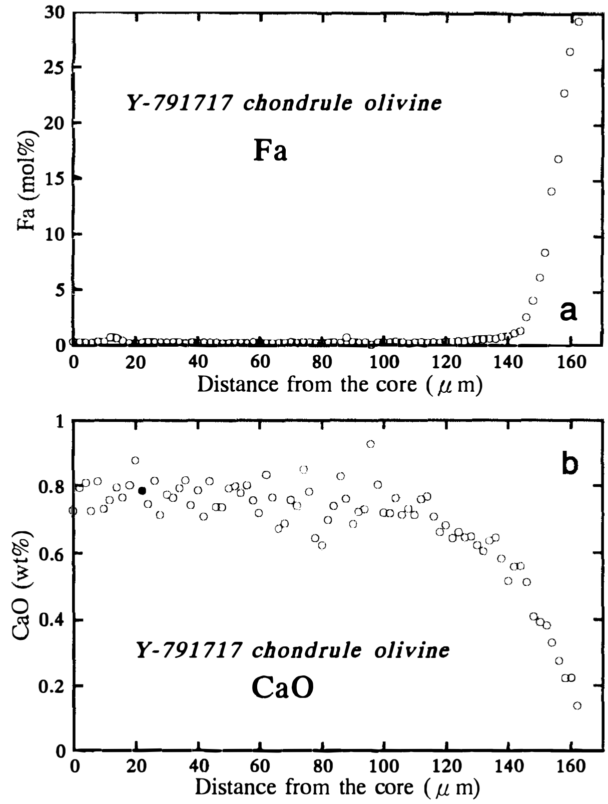

Fig. 5. Observed (open circles) zoning profiles for (a) Fa components (mol%) and (b) CaO contents (wt%) in a chondrule olivine of Y-791717. The errors ($\pm 1\sigma$) based on counting statistics. Those for Ca contents are approximately 0.03 wt%.

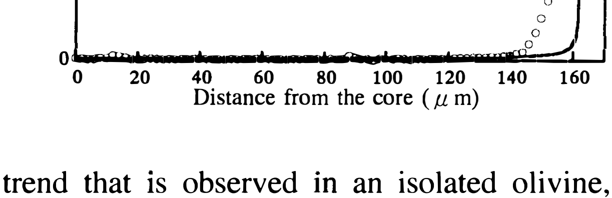

Fig. 6. Calculated (solid curve) and observed (open circles) zoning profiles for atomic FeO/MgO ratio in a chondrule olivine of Y-791717. The value of K_D (Fe/Mg) is the same as that used in Fig. 2. Since K_D (CaO) <1.0 is used in our calculations, we cannot fit profiles for the CaO content.

core to the rim. MnO shows the same trend that is observed in an isolated olivine, which ranges from < 0.15 to 0.25 wt%.

4.2.1. Fractional crystallization

The calculated FeO/MgO ratio does not accord with the observed one (Fig. 6). It was impossible to reproduce the observed zoning profile of the CaO content by calculating Rayleigh equation, because the value of distribution coefficient for CaO is <1.0, *i.e.* the CaO content should increase toward the rim (Fig. 5b).

4.2.2. Diffusive modification

The calculated zoning profiles well agree with the observed ones for both the Fa component (Fig. 7a) and CaO content (Fig. 7b). The temperature range 800–300°C also gives the best fit.

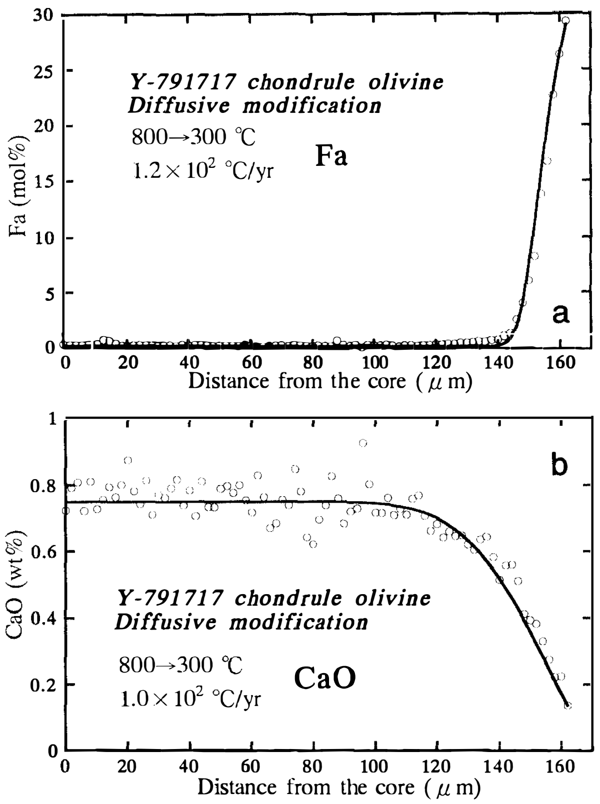

Fig. 7. Calculated (solid curves) and observed (open circles) zoning profiles for (a) Fa components (mol%) and (b) CaO contents (wt%) in an isolated olivine of Y-791717. Calculated profiles are obtained by a diffusive modification model. Diffusion coefficients are taken from the same references in Fig. 3.

5. Discussion

Previous studies have shown that the CO3 chondrites constitute a metamorphic sequence like type 3 ordinary chondrites (McSWEEN, 1977; SEARS *et al.*, 1980, 1991; KECK and SEARS, 1987; SCOTT and JONES, 1990).

SEARS *et al.* (1991) have proposed the definitions of petrographic types 3.0–3.9 for CO3 chondrites (Table 3 in their paper). They also obtained TL data for ten CO3 or CO3-like chondrites and recommended assignments of these chondrites to subtypes on the basis of their definitions. According to their recommendation, Y-791717 is classified as subtype 3.3, which shows that this meteorite has been thermally metamorphosed to a certain extent.

TL and other petrographic and compositional data do not allow us to discuss thermal histories in a more quantitative way. Quantitative studies of silicate zoning were performed by MIYAMOTO *et al.* (1986) for ordinary chondrites and by JONES and RUBIE (1991) for CO3 chondrites. MIYAMOTO *et al.* (1986) performed calculations to study the thermal conditions necessary to homogenize chondrule zoning profiles. JONES and RUBIE (1991) carried out similar calculations and estimated peak metamorphic temperatures of 470–490°C for ALHA77307 (subtype 3.1) and 510–520°C for Isna (subtype 3.7).

Our calculations indicate that a diffusive modification model successfully reproduces measured zoning profiles and that Y-791717 has been thermally metamorphosed. This result agrees with that obtained by SEARS *et al.* (1991). As mentioned in a pre-

Table 2. Calculated cooling rates (°C/year) of Y-791717 olivines.

Temperature	Isolated olivine		Chondrule olivine	
°C	Fa	CaO	Fa	CaO
1500–1000	7.0×10^6	1.3×10^5	1.8×10^7	5.3×10^4
1200–700	7.5×10^4	1.0×10^4	1.5×10^5	4.0×10^3
800–300	1.0×10^2	2.0×10^2	1.2×10^2	1.0×10^2
500–100	1.5×10^{-2}	1.0	1.5×10^{-2}	5.0×10^{-1}

vious section, we got the best fit between the calculated and observed zoning profiles in the temperature range 800–300°C, which generally corresponds to the peak metamorphic temperatures for CO3 chondrites estimated by JONES and RUBIE (1991). Table 2 shows cooling rates obtained by solving the diffusion equation in four different temperature ranges. The range 800–300°C also gives a similar cooling rate between isolated and chondrule olivines.

6. Conclusions

The following conclusions were derived from the results and discussion. In order to confirm these conclusions, however, there exists a need to investigate other grains from different sections of this meteorite.

(1) Chemical zoning of olivines in the Y-791717 chondrite is explained by a diffusive modification model better than by a fractional crystallization model, *i.e.* Y-791717 has been thermally metamorphosed.

(2) Thermal metamorphism of Y-791717 we demonstrated is consistent with that shown on the basis of TL studies.

(3) Among the four temperature ranges we calculated, the range 800–300°C gives the best agreement between calculated zoning profiles and observed ones, which is in accord with previous studies of the peak metamorphic temperatures for CO3 chondrites.

(4) A diffusive modification model is also confirmed by the fact that both isolated and chondrule olivines show a similar cooling rate in the temperature range 800–300°C.

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