COOLING RATES OF OLIVINE XENOCRYSTS IN THE EET79001 SHERGOTTITE

Hiroshi Kaiden, Takashi Mikouchi and Masamichi Miyamoto

*Mineralogical Institute, Graduate School of Science, University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113-0033*

Abstract: The chemical zoning profiles of olivine xenocrysts in lithology A of the Elephant Moraine (EET) 79001 basaltic shergottite have been measured in order to investigate its cooling history. Olivines are zoned from Fa_{23} in the cores to Fa_{44} in the rims. The major and minor element compositions of olivine xenocryst cores in EET79001 correspond to those of homogeneous olivines in the lherzolitic shergottites, reconfirming the previous studies. We assume that the initial profile of olivine was uniform and it was modified by atomic diffusion due to contact with the Fe-rich surrounding melt when olivine was incorporated as a xenocryst. Comparing the observed Fe zoning profiles with the calculated ones, we have estimated the minimum cooling rates of the xenocrystic olivines by numerically solving the diffusion equation. The inferred minimum cooling rates (0.07–0.5 °C) are faster than that for Zagami estimated from the width of pyroxene lamella, consistent with a hypothesis that EET79001 experienced significant undercooling unlike Shergotty and Zagami. We also performed the calculations by applying two different Fe-Mg interdiffusion coefficients to evaluate them. There is no significant difference in the curvature of the calculated profiles between the two diffusion coefficients, whereas one gives roughly fivefold higher cooling rates than the other.

1. Introduction

So far, twelve achondritic meteorites are recognized as SNC (Shergottites-Nakhlites-Chassignite) meteorites, which are inferred to have formed on Mars. Nowadays, they are also called "martian meteorites" and classified into five rock types on the basis of their textures, mineral assemblages and chemical compositions, *i.e.*, basalt, lherzolite, clinopyroxenite, dunite and orthopyroxenite (*e.g.*, McSween, 1994; Yanai, 1997). Several lines of evidence for a martian origin of SNC meteorites are discussed over these a few decades. The hypothesis is now almost accepted and useful information about martian geology have been deduced (*e.g.*, McSween, 1994). Furthermore, recent announcement of possible relict biogenic activity in a martian meteorite ALH84001 opened up a potential to discuss life on Mars (McKay *et al.*, 1996) although it has been under dispute (*e.g.*, Bradley *et al.*, 1997; McKay *et al.*, 1997).

An Antarctic meteorite Elephant Moraine (EET) 79001 is one of the martian meteorites and classified as a basaltic shergottite along with Shergotty, Zagami and Queen Alexandra Range (QUE) 94201. It contains two distinct igneous lithologies (designated "A" and "B") with a planar, non-brecciated contact. Lithologies A and B of EET79001 consist predominantly of clinopyroxene (pigeonite and augite) and maskelynite (shocked

plagioclase glass) and have many similarities in mineralogy to each other and to the other basaltic shergottites, but show textural and modal differences (STEELE and SMITH, 1982; McSWEEN and JAROSEWICH, 1983). For example, the grain size of lithology A is significantly finer than that of lithology B. The amount of maskelynite relative to clinopyroxene is higher in lithology B than in lithology A. Lithology A is a little more magnesian than lithology B. In addition, lithology A contains large olivine, orthopyroxene and chromite reaching ~5 mm across that are absent in the other basaltic shergottite including lithology B (STEELE and SMITH, 1982; McSWEEN and JAROSEWICH, 1983). Their compositions are clearly out of equilibrium with the surrounding melt and considered to be xenocrysts as their huge sizes suggest (STEELE and SMITH, 1982; McSWEEN and JAROSEWICH, 1983). Both lithologies are suggested to be petrogenetically related, probably through assimilation, fractionation from a similar parental magma, or partial melting of a similar source rock (McSWEEN and JAROSEWICH, 1983). It is also suggested that both lithologies probably formed from successive volcanic flows or multiple injections of magma into a small, shallow chamber (McSWEEN and JAROSEWICH, 1983). The xenocrysts in lithology A are important because they show a direct petrogenetic relationship to the lherzolitic martian meteorites as noted by McSWEEN and JAROSEWICH (1983). However, the origin of lithology A itself is still controversial due to their extremely small size of the grains and the presence of the xenocrysts. Recently, MITTLEFEHLDT *et al.* (1997) suggested that lithology A is a product of impact melting, whereas WARREN and KALLEMEYN (1997) argued that magma mixing is more likely than the impact melt (*e.g.*, WADHWA *et al.*, 1994).

Several quantitative studies on thermal histories of the basaltic shergottites have been carried out (JONES, 1986; BREARLEY, 1991; McCOY *et al.*, 1992; TREIMAN and SUTTON, 1992). Because they are largely on the basis of the textures and compositions of pyroxenes and/or maskelynites which are major minerals in these meteorites, estimation of cooling history using such procedures usually bears a large uncertainty. Thus, it is important to study zoning of olivine xenocrysts occurring in lithology A of EET79001 in the hope that they record an igneous history as well. The objective of the present study is to examine chemical zoning of olivine xenocrysts in lithology A of EET79001 shergottite and to constrain its thermal history. So far no quantitative data for cooling rate of EET79001 has been submitted except for a brief estimate by JONES (1986) and this study bears a great potential to constrain its cooling rate.

2. Samples and Analytical Techniques

EET79001 was found in a glacial moraine in Victoria Land, Antarctica, during the 1979–80 field season and is a 7.94 kg basaltic shergottite (SCORE and REID, 1981). Two polished thin sections of the meteorite (EET79001,88 and ,443) were supplied by the Meteorite Working Group. The EET79001 meteorite has been described in detail by STEELE and SMITH (1982) and McSWEEN and JAROSEWICH (1983).

Mineral compositions were determined using a JEOL JCXA-733 electron microprobe at the Ocean Research Institute, University of Tokyo. The accelerating voltage was 15 kV and the beam current was 12 nA on a Faraday cage. Thirteen major elements

(Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, Cr, V, Ni and P) were analyzed. Counting times at peak wavelengths were 20 s (10 s×2). The background intensity of each element was counted on both sides of the peak wavelength. X-ray intensities were corrected using a method by BENCE and ALBEE (1968). The chemical zoning profiles of olivine xenocrysts in lithology A of EET79001 were measured by line analyses by focused beam at intervals of 3 μm. The zoning profiles were measured along lines selected on the basis of backscattered electron images.

3. Calculation Procedures

It was assumed here that the compositional gradient of the Fa component (=100×Fe/ (Mg+Fe); mol%) of olivine xenocryst in EET79001 was controlled by atomic diffusion. In order to estimate the cooling rate of olivine xenocryst in EET79001, we analyzed the compositional gradient by solving the diffusion equation (MIYAMOTO et al., 1986; MIYAMOTO and TAKEDA, 1994).

The diffusion equation was numerically solved by using a finite difference approximation in spherical coordinates, taking into consideration the shape of olivine xenocrysts in EET79001:

$$\frac{\partial C}{\partial t} = \frac{1}{r^2} \left\{ \frac{\partial}{\partial r} \left(r^2 D \frac{\partial C}{\partial r} \right) \right\},$$

where C, r and t are the Fa component, position in spherical coordinate and time, respectively.

Initial condition is

$$C(r,0) = C_I(r),$$

where C_I is an initial concentration profile. Diffusion calculations were started by using a uniform initial profile which is determined by the core Fa composition of each olivine.

Boundary conditions are

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

$$C(R,t) = C_B,$$

where position R is at the interface between olivine and the adjacent matrix. C_B is the concentration at the grain boundary with the matrix. The constant concentration (C_B) was fixed to the concentration at the extreme rim of each olivine during diffusion calculations.

Although several expressions of the Fe-Mg diffusion coefficient have been reported, we have employed the ones determined by BUENING and BUSECK (1973) and MISENER (1974) here. The expressions of the Fe-Mg interdiffusion coefficient in olivine parallel to the c axis determined by BUENING and BUSECK (1973) are

$$D_{Fe}=10^2(f\,O_2)^{1/6}\exp(-0.045C_{Fe}-3.47)\exp[(-61.06+0.2214C_{Fe})/RT]\quad T\geq1125°C,\quad(1)$$

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

where D_{Fe} is the Fe-Mg interdiffusion coefficient in cm^2/s, $f\,O_2$ is the oxygen fugacity in atm, C_{Fe} is the Fa component in mol%, R is the gas constant and T is temperature in K. The diffusion coefficient in the c direction was used, because it is the largest among three directions and diffusive modification tends to be dominated by the largest diffusion coefficient among three directions although they do not differ greatly.

The Fe-Mg interdiffusion coefficient reported by MISENER (1974) is

$$D_{Fe}=10^{-2}(0.41+0.0112C_{Fe})\,\exp[(-58.88+0.0905C_{Fe})/RT],\qquad\qquad(3)$$

where 900 °C $\leq T \leq$ 1100 °C. The Fe-Mg interdiffusion coefficient in olivine depends on temperature, composition and oxygen fugacity (BUENING and BUSECK, 1973; eqs. (1) and (2)), whereas MISENER (1974) did not report a dependence on oxygen fugacity conditions for his experiments (eq. (3)). MIYAMOTO *et al.* (1986) corrected the eq. (3) to incorporate the $f\,O_2$ term. However, there is a typographical error in eq. (8) of MIYAMOTO *et al.* (1986), that is, the term "3.4538" was omitted. The correct expression is:

$$D_{Fe} = (f\,O_2)^{1/6}\,\exp[\ln(0.0041+0.000112C_{Fe})-3.4538]\,\exp[(-39.27+0.0905C_{Fe})/RT]$$

$$= 0.03163\times10^{-2}\,(f\,O_2)^{1/6}(0.41+0.0112C_{Fe})\,\exp[(-39.27+0.0905C_{Fe})/RT],\qquad(4)$$

Because coexisting Fe-Ti oxide (titanomagnetite and ilmenite) compositions in EET79001 suggest oxygen fugacity equilibration near that of the quartz-fayalite-magnetite (QFM) buffer (McSWEEN and JAROSEWICH, 1983), we calculated the temperature dependence of the oxygen fugacity using the $f\,O_2$-T relation for the QFM buffer assemblage in the temperature range of 600 °C to 1100 °C determined by WONES and GILBERT (1969).

$$\log(f\,O_2) = 9.00-25738/T.\qquad\qquad(5)$$

The pyroxene (core augite and pigeonite) compositions of lithology A of EET79001 suggest that the temperature at which pyroxene crystallized is about 1200 °C from two pyroxene geothermometry (LINDSLEY and ANDERSEN, 1983) although its composition is a little scattered due to their irregular zoning patterns. The crystallization experiment of the basaltic shergottite composition (Shergotty and Zagami) showed that liquidus temperature is around 1200 °C (STOLPER and McSWEEN, 1979). The compositions of coexisting Fe-Ti oxides in lithology A of EET79001 determine the temperature of 790 °C (McSWEEN and JAROSEWICH, 1983). Therefore, we calculated cooling rates in the temperature range of 1200–800 °C. Although we calculated down to temperature of 800 °C, our calculation gave little change of the profile at temperatures lower than 800 °C be-

cause atomic diffusion is only limited at low temperatures comparing with high temperatures. Thus, we believe that the minimum temperature (800 °C) corresponds to "closure temperature". Because olivine in lithology A is incorporated into the melt as a xenocryst, it is expected that olivine experienced atomic diffusion from temperatures higher than 1200 °C. Some olivine grains suggest evidence for partial dissolution. Therefore, the result from this calculation starting from 1200 °C gives the minimum cooling rate.

4. Results

4.1. Chemical zoning

The olivine xenocrysts in lithology A of EET79001 that we analyzed range from 0.5 mm to 3 mm in size. They are usually rounded in shape, suggesting interaction with the surrounding melt. Some olivines are faulted by shock. All the phases in lithology A, including the host pyroxene and maskelynite are severely shocked (i.e., undulatory extinction, polysynthetic twinning). The representative observed zoning profiles for olivine xenocrysts are shown in Figs. 1 and 2. Decrease of Mg and increase of Fe from the Mg-rich cores to Fe-rich rims are apparent in Mg and Fe maps (Fig. 3). Their compositional zoning ranges are Fa_{23-36}, Fa_{28-43} and Fa_{39-44}, respectively for a, b and c of Figs. 1 and 2. These compositional ranges are consistent with the analyses by Steele and Smith (1982) and McSween and Jarosewich (1983), whose maximum ranges of olivine compositions are Fa_{19-45} and Fa_{22-47}, respectively. Generally, larger grains have more magnesian compositions, indicating effect of off-center cut for grains. This caused more Fe-rich composition of olivine grain c than grains a and b in Figs. 1 and 2.

As noted by previous workers (Steele and Smith, 1982; McSween and Jarosewich, 1983), the olivine compositions in the poikilitic area of the lherzolitic shergottites (Allan Hills (ALH) 77005, Lewis Cliff (LEW) 88516 and Yamato (Y)-793605) correspond to those of olivine xenocryst cores with the most magnesian compositions in lithology A of EET79001 (Figs. 1 and 2). Unlike olivines in lithology A of EET79001, those in lherzolitic shergottites are fairly homogeneous in chemical compositions and the average olivine compositions of ALH77005, LEW88516 and Y-793605 are Fa_{26}, Fa_{31} and Fa_{31}, respectively (McSween et al., 1979; Harvey et al., 1993; Mikouchi and Miyamoto, 1997). Furthermore, minor element compositions of the olivine xenocrysts are also generally similar to those of olivine grains in the lherzolitic shergottites (Table 1). This fact reconfirms the idea that the xenocryst assemblage in lithology A of EET79001 represents a disaggregated plutonic rock (possibly the lherzolitic shergottites) assimilated by a basaltic shergottite magma (McSween and Jarosewich, 1983).

4.2. Cooling rates

Cooling rates that give the best fit between the calculated and observed profiles are provided in Table 2. Figure 1 shows the calculated and observed zoning profiles using two different diffusion coefficients. There are few differences in the curvature of the profiles between the Fe-Mg interdiffusion coefficient of Buening and Buseck (1973) and that of Misener (1974), while we obtained slightly different cooling rates of 0.5–3 °C/h
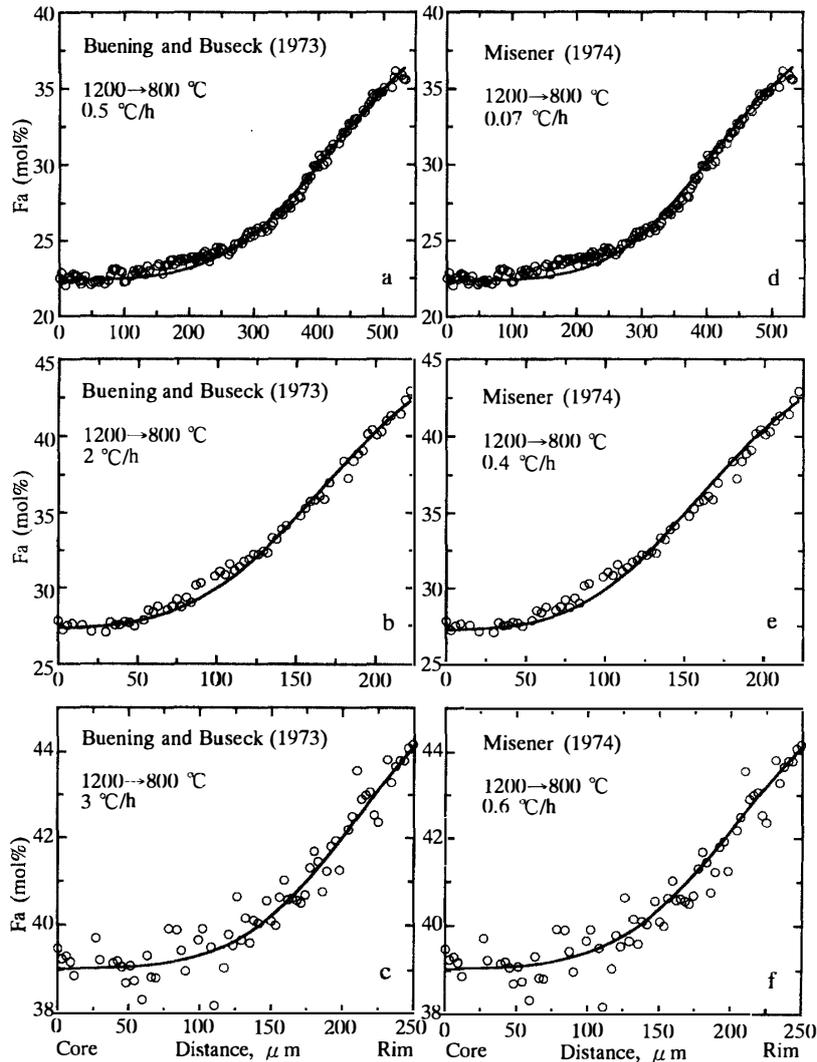
Fig. 1. Fe zoning profiles of the three different olivine xenocrysts in lithology A of the EET79001 basaltic shergottite. The compositional ranges are (a) Fa_{23-36} (b) Fa_{28-43} and (c) Fa_{39-44}. Open circles indicate the Fa component. Curves show calculated diffusion profiles. Numbers show the cooling rates from 1200 °C to 800 °C. Figures a–c are obtained by using the diffusion coefficient of BUENING and BUSECK (1973) and Fig. d–f are obtained by using the diffusion coefficient of MISENER (1974). There is no significant difference in the curvature between Fig. a–c and Fig. d–f, whereas the cooling rates of Fig. d–f (MISENER, 1974) are slower than those in Fig. a–c (BUENING and BUSECK, 1973).

for BUENING and BUSECK (1973) and 0.07–0.6 °C/h for MISENER (1974) (Fig. 1). Because Fe-rich olivines generally give faster cooling rates, the line profile having the most Mg-rich core gives the slowest cooling rate. Thus, the slowest cooling rates (0.5 °C/h from MISENER, 1974 and 0.07 °C from BUENING and BUSECK, 1973) correspond to the represen-
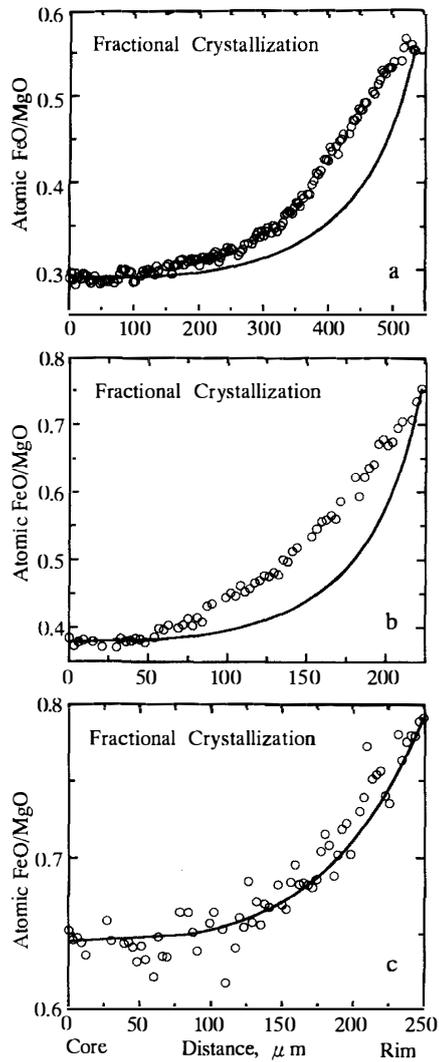
Fig. 2. Fe zoning profiles of the same olivines as Fig. 1. Curves show the profiles calculated by applying the Rayleigh fractional crystallization equation. The calculated profiles disagree with the observed ones, suggesting that the chemical zoning is of metamorphic origin (Fig. 1).
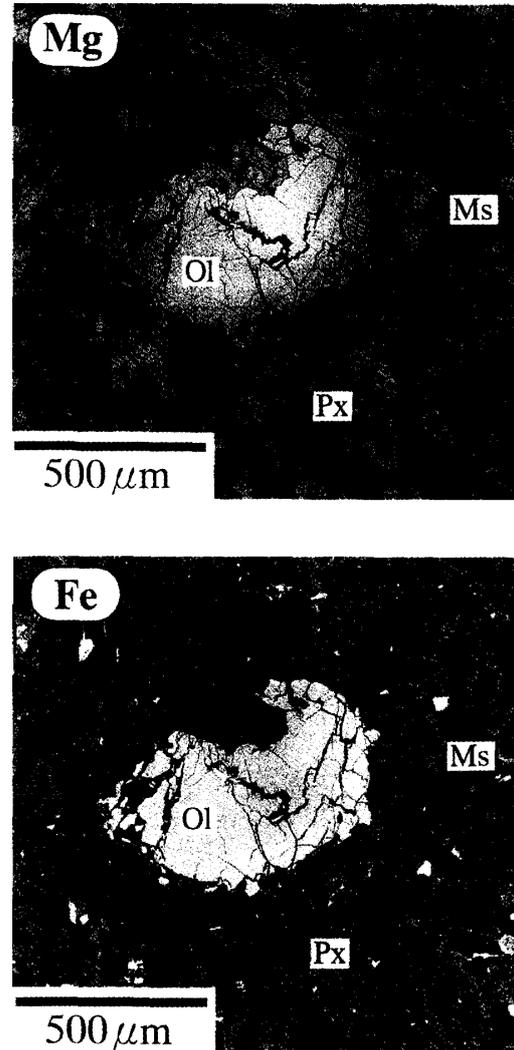
Fig. 3. Mg and Fe distribution maps of lithology A of EET79001. Brighter area shows higher concentration of each element. A large grain in the center is olivine. Note that olivine is zoned in both Mg and Fe from the Mg-rich and Fe-poor core to the Mg-poor and Fe-rich rim. Ol: olivine. Px: pyroxene. Ms: maskelynite. Scale bar is 500 μm.

Table 1.   Chemical composition of olivine in lithology A of EET79001 and lherzolitic shergottites (Core).

	Fa	CaO	MnO	NiO	Cr_2O_3
Lithology A EET79001	24	0.2–0.3	0.45	0.05–0.1	0.05–0.1
Lherzolitic shergottites	25–31	0.2–0.3	0.4	0–0.1	0–0.05

CaO, MnO, NiO, Cr_2O_3: wt%.

Table 2.   Comparison of cooling rates reported for the basaltic shergottites.

Cooling rate (°C/h)	Temperature	Method, mineral, etc.	Meteorite
0.02	1100–950	pyroxene exsolution lamellae	Zagami[1]
0.1–0.5	—	plagioclase	Zagami[2]
5–20	<1130–1200	pigeonite textures	Zagami[3]
0.07–0.6	1200–800	Fe-Mg interdiffusion in olivine*	EET79001[4]
0.5–3	1200–800	Fe-Mg interdiffusion in olivine†	EET79001[4]

*Diffusion coefficient of MISENER (1974).
†Diffusion coefficient of BUENING and BUSECK (1973).
[1]BREARLEY (1991); [2]McCOY et al. (1992); [3]TREIMAN and SUTTON (1992); [4]This study.

tative cooling rate of lithology A.

4.3. Iron diffusion coefficients

The Fe-Mg interdiffusion coefficient in olivine estimated by BUENING and BUSECK (1973) is about one order of magnitude larger than that by MISENER (1974) in the temperature range of this study. There is no significant difference in the curvature of the zoning profile between the two Fe-Mg interdiffusion coefficients, because both coefficients are formulated as a function of the Fe content in olivine. Since we assumed linear cooling, the difference in the cooling rates reflects the difference in the value of the diffusion coefficients.

4.4. Fractional crystallization

In order to test the validity of our assumption that the chemical zoning is of metamorphic origin, we also applied a methodology similar to that used in our previous study (KAIDEN et al., 1997), in which Rayleigh fractionation equation was employed (Fig. 2). From Figs. 1 and 2, it can be concluded that the zonation of the xenocrystic olivines is of metamorphic origin, and not the result of an igneous process.

5.   Discussion

Several authors have investigated the basaltic shergottites, especially Zagami, in order to reveal their crystallization histories (e.g., STOLPER and McSWEEN, 1979; TREIMAN and SUTTON, 1992; McCOY et al., 1992), and some of them have estimated the cooling rates (Table 2).

For example, BREARLEY (1991) suggested that the cooling rate of the Zagami shergottite is about 0.02 °C/h through the temperature interval of 1100–950 °C/h on the basis of the width of pyroxene exsolution lamellae in the pyroxene core and that Zagami has originated from a lava flow significantly thicker than 10 m or comes from a shallow intrusive body such as a sill or dike. McCOY et al. (1992) estimated cooling rates of 0.1–0.5 °C/h for Zagami based on sizes of the plagioclase (maskelynite) crystals and proposed that the Zagami shergottite experienced a two-stage magmatic history in which slow cooling occurred in a deep-seated magma chamber followed by rapid cooling in a shallow intrusion or thick lava flow. Cooling rates of 0.1–0.5 °C/h correspond to crys-

tallization during the second stage in a near-surface environment. On the other hand, Treiman and Sutton (1992) inferred cooling rates of 5–20 °C/h (<1130–1200 °C) from the textural comparison of Zagami with products from crystallization experiments of some lunar rocks and they found little evidence of a multistage cooling history as suggested McCoy *et al.* (1992).

Our calculation gives the first quantitative cooling rate of EET79001 (lithology A). Our results that the minimum cooling rate of olivine xenocrysts in EET79001 is 0.07–0.5 °C/h is clearly faster than the Zagami cooling rate (0.02 °C/h) estimated by Brearley (1991). Furthermore, our estimating cooling rate is as fast as that of Zagami (0.1–0.5 °C/h) for the second stage (rapid cooling) by McCoy *et al.* (1992). This is consistent with the suggestion by Mikouchi *et al.* (1997) that both lithologies of EET79001 experienced significant undercooling unlike Shergotty and Zagami as they show different textures and pyroxene and maskelynite zoning patterns from EET79001. However, our cooling rate is slower than fast cooling rate (5–20 °C/h) estimated by Treiman and Sutton (1992), probably due to uncertainty of their indirect estimation method.

6. Conclusions

The present investigation leads to the following conclusions.

(1) The compositions of olivine xenocryst cores in lithology A of EET79001 are similar to those of homogeneous olivines in the lherzolitic shergottites, reconfirming the idea that the xenocrysts represent disaggregated xenoliths of the lherzolitic shergottites as suggested by McSween and Jarosewich (1983).

(2) We have estimated cooling rates of olivine xenocrysts in the EET79001 basaltic shergottite by analyzing their chemical zoning profiles. The cooling rates that we obtained are faster than that for Zagami pyroxene core estimated by Brearley (1991) and roughly consistent with those for Zagami estimated by McCoy *et al.* (1992), who suggested its relatively rapid cooling in a near-surface environment as the second stage. Such cooling rates coincide with significant undercooling of EET79001 unlike Zagami proposed by Mikouchi *et al.* (1997).

(3) Two kinds of Fe-Mg interdiffusion coefficient in olivine we applied in the present study show no significant difference in the curvature of the profiles, whereas the coefficient reported by Buening and Buseck (1973) gives about fivefold higher cooling rates than that by Misener (1974).

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