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Oxygen three-isotope ratios of silicate particles returned from asteroid Itokawa by the Hayabusa spacecraft: A strong link with equilibrated LL chondrites

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ABSTRACT

Oxygen three-isotope ratios of four mineral phases (olivine, low-Ca and high-Ca pyroxene, and plagioclase) in seven silicate particles from asteroid Itokawa were measured to investigate oxygen isotope systematics of asteroidal materials. In order to obtain highly precise and accurate oxygen isotope ratios ($\sim \pm 0.3‰$ in $\delta^{18}O$), we used a new indium mounting method that minimizes potential instrumental mass fractionation due to surface topography. The oxygen isotope data of the seven Itokawa particles are distributed above the terrestrial fractionation line with indistinguishable $\Delta^{17}O(= \delta^{17}O - 0.52 \times \delta^{18}O)$ values of $+1.34 \pm 0.36‰$ (2SD; $n = 22$), which is similar to those of Itokawa particles analyzed by Yurimoto et al. (2011) and Nakamura et al. (2012). However, $\delta^{18}O$ values of the seven Itokawa particles are tightly clustered ($+3.9‰$ to $+5.9‰$ VSMOW) compared to previous analyses of the Itokawa particles ($+1.4‰$ to $+8.8‰$).

The average $\Delta^{17}O$ values and 2SD of the two equilibrated ordinary chondrites (EOCs), which were analyzed for comparison, are $+1.31 \pm 0.49‰$ for St. Séverin (LL6) and $+0.83 \pm 0.64‰$ for Guareña (H6). The $\Delta^{17}O$ values of the seven Itokawa particles are similar to those of St. Séverin. The average bulk $\delta^{18}O$ value of the seven Itokawa particles is estimated as $+4.8‰$, which is within the $\delta^{18}O$ range of bulk LL5 and LL6 chondrites. It is suggested that Itokawa particles are similar to those of equilibrated LL chondrites, which strengthens a link between asteroid Itokawa and equilibrated LL chondrites that fell to Earth.

The seven Itokawa particles and two EOCs have $\delta^{18}O$ values of high-Ca pyroxene that are lower than those of olivine, indicating that oxygen isotopes between the two mineral phases are not in equilibrium. Apparent oxygen isotope equilibrium temperatures estimated from a pair of low-Ca pyroxene and olivine are excessively higher than those from a pair of plagioclase and high-Ca pyroxene ($\sim 800 °C$) and peak metamorphic temperatures. Oxygen isotopes in olivine and low-Ca pyroxene do not represent equilibrium. On the other hand, oxygen isotope ratios in high-Ca pyroxene and plagioclase were mass-dependently fractionated accompanied by recrystallization (and possibly by diffusion) during thermal metamorphism. Values of $\delta^{18}O$ in high-Ca pyroxene were lowered by exchange, which may have resulted in the reverse $\delta^{18}O$ fractionation between olivine and high-Ca pyroxene.

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1. Introduction

The Hayabusa spacecraft returned dust particles from asteroid 25143 Itokawa in 2010 (Abe et al., 2011). Preliminary examinations show that the Itokawa particles resemble equilibrated LL chondrites based on the modal abundances of minerals, chemical compositions of major constituent minerals, minor element abun-

dances, and oxygen isotope ratios (Ebihara et al., 2011; Nakamura et al., 2011; Tsuchiyama et al., 2011; Yurimoto et al., 2011; Nakamura et al., 2012), which is consistent with the results of remote sensing measurements from the spacecraft (Abe et al., 2006; Okada et al., 2006). The presence of high concentrations of solar wind light noble gases in Itokawa particles indicates the particles have been exposed to solar wind on the surface of asteroid Itokawa (Nagao et al., 2011). Evidence of space weathering, which causes discrepancy of reflectance spectra between asteroids and meteorites (cf., Clark et al., 2002), was found as surface modifications

of Itokawa particles, e.g., Fe-rich nanoparticles in ferromagnesian silicates, which may have formed via in-situ reduction induced by solar wind ion implantation (Noguchi et al., 2011). Thus, preliminary examination confirmed that Itokawa particles are genuinely asteroidal surface materials, which strengthens a link between asteroids and meteorites.

As a part of preliminary examinations, Yurimoto et al. (2011) reported oxygen three-isotope ratios of 28 Itokawa particles measured by secondary ion mass spectrometer (SIMS), which include 33 spot analyses from olivine, low-Ca pyroxene and plagioclase. Oxygen isotope data of the Itokawa particles are distributed slightly above the TF (terrestrial fractionation) line in the oxygen three-isotope diagram, in which $^{18}O/^{16}O$ and $^{17}O/^{16}O$ ratios are converted to $\delta^{18}O$ and $\delta^{17}O$ (per mil deviations from Vienna Standard Mean Ocean Water, VSMOW; Baertschi, 1976). The average $\Delta^{17}O$ value ($= \delta^{17}O - 0.52 \times \delta^{18}O$) of the Itokawa particles is reported to be $+1.39 \pm 0.36‰$ (2SD; standard deviation; Yurimoto et al., 2011), which is within a range of bulk LL4–6 chondrites ($+1.26 \pm 0.24‰$; 2SD; Clayton et al., 1991). The $\delta^{18}O$ values of the Itokawa particles show a variation from $+1.4‰$ to $+8.3‰$ in a mass dependent manner and systematically increase with the order of olivine, low-Ca pyroxene, and plagioclase (Yurimoto et al., 2011). While the $\delta^{18}O$ ranges of low-Ca pyroxene and plagioclase in the Itokawa particles are similar to those in Ensisheim (LL6) analyzed as an analogue material (Yurimoto et al., 2011), $\delta^{18}O$ values of the Itokawa olivines ($+1.4‰$ to $+4.7‰$) are systematically lower than those of Ensisheim olivines ($+3.4‰$ to $+6.1‰$). Moreover, the average $\delta^{18}O$ value of the Itokawa olivines ($+3.0 \pm 2.2‰$; 2SD; $n = 19$) is lower than $\delta^{18}O$ values of olivine in LL5 (Olivenza; $+4.33‰$) and LL6 (St. Séverin; $+4.19‰$) chondrites (Onuma et al., 1972; Clayton, 1993; Yurimoto et al., 2011). Based on these data, Yurimoto et al. (2011) indicated oxygen isotope equilibration temperatures of 600–720 °C, which are lower than those estimated for LL5–6 chondrites (Clayton, 1993). However, given that olivine is the most abundant silicate mineral from Itokawa particles (64 vol%; Tsuchiyama et al., 2011, in press), the average oxygen isotope ratios of Itokawa particles could be significantly fractionated compared to bulk LL4–6 chondrites if olivine data truly represent that of olivine from Itokawa particles. Similar $\delta^{18}O$ variation ($+1.7‰$ to $+8.8‰$) along with positive $\Delta^{17}O$ values ($+1.4 \pm 1.7‰$ on average, 2SD) were observed from oxygen isotope analyses of four Itokawa particles (Nakamura et al., 2012), though the $\delta^{18}O$ values increase from low-Ca pyroxene to olivine, high-Ca pyroxene, and plagioclase unlike the $\delta^{18}O$ data in Yurimoto et al. (2011). While Nakamura et al. (2012) interpreted the $\delta^{18}O$ variation as a result of incomplete oxygen isotope exchange during the thermal metamorphism, Yurimoto et al. (2011) mentioned the possibility that part of the $\delta^{18}O$ variation could be caused by instrumental mass fractionation relating to irregularities of the sample surface owing to the difficulties of sample preparation for small particles. Thus, oxygen isotope ratios of Itokawa particles need to be further examined by carefully controlled SIMS analytical conditions.

Here we report new SIMS oxygen three-isotope analyses of seven Itokawa particles using an IMS-1280 at the University of Wisconsin (WiscSIMS laboratory) with precision and accuracy of 0.3‰ (2SD; Kita et al., 2009). We re-analyze five particles reported by Yurimoto et al. (2011) and two new particles. The total amount and size of collected Itokawa particles are very limited (cf., Tsuchiyama et al., 2011). SIMS analysis is the only technique capable of obtaining the oxygen isotope ratios of the Itokawa particles. Oxygen isotope data available for comparison were obtained from analyses of bulk samples and mineral separates of equilibrated LL chondrites (Clayton et al., 1991; Clayton, 1993), though Ensisheim (LL6) was analyzed using SIMS for comparison (Yurimoto et al., 2011). We analyzed oxygen isotope ratios of two equilibrated or-

dinary chondrites (EOCs), St. Séverin (LL6) and Guareña (H6), for comparison with the Itokawa particles.

2. Analytical procedures

2.1. Sample preparation

Itokawa particles are tiny (typically 10–100 µm in diameter; Tsuchiyama et al., 2011). In the past, custom-made disks with multiple holes, in which small disks containing samples were loaded, were used for SIMS oxygen isotope studies of such tiny samples including particles collected from comet Wild2, interplanetary dust particles, and Itokawa particles (Nakamura et al., 2008; Yurimoto et al., 2011; Nakashima et al., 2011a, 2011b, 2012a, 2012b). As described in Nakashima et al. (2011a), the accuracy of $\delta^{18}O$ measurements using multiple-hole disks is limited to ∼0.7‰ (2SD; 7-hole disks), most likely due to surface topography made by lip of the holes (typically ∼100 µm thick). In order to obtain highly precise and accurate oxygen isotope ratios (better than 0.3‰ in $\delta^{18}O$), we modified the sample mounting method without using a holder with multiple holes; an epoxy disk containing the Itokawa particle is pressed along with standard grains into indium inside of a 25 mm diameter disk so that sample and standard grains are on a single flat surface. Similar indium mounting methods have been applied previously to analyses at WiscSIMS (e.g., Nakashima et al., 2012b) and at other laboratories (e.g., Aubaud et al., 2007; Tenner et al., 2009; Nakamura et al., 2012).

Six of the allocated seven Itokawa particles were individually cast in the center of 6 mm epoxy disks (2 mm thickness; one particle in each disk). All the particles had a polished flat surface. We pressed the 6 mm disks into indium inside of 25 mm diameter aluminum disks (Fig. 1). Two small epoxy blocks (∼2 mm × 2 mm × 2 mm) that contain polished San Carlos olivine standard grains (∼1 mm in diameter) were also pressed into the indium mounts for standardization (mount type A; Table 1). The remaining one particle was prepared using a 6 mm epoxy disk, the same mounting techniques (Nakamura et al., 2011; Noguchi et al., 2011; Nakashima et al. 2011a, 2012a). A San Carlos olivine standard grain (∼500 µm in size) was embedded along with the particle in the 6 mm epoxy disk, so that only the epoxy disk was pressed into an indium mount (mount type B). The flatness of the entire aluminum disk including indium, sample particle, and San Carlos olivine grains was less than 40 µm. Detailed procedures for sample mounting methods are described in the Supplementary information.

We confirmed through the test analyses of indium mounts that (1) two San Carlos olivine grains mounted in the same 6 mm epoxy disk did not show distinguishable $\delta^{18}O$ values and that (2) instrumental bias is within 0.3‰ in $\delta^{18}O$ between San Carlos olivine grains in 6 mm epoxy disks and in epoxy blocks as long as the tilt of San Carlos olivine grains is less than 1 µm across the 1–2 mm diameter (see the Supplementary information). One of two standard grains of which tilt is within 1 µm across the 1 mm diameter was used for standardization in the respective Itokawa sample mounts.

2.2. Electron microscopy

Backscattered electron (BSE) images of the Itokawa particles were obtained after the SIMS analyses using a scanning electron microscope (SEM; Hitachi S3400) at University of Wisconsin, to avoid significant depressions or deformation of epoxy surrounding the Itokawa particles induced by exposure of particles to the electron beam that could cause a significant instrumental mass fractionation in oxygen isotope ratios (Kita et al., 2009). A newly prepared particle was observed briefly using SEM before SIMS
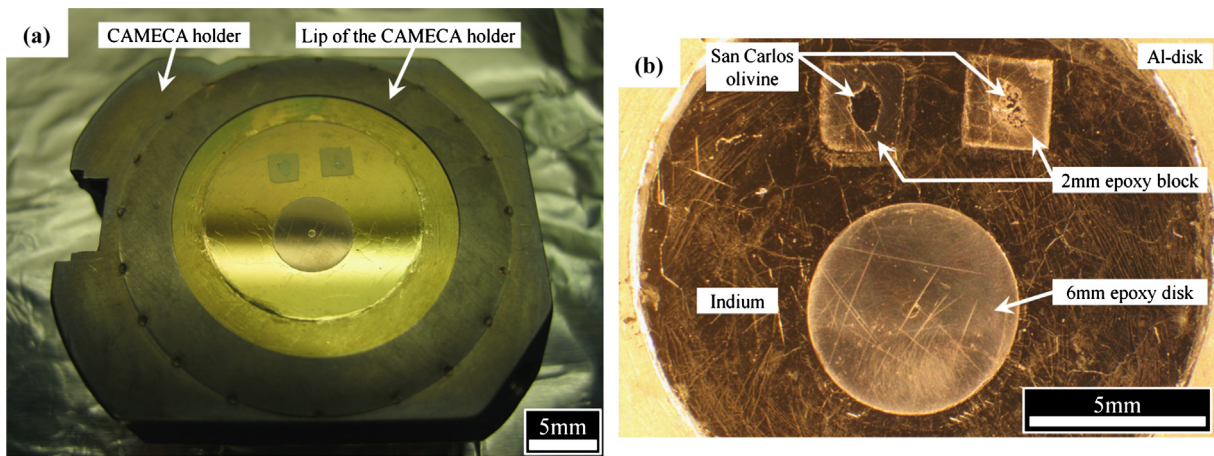
Fig. 1. Photograph of the indium mount (mount type A) in a CAMECA holder (a) and an expanded view of the center of the holder containing Itokawa particle RA-QD02-0017 mounted in an epoxy disk (b).

Table 1
Oxygen isotope ratios of the seven Itokawa particles measured using IMS-1280.

Sample name	Spot#	$\delta^{18}O \pm 2\sigma$ (‰)[a]		$\delta^{17}O \pm 2\sigma$ (‰)[a]		$\Delta^{17}O \pm$ 2SD (‰)		Target[b]	Mount type[c]
RA-QD02-0010	1	4.71	0.36	3.55	0.38	1.11	0.33	Fo_{71}	A
	2	4.80	0.36	3.96	0.38	1.47	0.33	Fo_{71}	
	3	4.73	0.36	4.10	0.38	1.64	0.33	Fo_{71}	
	4	5.89	0.36	4.16	0.38	1.10	0.33	$An_{11}Or_{5.4}$	
	5[d]	5.47	0.36	4.29	0.38	1.45	0.33	$An_{11}Or_{5.4}+Fo_{71}$	
	6	4.30	0.36	3.44	0.38	1.21	0.33	$En_{47}Wo_{44}$	
RA-QD02-0014	1	4.70	0.32	3.59	0.56	1.14	0.50	Fo_{72}	A
	2	3.91	0.32	3.46	0.56	1.42	0.50	Fo_{72}	
RA-QD02-0017	1	4.05	0.34	3.45	0.46	1.35	0.46	Fo_{71}	A
	2	4.09	0.34	3.62	0.46	1.49	0.46	Fo_{71}	
RA-QD02-0023	1	4.64	0.36	4.05	0.32	1.64	0.21	Fo_{71}	A
	2	4.62	0.36	3.72	0.32	1.32	0.21	Fo_{71}	
	3	4.25	0.36	3.74	0.32	1.53	0.21	Fo_{71}	
RA-QD02-0030	1	5.09	0.34	4.10	0.41	1.45	0.41	$En_{74}Wo_{1.8}$	A
	2	5.19	0.34	3.68	0.41	0.98	0.41	$En_{74}Wo_{1.8}$	
	3	4.91	0.34	3.68	0.41	1.12	0.41	$En_{74}Wo_{1.8}$	
	4	4.21	0.34	3.48	0.41	1.29	0.41	Fo_{71}	
	5	4.52	0.34	3.72	0.41	1.37	0.41	Fo_{71}	
RA-QD02-0047	1	4.89	0.35	3.92	0.43	1.38	0.39	Fo_{71}	A
	2	5.12	0.35	4.01	0.43	1.35	0.39	Fo_{71}	
RA-QD02-0196[e]	1	5.01	0.15	3.83	0.56	1.22	0.53	Fo_{71}	B
	2	4.94	0.15	4.09	0.56	1.52	0.53	Fo_{71}	
Average (olivine; $n = 16$)[f]		4.57	0.74	3.77	0.46	1.39	0.31		
Average (low-Ca pyroxene; $n = 3$)[f]		5.07	0.28	3.82	0.49	1.18	0.49		
Average ($n = 22$)						1.34	0.36		
Bulk (estimated)[g]		4.81	0.58	3.81	0.41	1.31	0.25		

[a] Confidence errors (95%; 2σ) associated with δ-values include external reproducibility and potential instrumental mass bias that was observed through the test analyses.
[b] Average (or representative) chemical compositions are shown (http://hayabusaao.isas.jaxa.jp/samples; Nakamura et al., 2011).
[c] Mount type A: San Carlos olivine standard grains and 6 mm epoxy disk containing an Itokawa particle are separately embedded in an indium mount. Mount type B: a 6 mm epoxy disk containing a San Carlos olivine grain and Itokawa particle is embedded singularly in an indium mount.
[d] Spot 5 in the Itokawa particle 0010 is a mixed phase between plagioclase and olivine with an ol/pl ratio of 1/9.
[e] The uncertainties associated with δ-values are two standard deviation (2SD).
[f] The uncertainties associated with average values are two standard deviation (2SD).
[g] The uncertainties associated with the estimated bulk oxygen isotope ratios include 2SD for average oxygen isotope ratios of respective mineral phases and error of volume fractions (10%; Tsuchiyama et al., in press).

analyses. Major elemental compositions of the new particle were obtained by semi-quantitative analyses using an energy-dispersive X-ray spectrometer (EDS), which were calibrated by comparison of elemental compositions of St. Séverin (LL6) obtained by EDS with those by electron microprobe.

For the oxygen three-isotope analysis of EOCs, we prepared a thin section of Guareña and one thick section of St. Séverin. Secondary electron (SE) and BSE images of silicate minerals (olivine, low-Ca and high-Ca pyroxene, and plagioclase) used for SIMS anal-

yses in the two meteorites were obtained using SEM and mineral identification was verified with EDS.

Major elemental compositions of the SIMS-analyzed minerals (near the SIMS pits) in the two EOCs were measured with an electron probe microanalyzer (EPMA; CAMECA SX-51) equipped with five wavelength-dispersive X-ray spectrometers (WDS) at University of Wisconsin. WDS quantitative chemical analyses were performed at 15 kV accelerating voltage and 10–20 nA beam current with a focused beam of approximately 1 μm in diameter (cf., Tenner et al., 2013).

2.3. Oxygen isotope analyses

Oxygen isotope ratios of the Itokawa particles and two EOCs were analyzed with the CAMECA IMS-1280 ion microprobe at the WiscSIMS laboratory (Kita et al., 2009). The analytical conditions and measurement procedures were similar to those in Kita et al. (2010). A focused Cs^+ primary beam was set to $\sim$10 μm × 12 μm and intensity of $\sim$3 nA. The $^{16}O^-$, $^{17}O^-$, and $^{18}O^-$ ions were detected simultaneously. Secondary ions of $^{16}O^-$ and $^{18}O^-$ were detected using two Faraday cups (FC) on the multiple collector trolleys, respectively, with mass resolving power (MRP) of $\sim$2200 (at 10% height). The FC at the ion optical axis and fixed position (mono collection detector) was used for detection of $^{17}O^-$ with MRP $\sim$5000 (at 10% height). Intensities of $^{16}O^-$ were $\sim$3 × 10^9 cps. The baselines of the FCs were measured during the presputtering (100s) in respective analyses and used for data correction. The contribution of the tailing of $^{16}O^1H^-$ interference to $^{17}O^-$ signal was corrected by the method described in Heck et al. (2010), though the contribution was negligibly small ($< 0.05‰$). Seven Itokawa particles and two EOCs were analyzed in three separate sessions (see the Supplementary Tables A1 and A2). After SIMS analyses, all SIMS pits were inspected using a SEM to confirm the analyzed positions.

Two to six analyses were performed for each Itokawa particle, bracketed by eight to nine analyses (four or five analyses before and after the unknown sample analyses) on the San Carlos olivine standard grains mounted in the same disks (Fig. 1). The external reproducibility of the running standards was 0.11–0.19‰ for $\delta^{18}O$, 0.28–0.56‰ for $\delta^{17}O$, and 0.21–0.53‰ for $\Delta^{17}O$ (2SD), which were assigned as analytical uncertainties of unknown samples (see Kita et al. 2009, 2010 for detailed explanations). An instrumental bias of as large as 0.3‰ in $\delta^{18}O$ was observed through the test analyses (Supplementary information) and is propagated as uncertainty (0.15‰ in $\delta^{17}O$) to those of δ-values of individual spot analyses in the mounts where the Itokawa particles and San Carlos olivine standard grains were not embedded in the same 6 mm epoxy disks (mount type A; Table 1). However, the instrumental bias is mass dependent and does not affect $\Delta^{17}O$.

For the EOC analysis session, eight to fourteen sets of unknown sample analyses were made, bracketed by eight sets of analyses on the running standard (San Carlos olivine). External reproducibility of the running standard was 0.23–0.62‰ for $\delta^{18}O$, 0.36–0.70‰ for $\delta^{17}O$, and 0.28–0.62‰ for $\Delta^{17}O$ (2SD). A drift of oxygen isotope ratios happened during San Carlos olivine standard analyses ($\sim$0.6‰ in $\delta^{18}O$) that bracketed the analyses of plagioclase in St. Séverin, which resulted in relatively large analytical uncertainty of 0.62‰ in $\delta^{18}O$ for the St. Séverin plagioclase data (Supplementary Table A2). Drift was less than 0.3‰ for other sample analyses. While most analyses were done within a few-mm radius of the center of the sample mounts, analyses of relatively minor mineral phases were done within 6 mm-radius of the center in which instrumental mass fractionation due to stage positions is insignificant (Kita et al., 2009).

We analyzed two olivine (Fo_{100} and Fo_{60}), four low-Ca pyroxene (En_{97}, En_{89}, En_{85}, and En_{70}), diopside, and five feldspar (An_{13}, An_{22}, $An_{35–38}$, Ab_{100}, and Or_{100}) standards (Valley and Kita, 2009; Kita et al., 2010) in the same sessions for correction of instrumental bias of olivine, pyroxene, and plagioclase (Supplementary Table A3).

3. Sample description

3.1. Itokawa particles

Seven Itokawa particles (Fig. 2) were allocated by JAXA for the oxygen isotope study, which include five particles analyzed in

Yurimoto et al. (2011) and two new particles, RA-QD02-0017 and -0196. Exposed surfaces of five particles (RA-QD02-0014, -0017, -0023, -0047, and -0196) are dominated by olivine, while those of the other two particles (RA-QD02-0010 and -0030) are composed of multiple minerals of olivine, low-Ca and high-Ca pyroxene, and plagioclase (Fig. 2). Opaque minerals such as chromite, kamacite, taenite, and troilite occur as accessory phases. Fa contents in olivine (27.9–29.3), Fs and Wo contents in low-Ca and high-Ca pyroxene ($Fs_{27.9–29.3}Wo_{1.3–1.8}$ and $Fs_{8.7–9.7}Wo_{40.5–43.8}$), and Ab and Or contents in plagioclase ($Ab_{83.2–84.1}Or_{5.4–5.5}$) are within the compositional ranges of olivine, pyroxene, and plagioclase in equilibrated LL chondrites (Brearley and Jones, 1998; Nakamura et al., 2011; http://hayabusaao.isas.jaxa.jp/samples). Some Itokawa particles reported in Nakamura et al. (2011) show lamellae in low-Ca pyroxene or contain glassy phases that are characteristic for poorly equilibrated Itokawa particles. Some olivine particles are slightly lower in Fa contents, implying weakly metamorphosed material, classified as petrologic type 4 (Nakamura et al., 2011). The seven particles we studied do not show any of these characteristics (Fig. 2), indicating that they are highly equilibrated particles.

3.2. Two equilibrated ordinary chondrites

Two EOCs, St. Séverin (LL6) and Guareña (H6) were selected in the present study. Clayton et al. (1991) reported the bulk oxygen isotope ratios, which are within the range of LL and H chondrites, respectively. We selected eight to nine grains of four major constituent mineral phases (olivine, low-Ca and high-Ca pyroxene, and plagioclase) for oxygen isotope analyses in the two meteorites, which are larger than SIMS spot size ($\geqslant$15 μm; Fig. 3). In type 6 chondrites, outlines of chondrules are not easily identified, though sometime they are recognized with low magnification imaging using SEM. In order to obtain a representative dataset, we avoided placing analyses in the interior of chondrules, though some analyses might be taken from unrecognized chondrule interiors.

Olivine and low-Ca pyroxene, which constitute $\sim$60–70 vol% of EOCs (McSween et al., 1991; Dunn et al., 2010), have grain sizes of 50–200 μm or larger (longest diameter; Fig. 3). High-Ca pyroxene and plagioclase are relatively minor, and the grains large enough for SIMS analyses ($\geqslant$30 μm) were not common.

Chemical compositions of the mineral phases analyzed for oxygen isotope ratios are summarized in Supplementary Tables A4–A5. Major-element compositions of olivine and low-Ca and high-Ca pyroxene are homogeneous and within the compositional ranges for LL and H chondrites, respectively (Brearley and Jones, 1998). Chemical compositions of plagioclase are less homogeneous, though within the range of equilibrated ordinary chondrites (Brearley and Jones, 1998).

4. Results of oxygen isotope analyses

4.1. Oxygen isotope ratios of the seven Itokawa particles

We made a total of 22 spot analyses in seven Itokawa particles, which include 16 spots from olivine (2–3 spots in individual particles), 3 spots from low-Ca pyroxene, 1 spot from high-Ca pyroxene, and 2 spots from plagioclase. Several pits overlapped cracks (e.g., Fig. 2c), though hydride correction to $^{17}O^-$ was negligibly small ($\sim$0.01‰). A summary of the 22 spot analyses taken from all seven particles is shown in Table 1; a complete data table is given in the Supplementary Table A1.

The oxygen isotope data are distributed around the Equilibrated Chondrite Line (ECL; defined by bulk sample analyses of EOCs; Clayton et al., 1991) and above the terrestrial fractionation (TF) line with a variation from +3.9‰ to +5.9‰ in $\delta^{18}O$ (Fig. 4a). The $\Delta^{17}O$ values range from +1.0‰ to +1.6‰, which are reproducible
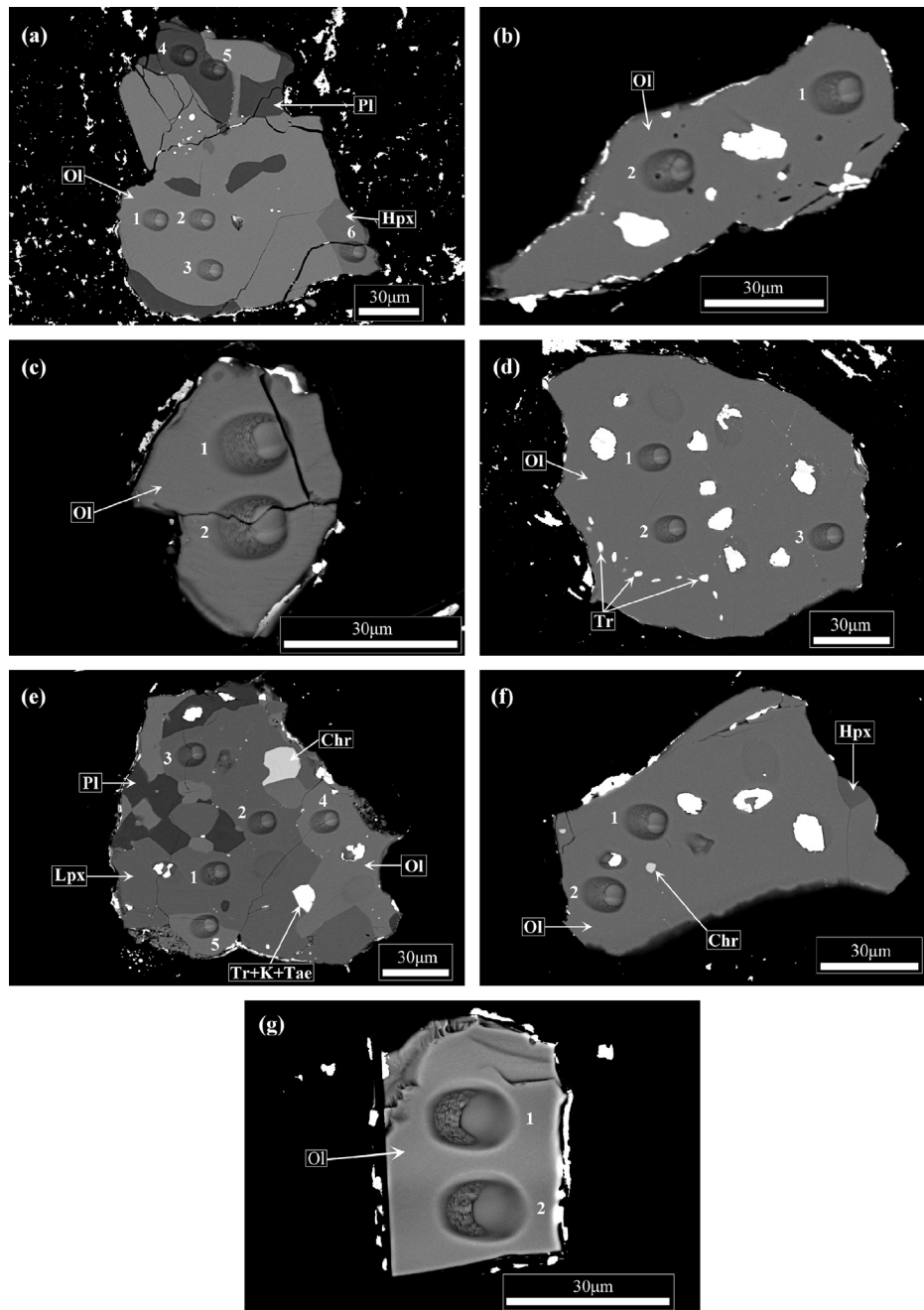
Fig. 2. BSE images of the Itokawa particles after oxygen isotope analyses; (a) RA-QD02-0010, (b) RA-QD02-0014, (c) RA-QD02-0017, (d) RA-QD02-0023, (e) RA-QD02-0030, (f) RA-QD02-0047, and (g) RA-QD02-0196. Numbers near the SIMS pits indicate spot numbers of SIMS analysis, which correspond to spot numbers in Table 1. White materials around and on the particles are remnant of Au-coating. Abbreviations: Ol, olivine; Pl, plagioclase; Hpx, high-Ca pyroxene; Lpx, low-Ca pyroxene; Tr, troilite; Chr, chromite; K, kamacite; Tae, taenite.
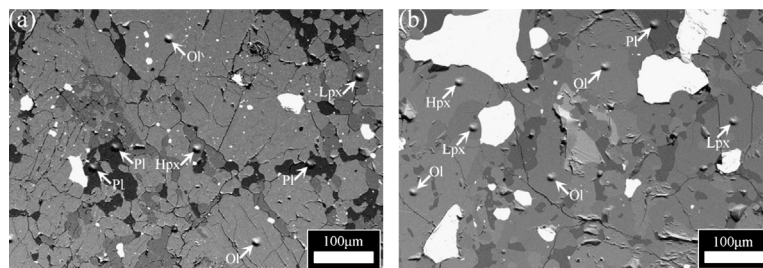
Fig. 3. BSE images of the two EOCs; (a) St. Séverin (LL6) and (b) Guareña (H6). SIMS pits are indicated by white arrows. Abbreviations: Ol, olivine; Lpx, low-Ca pyroxene; Hpx, high-Ca pyroxene; Pl, plagioclase.
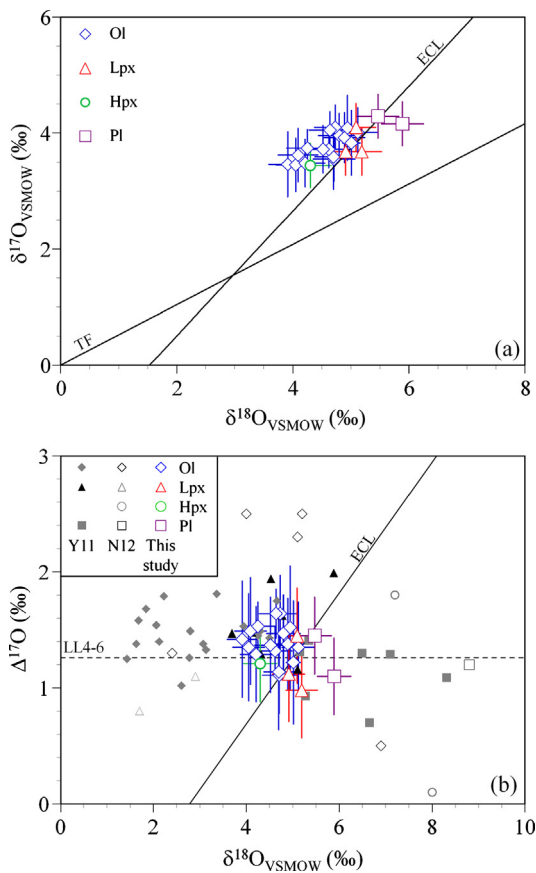
Fig. 4. Oxygen three-isotope ratios of the seven Itokawa particles (a) and comparisons between $\Delta^{17}O$ values and $\delta^{18}O$ values of the Itokawa particles in the present study and previous studies of Yurimoto et al. (2011) and Nakamura et al. (2012) (b). TF and ECL represent the terrestrial fractionation line and the equilibrated chondrite line (Clayton et al., 1991). The dashed line labeled LL4–6 is defined by average $\Delta^{17}O$ values of equilibrated LL chondrite data (Clayton et al., 1991). Literature data (Y11 and N12) are from Yurimoto et al. (2011) and Nakamura et al. (2012). Abbreviations: Ol, olivine; Lpx, low-Ca pyroxene; Hpx, high-Ca pyroxene; Pl, plagioclase.

within the analytical uncertainty. The average and 2SD of $\Delta^{17}O$ values of 22 spot analyses are $+1.34 \pm 0.36‰$, consistent with the results of Yurimoto et al. (2011) ($+1.39 \pm 0.36‰$; 2SD) and Nakamura et al. (2012) ($+1.4 \pm 1.7‰$; 2SD). In contrast, the $\delta^{18}O$ values in the present study are tightly distributed compared to the published $\delta^{18}O$ values ($+1.4‰$ to $+8.8‰$; Yurimoto et al., 2011; Nakamura et al., 2012) (Fig. 4b). Isotope data from olivine in the seven Itokawa particles are from $+3.9‰$ to $+5.1‰$ in $\delta^{18}O$, which are systematically higher by an average of $+4.57 \pm 0.74‰$ (2SD) than those ($+1.4‰$ to $+4.7‰$) in Yurimoto et al. (2011) (Fig. 4b). While it was reported that olivine in the two particles of RA-QD02-0010 and -0030 showed $\delta^{18}O$ values of $+2.8‰$ (Yurimoto et al., 2011), our analyses obtained $\delta^{18}O$ values of $\sim +4.8‰$ and $\sim +4.4‰$ from olivine in the same two particles (Table 1). Three data from low-Ca pyroxene in the particle RA-QD02-0030 (Fig. 2e) have $\delta^{18}O$ values from $+4.9‰$ to $+5.2‰$, while two data from olivine in the same particle have lower $\delta^{18}O$ values of $+4.2‰$ and $+4.5‰$. In RA-QD02-0010, one spot in high-Ca pyroxene and two spots in plagioclase were analyzed along with three spots in olivine (Fig. 2a). High-Ca pyroxene shows $\delta^{18}O$ value of $+4.3‰$, which is lower than those of olivine ($+4.7‰$ to $+4.8‰$; $n = 3$) and plagioclase ($+5.5‰$ and $+5.9‰$) in the same particle. One of the two pits on plagioclase ($\delta^{18}O$ of $+5.5‰$; spot 5 in Fig. 2a) overlapped neighboring olivine slightly (~ 10 vol% of the SIMS pit). Assuming that the neighboring olivine has $\delta^{18}O$ value of $+4.8‰$ which is an average $\delta^{18}O$ value of the three spots in the same particle,
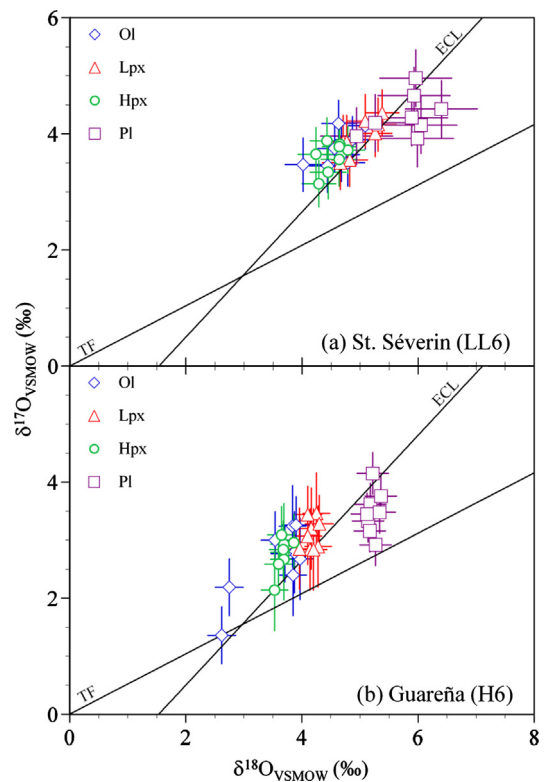

Fig. 5. Oxygen three-isotope ratios of St. Séverin (a) and Guareña (b). TF and ECL represent the terrestrial fractionation line and the equilibrated chondrite line (Clayton et al., 1991). Abbreviations: Ol, olivine; Lpx, low-Ca pyroxene; Hpx, high-Ca pyroxene; Pl, plagioclase.

the $\delta^{18}O$ value of pure plagioclase is estimated to be $+5.6‰$. The estimated $\delta^{18}O$ value is not used for the later discussion because volume fraction and $\delta^{18}O$ value of neighboring olivine cannot be evaluated precisely.

4.2. Oxygen isotope ratios of the two equilibrated ordinary chondrites

A total of 32–34 spot analyses were made in each of St. Séverin and Guareña, respectively, which include 8–9 spots from four minerals, olivine, low-Ca pyroxene, high-Ca pyroxene, and plagioclase. A summary of all analyses from the two meteorites is shown in Supplementary Tables A4–A5.

Most oxygen isotope data of the two EOCs are distributed along the slope $= 0.5$ lines above the TF line (Fig. 5). The average $\Delta^{17}O$ values and 2SD for St. Séverin are estimated as $+1.31 \pm 0.49‰$ ($n = 32$) (Table 2), which are consistent with the average $\Delta^{17}O$ value of bulk LL4–6 chondrites ($+1.26 \pm 0.24‰$; 2SD; Clayton et al., 1991) within the analytical uncertainties as well as SIMS data of chromites from St. Séverin ($+1.24 \pm 0.10‰$; 2SE; Heck et al., 2010). The average $\Delta^{17}O$ value and 2SD for Guareña is $+0.83 \pm 0.64‰$ ($n = 34$), which is consistent with that of bulk H4–6 chondrites ($\Delta^{17}O = +0.73 \pm 0.18‰$; 2SD; Clayton et al., 1991) within the analytical uncertainties. The $\delta^{18}O$ values of Guareña cluster for each mineral phase and increase in $\delta^{18}O$ from high-Ca pyroxene to olivine, low-Ca pyroxene, and plagioclase (Fig. 5b). The average $\delta^{18}O$ values of respective mineral phases increase in the order of high-Ca pyroxene, olivine, low-Ca pyroxene, and plagioclase (Table 2). The data from two spots on Guareña, which are from a single olivine grain, are lower in $\delta^{18}O$ compared to the cluster of Guareña olivines, though the texture and chemical compositions are similar to those of other olivine grains in Guareña (Supplementary Table A5). A similar systematic $\delta^{18}O$ increase is also seen for St. Séverin (Fig. 5a and Table 2). The $\delta^{18}O$ values of mineral sepa-

Table 2
Averaged oxygen isotope ratios of four mineral phases and estimated bulk oxygen isotope ratios in two EOCs.

Meteorite		$\delta^{18}O \pm 2SD$ (‰)		$\delta^{17}O \pm 2SD$ (‰)		$\Delta^{17}O \pm 2SD$ (‰)	
St. Séverin (LL6)	Olivine ($n = 8$)	4.63	0.64	3.75	0.58	1.34	0.46
	Low-Ca pyroxene ($n = 8$)	5.00	0.59	3.94	0.62	1.34	0.40
	High-Ca pyroxene ($n = 8$)	4.52	0.39	3.61	0.51	1.26	0.45
	Plagioclase ($n = 8$)	5.80	0.94	4.32	0.70	1.30	0.68
	Grand average ($n = 32$)					1.31	0.49
	Estimated bulk isotope ratios[a]	4.83	0.53	3.84	0.46	1.33	0.31
Guareña (H6)	Olivine ($n = 9$)	3.56	1.03	2.63	1.18	0.78	0.82
	Low-Ca pyroxene ($n = 9$)	4.16	0.22	3.10	0.51	0.93	0.50
	High-Ca pyroxene ($n = 8$)	3.67	0.19	2.75	0.59	0.84	0.53
	Plagioclase ($n = 8$)	5.23	0.18	3.48	0.75	0.77	0.74
	Grand average ($n = 34$)					0.83	0.64
	Estimated bulk isotope ratios[a]	3.96	0.58	2.90	0.63	0.84	0.43

[a] The uncertainty associated with the estimated bulk isotope ratios include 2SD for the average isotope ratios of respective mineral phases and 2SD for the volume fractions of four mineral phases (Dunn et al., 2010).
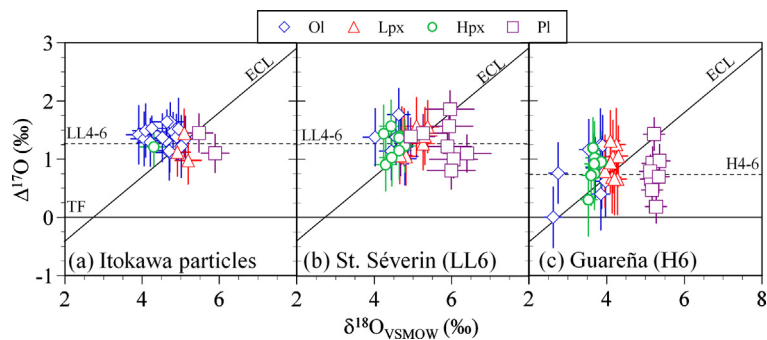

Fig. 6. Comparisons between $\Delta^{17}O$ values and $\delta^{18}O$ values of the Itokawa particles (a), St. Séverin (b), and Guareña (c). The dashed lines labeled LL4–6 and H4–6 is defined by average $\Delta^{17}O$ values of equilibrated LL and H chondrite data (Clayton et al., 1991). ECL represents equilibrated chondrite line (Clayton et al., 1991). Abbreviations: Ol, olivine; Lpx, low-Ca pyroxene; Hpx, high-Ca pyroxene; Pl, plagioclase.

rates of olivine (+4.19‰), pyroxene (mostly low-Ca; +4.99‰), and plagioclase (+6.33‰) from St. Séverin (Clayton, 1993) are generally similar to those of the average $\delta^{18}O$ values of corresponding mineral phases in the present study (Table 2).

5. Discussion

5.1. Oxygen isotope systematics of Itokawa particles and equilibrated ordinary chondrites

Oxygen isotope ratios of EOCs are characterized by positive $\Delta^{17}O$ values (Clayton et al. 1976, 1991). Three types of EOCs (H, L, and LL) have distinct $\Delta^{17}O$ values, and equilibrated LL chondrites have the highest $\Delta^{17}O$ values of +1.26‰ on average. It was reported that Itokawa particles have similar $\Delta^{17}O$ values from the preliminary isotopic examinations (+1.34 ± 0.36‰; 2SD; Yurimoto et al., 2011; +1.4 ± 1.7‰; 2SD; Nakamura et al., 2012; Fig. 4b), which we further confirmed with the higher precision analyses. Along with results of petrological and mineralogical examination (see Introduction), a close affinity of Itokawa particles to equilibrated LL chondrites is suggested. Here we further compare oxygen isotope systematics of Itokawa particles with those of St. Séverin (LL6) and Guareña (H6) (Fig. 6), of which all data obtained by SIMS analyses that enable us to observe a variation in oxygen isotope ratios in grain by grain at the μm-scale.

As shown in Fig. 6, the oxygen isotope data are distributed parallel to the TF line showing systematic increases of $\delta^{18}O$ with the order of high-Ca pyroxene, olivine, low-Ca pyroxene, and plagioclase (Table 2). Although the $\delta^{18}O$ value of high-Ca pyroxene is within the $\delta^{18}O$ range of olivine for Itokawa particles (Fig. 6a), the $\delta^{18}O$ value of high-Ca pyroxene is lower than those of olivine in the same particle (RA-QD02-0010; Table 1). The $\Delta^{17}O$ values of the seven Itokawa particles are similar to those of the LL chondrite,

St. Séverin, but significantly higher than those of the H chondrite, Guareña (Fig. 6). This is consistent with similarities of chemical composition between the Itokawa particles and LL5–6 chondrites (Nakamura et al., 2011).

The four mineral phases that we analyzed are major constituents of the Itokawa particles with volume fractions of 0.65 for olivine, 0.19 for low-Ca pyroxene, 0.03 for high-Ca pyroxene, and 0.11 for plagioclase (Tsuchiyama et al., in press). Based on the volume fractions and average $\delta^{18}O$ values of respective mineral phases (Table 1), the bulk $\delta^{18}O$ value of the Itokawa particles is calculated as +4.8‰ (concentrations of oxygen atoms in the four minerals are taken into account), which is within the $\delta^{18}O$ range of bulk LL5 and LL6 chondrites (+5.02 ± 0.42‰ and +4.92 ± 0.34‰; 2SD; Clayton et al., 1991). The bulk $\delta^{18}O$ values of the two EOCs are estimated in a similar fashion (volume fraction data are from Dunn et al., 2010); +4.8‰ for St. Séverin and +4.0‰ for Guareña (Table 2), which are in good agreement with those obtained by bulk sample analyses (Clayton et al., 1991). Although the number of analyses is limited ($n = 22$) and only highly equilibrated particles were analyzed, the Itokawa particles resemble equilibrated LL chondrites in terms of oxygen isotope systematics based on in-situ multiple spot analyses for $\Delta^{17}O$ and estimated bulk $\delta^{18}O$ values. Thus, our new oxygen isotope data strengthen link between asteroid Itokawa and equilibrated LL chondrites that fell to Earth, which has been suggested in the preliminary examination.

5.2. Thermal history and oxygen isotope ratios

Homogeneous chemical compositions of minerals in Itokawa particles have been interpreted as a result of thermal metamorphism in the LL chondrite parent asteroid (Nakamura et al., 2011). If the oxygen-bearing phases in Itokawa preserved oxygen isotope equilibrium from the peak metamorphic temperatures,

oxygen isotope ratios of four main silicate minerals should be mass-dependently fractionated with increasing $\delta^{18}O$ in the order of olivine, high-Ca pyroxene, low-Ca pyroxene, and plagioclase (cf., Clayton and Kieffer, 1991; Rosenbaum et al., 1994; Eiler, 2001). The inter-mineral $\delta^{18}O$ fractionations are larger at lower temperatures. Mineral separates from type 4–6 EOCs show a systematic increase of $\delta^{18}O$; $\delta^{18}O$ (Ol) $< \delta^{18}O$ (Lpx) $< \delta^{18}O$ (Pl), and the estimated temperatures are consistent among the three mineral pairs ($\sim$600–1000 °C; Clayton, 1993). Here, we examine inter-mineral $\delta^{18}O$ fractionations among four minerals from Itokawa particles and two EOCs, based on equilibrium isotope fractionations of two mineral pairs estimated from experimental calibrations of the isotope thermometers. We used calibration data for oxygen isotope fractionation among olivine, high-Ca pyroxene, and plagioclase from Clayton and Kieffer (1991) and those for low-Ca pyroxene-olivine from Rosenbaum et al. (1994).

Among these mineral pairs, we first look at temperatures estimated from high-Ca pyroxene and plagioclase, because their grain sizes become larger with petrologic type (cf., Brearley and Jones, 1998; Huss et al., 2006) due to crystal growth as metamorphic minerals during thermal metamorphism (e.g., Kovach and Jones, 2010). For Itokawa particle RA-QD02-0010, the fractionation of $\delta^{18}O$ values between plagioclase and high-Ca pyroxene is 1.6 ± 0.5‰, corresponding to the temperature of 750 ± 230 °C. Similar differences in the average $\delta^{18}O$ values of two minerals, 1.3 ± 1.0‰ and 1.6 ± 0.3‰, are obtained from St. Séverin and Guareña, respectively, corresponding to the estimated temperatures of 870^{+1120}_{-530} °C and 770 ± 100 °C. These temperatures are similar to those estimated from mineral chemistry (e.g., Kessel et al., 2007; Nakamura et al., 2011). Plagioclase crystallized from chondrule glass at peak metamorphic temperatures that are estimated as 725–742 °C for H6 and 800 °C for LL6 based on Si–Al ordering on the tetrahedral site of plagioclase, which may be preserved in a dry environment (Nakamuta and Motomura, 1999). This estimate is comparable with the apparent temperatures estimated from $\delta^{18}O$ fractionation between plagioclase and high-Ca pyroxene.

However, we found some problems in applying oxygen thermometry for other mineral pairs for both Itokawa particles and two EOC samples. First, the $\delta^{18}O$ values of high-Ca pyroxene and olivine are reversed; those of high-Ca pyroxene are lower than those of olivine (Fig. 6 and Table 2), indicating that oxygen isotopes between olivine and high-Ca pyroxene are not in equilibrium. Second, the difference between the average $\delta^{18}O$ values of low-Ca pyroxene and olivine are small ($\leqslant 1$‰), which resulted in unrealistic high nominal temperature estimates (Fig. 7) that exceed peak metamorphic temperatures ($\sim$800–1000 °C) of EOCs (Scott and Krot, 2003; Huss et al., 2006) and dry melting temperature of albitic plagioclase. We also infer that $\delta^{18}O$ values of olivine and low-Ca pyroxene in the Itokawa particles and two EOCs do not represent equilibrium. Oxygen isotope ratios of olivine in Itokawa particles as well as those of olivine grains in two type 6 chondrites show a significant variation (0.6–1‰ in 2SD) more than the reproducibility of the bracketing olivine standard (0.15–0.3‰). Thus, oxygen isotope ratios in olivine in these samples might be internally heterogeneous. The inconsistency of oxygen isotope fractionation between mineral pairs of high-Ca pyroxene-plagioclase and low-Ca pyroxene-olivine are presented in a concordance diagram (Fig. 7), in which the average $\delta^{18}O$ fractionations of these two-mineral pairs are compared; data from Itokawa particles and the two EOCs plot off systematically the concordant line, though with large uncertainty. We note that difference in $\delta^{18}O$ values between olivine and low-Ca pyroxene observed from Itokawa particles and two type 6 chondrites in this study ($\leqslant 1$‰) are in agreement with those of type 5–6 chondrites (0.7–0.9‰) by Clayton (1993) if the uncertainties of SIMS data are taken into consideration. Clayton (1993) estimated olivine-pyroxene temperatures to be 730–870 °C
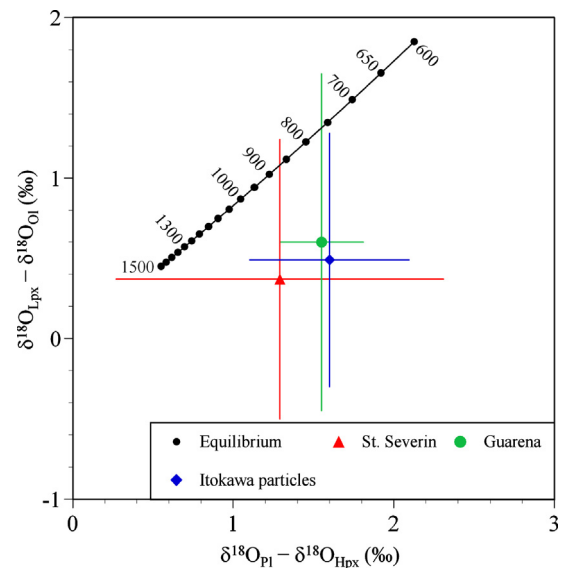

Fig. 7. Concordance diagram of Lpx-Ol and Pl-Hpx for the Itokawa particles and two EOCs. Oxygen isotope equilibrium fractionation data are calculated in 50 °C increments from 600 °C to 1500 °C based on the data from Rosenbaum et al. (1994) for a pair of low-Ca pyroxene and olivine and from Clayton and Kieffer (1991) for a pair of plagioclase and high-Ca pyroxene. Plagioclase is assumed to be $An_{11}Ab_{89}$. Numbers near the data points are temperatures at °C. The error bars are calculated from 2SD associated with the average $\delta^{18}O$ values of respective mineral phases. Measured $\delta^{18}O$ data of the seven Itokawa particles and two EOCs do not plot along the concordance line, which means the apparent temperatures estimated from the two pairs (Lpx–Ol and Pl–Hpx) do not match each other.

by applying diopside-olivine calibration (Clayton and Kieffer, 1991) that gives $\sim$300 °C lower temperatures than enstatite-olivine calibration by Rosenbaum et al. (1994).

It has been proposed that type 6 chondrites experienced metamorphic temperatures exceeding $\sim$800 °C for a longer time ($\sim$10 Ma; cf., Amelin et al., 2005; Huss et al., 2006; Kleine et al., 2008). In the absence of recrystallization and fast pathways of exchange, measured mineral fractionations and apparent temperatures reflect the diffusive exchange of each mineral with the grain boundaries during the cooling of the system (Eiler et al. 1992, 1993; Valley, 2001). One way to approximate this exchange is with the Dodson equation for closure temperatures (Dodson, 1973). Closure temperature for oxygen isotope exchange is an indication of each mineral's ability to exchange with adjacent mineral grains that are open to diffusion. Closure temperature varies as a function of diffusion coefficient (presumably dry) and grain sizes of the minerals, and cooling rate; larger grain size and higher cooling rate give higher closure temperatures (Dodson, 1973). While grain sizes of olivine and low-Ca pyroxene in the Itokawa particles and the two EOCs are typically 100 μm in radii (Figs. 2 and 3), those of plagioclase and high-Ca pyroxene are typically 10 μm in radii (see also Huss et al., 2006; Brearley and Jones, 1998). As shown in Table 3, albite has the lowest closure temperatures (T_C in Table 3) at any cooling rate from 1000 °C/Myr to 1 °C/Myr (cf., Taylor et al., 1987). In a two-mineral diffusive system, this would mean that apparent temperatures estimated from $\delta^{18}O$ fractionation between plagioclase and high-Ca pyroxene actually record the closure temperature of the mineral with the second lowest closure temperature, high-Ca pyroxene (see Valley, 2001). Olivine and low-Ca pyroxene have similar closure temperatures that are $\sim$100 °C higher than high-Ca pyroxene supporting the two-mineral approximation for these rocks. If the Itokawa particles and the two type-6 chondrites (St. Séverin and Guareña) experienced metamorphic temperatures exceeding 800 °C, plagioclase and high-Ca pyroxene might have exchanged oxygen isotopes to $\delta^{18}O$ values down to $\sim$ 800 °C during cool-

Table 3
Closure temperatures (T_C) for olivine, pyroxene, and albite at various cooling rates[a].

	D_0 (cm^2/s)	E (KJ/mol)	A	T_C (°C) 1 °C/Myr	10 °C/Myr	10^2 °C/Myr	10^3 °C/Myr	Reference
Olivine ($r = 100$ μm)	6.72×10^{-6}	318	55	800	869	948	1038	Gerard and Jaoul (1989)
Pyroxene ($r = 100$ μm)	4.3	457	55	855	909	967	1032	Ryerson and McKeegan (1994)
Pyroxene ($r = 10$ μm)	4.3	457	55	762	806	855	909	Ryerson and McKeegan (1994)
Albite ($r = 10$ μm)	2×10^{-16}	90	55	388	481	603	767	Matthews et al. (1994)

D_0 = pre-exponential factor in oxygen diffusion Arrhenius relation.
E = activation energy for diffusion of oxygen.
A = diffusional anisotropy parameter for sphere; here we assumed that the four mineral phases are spherical in shape.
[a] Pyroxene with 100 μm-radius is assumed to be low-Ca pyroxene and that with 10 μm-radius to be high-Ca pyroxene.

ing and retrograde metamorphism. Under these conditions, the mass-dependent fractionation of oxygen isotope ratios between plagioclase and high-Ca pyroxene at metamorphic temperatures results in lower δ^{18}O for high-Ca pyroxene and higher δ^{18}O for plagioclase (Clayton and Kieffer, 1991). Thus the apparent reversal of δ^{18}O fractionation between olivine and high-Ca pyroxene is the result of sub-solidus heating of an isotopically unequilibrated mineral pair.

6. Conclusions

We analyzed oxygen three-isotope ratios of four minerals (olivine, low-Ca and high-Ca pyroxene, and plagioclase) in seven Itokawa particles that were pressed into 25 mm flat indium mounts in order to minimize topography effects on instrumental mass fractionation. Two EOCs, St. Séverin (LL6) and Guareña (H6) were analyzed for oxygen three-isotope ratios for comparison. Oxygen isotope data of the seven Itokawa particles are tightly clustered near the intersection of the equilibrated LL chondrite line and the ECL (Clayton et al., 1991), in contrast to the earlier data, which are more widely dispersed (Yurimoto et al., 2011; Nakamura et al., 2012). The Δ^{17}O values of the seven Itokawa particles are nearly identical with the average value of $+1.34 \pm 0.36$‰ (2SD), which is consistent with those of St. Séverin analyzed in this study ($+1.31 \pm 0.49$‰) and Itokawa particles reported in Yurimoto et al. (2011) and Nakamura et al. (2012), but distinct from those of Guareña ($+0.83 \pm 0.64$‰). The estimated bulk δ^{18}O value of the Itokawa particles is $+4.8$‰, which is within the δ^{18}O range of bulk LL5 and LL6 chondrites (Clayton et al., 1991). The Itokawa particles resemble equilibrated LL chondrites in terms of oxygen isotope systematics based on multiple in-situ analyses and estimated bulk oxygen isotope ratios, which strengthens the link between asteroid Itokawa and equilibrated LL chondrites that fell to Earth.

The Itokawa particles and two EOCs show an apparently reversed δ^{18}O fractionation between olivine and high-Ca pyroxene, indicating that oxygen isotopes are not in equilibrium between the two mineral phases. Likewise, oxygen isotope ratios might be disequilibrium between low-Ca pyroxene and olivine mineral pair because of their small differences ($\leqslant 1$‰), which corresponds to temperatures higher than estimated peak metamorphic temperatures. In contrast, the mineral pair of plagioclase and high-Ca pyroxene yields $\sim$800 °C, consistent with mass-dependent fractionation during recrystallization (and possibly by diffusion) caused by thermal metamorphism.

Appendix A. Supplementary material

Supplementary material related to this article can be found online at http://dx.doi.org/10.1016/j.epsl.2013.08.009.

References

Abe, S., Mukai, T., Hirata, N., Barnouin-Jha, O.S., Cheng, A.F., Demura, H., Gaskell, R.W., Hashimoto, T., Hiraoka, K., Honda, T., Kubota, T., Matsuoka, M., Mizuno, T., Nakamura, R., Scheeres, D.J., Yoshioka, M., 2006. Mass and local topography measurements of Itokawa by Hayabusa. Science 312, 1344–1347.

Abe, M., Fujimura, A., Yano, H., Okamoto, C., Okada, T., Yada, T., Ishibashi, Y., Shirai, K., Nakamura, T., Noguchi, T., Okazaki, R., Zolensky, M.E., Sandford, S.A., Ireland, T., Ueno, M., Mukai, T., Yoshikawa, M., Yamada, T., Kuninaka, H., Kawaguchi, J., 2011. Recovery, transportation and acceptance to the curation facility of the Hayabusa re-entry capsule. Lunar Planet. Sci. XLII, 1638 (abstr.).

Amelin, Y., Ghosh, A., Rotenberg, E., 2005. Unraveling the evolution of chondrite parent asteroids by precise U–Pb dating and thermal modeling. Geochim. Cosmochim. Acta 69, 505–518.

Aubaud, C., Withers, A.C., Hirschmann, M.M., Guan, Y., Leshin, L.A., Mackwell, S.J., Bell, D.R., 2007. Intercalibration of FTIR and SIMS for hydrogen measurements in glasses and nominally anhydrous minerals. Am. Mineral. 92, 811–828.

Baertschi, P., 1976. Absolute ^{18}O content of standard mean ocean water. Earth Planet. Sci. Lett. 31, 341–344.

Brearley, A.J., Jones, R.H., 1998. Chondritic meteorites. In: Papike, J.J. (Ed.), Planetary Materials. In: Rev. Mineral., vol. 36. Mineralogical Society of America, Washington, DC, pp. 3-1–3-398.

Clark, B.E., Hapke, B., Pieters, C., Britt, D., 2002. Asteroid space weathering and regolith evolution. In: Bottke Jr., W.F., Cellino, A., Paolicchi, P., Binzel, R.P. (Eds.), Asteroids III. Univ. of Arizona Press, Tucson, AZ, pp. 585–599.

Clayton, R.N., 1993. Oxygen isotopes in meteorites. Annu. Rev. Earth Planet. Sci. 21, 115–149.

Clayton, R.N., Onuma, N., Mayeda, T.K., 1976. A classification of meteorites based on oxygen isotopes. Earth Planet. Sci. Lett. 30, 10–18.

Clayton, R.N., Kieffer, S.W., 1991. Oxygen isotopic thermometer calibration. In: Taylor Jr., H.P., O'Neil, J.R., Kaplan, I.R. (Eds.), Stable Isotope Geochemistry: A tribute to Samuel Epstein. In: Geochim. Soc. Spec. Publ., vol. 3, pp. 3–10.

Clayton, R.N., Mayeda, T.K., Goswami, J.N., Olsen, E.J., 1991. Oxygen isotope studies of ordinary chondrites. Geochim. Cosmochim. Acta 55, 2317–2337.

Dodson, M.H., 1973. Closure temperature in cooling geochronological and petrological systems. Contrib. Mineral. Petrol. 40, 259–274.

Dunn, T.L., Cressey, G., McSween Jr., H.Y., McCoy, T.J., 2010. Analysis of ordinary chondrites using powder X-ray diffraction: 1. Modal mineral abundances. Meteorit. Planet. Sci. 45, 123–134.

Ebihara, M., Sekimoto, S., Shirai, N., Hamajima, Y., Yamamoto, M., Kumagai, K., Oura, Y., Ireland, T.R., Kitajima, F., Nagao, K., Nakamura, T., Naraoka, H., Noguchi, T., Okazaki, R., Tsuchiyama, A., Uesugi, M., Yurimoto, H., Zolensky, M.E., Abe, M., Fujimura, A., Mukai, T., Yada, T., 2011. Neutron activation analysis of a particle returned from asteroid Itokawa. Science 333, 1119–1121.

Eiler, J.M., 2001. Oxygen isotope variations of basaltic lavas and upper mantle rocks. In: Valley, J.W., Cole, D.R. (Eds.), Stable Isotope Geochemistry. In: Rev. Mineral. Geochem., vol. 43. Mineralogical Society of America, Washington, DC, pp. 319–364.

Eiler, J.M., Baumgartner, L.P., Valley, J.W., 1992. Intercrystalline stable isotope diffusion: A fast grain boundary model. Contrib. Mineral. Petrol. 112, 543–557.

Eiler, J.M., Valley, J.W., Baumgartner, L.P., 1993. A new look at stable isotope thermometry. Geochim. Cosmochim. Acta 57, 2571–2583.

Gérard, O., Jaoul, O., 1989. Oxygen diffusion in San Carlos olivine. J. Geophys. Res. 94, 4119–4128.

Heck, P.R., Ushikubo, T., Schmitz, B., Kita, N.T., Spicuzza, M.J., Valley, J.W., 2010. A single asteroidal source for extraterrestrial Ordovician chromite grains from Sweden and China: High-precision oxygen three-isotope SIMS analysis. Geochim. Cosmochim. Acta 74, 497–509.

Huss, G.R., Rubin, A.E., Grossman, J.N., 2006. Thermal metamorphism in chondrites. In: Lauretta, D.S., McSween Jr., H.Y. (Eds.), Meteorites and the Early Solar System II. Univ. of Arizona Press, Tucson, pp. 567–586.

Kessel, R., Beckett, J.R., Stolper, E.M., 2007. The thermal history of equilibrated ordinary chondrites and the relationship between maturity and temperature. Geochim. Cosmochim. Acta 71, 1855–1881.

Kita, N.T., Ushikubo, T., Fu, B., Valley, J.W., 2009. High precision SIMS oxygen isotope analysis and the effect of sample topography. Chem. Geol. 264, 43–57.

Kita, N.T., Nagahara, H., Tachibana, S., Tomomura, S., Spicuzza, M.J., Fournelle, J.H., Valley, J.W., 2010. High precision SIMS oxygen three isotope study of chondrules in LL3 chondrites: Role of ambient gas during chondrule formation. Geochim. Cosmochim. Acta 74, 6610–6635.

Kleine, T., Touboul, M., Van Orman, J.A., Bourdon, B., Maden, C., Mezger, K., Halliday, A.N., 2008. Hf–W thermochronometry: Closure temperature and constraints on the accretion and cooling history of the H chondrite parent body. Earth Planet. Sci. Lett. 270, 106–118.

Kovach, H.A., Jones, R.H., 2010. Feldspar in type 4–6 ordinary chondrites: Metamorphic processing on the H and LL chondrite parent bodies. Meteorit. Planet. Sci. 45, 246–264.

Matthews, A., Palin, J.M., Epstein, S., Stolper, E.M., 1994. Experimental study of $^{18}O/^{16}O$ partitioning between crystalline albite, albitic glass, and CO_2 gas. Geochim. Cosmochim. Acta 58, 5255–5266.

McSween Jr., H.Y., Bennett III, M.E., Jarosewich, E., 1991. The mineralogy of ordinary chondrites and implications for asteroid spectrophotometry. Icarus 90, 107–116.

Nagao, K., Okazaki, R., Nakamura, T., Miura, Y.N., Osawa, T., Bajo, K., Matsuda, S., Ebihara, M., Ireland, T.R., Kitajima, F., Naraoka, H., Noguchi, T., Tsuchiyama, A., Yurimoto, H., Zolensky, M.E., Uesugi, M., Shirai, K., Abe, M., Yada, T., Ishibashi, Y., Fujimura, A., Mukai, T., Ueno, M., Okada, T., Yoshioka, M., Kawaguchi, J., 2011. Irradiation history of Itokawa regolith material deduced from noble gases in the Hayabusa samples. Science 333, 1128–1131.

Nakamura, E., Makishima, A., Moriguti, T., Kobayashi, K., Tanaka, R., Kunihiro, T., Tsujimori, T., Sakaguchi, C., Kitagawa, H., Ota, T., Yachi, Y., Yada, T., Abe, M., Fujimura, A., Ueno, M., Mukai, T., Yoshikawa, M., Kawaguchi, J., 2012. Space environment of an asteroid preserved on micrograins returned by the Hayabusa spacecraft. Proc. Natl. Acad. Sci. 109, E624–E629.

Nakamura, T., Noguchi, T., Tsuchiyama, A., Ushikubo, T., Kita, N.T., Valley, J.W., Zolensky, M.E., Kakazu, Y., Sakamoto, K., Mashio, E., Uesugi, K., Nakano, T., 2008. Chondrulelike objects in short-period comet 81P/Wild 2. Science 321, 1664–1667.

Nakamura, T., Noguchi, T., Tanaka, M., Zolensky, M.E., Kimura, M., Tsuchiyama, A., Nakato, A., Ogami, T., Ishida, H., Uesugi, M., Yada, T., Shirai, K., Fujimura, A., Okazaki, R., Sandford, S.A., Ishibashi, Y., Abe, M., Okada, T., Ueno, M., Mukai, T., Yoshikawa, M., Kawaguchi, J., 2011. Itokawa dust particles: A direct link between S-type asteroids and ordinary chondrites. Science 333, 1113–1116.

Nakamuta, Y., Motomura, Y., 1999. Sodic plagioclase thermometry of type 6 ordinary chondrites: Implications for the thermal histories of parent bodies. Meteorit. Planet. Sci. 34, 763–772.

Nakashima, D., Ushikubo, T., Rudraswami, N.G., Kita, N.T., Valley, J.W., Nagao, K., 2011a. Ion microprobe analyses of oxygen three-isotope ratios of chondrules from the Sayh al Uhaymir 290 chondrite using a multiple-hole disk. Meteorit. Planet. Sci. 46, 857–874.

Nakashima, D., Ushikubo, T., Zolensky, M.E., Weisberg, M.K., Joswiak, D.J., Brownlee, D.E., Matrajt, G., Kita, N.T., 2011b. High precision oxygen three isotope analysis of Wild 2 particles and anhydrous chondritic interplanetary dust particles. Lunar Planet. Sci. XLII, 1240 (abstr.).

Nakashima, D., Ushikubo, T., Zolensky, M.E., Kita, N.T., 2012a. High precision oxygen three-isotope analyses of anhydrous chondritic interplanetary dust particles. Meteorit. Planet. Sci. 47, 197–208.

Nakashima, D., Ushikubo, T., Joswiak, D.J., Brownlee, D.E., Matrajt, G., Weisberg, M.K., Zolensky, M.E., Kita, N.T., 2012b. Oxygen isotopes in crystalline silicates of comet Wild 2: A comparison of oxygen isotope systematics between Wild 2 particles and chondritic materials. Earth Planet. Sci. Lett. 357–358, 355–365.

Noguchi, T., Nakamura, T., Kimura, M., Zolensky, M.E., Tanaka, M., Hashimoto, T., Konno, M., Nakato, A., Ogami, T., Fujimura, A., Abe, M., Yada, T., Mukai, T., Ueno, M., Okada, T., Shirai, K., Ishibashi, Y., Okazaki, R., 2011. Incipient space weathering observed on the surface of Itokawa dust particles. Science 333, 1121–1125.

Okada, T., Shirai, K., Yamamoto, Y., Arai, T., Ogawa, K., Hosono, K., Kato, M., 2006. X-ray fluorescence spectrometry of asteroid Itokawa by Hayabusa. Science 312, 1338–1341.

Onuma, N., Clayton, R.N., Mayeda, T.K., 1972. Oxygen isotope temperatures of "equilibrated" ordinary chondrites. Geochim. Cosmochim. Acta 36, 157–168.

Rosenbaum, J.M., Kyser, T.K., Walker, D., 1994. High temperature oxygen isotope fractionation in the enstatite–olivine–$BaCO_3$ system. Geochim. Cosmochim. Acta 58, 2653–2660.

Ryerson, F.J., McKeegan, K.D., 1994. Determination of oxygen self-diffusion in åkermanite, anorthite, diopside, and spinel: Implications for oxygen isotopic anomalies and the thermal histories of Ca–Al-rich inclusions. Geochim. Cosmochim. Acta 58, 3717–3734.

Scott, E.R.D., Krot, A.N., 2003. Chondrites and their components. In: Davis, A.M. (Ed.), Meteorites, Comets, and Planets. In: Treatise on Geochemistry, vol. 1. Elsevier, BV, Amsterdam, pp. 143–200.

Taylor, G.J., Maggiore, P., Scott, E.R.D., Rubin, A.E., Keil, K., 1987. Original structures, and fragmentation and reassembly histories of asteroids: Evidence from meteorites. Icarus 69, 1–13.

Tenner, T.J., Hirschmann, M.M., Withers, A.C., Hervig, R.L., 2009. Hydrogen partitioning between nominally anhydrous upper mantle minerals and melt between 3 and 5 GPa and applications to hydrous peridotite partial melting. Chem. Geol. 262, 42–56.

Tenner, T.J., Ushikubo, T., Kurahashi, E., Kita, N.T., Nagahara, H., 2013. Oxygen isotope systematics of chondrule phenocrysts from the CO3.0 chondrite Yamato 81020: Evidence for two distinct oxygen isotope reservoirs. Geochim. Cosmochim. Acta 102, 226–245.

Tsuchiyama, A., Uesugi, M., Matsushima, M., Michikami, T., Kadono, T., Nakamura, T., Uesugi, K., Nakano, T., Sandford, S.A., Noguchi, R., Matsumoto, T., Matsuno, J., Nagano, T., Imai, Y., Takeuchi, A., Suzuki, Y., Ogami, T., Katagiri, J., Ebihara, M., Ireland, T.R., Kitajima, F., Nagao, K., Naraoka, H., Noguchi, T., Okazaki, R., Yurimoto, H., Zolensky, M.E., Mukai, T., Abe, M., Yada, T., Fujimura, A., Yoshikawa, M., Kawaguchi, J., 2011. Three-dimensional structure of Hayabusa samples: Origin and evolution of Itokawa regolith. Science 333, 1125–1128.

Tsuchiyama, A., Uesugi, M., Uesugi, K., Nakano, T., Noguchi, R., Matsumoto, T., Matsuno, J., Nagano, T., Imai, Y., Shimada, A., Takeuchi, A., Suzuki, Y., Nakamura, T., Noguchi, T., Abe, M., Yada, T., Fujimura, A., in press. Three-dimensional microstructure of samples recovered from asteroid 25143 Itokawa: Comparison with LL5 and LL6 chondrite particles. Meteorit. Planet. Sci., http://dx.doi.org/10.1111/maps.12177.

Valley, J.W., 2001. Stable isotope thermometry at high temperatures. In: Valley, J.W., Cole, D.R. (Eds.), Stable Isotope Geochemistry. In: Rev. Mineral. Geochem., vol. 43. Mineralogical Society of America, Washington, DC, pp. 365–413.

Valley, J.W., Kita, N.T., 2009. In situ oxygen isotope geochemistry by ion microprobe. In: Mineral. Assoc. Canada Short Course, Toronto, vol. 41, pp. 19–63.

Yurimoto, H., Abe, K., Abe, M., Ebihara, M., Fujimura, A., Hashiguchi, M., Hashizume, K., Ireland, T.R., Itoh, S., Katatyama, J., Kato, C., Kawaguchi, J., Kawasaki, N., Kitajima, F., Kobayashi, S., Meike, T., Mukai, T., Nagao, K., Nakamura, T., Naraoka, H., Noguchi, T., Okazaki, R., Park, C., Sakamoto, N., Seto, Y., Takei, M., Tsuchiyama, A., Uesugi, M., Wakaki, S., Yada, T., Yamamoto, K., Yoshikawa, M., Zolensky, M.E., 2011. Oxygen isotopic compositions of asteroidal materials returned from Itokawa by the Hayabusa Mission. Science 333, 1116–1119.