A systematic comparison of obsidian hydration measurements: the first application of micro-image with secondary ion mass spectrometry to the prehistoric obsidian

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Abstract

Archaeologists have long used obsidian hydration dating method to give chronometric dates for obsidian artifacts. Models using these equations independently employ different measurement systems, which are based on rim thicknesses determined by optical microscope and hydrogen depths measured by secondary ion mass spectrometry (SIMS), respectively, although the inconsistency of both measurements has been reported. Firstly, this paper describes a systematic comparison that was done on optical rim thicknesses and hydrogen depths by means of an isotope microscope, which provides micro-imaging with SIMS. Depth profiles of hydrogen were precisely obtained from the spots where optical measurements were taken on the archaeological obsidian flakes from two distinctive cultural horizons (older: Upper Paleolithic, younger: Initial Jomon) in the stratified open-air site of Jozuka in southern Kyushu (Japan). Secondarily, using the measurements of hydrogen depths that are the most consistent to the measurements of optical thicknesses, the estimated hydration rate of the Holocene (Initial Jomon) is slower than that of the Late Pleistocene (Upper Paleolithic), implying that the difference in hydration rates was due to the difference of intrinsic water content of obsidian and/or obsidian geochemistry. An application of micro-imaging with SIMS to measure hydrogen depths on obsidian shows promise as a tool for improving the practice of hydration dating and evaluating local climatic condition.

Keywords: obsidian; hydration; measurement; secondary ion mass spectrometry; micro-imaging

1. **Introduction**

Because of its easiness of observations, preparations, and availability of samples, archaeologists have used obsidian hydration dating (OHD). Since the earlier stage of the Japanese archaeological studies, OHD has been employed for constructing cultural chronologies (e.g., Suzuki 1971; Katsui and Kondo, 1976, see also Nakazawa, 2015). However, a rapid progress of tephrochronology since the 1970's has given general framework to allow to create regional chronologies of the Japanese prehistoric sites (e.g., Moriwaki et al., 2016), and this made archaeologists less relied on chronometric method to temporal significance on the archaeologically constructed unit (e.g., site, assemblage, artifact). Contrary, a progress of Paleolithic research over the last 70 years now gives rich but complex picture of Japanese Paleolithic archaeological record (Kaifu et al., 2015; Nakazawa, 2011, 2017), which further requires to explore reliable chronometric dating methods to understand Paleolithic in East Asia. Under this circumstance, use of ^{14}C dates has now become critical to give dates for the sites and assemblages to help to support various chronologies of the Japanese prehistory (e.g., Ono et al., 2002; Shoda, 2010; Nakazawa et al., 2011; Izuho and Kaifu, 2015; Morisaki and Natsuki, 2017). However, chronometric dates notably ^{14}C dates are not always available from archaeological sites and their reliability needs to be assessed by other methods. Moreover, given intensive exploitations of obsidian by the prehistoric populations lived in the Japanese Archipelago, it is worthwhile to explore the OHD for an alternative method.

Obsidian hydration has known as the diffusion of ambient water into a glass matrix of obsidian forms a hydration rim that is the function of the time elapsed since the fresh surface of obsidian has been exposed. The relationship between elapsed time and

thickness of the hydration rim on an obsidian flake gives the theoretical basis for the OHD. The traditional method for measuring hydration rim thickness is based on the optical principle that a microscopically observed hydrated layer appears due to the flux of light (Friedman and Smith, 1960). However, the optical method of measurements has been challenged by the new diffusion model explicating that the diffusion of molecular water into a glass solid is dependent on the concentration of intrinsic water in the obsidian (Anovitz et al., 1999; Liritzis, 2006; Novak and Stevenson, 2012; Rogers, 2008; Stevenson and Novak, 2011, see also Ambrose, 1976; Haller, 1963, Lee et al., 1974). In the new diffusion model, the depth profiles of the hydrogen on the hydrated obsidian surfaces diagnosed by the secondary ion mass spectrometry (SIMS) offer a critical method for evaluating variations in diffused water (e.g., Anovitz et al., 1999, 2004, 2006a, 2006b; Liritzis 2006; Liritzis and Laskaris, 2011; Riciputi et al., 2002; Steffen, 2005; Stevenson et al., 2001, 2004). Because currently two measurement systems are being used, an explicit comparison of the depth profiles of hydrogen and the optical rim thicknesses is necessary if we are to discuss how the two measurement systems are integrated. The primary goal of this paper is to make an explicit comparison of the optically measured hydration rim thickness and depth of hydrogen precisely assessed by the isotope microscope that equipped SIMS to create micro-images of hydrogen profiles (Yurimoto et al., 2003). The second goal is to give a gross estimate of the Pleistocene hydration rate that may be useful for evaluating paleoclimatic regimes.

2. An application of the secondary ion mass spectrometry (SIMS) to obsidian hydration dating method

At present, both traditional and new diffusion models have been employed in

obtaining obsidian hydration equations. For the traditional model, empirically developed quadratic equation has yielded dates based on the optically measured thickness of the hydration rim and time (Friedman and Smith, 1960; Friedman and Long, 1976). The equation is $x^2 = kt$

where x = rim thickness (μm), t = time, and k = diffusion rate.

In the quadratic equation, the thickness of the hydration rims created by stress birefringence in the optical principle (Anovitz et al., 1999; Michels et al., 1983; Liritzis, 2014) is measured under the polarized microscope (Friedman and Smith, 1960). Although the quadratic equation does not provide the best solution for some archaeological dates (e.g., Ridings, 1996; Riciputi et al., 2002), with refining the estimation of the effective hydration temperature (Rogers, 2007), the considerations of chemical difference (Suzuki, 1971; Friedman and Smith, 1976; Hughes, 1988; Watanabe and Suzuki, 2005; Behrens and Zhang, 2009), and the effect of the intrinsic water content of the obsidian (Ambrose, 1976; Stevenson et al., 1993, 1998; Steffen, 2005; Rogers, 2008, 2013; Rogers and Duke, 2011), the traditional model has been continuously improved to address various archaeological research questions (e.g., Ambrose, 1993; Hull, 2001; Dillian, 2002; Eerkens et al., 2008; Nakazawa, 2015; Tripcevich et al., 2012).

On the other hand, the new model that provides the concentration-dependent diffusion equation based on Fick's second diffusion law is, described as $\partial C/\partial t = \partial/\partial x(D\partial C/\partial x)$

where C is the concentration of hydrogen, x is the depth of hydrogen, t is the time, and D is the diffusion coefficient (Anovitz et al., 1999; Riciputi et al., 2002; Liritzis, 2014). The concentration-dependent diffusion equation describes the diffusion of water

molecule from the exposed surface to the inward unhydrated glass matrix. When the effective hydration temperature is constant, the rate of diffusion is largely dependent on the variability in the intrinsic water content (e.g., Anovitz et al., 1999; Delaney and Karsten, 1981; Haller, 1963; Zhang et al., 1997; Stevenson et al., 1998; Riciputi et al., 2002; Rogers, 2008; Behrens and Zang, 2009).

Since the proposal of a new diffusion model, the estimated concentration-dependent diffusion coefficient has been established often by SIMS in order to give an accurate hydration date (e.g., Anovitz et al., 1999; Liritzis, 2014; Riciputi et al., 2002). The fundamental reason to explore the SIMS profile readings for the depth of hydrogen in the new diffusion model is that it has great potential for understanding the surface dynamics of molecular water into glass (Anovitz et al., 1999, 2004, 2008; Liritzis and Diakostamatiou, 2002; Stevenson et al., 2004). Depth profiles of hydrogen on obsidian surfaces exhibits S-shaped (precisely it is a mirror image of S) curve, but they do not necessarily correspond to the optical boundary between the hydrated obsidian surface and the obsidian without hydration, thus weakening the reliability of the optical measurements in using the traditional model to give dates (Anovitz et al., 1999; Riciputi et al., 2002). While SIMS serves as a critical method for applying a new diffusion model to OHD, taking measurements of the depth of the diffused water molecules from the surface on a SIMS profile is not straightforward because the diffusion front shows a gradual decrease of hydrogen. Moreover, even in the equations that estimate diffusion coefficient based on gradient water profiles (Liritzis, 2006; Liritzis and Diakostamatiou, 2002; Riciputi et al., 2002), the depths of the water molecules are a prerequisite for computing hydration dates. Given the current situation in which both traditional and new diffusion models with corresponding analytical methods (i.e., optical microscopic

measurements and SIMS profiling) are juxtapose, the present study introduces the micro-imaging with SIMS, a new method of measurement that can bridge the two measurement methods.

3. Materials and methods

3-1. Samples from two temporal units at a single site of Jozuka, southern Kyushu, Japan

The study site is from southern Kyushu, a large island south of the Korean Peninsula and east of the southern China across the Tsushima Strait and the East China Sea, respectively (Fig. 1). Despite the fact that the archaeological sites in southern Kyushu have yielded abundant obsidian artifacts from the well-stratified open-air sites often blanketed by a series of the Late Pleistocene and Holocene tephra units, OHD has not been used for dating archaeological assemblages. Samples of obsidian artifacts for the present study were obtained from the two assemblages with reliable dates in the identical archaeological site of Jozuka (31° 36’40’’N, 130°57’30’’E) (Fig. 1). Jozuka is an open-air site characterized by multiple occupational levels from the Late Pleistocene to Holocene (Kagoshima Prefectural Archaeological Center, 2010). Artifacts and features were encompassed in the aeolian loam blanketed by multiple tephra layers that have known erupted dates. A total of three cultural horizons (i.e., Final Jomon, Initial Jomon, and Upper Paleolithic) were identified in the sequentially ordered lithostratigraphic units (Fig. 2). Because vertical separation of three cultural horizons is distinctive and no significant evidence of anthropogenic and natural disturbances is identified (Kagoshima Prefectural Archaeological Center, 2010), inter-stratigraphic mixture of artifacts between different cultural horizons is unlikely.

Study samples were obtained from two occupational levels: Level XVI, which is

culturally affiliated to the early Upper Paleolithic, and Level VII, the Initial Jomon period, a cultural period characterized by a subsistence economy based on hunting, gathering, and fishing assisted by the use of pottery (Kagoshima Prefectural Archaeological Center, 2010). Although, no chronometric dates were obtained from the lower levels at the Jozuka site, the bottom layer (Level XVIII) of the site has a marker tephra of AT, erupted at 30,000 cal. B.P. (Miyairi et al., 2004; Yokoyama et al., 2007; Smith et al., 2013), and Level XVI encompasses the tephra called P17, erupted ca. 26,000 cal. B.P. (Okuno, 2002) from the local volcano of Sakurajima, 30 km west of the study site of Jozuka (Fig. 1). In contrast, Level VII characterized by dense human occupations during the Initial Jomon has a total of 14 radiocarbon dates that were obtained from organic stains on pottery and features including pits, pit-houses, and stone heaps consisting of fire-cracked rocks (Table 1). Represented by the median date among the total of 14 radiocarbon dates obtained from the features in Levels VII and VIII, we treated 10,500 cal. B.P. as the date of the Initial Jomon occupation. Thus, two sets of obsidian samples were from human occupations that are 15,500 years apart. Because the temporally different samples are from the identical site, differences in the thermal histories between the two assemblages would be caused by soil temperatures that varied depending on the duration of artifacts' depositions (Jones et al., 1997; Ridings, 1991).

The optical measurements of the hydration rims were conducted under a polarized microscope (MT9300, Meiji Techno Co., LTD.) at the magnifications of 400×. Three measurements both on exterior (dorsal) and interior (ventral) surfaces of a single obsidian flake sample were recorded at the μm using the computer-assisted measuring devise (Art Measure, Artray Inc.). Observations and measurements on obsidian

hydration were exclusively conducted by the first author, nullified the inter-observer errors. After taking pictures of all measured spots on the rims, all SIMS profiles were taken within 140 μm range around the exact spots where the optical measurements were done (Fig. 3). Among the sampled obsidian flakes, thicknesses were all measured by optical microscope: three samples from the younger occupation and three samples from the older occupation at the study site of Jozuka were chosen for the SIMS analysis. A total of 13 SIMS profiles comprised of six measurements from the younger samples and seven measurements from the older samples were taken. To increase the efficiency in taking SIMS measurements, all samples were sliced into small pieces to embed them into a columnar epoxy.

3-2. Hydrogen imaging and secondary ion-mass spectrometry

Previous applications of SIMS on the hydrated surfaces of obsidian have demonstrated that hydrogen profiles are characterized by the S-shaped profile of water concentration as the function of depth. As Anovitz et al. (1999: 739) describes, concentration-dependent S-shaped profile has a typical pattern: first, water concentrations are initially flat or decrease slowly. Second, water concentration decreases rapidly. Third, water concentration decreases slowly into the background (see also Lirtzis 2006; Riciputi et al., 2002). However, it has not fully evaluated the extent to which the optical method of hydration measurements is reliable with respect to the measured hydrogen depth by SIMS. An earlier observation of hydrogen profiles of archaeological obsidian artifacts suggests that optically measured hydration rim thicknesses do not correspond to the depths of hydrogen (Anovitz et al., 1999). A more systematic comparison has demonstrated that optical measurements systematically

overestimate hydrogen depths (Riciputi et al., 2002: 1069; Stevenson et al., 2004: 564). In contrast, the other comparisons have shown that the optical measurements the underestimate hydrogen depths despite their correlation (Novak and Stevenson, 2012: 8-9; Stevenson et al., 2001: 112-113). Given an additional observation that the difference between the optical measurements and hydrogen depths becomes larger as the optical measurements increase, Stevenson et al. (2001: 114) notes that an optical boundary (i.e., Becke line [Anovitz et al., 1999: 744]) was observed at a point shallower than the actual diffusion front because a hydrogen profile becomes flat "within the region of the hydration rim diffusion front." The current uncertainty of correspondence between optical and hydrogen profiles are not only because of the difference in principles and models, but also because the spots where the measurements were taken were uncontrollable. Even though we have known that optically measured hydration thicknesses are often varied in a single specimen (e.g., Origer, 1989; Dillian, 2002; Nakazawa, 2015), current SIMS measurements are either better applied to a relatively flat surface (e.g., Liritzis and Laskaris, 2012; Novak and Stevenson, 2012) or to anonymous locations in a given specimen (e.g., Anovitz et al., 1999; Stevenson et al., 2004; Liritzis, 2014) that do not necessarily correspond to the spots where the optical measurements were taken. Thus, the reliability of the two methods needs to be evaluated by taking two kinds of measurements at an identical spot within a single hydration rim.

To obtain accurate hydrogen profiles, here, we used an isotope microscope in which the Cameca ims-1270 is equipped with Stacked CMOS-type Active Pixel Sensor (Yurimoto et al. 2003). The sample surface was homogeneously irradiated over a field area of diameter ~100 μm, using a broad O^- primary beam set to 23 keV and 20 nA.

Stigmatic images of the positive secondary ions of $^{1}H^{+}$ and $^{28}Si^{+}$ were acquired in each analyzed area. The exposure time was typically 500 s for $^{1}H^{+}$ and 10 s for $^{28}Si^{+}$. The lateral resolutions of the secondary ion images were ~0.5 μm using a contrast aperture of 50 μm in diameter. The isotope microscope is specifically designed to make micro-scale images from quantified elements by SIMS (e.g., Yurimoto and Nagashima, 2005; Kawasaki et al., 2012). In the present study, it enables us to capture elements on hydrated and unhydrated surface at the same spot where an optical measurement has been taken. The depth of the hydrogen is delimited in accordance with the imaged hydrogen concentration at the micro scale. The hydration concentration is clearly visible as a bright band in the micro-image (Fig. 4a). In Fig 4a, x is the point on the surface of obsidian and the perpendicular line that transects x on the diminishing margin of bright band is regarded as y, the hydration front. Then, the measured distance between x and y based on the micro-image in Fig. 4a gives the profile of the hydration concentration delimited by x and y (Fig. 4b). Profiles of the elements of interests (e.g., H, Si) can be repeatedly created along any of the lines on the images, using the image analysis program Image J2 (free software available at http://imagej.net/ImageJ2). These functions allow us to make an explicit comparison of hydrogen profiles and optical measurements.

4. Results and discussion

Thicknesses of the hydration rims and hydrogen depths compared among the 13 spots that were measured (Table 2, Fig. 5). Although measurement errors can be involved both for optical method and SIMS, because of its high precision the measured hydrogen depths would be less involved errors than the optical rim thicknesses. Thus, here we

treat that the hydrogen depths as the independent variable and the optical rim thicknesses as the dependent variable. Although a systematic difference between the optical rim thicknesses and hydrogen depths has been reported by Riciputi et al. (2002) and Stevenson et al. (2004), the plots of measurements in Figure 5 are more or less equally placed over and under the regression spline, while the specimens from the Upper Paleolithic level (Level XVI) are generally closer to the regression line than those from the Initial Jomon level (Levels VII, and VIII). This visual observation is further examined by linear regression analysis. Using the regression equation for the present sets of measurements: $Y = 2.155 + 0.713X$, the predicted rim thicknesses and raw residuals (d_{Y*X}) are calculated (Table 2, see VanPool and Leonard, 2011), where Y = rim thickness, X = hydrogen depth, $d_{Y*X} = Y_i - \hat{Y}$. Based on the raw residuals, the optical thicknesses for the specimens of Upper Paleolithic are thicker than the expected based on the hydrogen depths, suggesting that optical measurements overestimated the hydrogen depths. In contrast, the optical measurements for the specimens of Initial Jomon were thinner than the hydrogen depths, implying the optical measurements underestimated the hydrogen depths.

Because the hydration rate of obsidian was sensitively varied depending on temperature (Friedman and Long, 1976; Rogers, 2007), it is generally expected that hydration rate for the Holocene is faster than the Pleistocene. Temperature history is expected to be spatially unvaried at the study site of Jozuka because it is a single open-air site with multiple occupational levels from the Late Pleistocene to the Holocene (Upper Paleolithic to Jomon). Taking this advantage, here we give a gross estimation of hydration rate for the Late Pleistocene in the southern Kyushu through an assessment of the difference in the hydration rates between the Pleistocene and Holocene. An analysis

of standardized residuals (VanPool and Leonard, 2011: 211-213) is performed to extract the representative measurements to estimate the hydration rates (Table 2).

Because the standard residuals of the measurements from J-2445-v-1 and J-8641-d-2 are less variable than the other samples (Table 2), these two measurements are legitimately employed for estimating the Late Pleistocene and Holocene hydration rates of obsidian. Using the SIMS measurement of hydrogen depth for the Upper Paleoithic specimen J-2445-v-1 that retains the most consistent measurement between the optical hydration rim thickness and hydrogen depth, the hydration date is estimated by the equation: $x^2 = kt$. For the J-2445-v-1,

$$k_{UP} = x_{UP}{}^2 / t_{UP}$$

$$= (12.89)^2 / 26000$$

$$= 0.006390$$

$$= 6.39 \times 10^{-3}$$

where x_{UP} = 12.89 (μm) and t_{UP} = 26000 (years ago).

Thus, the hydration rate for the specimens of Upper Paleolithic level of the Jozuka site, southern Kyushu is 6.39 μm per 1000 years. This hydration rate is the averaged during the last 26,000 years of deposition, which encompasses both the Late Pleistocene and Holocene. What we are interested in, however, is the difference in hydration rates for the Late Pleistocene and Holocene. This requires us to isolate the Late Pleistocene hydration rate through an assessment of the Holocene hydration rate.

A hydration rate for the Holocene is estimated from the specimen of the Initial Jomon (10,500 years ago). Because of its proximity of measurements between microscopic thickness and hydrogen depth (Table 2), the measurement of J-8641-d-2 is used for an estimation of Holocene hydration rate. For the J-8641-d-2,

$k_J = x_J^2 / t_J$

$= (6.53)^2 / 10500$

$= 0.004061$

$= 4.061 \times 10^{-3}$

where $x_J = 6.53$ (μm) and $t_J = 10500$ (years ago).

Because the Holocene temperature is higher than the Pleistocene, it is expected that k_J is faster than k_{UP}. Contrary to this expectation, as shown above, k_{UP} estimated from Upper Paleoltihic specimen (J-2445) is faster than k_J using the Initial Jomon specimen (J-8641). This contradictory result can be explained by factors other than thermal histories, such as intrinsic water content (Ambrose, 1976) and geochemistry of obsidian (Suzuki, 1971). Because this is the pilot study, we have not performed geochemical analysis and measuring water content for the specimens. A study of geochemical analysis for the obsidian outcrops in southern Kyushu has distinguished a total of 10 sources (Mukai, 2008), suggesting that the obsidian specimens for the present study might be from multiple sources. Because the different obsidian sources have different diffusion rate (e.g., Michels et al., 1983; Watanabe and Suzuki, 2006), the slower rate of hydration for the Initial Jomon specimen (J-8641) and the faster rate of hydration for the Upper Paleolithic specimen (J-2445) could be due to the differences in intrinsic water content (Stevenson et al., 1993) and obsidian geochemistry. This needs to be investigated in the future research.

In the traditional model of OHD, k is a critical variable. In estimating k, temperature is given as time-averaged. While the global climatic records have shown the millennium-scale fluctuations of climatic changes (e.g., Yuan et al., 2004), the local climatic fluctuations would have been more effective to human behavior than the global

climatic changes (e.g., Nakazawa et al., 2011; Iizika and Izuho, 2017). In this sense, besides rigorous experimental approach (e.g., Anovitz et al., 2006a), an examination of hydration rate through an application of the traditional model of OHD to empirical archaeological data is also worthwhile to evaluate local climatic condition, particularly paleo-temperature regime.

5. Conclusion

The present study compared the measurements between optical rim thicknesses and hydrogen depths by taking an advantage of the isotope microscope that gives distinctive micro-images of hydrogen profiles at the exact spots where optical measurements were taken. This method not only increases the reliability of measurements, but also makes a deeper profile (> 10 μm) based on a high spatter rate lessen the duration of analysis. The systematic comparison of two kinds of measurements showed good correlation, implying that micro-imaging with SIMS is useful method to evaluate the extent to which the optical measurements are reliable. Using the reliable measurements assessed by the micro-imaging with SIMS, the estimated hydration rate can be validly evaluated. Imaging diffused hydrogen concentration on the surface of an archaeological obsidian artifact is an emerging methodological approach that will open new research avenues, therein improving the practice of OHD.

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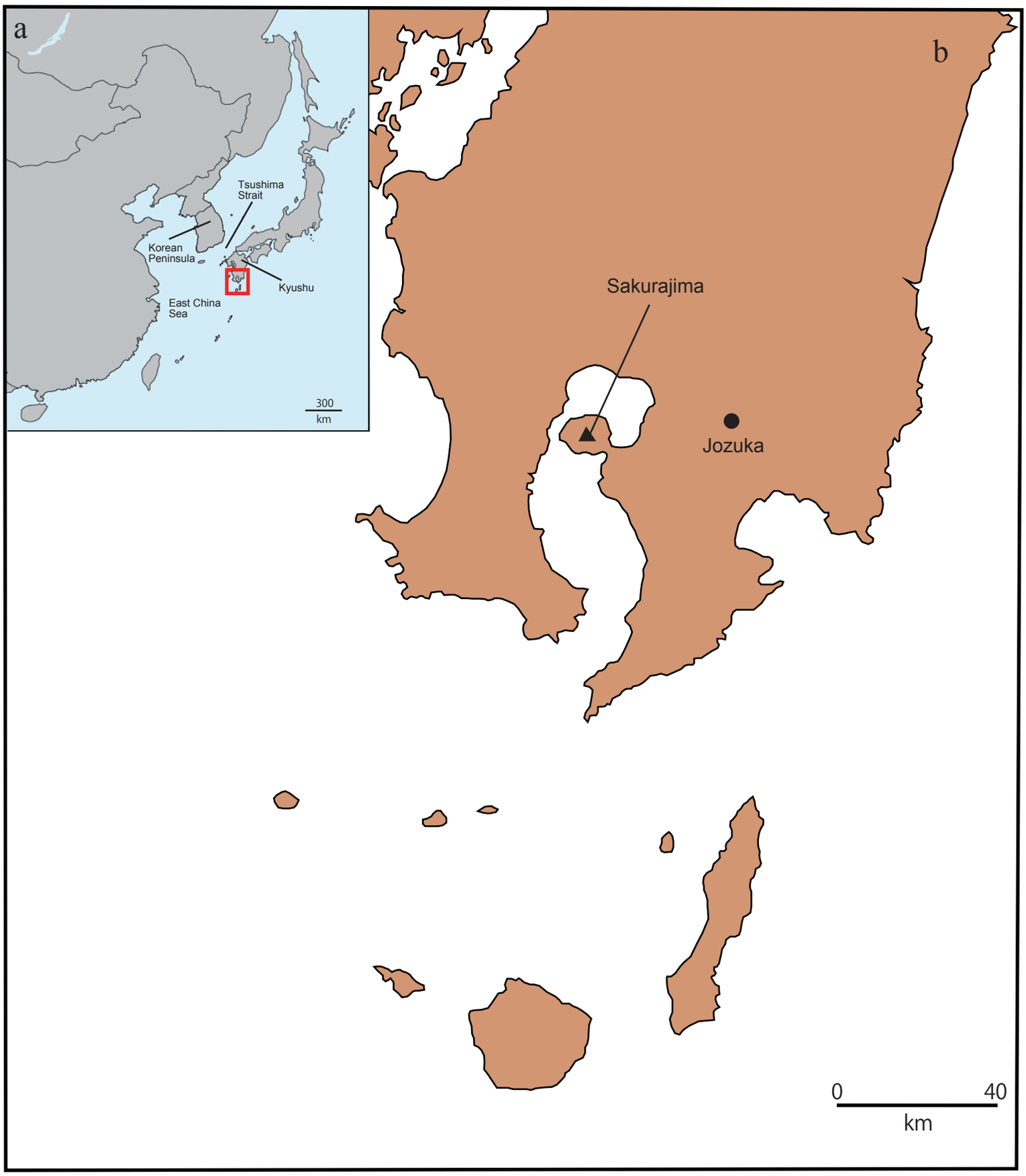
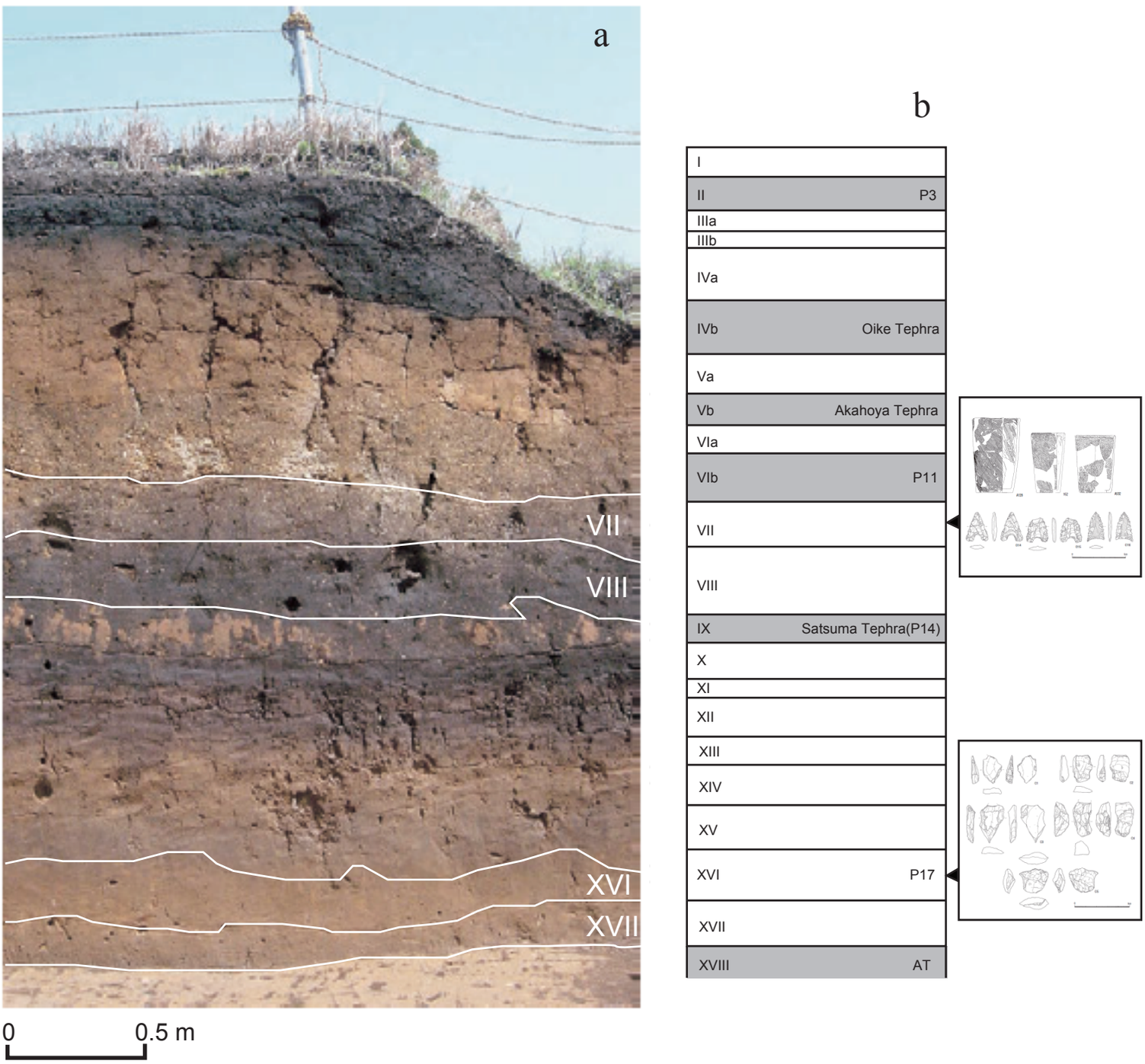

a
Tsushima
Strait
Korean
Peninsula
Kyushu
East China
Sea
300
km
b
Sakurajima
Jozuka
0
40
km

Figure 1


a
VII
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Vb
Akahoya Tephra
VIa
VIb
P11
VII
VIII
IX
Satsuma Tephra(P14)
X
XI
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XV
XVI
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XVIII
AT

Figure 2

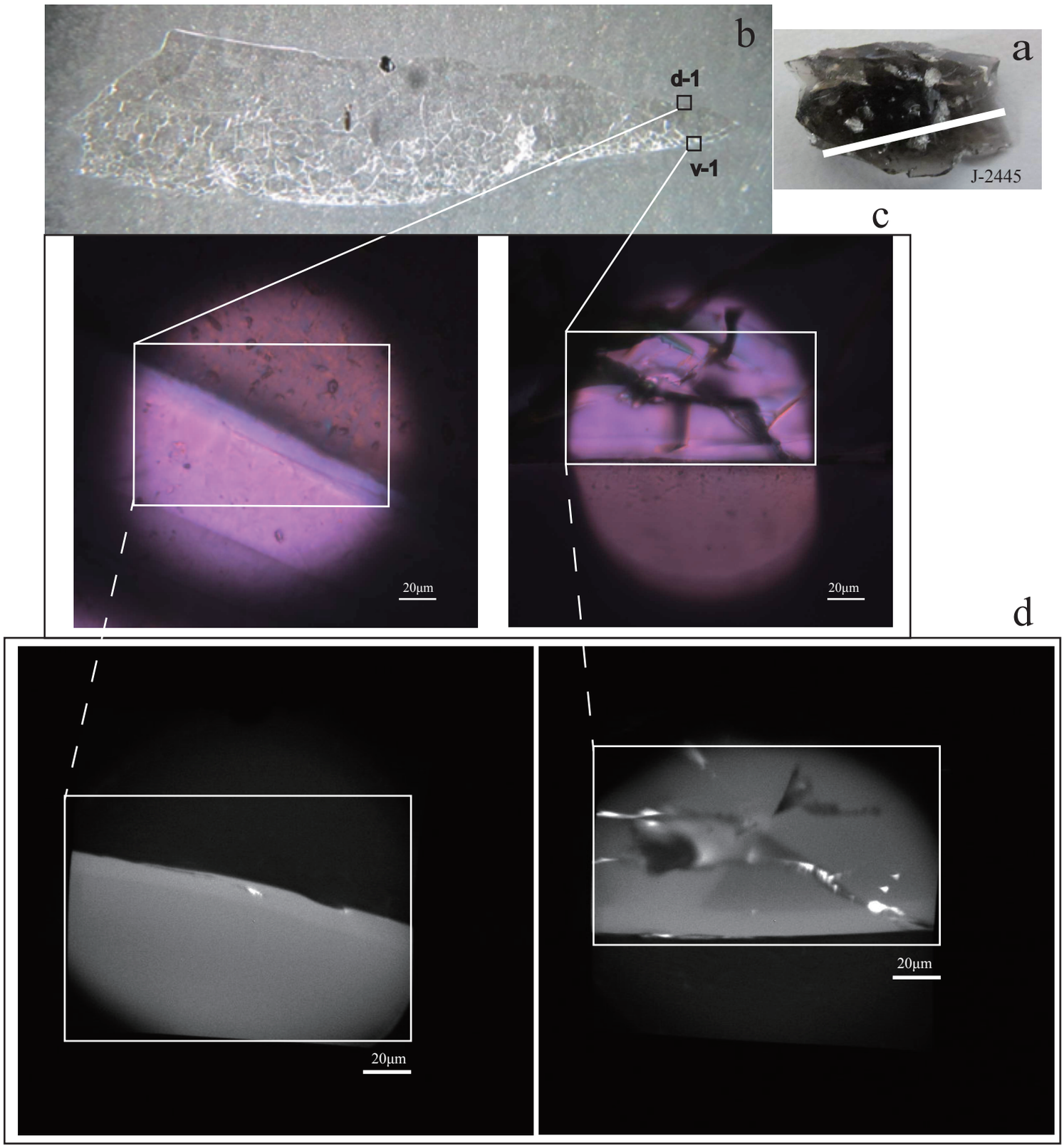

Figure 3

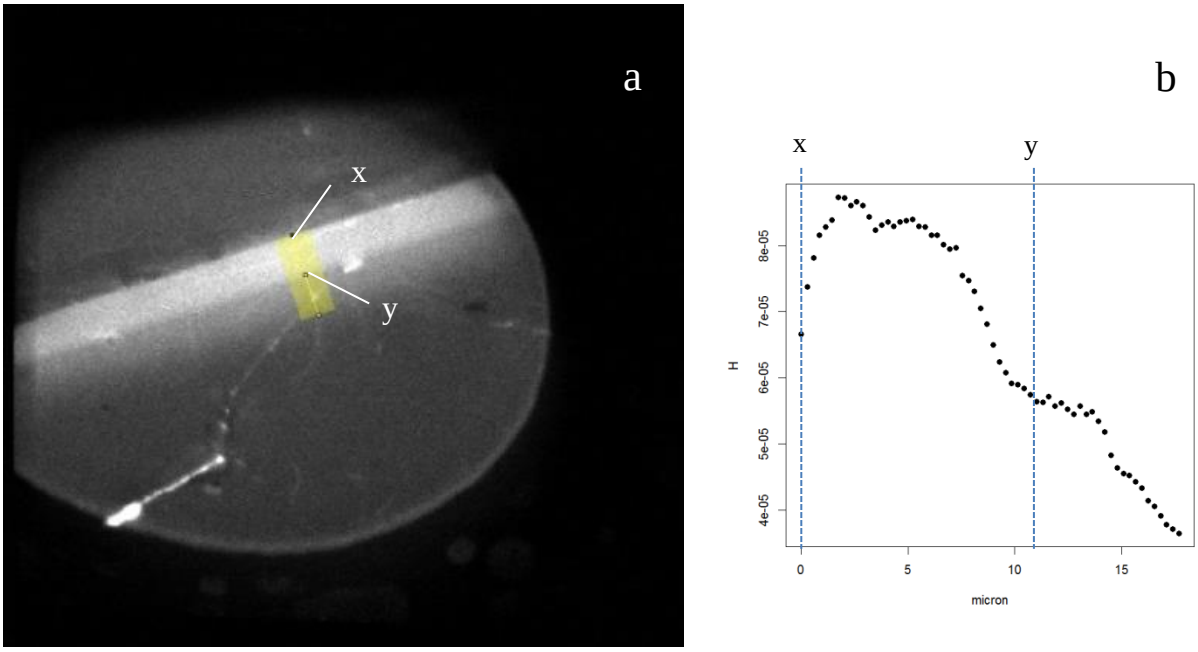

Figure 4

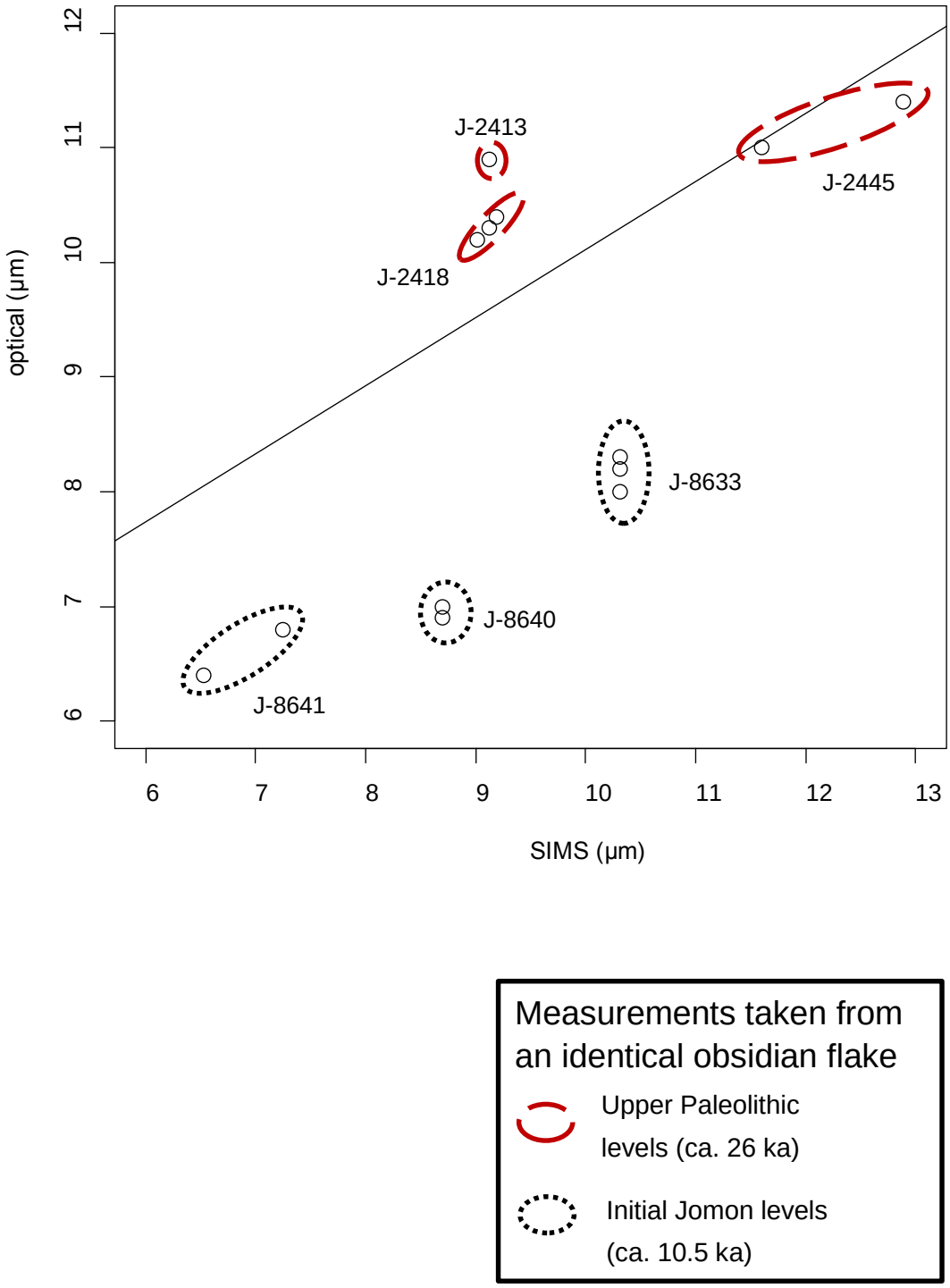
optical (µm)
SIMS (µm)
J-2413
J-2418
J-2445
J-8633
J-8640
J-8641
Measurements taken from an identical obsidian flake
Upper Paleolithic levels (ca. 26 ka)
Initial Jomon levels (ca. 10.5 ka)

Figure 5

Laboratory Number	Material Dated	Level	Associated features and artifacts	^{14}C Age BP	cal. B.P.
IAAA-82108	Charcoal	VII/VIII	Cobble concentration (#35)	8820±50	10155-9686
PLD-11056	Charred surface deposit	VII/VIII	Pottery	8875±35	10175-9793
IAAA-82106	Charcoal	VII/VIII	Pit-house (SH16)	8910±50	10204-9795
PLD-11055	Charred surface deposit	VII/VIII	Pottery	9195±40	10491-10247
IAAA-80833	Charcoal	VII/VIII	Pit-house (SH22)	9210±40	10496-10252
PLD-11054	Charred surface deposit	VII/VIII	Pottery	9220±40	10501-10258
IAAA-82107	Charcoal	VII/VIII	Cobble concentration (#25)	9310±40	10654-10303
IAAA-80835	Charcoal	VII/VIII	Pit-house (SH62)	9420±40	10752-10561
IAAA-80836	Charcoal	VII/VIII	Pit	9480±40	11068-10586
IAAA-82105	Charcoal	VII/VIII	Pit-house (SH04)	9480±40	11068-10586
PLD-11051	Charred surface deposit	VII/VIII	Pottery	9500±35	11070-10608
IAAA-80834	Charcoal	VII/VIII	Pit-house (SH31)	9500±40	11072-10605
PLD-11052	Charred surface deposit	VII/VIII	Pottery	9540±35	11081-10709
PLD-11053	Charred surface deposit	VII/VIII	Pottery	9750±35	11238-11136

Table 1. ^{14}C Dates from Levels VII and VIII (Initial Jomon occupation).

Sample	Age	A: microscopic thickness (μm) by optical microscope	B: hydrogen depth (μm) by SIMS	A - B	An evaluation of optical measurements
J-2413-d-3	26.5 ka	10.9	9.12	1.78	overestimate
J-2418-v-1	26.5 ka	10.4	9.19	1.21	overestimate
J-2418-v-2	26.5 ka	10.3	9.12	1.18	
J-2418-v-3	26.5 ka	10.2	9.02	1.18	
J-2445-d-1	26.5 ka	11	11.6	-0.6	underestimate
J-2445-v-1	26.5 ka	11.4	12.89	-1.49	
J-8633-d-3	10.5 ka	8.2	10.31	-2.11	underestimate
J-8633-v-1	10.5 ka	8	10.31	-2.31	
J-8633-v-2	10.5 ka	8.3	10.31	-2.01	
J-8640-d-3	10.5 ka	6.9	8.7	-1.8	underestimate
J-8640-v-2	10.5 ka	7	8.7	-1.7	
J-8641-d-2	10.5 ka	6.4	6.53	-0.13	underestimate
J-8641-v-2	10.5 ka	6.8	7.25	-0.45	

Table 2. Optical thickness compared with hydrogen depths, with an evaluation of microscopic measurements relative to hydrogen depths. Optical measurements and hydrogen depths are correlated at 5% level (Pearson's $r = 0.65$, $p = 0.016$).

Captions of figures and tables

Figure 1. Locations of southern Kyushu, the Jozuka site, and the related geographic locations. a: Map of Southeast Asia and the squared area is the southern Kyushu, b: southern Kyushu. Map of a is extracted from Wikimedia commons (https://commons.wikimedia.org/wiki/File:East_Asia_area_blank_CJK.svg)

Figure 2. Stratigraphic profile of the Jozuka, southern Kyushu. a: profile picture (from Kagoshima Prefectural Archaeological Center, 2010), b: schematic stratigraphic sequence. Shaded layers are pumice deposits. Obsidian flakes were sampled from Levels XVI and VII.

Figure 3. Optical hydration rims and corresponding micro-images of hydrogen on obsidian artifact (sample # J-2445). White line on obsidian flake (a) is at the location where thin section (b) was made. d-1 is a spot of measurement on ventral surface, and v-1 is that of ventral surface. (c) optical rim images. (d) micro-imaging.

Figure 4. (a) Micro-image of the hydrated surface, (b) SIMS hydrogen profile. x: at surface of obsidian. y: spot where hydrogen diminishes to background. Sample number is J-2413-d-3.

Figure 5. Plot of optical rim thicknesses against hydrogen depths (μm).

Table 1. ^{14}C Dates from Levels VII and VIII (Initial Jomon occupation).

Table 2. Measurements and related statistics for the samples from Jozuka site.

Note: The standard residual is calculated by the following equation: $SR = \frac{d_{Y*X}}{S_{Y*X}\sqrt{(1-h_i)}}$

where d_{Y*X} is raw residuals given as Y_i - $\hat{Y}$ as described above, hi is the leverage coefficient given as $h_i = \frac{1}{n} + \frac{(X_i - \hat{X})^2}{\sum x^2}$, S_{Y*X} is the mean square error given as $\sum_{i=1}^{n} \frac{(Y_i - \hat{Y})^2}{n-2}$