Methodological Issues for Characterisation and Provenance Studies of Obsidian in Northeast Asia

Edited by

Akira Ono Michael D. Glascock Yaroslav V. Kuzmin Yoshimitsu Suda



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This volume is dedicated to the Golden Anniversary celebrating the beginning of scientific obsidian provenance studies in 1964, with Professor Colin Renfrew FBA FSA (a.k.a. The Lord Renfrew of Kaimsthorn) and Professor Johnson R. Cann FRS as pioneers

Table of Contents

List of Contributors	iii
List of Figures and Photos	v
List of Tables	ix
Abbreviations	xi
Foreword Colin Renfrew	xii
Preface and Acknowledgements Akira ONO and Yaroslav V. KUZMIN	xvii
 Chapter 1 Introduction: Characterisation and Provenance Studies of Obsidian in Northeast Asia — the View from the Early 2010s Akira ONO, Yaroslav V. KUZMIN, Michael D. GLASCOCK, and Yoshimitsu SUDA 	1
Methodological Issues on Characterisation of Obsidian Sources in Northeast Asia	
 Chapter 2 Multi-Method Characterisation of Obsidian Source Compositional Groups in Hokkaido Island (Japan) Jeffrey R. FERGUSON, Michael D. GLASCOCK, Masami IZUHO, Masayuki MUKAI, Kejii WADA, and Hiroyuki SATO 	13
Chapter 3 Application of Internal Standard Method for Non-Destructive Analysis of Obsidian Artefacts by Wavelength Dispersive X-ray Fluorescence Spectrometry Yoshimitsu SUDA	
Chapter 4 The Effectiveness of Elemental Intensity Ratios for Sourcing Obsidian Artefacts Using Energy Dispersive X-ray Fluorescence Spectrometry: a Case Study from Japan Tarou KANNARI, Masashi NAGAI, and Shigeo SUGIHARA	47
Chapter 5 Chemical Composition of Obsidians in Hokkaido Island, Northern Japan: the Importance of Geological and Petrological Data for Source Studies Keiji WADA, Masayuki MUKAI, Kyohei SANO, Masami IZUHO, and Hiroyuki SATO	67

Chapter 6	
The Neutron Activation Analysis of Volcanic Glasses in the Russian Far East and Neighbouring	
Northeast Asia: a Summary of the First 20 Years of Research	85
Yaroslav V. KUZMIN and Michael D. GLASCOCK	
Chapter 7	
Geochemistry of Volcanic Glasses and the Search Strategy for Unknown	
Obsidian Sources on Kamchatka Peninsula (Russian Far East)	
Andrei V. GREBENNIKOV, Vladimir K. POPOV, and Yaroslav V. KUZMIN	
Provenance Studies of Archaeological Obsidian in Northeast Asia: Current Progress	
Chapter 8	
Identification of Archaeological Obsidian Sources in Kanto and Chubu Regions	
(Central Japan) by Energy Dispersive X-ray Fluorescence Analysis	
Nobuyuki IKEYA	
Chapter 9	
Integration of Obsidian Compositional Studies and Lithic Reduction Sequence	
Analysis at the Upper Palaeolithic Site of Ogachi-Kato 2, Hokkaido, Japan	125
Masami Izuho, Jeffrey R. FERGUSON, Michael D. GLASCOCK, Norivoshi ODA.	
Fumito AKAI, Yuichi NAKAZAWA, and Hiroyuki SATO	
Chapter 10	
Geoarchaeological Aspects of Obsidian Source Studies in the Southern Russian	
Far East and Brief Comparison with Neighbouring Regions	
Yaroslav V. KUZMIN	
Chapter 11	
The Paektusan Volcano Source and Geochemical Analysis of Archaeological Obsidians in Korea	
Jong-Chan KIM	
	150
Index	179

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List of Figures and Photos

Figure 1.1. The travel routes of the 2011 Workshop (by air and by land)	3
Figure 2.1. Map of Hokkaido obsidian sources and the location of Ogachi-Kato 2 site	14
Figure 2.2. Scatterplot of Rb vs. Sb concentrations from NAA for all obsidian sources in Hokkaido	17
Figure 2.3. Scatterplot of Mn vs. Fe concentrations from NAA for obsidian sources in Hokkaido	21
Figure 2.4. Scatterplot of Cs vs. Co concentrations from NAA for selected obsidian sources in Hokkaido	22
Figure 2.5. Scatterplot of Rb vs. Sr concentrations from ED-XRF for all sources in Hokkaido	22
Figure 2.6. Scatterplot of Sr vs. Zr concentrations from ED-XRF for obsidian sources in Hokkaido	23
Figure 2.7. Scatterplot of Sr vs. Fe concentrations from ED-XRF used to separate groups A and B	23
Figure 2.8. Scatterplot of Zr vs. Fe concentrations from ED–XRF used to separate the samples from Group A	24
Figure 2.9. Scatterplot of Fe vs. Rb concentrations from ED–XRF used to separate the remaining samples (see Figure 2.8) from Group A in Figure 2.7	24
Figure 2.10. Scatterplot of Rb vs. Sr concentrations from ED–XRF used to separate the first two source groups from Group B (see Figure 2.7)	25
Figure 2.11. Scatterplot of Zr vs. Y concentrations from ED–XRF showing the overlap of the remaining source groups (see Figure 2.10) in Group B in Figure 2.7	25
Figure 2.12. Bivariate plot of Sr vs. Zr concentrations showing all of the likely source reference groups [except for Tokachi (Mitsumata)] along with all of the artefacts from the Ogachi-Kato 2 site	29
Figure 2.13. Bivariate plot of Rb vs. Zr concentrations showing the separation of the two Oketo source groups at the Ogachi-Kato 2 site	30
Figure 3.1. Techniques and materials used in the present study	34
Figure 3.2. Locations of the major obsidian sources analysed in this study	35
Figure 3.3. Flaked obsidian from the Hoshikuso-toge, Wada-toge, Shirataki, and Quispisisa sources	35
Figure 3.4. Microphotograph, backscattered electron image, and element mappings of Fe for obsidian from the Shirataki source	35
Figure 3.5. Variation diagrams of measurement intensity vs. theoretical intensity for selective elements	38
Figure 3.6. Qualified values normalised multi-element diagrams compiling the calculated values of the reference materials of obsidian for the non-destructive analysis	40
Figure 3.7. Qualified values normalised multi-element diagrams compiling the results of quantitative analysis of flaked obsidian using the non-destructive method	43
Figure 3.8. The JR-1 normalised multi-element diagram compiling the representative values of the obsidian in major sources analysed by the Fusion Bead Method	43

Figure 3.9. The JR-1 normalised Y/Ca vs. Rb/Mn ratios variation diagram for obsidian from major sources analysed in the present study	44
Figure 4.1. Schematic diagram of obsidian occurrences in nature	49
Figure 4.2. Major obsidian sources in the Stone Age of Japan	50
Figure 4.3. Obsidian samples from the Akaishiyama and Takaharayama sources in three conditions	
Figure 4.4, A–B. The SiO ₂ variation diagrams for element concentrations of glass beads by WDXRF, and mirror surface and flake samples by EDXRF, from Akaishiyama and Takaharayama sources	54
Figure 4.5. Scatterplots of element concentrations for glass beads by WDXRF, and for mirror surface and flake samples by EDXRF, from Akaishiyama and Takaharayama sources	56
Figure 4.6. Scatterplots of intensity ratios for mirror surface and flake samples by EDXRF, from Akaishiyama and Takaharayama sources	56
Figure 4.7. Scatterplots of intensity ratios for obsidian artefacts found at the Yadegawa site, including those from an unknown source (modified from Nagai <i>et al.</i> 2012)	58
Figure 4.8, A–B. The SiO ₂ variation diagrams for major and trace elements in obsidian artefacts from an unknown source found at the Yadegawa site (modified from Nagai <i>et al.</i> 2012)	59
Figure 4.9. Obsidian sample which changed colour after X-ray irradiation by WDXRF	60
Figure 5.1. Map of obsidian sources in Hokkaido	68
Figure 5.2. The K–Ar age of obsidian sources in Hokkaido and the location of the Monbetsu-Kamishihoro graben (after Yahata 1997)	73
Figure 5.3. Microphotograhs of obsidian taken under open-polarised light from the Rubeshibe source, and from the Shirataki source (Tokachiishizawa Locality)	
Figure 5.4. The CaO/Al ₂ O ₃ vs. TiO ₂ /K ₂ O diagram of whole-rock composition for the Hokkaido obsidian sources.	
Figure 5.5. The MgO vs. CaO and TiO ₂ vs. Fe ₂ O ₃ * diagrams	
Figure 5.6. The Ba/Zr vs. Rb/Zr and Ba/Zr vs. Sr/Zr diagrams	
Figure 5.7. An example of glass analysis displayed in the Secondary Electron Images for the Shirataki obsidian	
Figure 5.8. The CaO/Al ₂ O ₃ vs. TiO ₂ /K ₂ O diagram of glass composition for the Hokkaido obsidian sources.	
Figure 5.9. The CaO vs. SiO ₂ , K ₂ O, FeO*, and Cl diagrams	82
Figure 5.10. Obsidian artefacts with polished mirror surfaces embedded in epoxy resin	82
Figure 6.1. Main primary obsidian sources in mainland Northeast Asia and adjacent regions	86
Figure 6.2. Bivariative plot (Mn vs. Rb) showing geochemical groups of northeast Asian obsidian	88
Figure 7.1. Selected obsidian sources on Kamchatka and archaeological sites with artefacts associated with them	
Figure 7.2. Major obsidian sources on the Kamchatka Peninsula (after Otchet 1992, modified)	
Figure 7.3. Schematic map of volcanic glass sources of the Ichinsky Volcanic Centre (after Otchet 1992, modified)	100
Figure 7.4. Bivariate plots showing geochemical groups of Kamchatkan obsidian	102
Figure 7.5. Bivariate plots showing geochemical groups of Kamchatkan obsidian	103
Figure 7.6. The Hf – Rb / 30 – Ta x 3 discriminant diagram for obsidian source samples and artefacts from Kamchatka and their tectonic position (after Grebennikov <i>et al.</i> 2010, modified)	103

Figure 7.7. The distribution of archaeological sites with obsidian artefacts of the KAM-02 group on Kamchatka, and location of the Bakening Volcano as their possible source (after Grebennikov <i>et al.</i> 2010, modified)	104
Figure 8.1. Major obsidian sources and areas in the Chubu and Kanto regions of Japan	112
Figure 8.2. Discrimination diagram of Rb x 100 / (Rb + Sr + Y + Zr) vs. Mn x 100 / Fe	113
Figure 8.3. Discrimination diagram of Sr x 100 / (Rb + Sr + Y + Zr) vs. log (Fe/K)	113
Figure 8.4. General stratigraphic sequence of the upper members of Ashitaka Loam at the piedmont of Mt. Ashitaka	115
Figure 8.5. Amount of obsidian from different sources in the cultural layers at the piedmont of Mt. Ashitaka	115
Figure 8.6. Location of obsidian sources in the northern part of the Izu Islands and the Izu Peninsula	116
Figure 8.7. Discrimination diagram of La/Hf vs. Ce/Th based on NAA for geological samples and artefacts of Doteue site (Layer BBV)	122
Figure 9.1. Topography of Hokkaido Island and location of the Ogachi-Kato 2 site	126
Figure 9.2. Distant view of the Ogachi-Kato 2 site	127
Figure 9.3. Geomorphological map of the Ogachi-Kato 2 site	127
Figure 9.4. Stratigraphic profile and artefact frequencies at the Ogachi-Kato 2 site	128
Figure 9.5. Distribution of refitted pieces at the Ogachi-Kato 2 site	129
Figure 9.6. Lithic specimens of the Ogachi-Kato 2 site showing small flake reduction sequence, flake reduction sequence, and microblade reduction sequence	130
Figure 9.7. Scatter diagram of the percentage of refitted pieces and the distances from the major primary obsidian sources (see Table 9.3)	133
Figure 9.8. Major lithic refits of the Ogachi-Kato 2 site	134
Figure 9.9. Bivariate plot of Sr vs. Zr concentrations showing all of the likely source reference groups (except for Tokachi-Mitsumata) along with all of the artefacts	137
Figure 9.10. Bivariate plot of Rb vs. Zr concentrations (in ppm) showing the separation of the two Oketo source groups	137
Figure 9.11. Lithic reduction sequences of the Ogachi-Kato 2 site; reduction flows are from left to right	139
Figure 10.1. Distribution of obsidian from the Basaltic Plateau source in Northeast Asia	146
Figure 10.2. Distribution of obsidian from the Paektusan source in Northeast Asia	146
Figure 10.3. Distribution of obsidian from the Shirataki and Oketo sources in Northeast Asia (selective sites, mainly beyond Hokkaido Island)	147
Figure 10.4. Distribution of obsidian from the Obluchie Plateau source in Northeast Asia	147
Figure 10.5. Sources of archaeological obsidian for the Kurile Islands	154
Figure 10.6. Percentage of sites/artefacts in the Russian Far East studied in terms of obsidian geochemistry	154
Figure 10.7. Contact zones of the obsidian networks in Northeast Asia	155
Figure 11.1. The position of archaeological sites and other places of interest	167
Figure 11.2. Locations sampled during the 2007 field trip to Paektusan Volcano	168
Figure 11.3. The REE concentrations of PNK obsidians normalised to the chondritic abundances (Thompson <i>et al.</i> 1983)	170
Figure 11.4. The result of PCA analysis using data given by Cho and Choi (2010) for the obsidians from four Palaeolithic sites (including the Kigok site)	170

Figure 11.5. Dendrogram of obsidians from the Kigok site obtained by cluster analysis using StatisXL	171
Figure 11.6. Dendrogram of obsidians from Neolithic sites in the southern part of Korea based	
on data in Cho et al. (2006) obtained by cluster analysis	172

Photo 1.1. The building of the Centre for Obsidian and Lithic Studies, Meiji University (Nagawa Town, Nagano Pref.)	
Photo 1.2. Participants of the 2011 Hokkaido Fieldtrip at the Akaishiyama (Summit) outcrop (Shirataki area), 30 October 2011	5
Photo 1.3. Excursion to the Hachigozawa outcrop (Shirataki area, Hokkaido), 30 October 2011	6
Photo 1.4. Excursion to the Ajisaitaki outcrop (Shirataki area, Hokkaido), 31 October 2011	6
Photo 1.5. Excursion to the Tokoroyama outcrop (Oketo area, Hokkaido), 1 November 2011	6
Photo 1.6. Excursion to the Tokachi-Mitsumata source (Hokkaido), 1 November 2011	6
Photo 1.7. Before the beginning of the ceremony of splitting the Shirataki obsidian sample for inter-comparison at the Centre for Obsidian and Lithic Studies on 6 November 2011	7

List of Tables

 Table 2.2. Current and previously published obsidian source names for Hokkaido Island	Table 2.1. Obsidian sources in Hokkaido Island described in this study and their locations	15
 Table 2.3. Element concentration means and standard deviations by NAA and ED–XRF for obsidian sources in Hokkaido. Table 2.4. Element concentrations by ED–XRF of artefacts from the Ogachi-Kato 2 site. Table 3.1. Results of quantitative analysis of obsidian using the Fusion Bead Method. Table 3.2. Results of quantitative analysis using the Internal Standard Method on polished slab obsidian specimens. Table 3.3. Results of quantitative analysis using the Internal Standard Method on flaked obsidian specimens. Table 3.3. Results of quantitative analysis using the Internal Standard Method on flaked obsidian specimens. Table 4.1. Element concentrations for major and selected trace elements in obsidian samples from Japanese sources. Table 4.2. The Mahalanobis distances of each cluster for the Akaishiyama and Takaharayama sources. Table 4.3. Element compositions of obsidian samples from the Tokachi and Nishiaomori areas (after Kannari <i>et al.</i> 2010). Table 4.4. Petrographic results of microscopic examination of obsidians from the Tokachi-Mitsumata and Amadanaigawa localities (after Nagai <i>et al.</i> 2012). Crystallite classification is based on Johannsen (1931). Table 5.1. List of Hokkaido obsidian sources. Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A. Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources. Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources in the Russian Far East and neighbouring Northeast Asia analysed by NAA. 	Table 2.2. Current and previously published obsidian source names for Hokkaido Island	16
 Table 2.4. Element concentrations by ED–XRF of artefacts from the Ogachi-Kato 2 site Table 3.1. Results of quantitative analysis of obsidian using the Fusion Bead Method Table 3.2. Results of quantitative analysis using the Internal Standard Method on polished slab obsidian specimens Table 3.3. Results of quantitative analysis using the Internal Standard Method on flaked obsidian specimens Table 4.1. Element concentrations for major and selected trace elements in obsidian samples from Japanese sources Table 4.2. The Mahalanobis distances of each cluster for the Akaishiyama and Takaharayama sources Table 4.3. Element compositions of obsidian samples from the Tokachi and Nishiaomori areas (after Kannari <i>et al.</i> 2010). Table 4.4. Petrographic results of microscopic examination of obsidians from the Tokachi-Mitsumata and Amadanaigawa localities (after Nagai <i>et al.</i> 2012). Crystallite classification is based on Johannsen (1931). Table 5.1. List of Hokkaido obsidian from the Akaigawa, Nayoro, Shirataki, Ikutahara, Rubeshibe, Oketo, Tokachi-Mitsumata, and Shikaribetsu sources. Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A. Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources Table 5.4. Whole-rock chemical compositions of besidian glass from the Hokkaido sources Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources	Table 2.3. Element concentration means and standard deviations by NAA and ED-XRF for obsidian sources in Hokkaido.	17
Table 3.1. Results of quantitative analysis of obsidian using the Fusion Bead Method	Table 2.4. Element concentrations by ED-XRF of artefacts from the Ogachi-Kato 2 site	
 Table 3.2. Results of quantitative analysis using the Internal Standard Method on polished slab obsidian specimens Table 3.3. Results of quantitative analysis using the Internal Standard Method on flaked obsidian specimens Table 4.1. Element concentrations for major and selected trace elements in obsidian samples from Japanese sources Table 4.2. The Mahalanobis distances of each cluster for the Akaishiyama and Takaharayama sources Table 4.3. Element compositions of obsidian samples from the Tokachi and Nishiaomori areas (after Kannari <i>et al.</i> 2010). Table 4.4. Petrographic results of microscopic examination of obsidians from the Tokachi-Mitsumata and Amadanaigawa localities (after Nagai <i>et al.</i> 2012). Crystallite classification is based on Johannsen (1931) Table 5.1. List of Hokkaido obsidian from the Akaigawa, Nayoro, Shirataki, Ikutahara, Rubeshibe, Oketo, Tokachi-Mitsumata, and Shikaribetsu sources. Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A. Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources. Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources. Table 6.1. Obsidian samples from the Russian Far East and neighbouring Northeast Asia analysed by NAA in 1992–2011. 	Table 3.1. Results of quantitative analysis of obsidian using the Fusion Bead Method	36
 Table 3.3. Results of quantitative analysis using the Internal Standard Method on flaked obsidian specimens	Table 3.2. Results of quantitative analysis using the Internal Standard Method on polished slab obsidian specimens	41
Table 4.1. Element concentrations for major and selected trace elements in obsidian samples from Japanese sources Table 4.2. The Mahalanobis distances of each cluster for the Akaishiyama and Takaharayama sources Table 4.2. The Mahalanobis distances of each cluster for the Akaishiyama and Takaharayama sources Table 4.3. Element compositions of obsidian samples from the Tokachi and Nishiaomori areas (after Kannari et al. 2010) Table 4.4. Petrographic results of microscopic examination of obsidians from the Tokachi-Mitsumata and Amadanaigawa localities (after Nagai et al. 2012). Crystallite classification is based on Johannsen (1931) fttt Table 5.2. The K–Ar ages of obsidian from the Akaigawa, Nayoro, Shirataki, Ikutahara, Rubeshibe, oketo, Tokachi-Mitsumata, and Shikaribetsu sources Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A. fttt Table 5.4. Whole-rock chemical compositions of obsidian glass from the Hokkaido sources fttt Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources ftttt Table 6.1. Obsidian samples from the Russian Far East and neighbouring Northeast Asia analysed fttttttttttttttttttttttttttttttttttt	Table 3.3. Results of quantitative analysis using the Internal Standard Method on flaked obsidian specimens.	42
Table 4.2. The Mahalanobis distances of each cluster for the Akaishiyama and Takaharayama sources ************************************	Table 4.1. Element concentrations for major and selected trace elements in obsidian samples from Japanese sources	51
 Table 4.3. Element compositions of obsidian samples from the Tokachi and Nishiaomori areas (after Kannari <i>et al.</i> 2010)	Table 4.2. The Mahalanobis distances of each cluster for the Akaishiyama and Takaharayama sources	57
 Table 4.4. Petrographic results of microscopic examination of obsidians from the Tokachi-Mitsumata and Amadanaigawa localities (after Nagai <i>et al.</i> 2012). Crystallite classification is based on Johannsen (1931) Table 5.1. List of Hokkaido obsidian sources Table 5.2. The K–Ar ages of obsidian from the Akaigawa, Nayoro, Shirataki, Ikutahara, Rubeshibe, Oketo, Tokachi-Mitsumata, and Shikaribetsu sources Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A. Table 5.4. Whole-rock chemical compositions of the Hokkaido obsidians by XRF. Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources. Table 6.1. Obsidian samples from the Russian Far East and neighbouring Northeast Asia analysed by NAA in 1992–2011. Table 6.2. Means and standard deviations of element concentrations for obsidian sources in the Russian Far East and neighbouring NORA . 	Table 4.3. Element compositions of obsidian samples from the Tokachi and Nishiaomori areas (after Kannari et al. 2010)	57
 Table 5.1. List of Hokkaido obsidian sources Table 5.2. The K–Ar ages of obsidian from the Akaigawa, Nayoro, Shirataki, Ikutahara, Rubeshibe, Oketo, Tokachi-Mitsumata, and Shikaribetsu sources Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A. Table 5.4. Whole-rock chemical compositions of the Hokkaido obsidians by XRF. Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources. Table 6.1. Obsidian samples from the Russian Far East and neighbouring Northeast Asia analysed by NAA in 1992–2011. Table 6.2. Means and standard deviations of element concentrations for obsidian sources in the Russian Far East and neighbouring Northeast Asia 	Table 4.4. Petrographic results of microscopic examination of obsidians from the Tokachi-Mitsumata and Amadanaigawa localities (after Nagai <i>et al.</i> 2012). Crystallite classification is based on Johannsen (1931)	58
 Table 5.2. The K–Ar ages of obsidian from the Akaigawa, Nayoro, Shirataki, Ikutahara, Rubeshibe, Oketo, Tokachi-Mitsumata, and Shikaribetsu sources. Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A. Table 5.4. Whole-rock chemical compositions of the Hokkaido obsidians by XRF. Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources. Table 6.1. Obsidian samples from the Russian Far East and neighbouring Northeast Asia analysed by NAA in 1992–2011. Table 6.2. Means and standard deviations of element concentrations for obsidian sources in the Russian Far East and neighbouring Northeast Asia 	Table 5.1. List of Hokkaido obsidian sources	69
Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A	Table 5.2. The K–Ar ages of obsidian from the Akaigawa, Nayoro, Shirataki, Ikutahara, Rubeshibe, Oketo, Tokachi-Mitsumata, and Shikaribetsu sources	71
 Table 5.4. Whole-rock chemical compositions of the Hokkaido obsidians by XRF	Table 5.3. Standard deviation of the chemical composition for reference sample HR-1A	74
 Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources	Table 5.4. Whole-rock chemical compositions of the Hokkaido obsidians by XRF	75
 Table 6.1. Obsidian samples from the Russian Far East and neighbouring Northeast Asia analysed by NAA in 1992–2011 Table 6.2. Means and standard deviations of element concentrations for obsidian sources in the Russian Far East and neighbouring Northeast Asia measured by NAA	Table 5.5. Summary of chemical compositions of obsidian glass from the Hokkaido sources	79
Table 6.2. Means and standard deviations of element concentrations for obsidian sources in the Russian Far East and neighbouring Northeast Asia measured by NAA	Table 6.1. Obsidian samples from the Russian Far East and neighbouring Northeast Asia analysed by NAA in 1992–2011	87
	Table 6.2. Means and standard deviations of element concentrations for obsidian sources in the Russian Far East and neighbouring Northeast Asia measured by NAA	89

Table 7.1. Ages determined by K-Ar method for obsidians from Kamchatka (after Budnitsky 2013) 105

Table 8.1. Areas and sub-areas of obsidian sources in the Chubu and Kanto regions	114
Table 8.2. NAA measurements for obsidian from Doteue site, Numazu City	116
Table 8.3. NAA measurements for obsidian from the Chubu and Kanto regions	117
Table 8.4. Comparison of identification the obsidian sources by NAA and EDXRF methods	122
Table 9.1. Lithic assemblage of the Ogachi-Kato 2 site	131
Table 9.2. Artefact frequency by recovery methods at the Ogachi-Kato 2 site	131
Table 9.3. Rate of refitted pieces of the Upper Palaeolithic sites on Hokkaido	132
Table 9.4. Lithic refits of the Ogachi-Kato 2 site	133
Table 9.5. Samples for obsidian source assignment at the Ogachi-Kato 2 site	135
Table 9.6. Elements concentrations by short-irradiated NAA for artefacts of the Ogachi-Kato 2 site	137
Table 9.7. Results of obsidian source assignment at the Ogachi-Kato 2 site	138
Table 10.1. Obsidian in prehistoric cultural complexes of Northeast Asia	145
Table 10.2. Prehistoric sites in Primorye Province with obsidian artefacts and their sources	148
Table 10.3. Prehistoric sites in Sakhalin Island with obsidian artefacts and their sources	150
Table 10.4. Prehistoric sites in the Amur River basin with obsidian artefacts and their sources	152
Table 10.5. Prehistoric sites on the Kurile Islands with obsidian artefacts and their sources	153
Table 11.1. The matrix dependence of Fe concentration in PIXE measurement	169
Table 11.2. The ICP–MS results for geological samples collected during the 2007 Paektusan fieldtrip (labelled as "present study") compared with the NAA results of Popov <i>et al.</i> (2005)	169
Table 11.3. The results of ICP–MS analysis of the obsidian source samples from Kyushu Island, Japan	172
Table 11.4. Results of the present LA–ICP–MS analysis of obsidian from the Little Glass Buttes and Sierra de Pachuca by the Korean Basic Science (KBS) Facility, compared with the previous ICP–MS results at the Orleans Laboratory (Glascock 1999; Gratuze 1999)	173
Appendix. Table 1. Pyroclastic debris from the Paektusan Volcano collected during the 2007 fieldtrip (see Figure 11.2 for sampling locations)	178

Abbreviations

AD —	Anno Domini, i.e., years after the birth of Jesus Christ
a.k.a. —	also known as
a.s.l. —	above sea level
BP —	"before present", age in uncalibrated radiocarbon years as received from the laboratory
ca. —	circa, i.e., approximately
cal BP —	years before AD 1950, as applied to calibrated radiocarbon ages
CRDF —	Civil Research and Development Foundation
e.g. —	exempli gratia, i.e., for example
EDXRF, ED–XRF –	Energy Dispersive X-ray Fluorescence
EPMA —	Electron Probe Microanalysis
FEB RAS —	Far Eastern Branch of the Russian Academy of Sciences
hXRF —	handheld X-ray Fluorescence
i.e. —	<i>id est</i> , that is to say
ICP-MS —	Inductively Coupled Plasma – Mass Spectrometry
KAKENHI —	Grant-in-Aid for Scientific Research; from Japan Society for Promotion of Science
LA-ICP-MS —	Laser Ablation Inductively Coupled Plasma – Mass Spectrometry
Ма —	million years ago
MEXT —	Ministry of Education, Culture, Sport, Science, and Technology of Japan
	(also known in Japanese as Mombu Kagakusho)
NAA —	Neutron Activation Analysis
OIS —	Oxygen Isotope Stage
PCA —	Principal Component Analysis
PI —	Principal Investigator
PIXE —	Proton-Induced X-ray Emission
ppm —	parts-per-million, or per mille
Pref. —	Prefecture
PXRF, pXRF —	portable X-ray Fluorescence
REE —	rare-earth elements
RFFI —	Russian Foundation for Fundamental Investigations (also known as Russian Foundation for Basic Research [RFBR])
SB RAS —	Siberian Branch of the Russian Academy of Sciences
SRM —	standard reference material
US NSF —	United States National Science Foundation
USGS —	United States Geological Survey
vol.% —	volume percent
vs. —	versus, i.e., against
WDX, WDXRF —	Wavelength Dispersive X-ray Fluorescence
wt.% —	weight percent
WWII —	Second World War
XRF —	X-ray Fluorescence

Chapter 7 GEOCHEMISTRY OF VOLCANIC GLASSES AND THE SEARCH STRATEGY FOR UNKNOWN OBSIDIAN SOURCES ON KAMCHATKA PENINSULA (RUSSIAN FAR EAST)

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Abstract: The 2013 state-of-the-art in obsidian geology and geochemistry of Kamchatka Peninsula (northern Russian Far East) is presented. General information on volcanic geology of Kamchatka is given, and major obsidian sources studied by our team since 2003 are briefly described. A strategy for the search of the unknown primary sources of obsidian on Kamchatka (i.e., those for which the precise position is not established) is proposed. It is based on the following criteria: 1) general geological structure and the history of geological development; 2) geochemical typification of volcanic rocks and glasses; and 3) absolute age of both geological and archaeological obsidians. Using the data available and its analysis, possible primary sources for archaeological obsidian on Kamchatka are suggested. It now requires verification by the means of fieldwork.

Keywords: Obsidian, Geochemistry, Volcanic Geology, Source Identification, Neutron Activation Analysis, Potassium–Argon Dating, Kamchatka Peninsula, Russian Far East

INTRODUCTION

Information on the geochemistry of volcanic rocks, specifically glasses which reflect the initial composition of "frozen" eruptive magmas, is very important for studying the conditions of the creation and evolution of magmatic melts. Also, geochemical data have a superior importance for studying the sources of archaeological obsidian. The determination of obsidian sources for prehistoric tool assemblages allows researchers to reconstruct the directions of ancient migrations and contacts. Recent progress in these fields in Northeast Asia can be found in the volume edited by Kuzmin and Glascock (2010).

In the northern Russian Far East, the Kamchatka Peninsula is one of the most promising areas for obsidian provenance studies due to an abundance of volcanic glass sources and their extensive use by prehistoric people. Since the early 1900s, obsidian artefacts have been discovered at more than 800 archaeological sites on Kamchatka (see Grebennikov et al. 2010, 91). Volcanic glasses of this region have been systematically studied by our group since 2003 (see Glascock et al. 2006; Kuzmin et al. 2008; Popov et al. 2007). As a result, an extensive Database containing information on the geochemical composition of about 500 samples was created for the first time. Based on the data obtained, volcanic glasses from Kamchatka were divided into 16 geochemical groups. Seven of them include both geological and archaeological samples, and correspond to the main obsidian sources used by prehistoric people (Figure 7.1). The other seven groups consist of 'archaeological' obsidian (i.e., artefacts) only, and the primary sources for these groups are unknown so far. Two groups are represented by solely geological source samples which were not used by ancient people (Figure 7.1) (see details in Grebennikov et al. 2010).

The Kamchatka Peninsula in the Northwestern Pacific stretches approximately 1200 km in SSW-NNE directi-

on, and is flanked by the Bering Sea in the east, the Sea of Okhotsk in the west, and the open Pacific Ocean in the south (Figures 7.1–7.2). The main geomorphic features of the region are two mountain ranges, Central [Sredinniy] and Eastern [Vostochniy], with a sedimentary basin between them occupied by the Kamchatka River. From a tectonic point of view, the Kamchatka Peninsula sits on the boundary between the Pacific and Eurasian plates. This is one of the most active volcanic arcs in the world, and at least 28 modern volcanoes are known in the region (Fedotov and Masurenkov 1991). Most of the Kamchatkan terrain consists of Cenozoic volcanic rocks, with some sedimentary and volcanic-sedimentary formations (Khain 1994). Volcanic glasses (obsidians and perlites) are widely distributed on Kamchatka, and they are part of the dacitic-rhyolitic volcanic complexes of Neogene-Pleistocene age (Shevchuk 1981).

Nowadays, about 30 sources of high and medium quality volcanic glasses are known on Kamchatka (Figure 7.2). In the Central Kamchatkan Volcanic Belt corresponding to the Central Range obsidian-bearing volcanic formations are dated to Oligocene–Neogene times; and in the Eastern Kamchatkan Volcanic Belt occupied by the Eastern Range obsidian is known mainly among the Pleistocene rocks. In southern Kamchatka, obsidian-containing rocks are dated to the Pliocene–Pleistocene. Volcanic glasses on Kamchatka occur in extrusive domes, lava and pyroclastic flows, and in the pyroclastic products (as tephras and pumice tuffa fragments). According to their chemical composition, volcanic glasses correspond to dacites and rhyolites.

In this chapter, we summarise the results of research in obsidian geology and geochemistry of the Kamchatka Peninsula as of 2013, and present an attempt to create a search strategy for the still unknown primary sources by means of geochemical typification and geochronological examination of both archaeological and geological obsidians.



Figure 7.1. Selected obsidian sources on Kamchatka and archaeological sites with artefacts associated with them. Major tectonic zones of Kamchatka are indicated by grey shadings. 1 – archaeological sites; 2 – obsidian sources (black stars are primary sources of archaeological obsidian, and grey stars are geological sources not used in prehistory)

GEOLOGICAL HISTORY OF KAMCHATKA: A SHORT OUTLINE

Kamchatka Peninsula together with the Kurile Islands is usually considered as a single island arc system; however, the tectonic position of Kamchatka is more complicated. The Kurile–Kamchatkan Island Arc system consists of a typical island arc (the Kuriles) and an active continental margin (Kamchatka). In the north it meets the Aleutian Island Arc at an almost right angle. Three island arcs of different ages are distinguished on Kamchatka (Avdeiko *et al.* 2006). The most ancient one is the Western



Figure 7.2. Major obsidian sources on the Kamchatka Peninsula (after Otchet ... 1992, modified). 1 – Tolmachev Dol (Chasha Maar); 2 – Nachiki Stream; 3 – Taburetka River; 4 – Nachiki (Shapochka Summit); 5 – Karimsky Volcano; 6 – Krasheninnikov Volcano; 7 – Khangar Volcano (Southern); 8 – Khangar Volcano (Central); 9 – Khangar Volcano (Eastern); 10 – Khangar *Volcano (Northern); 11 – Gigigilen; 12 – Payalpan;* 13 – Maly Payalpan; 14 – Nosichan; 15 – Polyarnaya Summit; 16 – Tynya Summit; 17 – Belogolovaya Vtoraya River; 18 – Kunkhilok; 19 – Sedanka; 20 – Itkavayam (Southern); 21 – Itkavayam (Northern); 22 – Kevenei (Northern); 23 – Kevenei (Western); 24 – Levye Nachiki; 25 – Levoe Khailuli Plateau; 26 – Maryavaam; 27 – Palana (Southern) and Korkavayam; 28 – Palana 1; 29 – Posledny Stream; 30 – Vanyavaam; 31 – Kichiga *River, right side; 32 – Belaya River headwaters; and*

Kamchatkan Volcanic Arc of late Cretaceous age. In the Oligocene – early Miocene, the Central Kamchatkan and the Southern Kamchatkan island arc systems existed, with a wide Malki–Petropavlovsk Zone of tectonic dislocations between them. In the middle Miocene – early Pliocene, due to the displacement of the subduction zone

33 – Kichiga River, left side

to its present position, the Eastern Kamchatkan Volcanic Belt emerged. The late Pleistocene – Holocene volcanism progressed not only in the frontal and rear parts of the Eastern Kamchatkan Volcanic Belt, but also in the Central Range. In southern Kamchatka, the volcanic belt coincided with the Oligocene – early Miocene volcanic zone.

The Central Kamchatkan and Southern Kamchatkan Volcanic Belts

The geological evolution of the Kamchatkan Island Arc in the Oligocene–Miocene is connected to the formation of surface volcanism in the central and southern parts of the peninsula. The Central Kamchatkan Volcanic Zone (hereafter – the Central Range; see Figure 7.1) stretches from the Kamchatka Isthmus to the Malki–Petropavlovsk Zone. The Central Range appeared in the late Paleogene as the horst–anticline uplifts composed of late Mesozoic folded complexes.

The Southern Kamchatkan Volcanic Zone (see Figure 7.1, "Southern Kamchatka") extends for 230 km from the upper reaches of the Paratunka and Plotnikova rivers (the latitude of Petropalvovsk-Kamchatskiy) southward to the Lopatka Cape, and ranges in width from 10 to 45 km. In contrast to the Central Range, the formation of this zone extended to the middle Miocene and even up to the Pliocene in the extreme south, in the tectonic settings of a typical island arc. It existed as a chain of volcanic islands surrounded by shallow waters (Khanchuk 2006).

The geological history of both volcanic zones on Kamchatka is notable for two major stages of volcanism. The first stage is dated to the late Oligocene – early Miocene. Volcanic rock formations accumulated at that time in the Central Range are represented by two suites of the Anavgai Complex. According to the chemical composition of effusive rocks, the lower (Krapivina) suite is dominated by andesites and basaltic andesites, with some basalts and their tuffs, sand tuffs, and aleurolites. The upper (Berezovka) suite consists of two parts according to their composition: 1) a lower part, composed predominantly of andesite–dacite lavas and tuffs about 800 m thick; and 2) an upper part, represented by volcanic-sedimentary rocks about 500 m thick.

The second stage of rock formation is related to the most powerful flare-up of surface volcanism which occurred in the late Miocene – Pliocene, and resulted in the formation of the Alnei Series. Volcanic rocks are represented by basaltic, andesitic, and dacitic lava flows and subvolcanic bodies, ignimbrite sheets, and detached tuff horizons. According to Leonov *et al.* (2008), the age of the Central Range ignimbrites corresponds to the lower Pliocene, ca. 3.5–5.7 Ma.

It should be noted that an independent phase of volcanism within the Central Range in the Pleistocene–Holocene resulted in the formation of volcanic structures recognised as the Pleistocene Volcanic Belt. The most abundant primary occurrences of obsidian are associated with products of the Oligocene–Pliocene and Pleistocene–Holocene phases of acidic volcanism in the Central Range.

The Eastern Kamchatkan Volcanic Belt

The Eastern Kamchatkan Volcanic Belt stretches along the eastern coast of Kamchatka for about 850 km in NNE direction, and ranges in width from 50 to 100 km (Figure 7.1, "Eastern Range"). It was formed during the last 50,000-60,000 years, and is composed of large volcanic edifices such as shield volcanoes, stratovolcanoes, and calderas, as well as a multitude of smaller volcanic structures like maars, explosive funnels, and extrusive domes. The volume of volcanic products is ca. 14,000-15,000 km³, and it covers a territory of about 15,000 km² (Fedotov and Masurenkov 1991). Shield volcanoes and stratovolcanoes consist mostly of basalts and andesites; dacites and rhyolites are also widespread. Volcanic glasses (obsidians and perlites) are related to some types of these rocks in the Uzon Caldera and the Karymsky Volcanic Centre.

MATERIALS AND METHODS

The geochemical study of volcanic glasses was conducted using Neutron Activation Analysis (henceforth NAA). The NAA is one of the most advanced methods to study the chemical composition of volcanic glasses, with sensitivity limits for most elements in the parts-per-billion to parts-per-million ranges. The advantage of NAA is that one can use small samples (starting from 10-20 mg) to determine the content of more than 25 chemical elements, including rare-earth ones, in order to reveal a unique geochemical 'fingerprint' of a particular volcanic glass source. For our study, NAA analysis was performed at the Archaeometry Laboratory, University of Missouri Research Reactor Center (hereafter - MURR) in Columbia, Missouri (USA).

In total, about 500 samples of obsidian from Kamchatka were studied in 2003-11. Some of them were collected by our team during fieldwork campaigns in 2004-5. Several colleagues from the Institute of Volcanology and Seismology (Far Eastern Branch of the Russian Academy of Sciences) in Petropavlovsk-Kamchatskiy and from the Institute of Geochemistry (Siberian Branch of the Russian Academy of Sciences) in Irkutsk (both in Russia), contributed to our collection of obsidian from primary Kamchatkan sources. Archaeological samples (obsidian artefacts from the final Palaeolithic - Palaeometal sites) were collected by Dr A. V. Ptashinsky who participated in our studies (see Glascock et al. 2006; Grebennikov et al. 2010, 91; Kuzmin et al. 2008); other samples were obtained by us in 2005 from the collection of the late Prof. Nikolai N. Dikov stored at the Northeastern Multidisciplinary Research Institute (Far Eastern Branch of the Russian Academy of Sciences) in Magadan, Russia, including the Ushki cluster (see Kuzmin et al. 2008).

The samples were cleaned to rid the surface of contaminants, and then divided into aliquots of 25–50 mg each. Specimens were exposed to thermal neutrons in the reactor; after that, the abundance of up to 28 chemical elements (Al, Cl, Dy, K, Mn, Na, Ba, La, Lu, Nd, Sm, U, Yb, Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, and Zr) was determined. Data about the content of all these elements can be obtained using long-irradiation of samples. For some samples, only short-irradiation was applied, and the content of seven elements was measured: Al, Ba, Cl, Dy, K, Mn, and Na. Details on the NAA method can be found elsewhere (e.g., Glascock *et al.* 2007; Malainey 2011; Pollard *et al.* 2007; see also Grebennikov *et al.* 2010, 91).

Statistical grouping, based on bivariate and triangle plots, and cluster and discriminant classification analyses, was performed with the help of GAUSS software (available from the MURR; Internet access: http://www.missouri.edu/~glascock/profile.htm), to indicate within a 95% degree of probability the major geochemical groups reflecting obsidian sources (see details in Glascock *et al.* 1998). As a result, the individual sources were securely identified.

The potassium-argon (K-Ar) dating of obsidian samples was carried out by the Laboratory of Stable Isotopes of the Far Eastern Geological Institute, Far Eastern Branch of the Russian Academy of Sciences (hereafter - FEB RAS) in Vladivostok, Russia. In order to measure the content of radiogenic Ar, an original Continuous-Flow Gas Chromatography/Isotope-Ratio Mass Spectrometry (CF-GC-IRMS) with laser ablation method, developed by the staff of this Laboratory, was applied (Ignatiev et al. 2010; Budnitsky 2013). The isotope composition of Ar was investigated using a MAT-253 Mass Spectrometer (Thermo Scientific Co.); the content of K was measured with the Atomic Absorption Spectrophotometry method at the Laboratory of Analytical Chemistry, Far Eastern Geological Institute FEB RAS.

PRIMARY SOURCES OF OBSIDIAN ON KAMCHATKA: RECENT STATUS

Seven geochemical groups containing both archaeological and geological obsidians were established by our team on Kamchatka (Figure 7.1). Four groups are directly attributed to primary sources in the Central Range, with precisely known locations: 1) Itkavayam Volcano (group KAM-03); 2) Payalpan Volcano (KAM-05); 3) Belogolovaya Vtoraya River source (KAM-07); and 4) Nosichan Volcano (KAM-16). The Karymsky Volcano source (group KAM-09) was identified in the Akademii Nauk [Academy of Sciences] Caldera which is a part of the Karymsky Volcanic Centre in the Eastern Range. Two primary sources were identified in southern

Kamchatka, the Nachiki Volcano (group KAM-06) and the Tolmachev Dol Volcano (KAM-11).

The Central Range

The majority of obsidian sources on Kamchatka are located in the Central Range (Figures 7.1–7.2). They are situated at higher elevations within the mountain plateaus covered with tundra, as open-air scatters of colluvial origin. Dacitic and rhyolitic obsidians are presented by blocks and big chunks. The colour and structure of obsidian varies, and in some places the iridescent kinds are found.

The Itkavayam Volcano Source Group

In the northern part of the Central Range, more precisely the headwaters of the Vayampolka and Kutina rivers, the Itkavayam obsidian source group is located (Figure 7.2, Nos. 20–21). It consists of at least four sub-sources on the slopes of Ritman Volcano (Otchet ... 1992; Shevchuk 1981). The first sub-source, at the headwaters of the Itkavayam River, is a 200 m thick deposits which originated from the Obsidianovy Volcano due to a circular fracture on the slopes of the Ritman Volcano. The obsidian-bearing rocks form a plateau-like upland. The thickness of several alternating obsidian layers ranges from 0.3-0.4 to 15 m. Obsidians are blackcoloured, transparent in thin sections, and sometimes banded due to light and dark streaks. Obsidians have a strong glassy lustre and shell-like fracture with sharp edges. Red and mahogany coloured obsidians, with the colours due to the presence of dusty and flaky hematite, were also observed.

The second sub-source is located 2.5 km SW of the first one. It is composed of sub-horizontally bedded lava flows, with its thickness ranging from 3-5 to 5-15 m; the aggregated beds are up to 200 m thick. The lower part of the obsidian-bearing stratum (70 m in thickness) consists of mainly black obsidian, with thin red mahogany coloured bands. The upper part of the stratum is composed of pure black volcanic glass with small plagioclase impregnations. Black obsidians are characterised by brittleness, a dull lustre, and an almost absolute lack of the distinct shell-like fracture. It is worth noting that the obsidians of the second sub-source differ from obsidians of the first one by their lower silica contents (Otchet ... 1992).

The third sub-source of the Itkavayam obsidian group was found on the southeastern slope of the Ritman Volcano, in a valley of one of the Keveneivayam River tributaries. The obsidian flows occupy a territory of 4 km²; several of them are up to 30–60 m thick. The obsidians have a distinct black colour, a glassy lustre, and a shell-like fracture, with small plagioclase inclusions occupying 5–10% of the rock volume.

The fourth sub-source is located on the southeastern slope of the Ritman Volcano in the valley of a small stream, a tributary of the Keveneivayam River, and is represented by blocks of eluvium consisting of black glassy obsidian. This locality covers an area of up to 4 km². N. T. Demidov and his colleagues (see Otchet ... 1992, 421) suggested that these obsidians initially formed the top of a series of lava flows which later underwent intensive glacial weathering. The thickness of the flows remains unknown.

Obsidian Sources of the Ichinsky Volcanic Centre

The Ichinsky cluster of obsidian sources is situated in the middle sector of the Central Range (Figure 7.2, Nos. 11–17). This is the largest single area with volcanic glasses on Kamchatka, and it covers a territory of ca. 700 km². In the vicinity of the Ichinsky Volcano with an elevation of 3621 m above sea level (Figure 7.3, see lower left corner), situated on the western slope of the Central Range, there are at least 11 distinct volcanic glass sources, namely Belogolovaya Vtoraya River, Tynya, Polyarnaya, Nosichan, Payalpan, Maly Payalpan, Galdavit, Studeny, Zemnoy Creek, Zemnoy Summit, and Gigigilen (Figure 7.3). This information is based on the inventory of volcanic glass sources generated by the Geological Survey of Russia (Otchet ... 1992).

Obsidians from three of these sources — Payalpan (group KAM-05), Belogolovaya Vtoraya River (KAM-07), and Nosichan (KAM-16) — have been identified in archaeological collections (Figure 7.1; see also Grebennikov *et al.* 2010). The volcanic glass corresponds mainly to dacite–rhyolites of the upper part of the Alnei Series of late Miocene age (Sheimovich and Patoka 2000). Some sources, such as the Belogolovaya Vtoraya River, may have been created approximately 2.5 Ma ago.

The Payalpan is the major volcanic glass source in Kamchatka, and it is famous because of a rare decorative variety of blue obsidian. The Payalpan source of Pliocene age is located 25 km NE of the Ichinsky Volcano, on the western slope of the Maly Payalpan Volcano (Figure 7.3, No. 5). Our microscopic study shows that the blue shade of this obsidian is defined by the colour of fluidal lines of crystallites rather than by the ore dust impurity, as it was previously suggested by Eremina (2009). Obsidian deposits at the Payalpan source are associated mainly with the upper Pliocene sub-volcanic rhyolitic domes and effusive formations like sheets and covers of lava, tuff, tuff breccia, and ignimbrite (Figure 7.3). The obsidian layers here are generally not thick, at 1–2 m on average. Obsidian occurs mainly as individual layers, and also as sets of extended, squeezed, and contiguous lenses in rhyolites; small obsidian flows are also known. The richest in blue obsidians are colluvial deposits on the banks of the Obsidianovy Creek, with a diameter of pieces from 3-5 to 50 cm. These deposits are located so close to the primary rhyolitic extrusion that some researchers suggested an extrusive genesis of obsidian (see Otchet ... 1992). However, this issue is still uncertain due to insufficient data on the depositional conditions and characteristics of obsidian bodies, and the abundance of lenses of brecciated obsidians in pyroclastic deposits. The

obsidians vary in colour and texture: there are dark-grey, black, and greenish massive obsidians; and finely fragmented reddish-brown and bluish-banded ones.

The Belogolovaya Vtoraya River source (Figure 7.3, No. 1) is a set of lenses and layers of obsidians embedded in effusive and pyroclastic rocks of moderately acidic composition. Obsidian lenses are found in the upper part of the dacitic lava flow outcrop of middle Pleistocene age, as scatters of colluvium on steep slopes of the Tynya Summit (Figure 7.3, No. 2). Volcanic glass is mostly black and with cracks, and contains plagioclase phenocrysts. Other varieties are represented by brownish and mahogany coloured obsidians with black inclusions.

On the right bank of the Nosichan River and in the vicinity of the Polyarnaya Summit (Figure 7.3, Nos. 3–4), there are small obsidian scatters and rare primary outcrops in the form of lenticular beds and dikes of Pliocene age. They are from 4–5 to 8 m thick (at bulges), and up to 270 m long. All locales are genetically related to rhyolitic extrusions, and are characterised by multi-coloured volcanic glasses: mostly black glass (both transparent and smoky), and, more rarely, amber, brown, and lilac ones. The size of non-rounded obsidian fragments is predominantly 0.5–2.5 cm; pieces of up to 10 cm in diameter are rare.

The Khangar Volcano Source

South of the Ichinsky cluster, there is another obsidian source in the caldera of the Khangar Volcano (Figure 7.2, Nos. 8–10). The recent crater was formed as a result of an eruption at about 6900 BP (Melekestsev *et al.* 1996). According to data collected by the Geological Survey of Russia (see Otchet ... 1992), there are several obsidian outcrops inside the caldera. They are related to extrusive dacites and represented by lenses, dikes, and beds of Pleistocene volcanic rocks, created after apical explosion of the caldera but before the formation of the recent crater in the mid-Holocene. Fissured and massive volcanic glasses are mainly black and fallow in colour; brown and blue kinds are rarer.

The Eastern Range

This part of Kamchatka has several active volcanoes, such as Krasheninnikov, Karymskaya Sopka, Avachinskaya Sopka, and others (see Fedotov and Masurenkov 1991). Several volcanic glass sources are known in the central part of the range, and they are correlated to the Pleistocene phase of the acidic ignimbrite volcanism. Glasses are mainly perlites, and one of the best-known sources is situated in the Uzon Caldera.

The Krasheninnikov Volcano obsidian source (Figure 7.2, No. 6) is a series of lava flows 100–200 m long and 5–20 m thick of early-to-middle Pleistocene age. Obsidian occurs as thin layers inside these volcanic rocks, and it is mainly dark-grey and rarely brick-red in colour.



Figure 7.3. Schematic map of volcanic glass sources of the Ichinsky Volcanic Centre (after Otchet ... 1992, modified).
1-3 – Holocene deposits: 1 – alluvial and glacial deposits; 2 – upper basaltic strata; 3 – lower basaltic strata;
4 – lower Pleistocene basalts; 5 – upper Pleistocene basaltic andesites and scoriae; 6 – upper Pleistocene – Holocene andesites and dacites; 7 – middle Pleistocene dacites and ignimbrites; 8 – Holocene rhyolites and dacites; 9 – middle Pleistocene rhyolites and dacites; 10 – trachytes and trachyandesites; 11 – andesites; 12 – dacites; 13 – rhyolites; 14 – Miocene – Pliocene basaltic andesites, andesites, dacites, tuffs, tuff breccias, and ignimbrites of the Alnei Series; 15 – subvolcanic bodies; 16 – borders of volcano-tectonic calderas; 17 – volcanic glass sources: 1 – Belogolovaya Vtoraya River; 2 – Tynya Summit; 3 – Polyarnaya Summit; 4 – Nosichan; 5 – Payalpan; 6 – Maly Payalpan; 7 – Galdavit; 8 – Studeny; 9 – Zemnoy Creek; 10 – Gigigilen; and 11 – Galdavit Creek

Seven primary outcrops of obsidian are found, 0.8–2 m thick and up to 5 m long, and they are black, massive, and dotted with transparent insets (Otchet ... 1992).

Another obsidian source is known in the Karymsky Volcanic Centre (Figure 7.2, No. 5). Here pure obsidians are embedded in the pumice "noble" tuffa of the Odnoboky Volcano, dated to ca. 100,000 years ago (Masurenkov 1980). The younger pyroclastic pumices of the Akademii Nauk Caldera, dated to ca. 28,000–40,000 years ago, also contain obsidian fragments. The texture is massive, with a transparent thin edge, and black in colour. Obsidian is plentiful on the modern shore of the caldera lake.

Southern Kamchatka

South of the city of Petropavlovsk-Kamchatskiy, several volcanic glass sources of Neogene and Pleistocene age are known. One of the largest is the Nachiki source of perlites and pure obsidians as a part of extrusive dome of the Shapochka Volcano (Figure 7.1; Figure 7.2, No. 4), dated to the Pliocene. A distinct feature of the Nachiki source is the presence of plagioclase and pyroxene phenocrysts in the black glass matrix. Natural outcrops of this source are visible at the top of the Nachiki Summit as a sheet of volcanic glasses representing the selvage of chilled extrusive rhyolites. The obsidian and perlite deposits have a complex structure. The obsidian is black, whereas the perlites have a lighter colour (greyish-black) and they are weakly transparent and gently banded. Perlite from the Nachiki source is a subject of commercial mining due to its superior quality for the production of thermal insulation materials.

The second obsidian source is situated on the watershed of the Bannaya and Plotnikova rivers, and is named by us the Bannaya River (Figure 7.1). Numerous nodules of high quality transparent obsidian (up to 3–7 cm in diameter) are visible in the rhyolites and perlites of the extrusive dome of the Yagodnaya Summit.

The third source, Chasha Maar, is located to the west of the Gorelaya Sopka Volcano in the Tolmachev Dol River valley (Figure 7.2, No. 1). It originated from the slaggy lava cone of the Chasha Maar dated to ca. 4600 BP (Dirksen *et al.* 2002). Among the fragments of volcanic tephra, large (up to 30 cm long) pieces of obsidian of unusual light grey colour were found.

SEARCH STRATEGY FOR UNKNOWN OBSIDIAN SOURCES ON KAMCHATKA PENINSULA

Prior to the description of the search strategy for still unknown obsidian sources, it should be highlighted that the majority of obsidian sources on Kamchatka consist of several sub-sources separated from each other by often considerable distances, and they occur within volcanoes in a variety of forms: as extrusive bodies, lava sheets, and pyroclastic deposits. They reflect, as a rule, different formation stages of the volcano and may also differ in chemical composition. Unfortunately, we had no opportunity for detailed sampling of obsidians (including assignment of samples to particular strata) from many sub-sources due to their inaccessibility without helicopter transport. Also, obsidian samples collected by other researchers without precise pinpointing to a particular layer in the volcanic deposits are frequently used in our study. As a result, these circumstances limit to some extent the possibility to identify the exact primary sources of obsidian artefacts.

As was discussed earlier (see Glascock *et al.* 2006; Grebennikov *et al.* 2010; Kuzmin *et al.* 2008; Popov *et al.* 2007), primary ('geological') sources of obsidian on Kamchatka have been studied insufficiently in comparison to obsidian artefacts. There are at least seven geochemical groups of obsidian on Kamchatka identified only in prehistoric assemblages (Grebennikov *et al.* 2010; Kuzmin *et al.* 2008), and the location of their sources is still unknown. A similar situation can be observed in neighbouring Alaska where geochemical analysis of obsidian artefacts shows that they are derived from at least 25–30 primary sources, but less than ten have been precisely located so far (see Reuther *et al.* 2011).

Due to the large number of obsidian sources on Kamchatka, more research is still needed to correlate the archaeological volcanic glasses with the sources. On the one hand, geochemical data and the spatial distribution of archaeological sites allowed us to suggest possible localisation for the unknown sources; the first attempt was done by Grebennikov et al. (2010, 104). On the other hand, additional information is still necessary to determine the position of primary sources with a satisfactory degree of precision, in order to be able to visit them in the future and to conduct detailed studies. This situation, along with the fact that many of the obsidian sources on Kamchatka are still not sampled (see Figure 7.2), is the reason why we put forward the task of identification of the currently unknown primary obsidian locales with a minimal amount of labour and finance expenditure necessary for fieldwork on the large and logistically extremely difficult Kamchatkan terrain.

For this purpose, we have developed a search strategy based upon the existing geochemical data of geological archaeological obsidians and from Kamchatka (Grebennikov et al. 2010). In the quest for unknown archaeological obsidian sources, we use two important parameters: 1) the geochemical typification of volcanic rocks and glasses; and 2) the absolute age of archaeological and geological obsidians. For the first task, all possible geological data were analysed. As for the second task, age determination for archaeological obsidians and their assignment to volcanic glass outcrops of appropriate age was undertaken. Chronological study is also necessary to confirm that obsidian artefacts belong to a particular volcanic structure. To solve the problem of age correlation between volcanic glasses from geologic sources and archaeological sites, K-Ar dating of obsidians was conducted (Budnitsky 2013).

GEOCHEMICAL CRITERIA FOR IDENTIFICATION OF UNKNOWN OBSIDIAN SOURCES

The KAM-01, KAM-04, KAM-10, and KAM-14 Groups

The KAM-01, KAM-04, KAM-10, and KAM-14 groups have a Nb/Zr ratio of around 0.04, which is typical for volcanic rocks of the Eastern Kamchatkan Volcanic Belt. It should be noted that archaeological sites with artefacts belonging to these groups (see Grebennikov *et al.* 2010, 107–10) are in the vicinity of the Karymsky source (group KAM-09), which has a similar Nb/Zr ratio. Additionally, the chemical composition of these groups is very similar to the KAM-09 group (Figures 7.4–7.6). Based on current information, we assume that the primary obsidian sources for all of these groups are situated somewhere in eastern Kamchatka.

The KAM-02 Group

The most enigmatic geochemical group of Kamchatkan archaeological obsidian is KAM-02. Artefacts belonging to it are found at the majority of sites in southern and southeastern Kamchatka (Figure 7.7). For this group, the high concentrations of K, high-field-strength elements (Zr, Hf, Ta, and Th), and rare-earth elements, are considered typical for within-plate granites. Volcanic glass of the KAM-02 group plotted on the Hf–Rb–Ta

diagram corresponds to the Eastern Kamchatkan Volcanic Belt (Figure 7.6). Besides this, volcanic glasses from eastern Kamchatka (Uzon Caldera and Odnoboky Volcano in the Karymsky Volcanic Centre) are characterised by minimal Nb/Zr ratios, and this is similar to the KAM-02 group. However, based on the majority of geochemical plots the obsidian of this group is closer geochemically to volcanic glasses from southern Kamchatka or falls into outliers. In Figures 7.4–7.5, it is clear that volcanic glasses from eastern and southern Kamchatka, and the Central Range create separate clusters (divided by empiric lines, see Figure 7.5), depending on the content of chemical elements. Probably, this feature reflects the specifics of primary magma sources that determine the formation of obsidians in these regions.

One of the specific features of the Kamchatka Peninsula is that besides the proper island arc volcanism in the boundary region between two convergent tectonic plates, a different type of volcanic activity is also known, and it is petrologically and geochemically close to the withinplate geodynamic settings (Khanchuk 2006). The Bakening Volcano, located between the Central Kamchatkan Basin and the Eastern Range, is one of such structures (Figure 7.7). Here, volcanic rocks are represented by the Miocene–Pliocene calc-alkali basalts of the Paratunka and Alnei series, and by the late Pliocene – early Pleistocene sub-alkali rocks enriched with high-charged elements (Dorendorf *et al.* 2000). The



Figure 7.4. Bivariate plots showing geochemical groups of Kamchatkan obsidian (ellipses indicate 95% confidence level)



Figure 7.5. Bivariate plots showing geochemical groups of Kamchatkan obsidian (ellipses indicate 95% confidence level)



Figure 7.6. The Hf – Rb / 30 – Ta x 3 discriminant diagram for obsidian source samples and artefacts (groups KAM-01 through KAM-16) from Kamchatka and their tectonic position (after Grebennikov et al. 2010, modified). I – volcanic glasses from the Eastern Range; II – volcanic glasses from southern Kamchatka; III – volcanic glasses from the Central Range



Figure 7.7. The distribution of archaeological sites with obsidian artefacts of the KAM-02 group (black circles) on Kamchatka, and location of the Bakening Volcano (black star) as their possible source (after Grebennikov et al. 2010, modified)

volcano is situated in the headwaters of the Srednaya Avacha River. Several archaeological sites with obsidian of the KAM-02 group are located at the mouth of the Avacha River which originates from the confluence of the Srednaya Avacha and Levaya Avacha rivers (Figure 7.7). Along with the stratovolcano of Bakening, the watershed of these rivers has a multitude of monogenic rhyodacite volcanic domes, so-called *tuyas*. Dorendorf *et al.* (2000, 135) recorded the black phenocryst-free obsidian among the tuya rocks. It is therefore quite possible that the source of the KAM-02 group is located in this area.

The KAM-15 Group

According to the geochemical data, the KAM-15 group has some resemblance to the Belogolovaya Vtoraya River

source (group KAM-07) and corresponds to obsidians of the Central Range (Figure 7.4). This fact can be used to tentatively place the source of the KAM-15 group in the Ichinsky Volcano region.

AGE OF OBSIDIAN AS A CRITERION FOR THE SEARCH OF UNKNOWN SOURCES

Geological Samples

The obsidians for age determination were selected from the Ichinsky Volcanic Centre, Lake Palana, Nachiki, and the Yagodnaya Summit, which are among the most important obsidian outcrops of Kamchatka. The late Pleistocene – Holocene volcanic glasses from the Chasha Maar, Karymsky, Khangar, and other volcanoes were excluded from this study because of their relatively young geological age, which cannot be determined by the K–Ar method with the necessary precision.

The obsidian outcrops mentioned above (except for the Yagodnaya Summit) have not been dated by isotopic methods before, and their ages remained the subject of dispute because of a lack of geochronological data for young volcanic rocks on Kamchatka. In recent years, however, the situation has changed considerably. New argon-argon (Ar-Ar) age determinations for ignimbrites were obtained for the eastern and southern parts of Kamchatka as well as for the Central Range (Bindeman et al. 2010; Leonov and Rogozin 2010; Leonov et al. 2008). According to these studies, the oldest ignimbrites are now known in the Central Range (dated to ca. 3.5-5.7 Ma ago), and ignimbrites from eastern and southern Kamchatka are younger than 3 Ma. This is an important fact because ignimbrite volcanism was generally accompanied by and ended with the intrusion of extrusive rhyolites; and the outcrops of volcanic glasses (obsidians and perlites) are often found in direct association with ignimbrites.

The Lake Palana obsidian outcrop is located in the Palana River headwaters (northern part of the Central Range), and is represented by obsidian dikes and beds in volcanic rocks of the Alnei Series (Shevchuk 1981). The age of the obsidian obtained, ca. 5.57 Ma (Table 7.1), confirms the earlier conclusion by Leonov *et al.* (2008) about the early Pliocene acidic volcanism in the Central Range.

The Ichinsky Volcanic Centre in the middle section of the Central Range has more than ten primary obsidian outcrops (see above). Although the geology of igneous rocks in this region is well-studied, it was still necessary to obtain an age determination for the obsidian. We analysed five obsidian samples from the main outcrops. Two of them, from the Payalpan and the Belogolovaya Vtoraya River sources, revealed excess air argon. Therefore, these samples are unsuitable for age determination by the K–Ar method. Three other samples (from the Dimshikan, Bystraya River, and Nosichan outcrops) were successfully dated.

Sample ID	Age, Ma	Source Name and/or Geochemical Group No.	Location of Source
Geological samples			
G-7	5.57 ± 0.16	Lake Palana	Central Range (north)
G-1	2.78 ± 0.14	Bystraya River	Central Range (middle)
KTE-4	2.77 ± 0.085	Dimshikan	Central Range (middle)
KLD-2	1.31 ± 0.087	Nosichan (KAM-16)	Central Range (middle)
РК-3-1	3.06 ± 0.19	Bannaya River	Southern Kamchatka
Archaeological samples			
КР-3-1	5.90 ± 0.18	KAM-08	Central Range (north) or Kamchatka Isthmus?
КР-3-1	6.32 ± 0.18	KAM-08	Central Range (north) or Kamchatka Isthmus?
КР-20-6	3.27 ± 0.09	KAM-10	Eastern Kamchatka? [Stol Summit, age of 3.71 ± 0.08 Ma; Bindeman <i>et al.</i> (2010); Leonov <i>et al.</i> (2008)]
KP-1-1	1.94 ± 0.057	KAM-01	Southern Kamchatka? [Karymshina Caldera, age of ca. 1.78–1.81 Ma; Leonov <i>et al.</i> (2008)]

Table 7.1. Ages determined by K-Ar method for obsidians from Kamchatka (after Budnitsky 2013)

The Dimshikan outcrop is located in the headwaters of the Dimshikan River, a tributary of the Bystraya River in the Central Range. It is represented by lens-like obsidian layers within the rhyolite lava flows of the Alnei Series. The result of K-Ar dating, ca. 2.77 Ma (Table 7.1), testifies that rhyolites and the related volcanic glasses were formed in the late Pliocene, and this corresponds to the Alnei Phase of Kamchatkan volcanism (Bindeman et al. 2010). The Bystraya River obsidian outcrop is situated in the upper reaches of the river basin. Volcanic glasses can be found as a sheet in the sequence of acidic rocks of the Alnei Series. These rocks of unusual light-brown colour contain up to 10% of plagioclase phenocrysts. The absolute age of ca. 2.78 Ma (Table 7.1) corresponds to the Alnei Phase. The Nosichan obsidian outcrop belongs to the middle Pleistocene extrusive rhyolites according to the available data (Otchet ... 1992). However, dating of this obsidian revealed an early Pleistocene age of the rhyolite extrusion, ca. 1.31 Ma (Table 7.1).

Leonov *et al.* (2008) determined the age of ignimbrites in the Nosichan Volcano area as 4.02 ± 0.12 Ma (an obsidian fragment in welded tuff was dated). The results obtained by our group testify that extrusive rhyolites are not connected to the Pliocene phase of the ignimbrite volcanism that occurred in the Central Range. The time of origin for obsidians at the Nosichan Volcano corresponds to ignimbrites of the Kronotsk–Gamchen volcanic structure in the Eastern Kamchatkan Volcanic Belt and of the Bannaya River basin in southern Kamchatka (Leonov *et al.* 2008). We suggest that obsidians of the Nosichan Volcano were formed during the early Pleistocene phase of acidic volcanism in the Central Range.

Archaeological Samples

Out of seven geochemical groups consisting entirely of archaeological obsidian, four samples were analysed

(Table 7.1). The data obtained reflect ages of three volcanic glass sources from unknown locales. The KAM-01 group is the largest in terms of the number of samples: 113 artefacts from 20 archaeological sites, with most of them from southern Kamchatka (see Grebennikov et al. 2010, 107). The KAM-01 obsidians correspond to volcanic glasses from the Eastern Kamchatkan Volcanic Belt (see above). For dating, an obsidian artefact from the Avacha site was selected (KP-1-1, Table 7.1). The age of this specimen, ca. 1.94 Ma, indicates that the primary source of volcanic glass is of early Pleistocene age. This epoch is known for powerful ignimbrite eruptions which affected both eastern and southern Kamchatka. In particular, ignimbrites of the Karymshyna Caldera in southern Kamchatka were formed during the period of 1.78-1.81 Ma ago (Table 7.1). According to information provided by V. L. Leonov (personal communication, 2012), older rhyolite extrusions dated to ca. 2-3 Ma ago are known in the vicinity of this caldera. All these data help our group to plan a fieldwork campaign within the boundaries of the Karymshyna Caldera in the near future.

The KAM-10 group of archaeological obsidians is represented by 52 samples from 10 sites, compactly distributed along the Kamchatka River; the only exception is the Lisy site at the southern end of the Kronotsk Peninsula (Grebennikov et al. 2010). An obsidian artefact from the Anavgai 2 site was chosen for dating as typical for this group. The age obtained, ca. 3.27 Ma (KP-2-6; Table 7.1), testifies that the primary obsidian source is dated to the late Pliocene. Close correlation exists between the geochemical composition of obsidians of this group and volcanic glasses of the Eastern Kamchatkan Volcanic Belt (see above). The data about the age of the KAM-10 obsidian allows us to suggest a possible connection between the primary source and the Pliocene ignimbrite volcanism of the Karymsky Volcanic Centre. For example, the ignimbrite strata of the Stol Summit situated on the watershed of the Levaya Zhupanova and Pravaya Zhupanova rivers contain welded tuffs and obsidian fragments dated to ca. 3.71 Ma ago (Table 7.1). Besides this, near the Anavgai 2 site on the western slopes of the Eastern Range there are outcrops of obsidian of the same age (V. L. Leonov, personal communication 2012).

The KAM-08 group consists of nine volcanic glass samples from the Pakhachi, Vaimitangin, and Penzhina archaeological sites in northern Kamchatka (also called Koryak Region) (Grebennikov et al. 2010, 113). We analysed two kinds of obsidian artefacts from the Pakhachi site: 1) translucent volcanic glass; and 2) poorly translucent (with abundant ore mineral spots) volcanic glass, and determined two ages corresponding to the late Miocene: ca. 5.90-6.32 Ma (KP-3-1; Table 7.1). According to the data obtained, the primary source of obsidian for this group may occur at one of the volcanic structures of the Central Range. However, based on the overall distribu-tion of artefacts assigned to this source (see Grebennikov et al. 2010, 113), it seems very likely that it is located north of the Kamchatka Isthmus, or within this area.

CONCLUSIONS

Knowledge of geology and volcanology in regions with abundant obsidian artefacts is one of the major requirements for understanding the genesis and exact location of primary volcanic glass sources as well as the patterns of obsidian exploitation by prehistoric people. Using the information on the geological structure of the territory under investigation, it is possible to establish the criteria for analysis of geochemical data for both geological and archaeological obsidians, in order to pinpoint the original outcrops which were used by ancient populations to acquire valuable raw material (see also Wada *et al.*, this volume). This is especially necessary for regions with a complex geological structure and a multitude of obsidian sources, and the Kamchatka Peninsula of the northern Russian Far East is one of these territories.

The age determinations for both geological and archaeological obsidians used in our study are in good accordance with the results of geochemical typification of volcanic glasses from Kamchatka. The combination of these approaches along with features of spatial distribution of obsidian with different geochemical signatures at archaeological sites allows us to propose a strategy for the search of the unknown sources of archaeological obsidian. As a result of its application, we suggest the localisations of primary sources for different geochemical groups of archaeological obsidian: 1) the Karymshina Caldera and its vicinity (southern Kamchatka) for the KAM-01 group; 2) the vicinity of the Stol Summit (Karymsky Volcanic Centre, the Eastern Range) for the KAM-04, KAM-10, and KAM-14 groups; 3) rhyodacitic domes (tuyas) of the Bakening Volcano (between the Eastern and Central ranges in the upper reaches of the Kamchatka River) for the KAM-02 group; 4) the Kamchatka Isthmus (northern part of the Central

Range) for the KAM-08 group; and 5) the vicinities of the Ichinsky Volcano (middle part of the Central Range) for the KAM-15 group.

We are fully aware that only extensive fieldwork, including collection and analyses of additional samples of volcanic glass from the above mentioned localities, can prove the reliability of our suggestions. We are strongly aiming to complete this task in the near future with the help of colleagues from Russia, USA, and Japan.

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