Online resource 1 to a paper

"Early Holocene M~6 explosive eruption from Plosky volcanic massif (Kamchatka) and its tephra as a link between terrestrial and marine paleoenvironmental records"

International Journal of Earth Sciences

Authors: Vera Ponomareva, Maxim Portnyagin, Alexander Derkachev, I.Florin Pendea, Joanne Bourgeois, Paula J. Reimer, Dieter Garbe-Schönberg, Stepan Krasheninnikov, Dirk Nürnberg

Corresponding author: Vera Ponomareva

Institute of Volcanology and Seismology

E-mail: vera.ponomareva1@gmail.com

Details of the EMP and LA-ICP-MS settings and data processing

Volcanic glass and minerals were analyzed using JEOL JXA 8200 electron microprobe equipped with five wavelength dispersive spectrometers including 3 high-sensitivity ones (2 PETH and TAPH) at GEOMAR (Kiel). The analytical conditions for glasses were 15 kV accelerating voltage, 6 nA current and 5 μm electron beam size. Counting time was 10/10 s (peak/background) for Na, 20/10s for (Si, Al, Fe, Mg, Ca), 30/15 s for K, Ti, Cl, S and 40/20 s for Mn and F. Basaltic glass (USNM 113498/1 VG-A99) for Ti, Fe, Mg, Ca, P, rhyolitic glass (USNM 72854 VG568) for Si, Al, Na, K, scapolite (USNM R6600-1) for S and Cl, all from the Smithosonian collection of natural reference materials (Jarosevich et al., 1980), rhyolitic glass KN-18 (Mosbah et al., 1991) for F and synthetic rhodonite for Mn were used for calibration and monitoring of routine measurements. Two to three analyses of all standard glasses and scapolite were performed at the beginning of analytical session, after every 50-60 analyses and at the end. The data reduction included on-line CITZAF correction (Armb, 1995) and small correction for systematic deviations (if any) from the reference values obtained on standard materials. The later correction did not exceed 5 % relative for all elements and allowed to achieve the best possible accuracy of the data and long-term reproducibility. The INTAV intercomparison of electron-beam microanalysis of glass by tephrochronology laboratories (Kuehn et al., 2011) revealed no systematic error for glasses compositions analyzed at GEOMAR lab (coded as lab #12).

During the data reduction we excluded EMP analyses with the totals lower than 94 wt%, which resulted from possible unevenness of sample surface, entrapment of voids or epoxy during analysis of very small glass fragments. The latter has been also identified by unusually

high measured chlorine concentrations, which resulted from 3-4 wt% of Cl in the epoxy resin used in the course of this study (Buehler EpoThin). Analyses contaminated by occasional entrapment of crystal phases, usually microliths of plagioclase, pyroxene or Fe-Ti oxides, were identified on the basis of excessive concentrations of Al_2O_3, CaO or FeO (and TiO_2), respectively, compared to the prevailing composition of glasses in every sample. Because volcanic glasses can be hydrated over time during post-magmatic interaction with meteoric or sea water or contain significant but variable amount of H_2O, not completely degassed during eruption, all analyses were then normalized to anhydrous basis. The original totals measured by EMP are given in Online Resource 3.

Minerals were analyzed at 100 nA (olivine), 50 nA (Fe-Ti oxides) and 20nA (other minerals) and focused to 1 μm electron beam. Counting time was 20/10 s (peak/background) for all elements. Smithsonian standards of olivine (San Carlos olivine USNM 111312/444), plagioclase (USNM 115900) pyroxene (Kakanue Augite USNM 12214), hornblende (Arenal hornblende USNM 111356, Kakanue hornblende USNM 143965), chromite (Caledonia chromite USNM 117075) and ilmenite (USNM 96189) (Jarosevich et al., 1981) were used for standardization and reference (Online Resource 2).

Trace elements in glasses were analysed by laser ablation – inductively coupled plasma – mass spectrometry (LA-ICP-MS) using a 193nm excimer laser with a large volume ablation cell (Zürich, Switzerland) coupled with a quadrupole-based ICP-MS (Agilent 7500cs) at the Institute of Geosciences, CAU Kiel, Germany. *In situ*-microsampling was done with 50 μm pit size and 10Hz pulse frequency at 10 J cm^{-2}. The generated aerosol was transported with 0.75 L min^{-1} He and mixed with 0.6 L min^{-1} Ar prior to introduction into the ICP. The ICP-MS was operated under standard conditions at 1500W and optimized for low oxide formation (ThO/Th <0.8%). The GLITTER software package (Access Macquarie Ltd.) was used for data reduction of the time-resolved measurements. The blank signal was measured 20 s prior to each ablation and used for calculation of the actual detection limits. For sample data integration the time window of approx. 60 s was individually adjusted for each run. Calcium (44 m/z) was used for internal standardization utilizing pre-analyzed data from electron probe microanalysis (EPMA). The NIST 612 glass (preferred values from Pearce et al., 1997; Jochum et al., 2011; GeoRem, 2011) was used for calibration of the integrated raw data and re-analysed in triplicate with every batch of 20 sample acquisitions. International rock glass standards (USGS BCR-2G and MPI-DING glass KL-2G; Jochum et al., 2006; GeoReM, 2011) have been analysed as unknown samples in one series with tephra samples for check of accuracy. Analytical precision of five to six runs of the standard glasses was <5 % for most elements. To eliminate possible entrapment of crystal phases during tephra glass analyses,

additional quality test has been applied by comparing Si and Ti concentrations measured by LA-ICP-MS with those obtained by EMPA on the same glass shard. Analysis was accepted as representative for pure glass if the Si and Ti concentrations measured by LA-ICP-MS and EMP agree within 15%. The final LA-ICP-MS data represent background-subtracted averages of four to five individual sample acquisitions which passed the quality test.

References

Armb JT (1995) CITZAF: A package of correction programs for the quantitative electron microbeam X-ray analysis of thick polished materials, thin films, and particles. Microbeam Analysis 4: 177-200

GeoReM (2011) Geological and Environmental Reference Materials, http://georem.mpch-mainz.gwdg.de/ (accessed by 2011)

Jarosewich EJ, Nelen JA, Norberg JA (1980) Reference samples for electron microprobe analysis. Geostandards Newsletter 4: 43-47

Jochum KP, Stoll B, Herwig K, Willbold M, Hofmann AW, Amini M, Aarburg S, Abouchami W, Hellebrand E, Mocek B, Raczek I, Stracke A, Alard O, Bouman C, Becker S, Dücking M, Brätz H, Klemd R, de Bruin D, Canil D, Cornell D, de Hoog C-J, Dalpé C, Danyushevsky L, Eisenhauer A, Gao Y, Snow JE, Groschopf N, Günther D, Latkoczy C, Guillong M, Hauri EH, Höfer HE, Lahaye Y, Horz K, Jacob DE, Kasemann SA, Kent A J R, Ludwig T, Zack T, Mason PRD, Meixner A, Rosner M, Misawa K, Nash BP, Pfänder J, Premo WR, Sun WD, Tiepolo M, Vannucci R, Vennemann T, Wayne D, Woodhead J D (2006) MPI-DING reference glasses for in situ microanalysis: new reference values for element concentrations and isotope ratios. Geochem Geophys Geosyst, 7. doi:10.1029/2005GC001060.

Jochum K P, Weis U, Stoll B, Kuzmin D, Yang Q, Raczek I, Jacob DE, Stracke A, Birbaum K, Frick DA, Günther D, Enzweiler J (2011) Determination of reference values for NIST SRM 610–617 glasses following ISO guidelines. Geostandards and Geoanalytical Research. doi: 10.1111/j.1751-908X.2011.00120.x

Mosbah M, Metrich N, Massiot P (1991) PIGME fluorine determination using a nuclear microprobe with application to glass inclusions. Nuclear Instruments and Methods in Physics Research, B58:. 227-231

Pearce NJG, Perkins WT, Westgate JA, Gorton MP, Jackson SE, Neal CR, Chenery SP (1997) A compilation of new and published major and trace element data for NIST SRM 610 and NIST SRM 612 glass reference materials. Geostandards Newsletter 21: 115–144