

Separation and Analysis of Thera Volcanic Glass by INAA, XRF and EPMA

Petra Schmid¹, Claudia Peltz¹, Vera M. F. Hammer², Erich Halwax³, Theo Ntaflos⁴, Peter Nagl⁴, and Max Bichler^{1,*}

¹ Atominstytut der Österreichischen Universitäten, TU Wien, Stadionallee 2, A-1020 Wien, Austria

² Naturhistorisches Museum, Mineralogisch-Petrographische Abteilung, Burgring 7, A-1010 Wien, Austria

³ Institut für Mineralogie, Kristallographie und Strukturchemie, TU Wien, Getreidemarkt 9, A-1060 Wien, Austria

⁴ Institut für Petrologie, Universität Wien, Althanstraße 14, A-1090 Wien, Austria

Abstract. Pumice from the “Minoan eruption” on Thera (Cyclades, Greece) was investigated to reveal the differences between the composition of the bulk material, which contains a certain percentage of crystallites, and the pure glass phase. This is important for the identification of vitric tephra layers found in the Eastern Mediterranean region in archaeological context and in deep sea drilling cores. Eruption products, deposited at some distance, have usually lost their crystalline fraction due to gravity separation and consist only of glass shards. Only major element distributions in such layers and in pumiceous glass phases have been published up to now, but these data are not sufficient for a reliable identification of the volcanic source, as several other eruptions are known to have produced chemically very similar layers in this region (Milos, Nisyros, Yali, Kos). Therefore, a technique has been developed to separate the glass phase from the primary pumice to reveal differences in the trace element distributions obtained by instrumental neutron activation analysis (INAA). X-ray diffractometry and microscopical techniques were applied to check the purity of this fraction. The concentrations of the major constituents, in particular Al, Ca, Fe, K, Mg, Mn, Na, Si, and Ti were determined by X-ray fluorescence (XRF) and electron probe microanalysis (EPMA), those of Al, Ba, Ca, Ce, Co, Cr, Cs, Dy, Eu, Fe, Hf, K, La, Lu, Mn, Na, Nd, Rb, Sb, Sc, Sm, Ta, Ti, Th, U, Yb and Zr by instrumental neutron activation analysis

and partly also by X-ray fluorescence. Subtle differences between the compositions of the glass phase and the bulk material are explained by differentiation during partial crystallization and their applicability to the classification of tephra layers is demonstrated.

Key words: Geochemistry; volcanology; INAA; pumice; Thera.

The “Minoan pumice deposit” (Upper pumice layer – Bo) on the Santorini archipelago (Greece) stems from the explosive eruption of the Thera volcano in the second millennium B.C. [1–4]. A volcanic explosion of this magnitude happens in several phases, during which tremendous amounts of lava, ash and rock are erupted [5–7]. During the first phase, the so-called Plinian phase, the eruption velocity and the height of the eruption column reach their maximum, with varying quantities of volcanic dust entering the high atmosphere. In this way the particles are transported over great distances and deposited as a practically synchronous tephra layer. This is due to the fact that the Plinian phase lasts only for a few hours or days [8]. Such layers can therefore be used as time markers in deep sea drilling cores and for the synchronization of local archaeological stratigraphies [9–12]. Usually, such different deposits show typical but often only subtle differences in their chemical compositions, so that an identification by their trace element distribution is possible [13–15]. However, previous studies have shown that the composition of tephra layers may change with the distance from the vent due to the progressive loss of a crystalline fraction [15–17]. The erupted material consists mainly of pumice, which is a

* To whom correspondence should be addressed

vesicular, light coloured volcanic rock with a certain percentage of crystallites in a glassy matrix. Mechanical stress during the eruption leads to the fragmentation of vesicle walls and the formation of an extremely fine grained glass fraction which is easily transported to high altitudes. With increasing distance from the volcano, the distribution of elements thus approaches that of the pure glass fraction. The Minoan pumice contains only relatively small (sub mm) crystallites while others, for example the Kos Plateau Tuff pumice, contain crystals up to several mm in length. The Minoan eruption of Thera was investigated because it produced a tephra layer in the Eastern Mediterranean in a period highly important for archaeological science. The layer has been found in deep sea drilling cores as well as in archaeological excavations [10, 12, 18]. This work provides the full element distribution of the bulk material and the glass phase that is necessary for an identification of tephra fallout in unknown sequences,

especially where there are only traces of tephra owing to the distance from the eruption centre.

Materials and Methods

Sample Preparation

The Minoan eruption produced the Upper pumice, which is subdivided into three layers that can be distinguished morphologically (Bo1, Bo2, Bo3). Nevertheless, previous work has shown that the composition of the pure pumice fraction varies only within a very narrow range [14, 15]. Only the first layer (Bo1), which is related to the Plinian phase of the eruption, is of interest for this investigation. Three representative samples of pure pumice were taken from Bo1, including one “average Bo1” sample averaged over the entire range of the Bo1-layer, and two samples from different Bo1 sites. Before sampling, weathered rock surfaces were

Table 1. Activation products, half-lives and gamma-energies used for pumice analyses

Element	Activation product	Half-life	γ -energy keV
Al	²⁸ Al	2.24 min	1779
Ba	¹³¹ Ba	11.7 d	496
Ca	⁴⁹ Ca	8.72 min	3084
Ce	¹⁴¹ Ce	32.5 d	145
Co	⁶⁰ Co	5.27 a	1173
Cr	⁵¹ Cr	27.7 d	320
Cs	¹³⁴ Cs	2.06 a	796
Dy	¹⁶⁵ Dy	2.3 h	95
Eu	¹⁵² Eu	13.5 a	1408
Fe	⁵⁹ Fe	44.5 d	1099
Hf	¹⁸¹ Hf	42.4 d	482
K	⁴² K	12.4 h	1525
La	¹⁴⁰ La	40.3 h	1597
Lu	¹⁷⁷ Lu	6.7 d	208
Mn	⁵⁶ Mn	2.6 h	1811
Na	²⁴ Na	15.0 h	1368
Nd	¹⁴⁷ Nd	11.0 d	531
Rb	⁸⁶ Rb	18.6 d	1077
Sb	¹²⁴ Sb	60.3 d	1691
Sc	⁴⁶ Sc	83.8 d	1120
Sm	¹⁵³ Sm	46.3 h	103
Ta	¹⁸² Ta	114.4 d	1189
Th	²³³ Pa ^a	27.0 d	312
Ti	⁵¹ Ti	5.8 min	320
U	²³⁹ Np ^a	56.5 h	278
Yb	¹⁶⁹ Yb	32.0 d	177
Zr	⁹⁵ Zr	64.0 d	757

^a ²³³Pa and ²³⁹Np are produced by the β -decay of ²³³Th (half-life 22.3 min) and ²³⁹U (half-life 23.5 min), which were formed by neutron capture of ²³²Th and ²³⁸U, respectively.

Table 2. Concentrations of elements in Santorini Bo1 bulk pumice obtained from 3 representative samples by INAA and XRF. For INAA, $\pm 1\sigma$ was used for the calculation of the error due to counting statistics, $\pm 3\sigma$ was used for the calculation of the detection limits. GSR 1-6 reference materials were used for the calculation of the XRF error bars

	NAA		XRF	
	err [%rel]		err [%rel]	
Major components (mass %)				
Al	7.57	0.2	7.44	3
Ca	1.70	14.2	1.6	2
Fe	2.24	0.2	2.22	3
K	2.36	4.2	2.4	2
Mg	n.d.		0.48	28
Na	3.39	0.2	3.4	5
Si	n.d.		31.3	3
Ti	0.22	22.5	0.27	4
Trace elements (mg/kg)				
Ba	557	2.4	479	11
Ce	61.2	0.5	59	23
Co	4.33	0.5		
Cr	1.79	12.8		
Cs	2.74	1.4		
Dy	5.65	10.0		
Eu	0.995	0.7		
Hf	7.42	0.4		
La	31.0	0.3	29	19
Lu	0.787	1.2		
Mn	632	0.9	671	1
Nd	31.4	8.5		
Rb	105	1.3	91	7
Sb	0.27	6.7		
Sc	9.90	0.1	7	12
Sm	6.06	0.2		
Ta	0.776	2.8		
Th	19.4	0.2		
U	5.74	2.7		
Yb	5.44	1.6		
Zr	280	3.8	286	7

removed to a depth of at least 150 mm. Sample surface cleaning was done by immersion in distilled water in an ultrasonic bath. The samples were then crushed with PE tools, dried at 110°, and homogenized by grinding in an agate mortar to a grain size < 3 µm.

To separate the pure glass phase, however, a representative part of the sample “average Bo1” was treated differently. To avoid destruction of the crystallites, the sample material was carefully crushed with PE tools instead of grinding. A fraction suitable for separation was obtained by sieving (1 mm). The separation technique imitates the natural process on a laboratory scale and is based on the fact that in an air flow crystallites are not transported as far as vitric particles because of their higher specific mass and their morphological properties. The separation is achieved by means of a rotating glass tube of 30 mm diameter through which a continuous flow of nitrogen transports the particles. By mounting the tube with an inclination of about 45° the material deposited in the tube is transported back to the input by gravity. The suspended fraction was collected on a filter. The purity of the separated fractions was checked by X-ray powder diffractometry and microscopy. The results obtained by X-ray diffractometry showed the glass fraction to contain less than 5% crystalline material. Additional observations with a polarization

microscope proved that the concentration of crystallites is lower than 1%. The particle size ranged from about 1–10 µm.

Analysis

The concentrations of the elements were determined by X-ray fluorescence (XRF, PHILIPS PW2400), electron probe micro-analysis (EPMA, CAMECA SX100) and instrumental neutron activation analysis (INAA). For the determination of the major constituents by XRF at the Institute of Petrology, University of Vienna, both glass and bulk samples were used in the form of fused pellets, prepared as follows: 1,2 g of the ignited sample were homogenized with 6 g lithium tetraborate (Merck Spectromelt A10) and 150 µl aqueous LiBr₂ solution (25%). The mixture is fused using a Philips Perl’X3 automatic bead machine under controlled conditions in a platinum-gold crucible and poured into a platinum-gold mould. For the determination of trace elements by XRF, powder pellets were produced by compaction (160 kN/cm²) of 10 g of the sample, homogenized with 0,5 ml of an aqueous solution of polyvinylalcohol (Merck Mowiol, 2%). For the measurement, a sequential X-ray spectrometer Philips PW2400 with a super-sharp end-window X-ray tube (Rh-anode) and a 3 kW

Table 3. Concentrations of elements in the glass fraction of the Bo1 pumice from Santorini as determined with NAA, XRF and EPMA

	NAA		XRF		Microprobe	
	err [%rel]		err [%rel]		err [%rel]	
Major components (mass %)						
Al	7.06	0.2	7.00	3	7.15	1.5
Ca	1.02	27.2	1.1	2	0.9	4.8
Fe	1.64	0.2	1.64	3	1.45	1.8
K	2.48	3.4	2.7	2	2.6	3.9
Mg	n.d.		0.28	28	0.15	7.1
Na	3.21	0.2	3.3	5	3.02	14.0
Si	n.d.		32.2	3	33.2	1.7
Ti	< 0.15		0.19	4	0.18	9.9
Trace elements (mg/kg)						
Ba	614	2.0				
Ce	64.9	0.4				
Co	2.30	0.8				
Cr	< 0.5					
Cs	3.10	1.2				
Dy	6.44	6.4				
Eu	0.906	0.8				
Hf	8.20	0.4				
La	33.7	0.3				
Lu	0.901	1.1				
Mn	490	0.9	542	1	573	2.4
Nd	31.8	7.8				
Rb	118	1.1				
Sb	0.30	4.7				
Sc	8.07	0.1				
Sm	6.65	0.2				
Ta	0.802	2.6				
Th	21.6	0.2				
U	6.49	2.3				
Yb	5.94	1.7				
Zr	309	3.5				

Table 4. Concentrations of elements in CANMET reference material SO1, analyzed both by INAA and XRF and comparison to referenced values [25]. For INAA, ± 1σ was used for the calculation of the error due to counting statistics

	Reference values	NAA	XRF	
			err [% rel]	
Major components (mass %)				
Al	9.31	9.37	0.4	9.37
Ca	1.76	1.75	13.2	1.76
Fe	6.00	5.96	0.2	6.02
K	2.64	2.64	8.4	2.65
Mg	2.31	n.d.		2.38
Na	2.00	2.01	0.6	2.03
Si	26.08	n.d.		26.04
Ti	0.52	0.51	22	0.53
Trace elements (mg/kg)				
Ba	870	868	3.2	816
Ce	102	113	0.6	115
Co	29	29	0.2	26
Cr	170	171	0.6	176
Cs	5.07	5.06	1.8	
Dy	4.5	4.7	28	
Eu	1.57	1.67	1.2	
Hf	2.50	2.36	2.6	
La	54	57	0.4	65
Lu	0.31	0.34	2	
Mn	852	865	1.6	852
Nd	44	47	4	
Rb	141	134	2.6	116
Sc	17.7	17.9	0.1	18
Sm	7.9	8.4	0.4	
Ta	0.70	0.68	8.2	
Th	12.4	12.5	0.6	
U	1.71	1.85	12.4	
Yb	2.24	2.30	2.6	
Zr	84	119	18	84

generator was used. The accompanying software was Philips SuperQ, V1.1d. Theoretical correction factors (Philips model) were applied for matrix correction [19, 20, 21] of major elements, the resulting concentration data were recalculated with consideration of the loss on ignition (LOI) using the program "Majors" [22]. Following the suggestions of Nisbet et al. [23], background correction for trace elements with larger analytical wavelengths than the Fe-K β absorption edge was performed using the Compton scattered radiation, other backgrounds were measured. Mass absorption coefficients calculated from the measured major element compositions were used for the correction of matrix effects. The resulting linear calibration curves are the base for the calculation of the trace element contents. All those calculations were done offline using the program "Traces" [22]. For both element groups a set of reference materials (IGGE GSR-1 to GSR-6) was used for the error calculation.

Glass analyses were carried out on polished thin sections at the Institute of Petrology, University of Vienna, using a Cameca SX100 electron microprobe equipped with four wavelength- and one energy-dispersive spectrometers. The acceleration voltage was 15 kV with beam current of 20 nA. Special measuring conditions (beam width 10 μ m, 15 kV, 7 nA, 2 s measuring time) were chosen for the determination of Na to avoid losses due to diffusion and evaporation effects. 40 measurements were performed to achieve acceptable counting statistics for Na, 6 measurement runs were done for the other elements. The standards were natural and synthetic minerals and glasses, matrix corrections were made by PAP (Pouchou and Pichoir) procedures [24].

For neutron activation analysis two irradiation cycles and four measurement runs were applied. About 150 mg of the samples and of suitable standards (BCR 142 Light Sandy Soil, NIST SRM 1633b Coal Fly Ash, and CANMET Reference Soil SO-1) were weighed into PE capsules and irradiated for 1 min in the irradiation position of the pneumatic transfer system of the TRIGA Mark-II reactor of the Atominstitut at a thermal neutron flux of $3,3 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. The first gamma spectrum was measured after a decay time of 5 min to determine Al, Ca and Ti. About 3 h later a second measurement was performed to quantify Dy, K, Mn and Na. For the determination of long-lived radionuclides about 150 mg of each sample and standard were sealed into SuprasilTM quartz glass vials and irradiated for 64 h in the ASTRA-reactor of the Austrian Research Centre Seibersdorf at a thermal neutron flux of $8 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. After a decay time of 7 days the activities of the medium-lived nuclides and after another 23 days the activities of the long-lived nuclides were measured. All measurements were performed with a 151 cm³ HPGe-detector connected to a PC-based multichannel analyzer. A preloaded filter and a loss free counting system improved the quality of the spectra obtained. Table 1 shows the activation products and the gamma-lines used for analysis.

Results and Discussion

The results are given in Table 2 (bulk material) and Table 3 (glass fraction). The trace-element concentra-

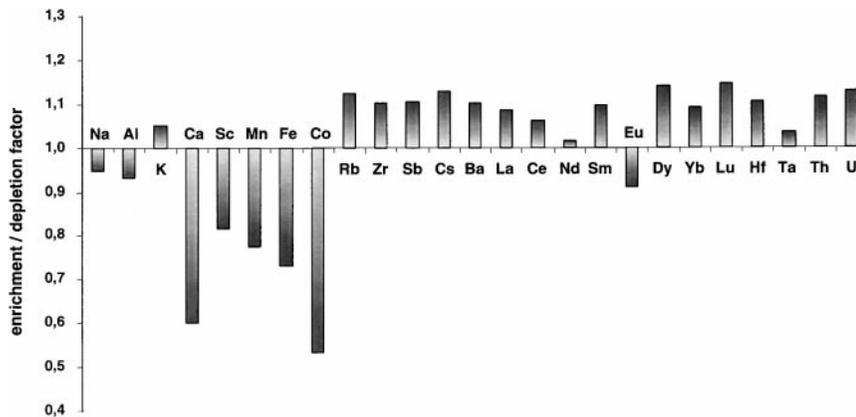


Fig. 1. Enrichment/depletion factors of elements in the glass fraction respective to the bulk material

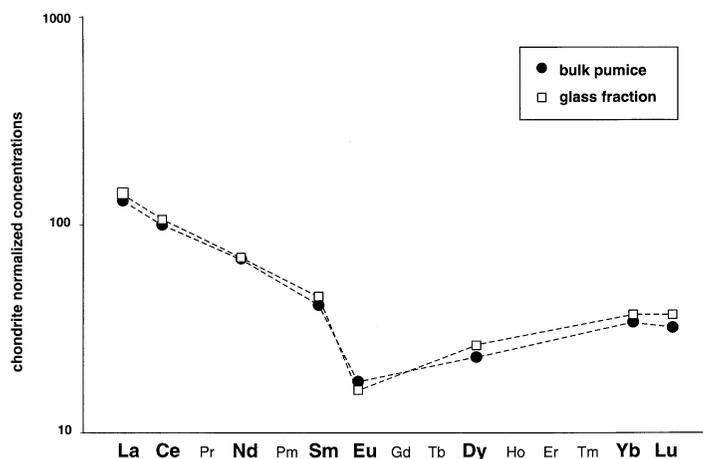


Fig. 2. Distribution patterns of chondrite-normalized rare earth element concentrations [30]

tions determined by INAA and XRF show a very good agreement. Likewise, the major element distributions obtained by these two techniques are in perfect accordance with the results of the microprobe. CANMET reference material SO1 was analyzed by

both INAA and XPF. The results obtained are given in Table 4 together with the referenced values [25]. The major constituent of the bulk material is glass. However other phases like quartz, plagioclase, pyroxene, apatite, ilmenite and titanomagnetite are

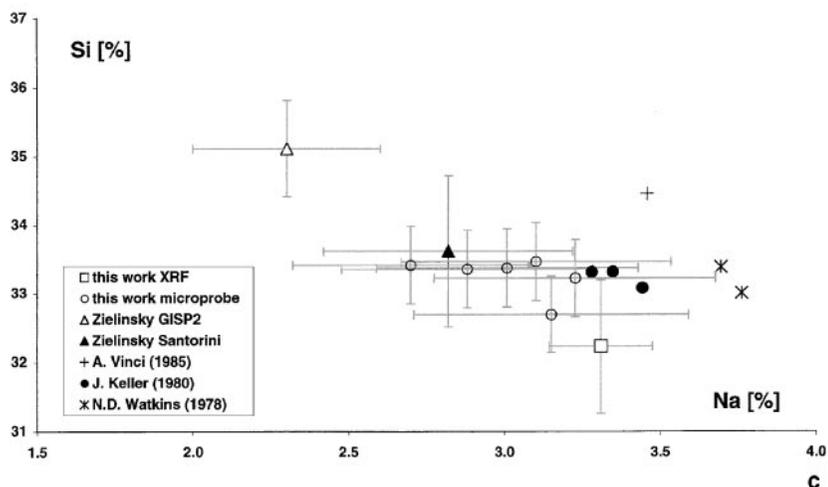
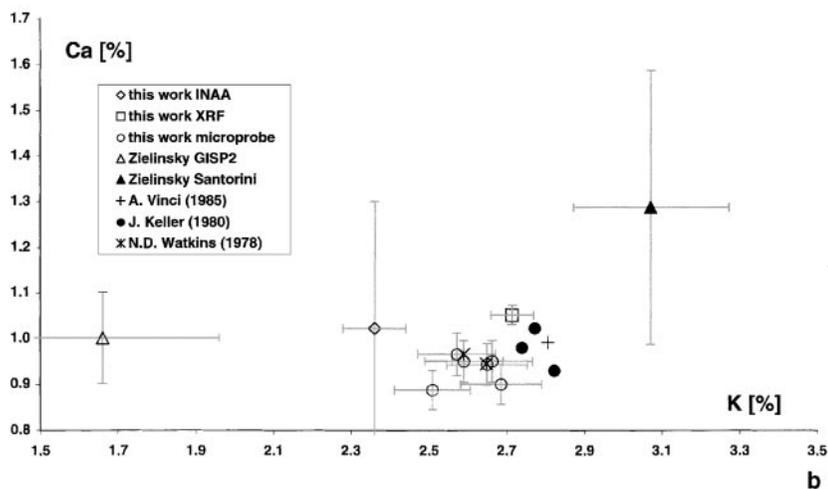
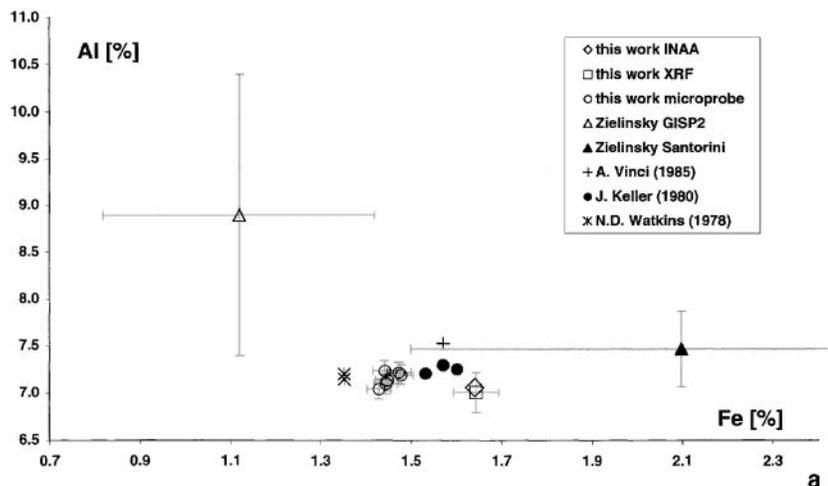


Fig. 3. Distribution of Al, Fe, Si, Na, Ca and K concentrations obtained by this work and EPMA values from other authors [10, 18, 28, 29]

also present. In comparison to the bulk material, the glass phase is slightly enriched in all elements but Al, Ca, Co, Eu, Fe, Mn, Na and Sc (Fig. 1). The depletion of the major elements Al, Ca, Fe, Mn and Na in the glass can be readily attributed to the presence of the above mentioned mineral phases. Co and Sc are compatible elements and therefore not expected to be partitioned into the liquid. The chondritic normalized REE concentrations (Fig. 2) show very clearly small but systematic differences between bulk material and glass. The pronounced negative Eu anomaly is attributed to the plagioclase fractionation which is normally expected in such highly evolved lavas. In contrast to these results, the element concentrations in the bulk material and the glass phase of pumice from other sources, for example from the island Kos, show more significant differences due to their higher content of mineral phases [15]. Work is in progress on the latter question and the separation techniques developed are being applied to pumice from different primary sources in the Aegean.

The comparison with analytical data from the literature shows perfect agreement [10, 14, 15, 18, 26–28]. Using microprobe techniques, Zielinsky and Germani [29] compared glass shards extracted from Greenland ice cores with original material from Santorini. They concluded that the particles from the ice core should not be related to the Minoan eruption. This suggestion is not supported by the results obtained from the separated glass fraction. It was found that, within the experimental error, only potassium is slightly different from the original Santorinian glass. Figure 3 shows a comparison of the results obtained in this work with those by other authors.

We conclude that the element concentrations in the glass phase and the bulk pumice of the “Minoan eruption” show only small differences and can thus be used for the reliable identification of tephra layers related to that eruption. INAA enables the choice of the most suitable elements for this identification work, which cannot be achieved by major element determinations alone. In this way it is possible to identify even very small quantities of the tephra fraction separated from the sediment. This research program together with the results presented will contribute significantly to our knowledge about the chronology and volcanic history of the Eastern Mediterranean. Further analogous separations are already being performed on pumice from other volcanic sources in

the Aegean Sea to extend the possibility of individual identification to all tephra deposits of the region.

Acknowledgements. This work was supported by the European Commission project Nr. 98/034065 and by the Austrian “Fonds zur Förderung wissenschaftlicher Forschung”, project Nr. 13151-SPR. The project “Thera Ashes” is supported also as a part of the Austrian Spezialforschungsbereich “Synchronization of Civilizations in the Eastern Mediterranean in the Second Millennium B.C.”.

References

- [1] P. P. Betancourt, *Archaeometry* **1987**, 29, 45.
- [2] M. Bietak, *Egyptian Archaeology* **1992**, 2, 26.
- [3] W. L. Friedrich, R. Friborg, H. Tauber, *Thera and the Aegean World II*. In: C. G. Dumas (Ed.) London (The Thera Foundation), 1980, p. 241.
- [4] C. U. Hammer, H. B. Clausen, W. L. Friedrich, H. Tauber, *Nature* **1987**, 328, 517.
- [5] H. Sigurdsson, S. Carey, J. D. Devine, *Thera and the Aegean World III, Vol. 2*. In: D. A. Hardy (Ed.) London (The Thera Foundation), 1990, p. 100.
- [6] R. S. J. Sparks, C. J. N. Wilson, *Thera and the Aegean World III, Vol. 2*. In: D. A. Hardy (Ed.) London (The Thera Foundation), 1990, p. 89.
- [7] D. M. Pyle, *Thera and the Aegean World III, Vol. 2*. In: D. A. Hardy (Ed.) London (The Thera Foundation), 1990, p. 113.
- [8] H. Pichler, W. L. Friedrich, *Thera and the Aegean World II*. In: C. G. Dumas (Ed.) London (The Thera Foundation), 1990, p. 15.
- [9] D. G. Sullivan, *Thera and the Aegean World III, Vol. 2*. In: D. A. Hardy (Ed.) London (The Thera Foundation), 1990, p. 114.
- [10] A. Vinci, *Mar. Geol.* **1985**, 64, 143.
- [11] P. M. Warren, H. Puchelt, *Thera and the Aegean World III, Vol. 3*. In: D. A. Hardy (Ed.) London (The Thera Foundation), 1990, p. 71.
- [12] T. Marketou, *Thera and the Aegean World III, Vol. 3*. In: D. A. Hardy (Ed.) London (The Thera Foundation), 1990, p. 100.
- [13] H. Pichler, W. Schiering, *Archäologischer Anzeiger*, Sonderdruck, 1980, p. 1.
- [14] M. Bichler, H. Egger, A. Preisinger, D. Ritter, P. Stastny, *J. Radioanal. Nucl. Chem.* **1997**, 224, 7.
- [15] C. Peltz, P. Schmid, M. Bichler, *J. Radioanal. Nucl. Chem.* **1999**, 242/2 (in press).
- [16] W. Larsson, *Bull. Geol. Lust. Upsala* **1936**, 26, 27.
- [17] R. L. Hay, *Jour. Geol.* **1959**, 67, 540.
- [18] N. D. Watkins, R. S. J. Sparks, H. Sigurdsson, T. C. Huang, A. Federman, S. Carey, D. Ninkovich, *Nature* **1978**, 271, 122.
- [19] W. K. De Jongh, *X-Ray Spectrom.* **1973**, 2, 151.
- [20] W. K. De Jongh, *Norelco Reporter* **1976**, 23, 26.
- [21] G. W. Lobeek, Philips Report, Publ. Nr 9498 700 00913, 1988.
- [22] K. Petrakakis, P. Nagl, 1998, pers. comm.
- [23] E. G. Nisbet, V. J. Dietrich, A. Esenwein, *Fortschr. Min.* **1979**, 57, 264.
- [24] J. L. Pouchou, F. Pichoir, *Electron Probe Quantitation*, In: K. F. J. Heinrich, D. E. Newbury (Eds.) Plenum Press, New York, 1991, p. 31.
- [25] K. Govindaraju (Ed.) *Geostandards Newsletter*, Special issue, **1994**, 18, 18.
- [26] C. J. Vitaliano et al., *Thera and the Aegean World III, Vol. 2*. In: D. A. Hardy (Ed.) London (The Thera Foundation), 1990, p. 53.

- [27] V. Francaviglia, B. Di Sabatino, *Thera and the Aegean World III, Vol. 2*. In: D. A. Hardy (Ed.) London (The Thera Foundation), 1990, p. 29.
- [28] J. Keller, *Thera and the Aegean World II*, In: C. G. Doumas (Ed.) London (The Thera Foundation), 1980, p. 49.
- [29] G. A. Zielinski, M. S. Germani, *J. Archaeolog. Sci.* **1998**, 25, 279.
- [30] S. Sun, W. F. McDonough, *Magmatism in the Ocean Basins*, A. D. Saunders and M. J. Norry (Eds.) Blackwell Scientific Publications, Oxford, *Geol. Soc. Spec. Pub.* **1989**, 42, 313.