Article

The Distal and Local Volcanic Ash in the Late Pleistocene Sediments of the Termination I Interval at the Reykjanes Ridge, North Atlantic, Based on Study of the Core AMK-340

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Abstract: Based on the geochemical analysis of the volcanic material from the sediment core AMK-340, central zone of the Reykjanes Ridge, we could detect two ash-bearing sediment units accumulated during the Termination I. They correlate to the Ash Zone I in the North Atlantic Late Quaternary sediments having an age of 12170-12840, within the Younger Dryas cold chronozone, and 13600-14540 years, within and Bølling-Allerød warm chronozone. The ash of the Younger Dryas unit is presented mostly by the mafic and persilicic material originated from the Icelandic volcanoes; Vedde Ash is presented in one sediment sample from this unit. The ash of the Bølling-Allerød unit is presented mostly by the mafic shards which are related to the basalts of the rift zone on the Reykjanes Ridge, having presumably the local origin. A detection of Vedde Ash helped to specify the timing of the previously reconstructed paleoceanographic changes for the Termination I in the point of study: a significant warming in the area could occur as early as 300 years prior to the end of the conventional Younger Dryas cold chronozone.

Keywords: tephra in marine sediments; Ash Zone I in North Atlantic; tephrochronology of Termination I

1. Introduction

Tephrochronology is a widely used tool for dating and correlating of the marine and terrestrial sediment sequences, especially within the Quaternary [1]. Recent detailed mineralogical and geochemical studies of the volcanic material revealed a high-resolution Late Pleistocene and Holocene chronostratigraphy for the North Atlantic [2-4]. Icelandic volcanoes are the major source of the ash in the marine sediments of the Nordic Seas and North Atlantic [5]. Extensive studies of the Icelandic soil, lake and shelf sediments documented >150 tephra layers formed during the Termination I and Holocene [6]. Thornalley et al. [7] detected numerous ash-bearing marine sediment layers south of Iceland within the last deglacial and Holocene time. Such data help to refine the regional and local sediment stratigraphy, and synchronize the paleoclimatic archives between the distal oceanic and land regions.

The aim of our study is to get an additional information on the occurrence and composition of the tephra in the North Atlantic sediments at the transition from the last glacial to the Holocene. The sediment core AMK-340 is situated in the central zone of the Reykjanes Ridge where an eruptive material is produced. Therefore, we try to recognize the different sources of the volcanic ash, local or distal ones. A geochemical analysis of the volcanic shards using the scanning electron microscopy will help to reveal the specific well-known tephra layers like the Vedde Ash which can be used for a refinement of the core stratigraphy and chronology of the local paleoceanographic changes.

2. Materials and Methods

The sediment core AMK-340 was obtained during the 4th cruise of the Russian RV "Akademik Mstislav Keldysh" [8] in the central part of the Reykjanes Ridge, North Atlantic south of Iceland (Fig. 1a): 58°30.6′ N, 31°31.2′ W, water depth of 1689 m, core length 387 cm. The core unit of 0-307 cm is composed of the white pelitic calcareous or weakly calcareous (foraminiferal-coccolith) oozes with a $CaCO_3$ content from 10-25 to 40-50%. In the lower core unit of 307-387 cm, a sediment color becomes mainly grey with thin alternation of greenish-grey, yellowish-grey, and dark almost black bands. This unit is enriched in the diatoms (sometimes up to 10-30%), the $CaCO_3$ content varies there between 5.5 and 20% [8]. A visual lithological description of the core exhibited no signs of the volcanic material.

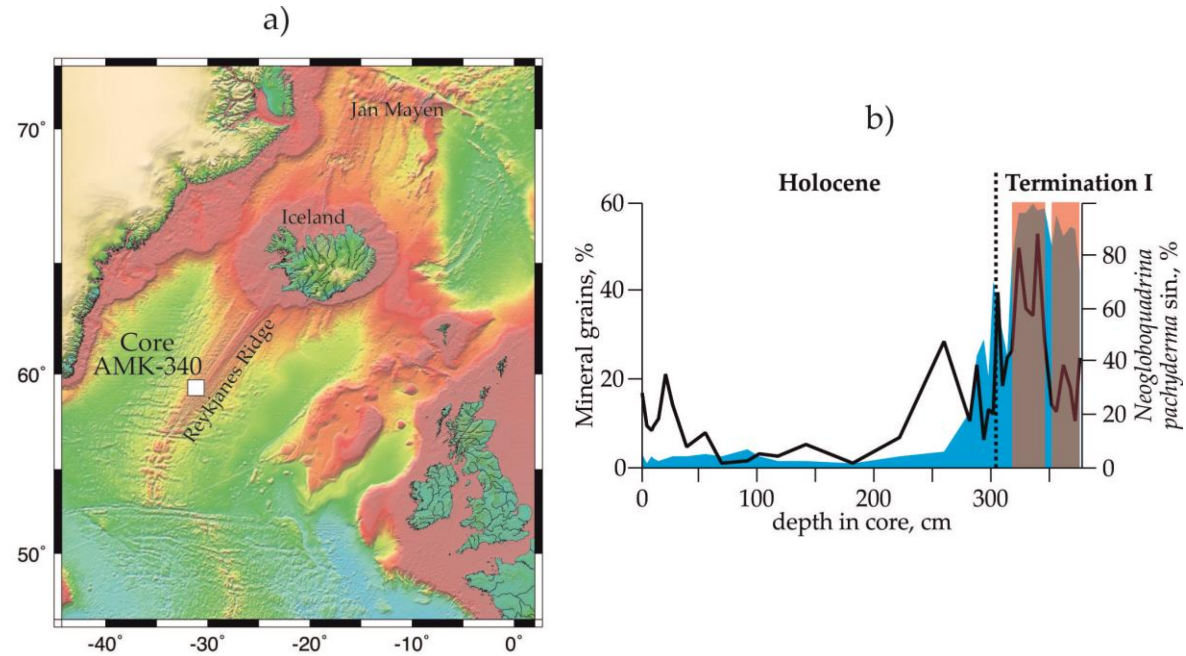

Figure 1. Sediment core AMK-340: a) geographic position (source of map is <https topex.ucsd.edu marine_topo jpg_images topo4.jpg>), b) position of the ash-bearing units within the core, blue-colorized graph is a distribution of the polar planktic foraminifera *Neogloboquadrina pachyderma* sinistral [9] as glacial marker, black line is a distribution of the mineral grains in the sediment fraction of >100 μm [9] as a marker of the ice-rafted material, red bars are the ash-bearing core units.

During the micropaleontological foraminiferal analysis of the core AMK-340 sediments under the stereomicroscope (Fig. 2), we could recognize a remarkable admixture of the eruptive shards in the sediment fraction of >100 μm from two core units (Fig. 1b), 323-340 cm (four samples 323-325,

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328-330, 334-336, and 338-340 cm) and 355-378 cm (four samples 355-357, 360-368, 370-372, and 376-378 cm). We analyzed those samples where a content of the eruptive material was >10-15% from the whole number of grains in the sediment fraction of >100 μm. The eruptive shards from every sample for the following studies of their chemical composition were picked out. All in all, 24 shards in the natural state, 25 shards from the core unit of 323-340 cm and 16 shards from the core unit of 355-378 cm in the polished thin sections were analyzed. The chemical composition of the shards was examined (1) by a scanning electron microscope CamScan MV2300 with energy dispersive analysis system INCA in the Geological Institute of the Russian Academy of Sciences, Moscow, Russia, (shards in the natural state), and (2) by the scanning electron microscope VEGA3 TESCAN with energy dispersive analysis system INCA in the Institute of Oceanology of the Russian Academy of Sciences, Moscow, Russia, (shards in the polished thin sections). The regular microphotographs of the sediment fractions were made on the stereomicroscope ZEISS Stemi 508 equipped by the camera AxioCam Icc5.

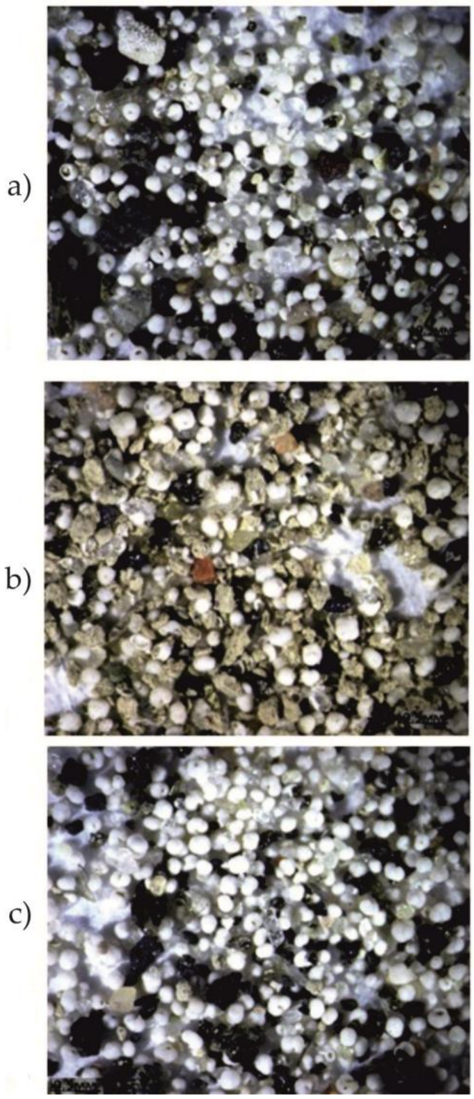

Figure 2. Microphotographs of the sediment fraction >0.1 mm: a) core sample of 323-325 cm, b) sample of 328-330 cm, c) sample of 338-340 cm.

An age model of the core AMK-340 was developed on the linear interpolation between four AMS ^{14}C-datings [9] taking into account five old conventional ^{14}C-datings [10-11]. The core spans time interval of the last appr. 14500 years or the Termination I and Holocene. A possible detection of the Vedde Ash with the age of 12170 years [3, 12-13] in the sample 323-325 cm (see Discussion section) allows us to make more accurate age model of the sediment core AMK-340 for the time interval of the Termination I (sharp warming with the climatic fluctuations between the Last Glacial Maximum and Holocene). From new calculations regarding the Vedde Ash detection, the lower time limit of the core AMK-340 is 14540 years B.P. The core units of 323-340 and 355-378 cm can have the age of 12170-12840 and 13600-14540 years, respectively.

3. Results

3.1. Morphological types of the eruptive material in the studied sediment samples

Angular fragments of the pumiceous basalts and basaltic andesits, black and sometimes greenish, aphanitic (microlitic) and porous, with cavities filled by the light volcanic ash and sometimes by the fragmented diatom frustules (Fig. 3).

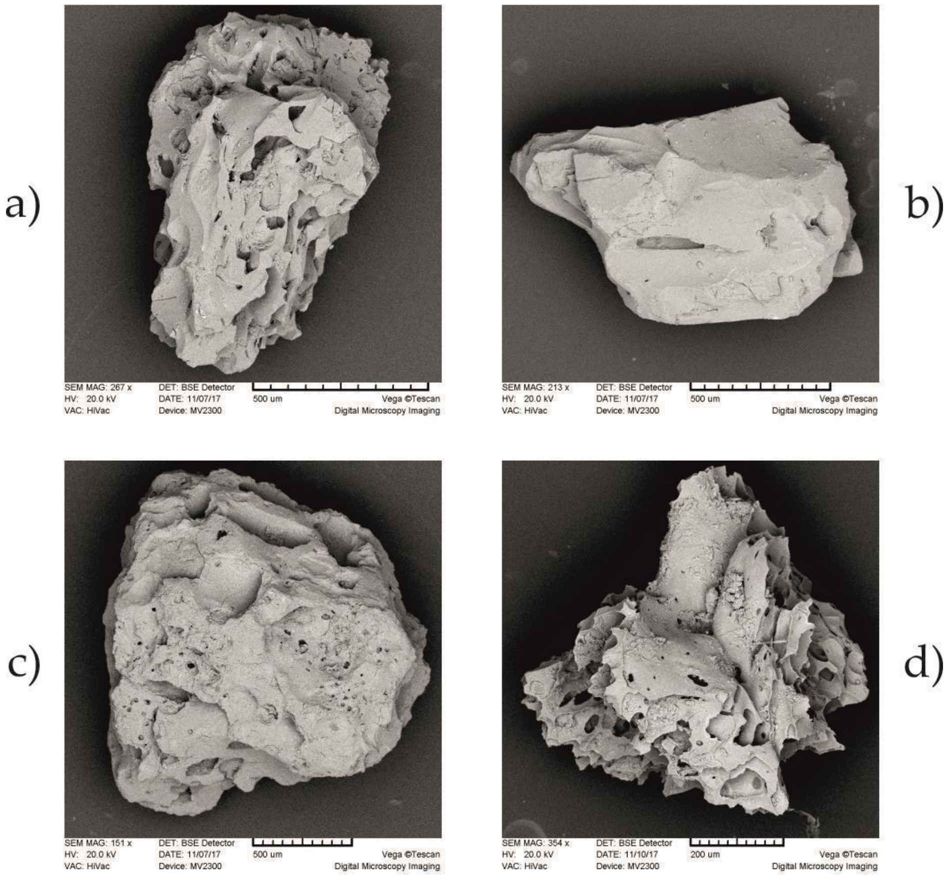

Figure 3. Scanning electron microphotographs of the basalt and andesitic basalt ash shards from the core unit of 323-340 cm: a) vesicular black basalt glass with SiO_2 of 49.10 to 57.15% in the sample of 323-325 cm, b) massive black semi-transparent glass with SiO_2 of 49.45% in the sample of 323-325 cm, c) vesicular black shard (SiO_2 of 50.22%) with cavities filled by the andesitic (SiO_2 of 55.79%) and persilicic (SiO_2 of 63.89-65.97%) dust in the sample of 323-325 cm, d) highly vesicular dark-green semi-transparent andesitic basalt glass with SiO_2 of 52.52% in the sample of 334-336 cm.

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Angular transparent/subtransparent fragments of the persilicic glass, olive and bottle-green, elongate (columnar) with rough scratching on the surface parallel to the elongation, or having an irregular shape, aphanitic (Fig. 4).

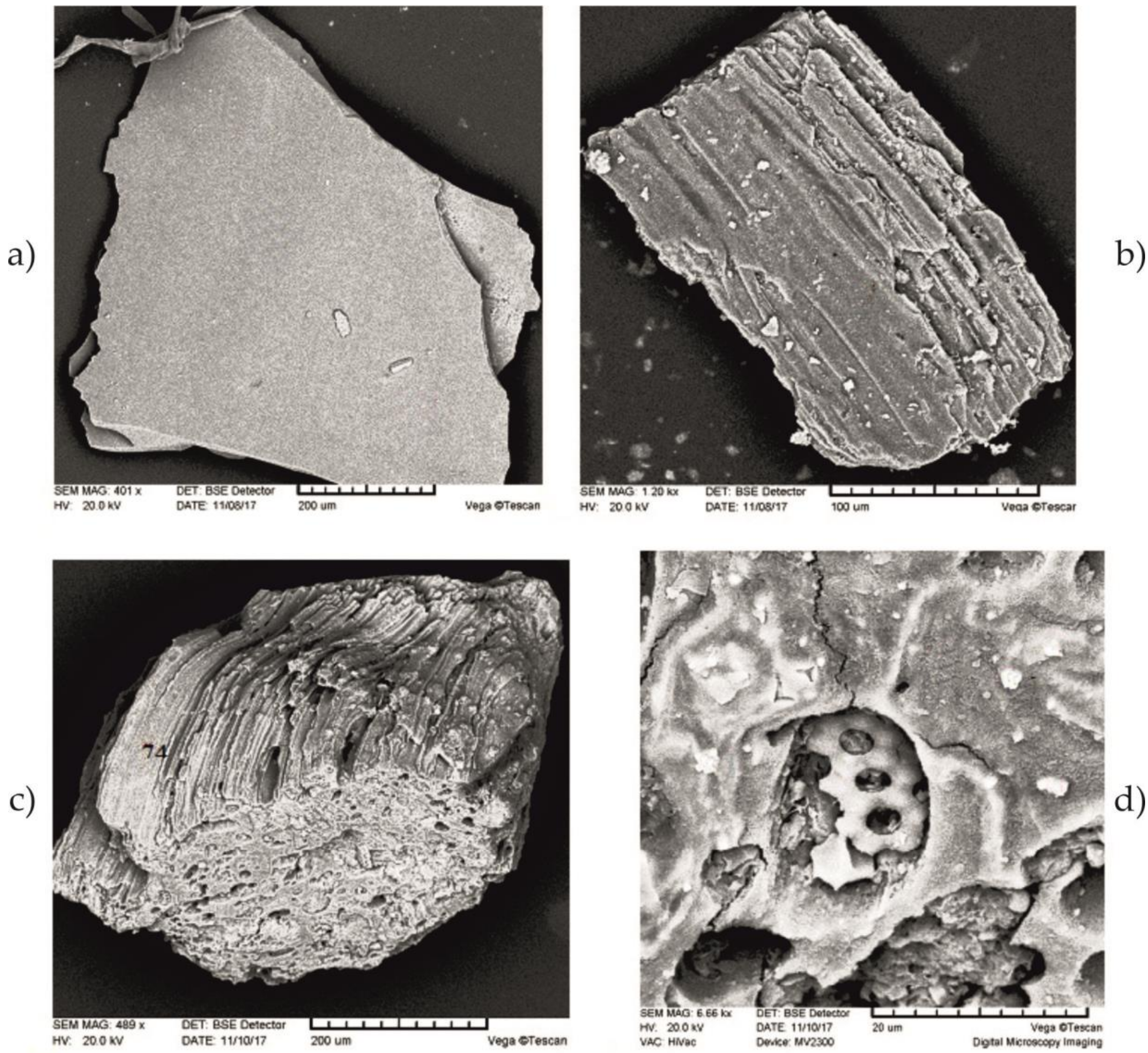

Figure 4. Scanning electron microphotographs of the persilicic ash shards from the core unit of 323-340 cm: a) angular dense greenish transparent glass with a median content of SiO_2 of 76.37% in the sample of 323-325 cm, b) rectangular light semi-transparent dense foliated shard with SiO2 of 75.57-76.88% in the sample of 328-3330 cm, c) and d) general view and fragment, respectively, of vesicular greenish semi-transparent glass (SiO_2 of 70.38%) in the sample of 334-336 cm, with layered andesitic insertions (SiO_2 of 55.90%) and titanomagnetite crystals and fragments of diatom frustules.

Pisolites as rounded/semi-rounded grains and fragmentary grains, light (almost white), massive and occasionally porous, composed of the persilicic and andesitic ash with inclusions of the fragmented diatom frustules, titanomagnetite and quartz (Fig. 5b-d).

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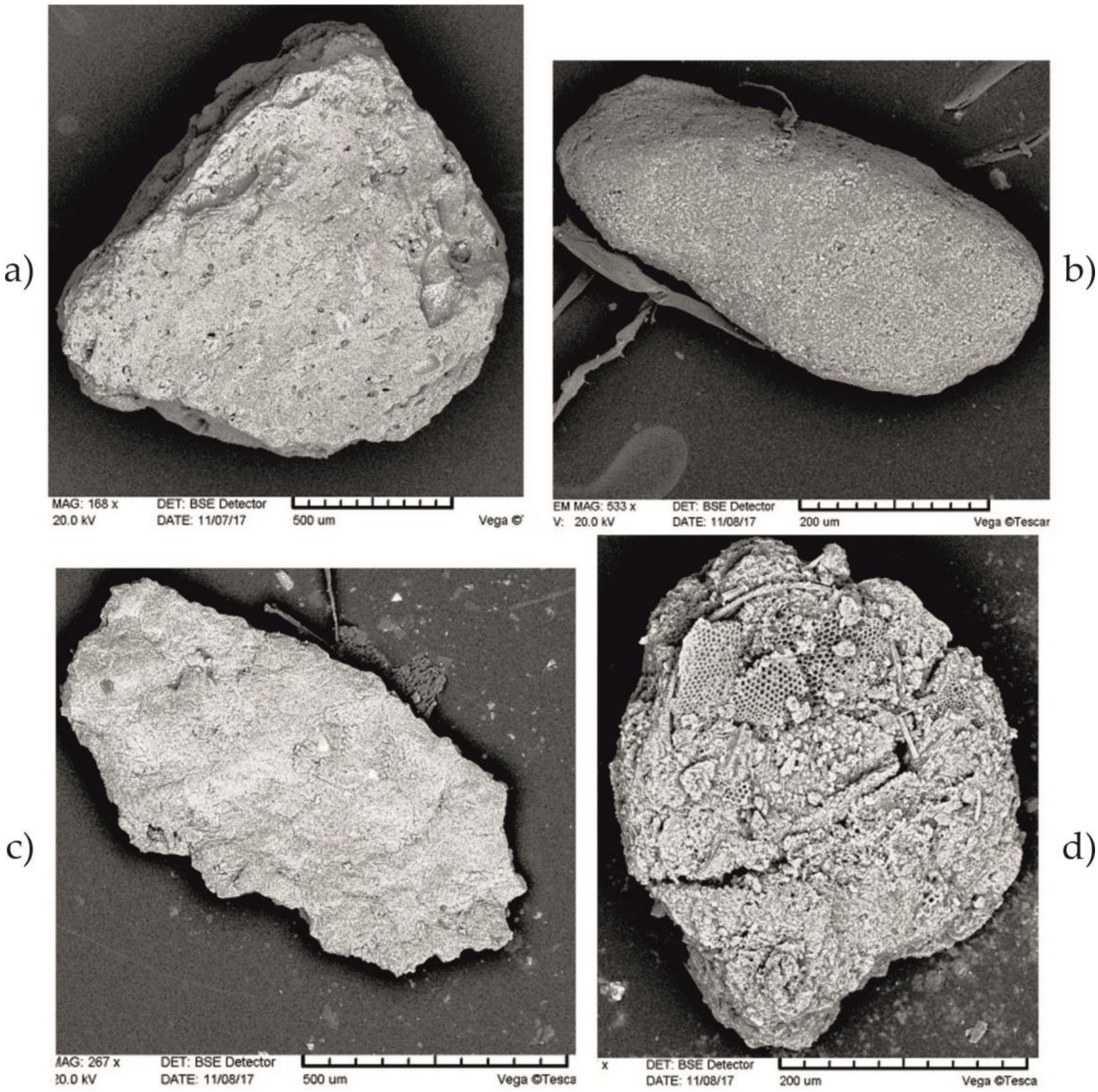

Figure 5. Scanning electron microphotographs of the andesitic ash shards and pisolites from the core unit of 323-340 cm: a) rounded fine-pored black heterogeneous andesitic shard with SiO_2 of 53.30-53.66% in the sample of 323-325 cm, the sheet-like fragments with higher SiO_2 of 55.50-56.05% and small ilmenite crystals are included, b) light pisolite composed of the andesitic basalt ash dust with SiO_2 of 62.03-65.98% in the sample of 323-325 cm, small titanomagnetite crystals are included, c) light loose grain composed of the andesitic basalt ash dust in the sample of 328-330 cm, small ilmenite and titanomagnetite crystals are included, d) white pisolite composed of the diatom frustules fragments and volcanic dust in the sample of 328-330 cm.

Pisolites as semi-rounded/non-rounded grains, black, composed of the andesitic and mafic ash with inclusions of the fragmented diatom frustules, quartz and pyroxene (Fig. 5 and 6a-b, 6d).

In addition, mostly rounded, transparent, colorless sometimes rose or yellow-brown (ferruginized) quartz.

What are pisolites in our samples?

Part of the ash material is the rounded and semi-rounded aggregates of the very thin, usually slightly cemented ash particles in size of ≤50 μm having the various composition with a sometimes substantial admixture of the fragmented diatom frustules, sponge spicules and other microfossils. We assign them as pisolites or ash shatters. They are aggregates of thin volcanic ash which can be

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formed during the penetration of the rain drops within the ash clouds, also during the vapor condensation on the ash particles in the eruptive clouds [14-17]. According the classification of the volcaniclastic material in [18], particles <0.1 mm are the fine-grained ash dust. This material appears at the andesite volcanic eruptions, and an area of its dispersal is unlimited. It can be contaminated by the terrestrial particles (e.g., minerals, fresh-water diatoms) during the eolian transport and by the marine particles (e.g., microfossils) during the sedimentation in the ocean.

We could recognize two types of pisolites in our samples: 1) semi-rounded, black, dense, sometimes pumiceous aggregates of the mixed composition, and 2) rounded, white, loose aggregates of the intermediate composition (Fig. 5 and 6).

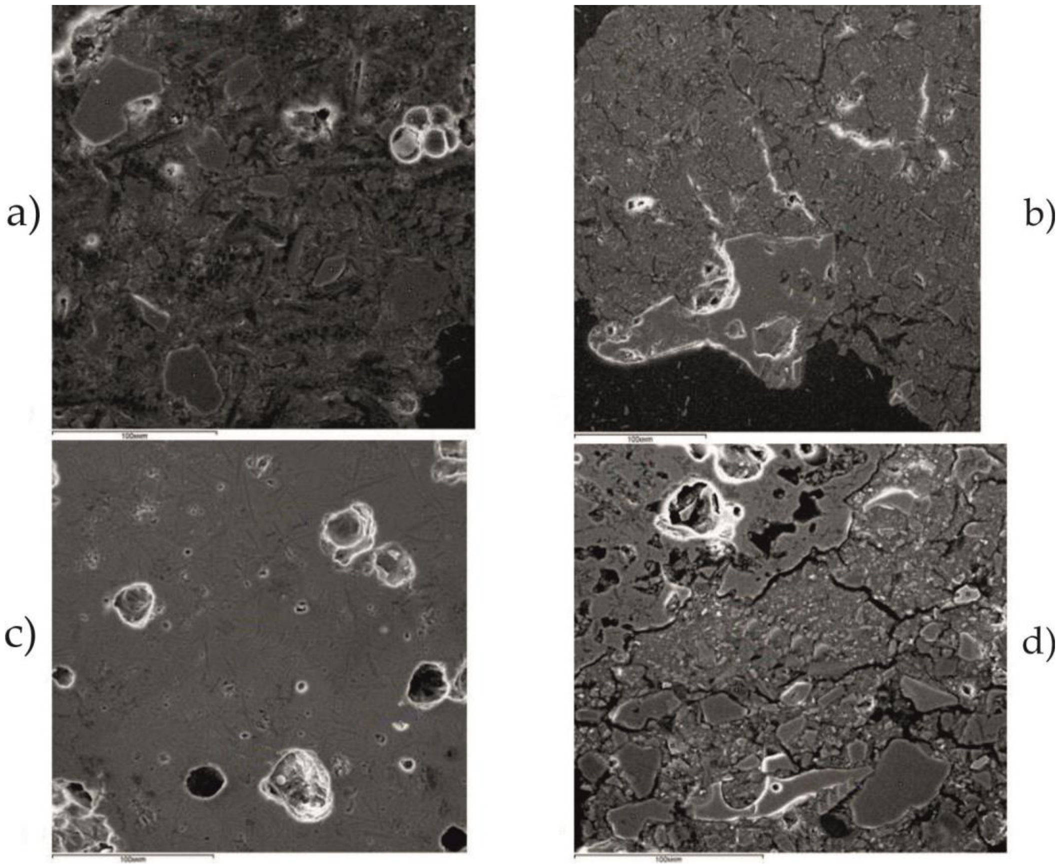

Figure 6. Scanning electron microphotographs of the basalts and pisolites of the andesitic and mafic composition on the polished thin sections from the core unit of 323-340 cm: a) irregularly elongated non-rounded black grain composed of mainly andesitic (SiO_2 of 52.39-58.97%) and sometimes persilicic (SiO_2 of 64.94%) dust in the sample of 328-330 cm, larger mafic shards, quartz and microfossil fragments are included, b) semi-rounded black shard composed of the andesitic ash dust with SiO_2 in the mean of 57.5% in the sample of 328-330 cm, occasional larger basalt shards with SiO_2 of 49.22% are included, c) microlitic basalt glass with SiO_2 in the mean of 50.31% in the sample of 328-330 cm, microlites are intermediate/mafic plagioclase, d) semi-rounded black shard composed of the andesitic ash dust with SiO_2 of 54.83% in the sample of 338-340 cm, occasional larger basalt fragments with SiO_2 in the mean of 50.52% and some Fe oxides (?) are included.

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3.2. Distribution of the eruptive material in the studied sediment samples

3.1.1. Core unit of 323-340 cm with an age of 12170-12840 years

We found here the abundant ash particles and pisolites, together with the foraminiferal shells, from 0.1-0.5 to 2-2.5 mm sometimes up to 6.5 mm in size (Fig. 2). Black fragments (basalts, andesito-basalts, pisolites of the intermediate and mafic composition) prevail in the upper and lower parts of the unit, samples of 323-325 and 334-336 cm, respectively, with a content of 30-40% of the whole sediment fraction (Fig. 2). The largest fragments of >1-5 mm in size are typical for the upper part of the unit.

The content and size of the black eruptive fragments decrease sharply in the sample of 328-330 cm; they comprise 5-10% of the sediment fraction, and their size normally is <0.5-1 mm. In this sample, the light pisolites of 0.25-0.5 mm in size, composed of the persilicic and andesitic ash with quartz, do prevail reaching 50-70% of the sediment fraction.

The content of the volcanic particles in the lowermost part of the unit, sample 338-340 cm, decreases significantly down to 8-10% of the sediment fraction. They are presented mostly by the black volcanic glass with an admixture of the olive-green ash, white pisolites of the persilicic composition, quartz, rare fragments of the pyroxene and plagioclase. Size of the particles rarely exceeds 1 mm with a maximum up to 2.5 mm.

3.1.2. Core unit of 355-378 cm with an age of 13600-14540 years

The eruptive material is presented by the sharply angular mainly pumiceous black basalt fragments with a white ash dust in the cavities, the semi-transparent bottle-green, sometimes yellowish mafic glass particles, quartz, feldspar, and sporadic semi-rounded white pisolites composed of the persilicic and andesitic ash dust (Fig. 7). In the analyzed sediment fraction, fragments of the eruptive rocks and minerals are larger compared to the biogenic particles being of 0.5-1 mm, occasionally 2-4 mm in size. The eruptive material within the unit is distributed irregularly with highest amounts up to 20-25% of the sediment fraction in the middle (sample 360-362 cm) and lower (sample 376-378 cm) parts; its content in other samples stands at 5-10%.

3.2. Chemical composition of the volcanic material in the studied samples

3.2.1. Core unit of 323-340 cm with an age of 12170-12840 years

3.2.1.1. Sample 323-325 cm

Basalt fragments, which prevail here, have typical content of SiO_2 from 49.05 to 51.67%, degraded concentration of K_2O from 0 to 0.91%, and high TiO_2 amount from 1.49% to 5.43%. TiO_2 content drops down to 0.68% in some grains with highest SiO_2 concentration. Glass composition on the surface of one shard can vary in some cases from basaltic with SiO_2 of 49.10% to andesitic with SiO_2 of 57.15% (Fig. 3a). Cavities of the black pumiceous basalt fragments are filled in many cases by the volcanic ash dust of the different composition, from the andesitic one with SiO_2 of 55.79% to persilicic one with SiO_2 of 63.89% and 65.97% (Fig. 3c).

Rhyolites (volcanic persilicic shards) are less numerous than the basaltic fragments. We analyzed a chemical composition of one grain (Fig.4a) where SiO_2 and K_2O content is high up to 76.37% and 3.92%, respectively. TiO_2 is not found.

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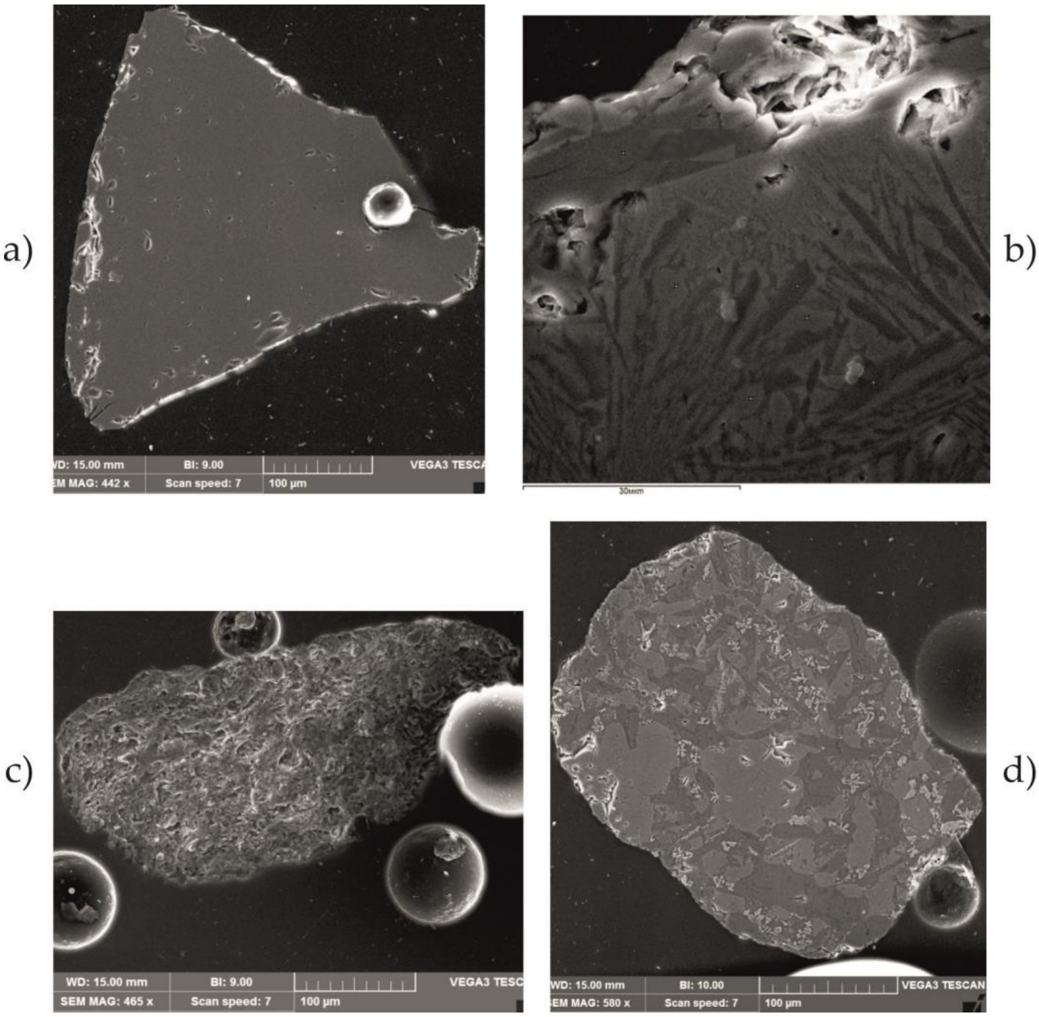

Figure 7. Scanning electron microphotographs of the eruptive shards on the polished thin sections from the core unit of 355-378 cm: a) andesitic basalt shard with SiO_2 of 52.60% in the sample of 355-357 cm, b) microlitic andesitic basalt glass shard with SiO_2 of 51.68% in the sample of 366-368 cm, intermediate/mafic crystals of plagilclase are included, c) persilicic pisolite with SiO_2 of 79.1% in the sample of 370-372 cm, some plagioclase (?) crystals are included, d) dark-grey andesitic pisolite with SiO_2 of 53.38-56.96% in the sample of 376-378 cm, light-grey basalt fragments (SiO_2 of 50.42-51.81%) are included.

Pisolites, which are presented here mostly by the white rounded loose intermediate variety (Fig. 5 and 6), are composed of the ash dust with SiO_2 content from 53.30-53.66 to 58.18% with occasional inclusions of the titanomagnetite. Black pisolites have fragments of the mixed mafic (SiO_2 of 42.08-50.76%) to persilicic (SiO_2 of 65.49% in average) composition.

3.2.1.2. Sample 328-330 cm

Most part of the volcanic material is presented by pisolites predominantly of the intermediate-persilicic composition (Fig. 5c-d) similar to those in the sample 323-325 cm. Ash dust in pisolites has SiO_2 content of 62.03-65.98%. Inclusions in pisolites are small crystals of titanomagnetite and ilmenite, and diatom frustules (Fig. 5d).

We found also pisolites of the mixed composition with the andesitic (SiO_2 of 58.97%) and persilicic (SiO_2 of 64.94%) ash dust, larger andesitic basalt particles (SiO_2 in the mean of 52.39%),

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occasional quartz inclusions and high admixture of the microfossil fragments (mostly diatoms) (Fig. 6a). Most black pisolites consist of the intermediate ash dust with SiO_2 in the mean of 57.5% and occasional larger basalt particles (Fig. 6b) with SiO_2 of 49.22%.

In addition, there are sporadic mafic with SiO_2 of 52.04%, intermediate with SiO_2 of 61.22%, and persilicic ash shards, the latter with high concentration of SiO_2 and K_2O, of 75.11% in average and up to 4.88%, respectively. Some mafic shards are microlithic (Fig. 6c) and consist of the basalt glass with SiO_2 in the mean of 50.31% and thin mafic plagioclase microliths.

3.2.1.3. Sample 334-336 cm

Eruptive material consists predominantly by the ash shards of the mafic (Fig. 3d) with SiO_2 of 50-51%, persilicic with SiO_2 of 70.49-75.26% and K_2O up to 3.39%, and mixed (Fig. 4в, г) composition. Less often, the andesitic basalt shards with SiO_2 of 52.78% occur. The persilicic shards are notable here for their elongate shape, presence of the lengthwise scratching, dense texture. Basalt shards have irregular shape and are pumiceous (Fig. 3 and 4). Shards of the mixed composition are close to the persilicic ones in the shape; on their transverse shear surfaces, we could see many small round cavities (bubbles) filled by the fragmented diatom frustules (Fig. 4c-d).

Some pisolites, consisted of thin andesitic ash dust with SiO2 of 59.94 % and abundant diatom fragments, were found.

3.2.1.3. Sample 338-340 cm

Basalt shards with SiO_2 of 50.17-51.01%, low K_2O content of <1%, and high TiO_2 concentration up to 4.44% prevail in the sample. Andesitic basalt shards with SiO_2 of 53.46%, and sharply angular transparent persilicic glass shards with SiO_2 of 71.45-71.84% are less numerous. The latter have relatively high K_2O content of 3.31-3.48%.

Sporadic black semi-rounded grains of the isometric or oval form are pisolites consisted of the andesitic ash dust with SiO_2 of 52.56-56.30% and occasional larger basalt shards (Fig. 6d) with SiO_2 in the mean of 50.52%.

3.2.1. Core unit of 355-378 cm with an age of 13600-14540 years (Fig. 7).

We analyzed 16 eruptive grains in the polished thin sections from 4 samples at 355-357, 360-368, 370-372, and 376-378 cm. Most part of them is the andesitic basalt shards (Fig. 7a) with SiO_2 of 52.5%; they were found in all samples of this core unit. The sample 355-357 cm contains also andesitic volcanic shards with SiO_2 of 53.26 %, microlithic basalt shards with SiO_2 in the mean of 51.68% on three analyses, and intermediate-mafic plagioclase crystals (Fig. 7b). In the sample of 370-372 cm, we found the persilicic glass shard with SiO_2 of 66.90-67.65% and very high K_2O concentration up to 7.93%, and the persilicic pisolite (Fig. 7c) with SiO_2 of 79.1% and with intruded plagioclase. The sample 376-378 cm has the andesitic pisolites with SiO_2 of 53.38-56.96 % or in the mean of 55.17% and with intruded basalt fragments (SiO_2 of 50.42-51.81% or in the mean of 51.12%) and titanomagnetite (Fig. 7d), and basalt shards with SiO_2 of 45.88%.

4. Discussion

Mangerud et al. [19] and Kvamme et al. [20] summarized findings of the Vedde Ash, started as early as in 1940th, within the Younger Dryas chronozone sediments in the North Atlantic, Nordic Seas and surrounding European continental areas. Ruddiman and Glover [21] described a rhyolitic ash bed in the pre-Holocene sediments from the North Atlantic which can be assigned as the regional Ash Zone I. As the authors suggested, this ash bed must be mostly ice-rafted, and the ash could be mixed through the sediment thickness of dozens of centimeters. In our core AMK-340 the thickness of the ash-bearing sediments from two core units is 40 cm within the time interval of appr. 12100-14500 years B.P. Bond et al. [22] and Thornalley et al. [7], as earlier Kvamme et al. [20], demonstrated a complicated geochemical composition of the ash beds in the Ash Zone I. The Vedde Ash cannot be a simple synonym of the Ash Zone I. The latter contains the volcanic material originated at different times from different Icelandic volcanoes and, probably, other sources. Based on studies of our core, we can give more results on the differentiation of the ash within the Ash Zone I in the open North Atlantic.

The diagram SiO_2 *versus* K_2O on the Fig. 8 shows that most analyzed volcanic grains from the core unit of 323-340 cm suit the ash material from the Icelandic volcanoes eruptions.

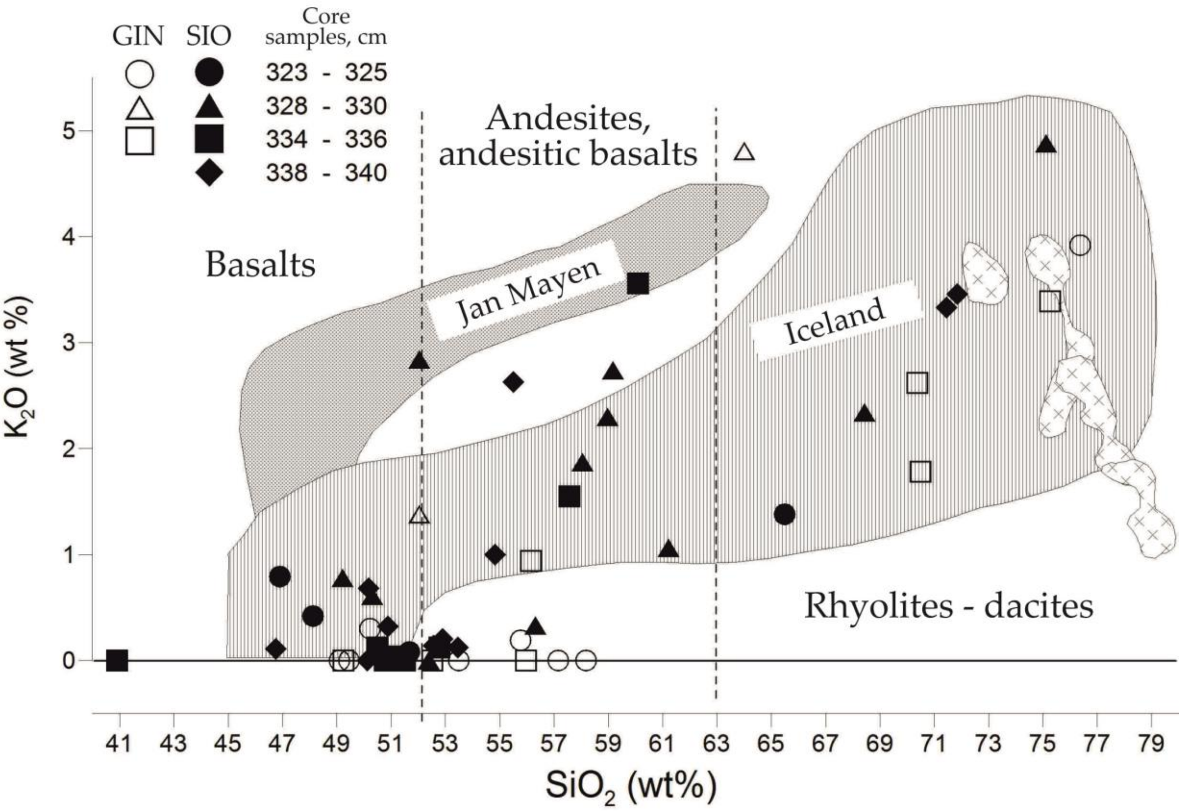

Figure 8. Position of the eruptive shards from the ash-bearing core unit of 325-340 cm in the binary SiO_2/K_2O system according [23]. Areas of the volcanic material from different sources are indicated according [24-25].

The sample of 323-325 cm contains the basalt shards and pisolites enriched in TiO_2, occasional rhyolites with the elevated K_2O and high FeO concentrations. Such ash composition is typical for the Vedde Ash whose age in the Greenland ice-core chronology appear to be 12170±57 years [3, 12-13]. A source of the eruptive material for the Vedde Ash can be Katla volcanoe in the southern Iceland [20, 27]. In addition, we found some intermediate ash shards, also as dust in pisolites, with low K_2O content, but their origin is unclear.

In the core unit of 328-335 cm with the corrected age estimate of appr. 12700-12900 years, the ash is presented mainly by the andesitic pisolites with the admixture of the basalts and rhyolites. Most of them suit the material from the Icelandic volcanoes. But some basalt fragments with the elevated K_2O in the andesitic pisolites can be related to the Jan Mayen volcanoes (Fig. 8). A common

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occurrence of the marine microfossil (diatom) fragments inside pisolites and ash shard cavities may suggest that the marine transportation and sedimentation could influence in a large degree an accumulation of the volcanic material in the area of study. However, we cannot be sure of the Jan Mayen origin of the above-mentioned andesitic pisolites because Abbot and Davies [3] noted that it is rare to find the Jan Mayen volcanic deposits in the distal areas.

The ash in the core unit of 355-378 cm with an age of 13600-14540 years differs from that in the core unit of 323-340 cm with an age of 12170-12840 years.

In the samples of 355-368 cm and 376-378 cm with an age of 13600-14100 and 14540 years, respectively, we can see a dominance of the basalt and andesitic basalt shards with SiO_2 of 52.32-53.13%, FeO of 9.71-11.13%, MgO of 6.31-8.69%, and K_2O of <1%. On the geochemical composition they are close to the tholeitic basalts and basalt glass in the rift zone of the Reykjanes Ridge [8] (Fig. 9), but differ from them by higher SiO_2 concentration. SiO_2 content is 49.76% and 50.56% in average in the tholeitic basalts and in the basalt shards of the Reykjanes Ridge, respectively. It is possible that the ash in the core unit of 355-378 cm is mainly the local eruptive material originated by the volcanism and tectonics in the Reykjanes Ridge rift zone [8], and transformed under an influence of the acidic hydrothermal fluids during the sedimentation.

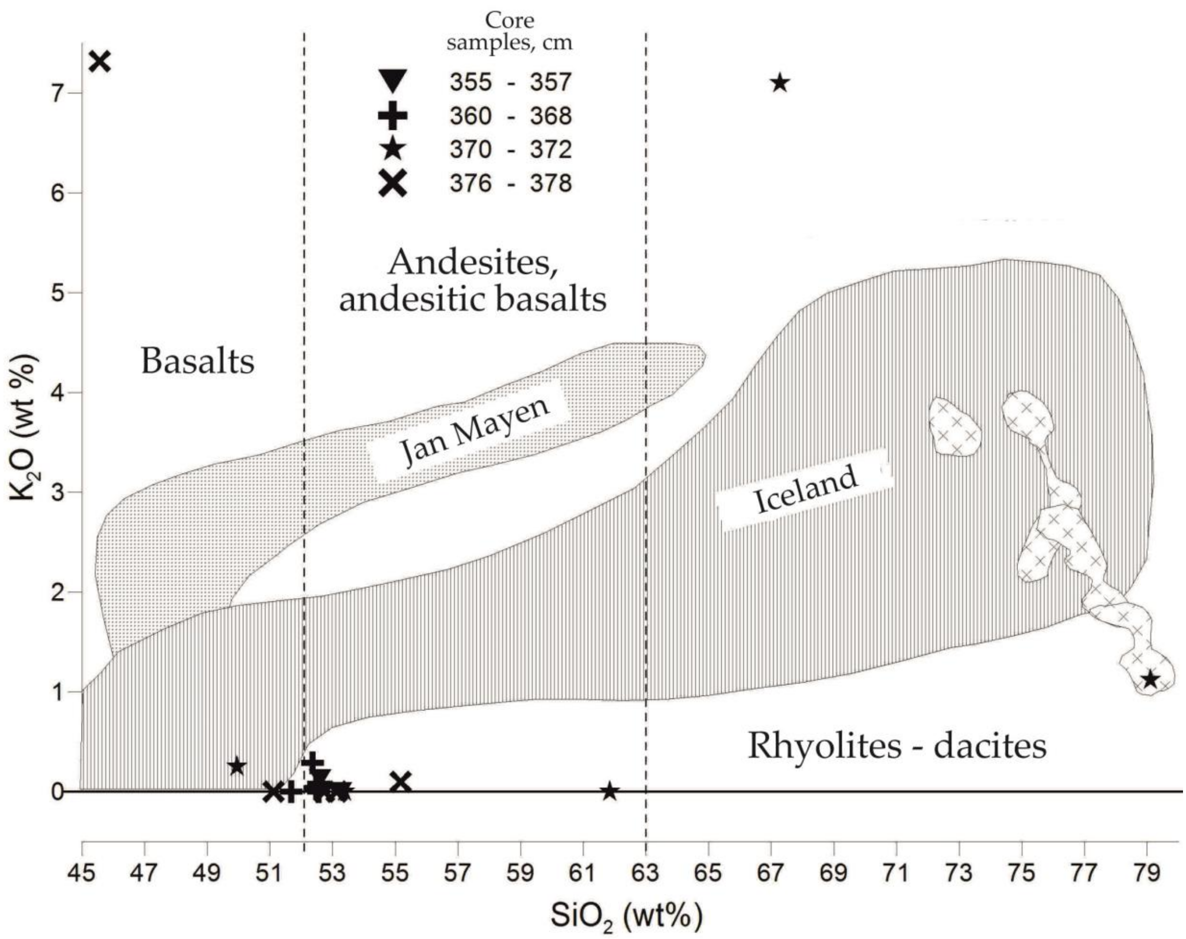

Figure 9. Position of the eruptive shards from the ash-bearing core unit of 355-378 cm in the binary SiO_2/K_2O system according [23]. Areas of the volcanic material from different sources are indicated according [24-25].

Other ash material in the core unit of 355-378 cm is (1) mafic shards with decreased SiO_2 of 45.88% in the lowermost sample of 376-378 cm, and (2) persilicic glass with SiO_2 of 67.65% and high K_2O concentration in the sample of 370-372 cm; source of both is unclear. Persilicic pisolites in the

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sample of 370-372 cm and mafic pisolites with SiO_2 of 51.12% in the sample of 376-378 cm were possibly originated from the Icelandic volcanoes, but the source of the andesitic pisolites with SiO_2 of 55.17% in the sample of 376-378 cm is not defined and could be more distal.

The Vedde Ash occurrence in the sediment sample of 323-325 cm made it possible to re-estimate the timing of the paleoenvironmental changes during the Younger Dryas chronozone (Glacial Stadial 1 in Rasmussen et al. [13]), which were reconstructed for the core AMK-340 [9]. Matul et al. [9] assigned the pre-Holocene warming at the Reykjanes Ridge in the North Atlantic within the Younger Dryas cold chronozone to the time interval of 12500-12200 years B.P. or significantly earlier than the beginning of the Holocene (11700 years B.P.). Now, we can assume that this change occurred 12200-12000 years B.P. which was anyways 300 years prior to the Holocene start.

5. Conclusions

Two sediment units of the core AMK-340, Reykjanes Ridge, North Atlantic, contain a significant amount of the volcanic ash. They can be related to the Ash Zone I in the North Atlantic Late Quaternary sediments. The ash-bearing sediments of the core were accumulated within the time intervals of 12170-12840 and 13600-14540 years B.P. or within the Younger Dryas cold chronozone and Bølling-Allerød warm chronozone, respectively.

The ash in the core AMK-340 within the Younger Dryas unit is presented mostly by the mafic and persilicic material originated from the Icelandic volcanoes, and ice-rafted to the point of study. In one sediment sample we could detect the bimodal Vedde Ash.

The ash in the core AMK-340 within the Bølling-Allerød unit is presented mostly by the mafic shards which are close to the basalts and basalt glass of the rift zone on the Reykjanes Ridge, i.e., have presumably the local origin.

In some samples of both units we found pisolites aggregated of the andesitic ash dust with inclusions of the persilicic/mafic particles and fragments of the marine diatom frustules. An origin of these pisolites is unclear.

A detection of the Vedde Ash helped to specify the age model of the core AMK-340 for the Termination I time interval. Timing of the previously reconstructed paleoceanographic changes can be modified, but, anyways, a significant warming in the area could occur as early as 300 years prior to the end of the conventional Younger Dryas cold chronozone.

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References

1. Lowe, D.J. Tephrochronology and its application: a review. *Quat. Geochronol.* **2011**, *6*, 423.

2. Turney, S.M., Lowe, J.J., Davies, S.M., Hall, V.A., Lowe, D.J., Wastegård, S., Hoek, V.Z., Alloway, B.V. Tephrochronology of Last Termination sequences in Europe: a protocol for improved analytical precision and robust correlation procedures (a joint SCOTAV-INTIMATE proposal). *J. Quat. Sci.* **2004**, *21*, 335-345.
3. Abbott, P.M., Davies, S.M. Volcanism and the Greenland ice-cores: the tephra record. *Earth-Science Rev.* **2012**, *115*, 173-191.
4. Bourne, A.J., Cook, E., Abbot, P.M., Seierstad, I.K., Steffensen, J.P., Fischer, H., Schnupback, S., Davies, S.M. A tephra lattice for Greenland and a reconstruction of volcanic events spanning 25–45 ka b2k. *Quat. Sci. Rev.* **2015**, *118*, 122-141.
5. Thordarson, T., Höskuldsson, A. Postglacial volcanism in Iceland. *Jökull* **2008**, *58*, 198-228.
6. Gudmundsdóttir, E.R., Larsen, G., Björck, S., Ingólfsson, Ó., Striberger, J. A new high-resolution Holocene tephra stratigraphy in eastern Iceland: Improving the Icelandic and North Atlantic tephrochronology. *Quat. Sci. Rev.* **2016**, *150*, 234-249, https://doi.org/10.1016/j.quascirev.2016.08.011.
7. Thornalley, D.J.R., McCave, I.N., Elderfield, H. Tephra in deglacial ocean sediments south of Iceland: Stratigraphy, geochemistry and oceanic reservoir ages. *J. Quat. Sci.* **2011**, *26*, 190-198.
8. Lisitzin, A.P., Zonenshain, L.P., Eds. *Rift zone of the Reykjanes Ridge: tectonics, magmatism, conditions of sedimentation.* Nauka Press: Moscow, Russia, 1990; 239 pp. [In Russian].
9. Matul, A., Barash, M.S., Khusid, T.A., Behera, B., Tiwari, M. Paleoenvironment Variability during Termination I at the Reykjanes Ridge, North Atlantic. *Geoscience*s **2018**, *8*, article 375. DOI: 10.3390/geosciences8100375.
10. Matul, A. Late Quaternary paleoceanology of the North Atlantic based on radiolaria analysis data. *Oceanology* **1994**, *34*, 550-555.
11. Matul, A. On the problem of paleoceanological evolution of the Reykjanes ridge region (North Atlantic) during the last deglaciation based on a study of radiolaria. *Oceanology* **1994**, *34*, 806-814.
12. Mortensen, A.K., Bigler, M., Grönvold, K., Steffensen, J.P., Johnsen, S.J. Volcanic ash layers from the Last Glacial Termination in the NGRIP ice core. *J. Quat. Sci.* **2005**, *20*, 209-219.
13. Rasmussen, S.O., Bigler, M., Blockley, S.P., Blunier, T., Buchardt, S.L., Clausen, H.B., Cvijanovic, I., Dahl-Jensen, D., Johnsen, S.J., Fischer, H., et al. A stratigraphic framework for abrupt climatic changes during the Last Glacial period based on three synchronized Greenland ice-core records: refining and extending the INTIMATE event stratigraphy. *Quat. Sci. Rev.* **2014**, *106*, 14-28. http://dx.doi.org/10.1016/j.quascirev.2014.09.007.
14. Lyakhovich, V.V. On pisolitic tufa on the Siberian platform. *Doklady AN SSSR* **1956**, *110*, 137-139. [In Russian].
15. Moore, J.Y., Peck, D.L. Accretionary lapilli in volcanic rocks of the Western Continental United States. *J. Geol.* **1962,** *70*, 182-194.
16. Kotova, L.N. Ash lapilli from Devonian volcanogenic-sedimentary series of Tarbagai Ridge. *Lithol. Mineral Resour.* **1966**, *2*, 58-64. [In Russian].
17. Shcherbakova, M.N. Ash rain in volcanogenic sediments of near-Balkhash (Kazakhstan). *Lithol. Mineral Resour.* **1972**, *1*, 155-160. [In Russian].

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Peer-reviewed version available at *Geosciences* **2019**, *9*, 379; doi:10.3390/geosciences9090379

18. Dzozenidze, G.S., Markhinin, E.K. Volcanoclastic products and problem of their evolution. In *Problems of the volcanogenic-sedimentary lithogenesis*. Nauka Press: Moscow, Russia, 1974, pp. 4-12. [In Russian].
19. Mangerud, J., Lie, S.E., Furnes, H., Kristiansen, I.L., Lømo, L. A Younger Dryas Ash Bed in western Norway, and its possible correlations with tephra in cores from the Norwegian Sea and the North Atlantic. *Quat. Res.* **1984**, *21*, 85-104.
20. Kvamme, T., Mangerud, J., Furnes, H., Ruddiman, W.F. Geochemistry of Pleistocene ash zones in cores from the North Atlantic. *Norsk Geologisk Tidsskrift* **1989**, *69*, 251-272.
21. Ruddiman, W.F., Glover, L.K. Vertical mixing of ice-rafted volcanic ash in north Atlantic sediments. *Geol. Soc. Am. Bull.* **1972**, *83*, 2817-2836.
22. Bond, G.C., Mandeville, C., Hoffmann, S. Were rhyolitic glasses in the Vedde ash and in the North Atlantic's Ash Zone 1 produced by the same volcanic eruption? *Quat. Sci. Rev.* **2001**, *20*, 1189-1199.
23. Le Maitre, R.W., Bateman, P., Dudek, A., Keller, J., Lameyre, J., Le Bas, M.J., Sabine, P.A., Schmid, R., Sorensen, H., Streickeisen, A., Woolley, A.R., Zanettin, B. *A Classification of Igneous Rocks and Glossary of Terms*. Blackwell Scientific Publications: Oxford, UK, 1989; 193 p.
24. Mutschler, F.E., Rougon, D.J., Lavin, O.P., Hughes, R.D. PETROS – A data bank of major element chemical analyses of igneous rocks for research and teaching (version 6.1). NOAA, National Geophysical and Solar-Terrestrial Data Center, Boulder, CO. 1981.
25. Wallrabe-Adams, H.J., Lackschewitz, K.S. Chemical composition, distribution, and origin of silicic volcanic ash layers in the Greenland – Iceland – Norwegian Sea: explosive volcanism from 10 to 300 ka as recorded in deep-sea sediments. *Mar. Geol.* **2003**, *193*, 273-293.
26. Mortensen, A.K., Bigler, M., Grönvold, K., Steffensen, J.P., Johnsen, S.J. Volcanic ash layers from the Last Glacial Termination in NGRIP ice core. *J. Quat. Sci.* **2005**, *20*, 209-219.
27. Lacasse, C., Sigurdsson, H., Johanntson, H,Paterne, M, Carey, S. Source of Ash Zone 1 in North Atlantic. *Bull. Volcan.* **1995**, *57*, 18-32.