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Rittmann volcano, Antarctica as the source of a widespread 1252 ± 2 CE tephra layer in Antarctica ice

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ABSTRACT

Tephra occur in many ice cores from Antarctica and are important time markers that assist in correlations between cores and in dating their valuable climate records. Major element compositions of glass shards in a trachytic tephra found in ice cores drilled at WAIS Divide, Roosevelt Island and Styx Glacier, and blue ice patches at Brimstone Peak and the Rennick Glacier in Victoria Land, are similar and suggest they are the same tephra. The composition of the tephra is also similar to tephra layers reported in 3 others ice cores from the East and West Antarctica Ice Sheets. In the WAIS Divide WDC06A ice core the tephra is dated as 1252 ± 2 CE. The distribution of the tephra implies a source in northern Victoria Land, Antarctica. The Pleiades, Mt. Melbourne and Rittmann volcano in northern Victoria Land all have evidence of recent eruptive activity which has resulted in the occurrence of trachytic tephra in ice cores, blue ice/snow areas and as surficial tephra layers. Although there is a significant area of geothermal activity at Mt. Rittmann, until now there has been no evidence of any recent eruptive activity. A pyroclastic breccia, with glassy fiamme-like clasts was formed by an explosive eruption from Rittmann volcano. Analyses of the glass clasts and whole rock analyses of some lava samples have trachytic compositions very similar to the 1252 CE tephra. Rittmann volcano is now considered the source of this tephra, which is here named the Rittmann tephra. Rittmann tephra is spread over 2000 km and the 8 known occurrences makes it the most widely correlated tephra layer in Antarctic ice and a valuable marker layer. The wide distribution implies a large possibly Plinian eruption which makes it the largest known eruptions from any Holocene volcano in the western Ross Sea area. This discovery of young explosive eruptions from Rittmann volcano and other northern Victoria Land volcanoes show that there is a significant volcanic hazard from these volcanoes especially to aircraft operations.

1. Introduction

Tephra are pyroclastic ejecta that are erupted explosively from volcanoes (Alloway et al., 2013). The ejected tephra are transported through the atmosphere typically as a volcanic ash cloud and depending on the size of the eruption and wind conditions can be dispersed thousands of kilometers from the erupting volcano (Shane, 2000). Tephra provide valuable marker horizons in stratigraphic studies and when dated by various methods they provide valuable isochrons that can be correlated to distal geologic environments.

Ice is the perfect medium to preserve tephra and even thin and fine-grained cryptotephra are well preserved and are easily identified and extracted for analysis (Iverson et al., 2017a). Furthermore, ice cores can be dated by counting annual snow accumulation layers and annual chemical signals like oxygen isotopes and sulfate cycles (e.g. Taylor et al., 2004; Sigl et al., 2014; Winstrup et al., 2017). It is therefore possible to date Holocene and late Pleistocene tephra in ice cores to a precision of a year or two, which makes them valuable as precise time horizons. Tephra layers in ice cores can also be correlated by their lithology, mineralogy, and geochemical composition of their glassy ash particles (e.g. Kyle et al., 1981; Palais et al., 1987, 1988; Dunbar and Kurbatov, 2011; Narcisi et al., 2012; Dunbar et al., 2017). With the precise chronology in some ice core this allows the tephra record to be correlated to known historic eruptions. Tephra are valuable in providing correlations between individual ice cores. An excellent example was the "mysterious" 1257 CE tephra and sulfate signal that has been known in Greenland and Antarctic ice cores for decades (Oppenheimer, 2003). Lavigne et al. (2013) finally solved the mys-

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Fig. 1. Location maps. (a) Victoria Land showing the location of the ice cores at Styx Glacier and Talos Dome, the "active" volcanoes of The Pleiades, Rittmann volcano, Mt. Melbourne and Erebus volcano and tephra layers in sediment cores (Del Carlo et al., 2015) from the Ross Sea and (b) Location of "active" volcanoes and ice cores from Antarctica containing the Rittmann tephra.

tery and identified Samalas volcano in Indonesia as the source and showed the chemical composition of tephra at the volcano were like glass shards in ice cores from South Pole and Greenland (Palais et al., 1992).

In this study we correlate a trachytic tephra layer found in ice cores from the East and West Antarctic Ice Sheet, Rossevelt Island and the Styx Glacier, northern Victoria Land and in two blue ice patches in Victoria Land. We analyzed glass clasts (fiamme) and whole rock samples in a volcanic breccia from Rittmann volcano and found glass and whole rock sample compositions at Rittmann volcano that overlap within analytical error to the glass shards in the englacial tephra. Based on the compositions of glass in pumice lapilli from The Pleiades and Mt. Melbourne we can discount them as the source volcano of the tephra and propose Rittmann volcano as the eruptive source. This has major implications to the nature of volcanism in Antarctica and suggests that Rittmann volcano had one of the largest Holocene eruptions in Antarctica history. We here informally name the tephra as the Rittmann tephra.

2. The Rittmann (1252 CE) tephra

The Rittmann tephra was first described by Narcisi et al. (2001) at a depth of 85.82 m in a 90 m ice core drilled at Talos Dome in northern Victoria Land (Fig. 1). They found a coarse ash tephra and suggested the age was 1254 ± 2 CE by counting annual sulfate layers in the ice core. SEM studies showed the volcanic particles ranged from a few μm (microns) to about 200 μm and were volcanic glass shards with vesicles and some pumiceous ash. Narcisi et al. (2001) noted that the "eruption may represent the most important volcanic explosion in the Melbourne volcanic province during the last eight centuries". They considered a volcano in northern Victoria Land was the source of the tephra and compared their scanning electron microscope (SEM) and microprobe analyses of the glass shards with whole rock compositions of lavas from Mt. Melbourne, The Pleiades and Mt. Rittmann. The tephra compositions were shown to be like rocks from The Pleiades and Mount Rittmann, both about 200 km from Talos Dome (Fig. 1).

Dunbar et al. (2003) analyzed tephra from 97.2 and 97.45 m in the Siple Dome B ice core and from 79.155 meters in the Taylor Dome core and suggested they were correlative. They argued for an eruption age of between 703–709 years prior to 1995 (1289 CE). Dunbar et al. (2003) did not recognize the correlation with the 1254 ± 2 CE layer in Talos Dome but suggested the tephra was from The Pleiades volcanic center in northern Victoria Land.

Narcisi et al. (2012) further commented on the Rittmann tephra in a new Talos Dome ice core noting it represented a valuable stratigraphic marker across the Antarctic ice sheets as it correlated with tephra layers in the Siple Dome B and Taylor Dome ice cores described by Dunbar et al. (2003). Narcisi et al. (2012) also suggested an age for the tephra of 694 ± 7 before 1950 (1256 CE).

Dunbar et al. (2010) reported on occurrences of tephra in WAIS Divide ice cores. Here we report the first analyses of the Rittmann tephra in these ice cores. The Rittmann tephra occurs in two WAIS Divide cores (WDC05-190.37 m and WDC06A-190.80 m). They are geochemically the same and are identified as the same tephra. The WDC06A-190.80 m tephra layer has an age of 1252 ± 2 CE, based on the combination of annual layers of dust, ice chemistry and electrical conductivity records (Sigl et al., 2015). The tephra layer is five years older than the well dated 1257 CE Samalas eruption that produced the 1258/1259 sulfate spike in ice cores (Sigl et al., 2015; Lavigne et al., 2013).

The Rittmann tephra occurs in the RICE ice core drilled on Rossevelt Island (Bertler et al., 2018). It occurs at a depth of 165.00–165.02 m and was initially characterized by Kalteyer (2015) and published in Iverson et al. (2017a). The tephra is extremely important as it was a critical identification that was used to calibrate the time scale of the RICE core (Winstrup et al., 2017).

3. Recent volcanic activity in northern Victoria Land

Quaternary volcanism is widespread in Antarctica and is important in the western Ross Sea (Kyle, 1990a) and Marie Byrd Land (LeMasurier, 1990) and six subaerial active volcanoes are known (Fig. 1). Several potentially active subglacial volcanoes have been recognized beneath the West Antarctica ice sheet (Iverson et al., 2017b; Van Wyk de Vries et al., 2017). Active volcanoes in northern Victoria Land, are Taygete Cone at The Pleiades (Kyle, 1982; Esser and Kyle, 2002), Mt. Rittman (Bonaccorso et al., 1991) and Mt. Melbourne (Nathan and Schulte, 1967; Lyon and Giggenbach, 1974; Wörner and Viereck, 1989). Of these volcanoes, Rittmann is the focus of this study as we suggest it is the source of the proposed Rittmann tephra.

Mt. Rittmann and surrounding nunataks, are here named and referred to informally as Rittmann volcano, was discovered in 1988/1989 by the fourth Italian expedition to North Victoria Land (Armienti and Tripodo, 1991). Later, in the 1991/1992 field season an Italian expedition found fumaroles and ground heated by geothermal activity at Mt. Rittmann (Bonaccorso et al., 1991). Armienti and Tripodo (1991) recognized Rittmann volcano has a 2-km summit caldera but gave no detailed field description of the outcropping rocks. They noted the rim of the caldera was made up of volcanic breccia containing xenoliths and pumice. Armienti and Tripodo (1991) made whole rock major and trace element analy-

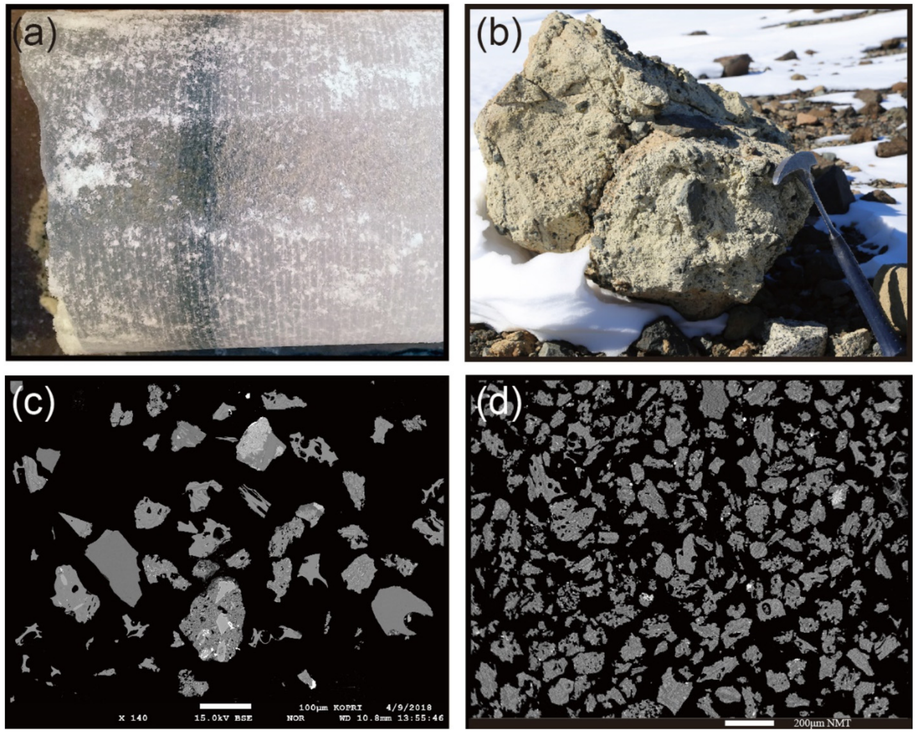

Fig. 2. Samples analyzed in this study. (a) 99.18 m tephra layer from the Styx ice core, (b) Rittman ignimbrite sample containing fiamme glasses, (c) and (d) SEM images of glass shards of the Styx 99.18 tephra and englacial tephra (BIT106) from a blue ice patch near Brimstone Peak, respectively.

ses and microprobe analyses of mineral phases from lava samples collected from Rittmann volcano.

The Pleiades is a 13 km long volcanic complex consisting of a stratovolcano and numerous domes and cones in northern Victoria Land (Fig. 1) (Kyle, 1982, 1990b; Kim et al., 2019). Fifteen $^{40}Ar/^{39}Ar$ ages (Esser and Kyle, 2002) range back to 847 ka. Taygete Cone is a trachytic endogeneous dome and the lava has a $^{40}Ar/^{39}Ar$ age of 6 ± 6 (2σ) ka. Whole rock ^{36}Cl exposure ages range from 6–10 ka (Kyle, unpublished data) also indicating an eruption less than 12 ka ago. Pumice lapilli, similar in compositional to lava at Taygete Cone lava, are scattered over the southern part of The Pleiades. The lapilli are evidence of a recent large explosive eruption which should have resulted in widespread deposition of tephra.

Mt. Melbourne is a 2732 m high alkaline stratovolcano composed of scoria cones, domes, lava flows and various pyroclastic deposits (Wörner and Viereck, 1989; Giordano et al., 2012). Fumarolic activity, geothermal ice caves, englacial tephra and welded pumice layers are evidence of recent explosive activity. Giordano et al. (2012) reported $^{40}Ar/^{39}Ar$ ages of 50 ± 70 and 35 ± 22 ka on feldspar separates from summit pumice deposits. Recent eruption products, pumice lapilli layers and several englacial tephra layers near Baker Rocks and Edmonson Point provide evidence of a recent explosive eruption of Mt. Melbourne. Narcisi et al. (2012) examined a rich tephra record in an ice core from Talos Dome (Fig. 1) and suggested many tephra were erupted from Mt. Melbourne.

4. Samples

A tephra layer (Fig. 2a) was sampled from 99.18 m depth in a 210.5 m deep ice core drilled in the 2014–2015 Antarctic summer field season on the Styx Glacier (Fig. 1), 85 km north of Jang Bogo Station (Han et al., 2015). Particles in the tephra range from several tens of microns up to 200 microns in size and are mostly composed of glass and microlite rich shards and minor lithic and mineral ash particles (Fig. 2c). The glass shards show arcuate edges, a typical appearance of primary juvenile material from an explosive eruption.

Two tephra samples from the WAIS Divide ice cores were analyzed and are comprised of fine-grained glass shards with arcuate edges and y-shaped septum. Most of the shards are between 10–40 microns with a few 70 microns in length. A tephra sample from the RICE ice core (Bertler et al., 2018) has shards similar in shape to those in the WAIS ice cores but there are rare shards > 100 micron. Pumiceous ash and shards with microlites are rare in both West Antarctic ice core sites.

Englacial tephra from a blue ice patches near Brimstone Peak (BIT106) and the Rennick Glacier (Fig. 1, Table S2) were analyzed and they have similar appearances and grain size (see the samples section in Table S2 for location and grain size data). The tephra contain glass shards, rare crystals and abundant crystallized shards full of microphenocrysts (Fig. 2d). The samples are strikingly similar in appearance and grain size to the tephra sample from the Styx ice core (Table S2). Samples of volcanic breccia, pumice and lava flows were collected from Rittmann volcano. Some of the samples are tentatively identified as ignimbrites (Fig. 2b) and contain fiamme which we analyzed. Eight pumice lapilli from surficial deposits at The Pleiades, were analyzed as representative of the youngest Taygete Cone eruption. Two englacial pumiceous tephra from the flank of Mt. Melbourne were analyzed. The age of the tephra are unknown but as they are in glacial ice high up on the flank of the volcano they must be very young and we estimate them to be less than 1000 years old. The tephra have pumice and obsidian lapilli and ash sized glass shards and minerals grains.

5. Analytical methods

Glass from pumice, fiamme and tephra samples were analyzed using a 4 spectrometer Cameca SX-100 microprobe at N.M. Tech with a 15 kV acceleration voltage, 10 nA probe current and beam diameters of 10, 15 or 20 microns. The lab participated in the INTAV intercomparison of microprobe analyses of glass (Kuehn

Table 1
Analyses of the Rittmann tephra and correlative glass from Rittmann volcano.

Sample	1		2		3		4		5		6		7	
N	14	1σ	9	1σ	8	1σ	14	1σ	9	1σ	5	1σ	34	1σ
SiO_2	61.85	0.32	61.47	0.37	60.89	0.52	61.78	0.38	61.20	0.51	61.55	0.48	61.62	0.20
TiO_2	0.39	0.04	0.38	0.04	0.35	0.05	0.41	0.05	0.43	0.04	0.43	0.03	0.36	0.03
Al_2O_3	16.43	0.15	16.80	0.19	17.02	0.38	16.77	0.16	16.32	0.14	16.48	0.21	16.12	0.12
FeO	6.39	0.12	6.37	0.11	6.47	0.44	6.23	0.31	6.48	0.24	6.50	0.09	6.70	0.07
MnO	0.24	0.02	0.28	0.02	0.26	0.05	0.23	0.02	0.27	0.03	0.21	0.03	0.26	0.03
MgO	0.11	0.02	0.11	0.01	0.10	0.02	0.13	0.03	0.17	0.02	0.15	0.02	0.09	0.02
CaO	1.21	0.05	1.13	0.07	1.03	0.12	1.20	0.12	1.09	0.06	1.22	0.04	1.08	0.02
Na_2O	7.54	0.40	7.76	0.59	8.16	0.39	7.50	0.56	8.36	0.36	7.52	0.58	8.24	0.18
K_2O	5.42	0.09	5.31	0.11	5.23	0.25	5.35	0.12	5.23	0.09	5.52	0.24	5.15	0.06
P_2O_5	0.07	0.03	0.06	0.02	0.07	0.04	0.07	0.04	0.09	0.03	0.06	0.03	0.05	0.02
SO_2	0.03	0.01	0.04	0.02	0.05	0.02	0.03	0.02	0.03	0.01	0.03	0.03	0.04	0.01
F	0.26	0.06	0.29	0.06	0.18	0.09	0.20	0.11	0.34	0.08	0.28	0.09	0.27	0.03
Cl	0.21	0.01	0.15	0.07	0.34	0.12	0.21	0.02	0.18	0.02	0.20	0.03	0.19	0.01
−O=F, Cl	−0.16	0.02	−0.16	0.02	−0.15		−0.13	0.05	−0.18	0.03	−0.16	0.04	−0.16	0.01
Total	100.00		100.00		100.00		100.00		100.00		100.00		100.00	
FeO*									6.37					
Na_2O*									7.87					

ug/g	5*	7**
Sc	3.34	1.3
Cr	2	0.4
Co	1.0	1.7
Zn	142	149
Rb	93	93
Sr	31	2
Cs	1.32	1.6
Ba	99	10
La	85.5	87.2
Ce	169.6	169.0
Nd	66	69.7
Sm	13.4	13.3
Eu	2.10	1.4
Tb	1.78	1.7
Yb	5.00	5.2
Lu	0.73	0.8
Hf	13.23	13.7
Ta	7.91	10.8
Th	11.46	14.3
U	3.60	3.7

N = number of analyses in average. *INAA, **ICP-MS.
Major element analyses recalculated to 100%.

1. Styx Ice Core 99.18 m depth.
2. WAIS core, WDC05-190.81.
3. WAIS core, WDC06A-190.37.
4. RICE core AntT16 (Iverson et al., 2017a).
5. Englacial tephra (BIT106) in blue ice from Brimstone Peak (−75.8712 158.606).
6. Englacial tephra from the Rennick Glacier (−71.7007 161.81893).
7. Rittmann volcano glass (fiamme) (J16121105-2).
Individual analyses are given in the supplemental material (Table S2).

et al., 2011) and followed the recommendations proposed as part of the study. All the instrumental conditions, standards used, and analyses of secondary standards are given in detail in the Supplement Table S2. Individual analyses of samples are given in Supplement Tables S2 and S3. All analyses have been recalculated to 100% to allow comparison.

Whole rock samples from Rittmann volcano were analyzed for major elements by X-ray fluorescence (XRF) and for trace elements by ICP-MS. Analytical details and analyses of samples and standards are given in Supplement Table S4.

A bulk (100 mg) sample of the BIT106 tephra from Brimstone Peak was analyzed by instrumental neutron activation analysis at N.M. Tech. Details of the analytical procedures and analyses of standards are given in Supplement Table S5.

6. Results

6.1. Styx, WAIS, RICE ice cores

Glass shards (Fig. 2c) from the 99.18 m tephra in the Styx ice core are trachytic (Table 1; Fig. 3). The glass shards have a uniform composition with the standard deviations on the mean being within typical electron microprobe analytical uncertainty. The characteristic features of the analyses are the low CaO and high FeO contents (Fig. 4). The tephra is clearly different in composition to recent pumice erupted from The Pleiades and Mt. Melbourne (Table 2, Figs. 3, 4).

Analyses of glass shards from the two WAIS Divide ice core samples are trachytic (Table 1). Both tephra have similar grain sizes and morphology and the analyses overlap at one standard deviation. However, WDC05-190.37 shows more variation with respects to Na_2O than the adjacent WDC06A-190.8 tephra. Just like the Styx ice core tephra, CaO and FeO are the most useful oxides for differentiating this tephra from Mt. Melbourne and The Pleiades (Figs. 3 and 4).

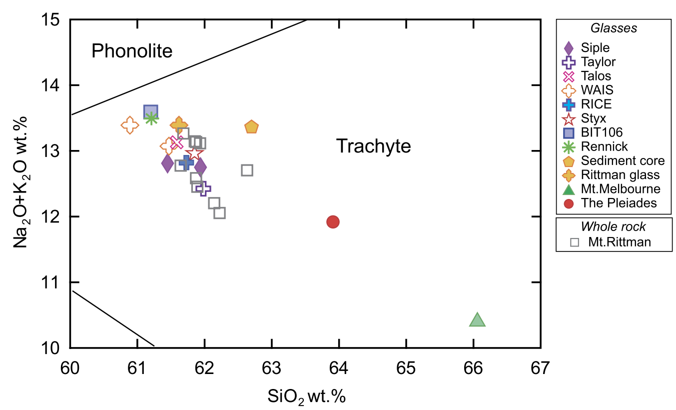

Fig. 3. Total alkali ($Na_2O + K_2O$) versus silica (SiO_2) classification plot (LeBas et al., 1986) of the Rittmann tephra and suggested correlatives. These are compared with fiamme glass and whole rock analyses (Table S4) from Rittmann volcano, and young pumice erupted from The Pleiades and Mt. Melbourne.

6.2. Blue ice tephra

Major element composition of glass shards from the englacial tephra samples from Brimstone Peak (BIT106) and the Rennick Glacier (Table 1; Figs. 3 and 4) are both similar to the Styx, WAIS and RICE ice core tephra and to published compositions of the Rittmann tephra from East and West Antarctica ice cores (Tables 1 and S1). Additionally, instrumental neutron activation analyses of a bulk (∼ 100 mg) sample of BIT106 is almost identical to the ICP-MS trace element analysis of glass clasts from Rittmann volcano (Table 1). BIT106 has slightly higher Sr, Ba and Eu contents suggesting the tephra is slightly enriched in feldspar, which is further supported by the abundance of microlites.

6.3. Tephra source volcanoes

An average composition (Table 1 analysis 7) of glass clasts (fiamme) from a pyroclastic breccia at Rittmann volcano is trachytic

Table 2
Analyses of recent tephra erupted from The Pleiades and Mt. Melbourne.

Sample	1		2		3		4		5		6	
N	15	1σ	12	1σ	10	1σ	11	1σ	14	1σ	8	1σ
SiO_2	63.92	0.57	64.70	0.24	64.85	0.21	65.26	0.33	66.06	0.23	66.13	0.47
TiO_2	0.30	0.03	0.25	0.10	0.23	0.05	0.23	0.05	0.26	0.03	0.28	0.04
Al_2O_3	17.50	0.25	15.70	0.14	15.72	0.10	15.83	0.19	15.46	0.13	15.50	0.15
FeO	4.36	0.23	5.76	0.16	5.91	0.11	5.75	0.11	5.54	0.12	5.60	0.17
MnO	0.18	0.03	0.14	0.03	0.15	0.02	0.14	0.02	0.14	0.02	0.16	0.03
MgO	0.20	0.06	0.18	0.02	0.19	0.02	0.18	0.03	0.07	0.02	0.06	0.02
CaO	1.21	0.10	1.84	0.08	1.90	0.06	1.88	0.02	1.75	0.06	1.76	0.03
Na_2O	6.40	0.27	5.85	0.17	5.55	0.22	5.13	0.45	5.35	0.21	5.00	0.54
K_2O	5.51	0.16	5.24	0.11	5.11	0.17	5.23	0.06	5.05	0.19	5.12	0.10
P_2O_5	0.07	0.03	0.05	0.02	0.08	0.02	0.06	0.02	0.03	0.02	0.06	0.02
SO_2	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
F	0.22	0.13	0.24	0.02	0.25	0.03	0.24	0.02	0.24	0.02	0.26	0.02
Cl	0.27	0.04	0.17	0.01	0.20	0.03	0.19	0.03	0.18	0.01	0.19	0.01
−O=F, Cl	−0.15	0.06	−0.14	0.01	−0.15	0.02	−0.14	0.01	−0.14	0.01	−0.15	0.01
Total	100.00		100.00		100.00		100.00		100.00		100.00	

1. Average composition of 8 pumice from The Pleiades (Table S2).
2. Composition of tephra sample A1602 from Mt. Melbourne (Table S3).
3. Composition of tephra sample A1604 from Mt. Melbourne (Table S3).
4. Composition of tephra sample A1605 from Mt. Melbourne (Table S3).
5. Composition of tephra sample A1620 from Mt. Melbourne (Table S3).
6. Composition of tephra sample A1621 from Mt. Melbourne (Table S3).

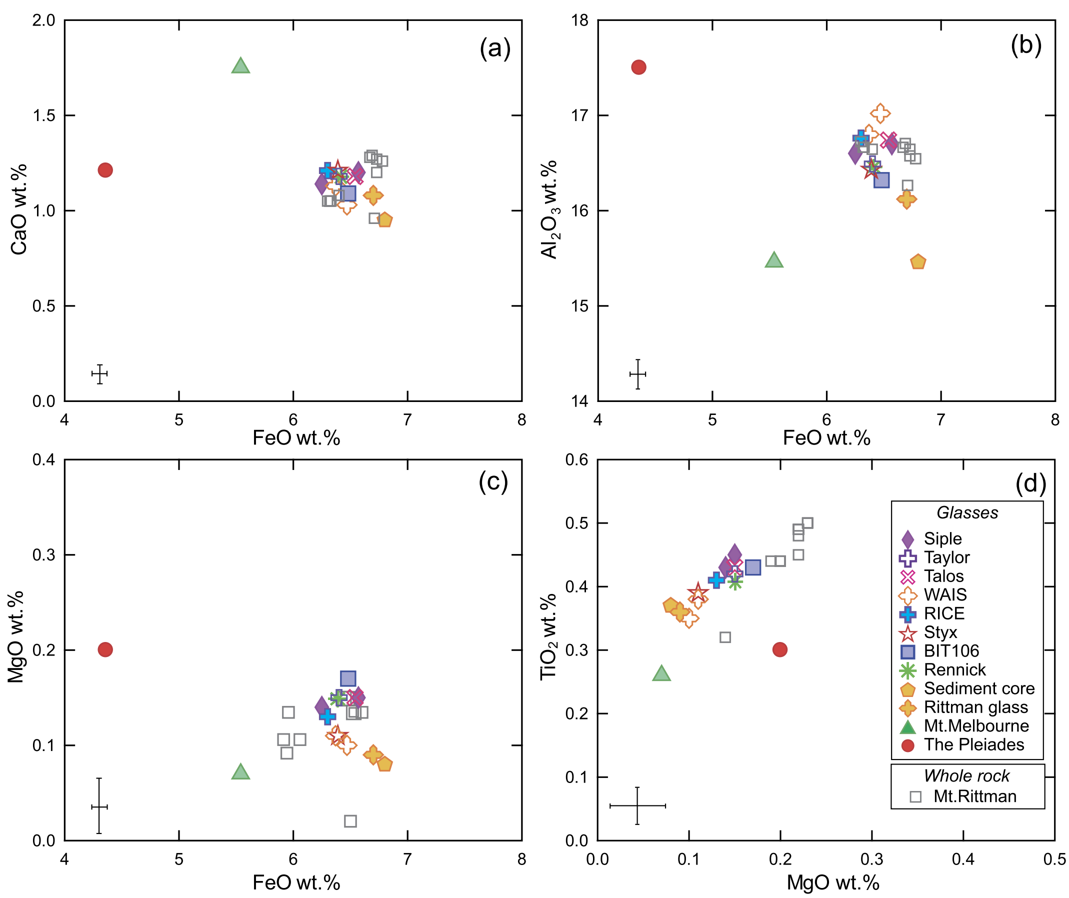

Fig. 4. Oxide variation diagrams comparing the composition of the Rittmann tephra and suggested correlatives. These are compared with fiamme glass and whole rock analyses (Table S4) from Rittmann volcano, and young pumice erupted from The Pleiades and Mt. Melbourne.

(Fig. 3) and show the characteristic low CaO and high FeO compositions of the distal Rittmann tephra (Fig. 4). In addition to the EMPA analysis of the fiamme, new whole rock analyses of nine trachytic samples from Rittmann volcano (Table S4) match the composition of the fiamme (Figs. 3, 4; Table 1). Earlier analyses of whole rock samples from Rittmann volcano (Armienti and Tripodo, 1991) have a wide range of trachytic and other compositions.

The matrix glass in eight pumice lapilli, which represent the most recent eruption at The Pleiades, are trachytic (Fig. 3) and uniform in composition (Table 2). The pumice is chemically similar to lavas from Taygete Cone, a young (< 12 ka) endogeneous dome (Kyle, 1982, 1986; Kim et al., 2019). Compared to the Rittmann tephra (Tables 1, S1), The Pleiades pumice are geochemically different with lower FeO and higher Al_2O_3 and MgO (Fig. 4).

Analyses of the glass in the pumice from 5 young tephra samples from Mt. Melbourne (Table 2) are trachytic (Fig. 3). Melbourne pumice samples are distinguished from the Rittmann tephra by their lower FeO and higher Al_2O_3 contents. The Melbourne pumice are also distinguished from The Pleiades pumice by lower FeO and TiO_2 contents (Fig. 4).

7. Discussion

The Rittmann tephra is present in three new ice core sites (Styx, WAIS Divide and RICE) and two blue ice areas (Brimstone and Rennick) (Table 1). All the tephra are trachytes using the standard total alkali versus silica plot (Fig. 3) as are the pumice from The Pleiades and Mt. Melbourne. Representative plots (Fig. 4) show the overlap in compositions of all the Rittmann tephra samples. CaO versus FeO plots (Fig. 4a) are widely used to discriminate tephra using geochemical data (e.g. Perkins et al., 1995). Both CaO and FeO have high analytical precision and there can be significant variations in the groundmass glass (which ultimately becomes the glass tephra shards) due to crystallization of mineral phases in the magma prior to eruption. All the Rittmann tephra have nearly identical FeO and CaO contents, within analytical error (Fig. 4a), which is the most compelling evidence that the proposed 8 Rittmann tephra are considered to be correlative. Other representative plots (Fig. 4b–d) show a little more spread in the tephra compositions but this can in part be related to analytical uncertainties and the low abundances of components like MgO and TiO_2 which have higher analytical uncertainties. When compared to the published analyses of the Rittmann tephra (Table S1) the similarity between all the analyses is obvious.

Perkins et al. (1995) devised a statistical procedure to provide a numerical assessment of the similarity in composition between geochemical compositions of tephra. The statistical distance (SD) is the Euclidean distance in standard deviation units between chemical analyses. We compared 6 elements (TiO_2, FeO, MnO, MgO, CaO and Cl) in the samples and proposed correlatives. A SD value of 0 indicates elements concentrations are identical between samples and a SD of < 4 are consider statistically identical and < 10 are statistically similar. Most of the Rittmann tephra are statistically similar ($SD < 10$) to each other (see Supplemental Table S6). The Siple B sample has an $SD > 10$ relative to the WAIS06A and Talos Dome samples, but this may reflect the differences in the analytical labs, the age of the analyses and the occurrence of microlites in the glass shards. The Styx tephra is geochemically identical ($SD < 4$) to the Siple B-97.2, the Taylor Dome and RICE tephra samples. For other Rittmann tephra, except for WDC6A the SD are in the 6 to 9 range showing the Styx tephra is similar to them. Overall the SD data compliments the geochemical plots, the morphological data and the age constraints in the ice cores in showing the eight Rittmann tephra samples are correlatives and resulted from the same eruptive episode.

The source of the Rittmann tephra has until now been poorly known. Volcanoes in northern Victoria Land are the most likely source as no trachytic eruptions of this age are known in the McMurdo Sound area, which is volcanically active (Kyle, 1990c). The distribution of Rittmann tephra in ice cores from Taylor Dome, Styx Glacier, Talos Dome and West Antarctica (Fig. 1) also implies a source in northern Victoria Land (Dunbar et al., 2003; Narcisi et al., 2001, 2012). Rittmann volcano, The Pleiades and Mt. Melbourne in northern Victoria Land (Fig. 1) are young “active” volcanoes which have erupted trachytic tephra in the Holocene and are potential sources for the Rittmann tephra. The new data presented here show tephra and whole rock compositions from the 3 volcanic centers (Tables 2 and S4; Fig. 4) are distinct and these new data provide better opportunities to correlate ice core tephra with their eruptive source volcano. The Pleiades has previously been proposed as the source of the Rittmann tephra (Dunbar et al., 2003). The SD values for The Pleiades pumice compared to the Rittmann tephra samples range from 6.8 to 14 suggesting they may be correlative based on concentrations of 6 elements. However, the plots of FeO versus CaO (Fig. 4a) show they are significant differences between The Pleiades, and we discount this as the source of the Rittmann tephra. Mt. Melbourne can be ruled out as the source of the Rittmann tephra as SD values range from 44 to 57 and the plots (Fig. 4) graphically show there is no correlation.

Comparing glass analyses from pyroclastic breccias at Rittmann volcano, to the distal Rittmann tephra samples, the SD values range from 3.33 (considered identical) to 10.43. Most SD values are < 10 so we consider this as strong evidence that the tephra was in fact erupted from Rittmann volcano and the breccias may represent a proximal deposit of the Rittmann tephra eruption. Thus, the match in compositions of the RICE, Styx and WAIS tephra, other occurrences of Rittmann tephra in East and West Antarctic ice cores (Table S1) and the 2 blue ice occurrences with the glass from Rittmann volcano is compelling (Table 1; Figs. 3 and 4). Additionally, the correlation is strengthened with new whole rock analyses of lava samples (Table S4; Figs. 3 and 4) from Rittmann volcano. The trace element analysis of the glass from Rittmann volcano (ICP-MS) is nearly identical to an analysis of a bulk trace element (INAA) composition sample of the blue ice tephra (BIT106) from Brimstone Peak (Table 1, samples 5 and 7). The correlation of these distal tephra to the proximal breccias from Mt. Rittmann are made on the basis of glass major element analysis, however the similar trace composition, although from two different methods, of the samples strengthens the major element observations.

Del Carlo et al. (2015) describe 8 tephra layers in Holocene-Late Pleistocene marine sediment cores in the western Ross Sea (Fig. 1). One of the tephra, sample NW2-0-13 is described as a poorly sorted coarse ash. It occurs in the top 13 cm of the core and therefore represents the youngest sediment at the coring site. The layer contains 77% pumice and 20% lithic fragments. Two alkali feldspar separates from NW2-0-13 were dated by $^{40}Ar/^{39}Ar$ and have a mean age of 24.7 ± 5.3 ka. Another tephra in core NW31 (sample 42–61 cm depth) is a coar se to medium ash and Del Carlo et al. (2015) correlate it with the NW2 sample. Four feldspar samples from NW31-42-61 give a mean $^{40}Ar/^{39}Ar$ age of 21.2 ± 6.4 ka. A ^{14}C age on sediment from directly above the NW31 layer has an age of 7.6 ka. It seems likely that the tephra is thus < 7.6 ka. Microprobe analyses of the two tephra are similar and support their correlation. More importantly the 2 tephra have Rittmann like geochemical signatures (Figs. 3 and 4). Although it is tempting to correlate the marine tephra with the Rittmann tephra the SD data are between 11 and 20 when compared to the tephra (Table S6). The correlation would also require the radiometric ages to be incorrect. This marine tephra does not correlate with The Pleiades or Melbourne tephra deposits, but it does show many similarities to the Rittmann glass which it has an SD of 11.6. This compares to SD values of 63 and 22 between the Melbourne and The Pleiades tephra, respectively. It seems likely the two marine tephra are from Rittmann volcano but may represent precursor activity prior to the 1252 CE Rittmann tephra eruption.

The recognition that Rittmann volcano is the source of the 1252 CE Rittmann tephra has implications for the volcanic activity at this relatively unknown volcano. As the Rittmann tephra is dispersed over 2000 km from Rittmann volcano this necessitates a significant eruption. It is highly likely that the Rittmann tephra resulted from a Plinian-style eruption. Armienti and Tripodo (1991) noted that Rittmann volcano is defined by a 2 km diameter caldera. We speculate that the caldera may be the result of the Rittmann tephra eruption, but until new field work is done this will remain somewhat inconclusive. Small nunataks around the rim of the caldera have volcanic breccias containing pumice and glass. We believe some of these breccias are ignimbrites formed from pyroclastic flows and the glass we analyzed (Table 1) are fiamme. Mt. Rittmann, the largest nunatak on the caldera rim, currently has geothermal activity with fumaroles and warm steaming ground (Bonaccorso et al., 1991). Whether this geothermal activity is residual from the 1252 CE eruption or more recent activity is unknown. It is likely that minor eruptive activity may have continued for some time after the 1252 CE eruption and that some of the volcanic deposits on the caldera rim are younger than 1252 CE.

Finally, it is worth noting that the recognition of the size and nature of the Rittmann 1252 CE eruption begs the question "could it happen again without much warning". The isolation of Rittmann volcano and The Pleiades, well removed from scientific stations, and the lack of any monitoring make them a potential volcanic hazard. Rittmann volcano is slightly to the west and up wind of the main aircraft route used to support activities at the US McMurdo Station. With the advent of an increasing number of flights to McMurdo Station during the darkness of winter some consideration should be given to understanding the potential risk to aircraft operations in the area (Miller and Casadevall, 2000; Prata and Tupper, 2009).

8. Conclusions

Our comprehensive set of geochemical data of tephra and rock samples from northern Victoria Land volcanoes shows that Rittmann volcano is almost certainly the source of a widespread tephra erupted in 1252 ± 2 CE. Further characterization and confirmation of the proposed correlations could be made by the addition of trace element analyses of the tephra. Trace element data, although less precise than some of the major element analyses, may also indicate if there were multiple eruptions and the possibility of several eruption clouds which could help explain the wide distribution of the tephra. This study demonstrates the power and value of tephrochronology to glaciology and volcanology studies in Antarctica. The value of time planes that can tie volcanoes to the valuable climate records in ice cores cannot be over-emphasized. Also, the value of the high precision time provided by the chronology in ice cores makes possible a new improved understanding of the age of the relatively unknown Rittmann volcano. Much remains to be learnt about Rittmann volcano. It is poorly exposed in only a few small outcroppings, so a full understanding will not come until geophysical methods are used to examine the subglacial morphology and confirm the presence of a caldera. Aeromagnetic data can also confirm the presence of subglacial volcanic rocks. Clearly Rittmann is the source of the 1252 CE tephra making it one of the largest Holocene volcanic eruptions in Antarctic. Rittmann is likely to have had a considerable eruptive history prior to 1252 CE. Further field work and dating of the volcanic rocks will help confirm our hypothesis that Rittmann erupted in 1252 CE and should also uncover the early volcanic history.

The Rittmann tephra has been known for almost 20 years and although sources had been proposed these were speculative and based on very little factual data. Now that we have determined the source of the Rittmann tephra it has the capacity to provide climate information. Grain size data on the tephra should be able to provide information on the eruption column heights. The dispersal of the tephra and its distribution as a function of wind speed and directions. With further characterization of the tephra properties combined with dispersal patterns, information on wind direction and speed can be determined and allow comparison of paleo-weather patterns with the present weather patterns which are subject to change as global climate changes occurs.

We have shown the presence of the Rittmann tephra in blue ice near Brimstone Peak and the Rennick Glacier in Victoria Land. The tephra is valuable in providing a time plane for these blue ice areas. It is highly likely the tephra will be identified elsewhere and provide age control for other blue ice patches.

The Rittmann tephra is now found in six ice cores, and two blue ice areas throughout northern Victoria Land to West Antarctica, making it the most widely correlated tephra in Antarctica. The timing, size and distinct chemistry of the 1252 eruption of Rittmann make it a valuable marker layer that should be targeted in any future ice core, and blue ice tephra projects.

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Appendix A. Supplementary material

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