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Iridium enrichment in volcanic dust from blue ice fields, Antarctica, and possible relevance to the K/T boundary event

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Blue ice fields in Antarctica, well known as stranding zones of Antarctic meteorites, contain ice that is several tens to hundreds of thousand years old, which records numerous events that have taken place since its formation. Among the most important structures on the ice fields are dust bands which are mostly of volcanic origin and consist of small volcanic glass shards and lithic fragments. Petrographic and chemical studies of a number of dust bands during earlier investigations have shown that significant ash layers are deposited at distances of up to several thousand kilometers from the source volcanoes. Samples of dust layers taken in the Lewis Cliff/Beardmore Glacier area in Antarctica, analyzed in the course of this work for major and trace elements, were identified as consisting of volcanic ash, probably originating from the Pleiades (Melbourne volcanic province, northern Victoria Land). Some of these dust samples were found to contain iridium in concentrations of up to 7.5 ppb. A positive correlation between Ir and Se as well as enrichments in As, Sb, and other volcanogenic elements has been observed. The dust samples investigated here have very small grain size, consistent with the distance from the source volcanoes. The small grain size of the dust suggests that the Ir enrichment is a surface effect, and was probably caused by condensation from a vapor phase. This is the first time that significant Ir enrichments have been found in volcanic dust which demonstrates that Ir (and possibly also other platinum group metals) may be present in some volcanic ash deposits, although this has been doubted by the proponents of the "pure" impact theory for the K/T boundary event. The results of this study suggest that the Ir in the K/T boundary clays is not necessarily of cosmic origin, but alternatively may have originated from mantle reservoirs that were tapped during extensive volcanic eruptions, which may have been triggered by impact events.

1. Introduction

Dust layers in Antarctic ice have been found in ice cores and in blue ice fields [1–6]. It is not easy to differentiate between the different sources of the dust and other impurities contained in the ice. Two main sources are possible: (1) material from subglacial bedrock scraped up by the movement of the glacier, and (2) volcanic ash deposited on the ice after large-scale eruptions of Antarctic (or sub-Antarctic) volcanoes. Other possible (but less frequent) sources of soluble or insoluble ice impurities are windblown continental material, marine aerosols, artificial (man-made) contaminants (e.g., space-craft debris), or cosmic particles. Sediment derived from subglacial bedrock is usually found in ice under moraines that develop above subglacial topographic ridges leading to retardation and subsequent upward movement of the ice flow, or close to barriers obstructing the glacial flow.

Volcanic ash is deposited all over Antarctica following large eruptions and transport within the Antarctic katabatic wind system. Dust layers in ice cores throughout Antarctica have been identified as being mostly of volcanic origin. For that reason they are also called tephra layers. In many cases, chemical and petrological studies have been used to correlate the tephra layers with specific volcanic eruptions in Antarctica [3–7]. For example, the volcanic glass shards in the Byrd Station ice core, studied by Kyle et al. [3], were attributed to Mt. Takahe, a volcano at about 450 km from Byrd Station in Marie Byrd Land. Most ice cores only date back several hundred to a few thousand years, so they only record more recent eruptions (with the exception of the Vostok core).

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Dust bands cropping out on bare blue ice fields in Antarctica have received less attention, although their presence has very interesting implications. Keys et al. [8] studied dust bands on ice fields at the Skelton Neve and the Kempe Glacier (South Victoria Land) and found that some consist of dolerite debris and have formed from local bedrock, while others are of volcanic origin probably originating from volcanoes belonging to the McMurdo Volcanic Group.

Blue ice fields have become very important since they have been found to be major sources of meteorites. Since 1969, expeditions mainly from the United States of America and Japan, have collected several thousand new meteorite specimens which provided important material for planetary and even lunar studies [9–13]. The accumulation of meteorites on the blue ice fields requires a concentration mechanism involving meteorite transport within the ice. Only in special areas, where the ice flow is obstructed by subglacial topographic features or mountain ranges and the ice is ablated by strong katabatic winds, do the meteorites reach the surface [14]. These areas are blue ice fields and are called meteorite stranding surfaces and all observations on these surfaces have direct bearing on the concentration mechanism of Antarctic meteorites [15].

Since the ice exposed in the ice fields is up to several hundred thousand years old [16–18], the dust bands in these areas are usually older than the ones in ice cores. Dust bands in the ice fields often run perpendicular to the direction of the ice flow, but may curl back occasionally, reflecting changes in the direction of the ice movement. They are usually about 10–30 cm wide and pinch and swell over distances of a few hundred to one thousand meters. Since they represent layers (or tephra sheets) within the ice, they may have variable angles of dip ranging from vertical to near horizontal. Dust bands from several blue ice fields have been studied and identified as being mostly of volcanic origin. This includes material from the well known meteorite accumulation areas of the Allan Hills in South Victoria Land and the Yamato Mountains in Queen Maud Land [4,19].

2. Samples and methods

During a recent field expedition to Antarctica, samples of dust bands were collected from blue ice fields in the Lewis Cliff area (Walcott Neve/Beardmore Glacier region). The main purpose of the expedition was to search for Antarctic meteorites [12]. Fig. 1 shows the geographical location of the sites discussed here as well as the locations of the two other important meteorite ice fields (Allan Hills, Yamato Mountains) and the locations of Cenozoic volcanoes. Several of these volcanoes have been identified as the sources for some of the dust bands, specifically The Pleiades, a volcanic group within the Melbourne volcanic province, which are considered to be the most probable source of the Lewis Cliff dust band samples.

The dust band samples were cut with a chain saw in blocks measuring about 50×50 cm and put into specially cleaned plastic bags. The dust was then isolated in the field under clean and contamination-free Antarctic conditions by slowly melting the ice and then decanting the water.

Chemical analyses were made for major and trace elements to determine the composition of the dust. Major elements were determined by electron microprobe analyses of individual dust particles [6]. The trace element analysis were made using instrumental neutron activation analysis (INAA) with synthetic and natural (meteoritic) standards. The preparation of the dust samples was performed in a contamination-free environment on a clean bench, following by immediate sealing in clean polyethylene vials, so that any laboratory contamination was excluded. The dust samples were examined prior to their chemical analysis by optical microscopy to ensure that they were pure volcanic dust and did not contain cosmic particles.

3. Results and discussion

Chemical data have been used to correlate tephra layers in the blue ice fields with specific Cenozoic volcanoes in Antarctica and in sub-Antarctic regions. In some cases the proposed source volcanoes are at distances of several thousand kilometers from the sites of the dust bands. For example, the tephra layers in the ice near the Yamato Mountains, have the composition of island arc tholeiite and, for that reason, were correlated with volcanoes of the South Sandwich Islands, which are about 3000 km northwest in the

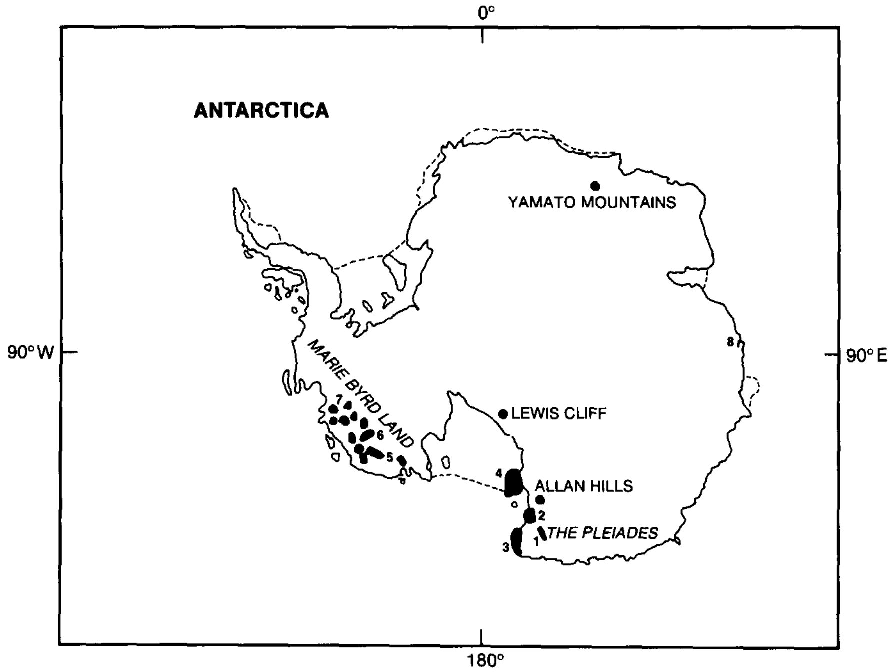

Fig. 1. Map of Antarctica, showing the locations of the Yamato Mountains, the Allan Hills, and the Lewis Cliff. Cenozoic volcanic provinces are numbered (*1* = The Pleiades; *2* = Mt. Melbourne; *3* = Hallet volcanic province; *4* = McMurdo volcanic province; *5* = Mt. Berlin; *6* = Executive Committee Range; *7* = Mt. Takahe; *8* = Gaussberg). The Pleiades volcanic group is the most probable source for the Lewis Cliff dust bands.

sub-Antarctic region [4,20]. Volcanic dust from the Allan Hills consists of alkalic material and may have a more local source in the Victoria Land region [19,20].

Petrological studies of dust from the Lewis Cliff tephra layers indicate that they consist predominantly of brown to black glass shards. Crystal fragments such as feldspar, plagioclase, and olivine

TABLE 1

Major element composition of volcanic glass shards from Lewis Cliff dust band samples, obtained by electron microprobe analysis [6]. The dust is a mixture of different components which are clearly of volcanic origin and may be correlated with basanites, K-trachytes, and peralkaline K-trachytes from The Pleiades, Mt. Melbourne Volcanic Group, northern Victoria Land [a]

	Lewis Cliff volcanic glass shards						The Pleiades volcanic rocks [b]		
	86-1-10	86-1-12	86-3-16	17-3-12	17-02-9	86-1-9	K-trachyte	peralkaline K-trachyte	basanite
SiO_2	58.4	58.5	64.7	64.4	44.4	44.1	60.0	64.4	44.3
TiO_2	1.07	0.83	0.23	0.64	4.16	3.10	0.70	0.14	3.66
Al_2O_3	17.4	17.8	17.8	15.2	14.7	11.3	17.7	16.9	14.8
FeO	6.74	6.80	3.37	9.17	12.7	17.7	5.70	3.64	12.2
MnO	0.21	0.32	0.03	0.31	0.19	0.29	0.17	0.15	0.20
MgO	1.00	0.75	0.38	0.06	5.09	12.1	0.75	0.08	7.21
CaO	2.82	3.04	1.28	1.60	10.5	6.40	2.47	0.93	11.0
Na_2O	4.07	6.08	8.37	4.02	4.19	3.19	7.09	8.26	3.80
K_2O	4.20	5.37	3.28	4.39	1.20	0.92	4.74	5.24	1.74

[a] All data in wt.% all Fe as FeO.
[b] From Kyle [32].

are also present as minor components. The presence of glass shards indicates that the samples are of volcanic origin. Further evidence for the volcanic origin of the samples comes from the chemical composition of the glass shards.

The analyses of individual glass shards reveal the presence of at least three different components. Table 1 gives the major element compositions of several glass shards from the Lewis Cliff tephra layers, together with data for volcanic rocks from The Pleiades, which are the most probable source volcanoes of these dust bands. The glass composition consists of basanite, K-trachyte, and peralkaline K-trachyte, respectively [6]. The correlation between the dust samples and rocks from The Pleiades is very good.

The grain size of the Lewis Cliff dust ranges from about 2 to 25 μm, with most shards in the 2–10 μm range. Thus they are much smaller than dust particles in the Allan Hills or Yamato Mountains dust bands (which are usually between 10 and 100 μm in diameter). The small grain size is consistent with a distant source in The Pleiades, which are at a distance of about 1500 km. Ash erupted from these volcanoes had to travel a long distance by being injected into the stratosphere, which caused survival of only the small grains, while the large particles settled out closer to the source.

The rather surprising result of the present trace element analyses is the detection of measurable quantities of Ir in most of the dust band samples. The results of the Ir determinations, together with several other typical trace elements, are given in Table 2. A non-volcanic dust band, which consisted of sandstone from the bedrock, was also analyzed and did not contain Ir above the limit of detection (0.5 ppb for the INAA method). The high Ir abundance in the volcanic dust (up to 7.5 ppb) is an interesting result and is the first time that Ir has been found in volcanic ash deposited far from the source volcano. The unique environment of Antarctica has allowed the preservation of material from individual volcanic eruptions without contamination from other sources. Since there is an inverse correlation of the Ir content with grain size in samples 86-3 and 86-4, the Ir in the volcanic dust appears to be surface-correlated.

TABLE 2

Concentration of several trace elements in samples from dust bands from the Lewis Cliff/Beardmore Glacier area, Antarctica

	Ir (ppb)	Au (ppb)	Se (ppm)	Sb [a] (ppm)	As [a] (ppm)
ICE 86-1	3.5	14	11.0	11.0	6.7
ICE 86-3	7.5	21	21.8	8.0	0.31
ICE 86-4	7.0	28	20.5	11.1	5.5
ICE 17-03	4.4	11	16.0	7.5	7.6

[a] From Koeberl et al. [6].

Iridium enrichments have been found in volcanic exhalations and aerosols from the Kilauea volcano, Hawaii [21,22]. Other volatile and typical volcanogenic elements (like Se, Hg, Cd, Au, As, Sb, as well as the halogens) are also enriched in the aerosols [21]. Zoller et al. [21] speculated that the iridium may be mobilized in the form of a volatile fluorine complex together with some of the other elements. Surface-correlated elements would show considerable enrichments at small grain sizes, not unlike that observed in lunar volcanic glass (e.g., Apollo 15 green glass and Apollo 17 orange glass) [23]. Antarctic volcanic dust with larger average grain sizes (e.g. at the Allan Hills) is not known to contain measurable quantities of Ir. The larger grains presumably settled out before reaching the Lewis Cliff area due to the long distance from the source volcano. If the Ir is surface-correlated, which seems most likely, then the highest Ir enrichment is expected to occur in the smallest grain size fraction. The data for the Lewis Cliff dust indicate that the Ir enrichment of the glass shards is most likely caused by condensation of a volatile Ir complex onto the dust particles in the outer parts of an eruption plume. Fig. 2 shows that Ir displays a positive correlation with Se, while the other elements given in Table 2 are enriched irregularly. However, the same elements are also enriched in Kilauea volcanic aerosols [21,22].

The discovery of Ir enrichments in volcanic ash in Antarctica may have some bearing on the interpretation of the Cretaceous–Tertiary (K/T) boundary, which is well known to show considerable enrichment of Ir. Multi-element studies of material from different K/T boundaries have shown enrichments not only for Ir, but also for Se, Sb, As, Cr, and several other elements [24–26]. Some K/T boundary layers exhibit a positive correlation between Ir and Se (e.g. the Lattenge-

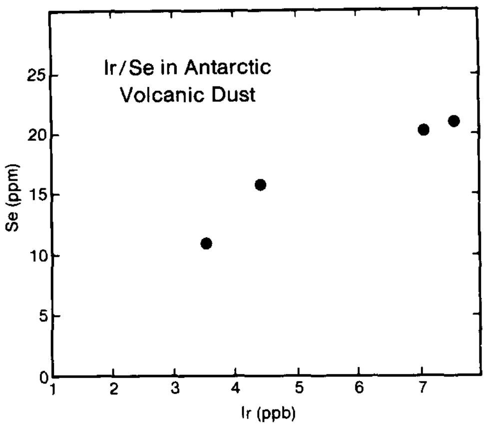

Fig. 2. A positive correlation between Ir and Se is visible for the dust samples from the Lewis Cliff region, Antarctica.

birge section, [26]). This correlation is also present for the Lewis Cliff volcanic ash. As in the Kilauea aerosols, the Ir/Au ratio in the Lewis Cliff volcanic dust is nonchondritic. Instead, Au is more enriched than Ir, which is to be expected because Au is more mobile and volatile than Ir. It is very easy to introduce Au in the terrestrial environment.

4. Conclusions

The present study demonstrates that Ir concentrations range up to 7.5 ppb in volcanic ash recovered from dust bands in ice fields in the Lewis Cliff/Beardmore Glacier area, Antarctica. This ash probably originated from a group of volcanoes called The Pleiades in northern Victoria Land and was deposited several tens of thousands of years ago. The Ir enrichment, as well as similar enrichments in Se, Au, Sb, and As are surface-correlated and were detected in this case only because of the small average grain size of the particles, while samples with larger average grain sizes may not show a similar enrichment.

In the non-Antarctic environment a surface-enriched Ir complex would be mobilized, transported, and ultimately concentrated in a carrier phase. A similar mobilization of Ir and other elements was suggested by Schmitz et al. [27] to explain the high concentration of Ir in organic phases in clay at the Stevns Klint boundary. On the other hand, the mineralogical record at the K/T boundary favors a large-scale meteorite impact (e.g., [28,29]). Therefore a combination of impacts and volcanism is a probable explanation of geochemical and mineralogical features of the K/T boundary. Candidates for impact craters at the time of the K/T boundary are rare. The Manson structure, Iowa, U.S.A. [30], and the Kara double impact structure, U.S.S.R. [31], have been suggested, although the Kara craters may be too old [31].

The cold and dry environment of Antarctica led to the preservation of these geochemical signatures. It was estimated earlier [22] for the Ir found in Kilauea emissions that only a small percentage of the Ir in the source basalt is necessary to explain the abundances observed in the gas phase. The Ir content of the source rocks from The Pleiades is not known, but is probably in the same range as for other volcanic rocks (about 0.5–0.05 ppb). The volcanic dust deposits found in Antarctica demonstrate that it is not necessary to have violent (silicic) volcanic eruptions to distribute large quantities of dust over several thousand square kilometers. Therefore the Ir enrichment in clays at the K/T boundary layers is not necessarily of cosmic origin, but may have originated from large mantle reservoirs that were tapped during periods of extensive basaltic volcanic eruptions. The similarity of geochemical signatures (Ir, As, Au, Sb, Se enrichments, Ir/Se correlation) is in agreement with this suggestion.

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