

Obsidian floater washed up on a beach in the Chatham Islands: geochemical composition and comparison with other volcanic glasses

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ABSTRACT: A large block of pumice with a thick layer of volcanic glass attached to one side was found on a beach in the Chatham Islands. The geochemical signature of the specimen was most unusual: it proved to be a peralkaline phonolite with a negative europium anomaly. Since there was no obvious eruptive event that might have been the source of the floating object, identification of its geographic source involved a series of steps that progressively narrowed in on fewer and fewer potential sources. This process eventually pointed most strongly to McDonald Island in the Antarctic region southwest of Australia. This was confirmed only after unpublished geochemical data for the island were found. The process of identification described could have wider application when trying to find the volcanic source of obsidian artefacts with greater certainty.

KEYWORDS: obsidian, pumice, Chatham Islands, McDonald Island, geochemistry, Pacific archaeology, sourcing model.

Introduction

This paper is about the identification of the geographic source of a piece of rock, embedded in pumice, which had floated to the location where it was found.

During the course of the research it became apparent that the process by which the conclusion was reached was of wider scientific interest than the identification itself. Normally, all that is needed to reach a conclusion with certainty in a case like this is a search among rocks with characteristics similar to those of the specimen in question, until an identical match is found. In this case, however, it was clear that there were a number of places with rocks very similar to that being studied. The process by which an

exact match could be made was therefore not at all straightforward, and is described in full.

Some years ago, a block of obsidian attached to a large band of pumice was found on a beach at Waitangi West in the Chatham Islands. It was collected by Pat Tuanui or his son Patrick and placed in their garden at Waihi in about 2008 or 2009. Since the piece was found on a beach, it was assumed that it had floated in sea water from its volcanic source, but where that source might be was an open question. It seemed possible that the piece had come from the unconfirmed submarine source of obsidian on Chatham Island itself, recorded by geologist Julius von Haast (1885: 26): ‘The Morioris also used flint “mataa”, which they split



Fig. 1 Several views of the obsidian floater from the Chatham Islands. Maximum dimension *c.* 200 mm.

into thin, irregular, wedge-like shapes, as knives, there being no volcanic glass (“tuhua”) obtainable in any quantity, although a reef of it is thought to exist under water at the south-east corner of the island at Manukau.’

Quite a few obsidian artefacts have previously been found in the Chatham Islands, although none has been excavated in a controlled archaeological context, so their ages and cultural associations are unknown. Analysis of these surface finds by PIXE-PIGME has shown that most derive from the volcanic source on Mayor Island (Tuhua) in New Zealand’s Bay of Plenty, but some artefacts could not easily be matched to known sources (Leach *et al.* 1986). It was possible that some of these artefacts might derive from the supposed submarine source off Manukau Point. Clearly, it would be useful to have this block of floating pumice and obsidian examined for its chemical properties in an effort to locate its original volcanic source.

Rhys Richards became aware of the Chatham Island block and gave it to Hamish Campbell for analysis. He confirmed that it did indeed float in sea water. He gave a piece of the pumice to Katherine Holt for analysis; Foss Leach was subsequently given permission to carry out further analyses of a small sample of the obsidian. The GNS Science Petrology Collection number P81381 was allocated to the block (the catalogue numbers of all samples analysed are given in Appendix 1). The entire block weighed 1271.93 g, and the piece of obsidian removed for analysis weighed 71.38 g.

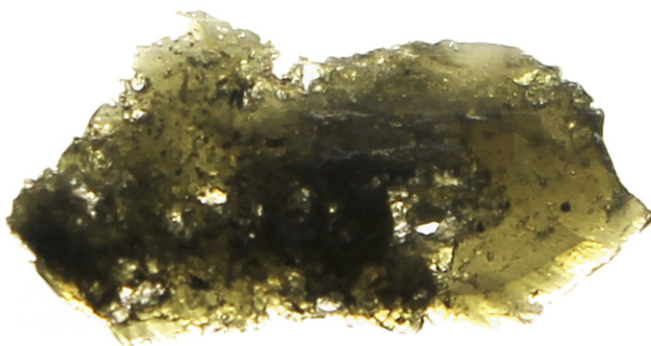


Fig. 2 The obsidian is olive-green in transmitted sunlight. Length 12 mm.

Physical description of the obsidian floater

The block is illustrated in Fig. 1, from which it can be seen that the bulk is pumice with only a small band of obsidian along one side. The maximum dimension is about 200 mm. A small, thin flake of obsidian was removed for analysis and photographed under transmitted sunlight (Fig. 2). This is clearly olive-green, similar in hand specimen to many obsidian artefacts that have been found in the past in the Chatham Islands, and also in New Zealand and further afield in the South Pacific. Such olive-green obsidian artefacts are frequently declared to be of Mayor Island (Tuhua) origin

Table 1 Electron microprobe analysis of pumice from the Chatham Islands obsidian floater, carried out and presented by Katherine Holt of Massey University, New Zealand.

Sample	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₃	Cl	Cr ₂ O ₃	NiO	TOTAL
Ch098	55.67	0.42	19.98	3.80	0.14	0.30	1.29	11.34	5.99	0.07	0.00	0.86	0.00	0.14	100.00
Ch098	55.92	0.36	20.14	3.67	0.08	0.22	1.33	11.25	5.84	0.21	0.04	0.79	0.00	0.13	100.00
Ch098	55.84	0.40	19.99	3.73	0.15	0.31	1.32	11.18	5.90	0.25	0.00	0.92	0.00	0.00	100.00
Ch098	56.01	0.43	20.12	3.58	0.11	0.30	1.38	11.07	5.92	0.02	0.00	0.93	0.09	0.04	100.00
Ch098	55.67	0.47	20.12	3.80	0.13	0.28	1.35	11.12	5.92	0.16	0.00	0.86	0.11	0.00	100.00
Ch098	55.47	0.46	19.98	3.64	0.12	0.41	1.40	11.29	6.01	0.15	0.00	0.95	0.00	0.11	100.00
Ch098	55.83	0.61	20.02	3.90	0.00	0.30	1.29	11.06	5.84	0.25	0.00	0.85	0.05	0.00	100.00
Ch098	55.58	0.42	19.93	3.95	0.18	0.41	1.23	11.23	5.91	0.23	0.00	0.82	0.00	0.11	100.00
Ch098	55.88	0.36	20.12	3.88	0.09	0.28	1.31	11.19	5.97	0.04	0.02	0.84	0.01	0.00	100.00
Ch098	55.83	0.45	20.16	3.84	0.08	0.32	1.31	11.05	5.91	0.09	0.00	0.75	0.00	0.20	100.00
Ch098	55.89	0.43	20.15	3.75	0.20	0.32	1.26	11.14	5.97	0.09	0.00	0.80	0.00	0.00	100.00
Ch098	56.14	0.37	20.00	3.40	0.00	0.29	1.32	10.97	6.02	0.43	0.00	0.85	0.04	0.16	100.00
Ch098	55.98	0.35	19.88	3.90	0.08	0.36	1.25	11.07	5.82	0.41	0.00	0.91	0.00	0.00	100.00
Ch098	55.81	0.31	20.04	3.80	0.11	0.23	1.35	11.36	5.89	0.23	0.00	0.83	0.04	0.00	100.00
Ch098	55.87	0.49	19.95	3.82	0.11	0.36	1.27	11.36	5.77	0.14	0.00	0.80	0.05	0.00	100.00
Ch098	55.42	0.53	20.12	3.75	0.19	0.41	1.28	11.07	6.08	0.16	0.00	0.92	0.00	0.06	100.00
Ch098	55.64	0.39	20.15	3.86	0.13	0.41	1.38	11.07	5.78	0.16	0.00	0.88	0.05	0.09	100.00
Ch098	56.00	0.48	20.07	3.70	0.14	0.32	1.31	11.05	5.90	0.16	0.00	0.87	0.00	0.00	100.00
Mean	55.803	0.429	20.051	3.765	0.113	0.324	1.313	11.159	5.913	0.181	0.003	0.857	0.024	0.058	
SD	0.193	0.072	0.088	0.134	0.055	0.059	0.047	0.121	0.084	0.111	0.010	0.054	0.035	0.068	

by archaeologists without any definitive test being carried out. Some sources of obsidian in Northland have similar coloration in transmitted light. This present piece does not come from either Northland or Mayor Island (Tuhua), as will be shown below.

Electron microprobe analyses of the pumice fraction

Eighteen spots on the sample were analysed on an EDS Jeol JXA-840A electron microprobe (EMP) at the University of

Auckland. The assays were collected using a Princeton GammaTech Prism 2000 Si (Li) EDS X-ray detector using a 20 µm defocused beam, an accelerating voltage of 12.5 kV, a beam current of 600 pA and a live count time of 100 seconds. The EMP results are presented in Table 1.

The analyses were made on a small sample (~1 g) of the pumice, that is, of the vesiculated portion of the boulder. The analyses are normalised to 100% water-free (water content ~1–2% in most samples). High sodium and chlorine values possibly indicate that the samples were not cleaned adequately before analysis. But even when taking

this into account, the pumice still appears to have a strange composition. It was initially thought that the pumice might be phonolitic, so the results were given to Rob Stewart, associate professor of earth sciences at Massey University, for comment. His response was:

This comes out as a phonolite alright, but there are some peculiarities. I would expect about 7–8% Na₂O max. The chlorines look rather high at just under 1% – I would expect < about 0.1%, which might explain some of the high Na. Apparently no sulphate though. Peculiar. The normative analysis shows about 25% nepheline, which indicates that it is strongly under-saturated wrt [with respect to] silica. The other peculiarity is that it is a pumice; most phonolites are crystalline. Phonolite would suggest one of the oceanic islands like Tristan de Cunha, Kerguelen, Heard Island, etc. (pers. comm. to Holt, 2012)

X-ray fluorescence and neutron activation analyses of the glass fraction

In order to get the most reliable results across a wide range of elements, both wavelength-dispersive X-ray fluorescence (XRF) analysis and neutron activation analysis (NAA) were carried out, the former at the Geochemistry Laboratory, Department of Geological Sciences, University of Canterbury, and the latter at the Department of Environmental, Earth and Atmospheric Sciences at the University of Massachusetts Lowell. The results are given in Tables 2 and 3. Initial comments on these results were as follows:

This specimen has a very strange composition – my first reaction was that this is not a natural magmatic composition. The silica suggests a trachybasalt composition but the alkalis are astonishingly high. I note that it is described as a ‘floater’ on the sample bag – does that mean that it is floating pumice? Analysis of floating pumice often includes a significant contribution from sea salt – just an idea. It is peralkaline – the Zr, Nb and Th confirm that but the Al is very high which smacks of feldspar accumulation. (Steve Weaver, pers. comm. to Leach, 5 March 2013)

A number of colleagues who are experts in the field of geochemical analysis of volcanic glasses (Ray Macdonald, University of Lancaster; Peter Kelly, United States Geological Survey Volcano Emissions Project; and Christian Reepmeyer and Wallace Ambrose, both of Australian National University) were provided with the XRF and NAA results and consulted for their opinions. All commented on the

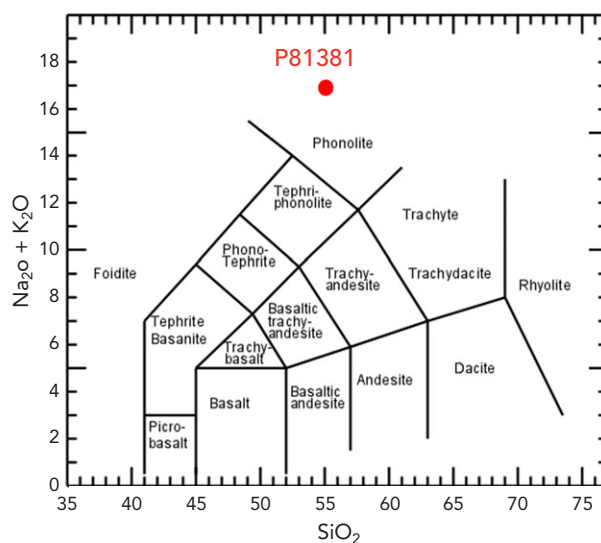


Fig. 3 The floater from the Chatham Islands (P81381) is definitely a phonolite according to the International Union of Geological Sciences classification of volcanic rocks.

unusual composition and none could identify the source. One authority thought the glass fraction might even be a man-made glass. The composition of the specimen was unquestionably different from the earlier-studied obsidian artefacts from the Chatham Islands that could not be matched to known volcanic sources.

Before trying to track down the volcanic source of this floating object, it was necessary to clarify some basic characteristics of the object.

Trachybasalt or phonolite? Alkaline or peralkaline?

The first thing that needed clarification was the kind of rock this glass came from. A commonly used system for the classification of volcanic rocks was proposed by the International Union of Geological Sciences (IUGS), called the total alkali versus silica (TAS) schema (Le Bas & Streckeisen 1991: 830, fig. 5). By this classification, the floater from the Chatham Islands is clearly phonolite (Fig. 3).

The next thing that needed clarification was whether the rock is peralkaline or not. This was also easily decided – if the agpaite index of a rock is greater than 1.0, then it is peralkaline. The agpaite index is the molar ratio of (Na₂O + K₂O)/Al₂O₃. Using the XRF results for P81381 in Table 3, it can be seen that Na₂O = 11.50%, K₂O = 5.50%, and Al₂O₃ = 20.33%. The molecular weights of the three

Table 2 Neutron activation analysis of various samples, including the Chatham Islands obsidian floater (P81381), carried out and presented by the Department of Environmental, Earth and Atmospheric Sciences at the University of Massachusetts Lowell. Details of samples are given in Appendix 1 (dash = not determined; nd = not detected).

Element	5105	ANU 306	ANU 306	5145	5145	302	302	AI 1991	AI 1991	GX 219	MAC 18E	P 81381	RGM- 1	STM- 1	Units
Fe	3.23	2.26	2.3	0.85	0.92	1.03	1.03	1.44	1.5	40063	46482	29004	1.28	3.72	ppm
Na	3.33	4.47	4.56	2.97	3.04	3.75	3.94	3.64	3.71	27239	33106	81501	3	6.53	ppm
K	—	—	—	—	—	—	—	—	—	5295	9535	49672	—	—	ppm
Sc	0.29	5.4	5.55	4.12	4.36	2.93	3.04	4.3	4.47	22.515	19.535	1.483	4.5	0.63	ppm
Cr	9.1	nd	nd	nd	nd	nd	nd	2.1	2.3	nd	0.893	8.167	3.4	1.9	ppm
Mn	445	372	371	134	126	145	146	215	217	—	—	—	272	1671	ppm
Co	0.5	0.52	0.51	0.61	0.67	0.5	0.5	1.43	1.49	7.57	5.24	2.97	1.97	0.8	ppm
Ni	—	—	—	—	—	—	—	—	—	nd	9	13	—	—	ppm
Zn	93	61	60	32	nd	27	29	35	37	91	129	150	34	105	ppm
Rb	129	128	112	54	54	136	130	146	141	4.4	24.6	213	147	120	ppm
Cs	4.7	4.5	4.5	1.5	1.6	3.9	4.1	1.8	2.1	0.69	0.94	6.65	9.8	1.5	ppm
Sr	nd	nd	nd	176	196	89	74	nd	47	96	160	137	128	718	ppm
Ba	58	286	266	551	568	895	877	734	737	215	453	nd	832	573	ppm
La	1679	51.3	52.4	13.3	14.1	31.5	32.7	39.2	39.7	4.5	10	121	24.8	142	ppm
Ce	2046	109	116.3	27.7	30.8	61.9	64.9	73.7	76.9	12	24.6	170	47.3	246	ppm
Nd	499	53.7	53	14.6	15.2	32.6	30.3	29.1	34.7	10.7	19.7	44.6	22	82	ppm
Sm	40.9	10.2	10.1	2.98	3.09	5.06	4.89	5.61	5.9	3.61	6.11	5.92	4.1	12.4	ppm
Eu	4.84	0.57	0.56	0.65	0.67	0.87	0.91	0.98	1.01	1.15	1.82	1.02	0.59	3.4	ppm
Gd	32	8.8	9	3.1	3.1	4	4.5	5.3	5.8	5.5	8.2	5.1	4	9.1	ppm
Tb	4.31	1.87	1.86	0.46	0.48	0.69	0.69	1.02	1.05	0.92	1.27	0.85	0.63	1.56	ppm
Ho	—	—	—	—	—	—	—	—	—	1.3	1.8	1.15	—	—	ppm
Tm	2.2	1.18	1.23	0.27	0.29	0.36	0.41	0.55	0.56	0.6	0.8	0.46	0.37	0.7	ppm
Yb	13.7	9.27	9.18	2.45	2.49	2.52	2.57	4.21	4.31	4.3	5.3	3.5	2.62	4.59	ppm
Lu	1.79	1.23	1.25	0.38	0.38	0.38	0.37	0.58	0.59	0.62	0.81	0.47	0.4	0.62	ppm
Zr	885	588	603	125	149	262	263	225	197	34	98	2350	205	1112	ppm
Hf	24.6	20.4	20.8	3.65	3.89	7.39	7.87	8.29	8.36	2.24	3.7	35	5.87	27.8	ppm
Ta	5.97	1.86	1.85	0.16	0.16	0.79	0.79	3.15	3.26	0.048	0.087	13.74	0.99	19.1	ppm
Th	42.7	18.7	18.9	2.7	2.79	12.52	13	11.5	11.7	0.61	1.38	52	14.8	30.5	ppm

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Table 2 Neutron activation analysis of various samples, including the Chatham Islands obsidian floater. *Continued from previous page*

Element	5105	ANU 306	ANU 306	5145	5145	302	302	AI 1991	AI 1991	GX 219	MAC 18E	P 81381	RGM- 1	STM- 1	Units
U	4.62	5.19	5.11	1.75	1.5	3.59	3.39	2.81	2.89	0.2	0.49	15.3	5.75	8.4	ppm
As	—	—	—	—	—	—	—	—	—	5.3	2.2	6.6	—	—	ppm
Sb	0.4	0.4	0.5	0.3	0.3	0.2	0.3	0.3	0.2	0.17	0.01	0.57	1.3	1.7	ppm
W	—	—	—	—	—	—	—	—	—	0.19	nd	10.7	—	—	ppm
Ir	—	—	—	—	—	—	—	—	—	nd	4.8	5.2	—	—	ppb
Au	—	—	—	—	—	—	—	—	—	nd	3.5	nd	—	—	ppb

Chondrite normalised values (Nakamura 1974)

Element	5105	ANU 306	ANU 306	5145	5145	302	302	AI 1991	AI 1991	GX 219	MAC 18E	P 81381	Nakamura
La	5087.9	155.5	158.8	40.3	42.7	95.5	99.1	118.8	120.3	13.6	30.3	366.7	0.33
Ce	2365.3	126.0	134.5	32.0	35.6	71.6	75.0	85.2	88.9	13.9	28.4	196.5	0.865
Nd	792.1	85.2	84.1	23.2	24.1	51.7	48.1	46.2	55.1	17.0	31.3	70.8	0.63
Sm	201.5	50.2	49.8	14.7	15.2	24.9	24.1	27.6	29.1	17.8	30.1	29.2	0.203
Eu	62.9	7.4	7.3	8.4	8.7	11.3	11.8	12.7	13.1	14.9	23.6	13.2	0.077
Gd	115.9	31.9	32.6	11.2	11.2	14.5	16.3	19.2	21.0	19.9	29.7	18.5	0.276
Tb	91.7	39.8	39.6	9.8	10.2	14.7	14.7	21.7	22.3	19.6	27.0	18.1	0.047
Ho	nd	nd	nd	nd	nd	nd	nd	nd	nd	18.6	25.7	16.4	0.07
Tm	73.3	39.3	41.0	9.0	9.7	12.0	13.7	18.3	18.7	20.0	26.7	15.3	0.03
Yb	62.3	42.1	41.7	11.1	11.3	11.5	11.7	19.1	19.6	19.5	24.1	15.9	0.22
Lu	52.6	36.2	36.8	11.2	11.2	11.2	10.9	17.1	17.4	18.2	23.8	13.8	0.034

molecules are 61.98, 94.20 and 101.96, respectively. The agpaitic index for this rock is therefore $(0.1855 (11.50/61.98) + 0.0584 (5.50/94.2))/0.1994 (20.33/101.96) = 1.223$. This makes it definitely peralkaline, thereby helping to narrow down the search for the source.

One other useful thing to consider is the rare earth element pattern (REE). Comparison of these patterns has often been found useful in matching a specimen to its source (Collerson & Weisler 2007: 1910).¹ The REE pattern of various obsidians is illustrated in Fig. 4. The obsidian from the Chatham Islands floater shows clear Eu depletion.

The origin of the pumice and glass *a priori* or *a posteriori*?

The Chatham Islands floater is not the first recorded example of a large block of pumice carrying obsidian to distant shores. Spennemann found a similar piece with a maximum dimension of 32 cm during an archaeological survey on Knox Atoll, also known as Nadikdik, in the Marshall Islands in Micronesia. Identification of the source of this piece was quite simple because its chemistry was identical to those of specimens in an existing database of

Table 3 Wavelength-dispersive X-ray fluorescence results from various samples, including the Chatham Islands floater (P81381), presented by the Geochemistry Laboratory, Department of Geological Sciences, University of Canterbury, New Zealand (35504A, two small pieces combined from the source on Macauley Island, MAC18A (AH594), 3151 mg, and MAC18D, 2050 mg; 35505A, part of GX223B from the source on Raoul Island, 12,269 mg; 35506A, part of P40908, also from the source on Raoul Island, 6584 mg; 35507A, part of P81381, Chatham Island obsidian floater, 7684 mg).

Element	Unit	35504A	35505	35506A	35507A (P81381)	Element	Unit	35504A	35505	35506A	35507A (P81381)
SiO ₂	%	69.31	67.06	67.33	55.03	Ni	ppm	5	<3	<3	17
TiO ₂	%	0.65	0.63	0.63	0.48	Zn	ppm	118	91	92	157
Al ₂ O ₃	%	13.36	14.71	14.54	20.33	Zr	ppm	155	74	75	2097
Fe ₂ O ₃ T	%	5.67	6.07	6.05	4.35	Nb	ppm	2	<2	<2	282
MnO	%	0.16	0.16	0.16	0.14	Ba	ppm	417	209	234	<20
MgO	%	0.79	1.45	1.40	0.62	La	ppm	12	10	8	118
CaO	%	3.36	5.22	5.15	1.49	Ce	ppm	38	28	19	205
Na ₂ O	%	4.65	3.92	3.95	11.50	Nd	ppm	15	13	<10	42
K ₂ O	%	1.56	0.61	0.61	5.50	Ga	ppm	16	15	15	47
P ₂ OS	%	0.17	0.15	0.16	0.10	Pb	ppm	8	5	6	42
LOI	%	0.18	-0.17	-0.05	0.30	Rb	ppm	28	9	9	223
Total	%	99.86	99.81	99.92	99.83	Sr	ppm	171	165	166	114
V	ppm	24	54	53	22	Th	ppm	3	<1	1	57
Cr	ppm	6	7	6	17	Y	ppm	54	40	41	39

obsidian sources. Edax SEM analysis showed the source to have been the Tulumano volcano near Manus Island in Papua New Guinea (Spennemann 1996: 30–31). That is a great-circle distance of about 2800 km. A similar large floating block of obsidian was found on Koil, one of the islands in the Schouten island group in the East Sepik area of Papua New Guinea (Ambrose *in* Spennemann 1996). This specimen was also sourced to the Tulumano volcano, which in this case was relatively nearby.

The chemistry of the Chatham Islands floater is far from familiar and it clearly was not going to be so easy to identify its source. Quite often in the past, following a major volcanic eruption somewhere in the world, pumice has turned up on distant beaches and geologists have collected samples and matched their chemistry to the volcano involved. In cases like this, identification is simple because one has *a priori* information against which to test the object. The situation

is quite different when there has been no recent eruption against which to test. In the case of the Chatham Islands sample, the source could be identified only *a posteriori*, that is, after gathering evidence from diverse sources and carrying out some form of definitive comparison and test against each. An important question here is: how big should this universe of sources be? Could this universe be narrowed down or should all possible sources be considered?

Such a situation was presented in a study by Jokiel & Cox (2003), in which they set out to identify the sources of numerous pieces of pumice that had drifted to beaches on Hawai'i and Christmas Island over an unknown period of time, and for which they could make no *a priori* assumptions on the original sources that might be involved. They carried out XRF analysis of 41 pumice specimens, about half from each island group. They then used information from a pumice source characterisation study by Frick & Kent

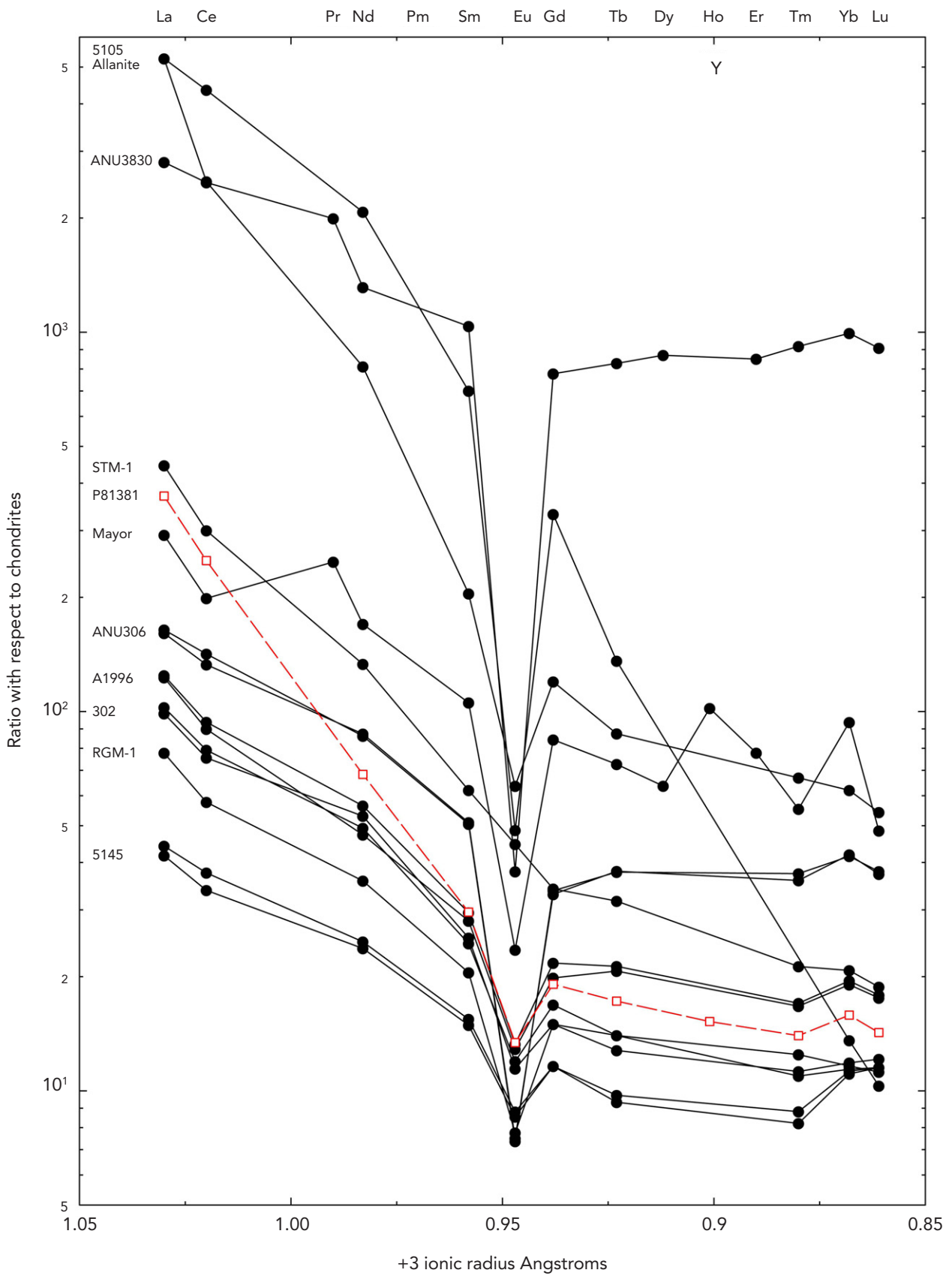


Fig. 4 The floater from the Chatham Islands shows europium (Eu) depletion. Details of samples are given in Appendix 1.

Table 4 Pumice oxide values for six geochemical groups (from Jokiel & Cox 2003).

Group	Fe ₂ O ₃	K ₂ O	TiO ₂	Na ₂ O/CaO
A: South Sandwich Islands	2.80–3.80	0.50–1.00	0.20–0.35	1.2–2.6
B: South Atlantic Ocean Ridge	1.70–2.50	3.50–7.00	0.20–0.45	8–9
C: South Indian Ocean Ridge	4.00	0.50–1.00	0.40–0.50	1
D: Tonga Trench	5.30–10.00	0.50–1.00	0.40–0.90	0.4–1
E: Krakatau, Indonesia	2.80–4.80	1.60–3.00	0.60–1.00	1.2–2.9
F: San Benedicto Island, Mexico	3.50–5.60	3.20–5.00	0.30–0.60	2.9–10

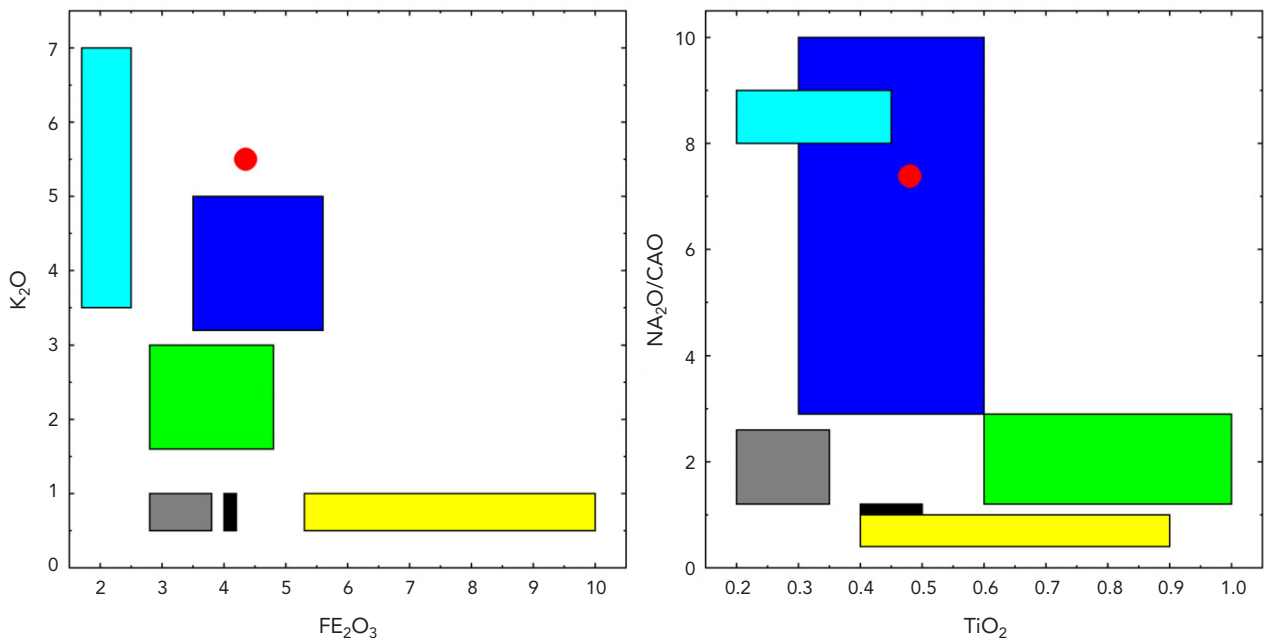


Fig. 5 Classification of major groups of pumices by oxide values: South Sandwich Islands (grey); South Atlantic Ocean Ridge (cyan); South Indian Ocean Ridge (black); Tonga Trench (yellow); Krakatau, Indonesia (green); San Benedicto Island, Mexico (blue). The floater from the Chatham Islands is indicated by the red circle.

(1984), augmented by some newer data, as a database with which to help identify their beach samples. Six geochemical groups were distinguished and linked to eruptions in the Indian, Atlantic and Pacific oceans (Jokiel & Cox 2003: 125, table 2). These are outlined in Table 4. It is a most instructive set of information.

The floater from the Chatham Islands is also plotted on Fig. 5, to show its possible allocation to any one of these six groups. In the first part of the graph, the floater plots outside the distribution of any known source group, and in the

second it plots inside the distribution of the San Benedicto Island volcanic source in Mexico.

So, can we conclude then that this floater derives from the volcanic source of San Benedicto Island? A more careful look shows that this not so. Jokiel & Cox (2003) obtained the data for their analysis from a paper by A.F. Richards, who describes the lithics on this island as consisting of trachybasalts, trachyandesites, sodic-trachites and sodic-rhyolites (Richards 1966: 384 ff.), with no mention of phonolites. He provides oxide data for 28 samples from the island, of

Table 5 Oxide values and agpaitic index (AI) of 11 peralkaline pumices from San Benedicto Island, Mexico, compared with the Chatham Islands floater.

Sample	Na ₂ O	K ₂ O	Al ₂ O ₃	AI
Chathams	11.50	5.50	20.33	1.22
Benedicto	4.34	2.66	8.53	1.17
Benedicto	4.64	2.64	8.90	1.18
Benedicto	7.30	4.25	15.27	1.09
Benedicto	4.70	3.70	8.47	1.39
Benedicto	4.97	3.76	8.69	1.41
Benedicto	7.58	3.61	14.36	1.14
Benedicto	4.50	3.24	8.21	1.33
Benedicto	6.42	4.98	14.59	1.09
Benedicto	4.75	4.43	7.72	1.63
Benedicto	5.71	4.65	13.96	1.03
Benedicto	4.24	3.86	7.39	1.51

which only 11 are peralkaline. These are listed with the Chatham Islands sample in Table 5, together with the data for Na₂O, K₂O, Al₂O₃ and the agpaitic index. Simple inspection of this table shows that the floater cannot possibly come from this source in Mexico. In short, the classification provided in Fig. 5 is unduly simplistic. In the absence of *a priori* information, such as the knowledge of a recent pumice-bearing volcanic eruption, reliable identification of a single beach-collected specimen of pumice (with or without obsidian attached) is no simple task.

If we accept the identifications that were made of the pumices on the beaches on Hawai'i, 72% of the pumice had found its way from the subantarctic South Sandwich Islands (Jokiel & Cox 2003: 128), a great-circle distance of 13,600 km. However, in reality the distance would have been a lot greater than that, as the pumice would have had to travel eastward along the Antarctic Circumpolar Current, then northward up the west coast of South America on the Humboldt Current, and then finally westward along the North Equatorial Current. There are many historical examples of very long distance journeys of floating objects on the oceans of the world. For example, one of the famous

so-called 'talking boards' from Easter Island, carved with hieroglyphics, was found to have been made from European ash (*Fraxinus excelsior*) (Fischer 1997: 497). It was probably originally an oar blade, and may well have found its way on sea currents all the way from some European shore.

So in a case like the floater from the Chatham Islands, the reality is that such a specimen could, in theory, have come from just about any volcano in the world so long as that volcano is close enough to the sea for the pumice it produces to be carried off by ocean currents.

How do we know when we have found the correct answer?

This raises an important question: how can we determine whether a specimen matches a particular source? Whether a source is the origin of an isolated piece partly depends upon having reliable information on the amount of variation of source composition. If the piece has, say, 3.5 ppm of an element and the source being considered has 35 ppm of the same element, could the piece realistically belong to that source, which has 10 times the concentration of the element? That depends entirely on the variability of the source. For example, if the mean concentration is 35 ppm and the standard deviation is 48 ppm, then clearly 3.5 ppm is within the range of variation.

When detailed research has been carried out on the chemical composition of a large number of samples from any particular source of volcanic glass, it is possible to use powerful parametric statistics, including multivariate methods such as discriminant analysis, to provide a probability that such an unknown belongs to this or that source. A simple, and very effective, test would be to ascertain whether the composition of a single element in the unknown is X units of standard deviation from the mean composition of a particular source. If X is, say, more than 3 units of standard deviation from the source mean, it would be reasonable to consider rejecting that source. On the other hand, if it was only 0.5 units of standard deviation from the source mean, then one could start to think that this could be the source. If such a simple test is repeated for several elements, confidence of source may be increased or decreased. Unfortunately, very few sources of volcanic glass have been intensively studied in this manner, effectively prohibiting the use of even simple parametric statistical tests, let alone multivariate ones. Published archaeological

literature on sourcing using chemical fingerprinting is filled with examples that ignore this.

The floater that ended up in the Chatham Islands poses quite a challenge, because a large universe may need to be searched to try to find the correct match. What to do?

One possibility is to narrow down the options by devising a simple test that helps to filter out really unlikely volcanic sources in the larger universe so one can focus attention on a smaller number with more similar chemical fingerprints. The test devised here examined the proportional difference between elements of individual specimens against the floater. Thus, a mean and standard deviation were calculated of the proportional difference between pairs of specimens using all elements available.

When comparing the floater with a sample from a single volcanic source, this was the procedure followed: for element 1, the concentration in the floater = C1, and the concentration of a sample from the source being considered = C2. The absolute difference, $1 = \text{abs}(C2 - C1)$. The proportional difference is $1/C1$. Such a method standardises differences, so that an element at, say, a concentration of 12 ppm will have the same weight as another element that is at 2000 ppm. After calculating this proportional difference for as many elements as possible, one can calculate a mean and standard deviation of the proportional difference. This then is a suitable measure of the overall difference between two individual samples, which for want of a suitable short name will be called the mean proportional difference (MPD). The measure shares some features with the chi-squared test but has no probability distribution. Although it is a crude measure, it should help to narrow down the size of the universe to a smaller set of more likely candidates for the true source. It is important to realise that this measure is very sensitive to the number of elements from which it can be calculated; the more elements involved, the better. Conversely, if only a few elements are involved in a comparison, little credence can be given to low values of mean and standard deviation.

In the case of the Chatham Islands floater, the first comparisons were made using information about volcanic glasses from the general area of New Zealand (Fig. 6). Information is available from NAA analysis for 32 sources and 23 elements (Leach & Warren 1981; Leach 1996). The analysis of the floater produced information on 44 elements when the XRF and NAA data were combined. Of these 44 elements, only 19 of the 23 available from the New Zealand sources are also common to the floater.

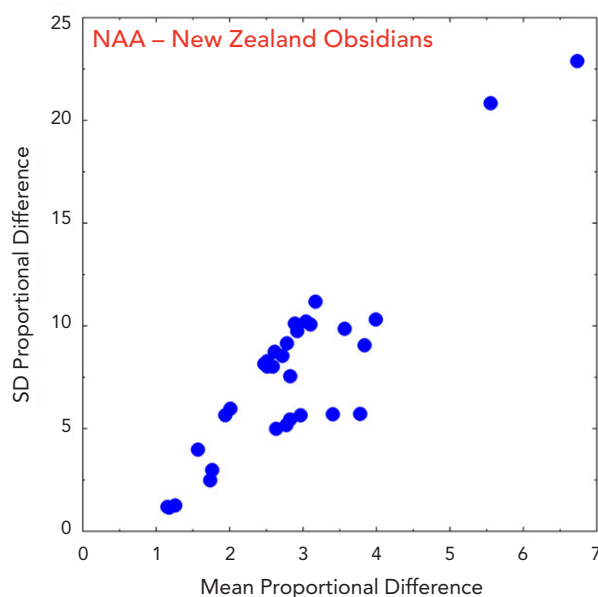


Fig. 6 Comparison of the floater from the Chatham Islands with New Zealand volcanic glasses using neutron activation data. The floater is situated at the origin ($x,y = 0,0$).

Table 6 Mean proportional differences between Mayor Island (Tuhua) obsidian samples and the Chatham Islands floater using neutron activation analysis data.

Mean	SD	Source
1.259	1.257	Mayor Island (Tuhua) Green
1.153	1.188	Mayor Island (Tuhua) Honey
1.175	1.151	Mayor Island (Tuhua) Yellow

Most of these sources have little similarity with the Chatham Islands floater. The sources whose chemistry is closest to the floater have concentrations that are, on average, more than 100% greater or smaller across all 19 elements ($\text{MPD} > 1.0$). Thus, all 32 sources are effectively ruled out. It is of passing interest that the three sources most similar to the floater are the three types of obsidian from Mayor Island (Tuhua), although there is no possibility that one of these could be its source. The element composition of the floater is very different to Mayor Island (Tuhua) obsidian.

The next data considered were from the wider Pacific region. Information on 18 elements is available from PIXE-PIGME analysis of 53 sources through the Pacific (Bird *et al.* 1981; Duerden *et al.* 1979; Duerden *et al.* 1987). Of the

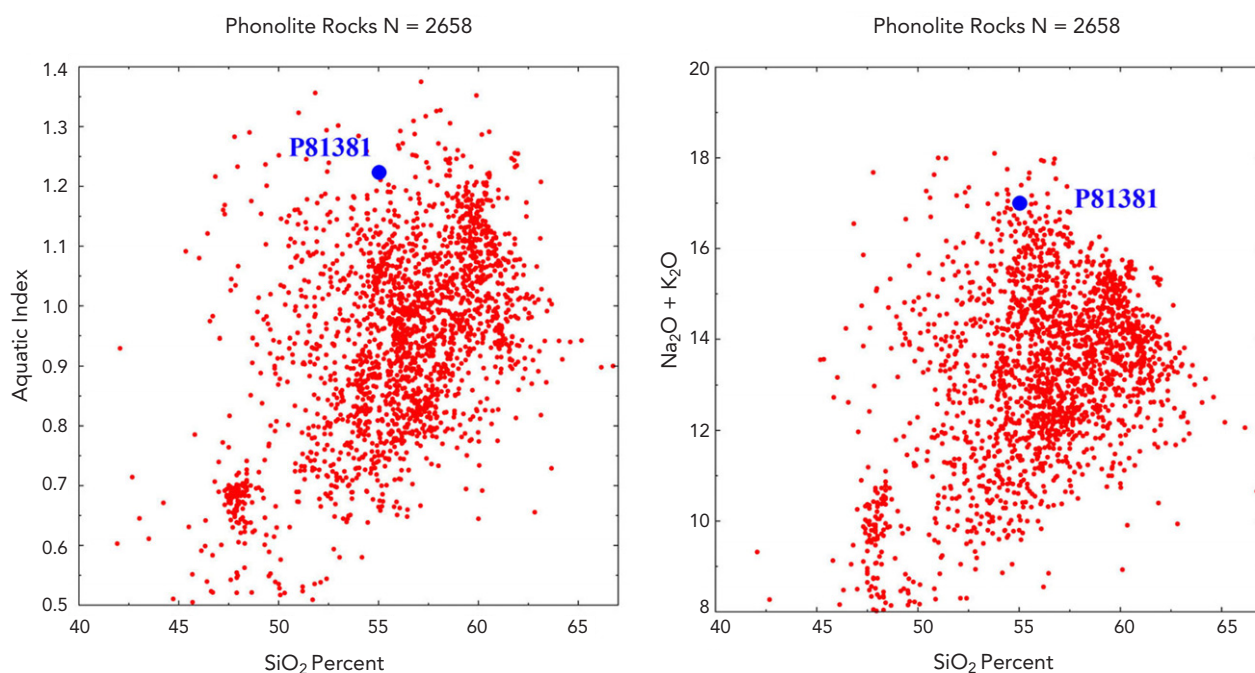


Fig. 7 The floater from the Chatham Islands compared with other phonolites.

44 elements available for the floater, it has only nine in common (Zn, Ga, As, Pb, Rb, Sr, Y, Zr, Nb) with the 18 available for these sources. Although the MPD was calculated for these sources, the nine elements were too few for any useful conclusions to be drawn. This shows the insensitivity of this crude statistic when only a small number of elements is involved. PIXE-PIGME data are also available for the same 18 elements for 15 obsidian sources from the islands of Japan. Once again, though, only nine were in common with those available for the floater, which was inadequate for meaningful comparison using the simple proportional statistic. It was decided to set aside the MPD at this stage and instead try to narrow down the large universe of possible volcanic sources using a different procedure based upon the geochemical character of the floater.

It has already been shown above that the floater is from a phonolite source, it is peralkaline with an agpaite index of 1.22, and it has a notable Eu depletion in the REE pattern. These three characteristics suggested another approach to narrow down the search for the source. That is, to search among published geochemical data for samples with these specific features. In addition to the published data, there is a large database known as GEOROC (Geochemistry of Rocks of the Oceans and Continents), which is maintained by the Max Planck Institute for Chemistry in Mainz and is available for searching online.²

The element composition of as many phonolites as possible was culled from published literature and the GEOROC database. This resulted in the tabulation of element data from 2658 samples of phonolite for careful scrutiny (Fig. 7).

It will be obvious from Fig. 7 that the Chatham Islands floater has very unusual characteristics, plotting out on the periphery of the distribution of phonolites.

Several computer programs were written in Turbo Pascal 5 to select only samples within a certain (fairly large) range of the key elements that were thought to be especially characteristic of the floater. The filters adopted are listed below:

Element	Floater	Minimum	Maximum
SiO ₂	55.03%	50	60
Al ₂ O ₃	20.33%	17	23
K ₂ O	5.50%	4	7
Na ₂ O	11.50%	9	13
Zr	2097 ppm	1800	3000
Nb	282 ppm	180	400
Th	57 ppm	40	100

All samples that had element concentrations outside all seven of these filters were rejected as possible sources of the floater. It was expected that this would leave a small percentage of the original 2658 specimens. Rather surprisingly, these wide

Table 7 Mean proportional differences between the five closest phonolite samples and the Chatham Islands floater.

Mean	SD	Source
0.739	0.941	MB35.2, Mt Sidley, Antarctica
0.653	0.806	MB35.5, Mt Sidley, Antarctica
0.482	0.715	11290, Ormonde seamount
0.308	0.288	65124, McDonald Island
0.534	0.396	GH11, sryan volcanic field, Libya

filters rejected all but five specimens (Fig. 8, Table 7), the details of which are as follows:

MB35.2 from Mt Sidley, Marie Byrd Land, Antarctica (Panter *et al.* 1997: 1231, table 3).

MB35.5 from Mt Sidley, Marie Byrd Land, Antarctica (Panter *et al.* 1997: 1231, table 3).

11290 from the seamount Ormonde, Gorrige Bank (west of the Strait of Gibraltar) (Bernard-Griffiths *et al.* 1997: 118, table 2).

65124 from McDonald Island, near Heard Island (Barling *et al.* 1994: 1024, table 1).

GH11 from the Gharyan volcanic field, Libya (Lustrino *et al.* 2012: 221, table 1).

It should not be thought that this MPD statistic alone is adequate to identify the source of an isolated sample, such as this floater. As pointed out above, the MPD is only really useful for rejecting potential sources that are unlikely to be the actual source. In this respect, the MPD statistic proved useful. At this stage, it remained to be seen whether any one of the five remaining samples could be the source of the floater.

The element composition of each of the five specimens is given in Table 8 alongside the values of the floater for direct comparison. The possibility that some volcanic rocks as remote as Libya and a seamount near Gibraltar could have a geochemical signature similar to this floater was initially very surprising, but whether they really were similar remained to be seen. Making sense of such a mass of figures is not easy, and it was useful to calculate the individual proportional difference (IPD) for each element for each sample. The plus or minus difference is $2 = (C2 - C1)$, and

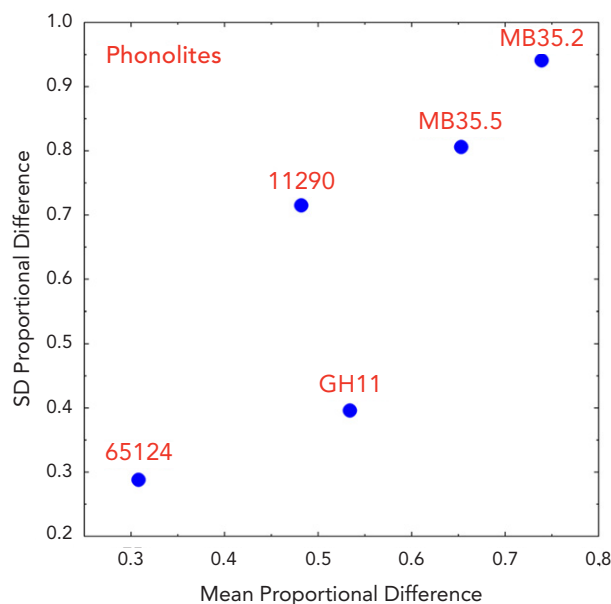


Fig. 8 The difference from the Chatham Islands floater of the five phonolites with the closest chemical composition.

the individual proportional difference is $2/C1$. These data are plotted in Fig. 9.

All individual values in Fig. 9 are plotted using the same scale, so that one can make a direct comparison of the pattern from one sample to another. For example, for the Ormonde seamount specimen, barium (Ba) shows a value of +4.05, which means that this specimen contains four times as much Ba as the floater (101 ppm, cf. 20 ppm: $(101 - 20)/20 = 4.05$).

It can readily be seen from this illustration that the specimen from McDonald Island gave the lowest value for the MPD, as the variation around the central line (representing the floater) is much smaller than for any of the other four specimens. The important question is: how big is small? To answer that we must return to the issue raised earlier relating to the use of parametric statistics to assess the probability that McDonald Island is indeed the correct source of the floater.

To the best of our knowledge, chemical data from which to gain some understanding of chemical variation have been published from only four samples of phonolite from McDonald Island. These are given in Table 9 and are taken from Barling *et al.* (1994: 1024, table 1). In spite of the fact that the data in Table 9 are patchy, they could be used to assess the range of results for any one element and, where possible, calculate a mean and standard deviation using Bessel's correction for small samples. It was then possible to

Table 8 Element composition of the Chatham Islands floater (P81381) and the five most similar phonolite samples (note: the values given for P81381 here are the average of the X-ray fluorescence analysis and neutron activation analysis determinations). Details of samples are given in Appendix 1.

Element	P81381	MB35.2	MB35.5	11290	65124	GH11
Na ₂ O	11.24	9.06	9.41	10.10	10.33	9.61
MgO	0.62	0.04	0.00	0.07	0.17	0.04
Al ₂ O ₃	20.33	19.17	19.49	22.10	20.83	19.88
SiO ₂	55.03	57.02	56.71	55.80	57.25	59.80
P ₂ O ₅	0.10	0.15	0.12	0.01	0.05	0.02
K ₂ O	5.74	5.19	5.39	5.03	6.15	5.24
CaO	1.49	1.43	1.20	0.20	0.94	1.10
Sc	1.48	1.10	0.80	0.00	0.00	0.00
TiO ₂	0.48	0.25	0.19	0.30	0.38	0.20
V	22.00	0.00	0.00	37.00	4.00	0.00
Cr	12.58	0.00	0.00	9.00	3.00	0.00
MnO	0.14	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	4.25	0.00	0.00	0.00	0.00	0.00
Co	2.97	0.00	0.00	2.00	0.00	0.00
Ni	15.00	6.00	7.00	5.00	2.00	0.00
Zn	153.50	185.00	186.00	155.00	137.00	177.00
Ga	47.00	44.00	44.00	52.00	41.00	53.00
As	6.60	8.90	8.70	0.00	0.00	0.00
Rb	218.00	234.65	252.80	263.00	145.00	237.00
Sr	125.50	47.96	4.20	77.40	141.00	6.00
Y	39.00	107.00	109.00	17.00	26.00	64.00
Zr	2223.50	1869.00	2018.00	1886.00	2340.00	1957.00
Nb	282.00	341.00	369.00	304.00	297.00	398.00
Sb	0.57	0.50	0.60	0.00	0.00	0.00
Cs	6.65	4.99	6.27	0.00	0.00	3.60
Ba	20.00	105.00	0.00	101.00	1.49	7.00
La	119.50	172.65	176.80	37.60	101.00	243.60
Ce	187.50	312.00	325.00	68.40	149.00	367.50

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Table 8 Element composition of the Chatham Islands floater (P81381). *Continued from previous page*

Element	P81381	MB35.2	MB35.5	11290	65124	GH11
Nd	43.30	102.75	112.00	17.60	34.40	79.70
Sm	5.92	18.71	19.88	2.77	4.98	10.60
Eu	1.02	1.77	1.27	0.85	1.39	1.00
Gd	5.10	0.00	0.00	2.82	3.88	8.00
Tb	0.85	2.95	2.91	0.00	0.00	1.50
Ho	1.15	0.00	0.00	0.00	0.00	1.90
Tm	0.46	0.00	0.00	0.00	0.00	1.10
Yb	3.50	11.26	11.90	3.01	2.80	7.20
Lu	0.47	1.59	1.76	0.52	0.43	1.00
Hf	35.00	36.95	40.45	0.00	0.00	40.00
Ta	13.74	21.75	24.20	0.00	0.00	21.80
W	10.70	0.00	0.00	0.00	0.00	0.00
Ir	5.20	0.00	0.00	0.00	0.00	0.00
Pb	42.00	27.00	26.00	27.00	0.00	22.20
Th	54.50	42.80	47.70	43.00	53.00	48.70
U	15.30	12.70	14.50	18.10	0.00	16.20

examine the individual element values of the floater and obtain a probability that each result was consistent with the four samples from McDonald Island. The results of this test are presented in Table 10. For example, if the element value for the floater lies within the McDonald Island mean $\pm 2SD$, it is within the 95% probability range, or $p = 0.05$. In cases where the floater was within the simple range of the minimum and maximum for McDonald Island, this is simply taken to be $p = 0.10$, since probability calculation would be meaningless.

The results in Table 10 give some confidence that McDonald Island could well be the source of the floater. However, there are four elements that have suspiciously high ppm values in the floater. These are shown in Table 11.

The value for the element rubidium (Rb) in the floater is almost double that of the four McDonald Island samples. These four values are certainly very close to each other

and may not be fully representative of the true range for the source. When an extensive series of analyses is undertaken for any one source of volcanic glass, a much larger range is found. For example, Weaver's analyses of 149 pieces of Mayor Island obsidian shows an order of magnitude range for Rb of 11–164 ppm (mean and standard deviation = 114.7 and 37.1) (Weaver, pers. comm. to Leach, 2013). Two values are available for the floater, and these are perfectly consistent: XRF = 223 ppm and NAA = 213 ppm, giving an average of 218 ppm. In spite of the reservation that if more data were available the range of Rb might be higher for McDonald Island phonolites, the value for the floater does look too large to be from this source.

The differences between the floater and the McDonald Island samples for the elements yttrium (Y), caesium (Cs) and gadolinium (Gd) are much smaller, but even here there is cause for concern. One more point needs to be made:

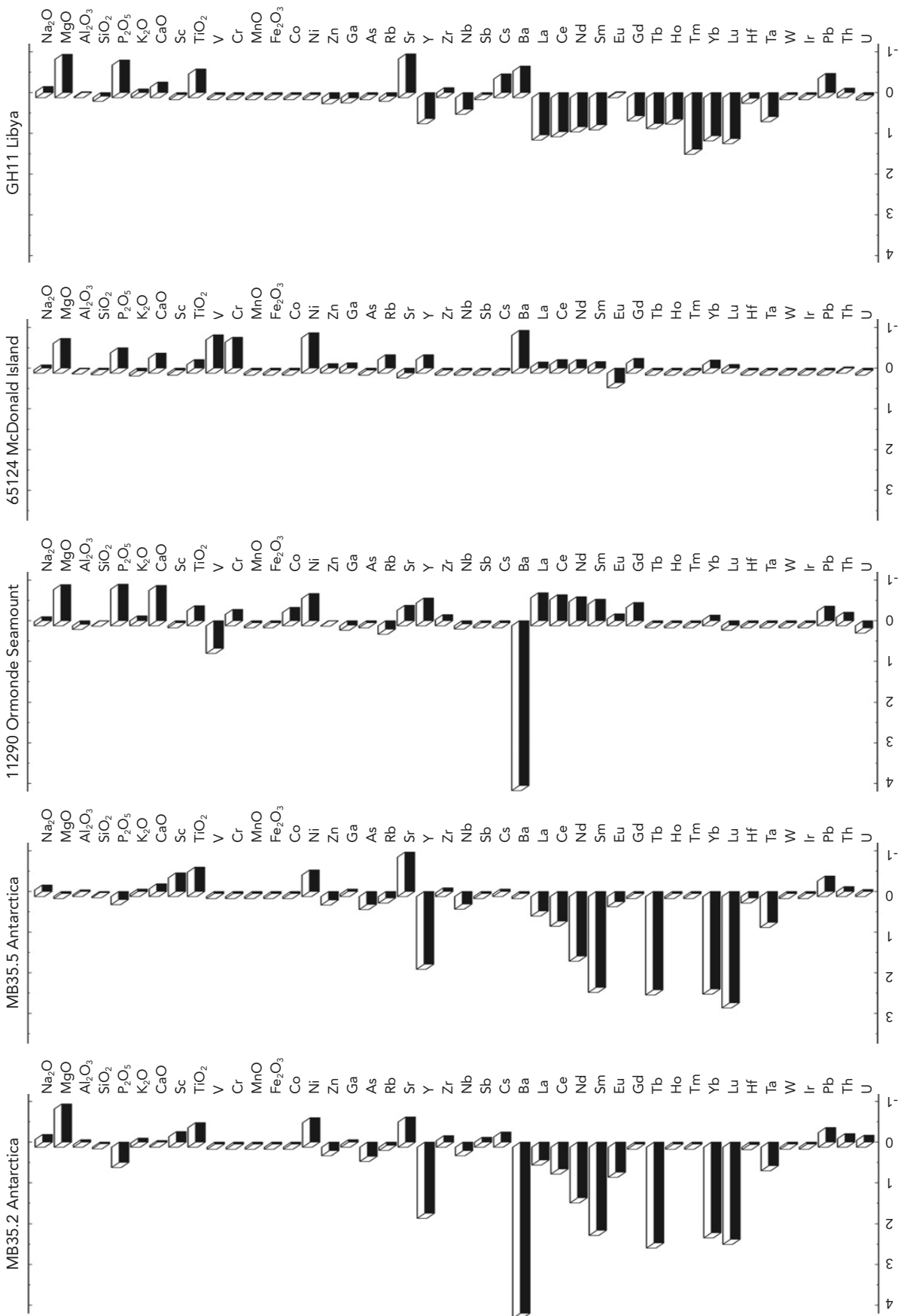


Fig.9 The individual proportional differences of the elements for each of the five most similar samples to the Chatham Islands floater. Proportional values to the left of the central line are greater than the floater, while those to the right are less than the floater.

Table 9 Analyses of McDonald Island phonolites (from Barling *et al.* 1994).

Element	Unit	65119	65133	65124	65125
SiO ₂	Wt%	54.36	57.14	57.25	57.33
TiO ₂	Wt%	1.65	0.77	0.38	0.92
B ₂ O ₃	Wt%	0	0	0	0
Al ₂ O ₃	Wt%	19.43	21.7	20.83	19.73
Cr ₂ O ₃	Wt%	0	0	0	0
Fe ₂ O ₃	Wt%	0.88	0.57	0.62	0.64
FeO	Wt%	4.47	2.91	3.16	3.27
FeOT	Wt%	0	0	0	0
CaO	Wt%	3.6	1.7	0.94	2.15
MgO	Wt%	1.8	0.84	0.17	1.26
MnO	Wt%	0.08	0.08	0.11	0.1
K ₂ O	Wt%	6.5	6.93	6.15	5.99
Na ₂ O	Wt%	6.75	7.22	10.33	8.36
P ₂ O ₅	Wt%	0.48	0.14	0.05	0.24
V	ppm	81	23	4	46
Cr	ppm	15	11	3	16
Ni	ppm	16	15	2	13
Cu	ppm	16	9	3	13
Zn	ppm	81	87	137	87
Ga	ppm	26	30	41	34
Rb	ppm	144	142	145	143
Sr	ppm	1129	1027	141	775
Y	ppm	21	19	26	16
Zr	ppm	738	1008	2340	1228
Nb	ppm	135	163	297	120
Cs	ppm	1.19	0	0	2.48
Ba	ppm	401	162	1.49	204
La	ppm	69.8	72	101	58.62
Ce	ppm	136	134	149	100.09

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Table 9 Analyses of McDonald Island phonolites (from Barling *et al.* 1994). *Continued from previous page*

Element	Unit	65119	65133	65124	65125
Nd	ppm	52.1	0	34.4	32.41
Sm	ppm	8.47	0	4.98	5.33
Eu	ppm	2.71	0	1.39	1.62
Gd	ppm	0	0	3.88	3.35
Dy	ppm	4.54	0	3.99	3.14
Er	ppm	2.12	0	2.66	1.6
Yb	ppm	1.67	0	2.8	1.65
Lu	ppm	0.245	0	0.43	0.264
Pb	ppm	0	0	0	32
Th	ppm	15	22	53	30
U	ppm	0	0	0	4

Table 10 Probability that the source of the Chatham Islands floater (P81481) is a McDonald Island phonolite ('above' = greater or less than 2 sigma from mean).

Element	Unit	P81481	N	Min	Max	Mean	SD	Prob
Na ₂ O	Wt%	11.24	4	6.75	10.33	8.17	1.59	$p=0.05$
MgO	Wt%	0.62	4	0.17	1.80	1.02	0.69	$p=0.10$
Al ₂ O ₃	Wt%	20.33	4	19.43	21.70	20.42	1.04	$p=0.10$
SiO ₂	Wt%	55.03	4	54.36	57.33	56.52	1.44	$p=0.10$
P ₂ O ₅	Wt%	0.10	4	0.05	0.48	0.23	0.19	$p=0.10$
K ₂ O	Wt%	5.74	4	5.99	6.93	6.39	0.42	$p=0.05$
CaO	Wt%	1.49	4	0.94	3.60	2.10	1.12	$p=0.10$
TiO ₂	Wt%	0.48	4	0.38	1.65	0.93	0.53	$p=0.10$
MnO	Wt%	0.14	4	0.08	0.11	0.09	0.02	$p=0.01$
Fe ₂ O ₃	Wt%	4.25	0	0.00	0.00	0.00	0.00	—
Sc	ppm	1.48	0	0.00	0.00	0.00	0.00	—
V	ppm	22.00	4	4.00	81.00	38.50	33.13	$p=0.10$
Cr	ppm	12.58	4	3.00	16.00	11.25	5.91	$p=0.10$
Co	ppm	2.97	0	0.00	0.00	0.00	0.00	—

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Table 10 Probability that the source of the Chatham Islands floater (P81481). *Continued from previous page*

Element	Unit	P81481	N	Min	Max	Mean	SD	Prob
Ni	ppm	15.00	4	2.00	16.00	11.50	6.45	$p=0.10$
Zn	ppm	153.50	4	81.00	137.00	98.00	26.15	$p=0.01$
Ga	ppm	47.00	4	26.00	41.00	32.75	6.40	$p=0.01$
As	ppm	6.60	0	0.00	0.00	0.00	0.00	—
Rb	ppm	218.00	4	142.00	145.00	143.50	1.29	Above
Sr	ppm	125.50	4	141.00	1129.00	768.00	443.69	$p=0.05$
Y	ppm	39.00	4	16.00	26.00	20.50	4.20	Above
Zr	ppm	2223.50	4	738.00	2340.00	1328.50	703.48	$p=0.10$
Nb	ppm	282.00	4	120.00	297.00	178.75	80.82	$p=0.10$
Sb	ppm	0.57	0	0.00	0.00	0.00	0.00	—
Cs	ppm	6.65	2	1.19	2.48	1.84	0.64	Above
Ba	ppm	20.00	4	1.49	401.00	192.12	164.34	$p=0.10$
La	ppm	119.50	4	58.62	101.00	75.35	18.07	$p=0.01$
Ce	ppm	187.50	4	100.09	149.00	129.77	20.88	$p=0.01$
Nd	ppm	43.30	3	32.41	52.10	39.64	10.84	$p=0.10$
Sm	ppm	5.92	3	4.98	8.47	6.26	1.92	$p=0.10$
Eu	ppm	1.02	3	1.39	2.71	1.91	0.71	$p=0.05$
Gd	ppm	5.10	2	3.35	3.88	3.62	0.27	Above
Tb	ppm	0.85	0	0.00	0.00	0.00	0.00	—
Ho	ppm	1.15	0	0.00	0.00	0.00	0.00	—
Tm	ppm	0.46	0	0.00	0.00	0.00	0.00	—
Yb	ppm	3.50	3	1.65	2.80	2.04	0.66	$p=0.01$
Lu	ppm	0.47	3	0.24	0.43	0.31	0.10	$p=0.05$
Hf	ppm	35.00	0	0.00	0.00	0.00	0.00	—
Ta	ppm	13.74	0	0.00	0.00	0.00	0.00	—
W	ppm	10.70	0	0.00	0.00	0.00	0.00	—
Ir	ppm	5.20	0	0.00	0.00	0.00	0.00	—
Pb	ppm	42.00	1	32.00	32.00	0.00	0.00	—
Th	ppm	54.50	4	15.00	53.00	30.00	16.51	$p=0.05$
U	ppm	15.30	1	4.00	4.00	0.00	0.00	—

Table 11 Four elements in the Chatham Islands floater (P81381) have suspiciously greater values compared to the only available results for phonolite samples from McDonald Island.

Element	P81381	65119	65133	65124	65125
Rb	218	144	142	145	143
Y	39	21	19	26	16
Cs	6.65	1.19	0	0	2.48
Gd	5.1	—	—	3.88	3.35

it will be recalled that the floater shows an Eu anomaly (Fig. 4), whereas a plot of these samples of phonolite from McDonald Island does not give the same result. In summary, at this point, even though McDonald Island did look as if it might be the source of the floater, little confidence could be had in this on the basis of the existing published information about McDonald Island. It was therefore necessary to delve further.

Jane Barling's published data (Barling *et al.* 1994) derive from her Ph.D. thesis (Barling 1990), and there have been other expeditions to the island and its vicinity since then. It seemed possible that more samples might have been collected from the area, but not fully published. A great deal has been published about the Kerguelen Plateau, which is the submarine feature on which McDonald Island lies. It has even been suggested that this plateau is the fabled Atlantis that featured in the dialogues of Greek philosopher Plato, including *Timaeus* (c. 360 BC). A wider literature search revealed an alkali versus silica plot that had 19 specimens labelled as McDonald Island phonolites (Verwoerd *et al.* 1990: fig. F6.3). Data for only one specimen were published by the authors – sample 65125 – which is one of the specimens cited above from Barling's research. Verwoerd had retired 20 years previously but was kind enough to provide additional information to the effect that the samples in question may have derived from a trip in 1980: 'Since their initial sighting in 1854 there have been only two recorded landings on the McDonald islands: The first in 1971 and the second in 1980. It was during the latter visit that the only samples from the islands were collected, by Clarke (Clarke *et al.* 1983)' (Verwoerd *et al.* 1990: 441).

The paper by Clarke *et al.* (1983) gives a similar alkali versus silica plot from what are probably the same phonolite specimens, but provides no data.

There was a more recent expedition to McDonald Island, in March 1997, and a related reference was found to an unpublished paper by Collerson (1997). The librarian of the Australian Antarctic Division reported, 'Unfortunately, we do not hold this unpublished report. It was not deposited with Library Services nor AAD's Records area' (Egan Library manager, pers. comm. to Leach 2014). There are also several citations of a paper by Collerson *et al.* (1998), but this contained a graph with no data. Kenneth Collerson was written to in order to obtain the data referred to in the paper, but he could not find them. Marcel Regelous, one of the junior authors of the paper, was then approached. This time some really useful information was forthcoming. Further geochemical analysis of samples from the area had been carried out, but had never been published. The analyses were of both pumice and rock samples: 'The very fresh pumice samples we analyzed were collected in 1997 by an Australian research ship from the sea in the neighbourhood of McDonald Island, which was apparently active at the time. I was not on the ship, but was given the samples to analyze' (Regelous, pers. comm. to Leach, 2014). The unpublished data related to six pumice samples taken from the sea close to McDonald Island and 33 rock samples from Heard Island. The REE pattern is given in Fig. 10.

The REE pattern of the floater is indistinguishable from those of the other pumice samples. The Eu depletion, previously noticed in the floater, is present in these pumices and absent in the phonolite rocks. The NAA analysis of the floater did not resolve concentrations for praseodymium (Pr), dysprosium (Dy) or erbium (Er), which explains the small deviations from the lines of the pumice samples in Fig. 10. The results of two pumice samples are almost identical to two others, which is why only four pumice specimens are clearly distinguishable on the plotted data.

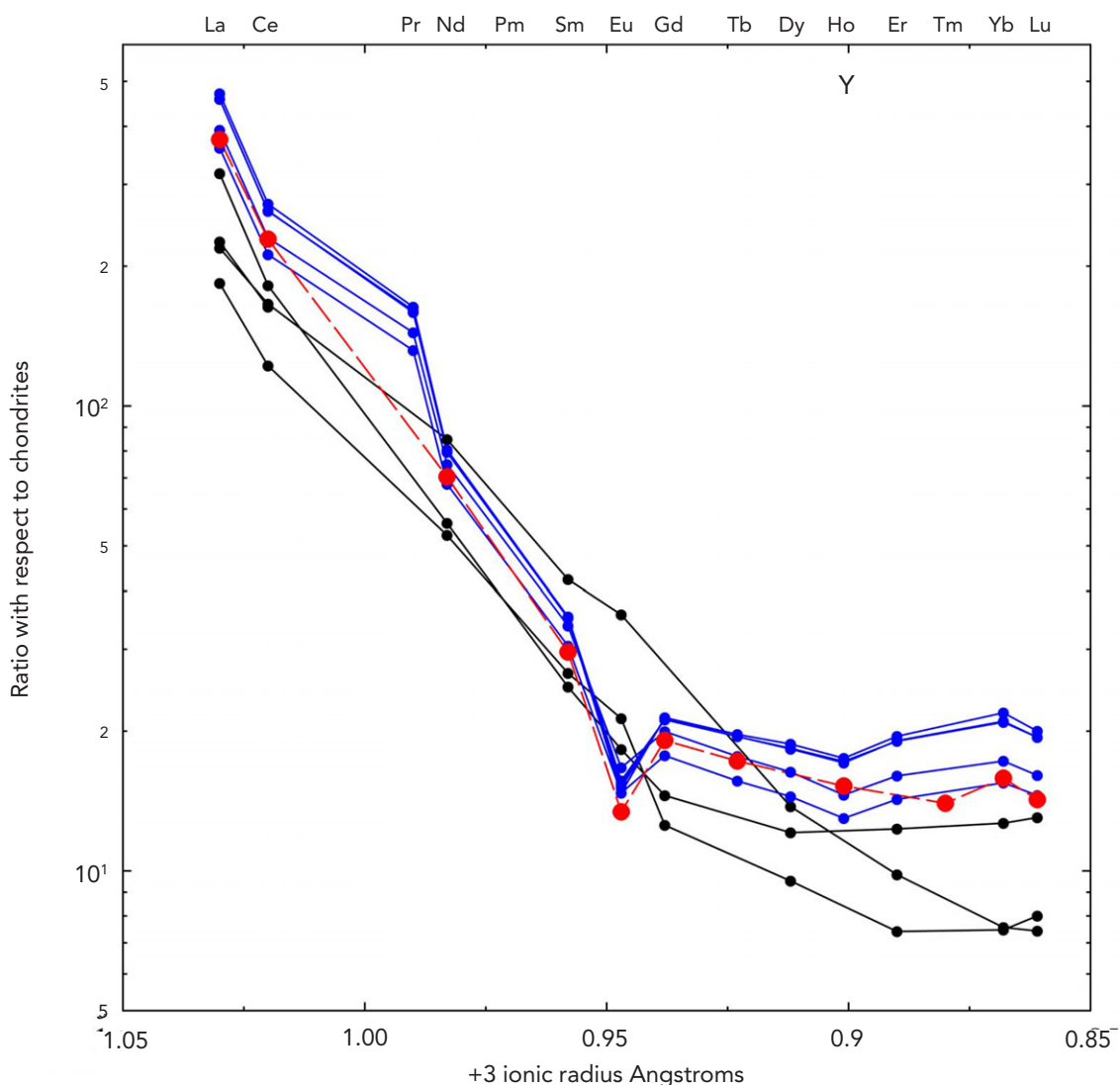


Fig. 10 Rare earth element plot of six pumice samples (blue) taken from the sea off McDonald Island March 1997 (courtesy of Marcel Regelus), together with three phonolites (black) from McDonald Island collected by Ian Clarke in 1980 and published by Barling *et al.* (1994). The red sample is the floater from the Chatham Islands. (Note that the results for two pumice samples are almost identical to two others, which is why only four blue plots are visible on the graph.)

The alkali and silica data of these pumices were compared with those of the floater glass and pumice fractions (Table 12), and plotted in Fig. 11. As with the floater, all pumice specimens are both phonolite and peralkaline (agpaite index ranging from 1.29 to 1.65). The spread of values in the plot gives considerable confidence that the floater is consistent with this source.

The geochemical data for these six pumice specimens are presented in Table 13, together with means and standard deviations, and the average values for the floater. It remains to assess how similar the floater is to these pumices. Table 13

is a bewildering mass of figures and one must adopt a systematic method of checking the data from one object against the data amassed from a possible source; simple eye-balling is not good enough. As mentioned above, discriminant functions are often used by archaeologists to ascertain the source of obsidian artefacts, but this is reliable only when the underlying assumptions of this method are met. One of these is a uniform variance and covariance matrix across all variables. A glance at Table 13 shows this to be manifestly false (the standard deviation values range more than two orders of magnitude). A revised discriminant

Table 12 The alkali and silica data of six pumices collected in 1997 from the sea in the neighbourhood of McDonald Island compared with those of the glass and pumice fractions of the Chatham Islands floater (data provided by Regelous, pers. comm. to Leach, 2014).

Catalogue no.	SiO ₂	Al ₂ O ₃	K ₂ O	Na ₂ O	Na ₂ O + K ₂ O	Agpaitic index
HI1	52.30	18.55	3.58	16.29	19.87	1.65
HI2	54.46	19.82	5.69	12.45	18.14	1.34
HI3	54.64	20.04	5.87	11.96	17.83	1.30
HI4	51.54	18.25	4.06	19.10	23.16	1.96
HI5	54.89	20.22	5.83	12.04	17.87	1.29
HI6	54.58	19.39	5.11	12.64	17.75	1.36
Floater glass	55.03	20.33	5.74	11.24	16.98	1.22
Floater pumice	55.80	20.05	5.91	11.16	17.07	1.23

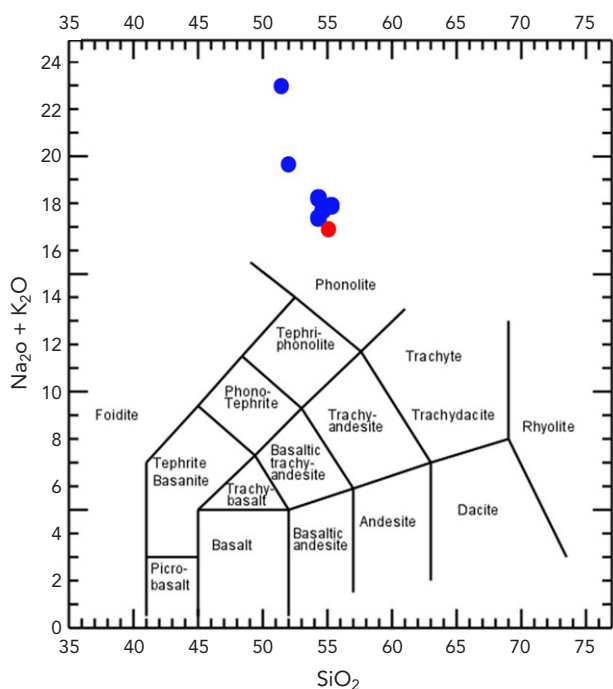


Fig. 11 Six pumice specimens from McDonald Island (blue) and the floater from the Chatham Islands (red).

function method called Popper’s razor helps to overcome some of these objections (Leach & Manly 1982), but in this case information was available for only six specimens of the putative source and it hardly seemed appropriate to

resort to such a complex method. A simpler approach was therefore adopted.

This was similar to what was done before when looking at the individual proportional differences between a series of samples. In this case, however, there is just one sample (the floater), and six samples that are known to belong to one source. Therefore, the means and standard deviations of the source samples were calculated. The standard deviations were then standardised as a proportion of the mean for each element. This permits us to visualise the variability of any one element using a standard point of reference. This is presented in Fig. 12. For clarification, take Na₂O as an example. From Table 13, we can see that the mean is 14.08% with a standard deviation of 2.95%. The standard deviation as a proportion of the mean is 0.21. So the 95% confidence limits are the mean ± 0.42. This is similar to so-called standard scores, or Z-scores. Also plotted on Fig. 12 is the difference between the value for the floater and the mean of the six pumices, as a proportion of the mean. This allows us quickly to visualise where any problems might lie in matching the specimen to the source. The sum of all proportional differences is -0.87 across 32 elements, averaging -0.03. This shows that the floater is very slightly lighter on average than the pumices.

Happily, all but one value lies within the 95% confidence limits of the distribution for each of the 32 elements plotted. The one outlier is vanadium (V). The individual values of

Table 13 The six McDonald Island pumice samples and the Chatham Islands floater (P81381).

Element	HI1	HI2	HI3	HI4	HI5	HI6	Mean	SD	P81381
SiO ₂	52.30	54.46	54.64	51.54	54.89	54.58	53.74	1.43	55.03
TiO ₂	0.63	0.53	0.54	0.29	0.47	0.54	0.50	0.11	0.48
Al ₂ O ₃	18.55	19.82	20.04	18.25	20.22	19.39	19.38	0.81	20.33
Fe ₂ O ₃	4.89	4.80	4.60	4.55	4.42	4.97	4.71	0.21	4.25
MnO	0.14	0.15	0.14	0.17	0.14	0.16	0.15	0.01	0.14
MgO	1.49	0.52	0.58	0.87	0.46	0.89	0.80	0.38	0.62
CaO	1.99	1.49	1.52	1.15	1.44	1.61	1.53	0.27	1.49
Na ₂ O	16.29	12.45	11.96	19.10	12.04	12.64	14.08	2.95	11.24
K ₂ O	3.58	5.69	5.87	4.06	5.83	5.11	5.02	0.98	5.74
P ₂ O ₅	0.15	0.09	0.11	0.03	0.08	0.10	0.09	0.04	0.10
Li	58.15	59.38	58.77	47.78	42.73	64.73	55.26	8.25	0.0
Be	23.06	23.89	23.47	18.37	16.55	25.76	21.85	3.57	0.0
Sc	1.19	1.25	1.22	5.16	4.75	1.01	2.43	1.96	1.48
V	8.26	8.50	8.38	17.40	13.48	5.67	10.28	4.31	22.00
Cr	10.21	10.43	10.32	11.08	19.44	6.21	11.28	4.36	12.58
Co	3.23	3.20	3.22	4.58	6.55	2.01	3.80	1.57	2.97
Ni	16.24	16.10	16.17	10.75	35.19	5.43	16.65	10.05	15.00
Cu	9.90	10.35	10.12	12.47	10.04	8.09	10.16	1.40	0.0
Zn	173.22	173.91	173.57	144.69	130.54	176.45	162.06	19.49	153.50
Ga	51.32	52.75	52.04	45.05	42.86	55.11	49.86	4.79	47.00
Ge	0	0	0	0	0	0	0	0	0.0
As	0	0	0	0	0	0	0	0	6.60
Rb	242.10	243.79	242.94	224.75	215.93	256.96	237.75	14.81	218.00
Sr	72.81	72.87	72.84	154.75	132.13	47.30	92.12	41.59	125.50
Y	37.27	37.22	37.24	32.78	29.67	38.83	35.50	3.51	39.00
Zr	2868.25	2884.37	2876.31	2285.03	2089.13	3002.64	2667.62	380.54	2223.50
Nb	348.27	350.82	349.54	278.92	255.85	364.63	324.67	45.35	282.00
Sb	0	0	0	0	0	0	0	0	0.57
Cs	5.62	5.62	5.62	4.46	3.99	5.89	5.20	0.78	6.65

continued on following page

Table 13 The six McDonald Island pumice samples and the Chatham Islands floater (P81381). *Continued from previous page*

Element	HI1	HI2	HI3	HI4	HI5	HI6	Mean	SD	P81381
Ba	31.66	31.76	31.71	83.07	59.05	19.43	42.78	23.67	20.00
La	146.00	146.10	146.05	125.23	114.62	150.11	138.02	14.50	119.50
Ce	215.37	215.90	215.64	188.64	173.70	223.27	205.42	19.59	187.50
Pr	19.42	19.25	19.33	17.41	15.94	19.77	18.52	1.51	0.0
Nd	49.05	48.91	48.98	46.03	41.75	49.50	47.37	3.02	43.30
Sm	7.05	7.00	7.03	6.74	6.10	7.03	6.83	0.37	5.92
Eu	1.19	1.15	1.17	1.27	1.12	1.12	1.17	0.06	1.02
Gd	5.65	5.67	5.66	5.33	4.73	5.71	5.46	0.38	5.10
Tb	0.96	0.96	0.96	0.87	0.77	0.97	0.92	0.08	0.85
Dy	6.06	6.04	6.05	5.39	4.77	6.19	5.75	0.56	0.0
Ho	1.30	1.29	1.29	1.10	0.98	1.32	1.21	0.14	1.15
Er	4.11	4.12	4.12	3.46	3.08	4.21	3.85	0.47	0.0
Tm	0	0	0	0	0	0	0	0	0.46
Yb	4.62	4.64	4.63	3.81	3.42	4.84	4.33	0.57	3.50
Lu	0.64	0.64	0.64	0.53	0.48	0.66	0.60	0.07	0.47
Hf	49.80	50.05	49.92	39.71	35.76	51.81	46.17	6.70	35.00
Ta	17.40	17.42	17.41	14.15	13.01	18.07	16.24	2.11	13.74
W	0	0	0	0	0	0	0	0	10.70
Ir	0	0	0	0	0	0	0	0	5.20
Pb	50.75	50.59	50.67	42.61	38.10	52.68	47.57	5.82	42.00
Bi	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.0
Th	70.84	70.12	70.48	55.22	49.76	71.96	64.73	9.66	54.50
U	19.12	18.95	19.04	15.03	13.57	19.56	17.55	2.56	15.30

this element for the six pumices are: 8.26, 8.50, 8.38, 17.40, 13.48 and 5.67, with a mean of 10.28 and standard deviation of 4.31; and the floater was 22 ppm. The difference from the mean is 11.72 ppm, which as a proportion is 1.14. The standard deviation expressed as a proportion from the mean is 0.42. So, the floater is 2.7 units from the mean (1.14/0.42). That is, between 95% and 99% confidence limits, which is still within acceptable statistical limits to the

source, but only just. In passing, it is worth mentioning that the four phonolite rocks from McDonald Island had a large range of values for V: 81 ppm, 23 ppm, 4 ppm and 46 ppm (Table 9).

We think we can safely say that this match of object to source is definitely as good as it gets. The REE pattern fits, the type of rock fits, and the major and trace element values fit. It can be stated with a strong sense of certitude that the

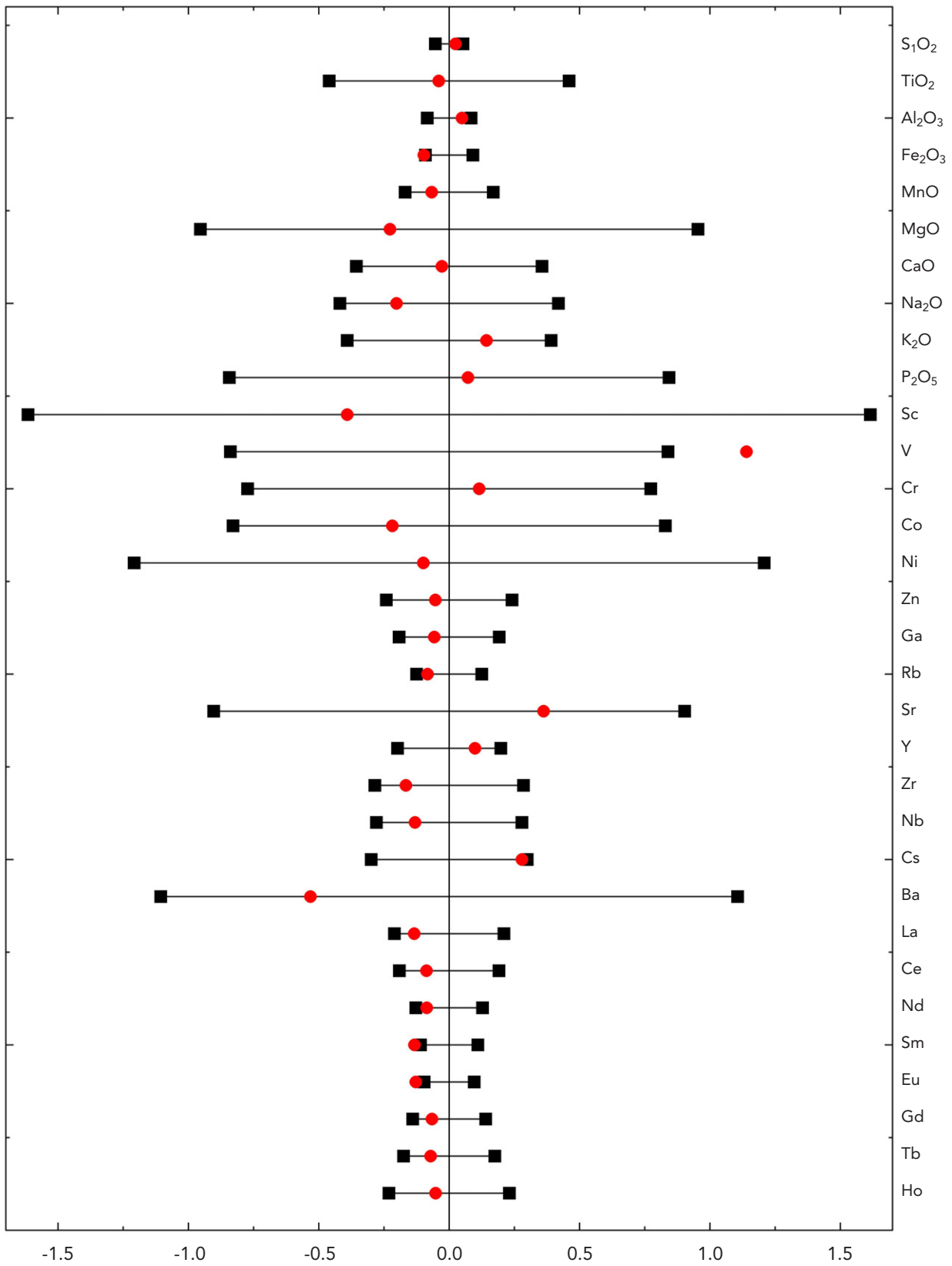


Fig. 12 Standardised plot of the mean and two standard deviations ranges of the McDonald Island pumices. The red dots are the floater from the Chatham Islands plotted on the same scale.

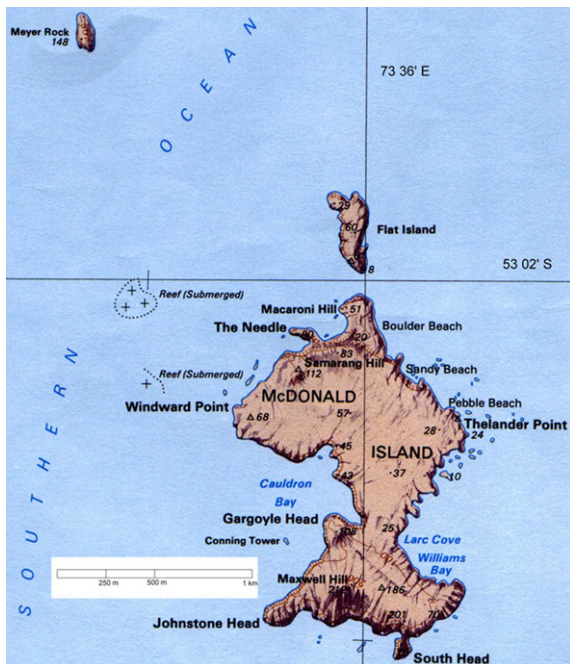


Fig. 13 (*left*) Map of McDonald Island before the recent volcanic activity (photo: Heritage Expeditions 2002).



Fig. 14 (*right*) McDonald Island as it appears today (photo: Google Earth/Digital Globe).

floaters found in the Chatham Islands came from the same source as the six pumice specimens collected in the sea at McDonald Island.

Some further observations

McDonald Island is a small island in the South Indian Ocean at 53°2'S and 72°36'E, lying 45 km to the west of the larger Heard Island. Fig. 13 shows how the island appeared before 2001.

A detailed description of the history of the two islands can be found in Quilty & Wheller (2000). It appears that McDonald Island has been visited only twice. There are reports of large quantities of pumice being washed up on the shores of Heard Island in 1992, which were stated to be chemically identical to the phonolite rocks on McDonald Island. At the time, it was thought that these rafts may have been from a submarine eruption, but in 1997 active steam plumes were seen at the north end of McDonald Island, suggesting subaerial eruption (Quilty & Wheller 2000: 3).

In 1997, two passing ships in the area reported eruptive behaviour on McDonald Island, and a satellite image in 2001 showed that the island had doubled in size (compare Figs 13 and 14). Stephenson *et al.* (2005) documented these huge changes when they sailed within about 1 km of

McDonald Island on their way to Heard Island on board the cruise ship *Akademik Shokalskiy*, operated by Heritage Expeditions of New Zealand.

It should be noted that pumice from McDonald Island is not the only pumice to have washed ashore on Heard Island. The 1962 eruption in the South Sandwich Islands in the southern Atlantic released vast quantities of pumice (Gass *et al.* 1963), and some of this found its way to Heard Island, about 6400 km distant, in 1963. Chemical analysis showed this to be dacite high in silica. This same pumice also turned up on Australian coasts from 1963 to 1967, and on the Juan Fernández Islands off Chile in 1965 (Sutherland & Olsen 1968). It has also turned up in New Zealand (Coombs & Landis 1966) and Hawai'i (Jokiel & Cox 2003).

These landfalls are bound to have been made courtesy of the Antarctic Circumpolar Current (Fig. 15), which sweeps around Antarctica in a clockwise direction and is one of the largest ocean currents. Sailors frequently make use of the current and its associated westerly winds, which assist any voyage from west to east in southerly waters.

It is therefore not surprising that this piece of pumice with glass attached from McDonald Island ended up in the Chatham Islands, a great-circle distance of at least 7400 km. The pumice was presumably ejected during the massive changes that took place on McDonald Island sometime

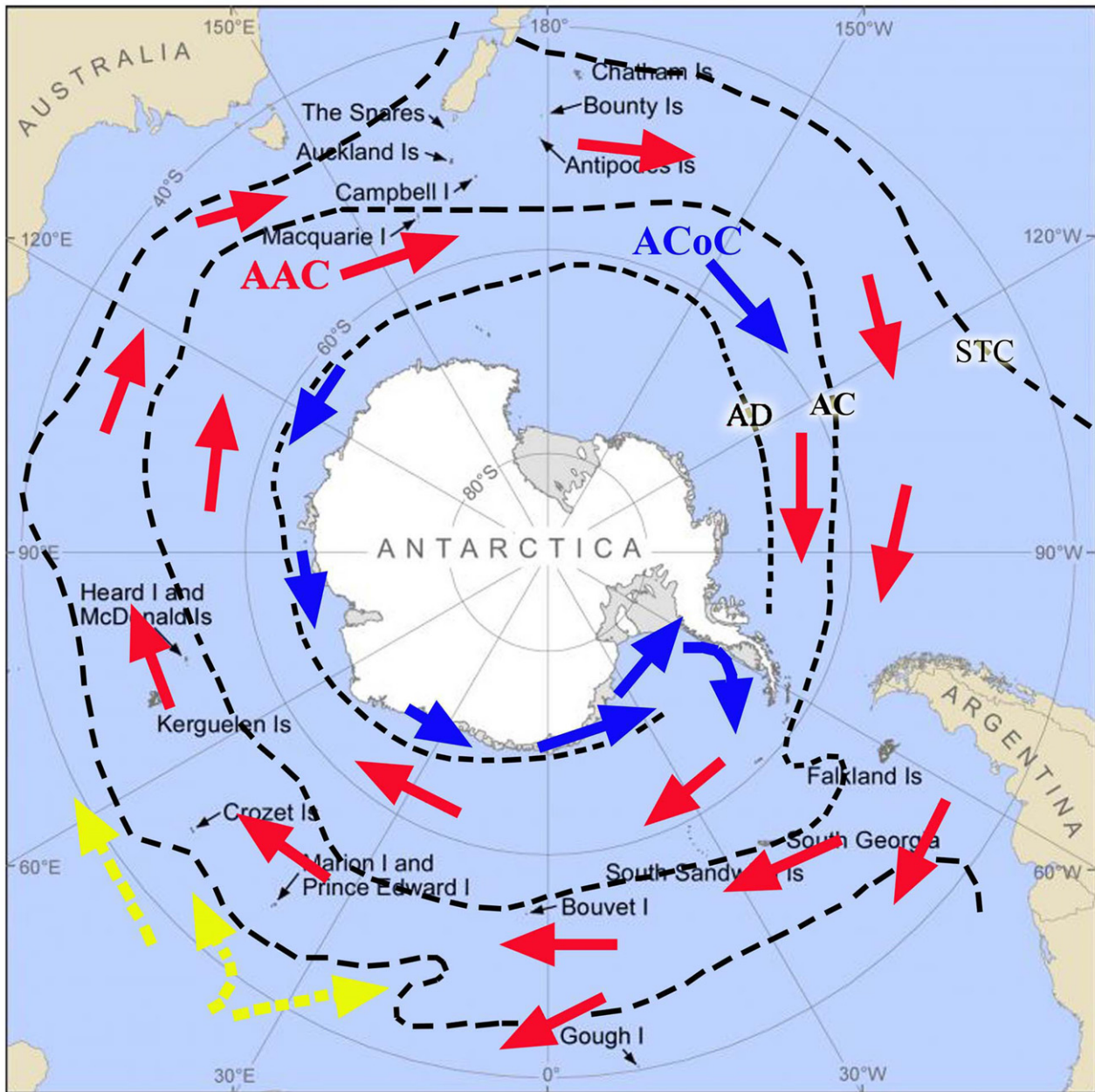


Fig. 15 Major currents and fronts in the Southern Ocean and subantarctic region: Antarctic Circumpolar Current (AAC), Antarctic Coastal Current (ACoC), Antarctic Divergence (AD), Antarctic Convergence (AC), Subtropical Convergence (STC).

between 1997 and 2001. According to Rhys Richards, the pumice was found some years before it was retrieved for analysis in 2008–09. Unfortunately, we will probably never know exactly how long it took to make the journey.

Acknowledgements

The senior author would like to thank his colleagues for their contributions to this complex research project: Rhys

Richards for permission to carry out analysis of the obsidian floater from the Chatham Islands; Hamish Campbell for access to the specimen and his enthusiasm for the project; Katherine Holt for EMP analysis of the pumice; Steve Weaver for XRF analyses; Nelson Eby for NAA analysis; and Marcel Regelous for the unpublished geochemical data of samples from McDonald Island. Thanks are also due to Barry Weaver of the School of Geology and Geophysics, University of Oklahoma, USA, for supplying analytical data

on obsidian from Ascension Island. Finally, the assistance of Janet Davidson is acknowledged for her help with checking and editing the content of this paper.

Notes

- 1 A europium (Eu) anomaly occurs when there is a striking difference in the concentration of Eu relative to the other rare earth elements. It is said to be positive if Eu is enriched, or negative if it is depleted. Some rocks are known to have a negative or positive Eu anomaly and some not.
- 2 <http://georoc.mpch-mainz.gwdg.de/georoc>.

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Appendix 1: Details of samples in this report

11290	Ormonde seamount, Gorringe, Strait of Gibraltar
302	Igwageta, Fergusson Island
35504A	Macauley Island source
35505A	Raoul Island source
35506A/P40908	Raoul Island source
35507A/P81381	Chatham Island floater
5105	Emily Bay, Norfolk Island artefact, Atholl Anderson
5145	DAFF site, Papua New Guinea, Matt Spriggs
65119, 65124, 65125, 65133	McDonald Island
AI991	Wekwok standard 2000
ANU306	Numanuma, East Fergusson Island
ANU3830	Nowak 3, Choiseul, Papua New Guinea, Matt Spriggs
GH11	Gharyan, Libya
GX219	Raoul Island source
MAC18E	Macauley Island source
Mayor Island	Obsidian standard
MB35.2	Mt Sidley, Marie Byrd Land, Antarctica (Panter <i>et al.</i> 1997)
MB35.5	Mt Sidley, Marie Byrd Land, Antarctica (Panter <i>et al.</i> 1997)
P81381	Chatham Islands floater
RGM-1	USGS Geochemical Standard: rhyolite, Glass Mountain
STM-1	USGS Geochemical Standard: peralkaline nepheline syenite, Table Mountain