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Potassium isotope abundances in Australasian tektites and microtektites

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Abstract–We report electron microprobe determinations of the elemental compositions of 11 Australasian layered tektites and 28 Australasian microtektites; and ion microprobe determinations of the $^{41}K/^{39}K$ ratios of all 11 tektites and 13 of the microtektites. The elemental compositions agree well with literature values, although the average potassium concentrations measured here for microtektites, 1.1–1.6 wt%, are lower than published average values, 1.9–2.9 wt%.

The potassium isotope abundances of the Australasian layered tektites vary little. The average value of $\delta^{41}K$, $0.02 \pm 0.12‰$ (1σ mean), is indistinguishable from the terrestrial value (= 0 by definition) as represented by our standard, thereby confirming four earlier tektite analyses of Humayun and Koeberl (2004). In agreement with those authors, we conclude that evaporation has significantly altered neither the isotopic nor the elemental composition of Australasian layered tektites for elements less volatile than potassium.

Although the average $^{41}K/^{39}K$ ratio of the microtektites, $1.1 \pm 1.7‰$ (1σ mean), is also statistically indistinguishable from the value for the standard, the individual ratios vary over a very large range, from $-10.6 \pm 1.4‰$ to $+13.8 \pm 1.5‰$ and at least three of them are significantly different from zero. We interpret these larger variations in terms of the evaporation of isotopically light potassium; condensation of potassium in the vapor plume; partial or complete stirring and quenching of the melts; and the possible uptake of potassium from seawater. That the average $^{41}K/^{39}K$ ratio of the microtektites equals the terrestrial value suggests that the microtektite-forming system was compositionally closed with respect to potassium and less volatile elements. The possibility remains open that $^{41}K/^{39}K$ ratios of microtektites vary systematically with location in the strewn field.

INTRODUCTION

Microtektites make up a major fraction of the mass of the Australasian and other tektite fields (Glass 1982). We decided to measure potassium isotope abundances in Australasian microtektites partly to fill a knowledge gap, but also out of our suspicion that evaporation from the molten precursors of tektites ought to have had some effect on their isotopic compositions.

Arguments about large evaporative losses or "vapor fractionation" from tektites began 40 years ago. Walter and Clayton (1967) argued for vapor fractionation based on high-temperature laboratory studies of silicate melts. Their work showed a correlation between increasing $^{18}O/^{16}O$ ratios and decreasing SiO_2 concentrations. Such a relationship had previously been found for one group of tektites, bediasites. It would hold if oxygen had evaporated freely from the tektite melts. Walter (1967) argued that Australasian tektites also lost material due to evaporation.

Although plausible, the vapor fractionation hypothesis for tektites has fared poorly. Molini-Velsko et al. (1982) reported that the heavier isotopes of silicon are depleted in bediasites. Vapor fractionation would have caused enrichment. Molini-Velsko and co-workers concluded that the bediasites acquired their isotopic abundances not through evaporative losses, but from their source material. Esat and Taylor (1987) observed at most small variations in the $^{26}Mg/^{24}Mg$ ratios of Ivory Coast and Australasian microtektites and of flanged Australite buttons. Based on these results they ruled out vaporization losses for magnesium. In a study of moldavites, Engelhardt et al. (1987) reported several geochemical trends inconsistent with control by vaporization.

Searching for isotope fractionation of boron, a moderately volatile element, Chaussidon and Koeberl (1995) analyzed tektites and other natural glasses. The small variations in ^{11}B abundances found did not follow the predictions of the Rayleigh law. These authors ruled out vapor fractionation of boron for most tektites. Humayun and Koeberl (2004) dealt the vaporization hypothesis another blow when they reported that four Australasian tektites contain isotopically normal abundances of potassium, another moderately volatile element.

The studies described above refer almost entirely to tektites of standard size and therefore leave microtektites largely unexamined. The Rayleigh law predicts that lighter isotopes evaporate preferentially, but only if the fluid a) is well stirred for b) long enough at c) high enough temperatures for there to be significant evaporation, and d) is under low ambient pressures. In discussing the lack of potassium isotope fractionation in conventional tektites, Humayun and Koeberl (2004) focused mainly on condition (c), above, i.e., on the likelihood that temperatures and hence potassium vapor pressures were too low for much evaporation to have occurred. This observation should apply a fortiori to the more refractory magnesium (see Esat and Taylor 1992; Alexander et al. 2002). They also noted, however, that the viscosity of the highly silicic tektite melts would discourage rapid diffusion, leading to a violation of condition (a) and confinement of any isotopic fractionation to a thin rind. Unsure of which constraint, (a) or (c), might have limited potassium isotopic fractionation in tektites, Humayun and Koeberl (2004) left open its possibility in the much smaller microtektites, where mixing could have been faster. They also noted that microtektites might have formed from droplets with a wider range of temperatures than did conventional tektites. Indeed, Koeberl et al. (1999) showed that high-magnesium (3.48–6.48 wt%) or bottle-green Australasian microtektites contain isotopically heavy Li. Subsequently Glass et al. (2004, their section 4.3.1) proposed that this group of objects formed by vapor fractionation of normal microtektites. Finally, the results of McDougall and Lovering (1969) point to a small but systematic deficiency of 2.5–7% in the K abundances of australite flanges relative to australite cores.

We present analyses of potassium isotope abundances and of elemental concentrations in several Australasian microtektites, which are similar to the Australasian microtektites described by Glass et al. (2004). Our main purpose was to test the hypothesis that evaporation from the melt caused the loss of potassium and enrichment of the heavier isotopes. As controls, we analyzed several Australasian layered tektites. Compared to Australasian splash-form tektites, the layered ones contain relatively high concentrations of the most volatile elements (the halogens, B, Cu, Zn, Ga, As, Se, Sb, and Pb; Koeberl 1992). Accordingly, the layered Australasian tektites seemed least likely to have experienced mass losses and attendant isotopic fractionation due to vaporization.

EXPERIMENTAL METHODS

Samples

Unless otherwise noted, all the samples described in this section came from the collection of one of the authors (B. P. G.).

We selected eleven hand specimens of Australasian layered tektites as controls, prepared polished thick sections at Rutgers University, and used them for both electron and ion microprobe analysis. In addition we analyzed a small fragment of an ablated tektite from the Central Indian Ocean (from M. Shyam Prasad, National Institute of Oceanography, Goa, India [Glass et al. 1996]) and a high-Mg tektite from Java, J35 from the collection of Dean Chapman (Chapman and Scheiber 1969).

All the microtektites came from the collection of B.P.G., already in the form of polished sections on two mounts labeled 589 and 633. All the microtektites were recovered from a total of six different piston cores taken in the Central Indian Ocean: 589-1,2,3 from core RC14-23; 589-4,5,6,7,8 from core V19-171; 589-9,10,11 from core V19-169, 589-12,13,14,15 from core MSN48-G; 633 1-7 from V29-39, 633 8-11 from MSN-48G, and 633 12,13 from RC14-24.

Ion Microprobe Analysis

We measured the isotope abundances of potassium with the Carnegie Cameca 6f ion microprobe, using a 12.5 kV O^- primary beam in the shaped or flat-bottomed illumination mode, a 10 kV secondary accelerating voltage, and a 50 eV energy window. We used a 100-µm field aperture and 2–5 min presputter to minimize the contribution from surface contamination to the analyses. Primary beam currents were ~1 nA and spot sizes were ~25 µm across. Each reported value is the average of 50 cycles of analysis. During each cycle ^{39}K and ^{41}K were analyzed for 1 and 5 s, respectively. For the microtektite analyses, ^{30}Si and ^{40}CaH were also monitored in every cycle for 1 s each. The mass resolution was 5000 and all interferences resolved (^{39}K from ^{23}Na^{16}O and ^{41}K from ^{25}Mg^{16}O and ^{40}Ca^{1}H). No significant tailing was observed. The potassium instrumental mass fractionation factor (IMF) was determined by analysis of the Standard 12 glass (see below). Comparisons with very similar results obtained for a rhyolite standard (see below) suggest that the IMF is not very sensitive to glass composition. The reproducibility (one standard deviation) of the standards was 0.4‰ for the Australasian layered tektite and 0.9‰ for the microtektite analyses. These values provide a lower bound on the errors inherent in any single measurement. Errors quoted below for individual measurements are all 1σ, and were obtained by combining, in quadrature, the uncertainties in the

IMF and the internal precision of the measurements. Alexander and Grossman (2005) and Yu et al. (2003) and references therein provide addition information on the ion microprobe methods.

Electron Microprobe Analysis

We included among our electron microprobe standards three samples with tektite-like composition. Two of them came from a collection of materials prepared by E. Jarosewich for the U.S. Natural History Museum (Washington, D.C.). USNM 2213 is an artificial glass fabricated by Corning Glass; USNM 72854 is a rhyolite collected at Yellowstone National Park and identified in some publications as VG 568. Jarosewich et al. (1980) give the chemical composition of this glass. To our knowledge, no potassium isotope data are available for it. The third tektite-like standard, Standard 12, is a glass that was fabricated by Corning Glass. Each microtektite mount included a small piece of Standard 12.

We determined the elemental composition of the samples in the course of several runs by using electron microprobes (EMPs) at Rutgers University and the Carnegie Institution of Washington, and a scanning electron microscope with an energy dispersive X-ray (EDX) analyzer at the University of Delaware. The EMP at Rutgers was run with an accelerating voltage of 15 kV and a defocused beam rastered to minimize loss of alkalis. We calibrated the Rutgers microprobe on standard silicates and reduced the data using conventional ZAF corrections (Boesenberg 1995; Boesenberg and Delaney 1997). Running conditions and data analysis procedures at the Carnegie EMP were similar. The EDX analyses from the University of Delaware (Table 2) are for layered tektites only. This work was done on crushed subsamples that were sieved; the 63–125 μm size fractions were separated into different density fractions using heavy liquids in an attempt to recover relict mineral grains. Glass fragments from each density fraction were mounted and polished. The EDX was a PGT (Princeton Gamma-Tech) System 4 used in combination with a Cambridge S90B SEM. The accelerating voltage was set at 25 kV. Samples were analyzed with the beam current adjusted so as to produce 2000 counts s^{-1}. Standard 12 was run before and after each sample run to correct for instrument drift. The standard and the sample compositions obtained by EDX were normalized to 100 wt%. The independently known oxide content of the standard was divided by the measured oxide content of the standard after normalization in order to get correction factors for each element. These correction factors were then multiplied by the normalized oxide contents of the samples to produce "standardized" sample compositions. The average composition of each sample is based on between 6 and 152 analyses.

For greater consistency with earlier results for microtektite compositions published by Glass and co-workers, we have normalized all Rutgers elemental concentrations for microtektites (but not for tektites) upward by a factor of 1.07. This adjustment increased the average sum of all oxide percentages to 99.4 wt% and, for the relevant electron microprobe run, brought the Rutgers analyses of Standard 12 into agreement with those of B. P. G.

RESULTS AND DISCUSSION

Australasian Tektites

Bulk Compositions

Table 1 gives the compositions of our standards. Table 2 gives the values of $\delta^{41}K$ and oxide compositions of eleven Australasian layered tektites. Overall, the elemental analyses from the three different electron microprobe laboratories agree well. The worst disagreements are for sodium for which the Rutgers analyses are systematically lower. For comparison, Table 2 includes the average elemental composition of Australasian layered tektites given by Glass et al. (2004) based on the earlier work of Glass and Koeberl (1989). We find, on average, higher SiO_2 concentrations (77.0 wt% versus 72.5 wt%) than they did, and correspondingly lower concentrations of most other elements. These differences are to be expected, as the layered tektites are rather heterogeneous both internally and from one sample to another. Koeberl (1992) attributed systematic differences in the elemental compositions of light and of dark layers to "incomplete mixing of different parent materials."

$\delta^{41}K$

We express the relative isotopic abundance of ^{41}K in terms of $\delta^{41}K$, which is calculated from the usual relation

$$\delta^{41}\mathrm{K}(‰) = \left(\frac{(^{41}\mathrm{K}/^{39}\mathrm{K})_{\mathrm{sample}}}{(^{41}\mathrm{K}/^{39}\mathrm{K})_{\mathrm{standard}}} - 1 \right) \times 1000 \qquad (1)$$

In calculating $\delta^{41}K$, we assume that our standard for potassium (standard 12) contains potassium with the average terrestrial $^{41}K/^{39}K$ ratio, the absolute value of which need not be specified for the present work. (For reference, the average (atomic) ratio is 0.0721677 [Böhlke et al. 2005]).

The potassium isotope ratios for the eleven Australasian layered tektites span a narrow range of values, from $\delta^{41}K$ = –0.38‰ for A-65 to +0.89‰ for TU-2, varying by approximately 1.3‰ overall (Fig. 1). In only one marginal case, TT-41, does our result differ from zero by more than two standard deviations. In agreement with Humayun and Koeberl (2004), we conclude that the potassium in layered type tektites is isotopically normal. We also conclude that for this set of samples, the statistical uncertainties of the measurements give one reasonable estimate of the overall 1σ reproducibility, about ±0.4‰.

Table 1. Electron microprobe standard compositions (wt%).

		SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Cr_2O_3	Total	Ref.
USNM 2213	Corning Glass	79.56	0.51	11.09	5.08	0.10	1.48	2.72	0.72	1.87	0.01	103.15	a
		75.75	0.50	11.34	4.90	0.11	1.51	2.66	1.06	1.88		99.82	b
USNM 72854	Rhyolite	78.03	0.08	12.33	1.16	0.01	0.03	0.45	2.84	4.49	0.00	99.41	a
		76.71	0.12	12.06	1.24	0.03	0.01	0.50	4.89	4.89		99.44	c
Glass Standard 12	Corning Glass	63.43	0.72	16.2	6.47	0.15	2.40	3.36	1.10	2.78	0.01	96.6	d
		60.8	0.43	15.6	6.32	0.16	2.52	3.19	1.03	2.73	0.01	92.7	a
		65.0	0.7	16.1	6.79		2.52	3.78	1.68	2.8		99.4	b

a = Rutgers University.
b = The Corning Glass Works.
c = See Boesenberg (1995).
d = Carnegie.

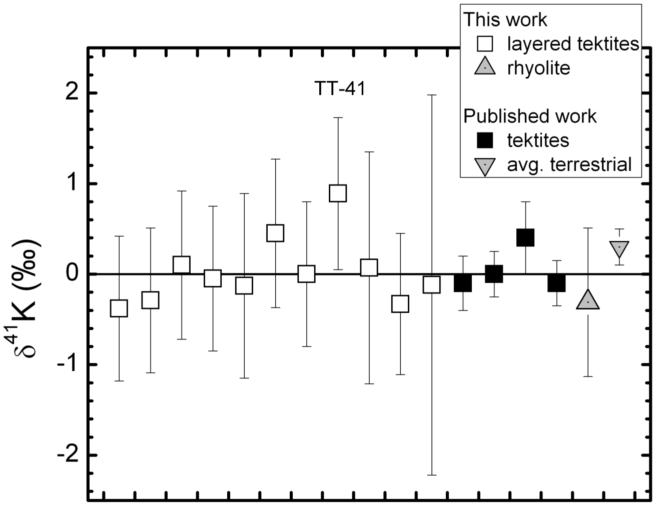

Fig. 1. Within the 2σ uncertainties, typically 0.8‰, the values of δ^{41}K in Australasian tektites are the same as the average terrestrial value. Results from published work are from Humayun and Koeberl (2004).

Australasian Microtektites

Elemental Compositions

Table 3 gives the oxide compositions and the values of δ^{41}K measured for fifteen microtektites on mount 589; Table 4 shows the oxide abundances measured for thirteen microtektites on mount 633. The results from the Rutgers and Carnegie electron microprobes generally agree well except for sodium. Agreement between our data and previously published compositions for Australasian microtektites is fairly good; differences are within the 1σ uncertainties and consistent with the wide range of compositions known for Australasian microtektites. To compare our average results (Table 3, note e) with the averages of Glass and Koeberl (2006) and Glass et al. (2004) (Table 3, notes f and g), we average the Carnegie data for mount 589 but exclude the high-Mg object 589-3 because of its unusually high Mg content. Our results agree with those of Glass et al. (2004) to within one standard deviation for all elements except Ca (1.5 σ). Glass and Koeberl (2006) quote somewhat higher values than ours for Na_2O (1.6 versus 0.75) and K_2O (2.9 versus 1.3), and a lower one for Mg (3.1 versus 4.7). Although the averages differ, the ranges observed for these three oxides are comparable for the most part (I=this work, II=Glass et al. (2004), III=Glass and Koeberl (2006)): Na_2O, 0.43–0.81(I); 0.22–1.69(II); 0.83–2.39(III); K_2O 0.8–2.14(I); 0.8–2.8(II); 1.07–4.54(III); MgO, 3.13–7.37(I); 2.11–7.99(II); 2.33–4.06. These comparisons include microtektites belonging to the "normal" and "intermediate Mg" groups, i.e., those with MgO < 8 wt%. We conclude that differences in the averages may be due to regional variations in composition.

In Fig. 2, we show the elemental data for microtektites and Australasian layered tektites normalized to abundances for the Earth's crust (Wedepohl [1981] as quoted in Lodders and Fegley [1998, p. 140]). The elements are plotted in order of increasing cosmochemical volatility, an order that need not apply strictly to the terrestrial setting but ought to be indicative. For all elements except moderately volatile Si and more volatile sodium and potassium, the concentrations in the microtektites exceed those in the Australasian layered tektites. In particular, for our set of samples, the average potassium abundance in microtektites is about 40% of its abundance in the Australasian layered tektites.

Previous studies have shown that the Al_2O_3, MgO, CaO, and Na_2O contents of the Australasian microtektites vary inversely with the silica content and that the trends match those of the Australasian tektites, but have greater scatter and extend to lower silica contents (Cassidy et al. 1969; Glass 1970, 1972). The major oxide contents of the Australasian tektites and microtektites suggest that the source rock was probably a sandstone with variable mixtures of a shale (clayey) component and a sand (quartz rich) component (Taylor 1962; Chao 1963; Schnetzler and Pinson 1963; Taylor and Kaye 1969; Glass et al. 2004). Our data are consistent with this conclusion.

Potassium Zoning Profiles

As expected, no variations of potassium concentration are apparent in scans taken across the small fragments of either the artificial glass standard 12 or of the Central Indian

Table 2. Elemental composition (wt%) and δ^{14}K (‰) of Australasian layered and other tektites.

Sample	Source location	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Cr_2O_3	Total	Ref.	δ^{41}K
A-65	Danang, Vietnam	76.29	0.70	10.76	3.77	0.06	1.62	1.55	1.54	2.50	0.01	98.80	a	−0.38 ± 0.40
		74.4	0.7	11.8	4.7	0.1	2.2	2.7	1.2	2.4		100.2	c	
C-2	Muong Nong, Laos	75.41	0.64	11.01	3.88	0.10	1.74	1.88	1.47	2.52	0.01	98.67	a	−0.29 ± 0.40
		73.0	0.7	12.2	4.9	0.1	2.1	2.3	1.7	2.6		99.6	c	
CG-1	Guandong, China	73.99	0.72	11.91	4.23	0.09	1.75	1.83	1.37	2.54	0.02	98.46	a	+0.10 ± 0.41
		74.9	0.7	11.5	4.6	0.1	1.6	1.8	1.6	2.7		99.5	c	
CNC-1	Hainan, China	75.49	0.59	11.34	4.14	0.10	1.78	1.89	1.13	2.44	0.01	98.92	b	−0.05 ± 0.40
		73.6	0.7	12	4.9		1.7	2.2	1.6	2.8		99.5	c	
MP-26	Muong Phin, Laos	75.80	0.74	11.35	3.87	0.05	1.66	1.11	1.49	2.49	0.01	98.57	a	−0.13 ± 0.51
		77.42	0.73	11.71	4.05	0.05	1.79	1.22	0.60	2.36	0.02	99.95	b	
		75.65	0.7	11.75	4.13		1.83	1.73	1.12	2.43		99.33	c	
TK-26	Nam Dan, Vietnam	77.16	0.64	10.62	3.88	0.09	1.42	1.10	1.22	2.47	0.01	98.61	a	+0.45 ± 0.41
		81.65	0.59	10.59	4.19	0.09	1.48	1.13	0.72	2.49		102.94	b	
		78.3	0.6	11.0	3.9		1.5	1.3	0.8	2.5		99.9	c	
TK-27	Nam Dan, Vietnam	78.04	0.75	11.93	4.44	0.09	1.78	1.84	0.89	2.50	0.01	102.27	b	0.00 ± 0.40
		76.3	0.7	10.9	4.6		1.5	1.4	1.4	2.5		99.3	c	
TT-41	Phang Daneg, Thailand	75.50	0.67	11.02	3.93	0.09	1.63	1.57	1.46	2.50	0.01	98.39	a	+0.89 ± 0.42
		76.4	0.6	11.8	3.9		1.8	1.9	1.1	2.5		100.0	c	
TU-2	Ubonratchathani, Thailand	78.21	0.69	11.21	4.16	0.09	1.72	1.64	0.83	2.44	0.01	101.01	b	+0.07 ± 0.64
		79.5	0.6	9.9	3.5		1.5	1.6	1.0	2.3		99.9	c	
TU-3	Ubonratchathani, Thailand	78.91	0.71	10.83	4.03	0.04	1.70	1.66	0.77	2.45	0.01	101.10	b	−0.33 ± 0.39
VC-9	Dalat, Vietnam	76.20	0.67	11.12	3.99	0.07	1.48	1.21	1.22	2.63	0.01	98.60	a	−0.1 ± 1.0
		79.04	0.72	11.57	4.03	0.08	1.46	1.15	0.92	2.68	0.01	101.66	b	
		76.4	0.6	11.0	4.5		1.5	1.5	1.2	2.6		99.3	c	
Avg a		75.78	0.66	11.09	4.06	0.08	1.60	1.60	1.35	2.45	0.01	98.67		
Avg b		78.39	0.68	11.31	4.15	0.08	1.67	1.50	0.84	2.48	0.01	101.12		
Avg c		76.82	0.64	10.96	4.28		1.54	1.6	1.2	2.54		99.58		
Avg all		76.95	0.66	11.13	4.15	0.08	1.61	1.57	1.13	2.48	0.01	99.76		
Layered		72.50	0.76	12.94	4.76		2.08	2.49	1.42	2.64	0.009	99.59	d	
586-1	Indian Ocean	72.62	0.59	10.54	5.20	0.09	3.56	2.09	1.02	2.05	0.04	97.79	a	
		69.36	0.76	13.52	6.33	0.10	4.36	3.60	0.64	2.18	0.04	100.89	b	
		68.7	0.63	13.3	6.33		3.82	3.74	0.92	2.00		99.44	f	
586-2	J35 High-Mg	74.64	0.59	10.95	5.64	0.11	3.98	2.35	0.75	2.05	0.04	101.10	b	
		73.1	0.66	10.9	5.68	0.11	3.65	2.32	1.15	2.10	0.04	99.71	e	

a = Carnegie. b = Rutgers. c = Dass (1999). d = Glass et al. (2004). e = Chapman and Scheiber (1969). f = Glass et al. (1996).

Table 3. Microtektite compositions[a] (wt%) for mount 589.

Sample	Core	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Cr_2O_3	Total
589-1	RC14-23	66.40	0.74	13.22	6.20	0.12	7.37	3.29	0.56	0.80	0.04	98.73
589-2	RC14-23	70.05	0.68	12.25	5.57	0.10	5.26	2.80	0.68	1.51	0.04	99.19
589-3	RC14-23	61.61	0.84	15.43	5.82	0.12	10.10	3.92	0.42	0.51	0.10	98.87
589-4	V19-171	66.36	0.77	14.54	5.94	0.11	5.36	2.79	0.65	1.22	0.04	97.78
589-5	V19-171	66.75	0.78	14.38	5.73	0.12	5.62	3.13	0.56	1.27	0.04	98.37
589-6	V19-171	60.89	0.99	19.93	5.67	0.13	5.03	3.61	0.54	0.89	0.03	97.71
589-7	V19-171	59.53	1.07	20.76	5.89	0.13	5.34	3.72	0.43	0.81	0.02	97.69
589-8	V19-171	67.28	0.73	12.42	6.65	0.12	7.34	3.26	0.49	1.09	0.10	99.48
589-9	V19-169	67.01	0.74	13.10	5.85	0.11	6.45	3.44	0.57	0.91	0.06	96.62
589-10	V19-169	68.04	0.75	14.09	5.25	0.11	4.67	3.53	0.62	1.28	0.03	97.36
589-11	V19-169	65.49	0.76	14.34	5.67	0.11	6.91	3.41	0.63	0.91	0.06	95.38
589-12	MSN48-G	69.19	0.70	12.92	5.27	0.10	5.69	2.82	0.56	1.09	0.03	98.38
589-13	MSN48-G	74.08	0.62	10.78	4.57	0.10	3.99	2.34	0.54	1.28	0.03	98.34
589-14	MSN48-G	70.62	0.70	12.50	5.00	0.10	5.13	2.79	0.63	1.22	0.03	98.72
589-15	MSN48-G	71.08	0.67	12.50	4.92	0.09	3.59	2.79	0.81	2.14	0.02	98.60
Average[b]		67.3	0.74	14.02	5.24	0.10	5.05	2.98	0.73	1.22	0.03	97.41
±		4.8	0.13	3.09	0.56	0.02	1.76	0.53	0.16	0.57	0.02	
Average[c]		66.8	0.79	14.57	5.74	0.12	6.33	3.32	0.46	1.12	0.05	99.24
±		4.2	0.12	2.77	0.57	0.01	1.96	0.51	0.09	0.55	0.03	
Average[d]		67.06	0.77	14.21	5.60	0.11	5.85	3.18	0.73	1.13	0.04	98.43
±		4.0	0.12	2.75	0.53	0.01	1.61	0.44	0.16	0.38	0.02	
Average[e]		67.7	0.75	13.9	5.20	0.10	4.7	2.9	0.75	1.3	0.03	97.36
±		4.8	0.16	3.3	0.60	0.02	1.4	0.5	0.16	0.6	0.02	
Average[f]		67.2	0.78	15.6	5.91	0.05	3.07	2.88	1.61	2.90		100.0
Average[g]		69.6	0.82	14.9	5.08		3.23	3.52	0.92	1.83		99.97

[a] Average of at least 4 analyses, two at Rutgers and two at Carnegie, except for 589-8, which was analyzed only at Rutgers.

[b] Average of all microtektites on mount 589 analyzed at Carnegie.

[c] Average of all microtektites on mount 589 analyzed at Rutgers and normalized to results for synthetic glass standard supplied by Glass B. P.

[d] Average of all electron microprobe data for microtektites on mount 589 excluding Na measured at Rutgers.

[e] Average of all microtektites on mount 589 analyzed at Carnegie except high-Mg microtektite 589-3.

[f] Average of Australasian microtektites from three sites in the South China Sea (Glass and Koeberl 2006, p. 312).

[g] Average for normal Australasian microtektites (Glass et al. 2004).

Table 4. Microtektite compositions[aa] (wt%) for mount 633.

Sample	Source location	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	K_2O	Cr_2O_3	Total
633-1	V29-39	64.55	0.73	14.21	8.09	0.14	5.46	3.47	2.01	0.07	99.38
633-2	V29-39	68.81	0.84	14.74	5.50	0.10	2.88	3.38	1.87	0.03	98.57
633-3	V29-39	66.68	0.79	14.48	6.80	0.12	4.17	3.43	1.94	0.05	98.98
633-4	V29-39	53.01	0.99	21.70	4.62	0.09	13.98	5.49	0.14	0.11	100.28
633-5	V29-39	72.36	0.73	12.40	4.03	0.09	6.14	3.09	0.93	0.03	100.12
633-6	V29-39	69.43	1.07	17.55	3.18	0.07	3.32	3.32	1.03	0.01	99.23
633-7	V29-39	60.22	0.48	16.20	6.24	0.12	12.56	4.72	0.29	0.15	101.22
633-8	MSN-48G	64.83	0.78	16.87	4.71	0.10	7.94	4.02	0.66	0.08	100.22
633-9	MSN-48G	60.78	0.78	14.70	5.20	0.09	2.53	4.53	2.71	0.02	92.07
633-10	MSN-48G	65.75	0.88	16.48	5.40	0.12	3.51	3.60	2.96	0.03	99.55
633-11	MSN-48G	75.32	0.60	10.80	4.65	0.09	4.33	2.53	1.47	0.04	100.25
633-12	RC14-24	70.33	0.72	13.24	5.61	0.11	2.90	2.89	2.57	0.04	98.95
633-13	RC14-24	72.69	0.42	13.84	5.77	0.11	3.38	3.17	1.91	0.03	101.77
Average[b]		66.5	0.75	15.2	5.4	0.10	5.6	3.7	1.6	0.05	99.3
±		6.0	0.18	2.7	1.2	0.02	3.7	0.8	0.9	0.04	
Average[c]		68.3	0.76	14.5	5.4	0.10	4.2	3.4	0.48	1.8	99.3
±		4.3	0.16	2.0	1.3	0.02	1.7	0.5	0.19	0.8	
Average[d]		67.2	0.78	15.6	5.91	0.05	3.07	2.88	2.90		100.0
±		4.0	0.08	2.6	0.68	0.02	0.48	0.89	0.74		

[a] Data from Rutgers only, typically at least two spots. Sodium data not reported (see section 3.1.2).

[b] Average of all microtektites on mount 633.

[c] Average omitting high-Mg microtektites 633-4 and 633-7.

[d] Average for Australasian microtektites from Glass and Koeberl (2006, p. 312).

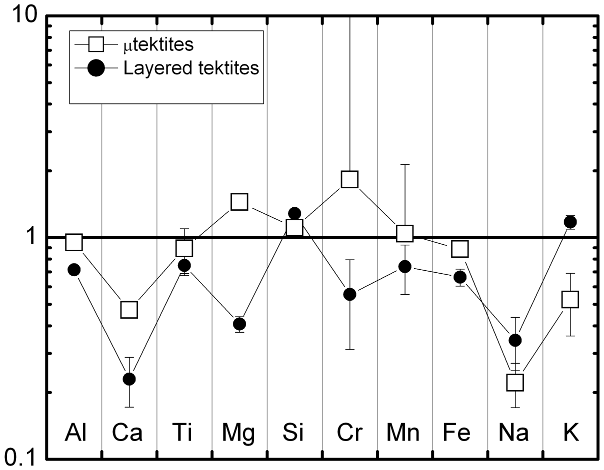

Fig. 2. In comparison to the average Australasian layered tektites, the average Australasian microtektites contain higher concentrations of more refractory elements and lower concentrations of Na and K. Elemental concentrations (E) are normalized to those of the Earth's crust (see text).

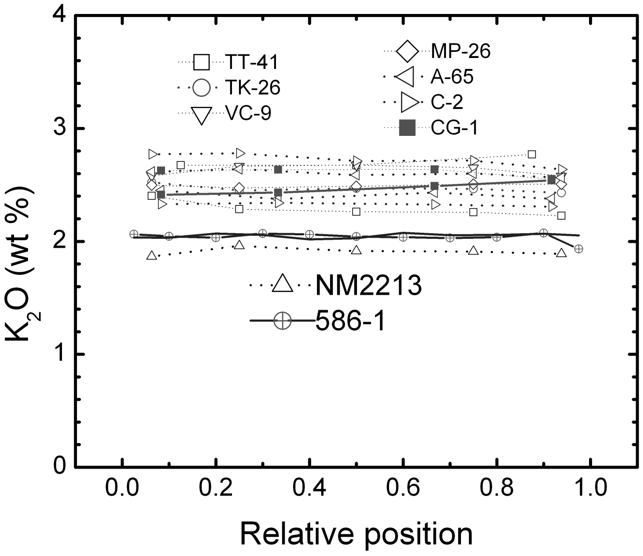

Fig. 3. K concentrations vary little in scans taken across Australasian tektites at the Carnegie Institution of Washington. Filled squares show results for two scans taken at right angles across CG1. Sample NM2213 is an artificial glass. The "relative position" is the distance along the traverse divided by the particle diameter; the relative positions of the two ends of a diameter are 0 and 1.

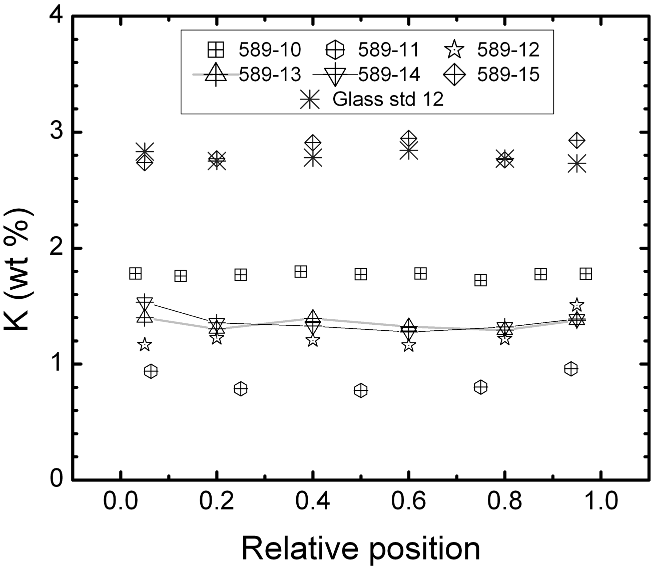

Fig. 4. Potassium profiles in microtektites on mount 589 measured at the Carnegie Institution of Washington. Evidence for potassium zonation is generally weak.

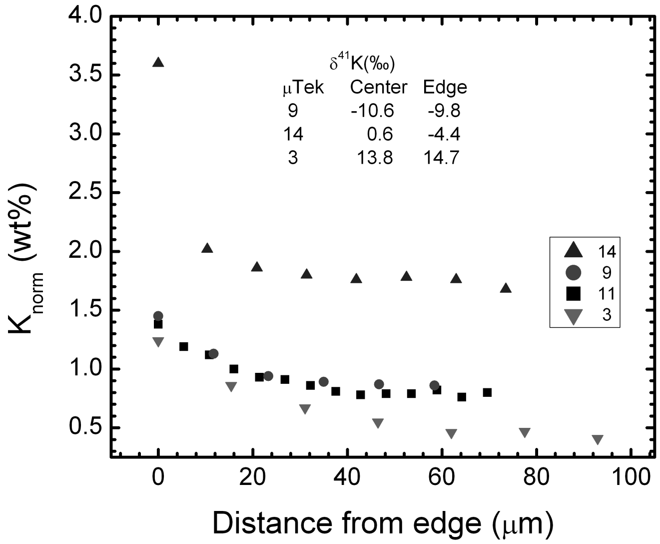

Fig. 5. Potassium profiles in microtektites measured at Rutgers University. Evidence for potassium zonation is stronger than seen in profiles measured at the Carnegie Institution. Potassium zonation does not appear to correlate with δ^{41}K.

Ocean tektite (586-1). Similarly, the K contents in the fragments of the Australasian layered tektites vary little, from ~2.3 wt% to 2.8 wt% (Fig. 3).

In contrast, in microtektites, the average potassium concentrations vary appreciably, from <1 wt% to 3 wt% (Tables 3 and 4), and the concentrations in the centers may be lower than those on the edges. Figs. 4 and 5 show potassium traverses taken at Carnegie and at Rutgers University, respectively. In the Rutgers profiles for four microtektites 3, 9, 11, and perhaps 14, the potassium content decreases appreciably with increasing depth (Fig. 5). Microtektites 11 and 14 were also profiled at Carnegie, although not necessarily along the same tracks. Towards the interior of sample 11, lower potassium concentrations are consistent with the Rutgers observations but the gradient is smaller, as it is for 14. In sum, for unknown reasons, data taken at Rutgers tend to show stronger zoning profiles than data taken at Carnegie.

In Fig. 6, we present again the center and edge data from the profiles discussed above, but in a different format. In particular, we plot the ratios of (K/Si) measured at the center

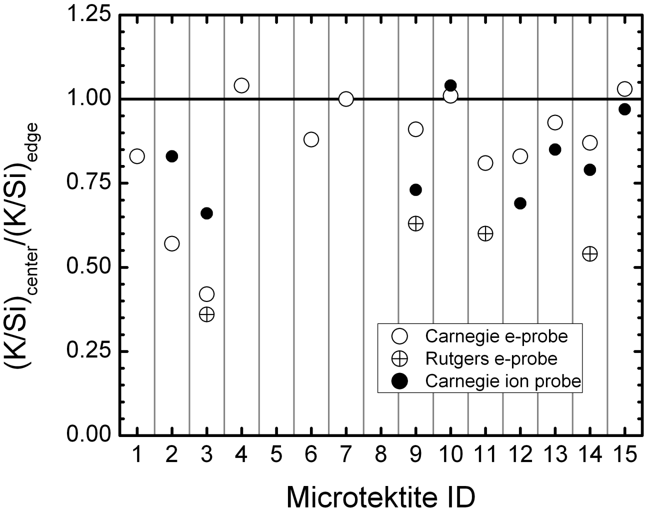

Fig. 6. Comparison of K/Si ratios in centers and edges of microtektites in mount 589 (see Table 3) measured by different methods and in different laboratories. Most of the variation in the ratios is due to changes in potassium signals. For several particles, the average potassium concentrations in the centers are lower than in the exteriors.

Table 5. Ion microprobe analyses of microtektites on mount 589.

Sample	Loc.	δ^{41}K (‰)	K/Si (wt/wt)
1	C	−3.1 ± 1.0	0.023
2	C	5.2 ± 0.9	0.028
2	E	0.4 ± 0.9	0.033
3	C	13.8 ± 1.5	0.008
3	E	14.7 ± 1.3	0.013
4	C	−1.2 ± 0.9	0.042
5	C	3.2 ± 0.9	0.029
6	C	3.3 ± 0.9	0.030
7	C	2.0 ± 0.9	0.032
9	C	−10.6 ± 1.4	0.011
9	E	−9.8 ± 1.5	0.016
10	C	0.1 ± 0.9	0.050
10	E	1.2 ± 0.9	0.048
11	C	0.5 ± 1.0	0.026
12	C	−1.9 ± 1.0	0.015
12	E	−5.0 ± 1.0	0.022
13	C	0.1 ± 0.9	0.026
13	E	−3.4 ± 1.0	0.031
14	C	0.6 ± 0.9	0.037
14	E	−4.4 ± 0.9	0.047
15	C	9.3 ± 0.9	0.079
15	E	9.7 ± 0.9	0.081

Loc. = location, C = center, E = edge.
Uncertainties of δ^{41}K are 1σ and are taken as the maximum of either the standard deviation for the six standards, or the uncertainty calculated from the data for the microtektite. The relative uncertainty of K/Si is ±10%.

to those measured at the edges, including now data for several microtektites where we made fewer than five spot measurements. Also shown are the K/Si ratios measured with the ion microprobe. Fig. 6 suggests that in six of thirteen microtektites on mount 589 (1, 2, 3, 11, 12, 14), the exteriors contain at least 20% more potassium than do the interiors. Microtektite 9 is a marginal case in that the Rutgers electron probe and the Carnegie ion probe indicate center-edge differences of more than 20%, while the Carnegie electron probe indicates a difference of about 10%.

δ^{41}K Measurements

The results of the δ^{41}K measurements for microtektites are shown referenced to the glass standard 12 in Table 5. With no correction for mass discrimination, six of seven temporally interleaved analyses of glass standard 12 yielded a nominal average value of δ^{41}K = −6.4‰ relative to the terrestrial ^{41}K/^{39}K atomic ratio of 0.0721677 (Böhlke et al., 2005). The standard deviation for these six measurements was 0.9 ‰, and the standard deviation of the mean, 0.4 ‰. To obtain δ^{41}K for the microtektite samples, we subtracted from their nominal δ^{41}K/^{39}K ratios (i.e., the ratios with no corrections for mass discrimination) the value δ^{41}K = −6.4 ± 0.4‰, (the average for glass standard 12). The average, the minimum, and the maximum 1σ uncertainties of δ^{41}K for the microtektites are 0.9‰, 0.6‰, and 1.5‰, respectively. These values are slightly larger than those for the tektites.

We analyzed material from the centers and edges of eight microtektites. No internal variation of δ^{41}K is apparent in microtektites 3, 9, 10, or 15. Two or more analyses of microtektites 2, 12, 13, and 14 differ by as much as 6‰. In these objects, the value of δ^{41}K at the edge is lower than at the center. These data for samples 2, 12, 13, and 14 raise a concern about possible matrix effects on our analyses. In particular, we recall that potassium concentrations on microtektite rims typically exceed those at the centers, perhaps as a result of seawater alteration. We cannot rule out such alteration as a cause of spurious measurements of δ^{41}K, but two lines of circumstantial evidence argue against it. First, as noted above, within the four microtektites 3, 9, 10, and 15 the measured values of δ^{41}K correlate poorly with absolute potassium concentrations and potassium depletions. Second, in comparing the average values of δ^{41}K among different microtektites, we see no correlation with potassium content. If alteration by seawater had introduced K at the surface, we would have expected to find smaller values of |δ^{41}K|. Still, in order to minimize doubt, below we consider "center" values of δ^{41}K for microtektites 2, 12, 13, and 14.

Isotopically Normal Potassium in Layered Tektites

Among the Australasian tektites, the layered ones have the highest volatile element concentrations and were probably heated least (Koeberl 1992, 1994). It seemed likely from the outset, therefore, that they would contain isotopically normal potassium. In fact, on average, the eleven tektites analyzed contain ^{39}K and ^{41}K in the normal isotope ratio. We therefore confirm the null results of Humayun and Koeberl (2004), who set an upper limit of 2% on the extent of potassium loss through free evaporation. It follows that elements less volatile than potassium—i.e., Fe, Si, Mg, Ca, Ti, and Al—likely underwent little or no net mass-dependent fractionation of their isotopes. Based on trends observed in laboratory experiments and in stony cosmic spherules [Taylor et al. 2005], we can extend the conclusion of Humayun and Koeberl (2004) to chromium (but not to monoisotopic sodium and manganese); we draw no conclusions about the retention of elements potentially more volatile than potassium, sulfur, copper, or zinc, for example.

Isotopically Fractionated Potassium in Some Microtektites

Figure 7 shows δ^{41}K values for both microtektites and layered tektites. The uncertainties for the microtektites are the larger of two values for each sample: either the uncertainty estimated from propagation of error for the microtektite, or 0.9‰, the standard deviation for the six measurements of the standards. Out of eight cases where we have isotopic analyses of microtektite edges and centers, four tektites have no significant difference δ^{41}K (C3,9,10,15) and four have lighter edges by 3–4‰ (C2, 12, 13, 14). As will be discussed later, these differences could be associated with alteration by sea water or condensation of potassium in the impact plume. To avoid this complication, we consider here only the core compositions.

To decide whether potassium has been fractionated in each microtektite, we set the criterion $|\delta^{41}\mathrm{K}| - 2\sigma > 0$. Based on the reproducibility of the standard for the microtektite analyses and the observation of small internal variations in δK in 589-15, we have adopted the relatively conservative 2σ value of 2×0.9‰ ~2‰. Using this approximate 2σ value, we would conclude that potassium was fractionated in 8 of the 13 microtektites analyzed, that is, not only in 3, 9, 15, which have very large fractionations, but also in 1, 2, 5, 6, and possibly 7. Our bias is that the large degrees of potassium isotope fractionation observed in microtektites 3, 9, and 15 makes it likely that smaller degrees of fractionation occur in other microtektites.

Variation of Potassium Concentrations and Potassium Isotope Fractionation among Australasian Microtektites

Evaporative losses may help explain why the average concentrations of K_2O in the microtektites analyzed are lower than values published for some other Australasian microtektites, (~1.4 wt% versus 1.8–2.9 wt%; Tables 3 and 4), although regional variation is another possibility.

In microtektites, the average value of δ^{41}K is 1.1 ± 6.1‰ if we include all results and 2.5 ± 4.4‰ if we exclude the rim measurements for 2, 12, 13, and 14. As in the layered tektites, these results are indistinguishable from the terrestrial value. In microtektites, however, the averages conceal significant excursions both above and below the terrestrial value.

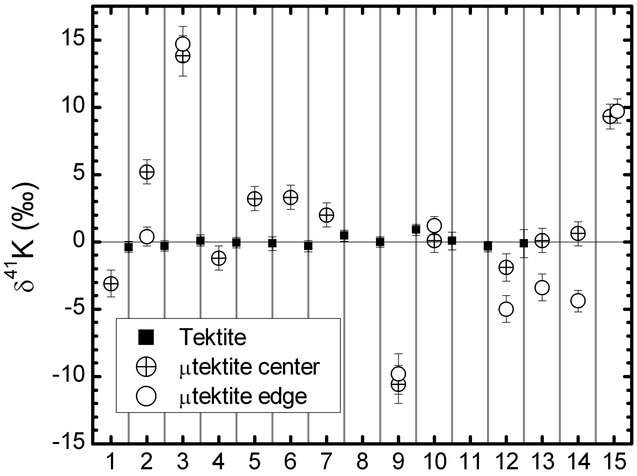

Fig. 7. Although the average value of δ^{41}K in the Australasian microtektites is close to zero, the individual results scatter over a much larger range than do those for the Australasian layered tektites.

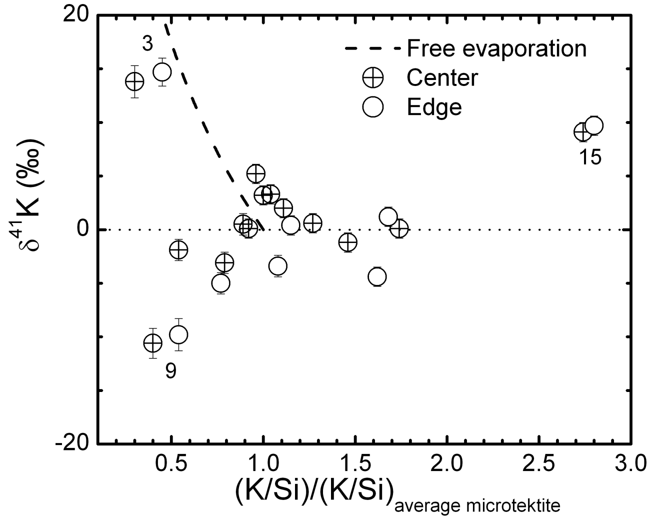

Fig. 8. If the values of δ^{41}K in microtektites were set in a free or Rayleigh evaporation, they should increase steadily as the fraction of potassium retained decreases, as indicated by the dashed line. We take as our measure of potassium retention the measured ratio of K/Si normalized to the average K/Si ratio of 14 Australasian microtektites, 0.032 ± 0.017, measured with the ion microprobe. Values of δ^{41}K do not track the Rayleigh curve well, but scatter about the terrestrial value.

We show next that our results for potassium follow the predictions of the Rayleigh equation for free evaporation to only a limited degree. According to the Rayleigh equation, we should have

$$\delta^{41}\mathrm{K} = 1000(f^{\alpha-1}-1)$$

where $\alpha = \sqrt{m\left(^{39}\mathrm{K}\right)/m\left(^{41}\mathrm{K}\right)}$, and f is the atom fraction of ^{39}K retained by the melt. Figure 8 shows these predictions, which require the following assumptions: 1) the droplets were well stirred during evaporation; and 2) all droplets had the same initial composition.

To compare the experimental data with the predictions of theory we need to assign a value of *f* to each microtektite. For this purpose we choose the quantity $(K/Si)_{measured}/(K/Si)_{average\ microtektite}$, where $(K/Si)_{measured}$ is taken from the ion microprobe data and $(K/Si)_{average\ microtektite}$ is set equal to 0.032 (mass/mass), the average for 14 microtektites on mount 589. Use of the elemental ratios, rather than the absolute concentrations of potassium, has the advantage of removing some of the experimental uncertainties that would be associated with quoting the absolute elemental concentrations. In particular, several uncertainties cancel out of the K/Si ratios because both the potassium and the silicon measurements were taken at the same time and place within each microtektite. The use of elemental ratios does require an additional but reasonable assumption, namely, that the evaporative losses of Si were small. Substitution of the electron microprobe data for the ion microprobe data does not alter our conclusions. We return below to the importance of the second assumption, the uniformity of the initial K/Si ratios in the source melt.

Although the potassium data for a few of the microtektites appear to follow the trend predicted by the Rayleigh equation for free evaporation, the potassium data for most of the microtektites do not. Specifically, positive and negative values of $\delta^{41}K$ occur with equal likelihood. We suggest that 1) the positive values of $\delta^{41}K$ reflect evaporative losses of potassium; and 2) the negative values of $\delta^{41}K$ arose in the plume that carried the microtektites away from the source crater. Some droplets that initially contained isotopically normal potassium underwent evaporation that left them enriched in ^{41}K to varying degrees. Most of the vaporized potassium subsequently condensed, some on droplets that had previously undergone evaporation and some on droplets that had not. The net effect was to conserve (within the limits of our uncertainties) the initial $\delta^{41}K/^{39}K$ ratio of the particle ensemble. Some microtektites on which extra potassium vapor condensed had their isotopic balance partly restored or may have become isotopically light as seen for the elements S, Cu, Zn, and Cd in lunar glass (Ding et al. 1983; Moynier et al. 2006; Schediwy et al. 2006). Light isotope enrichments would be stronger in liquids that by chance had low original potassium concentrations. It is also possible that the microtektites with $\delta^{41}K$ close to zero were heated less intensely and therefore retained their terrestrial potassium isotope ratios.

To some degree, the failure of the data to follow the predictions of the Rayleigh equation may owe to variations in the initial K/Si ratios of the melt droplets. No set of adjustments of the K/Si ratios chosen, however, can explain the existence of both negative and positive values of $\delta^{41}K$ in the context of a simple Rayleigh evaporation.

Table 6. Na_2O/K_2O in microtektites.

ID	Edge	Center	Center/edge
589-1	0.94	0.87	0.93
589-2	0.58	0.50	0.85
589-3	0.74	1.26	1.71
589-4	0.69	0.54	0.78
589-6	0.71	0.58	0.81
589-7	0.58	0.58	1.00
589-9	0.75	1.01	1.34
589-10	0.47	0.47	1.00
589-11	0.94	0.93	0.99
589-12	0.56	0.47	0.84
589-13	0.52	0.55	1.07
589-14	0.78	0.62	0.79
589-15	0.39	0.43	1.11

Data from Carnegie electron microprobe only.

Microtektites 3 and 15 have large positive values of $\delta^{41}K$ and occupy positions much further from the Rayleigh curve than do several other microtektites with positive values of $\delta^{41}K$. If our interpretation that heavy isotope enrichment reflects evaporation is correct, then these two objects must have had significantly higher initial K/Si ratios.

Effects of Seawater on Microtektites

We find higher potassium elemental concentrations in microtektite surfaces than in the interiors (Fig. 6). Our preferred explanation is condensation of potassium in the vapor plume followed by inward diffusion of potassium in some, but not all cases. Another possibility, however, is addition of potassium from seawater. We now examine briefly the interactions of microtektites with seawater.

In a study of 140 microtektites, Glass (1984) found that solution on the sea bottom removes between 1.8 and 16 μm (average ~7 μm) from microtektite surfaces. The amount of solution varies with the physical conditions (temperature, pressure, and perhaps flow rates). In particular, it seems to increase with decreasing water depth. These observations have implications for our work. First, they suggest that the solution process would have removed some volatile-rich surface layer that condensed on the microtektite surfaces. It follows that to preserve the light isotopic signatures observed in some microtektites, potassium must have diffused rapidly into the interior. Surface losses, however, cannot explain the surface enrichments in elemental potassium observed in some microtektites. We therefore look more closely at other possible chemical interactions between seawater and the surfaces of microtektites.

The chemical details of how terrestrial glass interacts with sea water depend on several factors (Stroncik and Schmincke 2002), among them the original composition of the glass. Basaltic glass from mid-ocean ridge basalts (MORBs) gains ten times the original potassium content but little or no sodium (Staudigel and Hart 1983). We infer that if alteration on the sea bottom increased potassium concentrations in the outer layer of microtektites, then the Na/K ratios should decrease toward the exterior, or at least not increase. To test this inference we use the Carnegie electron microprobe data. Only two of eleven microtektites, 589-3 and 589-9, show clear (>~12%) decreases in the Na_2O/K_2O ratio from center to edge (Table 6). In all other microtektites, Na/K ratios remain constant within the uncertainties of ~12% or increase. Except possibly for microtektites 3 and 9, we see no compelling evidence that the microtektites studied gained potassium from seawater.

Two circumstantial arguments support this conclusion: 1) the conditions at each microtektite collection site were the same. Accordingly but contrary to observation, one might expect alteration to affect all microtektites similarly, and 2) if hydration accompanied alteration by seawater, oxide totals for edges should be lower than those for interiors. We do not see such an effect.

We do not, however, rule out some isotopic exchange of potassium between microtektites and seawater.

δ^{41}K Variations in Microtektites

Our results show variations of both potassium concentration and δ^{41}K values within and among microtektites. For example, four tektites have no significant difference in their isotopes (3, 9, 10, and 15) and four have lighter edges by 3–4‰ (2, 12, 13, and 14). If our proposed explanations for these variations are correct, then we ought to be able to describe for each microtektite a plausible history that includes the evaporation of isotopically light potassium; condensation; partial or complete stirring, and quenching of the melts; and perhaps, the limited uptake of potassium from, or loss of Si to seawater. (Potassium in seawater is isotopically normal [Humayun and Clayton 1995], i.e., δ^{41}K = 0.) We propose broad-brush histories of individual microtektites in Appendix 1 and treat the history of microtektite 589-9 in detail in Appendix 2.

CONCLUSIONS

Elemental and isotopic analyses of potassium in Australasian layered tektites from Indochina produced no surprises. The compositional results match published values and the ^{41}K/^{39}K ratios equal the terrestrial value, as might be expected for the group of tektites that on average retains the highest concentrations of volatiles. We therefore confirm with our eleven new measurements the conclusions that Humayun and Koeberl (2004) drew based on measurements of four tektites of various types. In particular, the potassium isotope abundances indicate that the Australasian tektite melts lost little K due to evaporation.

Our results for microtektites lead to similar conclusions but by a more interesting route. By chance, the microtektites in which we analyzed potassium isotope abundances have a lower average potassium concentration than do those of Australasian microtektites from some other parts of the strewn field. For this reason they seemed a likely place to hunt for evaporative losses and elevated values of δ^{41}K. We found that the potassium isotope data scatter over an impressively wide range of both negative and positive values, from −10.6 ± 1.4‰ to +13.8 ± 1.5‰. We attribute the positive values to evaporative losses and the negative values primarily to the random condensation of vaporized, isotopically light potassium within the vapor plume that carried the microtektites along. Many of the microtektites that we analyzed—perhaps half of them—have non-zero values of δ^{41}K. These measurements carry information about microtektite formation histories and the study of a larger sample population seems warranted.

In summary, the suspicion expressed in the introduction, that evaporation should have some effect on microtektite isotope abundances, finds support in our results. This observation, however, should not disguise a key result: even for this potassium-poor set of microtektites, the mean ^{41}K/^{39}K ratio is the same as the terrestrial value within the uncertainties. As the microtektites analyzed for δ^{41}K are few in number (13) and come from a small geographical area, the mean may be biased. With this qualification, we conclude that evaporation had a limited overall effect on the average isotopic compositions of microtektites. We extrapolate from this result to suggest that it also had a limited effect on average elemental concentrations. It follows that measured microtektite compositions should reflect those of the source materials, at least for elements as or less volatile than potassium.

Some questions are unresolved. The concentrations of potassium tend to increase toward the surfaces of some microtektites. We have argued that many but not all of these increases resulted from the condensation of potassium. The possibility that other volatile elements condensed with potassium deserves consideration. To have survived the loss of surface material on the sea floor, however, measurable amounts of these other volatile elements would have to have diffused inward as rapidly as potassium through the melt. The role of alteration by seawater and possible solution of the outer layer of the microtektites needs further study. So too does the possible variation of isotopic fractionation with distance from the source crater, as thermal histories may relate systematically to fall location. Unfortunately all the samples analyzed to date came from sites about equidistant from the likely location of the source crater. Finally, we do not rule out the possibility of isotopic fractionation due to evaporation of elements more volatile than potassium (e.g., sulfur, copper, and zinc), or of systematic isotopic effects in restricted groups of microtektites (Koeberl et al. 1999).

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APPENDIX 1. MICROTEKTITE HISTORIES

589-1. We have no profiles for potassium or δ^{41}K. The available data are consistent with the condensation of isotopically light potassium, which mixed well with and dominated the potassium remaining after evaporation.

589-2. At the edge, the elemental potassium concentration is higher and the value of δ^{41}K is lower than at the center. This microtektite lost potassium through evaporation and accumulated a shell of isotopically light K, perhaps when the core had cooled so much that mixing could not occur. It may also have acquired some potassium from seawater.

589-3. This is a high-Mg microtektite. It has large and position-independent values of δ^{41}K of ~14 ± 0.5‰ and its potassium content is relatively low, 0.51 wt%, both of which are consistent with considerable evaporative losses. The higher concentration of potassium at the rim (1.1 wt%) versus center (0.3 wt%) is puzzling, but suggests incomplete mixing of condensed potassium.

589-4-7. Available data are consistent with small degrees of evaporation and condensation.

589-9. Potassium in microtektite 9 is isotopically light, δ^{41}K = −10.2 ± 0.5‰ and the isotopic analyses of edge and center analyses agree. The object appears to be compositionally typical of those studied. The average of the K_2O concentrations measured at Carnegie and Rutgers was 0.91 wt%. The Carnegie data show a small increase, about 10%, in potassium concentrations from center to edge; the Rutgers electron probe and the ion microprobe data show a larger one, about 35%.

589-10. We have no evidence of fractionation of potassium isotopes or variation in potassium concentration for this object. It probably cooled quickly.

589-12-14. In each of these objects, the potassium concentration is somewhat higher in the exterior and the value of δ^{41}K is negative. These results are consistent with condensation of isotopically light potassium, incomplete mixing before quenching, and no or a small addition of K from seawater.

589-15. Potassium in microtektite 15 is isotopically heavy, δ^{41}K = +9.1 ± 0.7‰, and we see no variation from edge to center. This result is consistent with the loss of potassium due to evaporation from the molten microtektite. For illustrative purposes, we model the loss as a free evaporation of potassium atoms with a fractionation factor set equal to $\sim\sqrt{m(^{39}\mathrm{K})/m(^{41}\mathrm{K})}$, where *m* is the atomic mass. From δ^{41}K = +9.1‰ and the Rayleigh equation (see, e.g., Davis and Richter 2005), we calculate a fractional potassium loss of 31%. The average of the K_2O concentrations measured with the electron microprobes at Carnegie and Rutgers was 2.14 wt% (Table 3) implying an initial K_2O concentration of 3.1%. This value is consistent with the range of K_2O concentrations observed for microtektites: 0.8–2.8 (Glass et al. 2004); 1.07–4.54 (Glass and Koeberl 2006). The potassium concentration measured with the ion microprobe, 3.7 wt%, was the highest measured by more than a factor of two. It implies an initial K_2O concentration of 6.5 wt%, which seems too high.

APPENDIX 2. MODEL CALCULATIONS

We explore a sequence of events that could explain the enrichment in light K isotopes in a microtektite, taking as an example microtektite 589-9, which contains approximately 1% elemental K (Table 3) and has a δ^{41}K value of ~10‰. As noted in Appendix 1, elemental K concentration shows some zonation, ~10% based on Carnegie electron microprobe data and ~35% based on Rutgers electron microprobe data. We do not discuss further the zonation of potassium, except to note that it could reflect incomplete inward mixing of K added to the surface of the object.

Figure 9 shows a proposed history in schematic form. We begin with a droplet of melt containing isotopically normal K. Evaporation from the droplet of melt leaves behind a fraction

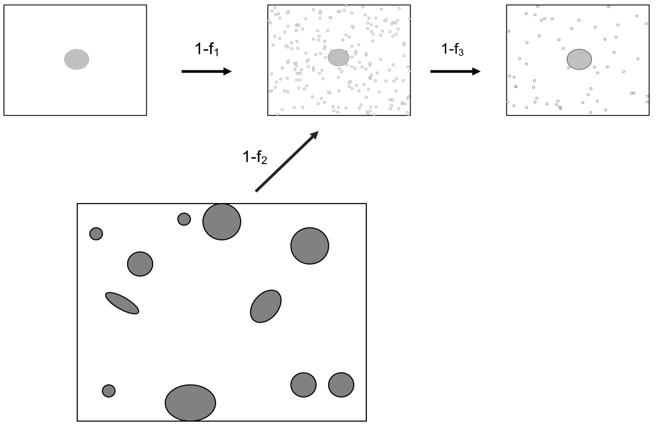

Fig. 9. A proto-microtektite and other liquid in the tektite plume lose fractions, $(1 - f_1)$ and $(1 - f_2)$, respectively, of their ^{39}K by free evaporation. A fraction $(1 - f_3)$ of that gaseous K then condenses kinetically back onto the proto-microtektite.

f_1 of the ^{39}K initially present. We assume that the application of the Rayleigh equation gives the corresponding retention of ^{41}K, namely f_1^{α}, where $\sqrt{m(^{39}\mathrm{K})/m(^{41}\mathrm{K})}$. Provided the gas initially present in the plume contained no K from other sources, the isotopic composition of the evaporated potassium follows from the conservation of mass. At the same time as the evaporation from the proto-microtektite took place, evaporation from other melt droplets added potassium to the plume. We assume that they (1) had a total mass equal to P times the mass of the proto-microtektite; and (2) retained a fraction f_2 of their ^{39}K along with corresponding (i.e., calculated from the Rayleigh equation) fraction of ^{41}K. Finally we suppose that the ^{39}K in the plume underwent a kinetically controlled condensation onto still-molten, but now somewhat cooler proto-microtektite. We postulate that the plume retained a fraction of f_3 of its ^{39}K and, again, the corresponding Rayleigh fraction of ^{41}K. We will ignore below the small effects on total K concentration due to the presence of ^{40}K.

What might have distinguished a microtektite such as 589-9 from other material with less or no fractionation of potassium isotopes? It could have been hotter initially and hence lost more potassium. Perhaps it then cooled some, although not enough to quench. In this condition, it could have entered a region of lower average temperature either because of its characteristic velocity or through turbulence. In this region, potassium enriched in light isotopes could have condensed on its surface and begun to diffuse inward.

The model described has six parameters—the weight percentages of potassium in the proto-microtektite and in the other melt droplets, respectively; the three fractions of ^{39}K retained; and a ratio that specifies the relative masses of the proto-microtektite and the other liquid material contributing to the budget of potassium (see below). Below we discuss choices of the parameters that could have led to the measured value of δ^{41}K in the object of interest in the framework of the Rayleigh equation. Before proceeding, however, we warn readers that the Rayleigh equation may not describe accurately either the evaporation or the condensation process.

We use the notation:

MW for molar mass
[K] for the mass fraction of potassium
Ab for terrestrial isotopic abundance
M for total mass
I for the isotope abundance ratio ^{41}K/^{39}K
n for amount (moles)
f_1 for the atomic fraction of ^{39}K retained by the prototektite melt
f_2 for the atomic fraction of ^{39}K retained by the liquid tektite material in the plume
f_3 for the atomic fraction of ^{39}K retained by the plume after some of it condensed on the prototektite melt
P for the mass ratio M_T/M_o, where the subscripts are defined below

and use the subscripts o for the proto-microtektite melt; μ for the (final) microtektite; T for the material that evaporated from other tektite material in the plume; 39 for ^{39}K; and 41 for ^{41}K.

From the definitions given above, we have the ancillary relations

$$n_{o,39} = M_o[\mathrm{K}]_o\mathrm{Ab}_{39}/\mathrm{MW}$$

$$n_{o,41} = n_{o,39}\ \mathrm{Ab}_{41}/\mathrm{Ab}_{39} = n_{o,39}\ I_o$$

$$I_\mu = n_{\mu,41}/n_{\mu,39}$$

$$n_{T,39} = PM_o[\mathrm{K}]_T\mathrm{Ab}_{39}/\mathrm{MW}$$

$$n_{T,41} = n_{T,39}\ \mathrm{Ab}_{41}/\mathrm{Ab}_{39} = n_{T,39}\ I_o$$

We assume normal initial isotopic abundances for all potassium in the source materials. Application of the Rayleigh equation and the requirement of mass balance give the following relations

$$n_{\mu,39} = f_1 n_{o,39} + (1 - f_3)[(1 - f_1)n_{o,39} + (1 - f_2)n_{T,39}] \quad \text{(A1)}$$

$$n_{\mu,41} = f_1^{\alpha} n_{o,41} + (1 - f_3^{\alpha})[(1 - f_1^{\alpha})n_{o,41} + (1 - f_2^{\alpha})n_{T,41}]$$
(A2)

where $\alpha = \sqrt{\mathrm{MW}_{39}/\mathrm{MW}_{41}} = \sqrt{38.96371/40.96183} = 0.975305$. The first term on the right of each equation is the potassium remaining in the proto-microtektite after evaporation; the second term is the contribution of the potassium lost from the proto-microtektite but now returning via condensation; and the third term is the contribution due to condensation of potassium that evaporated from other tektite melt in the plume. Introducing the relations between n_{39} and n_{41} yields Equations A1a and A2a:

$$n_{\mu,39} = f_1 n_{o,39} + (1 - f_3) \tag{A1a}$$

$$\left[(1 - f_1) n_{o,39} + (1 - f_2) P \frac{[\mathrm{K}]_T}{[\mathrm{K}]_o} n_{o,39} \right]$$

$$n_{\mu,39} = f_1^{\alpha} n_{o,39} + (1 - f_3^{\alpha}) \tag{A1b}$$

$$\times \left[(1 - f_1^{\alpha}) n_{o,39} I_o + (1 - f_2^{\alpha}) P \frac{[\mathrm{K}]_T}{[\mathrm{K}]_o} n_{o,39} I_o \right]$$

Dividing equation A2a by equation A1a we get for the final ^{41}K/^{39}K ratio over the initial (terrestrial) ^{41}K/^{39}K ratio:

$$\frac{I_\mu}{I_o} = \frac{f_1^{\alpha} + (1 - f_3^{\alpha}) \times \left[(1 - f_1^{\alpha}) + (1 - f_2^{\alpha}) P \frac{[\mathrm{K}]_T}{[\mathrm{K}]_o} \right]}{f_1 + (1 - f_3) \times \left[(1 - f_1) + (1 - f_2) P \frac{[\mathrm{K}]_T}{[\mathrm{K}]_o} \right]} \tag{A3}$$

We can solve Equation 3 for $P[\mathrm{K}]_T/[\mathrm{K}]_o$ in terms of I_μ/I_o. For compactness, we define

$$F_{1,39} \equiv f_1$$

$$F_{2,39} \equiv (1 - f_3)(1 - f_1)$$

$$F_{3,39} \equiv (1 - f_3)(1 - f_2)$$

$$F_{1,41} \equiv f_1^{\alpha}$$

$$F_{2,41} \equiv \left(1 - f_3^{\alpha}\right)\left(1 - f_1^{\alpha}\right)$$

$$F_{3,41} \equiv \left(1 - f_3^{\alpha}\right)\left(1 - f_2^{\alpha}\right)$$

Rearrangement of Equation 3 gives

$$\frac{M_T[\mathrm{K}]_T}{M_o[\mathrm{K}]_o} = \frac{\frac{I_\mu}{I_o}(F_{1,39} + F_{2,39}) - (F_{1,41} + F_{2,41})}{F_{3,41} - \frac{I_\mu}{I_o} F_{3,39}} \tag{A4}$$

where the measured quantity I_μ/I_o is related to the reported value of δ^{41}K through equation 1 of the main text.

We use Equation A4 to model how big a reservoir of material we must have to create a microtektite with a particular value of I_μ/I_o; that is, we will use Equation A4 to calculate $P = M_T/M_o$. First, however, we set some parameters. We have assumed that the gaseous potassium comes from the evaporation of tektite- or microtektite-like material. It seems reasonable, therefore, to adopt a K concentration $[\mathrm{K}]_T$ close to either ~2.2 wt%, the average value for tektites, or to ~2.0 wt%, the average literature value for all microtektites see (Table 3). For $[\mathrm{K}]_o$ in the proto-microtektite, we adopt 1.0 wt%, the potassium concentration for microtektite 589-9 measured with the electron microprobe (Table 3). We choose this value rather than one of the published averages for microtektites because it appears that our samples were atypically poor in potassium. Thus, we have $[\mathrm{K}]_T/[\mathrm{K}]_o = 2$, although any particular proto-microtektite could contain less or more potassium.

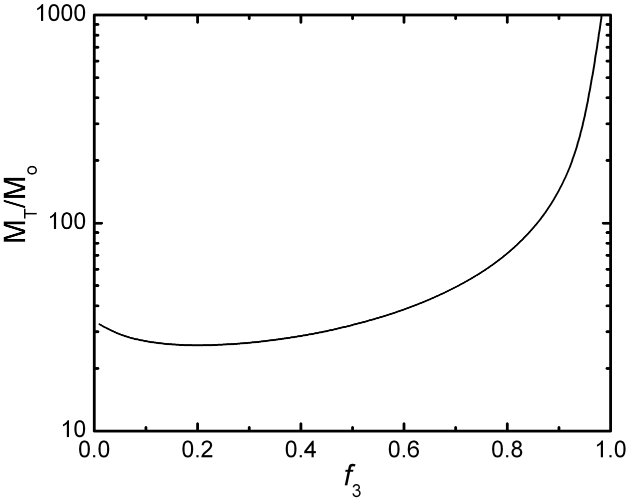

Fig. 10. In order to produce microtektite 589-9, for which $\delta^{41}\mathrm{K} = -10$‰, we add isotopically light potassium from the vapor plume. This new potassium must be evaporated from other liquid present in the plume and then condensed onto proto-589-9. Detailed modeling (Appendix 2) sets the ratio of the total mass of outside liquid required, $\mathrm{M_T}$, to the mass of the proto-microtektite, $\mathrm{M_o}$, as a function of the fraction of ^{39}K that the plume retains, f_3.

We turn next to the possible values of the fractions of potassium retained, beginning with f_1. As δ^{41}K is typically small for microtektites, we expect f_1 to be close to 1.0 in most cases and adopt $f_1 = 0.99$, although smaller values of f_1 would make it easier to explain zonation of elemental potassium. Similarly, from the experimental observation that the values of δ^{41}K for both tektites and microtektites are small, 0.02 ± 0.04‰ and 1.1 ± 1.7‰ respectively, we infer that f_2 is generally close to 1.0. Smaller values of f_2 would create a sizeable reservoir of isotopically heavy liquid in the plume, liquid that presumably would have quenched, but is not observed, at least among tektites. With $f_2 = 0.97$, we find $\delta^{41}\mathrm{K} = 0.75$‰ for the residual melt, a value acceptably close to zero.

The fraction f_3 sets the relative amount of gaseous potassium that the plume retained and that was lost to microtektites. The observation that the average measured values of δ^{41}K are close to zero for both tektites and microtektites suggests that the entire plume, gas + liquid + solid, lost little potassium. Perhaps counterintuitively, however, this observation does not constrain f_3. The reason is that the fraction of the total potassium in the gas phase is small—less than 1% with f_1 and $f_2 \sim 0.99$. Thus, the overall degree of potassium retention by the gaseous plume has a minimal effect on the K concentrations in the liquid or solid material. We therefore regard f_3 as free to take on any value between 0 and 1.0.

To summarize, we have set the values of four parameters, $[\mathrm{K}]_T = 0.02$, $[\mathrm{K}]_o = 0.01$, $f_1 \sim 0.99$, $f_2 \sim 0.99$, and have concluded that a fifth, f_3, may lie anywhere between 0 and 1. With these considerations in mind, we focus on microtektite 589-9 (δ^{41}K ~ −10‰; Table 5) and examine the behavior of the mass ratio $P = M_T/M_o$ as a function of f_3. Figure 10 shows that the smallest M_T/M_o ratio possible is about 23. Pushing the interpretative envelope, we might expect 1 in 23 microtektites to have δ^{41}K values of about −10‰ and the remaining 22 to have small values of δ^{41}K. We observed 1 in 14.

The discussion above makes no use of the measured value of $[\mathrm{K}]_\mu$. If we assume that potassium is the only volatile component in the proto-microtektite, then we have the relation

$$\frac{M_o}{M_\mu} = \frac{1 - [\mathrm{K}]_\mu}{1 - [\mathrm{K}]_o} \tag{A5}$$

Equation A5 has two implications. First, it shows that for measured values of $[\mathrm{K}]_\mu$ and choices of $[\mathrm{K}]_o$ less than ~10 wt%, the mass of the proto-microtektite will change little through loss or addition of potassium. Second, given a (measured) value of M_μ, and a set of fitting parameters, we always can find a value of M_o that will lead to the correct final concentration of potassium. The choice of M_o does not change δ^{41}K.

These calculations can be adjusted in several ways. For example, holding $f_1 = 0.99$ while decreasing the value of f_2 to 0.97 for the other tektite melt leads to a higher but still acceptably low value of δ^{41}K = 0.75‰, and lowers the minimum value of M_T/M_o to about 10 for $f_3 = 0.35$. Similarly, assuming the proto-microtektite was hot enough to lower the value of f_1 to 0.1, we find M_T/M_o ~10 for $f_2 = 0.99$ and $f_3 = 0.42$.