

Potassium isotopic composition of Australasian tektites

Munir HUMAYUN^{1+*} and Christian KOEBERL²

¹Department of Geophysical Sciences, The University of Chicago, Chicago, Illinois 60637, USA

²Department of Geological Sciences, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria

[†]Present address: National High Magnetic Field Laboratory and Department of Geological Sciences, Florida State University, Tallahassee, Florida 32310, USA; humayun@magnet.fsu.edu

*Corresponding author. E-mail: hum8@midway.uchicago.edu

(Received 13 August 2003; revision accepted 16 June 2004)

Abstract—We have analyzed the potassium isotopic composition of four tektites from the Australasian strewn field, spanning a wide diversity of thermal histories, inferred from textures and volatile element contents. Our results indicate no isotopic differences between tektites and terrestrial crustal rocks, placing stringent limits of $\leq 2\%$ loss of potassium during the brief duration of high temperature heating experienced by these samples. This confirms that the chemical composition of tektites is entirely a reflection of source rock composition and has not been modified by the tektite-forming process for elements less volatile than potassium. Losses of more volatile components, e.g., the halogens and water, are not precluded by the present data. Coupling a radiative cooling temperature-time path with potassium vapor pressure data indicates that tektite melt drops are not likely to develop bulk elemental fractionation during the brief heating episodes of tektites for peak temperatures < 2273 K. The extent of K isotopic fractionation is independent of droplet size but dependent on peak heating temperature. The exact peak temperature depends on the choice of vapor pressure data used for K, which need to be better constrained.

INTRODUCTION

Tektites and microtektites are natural glasses and an important group of distal impact ejecta. Tektites are currently known to occur in four strewn fields of Cenozoic age on the surface of the Earth (e.g., Koeberl 1986). Strewn fields can be defined as geographically extended areas over which tektite material is found. The four strewn fields are: the North American, Central European (moldavite), Ivory Coast, and Australasian strewn fields. Tektites found within each strewn field have the same age and similar petrological, physical, and chemical properties. Relatively reliable links between craters and tektite strewn fields have been established between the Bosumtwi (Ghana), the Ries (Germany), and the Chesapeake Bay (USA) craters and the Ivory Coast, Central European, and North American fields, respectively. The source crater of the Australasian strewn field has not been identified, yet. The Australasian strewnfield is the largest strewnfield in area (50 million km²) and probably in mass (10^{14} g) and has an age of 0.7 Ma (Glass et al. 1979).

Tektites are chemically homogeneous, often spherically symmetric natural glasses, with most being a few cm in size. Those found on land have commonly been classified into three groups: a) normal or splash-form tektites; b)

aerodynamically shaped tektites; and c) Muong Nong-type tektites (sometimes also called layered tektites). In addition to the “classical” tektites on land, microtektites from three of the four strewn fields have been found in deep-sea cores. They are generally less than 1 mm in diameter and show a somewhat wider variation in chemical composition than tektites on land but with an average composition that is very close to that of “normal” tektites. Microtektites occur in the stratigraphic layers of the deep-sea sediments that correspond in age to the radiometrically determined ages of the tektites found on land. Thus, they are distal ejecta and represent an impact marker. The geographical distribution of microtektite-bearing cores defines the extent of the respective strewn fields, as tektite occurrences on land are much more restricted. Furthermore, microtektites have been found together with melt fragments, high pressure phases, and shocked minerals and, therefore, provide confirming evidence for the association of tektites with a terrestrial impact event.

The major and trace element compositions of tektites are almost identical to the composition of the terrestrial upper crust (see, e.g., Taylor 1973; Koeberl 1986, 1992a, 1994). Mainly as a result of these chemical studies, it is now commonly accepted that tektites are the product of melting and subsequent quenching of terrestrial rocks during a

hypervelocity impact on the Earth. Tektites have been the subject of much study. For further details on tektites, see the reviews by, e.g., Koeberl (1994, 2001) and Montanari and Koeberl (2000).

Tektites have experienced severe heating, with temperatures in excess of 2000 °C (2273 K), but determining the role of selective chemical changes due to volatility has been contentious (Walter 1967; Walter and Carron 1964). Kinetic isotope fractionation during selective volatilization of elements from liquids has been well-documented by laboratory studies (Wang et al. 2001; Yu et al. 2003). The influence of vapor fractionation on tektite composition can, thus, be evaluated by comparing the stable isotopic composition of light elements with that of their source rocks. Oxygen and silicon show variations that cannot unambiguously be assigned to volatilization because of variability in source rock composition. The $\delta^{30}\text{Si}$ effects are small, and there are only few data (Molini-Vesko et al. 1982), making any interpretation difficult. In contrast, $\delta^{18}\text{O}$ data have a large range, generally lighter than source rock sediments by several permil (Taylor and Epstein 1966; Walter and Clayton 1967; Engelhardt et al. 1987). The lowering of $\delta^{18}\text{O}$ correlated with SiO_2 content has usually been explained as being due to meteoric porewaters present in sandy sedimentary rocks at the time of impact melting (e.g., Engelhardt et al. 1987; Koeberl et al. 1998), which provides a better explanation than vapor fractionation. The $\delta^{25}\text{Mg}$ values measured for microtektites and australite tektite flanges indicate less than 20% vaporization of tektite material (Esat and Taylor 1986, 1987; Esat 1988). No distinct effect was found by Chaussidon and Koeberl (1995) for boron isotopes, even though B is a volatile element.

The elements that are likely to be useful for establishing the role of evaporation would be those that are volatile, of low mass, and particularly, those that have a constant isotopic composition in terrestrial samples. One such element is potassium, which is moderately volatile under solar nebular conditions (volatilities under impact conditions are not known) and has a constant isotopic ratio in terrestrial samples (Humayun and Clayton 1995a). This paper reports precise determinations of the stable isotopic composition of potassium in several tektite samples and discusses the implications for the vapor fractionation of tektites. A preliminary report of the results was made by Humayun et al. (1994).

METHODS

Potassium has three naturally occurring isotopes: ^{39}K (93.2581%), ^{40}K (0.01167%), and ^{41}K (6.7302%). Due to the low abundance of ^{40}K and the presence of a significant interference from ^{40}Ca , it was only possible to measure the isotope ratio $^{41}\text{K}/^{39}\text{K}$, but for the present purposes, this is sufficient. Humayun and Clayton (1995a) have developed a mass spectrometric procedure to measure differences in the

isotopic ratio $^{41}\text{K}/^{39}\text{K}$ with a precision comparable to that of any element done by double spike TIMS (0.2 ‰/a.m.u.; 2σ), and an accuracy as good as the precision. The findings for a variety of chondrites, achondrites, and lunar materials and the cosmochemical consequences of these results were described by Humayun and Clayton (1995b). Further details can be found in Humayun (1994).

We have applied the same potassium isotopic techniques described by Humayun and Clayton (1995a) to investigate the role of volatilization in determining the composition of Australasian tektites. Four Australasian tektites, including one Muong Nong-type tektite, and three splash-form tektites were selected for analysis. The Muong Nong-type tektite (MN X-103) has been analyzed for trace element abundances (Glass and Koeberl 1989) and for Nd-Sr isotope systematics (Blum et al. 1992). It is the closest to a source composition for the Australasian strewnfield of any material, given the absence of an impact crater. Fresh interior chips of the tektites were dissolved in HF-HCl-HNO₃, dried, taken up in 0.1 M oxalic acid-HNO₃, and added to an ion exchange column (inner diameter = 11 mm) filled with 12 ml of AG 50W-X8 resin. The potassium was eluted with 0.5 N HNO₃, quantitatively recovered in the 80–250 ml fraction, with adequate separation from Na, Mg, Ca, and other potential interferences. The separated K was converted to 2% K Ba-borate glass and analyzed against our in-house standard, Merck Suprapur KNO₃, using the Chicago AEI IM-20 ion microprobe (see Humayun and Clayton [1995a] for more details). Potassium abundances in the tektites and K column yields were determined by flame emission photometry using a Perkin-Elmer 306 Atomic Absorption Spectrophotometer. The results for USGS Standards G-2 and BCR-1 are shown for comparison.

RESULTS AND DISCUSSION

The potassium isotopic composition is determined with precision and accuracy sufficient to recognize even a few percent loss of K, and terrestrial rocks of every kind thus far determined have identical $\delta^{41}\text{K}$, eliminating the uncertainties of source rock isotopic values (Humayun and Clayton 1995a). This allows us to determine the existence of kinetic isotope effects produced by the partial loss of potassium by distillation during high temperature processes, e.g., impact melting. Yu et al. (2003) showed that K follows the Rayleigh fractionation trend during selective distillation.

Data for the tektites, several terrestrial rocks, lunar soil (14163), and an average of terrestrial samples are given in Table 1 using delta-notation:

$$\delta^{41}\text{K} = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \times 1000$$

where R is the isotopic ratio ($^{41}\text{K}/^{39}\text{K}$), and the standard was a bottle of Merck Suprapur[®] KNO₃, used as an in-house standard by Humayun and Clayton (1995a, b). None of the

Table 1. Potassium isotopic composition of Australasian tektites, terrestrial samples and a lunar soil sample.

Sample	# points	K (wt%)	$\delta^{41}\text{K} \pm 2\sigma_n$ (‰)	%K volatilized ^a
MN X-103, Muong Nong	22	2.52	$-0.1 \pm 0.6\text{‰}$	≤ 2
AUS 9301, Australite	27	1.88	$+0.0 \pm 0.5\text{‰}$	< 2
T 9201, Thailandite	14	2.04	$+0.4 \pm 0.8\text{‰}$	< 5
P 9201, Phillipinite	26	1.85	$-0.1 \pm 0.5\text{‰}$	< 2
USGS G-2, Westerly granite ^b	20	3.64	$-0.1 \pm 0.7\text{‰}$	–
USGS BCR-1, Basalt ^b	82	1.43	$0.0 \pm 0.3\text{‰}$	–
Seawater, Pacific ^b	34	0.032	$+0.4 \pm 0.5\text{‰}$	–
Terrestrial average (n = 17) ^b	414	–	$+0.3 \pm 0.2\text{‰}$	–
14163 Lunar soil ^b	14	0.44	$+7.8 \pm 0.8\text{‰}$	~ 10

^aVolatilized amounts calculated assuming Rayleigh fractionation.

^bTerrestrial and lunar soil data from Humayun and Clayton (1995a).

tektite analyses deviate from the terrestrial composition within errors. We calculated the maximum degree of loss permitted by the errors, assuming Rayleigh distillation of single K atoms (the dominant species observed experimentally), and these are tabulated as well (generally $< 2\%$). This constraint could be relaxed if K volatilization occurred under conditions that did not satisfy those for Rayleigh fractionation, e.g., absence of internal mixing or presence of surrounding gas (Yu et al. 2003). This result sets stringent limits on the permissible losses of potassium, which, taken in conjunction with isotopic data on other elements, implies that selective distillation is small to non-existent for all major elements and for trace elements that are more refractory than potassium. Taylor (1973) and Blum et al. (1992) presented convincing arguments against the significant loss of more volatile alkalis, Rb and Cs. In particular, Blum et al. (1992) noted that loss of Rb by vapor fractionation would reset the Rb/Sr ages of tektites. They found Rb-Sr ages of about 165 Ma (interpreted to be that of Jurassic source rocks) instead of 0.7 Ma for Australasian tektites and argued against extensive volatile loss. Certain elements, e.g., water and halogens, do show marked depletions relative to sedimentary rocks (see, e.g., Koeberl 1992a), but such elements may have been lost at temperatures even below the glass transition temperature.

Chaussidon and Koeberl (1995) studied the variations of the abundances and isotopic composition of B in a flanged australite. $\delta^{11}\text{B}$ variations of only a few permil were found within the australite flange. The isotopic composition shows no correlation with the B contents or with the distance from the rim of the flange. The mean $\delta^{11}\text{B}$ value for the flanged australite is very similar to that of Muong Nong-type tektites ($-1.9 \pm 1.9\text{‰}$). Thus, Chaussidon and Koeberl (1995) concluded that vapor fractionation was unimportant for B during tektite formation. This is supported by the observation that B contents and the $\delta^{11}\text{B}$ values of the different samples from the Australasian tektite strewn field are not correlated with each other. Our present results for K support this conclusion.

There are two consequences of our observation that tektites are not chemically modified by the impact melting

process. First, in consideration of the chemical composition of tektites and inferences drawn from these regarding source compositions, the effect of selective volatilization can be neglected. Second, if impact melting does not affect the isotopic composition of K in large objects such as tektites, how about microtektites and lunar impact melt glasses? Studies of lunar soils (Humayun and Clayton 1995a) have shown large $\delta^{41}\text{K}$ enrichments for less than 15% chemical depletions of the K/U ratios. For instance, the lunar soil 14163 is chemically indistinguishable from KREEP but has a $\delta^{41}\text{K}$ value of $+7.8 \pm 0.8\text{‰}$. Thus, the absence of isotopic enrichments in potassium indicates chemical modifications too small to affect any discussion of the geochemistry of tektites, which must, therefore, entirely reflect source composition (exceptions previously noted). Finally, the absence of significant losses of volatiles from hot, molten spheres exposed to vacuum (or very low pressures) places constraints on the cooling rates of these liquid spheres.

A Model for Volatile Loss from Tektites

The K isotopic data show that tektites are not evaporation residues, and there has never been definitive chemical evidence for vapor fractionation of potassium or other alkalis. The significant question that arises is why do tektites not show greater chemical and isotopic signatures of volatilization? Presumably, the cooling rates of tektites may have been high enough to prevent significant losses of volatiles. We consider that tektites were ejected into ballistic flight through a low vacuum path in the atmosphere (e.g., Matsuda et al. 1993) and that the tektites experienced most of their potential volatile element loss under vacuum while cooling radiatively to space. Splash-form tektites, such as australite buttons, are considered to have been melted during atmospheric re-entry. The thermal effects in such a case are restricted to the flanges of the tektites, which were not analyzed during the present study. Analysis of a fusion crust from the Murchison meteorite by Humayun and Clayton (1995a) showed that melt ablation during atmospheric heating of meteorites had no detectable effect on the K isotopic composition of the fusion crust.

As a pedagogical exercise, below we calculated the expected chemical losses of potassium from a sphere of molten tektite composition at a peak temperature of 2000–2473 K, assuming radiative cooling (perfect black body) into space to the glass transition temperature (~ 950 K). There are few determinations of the vapor pressure of potassium and none at the temperatures of interest. Vapor pressures of potassium over silicate melts were determined by De Maria et al. (1971) and Gooding and Muenow (1976) for lunar basalt compositions and by Gooding and Muenow (1976, 1977) for molten chondrites and a tektite, at temperatures of ~ 1200 K. As vapor pressures increase exponentially with temperature, the available data were extrapolated from ~ 1200 K using the equation:

$$P = P_0 \exp\left(\frac{-\Delta E}{RT}\right) \quad (1)$$

where $P_0 = 3.4 \times 10^5 \text{ g cm}^{-1} \text{ s}^{-2}$, and $\Delta E/R = 21,000 \text{ K}$ is the activation energy divided by the gas constant. A significantly larger slope is exhibited by the tektite composition of Gooding and Muenow (1976), determined over the temperature range 1470–1150 K, which extrapolates to an extremely high vapor pressure at 2000–2473 K. Thus, the lower slopes characteristic of molten lunar basalts and chondrites were selected to yield an average slope and intercept compatible with the measurements. Calculations performed with the higher slopes result in complete loss of potassium from tektites, an effect that is not observed. It is imperative for future work to determine vapor pressures at the appropriate temperatures for tektite compositions.

The mass loss of potassium (dW) from a sphere of area (A) is given by:

$$dW = -AJdt$$

where J is the vaporization rate, given by:

$$J = \alpha P_{\text{vapor}} \sqrt{\frac{M}{2\pi RT}} \quad (2)$$

where P_{vapor} is the equilibrium vapor pressure of potassium, M is the molecular weight of the evaporating species, R is the gas constant, and T is the temperature in K. The Langmuir evaporation coefficient (α), has values between 0 and 1, with typical values for silicates of about 0.1. In the absence of direct measurements, $\alpha = 1$ was used (which overestimates the evaporation rate). The relative loss of potassium is then:

$$\frac{dW}{W} = -\frac{A}{C_0 \rho V} J \cdot dt \quad (3)$$

where W is the mass of potassium in the melt, ρ is density (2.5 g/cm^3), $V = 4\pi r^3/3$, and C_0 is the initial concentration of potassium (0.02 g/g). This simplifies to give:

$$d \ln W = -\left(\frac{3}{r}\right) \frac{\alpha P_{\text{vapor}}}{C_0 \rho} \sqrt{\frac{M}{2\pi RT}} dt \quad (4)$$

which can be integrated from $t = 0$ to t , $W = W_0$ to W , to give:

$$\ln\left(\frac{C}{C_0}\right) = -\frac{3\alpha}{C_0 \rho r} \int_0^t P_{\text{vapor}} \sqrt{\frac{M}{2\pi RT}} dt \quad (5)$$

where P is a function of T . The substitution of concentration of K (C) for mass of K (W) follows if the loss of major elements (O, Si, Al, etc.) can be neglected. The time elapsed since cooling began was calculated from a perfect black body radiative cooling model:

$$\frac{dQ}{dt} = 4\pi r^2 \sigma T^4 = -C_p m \frac{dT}{dt}$$

by substituting density and volume for mass followed by the separation of variables, which yields:

$$dt = \frac{-r \rho C_p T^{-4} dt}{3\sigma} \quad (6)$$

Substituting Equation 6 into Equation 5 to eliminate time as a variable and substituting Equation 1 for the dependence of vapor pressure on temperature yields:

$$\ln\left(\frac{C}{C_0}\right) = \frac{\alpha C_p P_0}{\sigma C_0} \int_{T_p}^T \exp(-\Delta E/RT) \sqrt{\frac{M}{2\pi RT}} T^{-4} dT \quad (7)$$

This expression is independent of radius of the molten sphere. Making the approximation that \sqrt{T} term can be treated as a constant, the relationship then becomes:

$$\ln\left(\frac{C}{C_0}\right) = \frac{\alpha C_p P_0}{\sigma C_0} \sqrt{\frac{M}{2\pi RT_{\text{avg}}}} \int_{T_p}^T \exp(-\Delta E/RT) T^{-4} dT \quad (8)$$

where T_{avg} is the average temperature over which the evaporation occurs. This equation has an analytical solution:

$$\ln\left(\frac{C}{C_0}\right) = \frac{\alpha C_p P_0}{\sigma C_0} \sqrt{\frac{M}{2\pi RT_{\text{avg}}}} \frac{1}{c^3} \left[2 \exp\left(-\frac{c}{T}\right) + 2 \exp\left(-\frac{c}{T}\right) \left(\frac{c}{T}\right) + \exp\left(-\frac{c}{T}\right) \left(\frac{c}{T}\right)^2 \right] \quad (9)$$

where $c = \Delta E/R$, and the integral is evaluated from T_p to T_g , the glass transition temperature.

The time scale for radiative cooling can be obtained by integrating Equation 6:

$$\int_0^t dt = \frac{-r \rho C_p}{3\sigma} \int_{T_p}^T T^{-4} dT$$

to yield:

$$t = \frac{r\rho C_p}{9\sigma} \left[\frac{1}{T^3} - \frac{1}{T_p^3} \right] \quad (10)$$

where r is radius, ρ is density, C_p is the heat capacity for silicate rock (10^7 erg g^{-1} K^{-1}), σ is the Stefan-Boltzmann constant (5.67×10^{-5} erg sec^{-1} cm^{-2} K^{-4}), and T_p is the peak temperature.

The analytical solution obtained for Equation 9 was evaluated at $T_p = 2000$ K, 2273 K, and 2473 K, down to the glass transition temperature. Arndt and Rombach (1976) found glass transition temperatures of 948–957 K for australites and phillippinites, and hence, the calculation was terminated at 950 K. The vapor pressure and mass loss rate of K becomes negligible at 950 K. The results of this are shown graphically in Fig. 2 for a sphere of 1 cm radius. The solution depends on the choice of P_0 , $\Delta E/R$, and T_p , the results of which are considered separately below.

It can be seen that increasing the peak temperature increases the magnitude of the final fractionation. Most of the K loss occurs in the first 3–5 sec before cooling reduces the vapor pressure of K to the extent that further losses of K become negligible. The final amount of K loss is translated into isotopic fractionation by assuming Rayleigh fractionation:

$$\frac{R}{R_0} = F^{\alpha-1}$$

with $\alpha = 0.9753$ (inverse square root of the masses of the K atoms), which is also shown in Fig. 2. The time scale is a function of droplet size and would be shorter for smaller droplets.

To better understand the effects of droplet size, peak temperature, and choice of vapor pressure data on the relative change in K concentration, it should be appreciated that the extent of volatile loss of K and, therefore, the final $\delta^{41}K$ depends on a competition between two important time scales, the radiative cooling time scale, which is:

$$t_{rad} = \frac{Q}{dQ/dt} = \frac{4\pi r^3 \rho C_p T}{4\pi r^2 \sigma T^4}$$

which simplifies to give:

$$t_{radiative} = \frac{r\rho C_p}{3\sigma T^3} \quad (11)$$

and the mass loss time scale:

$$t_{mass} = \frac{r\rho C_0}{3\alpha P_{vapor}} \sqrt{\frac{2\pi RT}{M}} \quad (12)$$

Since both time scales depend identically on the radius (r), the ratio of the two time scales is independent of radius. Thus, in

the manner in which this problem has been formulated, there is no dependence of K loss on tektite size. In Fig. 3, the time scales are shown for a droplet size of 1 cm as a function of peak heating temperature. The radiative cooling time scale depends on T^{-3} , but the mass loss time scale depends exponentially on T^{-1} . Thus, as peak temperature is increased, mass loss eventually dominates over cooling. Three values of the vapor pressure were evaluated, which include the fit used to solve Equation 9 above (b) and a lower (a) and upper (c) extreme to the experimental results of Gooding and Muenow (1976). From Fig. 3, it can be seen that the $\delta^{41}K$ of the final product depends on the vapor pressure extrapolation in an important way, since the upper extreme could produce measurable isotopic effects in potassium. Since the upper extreme is equivalent to a more volatile element, Fig. 3 also implies that elements more volatile than potassium may exhibit measurable concentration losses and accompanying isotopic fractionation.

Figure 2 shows that, for the choices of vapor pressure made here, the peak temperatures experienced by the Australasian tektite samples must have been 2273 K (2000 °C) or less. At higher peak temperatures, K isotopic effects might have been observed. The effect of decreasing the droplet size is to linearly shift the cooling times to shorter times. Thus, microtektites may be expected to exhibit an equally limited range of K isotopic compositions. This may not be the case if microtektites experienced a larger range of peak temperatures than those experienced by tektites.

Potassium isotopic compositions for impact melts covering Apollo 16 boulders (Fig. 1) are also isotopically normal, even though these glasses have been heated above the melting point in the high vacuum of the lunar surface. Thus, there is no fractionation involved in the production of glassy impact melts of macroscopic dimensions regardless of composition or the presence/absence of an atmosphere. There does not appear to be any greater prospect for finding K isotopically fractionated terrestrial impact melts. Terrestrial impact melts formed under atmospheric pressure and may have been subjected to weathering, all of which lunar impact melts have escaped. Terrestrial impact glasses have lost some water but not to the same degree as tektites (Koeberl and Beran 1988; Koeberl 1992b). These also have lower contents of boron and fluorine than typical sedimentary rocks but not as low as tektites (Matthies and Koeberl 1991). There is no greater indication of loss of potassium or other volatile elements than for tektites.

We note that, for such brief heating events as impacts, very viscous glasses, such as tektites and terrestrial impact melts, are not likely to be well-mixed by diffusion and that chemical losses may be restricted to an external rind (~ 25 μm), which may not be well-represented in our analyses. That will not affect our conclusions regarding the absence of a distillation effect on the bulk composition of tektite glasses. For typical diffusivities of K in silicic melts of 10^{-4} to

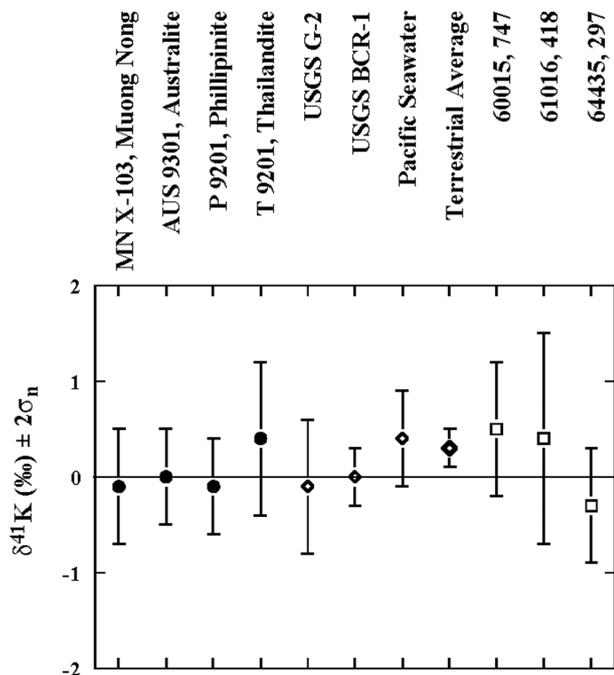


Fig. 1. Potassium isotopic compositions of tektites (filled circles, this study) compared with selected terrestrial samples (open diamonds) and impact melt coatings on Apollo 16 boulders (open squares). Terrestrial and lunar sample data from Humayun and Clayton (1995a).

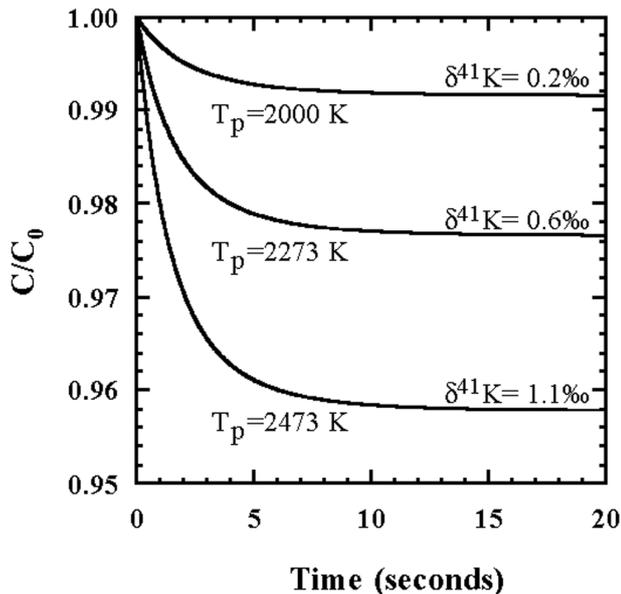


Fig. 2. Calculated potassium losses (C/C_0) occurring from a hypothetical 1 cm tektite droplet (2 wt% K) as a function of time. The droplet was assumed to be instantaneously heated to a peak temperature, T_p , of 2000, 2273, or 2473 K and then allowed to cool radiatively (see text) while experiencing thermal evaporation. The final $\delta^{41}\text{K}$ produced by Rayleigh fractionation is shown with each curve. Materials heated with $T_p < 2273$ K would not develop measurable K isotope mass fractionation effects.

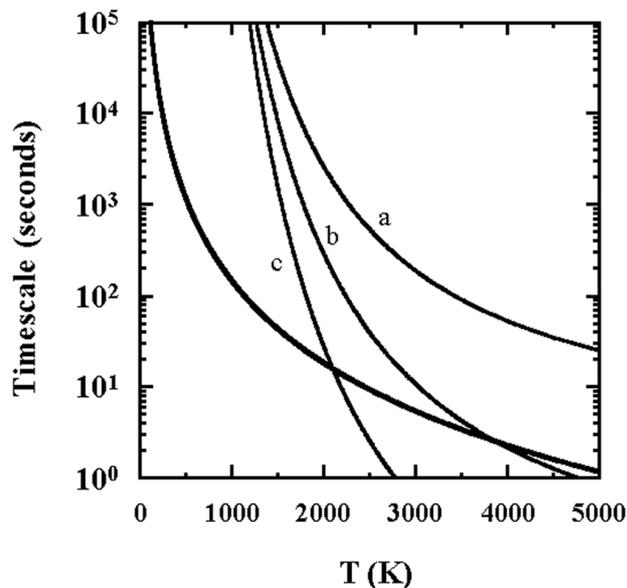


Fig. 3. Comparison between the time scale for radiative cooling (thick curve) with the time scales for mass loss as a function of temperature (thin curves) using the following vapor pressure information: a) $P_0 = 5.1 \times 10^3 \text{ g cm}^{-1} \text{ s}^{-2}$ and $\Delta E/R = 17,000 \text{ K}$; b) $P_0 = 3.4 \times 10^5 \text{ g cm}^{-1} \text{ s}^{-2}$ and $\Delta E/R = 21,000 \text{ K}$; and c) $P_0 = 2.6 \times 10^7 \text{ g cm}^{-1} \text{ s}^{-2}$ and $\Delta E/R = 25,000 \text{ K}$. The time scales of mass loss are longer than those of radiative cooling when $T < 2000 \text{ K}$ for all assumptions of the vapor pressure of potassium over tektite melts.

$10^{-5} \text{ cm}^2/\text{s}$ at $T \sim 2000 \text{ K}$ (e.g., Hofmann 1980), only melt droplets smaller than 0.01 cm (100 μm) might be diffusively mixed. In microtektites, the outer layers are likely to be dissolved away by seawater, and only those fractionations that are distributed throughout the body of the microtektites are likely to be discernable. Since microtektites are small enough to be diffusively mixed, if these objects exhibit measurable K isotopic fractionations, then it might imply that diffusion limited the extent of K losses from tektites. This would then imply that other elements that are more volatile than K would be similarly limited and that tektites provide accurate representations of their source composition because of the diffusion limit to losses of volatile elements. If this were the case, microtektites would not be suitable for establishing source compositions.

It should also be noted that the volatilization rate of K from silicate melts is a function of their oxygen fugacity, which may be different for tektites and for lunar glasses. The influence of oxygen fugacity on the magnitude of likely K isotope effects in tektites and lunar glasses is difficult to estimate in the absence of relevant experimental constraints but might be considered in more detailed explorations of this topic. The issue of why the lunar soil is isotopically fractionated in K remains. The soil is made up of many tiny glass particles, some of which show substantial chemical evidence of vaporization (McKay et al. 1991), but all of which are too small for individual isotopic analysis. The agglutinate glass is less than 1 μm in diameter and probably

less than 0.1 μm . As the glasses are too small to be diffusively limited, either higher peak temperatures, lower oxygen fugacity, or the absence of an atmosphere may have contributed to the observed K isotopic effects in lunar soils.

SUMMARY

The potassium isotopic composition for Australasian tektites is indistinguishable from that of terrestrial samples within 0.5–1.0‰, from which it is inferred that these tektites did not undergo significant vapor fractionation. These results are consistent with previous Mg and B isotopic studies but allow for volatile losses of water and halogens. This implies that the chemical compositions of tektites for alkalis, and more refractory elements, were controlled solely by source rock composition. A similar result is implied by the absence of K isotope fractionation in lunar impact melts.

A simple model of vapor fractionation during tektite genesis, using published determinations of the vapor pressure of potassium over silicate melts, and radiative cooling implies that silicate melt droplets are not likely to develop isotopic fractionation effects for peak $T \leq 2273 \text{ K}$ (2000 °C). At higher peak temperatures, silicate melt droplets might develop K isotope effects. Although no K isotope data presently exist for microtektites, a simple prediction is that there should be no measurable isotope effect, unless microtektites experienced higher peak heating temperatures. If tektites were simply diffusively limited, then microtektites might exhibit measurable K isotope effects.

Acknowledgments—We thank A. M. Davis for access to the ion microprobe and R. N. Clayton, S. R. Taylor, and Gidon Eshel for discussions on various aspects of this work. M. Humayun was supported by NASA NAGW 3345 (to R. N. Clayton) and by NASA NAG5-13133 (M. Humayun). C. Koeberl was supported by the Austrian Science Foundation, grant Y58-GEO. We thank Conel Alexander and an anonymous reviewer for their efforts, which substantially improved the manuscript, and we thank Ian Franchi for editorial handling of the manuscript.

Editorial Handling—Dr. Ian Franchi

REFERENCES

- Arndt J. and Rombach N. 1976. Derivation of the thermal history of tektites and lunar glasses from their thermal expansion characteristics. Proceedings, 7th Lunar and Planetary Science Conference. pp. 1123–1141.
- Blum J. D., Papanastassiou D. A., Koeberl C., and Wasserburg G. J. 1992. Nd and Sr isotopic study of Australasian tektites: New constraints on the provenance and age of target materials. *Geochimica et Cosmochimica Acta* 56:483–492.
- Chaussidon M. and Koeberl C. 1995. Boron content and isotopic composition of tektites and impact glasses: Constraints on source regions. *Geochimica et Cosmochimica Acta* 59:613–624.
- De Maria G., Balducci G., Guido M., and Piacente V. 1971. Mass spectrometric investigation of the vaporization process of Apollo 12 lunar samples. Proceedings, 2nd Lunar and Planetary Science Conference. pp. 1367–1380.
- Engelhardt W. V., Luft E., Arndt J., Schock H., and Weiskirchner W. 1987. Origin of moldavites. *Geochimica et Cosmochimica Acta* 51:1425–1443.
- Esat T. M. 1988. Physicochemical isotope anomalies. *Geochimica et Cosmochimica Acta* 52:1409–1424.
- Esat T. M. and Taylor S. R. 1986. Mg isotopic composition of Ivory Coast microtektites (abstract). 27th Lunar and Planetary Science Conference. pp. 210–211.
- Esat T. M. and Taylor S. R. 1987. Mg isotopic composition of microtektites and flanged australite buttons (abstract). 28th Lunar and Planetary Science Conference. pp. 267–268.
- Glass B. P. and Koeberl C. 1989. Trace element study of high- and low-refractive index Muong Nong-type tektites from Indochina. *Meteoritics* 24:143–146.
- Glass B. P., Swincki M. B., and Zwart P. A. 1979. Australasian, Ivory Coast, and North American tektite strewnfields: Size, mass, and correlation with geomagnetic reversals and other Earth events. Proceedings, 10th Lunar and Planetary Science Conference. pp. 2535–2545.
- Gooding J. L. and Muenow D. W. 1976. Activated release of alkalis during the vesiculation of molten basalts under high vacuum: Implications for lunar volcanism. *Geochimica et Cosmochimica Acta* 40:675–686.
- Gooding J. L. and Muenow D. W. 1977. Experimental vaporization of the Holbrook chondrite. *Meteoritics* 12:401–408.
- Hofmann A. W. 1980. Diffusion in natural silicate melts: A critical review. In *Physics of magmatic processes*, edited by Hargraves R. B. Princeton: Princeton University Press. pp. 385–417.
- Humayun M. 1994. Potassium isotope cosmochemistry: Implications for volatile depletion and origins of the Earth, Moon, and meteorites. Ph.D. Thesis, The University of Chicago, Chicago, Illinois, USA.
- Humayun M. and Clayton R. N. 1995a. Precise determination of the isotopic composition of potassium: Application to terrestrial rocks and lunar soils. *Geochimica et Cosmochimica Acta* 59:2115–2130.
- Humayun M. and Clayton R. N. 1995b. Potassium isotope cosmochemistry: Genetic implications of volatile element depletion. *Geochimica et Cosmochimica Acta* 59:2131–2148.
- Humayun M., Clayton R. N., and Koeberl C. 1994. Potassium isotopic composition of some Australasian tektites (abstract). 25th Lunar and Planetary Science Conference. pp. 581–582.
- Koeberl C. 1986. Geochemistry of tektites and impact glasses. *Annual Review of Earth and Planetary Sciences* 14:323–350.
- Koeberl C. 1992a. Geochemistry and origin of Muong Nong-type tektites. *Geochimica et Cosmochimica Acta* 56:1033–1064.
- Koeberl C. 1992b. Water content of glasses from the K/T boundary, Haiti: An indication of impact origin. *Geochimica et Cosmochimica Acta* 56:4329–4332.
- Koeberl C. 1994. Tektite origin by hypervelocity asteroidal or cometary impact: Target rocks, source craters, and mechanisms. In *Large meteorite impacts and planetary evolution*, edited by Dressler B. O., Grieve R. A. F., and Sharpton V. L. Special Paper 293. Boulder: Geological Society of America. pp. 133–152.
- Koeberl C. 1998. Identification of meteoritical components in impactites. In *Meteorites: Flux with time and impact effects*, edited by Grady M. M., Hutchison R., McCall G. J. H., and Rothery D. A. Special Publication 140. London: Geological Society of London. pp. 133–152.
- Koeberl C. 2001. The sedimentary record of impact events. In *Accretion of extraterrestrial matter throughout Earth's history*,

- edited by Peucker-Ehrenbrink B. and Schmitz B. Dordrecht: Kluwer Academic/Plenum Publishers. pp. 333–378.
- Koeberl C. and Beran A. 1988. Water content of tektites and impact glasses and related chemical studies. Proceedings, 18th Lunar and Planetary Science Conference. pp. 403–408.
- Koeberl C., Reimold W. U., Blum J. D., and Chamberlain C. P. 1998. Petrology and geochemistry of target rocks from the Bosumtwi impact structure, Ghana, and comparison with Ivory Coast tektites. *Geochimica et Cosmochimica Acta* 62:2179–2196.
- Matsuda J. I., Matsubara K., and Koeberl C. 1993. Origin of tektites: Constraints from heavy noble gas concentrations. *Meteoritics* 28: 586–589.
- Matthies D. and Koeberl C. 1991. Fluorine and boron geochemistry of tektites, impact glasses, and target rocks. *Meteoritics* 26:41–45.
- McKay D. S., Heiken G., Basu A., Blanford G., Simon S., Reedy R., French B. M., and Papike J. 1991. The lunar regolith. In *Lunar sourcebook*, edited by Heiken G., Vaniman D., and French B. M. Cambridge: Cambridge University Press. pp. 285–356.
- Molini-Vesko C., Mayeda T. K., and Clayton R. N. 1982. Silicon isotopes: Experimental vapor fractionation and tektites (abstract). *Meteoritics* 17:225–226.
- Montanari A. and Koeberl C. 2000. Impact stratigraphy: The Italian record. Heidelberg: Springer Verlag. 364 p.
- Taylor H. P. and Epstein S. 1966. Oxygen isotope studies of Ivory Coast tektites and impactite glass from the Bosumtwi Crater, Ghana. *Science* 153:173–175.
- Taylor S. R. 1973. Tektites: A post-Apollo view. *Earth Science Reviews* 9:101–123.
- Walter L. S. 1967. Tektite compositional trends and experimental vapor fractionation of silicates. *Geochimica et Cosmochimica Acta* 31:2043–2063.
- Walter L. S. and Carron M. K. 1964. Vapor pressure and vapor fractionation of silicate melts of tektite composition. *Geochimica et Cosmochimica Acta* 28:937–951.
- Walter L. S. and Clayton R. N. 1967. Oxygen isotopes: Experimental fractionation and variations in tektites. *Science* 156:1357.
- Wang J., Davis A. M., Clayton R. N., Mayeda T. K., and Hashimoto A. 2001. Chemical and isotopic fractionation during the evaporation of the FeO-MgO-SiO₂-CaO-Al₂O₃-TiO₂ rare earth element melt system. *Geochimica et Cosmochimica Acta* 65: 479–494.
- Yu Y., Hewins R. H., Alexander C. M. O'D., and Wang J. 2003. Experimental study of evaporation and isotopic mass fractionation of potassium in silicate melts. *Geochimica et Cosmochimica Acta* 67:773–786.
-