AN ANALYTICAL TECHNIQUE FOR THE ISOTOPIC ANALYSIS OF POTASSIUM IN METEORITIC AND PLANETARY MATERIALS; Munir Humayun[1], R. N. Clayton[1,2,3], and A. M. Davis[3]. Departments of [1]the Geophysical Sciences, and [2]Chemistry, and [3]Enrico Fermi Institute, University of Chicago, Chicago, IL 60637.

The depletion of volatile elements (condensation temperatures below those of Fo, En and Fe/Ni metal) affects nearly half the elements in the periodic table, and is one of two major chemical fractionation effects (siderophile element depletion is the other) seen in chondrites and differentiated planetary bodies. Despite the importance of this as a cosmochemical phenomenon, the processes responsible for volatile element depletion remain incompletely understood. The large range of observed effects can be accounted for by invoking a combination of two endmember mechanisms: two-component mixing, and physical processing of unfractionated chondritic material. These may take on a variety of forms, e.g. for two-component mixing this could be by mixing a high temperature volatile-free material with a low temperature C1 matrix-like material [1, 2]. Alternatively, the endmembers may be entirely hypothetically chosen [3] without reference to identifiable materials in meteorites, such as CAIs, chondrules or matrix. Physical processing has been conceived of as reevaporation of condensed material in nebular processes [4] (perhaps chondrule formation), and as metamorphism [5] or melting [6] on planetary bodies.

If physical processes (other than mixing) involving incomplete condensation or partial evaporation of volatiles, in the nebula or on small planetary bodies, are the dominant mechanisms, then it is possible that kinetic isotope effects have been induced in certain elements. Since volatile element depletion is evident on a planetary scale, isotopic compositions of certain volatile elements may differ from planet to planet (or meteorite), and in the case of chondrites may also be evident internally in different components. To be able to characterize a planet isotopically, a candidate element must not have large equilibrium isotope effects, and must have a well-understood geochemical behaviour. Certain elements such as Li, B, Cl, and S have widespread isotope fractionations within geological materials, and are unsuitable for this purpose. Other possibilities include K, Rb, Zn, and Se. Chalcophile and siderophile elements additionally show chemical depletions that cannot be unequivocally distinguished from volatility.

Lastly, the magnitude of a kinetic isotope effect is dependent on $\Delta M/M$ of the element concerned. We have, therefore, decided to investigate potassium, which is lithophile, and its extent of volatile depletion can be determined from K/La, or K/U ratios of differentiated planetary bodies. Potassium has three isotopes, 39 (93.2581 %), 40 (0.01167 %), and 41 (6.7302 %), but because of the low abundance of ^{40}K, we will only discuss the $^{41}K/^{39}K$ fractionation further. We report below on a method to accurately determine relative isotope fractionation in K, with a precision of about ±0.5 ‰ (±0.25 ‰/a.m.u., $2\sigma_M$) in a wide range of solar system materials. The method developed is a modification of the procedure used by Hinton *et al.* [7], employing the Chicago AEI IM-20 ionprobe. All mass spectrometric measurements are accompanied by instrumental mass fractionation, the correction of which is of paramount importance when attempting to search for intrinsic mass dependent isotope effects, particularly if these are comparable to or smaller than the instrumental effect. In the procedure developed by [7], this is done by running a standard of identical chemical composition under the same tuning conditions as the unknown.

In the present study, we have developed a method involving first the extraction of K from gram-size samples by conventional ion exchange techniques, followed by the conversion of the recovered KNO_3 to a borate glass, by melting with BaB_4O_7, prepared from Suprapur® reagents. The resultant glass bead is mounted on a glass slide along with standards and polished prior to ionprobe analysis. To avoid possible matrix effects, we always use a fixed chemical composition, i.e. 2 wt. % K. The precision attained is now reduced to a matter of the point to point reproducibility (of an isotopic measurement) on the same polished surface under identical tuning conditions. This precision is empirically determined by repeat measurements on a number of beads of the laboratory standard (Suprapur® KNO_3), and on other reagents or terrestrial materials.

In an older version of this procedure, we measured $\delta^{41}K$ [$=(R_{ij}/R_{ij}^{std}-1)\times1000$, where R_{ij}=41/39 ratio] using $Li_2B_4O_7$ glasses for a number of reagents and natural samples against Mallinckrodt® KCl (Table 1), and did not find any evidence for intrinsic isotopic fractionation. $Li_2B_4O_7$ glass was replaced with BaB_4O_7 glass, after it was observed that Li_2BO^+ interferences were not fully resolved at operating conditions of $M/\Delta M \approx 300$. This source of systematic error was kept to a minimum by using nearly constant $KNO_3/Li_2B_4O_7$ ratios. These did serve to demonstrate that a reproducibility of ≈±0.6 ‰ ($2\sigma_M$) can be obtained. In the BaB_4O_7 procedure, the only possible interference is B_2O^+, with $^{11}B^{10}B^{18}O^+/^{39}K^+$ of 10^{-8}. This peak is displaced by 58 millimass units from the center of the $^{39}K^+$ peak. Its effect is negligible.

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Besides interferences, the procedure may also introduce isotopic fractionation. There are two potential sources: ion exchange, and evaporation during melting. Isotope fractionation accompanying ion exchange separation of elements has been widely reported in the analytical literature [8]. It can be effectively dealt with by collecting the entire K fraction. In our procedures, a large ion exchange column is used, giving a chromatographically well-resolved K fraction, allowing essentially complete (≥98%) recovery. The effect of volatility during melting prior to glass formation has been carefully investigated, using $K_2B_4O_7$ and $KNO_3/Li_2B_4O_7$ mixture. Weight losses are determined gravimetrically, loss of NO_2 and H_2O from bubble formation in the melt, chemical loss of K by AAS, and isotopic fractionation by ionprobe analysis. It takes approximately 10 minutes to prepare a good melt bead. Longer melting for a period of hours to days results in detectable losses of K from the glass. Total losses of K after four days of melting were 22% of the initial concentration, and isotopic fractionation was ≤2.5 ‰. This is comparable to a calculated maximum effect assuming Rayleigh fractionation with a coefficient, $\alpha=(41/39)^{1/2}$, of 3.2 ‰. For the present procedure the fractional loss of K during the short melting period is much less than 10^{-3}, and the resultant isotope effect is entirely negligible. Finally, blanks during chemistry are kept to a minimum by the use of high purity reagents. The largest contribution is from the BaB_4O_7, and amounts to 5×10^{-4} of the sample K. The remaining blank is a factor of 10 smaller for most work.

Although we feel confident that with this procedure we can accurately measure relative isotopic differences between samples and a standard (in a manner analogous to gas source mass spectrometry), a test using separated isotopes is in progress. A number of natural materials, both terrestrial and extraterrestrial, are in the preparatory stages of analysis.

Scope: The present study, in addition to searching for isotopic fractionations in planetary and meteoritic samples, will also search for kinetic isotope fractionations within planetary bodies, particularly, a reinvestigation of the large reported effects in lunar soils and agglutinates [9, 10]. Since the discovery of the lunar Na/K exosphere, attention has once again been focussed on the lunar soils as possible sources of the exospheric alkali elements. This is consistent with earlier workers' assessment of loss mechanisms, that require ongoing processes, and provides a means of removing the volatilized elements by nonthermal loss from the lunar exosphere [11, 12]. The procedure we have developed is capable of further improvement in sample size, to eventually allow analysis of individual meteoritic components such as CAIs and chondrules.

References. [1] J. W. Larimer and E. Anders (1967) GCA 31, 1239-70; [2] L. Grossman and E. Olsen (1974) GCA 38, 173-187; [3] H. Wänke and G. Dreibus (1988) Phil. Trans. R. Soc. Lond. A 325, 545-557; [4] R. Wolf and E. Anders (1980) GCA 44, 2111-2124; [5] R. T. Dodd (1981) Meteorites, Cambridge Univ. Press, 368 p.; [6] D. W. Mittlefeldt (1987) GCA 51, 267-78; [7] R. W. Hinton *et al.* (1988) LPSC XIX, 497-8; [8] W. A. Russell and D. A. Papanastassiou (1978) Anal. Chem. 50, 1151-4; [9] E. L. Garner et al. (1975) Proc. Lunar Sci. Conf. 6, 1845-55; [10] S. E. Church et al. (1976) Proc. Lunar Sci. Conf. 7, 423-39; [11] A. E. Potter and T. H. Morgan (1988) Science 241, 675-80; [12] A. L. Sprague (1990) Icarus 84, 93-105.

Table 1. Isotopic compositions of natural samples vs. reagent Mallinckrodt® KCl.

Sample/Mallinckrodt® KCl	# of points analyzed	$\delta^{41}K\pm2\sigma_M$
Sylvite (Stassfurt, Germany)	n=12	- 0.1±0.9 ‰
Carnallite (Stassfurt, Germany)	n=15	+0.5±0.6 ‰
K-feldspar (Pegmatite, Baja Calif.)	n=12	+0.6±0.6 ‰