**POTASSIUM ISOTOPIC COMPOSITION IN STEPWISE DISSOLUTION OF ORGUEIL.** F. A. Podosek[1], R. H. Nichols[1], J. C. Brannon[1], and U. Ott[2], [1]McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130, USA, [2]Max-Planck-Institut fur Chemie, D-55128 Mainz, Germany.

The isotopic composition of K is of interest in several cosmochemical contexts. Fractionation effects, or lack thereof, set constraints on volatilization history [1]. Nuclear effects have also been observed: excesses of both $^{41}$K and $^{40}$K. Excess $^{41}$K is plausibly attributable to decay of short-lived $^{41}$Ca [2]; excess $^{40}$K attributable to cosmic-ray-induced nuclear reactions has also been observed, relatively modest enrichments in silicate meteorites and lunar samples [3–5] and huge enrichments in iron meteorites [6]. More generally, nucleosynthetic effects (isotopic anomalies) might be preserved in K just as they have been in other elements, with the added feature that because of the relatively short lifetime of $^{40}$K, anomalies might arise just from variable nucleosynthetic ages of presolar materials. Nevertheless, as far as we are aware no anomalies in K composition have been reported, specifically no deficiencies in $^{40}$K and no excesses in $^{40}$K other than those attributable to cosmic ray effects. Since the broad survey of Burnett et al. [3], however, samples investigated for possible anomalies at $^{40}$K have been quite limited, and motivated primarily by reports of unusually high K-Ar ages [7,8]. Precision of $^{40}$K analysis is limited by experimental factors arising in its low normal abundance (0.01%): In available published data error limits on potentially anomalous $^{40}$K abundance are reported as about one-half to one percent or higher.

We report here the results of K isotopic analyses of samples generated by stepwise dissolution of bulk Orgueil. This study is motivated by the observation of large isotopic anomalies in Cr in such samples [9,10] and the logic that there is presently no evident reason why such effects should be limited to Cr [10,11]. The samples studied are aliquots of the Orgueil-I dissolution series, for which chemical and other istopic data are reported elsewhere [10,11].

Potassium in these samples was chemically purified by ion-exchange chromatography. Isotopic analyses were performed by thermal ionization mass spectrometry in the Washington University Sector 54 instrument. Three different spectrometric precedures were used. The “IK40” procedure is a straightforward single-collector algorithm in which all isotopes are collected on the Daly detector, operated at 600 kcps ($6 \times 10^5$ counts per second, or about $10^{-13}$ amp) of $^{39}$K. “XKX2” is a mixed-mode algorithm, operated at $1.5 \times 10^{-12}$ amp of $^{39}$K, equivalently about 650 kcps of $^{41}$K), in which all three isotopes are first collected simultaneously, $^{40}$K in the Daly detector and the other two in Faraday cups), followed by simultaneous collection of $^{39}$K in a different Faraday cup and $^{41}$K in the Daly detector. The purpose of the $^{39}$K Daly measurement is to provide a “local” (approximately once per minute) calibration of Daly detector counting efficiency. (Over longer times, such as a few hours, Daly efficiency is not sufficiently stable to allow usefully precise data. This limitation precludes useful results, for example, for modes using larger beams and measurement of only $^{40}$K in the Daly). The third mode is “SK”, in which all three isotopes are simultaneously collected in Faraday cups, operated at a $^{39}$K beam intensity of $2 \times 10^{-10}$ amp.

Use of the Daly detector is important for the scarce isotope $^{40}$K, since it obviates the electrometer noise inherent in Faraday cup collection. For the two Daly modes, for example, the external precision (reproducibility) for $^{40}$K in calibration analyses is but little larger than the limit imposed by Poisson statistic, whereas for SK the $^{40}$K external precision is essentially the same as that for IK40 (about 12 ε, one sigma) despite a beam larger by a factor of 2000. For these analyses the Daly detector is preceded by a WARP (wide-angle retarding potential) “filter,” which reduces transmission of scattered ions. With the WARP, scattered $^{39}$K ions are essentially negligible for the fields at which the other isotopes are collected (Fig. 1).

Variations in $^{41}$K/$^{39}$K would be evident only if they exceeded the plausible range of variation of instrumental discrimination. No such effects were observed in any of the Orgueil-I samples, whence we may conclude that they have normal $^{41}$K/$^{39}$K, within a rather broad limit of about one percent.

Relative abundances of $^{40}$K were corrected for discrimination by assuming normal $^{41}$K/$^{39}$K. One dissolution fraction. Orgueil-I-4 (6N HCl at room temperature), yields results suggesting a 35–40 ε-unit excess of $^{40}$K (Fig. 2). One other fraction gives inconsistent results and six other have no $^{40}$K anomalies within limits of about 15 ε. (Fraction I-4 also exhibits excess $^{54}$Cr [10], but at a level small compared to the maximum effect in fraction I-6, which has normal $^{40}$K.)

It is not plausible to ascribe the apparent excess $^{40}$K to cosmic ray nuclear effects. For production rates as in other silicate meteorites [3] and a 10 Ma exposure age [12], $^{40}$K enrichment should be only $10^{-4}$ ε-unit for the whole rock. Cosmic-ray production of the apparent effect would thus require five to six orders of magnitude enrichment of Ca/K in fraction I-4, which appears highly unlikely.

The $^{40}$K excess must be considered only tentative because of potential interference at such a low-abundance isotope, The obvious candidate interferences are $^{40}$Ca and $^{24}$Mg$^{16}$O; neither species is expected under operating conditions for K, but the possibility cannot be dismissed out of hand. Possible interference from $^{40}$Ca is particularly troublesome because it is the dominant isotope of Ca and thus hard to monitor by other isotopes. Indeed, in both the IK40 and XKX2 analyses we would not be able to observe monitor peaks for Ca or MgO interferences accounting for 40 ε at mass 40. In the SK analyses, however, the absence of a signal at mass 42 (<1 cps) precludes any significant interference from either Ca or MgO at mass 40.

If the $^{40}$K excesses are real and fundamentally similar to those in Cr we might expect complementary deficiencies in other fractions. There is no suggestion of such deficiencies in the data, but if the effects scale like those in Cr the deficiencies would be only about 2 ε and thus unobservable.

**References:** [1] Humayun and Clayton (1995) GCA, 59, 2115. [2] Srinivasan et al. (1996) GCA, 60, 1823. [3] Burnett et al. (1966) JGR, 74, 1249. [4] Garner et al. (1975) Proc. LSC 6th, 1845. [5] Birck et al. (1977) Meteoritics, 12, 179. [6] Voshage and Feldman (1979) EPSL, 45, 293. [7] Stegmann and Begemann (1979) Nature, 282, 290. [8] Podosek et al. (1988) Nature, 334, 607. [9] Rotaru et al. (1992) Nature, 358, 465. [10] Podosek et al. (1997) MAPS, submitted. [11] Podosek et al., this volume. [12] Nichols et al. (1992) LPS XXIII, 987.

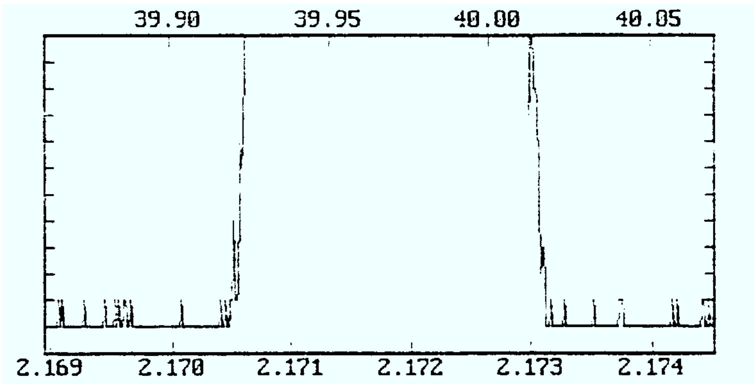


**Fig. 1.** Mass scan across $^{40}$K during XKX2 analysis of Orgueil-I-4. Bottom abscissa scale is Hall probe signal, top is equivalent mass. Ordinate ticks represent 5 cps (spikes to 5 cps reflect one count in 0.2 s integration time). $^{40}$K beam is about 1150 cps, $^{39}$K beam is about $10^7$ cps.

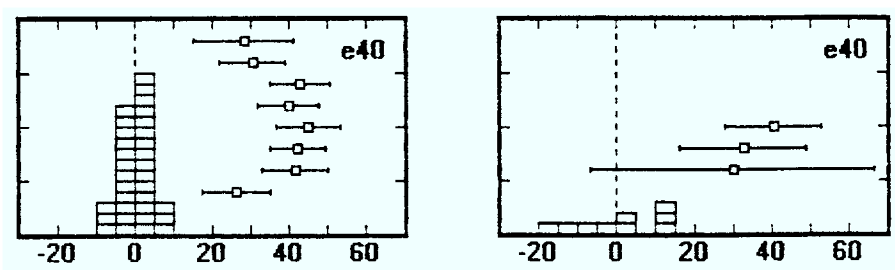


**Fig. 2.** Replicate analyses of Orgueil dissolution fraction I-4 using procedures XKX2 (left panel) and SK (right panel). Horizontal bars show two-sigma “internal” errors for $^{40}$K abundance. Abscissa scale in ε-units with origin defined by means of reagent calibrations (shown as histograms) for each procedure.