

**A NEW APPROACH TO IN-SITU K-Ar GEOCHRONOLOGY.** J.A. Hurowitz<sup>1</sup>, K.A. Farley<sup>2</sup>, N.S. Jacobson<sup>3</sup>, P.D. Asimow<sup>2</sup>, J.A. Cartwright<sup>4,2</sup>, J.M. Eiler<sup>2</sup>, G.R. Rossman<sup>2</sup>, Kathryn Waltenberg<sup>2</sup>, <sup>1</sup>Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA (joel.a.hurowitz@jpl.nasa.gov), <sup>2</sup>Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA, <sup>3</sup>NASA Glenn Research Center, Cleveland, OH, <sup>4</sup>Abteilung Biogeochemie, Max Planck Institut für Chemie, Mainz, Germany.

**Introduction:** The development of an in-situ geochronology capability for Mars and other planetary surfaces has the potential to fundamentally change our understanding of the evolution of terrestrial bodies in the Solar System. For Mars specifically, many of our most basic scientific questions about the geologic history of the planet require knowledge of the absolute time at which an event or process took place on its surface. For instance, what was the age and rate of early Martian climate change recorded in the mineralogy and morphology of surface lithologies (e.g., [1])? In-situ ages from a few select locations within the globally established stratigraphy of Mars would be transformative, enabling us to place *direct* chronologic constraints on the timing and rates of impact, volcanic, sedimentary, and aqueous processes on the Martian surface.

The current paradigm for establishing absolute ages on the Martian surface is through statistical methods based on lunar crater counting techniques. Progress has been made in previous decades, improving the precision of such estimates (e.g., [2]). However, precision is not equivalent to accuracy, and two inescapable facts regarding crater counting techniques remain: (1) “Any estimate of the Martian absolute chronology involves, implicitly or explicitly, an estimate of the Mars/Moon cratering rate ratio” [3]; and (2) Mars is geologically active, continually removing the record of craters and therefore causing bias towards younger ages. Thus, uncertainties on the accuracy of crater counting ages can exceed a factor of 2 in portions of Martian geologic history where constraints on crater flux are particularly poor. These issues will continue to cast doubt on crater age accuracy until radiometric age tie-points are provided for Mars.

Previous and ongoing efforts at the design of in-situ geochronology systems have targeted precisions of  $\pm 15\text{-}20\%$ . The new methodology we propose for measuring in-situ potassium-argon (K-Ar) ages has the potential to significantly improve on this measurement precision. Such improvements would increase the utility of in-situ ages for early Martian history, where crater counting methods are thought to be at their most accurate [3], and enable us to meaningfully address rates of processes on Mars.

#### *The Issue of Excess Ar in Shergottite Meteorites*

In discussions with our colleagues it is clear that there is a general uneasiness regarding the feasibility of accurately K/Ar dating Martian basalts. The reasons

for this uneasiness are most clearly stated in a series of papers by Bogard and colleagues [4-6]. The main concern is that the Ar/Ar ages of the most abundant class of SNC meteorites – the shergottites – are substantially older than their formation ages determined from other radiometric systems such as Sm/Nd, Rb/Sr and U/Pb. For example, Zagami is thought to have crystallized at 170 Ma, yet its Ar/Ar “age” (depending on what phase and what type of analysis is being considered) is more in the range of 300 Ma (and in some cases far older) [4]. Several studies have demonstrated that the cause of this discrepancy is excess Ar in the shergottites. This Ar is thought to be derived from shock implantation of atmospheric gases and from trapping of magmatic Ar [5, 7]. There are several reasons that we still believe that attempting K/Ar age determinations on Martian basalts is worthwhile:

1) Other classes of SNC’s give accurate K/Ar ages. For example, nakhlites and Chassigny yield Ar/Ar ages of about 1.35 Gyr, very similar to ages obtained from other techniques [8]. Thus it is not clear how pervasive this excess Ar problem really is in terms of the surficial coverage of Mars (as opposed to in the very unusual subset that has been launched to Earth). Specifically the shergottites are very shocked rocks (possibly associated with the launch event) and so may be expected to have larger amounts of shock implanted gases than typical surface basalts.

2) Bogard et al. [5] make the very curious observation that the amount of excess Ar in Shergottite mineral fractions is rather constant in their analyses, about  $1 \times 10^{-6} \text{ cm}^3 \text{ STP of } ^{40}\text{Ar}$ . This is important because in a basalt with a typical shergottite K concentration this is equivalent to about 200 Myr of Ar accumulation (i.e., the K/Ar age would be about 400 Myr instead of the “true” age of most shergottites of  $\sim 200$  Myr). However in a 2 Gyr basalt with the same K content and amount of excess Ar, the excess would yield just a 6% error in age (and this reduces to just 2% in a 3.5 Gyr basalt). In other words, the fact that the shergottites are so young is what makes this effect so noticeable. In our opinion an error of this magnitude is acceptable, since the fraction of extremely young basalts ( $< 500$  Myr) on the surface of Mars is almost certainly very low.

3) Bogard [6] notes the difficulty of obtaining the very high temperatures necessary to completely extract Ar from basaltic melts. Because we employ a flux-assisted digestion technique this issue is not relevant to our proposed approach (see below).

**A New Approach to K-Ar Geochronology:** We recognize that there are two major technical hurdles to making an accurate and precise in-situ K-Ar age measurement: (1) achieving melting temperature for rocks in order to quantitatively degas them of argon, and (2) measuring sample mass as a means of relating K-concentration to absolute abundance of argon. Here, we describe a new approach to in-situ measurement of K-Ar ages that solves both of these problems simultaneously.

In broad terms, our measurement protocol involves four steps. In step 1, a crushed or powdered sample is delivered to a crucible in a vacuum chamber, which has been loaded on Earth (i.e., prior to flight) with a lithium-based fluxing agent and a solid double-spike containing known amounts of isotopically enriched tracers of  $^{39}\text{Ar}$  and  $^{41}\text{K}$ . The  $^{39}\text{Ar}_{\text{spike}}/^{41}\text{K}_{\text{spike}}$  ratio is thus known, forming the basis of our age calculation (see below). In step two, the sample-flux-spike mixture is melted by heating the crucible with resistance heaters. The flux agent contains  $\text{LiBO}_2$ , which melts at  $849^\circ\text{C}$  and  $\text{Li}_2\text{B}_4\text{O}_7$ , which melts at  $920^\circ\text{C}$ . Heating to temperatures between  $950\text{--}1000^\circ\text{C}$  therefore readily achieves melting and isotopic homogenization of the sample-spike-flux mixture. In step three, the ratio of radiogenic  $^{40}\text{Ar}$  from the sample over  $^{39}\text{Ar}$  from the spike is measured on a mass spectrometer. Argon is quantitatively outgassed by melting of the sample, allowing us to solve for radiogenic  $^{40}\text{Ar}$  in the sample by measurement of the equilibrated sample/spike ratio. In the final step (4), the  $^{39}\text{K}_{\text{sample}}/^{41}\text{K}_{\text{spike}}$  ratio is analyzed via Knudsen Effusion Mass Spectroscopy (KEMS, [9]), using the same mass spectrometer as that used for the Ar-isotopic measurement. The measured K- and Ar-isotopic ratios are then used to solve for a whole rock age. We have validated each of the individual steps in this analytical procedure, as described below.

*Calculating K-Ar Ages using Double Isotope Dilution:* The K/Ar age equation is:

$$t = \frac{1}{\lambda} \ln\left(\frac{\lambda}{\lambda_e} \frac{^{40}\text{Ar}^*}{^{40}\text{K}} + 1\right)$$

where  $\lambda$  is the total  $^{40}\text{K}$  decay constant,  $\lambda_e$  is the decay constant for the electron capture decay mode that produces  $^{40}\text{Ar}$ ,  $t$  is the K/Ar age, and  $^{40}\text{K}$  and  $^{40}\text{Ar}^*$  are abundances in atomic units.  $^{40}\text{Ar}^*$  is the radiogenic daughter product, and is thus the  $^{40}\text{Ar}$  attributable to *in-situ* radioactive decay. Thus an age determination requires measurement of the  $^{40}\text{Ar}^*/^{40}\text{K}$  ratio.

K consists of three isotopes, with masses of 39 (93.3%), 40 (0.0117%), and 41 (6.73%). For isotope dilution K measurements,  $^{41}\text{K}$  of high isotopic purity

(>99%) is readily available. There are three stable isotopes of Ar (of masses 36, 38, and 40) and isotope dilution is usually done using  $^{38}\text{Ar}$  as a tracer. Since  $^{38}\text{Ar}$  is a useful indicator of cosmic ray exposure, we consider instead the use of synthetic  $^{39}\text{Ar}$ . This radioactive isotope has a half-life of 269 years and is routinely produced by neutron irradiation of  $^{39}\text{K}$  bearing substances.

When a spike containing the isotopic tracers  $^{41}\text{K}$  and  $^{39}\text{Ar}$  is added to the sample, and the combination fused to release and measure Ar isotopes and K-isotopes, the  $^{40}\text{Ar}^*/^{40}\text{K}$  ratio can be determined as follows (all variables are as defined in Table 1).

**Table 1. Definition of Variables**

$^{40}\text{Ar}^*$	in situ produced radiogenic Ar amount (unknown)
$^{39}\text{Ar}_{\text{spk}}, ^{40}\text{Ar}_{\text{spk}}$	amount of Ar isotope in spike
$^{40}\text{Ar}_m, ^{36}\text{Ar}_m, ^{39}\text{Ar}_m$	measured Ar amounts
$^{40}\text{Ar}_{\text{air}}, ^{36}\text{Ar}_{\text{air}}$	air-derived argon amounts
$R_{\text{air}} = (^{40}\text{Ar}/^{36}\text{Ar})_{\text{air}}$	Known
$R_{\text{spk}} = (^{40}\text{Ar}/^{39}\text{Ar})_{\text{spk}}$	independently determined
$R_m = (^{40}\text{Ar}/^{39}\text{Ar})_m$	Measured
$^{39}\text{K}_u, ^{40}\text{K}_u, ^{41}\text{K}_u$	amounts of K in unknown
$^{39}\text{K}_{\text{spk}}, ^{41}\text{K}_{\text{spk}}$	amounts of K in spike
$r_m = (^{39}\text{K}/^{41}\text{K})_m$	Measured
$r_{\text{spk}} = (^{39}\text{K}/^{41}\text{K})_{\text{spk}}$	independently determined
$r_{\text{nat}} = (^{39}\text{K}/^{41}\text{K})_{\text{nat}}$	natural K isotopic composition (known)
$r_{40} = (^{40}\text{K}/^{39}\text{K})_{\text{nat}}$	natural K isotopic composition (known)

First, for Ar:

$$^{40}\text{Ar}_m = ^{40}\text{Ar}^* + ^{40}\text{Ar}_{\text{air}} + ^{40}\text{Ar}_{\text{spk}} \quad (1)$$

$$^{36}\text{Ar}_m = ^{36}\text{Ar}_{\text{air}} \quad (2)$$

$$^{39}\text{Ar}_m = ^{39}\text{Ar}_{\text{spk}} \quad (3)$$

Where equation (1) is the mass balance for  $^{40}\text{Ar}$  and indicates that some of the  $^{40}\text{Ar}$  is derived from “contamination” with (terrestrial or martian) atmospheric argon. The the second and third equations indicate that all  $^{36}\text{Ar}$  is air-derived and all  $^{39}\text{Ar}$  is spike-derived. Combining these equations and the definitions in Table 1 yields:

$$^{40}\text{Ar}^* = \left(R_m - R_{\text{air}} \left(\frac{^{36}\text{Ar}}{^{39}\text{Ar}}\right)_m - R_{\text{spk}}\right) ^{39}\text{Ar}_{\text{spk}} \quad (4)$$

In the case of K:

$$^{39}\text{K}_m = ^{39}\text{K}_u + ^{39}\text{K}_{\text{spk}} \quad (5)$$

$${}^{41}K_m = {}^{41}K_u + {}^{41}K_{spk} \quad (6)$$

$${}^{40}K_u = r_{40} {}^{39}K_u \quad (7)$$

Where equations (5) and (6) reflect mass balance and equation (7) states that the isotopic composition of the unknown sample is that of natural potassium. Combining these equations and the definitions in Table 1 yields:

$${}^{40}K_u = r_{40} \left( \frac{r_{spk} - r_m}{r_{nat} - 1} \right) {}^{41}K_{spk} \quad (8)$$

Combining equations 4 and 8 yields the ratio from which the K/Ar age is determined:

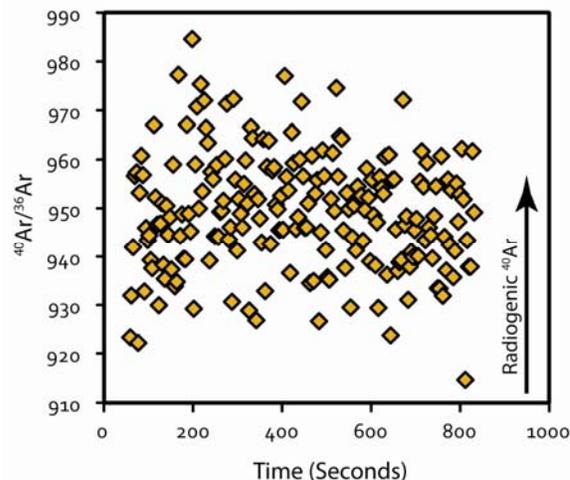
$$\frac{{}^{40}Ar^*}{{}^{40}K} = \frac{\left( R_m - R_{air} \left( \frac{{}^{36}Ar}{{}^{39}Ar} \right)_m - R_{spk} \right) \left( \frac{{}^{39}Ar}{{}^{41}K} \right)_{spk}}{r_{40} \left( \frac{r_{spk} - r_m}{r_{nat} - 1} \right)} \quad (9)$$

It is important to note that by using equation 9, the K/Ar age can be computed directly from measured isotopic ratios without knowledge of the mass of the sample or of the spike glass. This is a fundamental advantage of our age-dating technique, and is built on the fixed  ${}^{39}Ar_{spk}/{}^{41}K_{spk}$  ratio. Furthermore, because we only require the measurement of isotopic ratios with our technique, instrument calibration becomes much simpler or possibly even unnecessary.

*Synthesis of a Double Isotope Spike:* We have prepared an alkali-feldspar glass that contains the isotope dilution spikes  ${}^{41}K$  and  ${}^{39}Ar$ . The glass was prepared in a 2-step synthesis procedure. In the first step, pure oxide ( $SiO_2$ ,  $Al_2O_3$ ) and carbonate ( $Na_2CO_3$ ) components were fused at  $1150^\circ C$  in a Pt-crucible in an open-tube gas mixing furnace to form a melt. This melt was held above the liquidus for  $\sim 48$  hours and then quenched to form albite glass ( $NaAlSi_3O_8$ ). The product glass was then crushed with a mortar and pestle and mixed with KCl (obtained from the Oak Ridge National Laboratory) that is enriched in the  ${}^{41}K$  isotope (99.17%  ${}^{41}K$ ). This mixture was also loaded in a Pt crucible and fused at  $1150^\circ C$  into an open-tube gas mixing furnace that was continuously purged with a  $CO_2$ - $H_2$  gas mixture. The gas mixture was “tuned” to maximize  $pH_2O$  at  $1150^\circ C$  and remove Cl from the mixture as HCl vapor, leaving the K in the melt. Experiments at low  $pH_2O$  revealed that K is quantitatively lost from the melt owing to the relatively high volatility of KCl. The melt was held above the liquidus for  $\sim 96$  hours and then quenched to form a glass. Electron microprobe analysis of this glass indicates typical  $K_2O_{Total}$  concentra-

tions of 6-8 wt%. Because the KCl contains a trace of  ${}^{39}K$  ( $\leq 0.83\%$ ), the glass can be neutron irradiated using typical Ar-Ar irradiation conditions. This produces  ${}^{39}Ar$  in the glass by neutron capture, yielding our final double-isotope solid spike. Our synthetic glass was subjected to neutron irradiation for  $\sim 50$  hours in the Oregon State University TRIGA reactor.

*Argon Isotopic Measurements:* We have performed a variety of experiments designed to measure the Ar-isotopic composition of gases released from silicate materials fused in the presence of a Li-based fluxing agent (50% Li-metaborate, 50% Li-tetraborate). In early experiments, a K-feldspar sample was mixed with a SrCl tracer, in order to determine whether flux-assisted digestion of silicate minerals results in argon release at low temperatures ( $1000^\circ C$ ), and whether or not sample-tracer homogeneity is achieved by flux-assisted digestion. The results shown in **Fig. 1** indicate that Ar-release occurs during flux digestion. In addition, laser ablation ICP-MS analysis of the glass produced during this experiment has a homogeneous K/Sr ratio (not shown), demonstrating sample-spike equilibration during flux-assisted melting.



**Fig. 1:**  ${}^{40}Ar/{}^{36}Ar$  isotope ratio of K-feldspar measured as a function of time on a quadrupole mass spectrometer during flux-assisted digestion. The  ${}^{40}Ar/{}^{36}Ar$  ratio is significantly elevated relative to atmospheric ( ${}^{40}Ar/{}^{36}Ar=296$ ), indicating release of radiogenic  ${}^{40}Ar$  (i.e.,  ${}^{40}Ar^*$ ) from the sample.

In subsequent experimentation, we mixed a 132 Ma basalt obtained from the Parana basin of Brazil with our double-isotope spike and flux-melted the mixture at  $1000^\circ C$ . This yielded measurements of 60% radiogenic Ar from this young, low-K ( $< 0.5$  wt %  $K_2O$ ) basalt.

*Potassium Isotope Measurements with KEMS:* We have performed a series of experiments at the NASA Glenn Research Center that were designed to determine whether the application of KEMS could provide a suitable means of measuring the K-isotopic composition of vaporized K during low-temperature flux-assisted melting. Briefly, KEMS involves melting of the sample in a specially designed cell (in our case, made of Mo), production of a vapor that exits the top of the crucible in the Knudsen flow regime, line of sight ionization of neutral vapor species, and measurement of the ionized isotopes on a mass spectrometer, in our case a magnetic sector instrument [9]. The high resolution of the magnetic sector instrument allows separation of the  $^{39}\text{K}$  peak from background hydrocarbons, and hence more accurate measurements.

Our experimental results are shown on **Fig. 2**, which is a plot of measured  $^{39}\text{K}$  as a function of temperature for: (1) Parana basalt, (2) Parana basalt melted in the presence of flux, (3) non-isotopically enriched spike glass melted in the presence of flux, and (4) flux as a control. The salient results of these experiments can be summarized as follows: KEMS provides long lived (2-3 hours), stable  $^{39}\text{K}$  signals from all of the analyzed samples (except for the control, which contains no measureable K); K measurements can be made at low temperature ( $<1000^\circ\text{C}$ ) during flux assisted melting, (3) the onset of K-vaporization occurs at the same temperature for both the spike glass and the basalt during flux-assisted melting, indicating that equilibration of K-isotopes from sample and spike should be readily achievable.

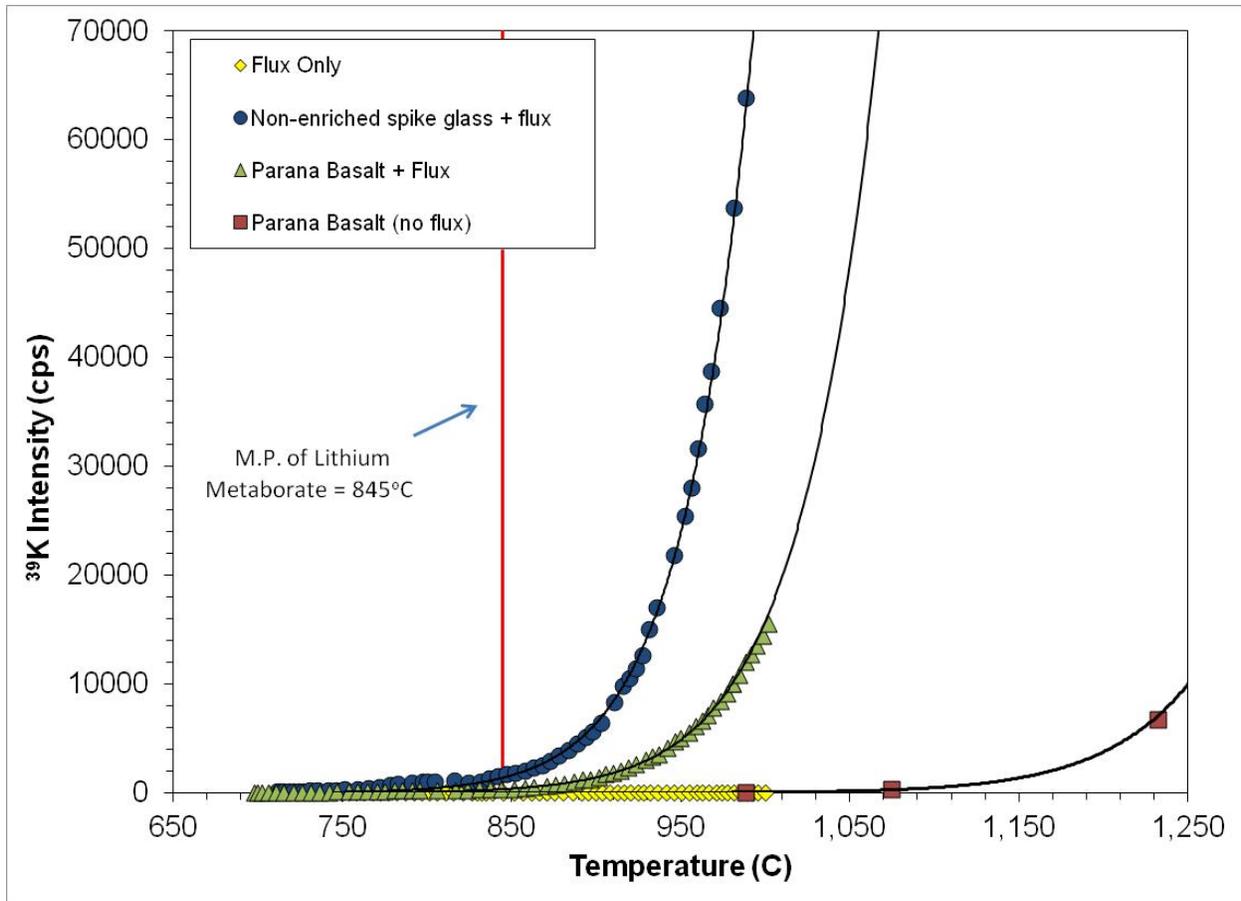
**Future Work:** Presently, we are synthesizing a second batch of an isotopically-enriched spike that will be used to produce our first age measurement using the methodology we have developed. This will be accomplished in a 2-step procedure in which a mixture of flux, Parana basalt, and spike glass are combined in a Knudsen cell crucible and melted in a furnace attached to a noble gas mass spectrometer in the Geological and Planetary Sciences Department at Caltech. The gases released following melting will be analyzed to measure the Ar-isotopic composition. The melt will then be quenched, and the Knudsen cell crucible containing the glass will be sent to NASA Glenn Research Center for measurement of the K-isotopic composition of the

glass using a KEMS instrument. From these isotope ratio measurements, the age of the Parana basalt sample will be computed.

Once we have successfully demonstrated an end-to-end age measurement using this technique, we will begin the construction of a single benchtop instrument that can accomplish the entire measurement in a single-step melting procedure. Due to the simplicity of our measurement technique, the benchtop instrument system will be relatively straightforward to build and operate. Essentially what we require is a resistance furnace, a line-of-sight ionizer, standard plumbing for enrichment and sequestration of noble gases, and a small mass spectrometer capable of measuring isotope ratios. From this basic benchtop architecture, we can design a suitably miniaturized instrument system for field testing and eventual flight prototyping.

In summary, we have developed an inherently simple experimental methodology that can be employed for the measurement of K-Ar whole rock ages on the surface of Mars, the Moon, and other Solar System bodies of interest. Our technique requires neither high fusion temperatures for Ar-release, nor a means of weighing aliquots of sample to relate K-concentration to Ar-abundance; both of which have been significant technical hurdles that have hampered previous attempts to produce in-situ instruments for K-Ar geochronology. This technique is applicable to materials with low-K concentrations, and requires only the measurement of isotope ratios, making in-flight mass spectrometer calibration simple or perhaps even unnecessary.

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**Fig. 2:**  $^{39}\text{K}$  signal measured on the NASA Glenn Research Center KEMS as a function of temperature. Note that the onset of  $^{39}\text{K}$  signal for flux assisted melting of basalt and spike occurs at 845°C, which is the melting point of the Li-metaborate flux.