

ENDEMIC ISOTOPIC ANOMALIES IN TITANIUM

F. R. NIEDERER, D. A. PAPANASTASSIOU, AND G. J. WASSERBURG

Division of Geological and Planetary Sciences,¹ Caltech

Received 1980 March 19; accepted 1980 May 9

ABSTRACT

Abundances of the titanium isotopes were determined using a new high-precision technique that shows terrestrial, lunar, and bulk meteorite samples to be indistinguishable. Ca-Al-Ti-rich inclusions in the Allende meteorite are found to contain Ti of widely varying isotopic composition reflecting the presence of at least three nucleosynthetic components. The anomalies in Ti appear to be relatively widespread and, when correlated with Ca data, provide a clue to nucleosynthesis in the neighborhood of the iron peak and to the late-stage nucleosynthetic processes which immediately preceded formation of the solar nebula.

Subject headings: meteors and meteorites — nucleosynthesis — solar system: general

I. INTRODUCTION

We report the discovery of variations in isotopic composition of titanium in four inclusions from the Allende meteorite. Extensive searches for isotopic anomalies have been carried out in meteorites, and clear evidence has been found in O, Ne, Mg, Ca, Kr, Sr, Xe, Ba, Nd, and Sm due to nuclear-astrophysical processes. Isotopic enrichments have been found in ²⁶Mg, ¹⁰⁷Ag, and ¹²⁹Xe due to decay of the short-lived progenitors ²⁶Al (0.7×10^6 yr), ¹⁰⁷Pd (6×10^6 yr), and ¹²⁹I (17×10^6 yr). As a result of these observations, it is widely believed that many isotopic effects result from the injection of freshly synthesized material from supernova sources into the ambient interstellar medium immediately prior to solar system formation. Two Ca-Al-Ti-rich inclusions (C-1 and EK-1-4-1) are of particular importance because almost every refractory element so far studied in these objects is isotopically anomalous. This may be used to search for regularities in the nuclear systematics as a function of atomic number and neutron number.

In this study we attempted to pursue a possible chain of nuclear reactions in the general region of the iron abundance peak. As Fe is in very low abundance in the "high-temperature" Ca-Al condensates, we chose to study Ti which is a major constituent of these materials. Although Ti is in the general region of the Fe peak, there is substantial uncertainty as to the nucleosynthesis of the Ti isotopes (Bodansky, Clayton, and Fowler 1968; Michaud and Fowler 1972; Howard *et al.* 1972; Cameron 1979). From previous studies it was known that Ca shows anomalies at masses 42 and 48 (Lee, Papanastassiou, and Wasserburg 1978; Lee, Russell, and Wasserburg 1979; Niederer and Papanastassiou 1979). It was plausible to suppose that anomalies should exist in Ti with atomic masses 46, 47, 48, 49, and 50. The solar ratio (⁴⁹Ti/⁴⁸Ca)_⊙ is 1.2 so that, for EK-1-4-1, addition of nuclei at ⁴⁹Ti or ⁵⁰Ti commensurate to those added at ⁴⁸Ca would cause effects

in ^{49,50}Ti at the level of ~ 15 parts per thousand. To carry out these experiments we applied chemical procedures directed toward separation of Ti and devised techniques which permit precise determination of Ti isotopic abundances. Most previous measurements of Ti were carried out at a level of precision which is far too low for the present purposes. The only recent measurements were by Heydegger, Foster, and Compton (1979), who measured a Ti⁺ ion beam with an ion yield (ions detected/atoms in the source) of 10^{-6} – 10^{-7} and obtained a precision of $\sim \pm 1$ part per thousand for an analysis. These workers inferred an isotopic shift in ⁵⁰Ti in Allende inclusions from a statistical analysis of their combined data from several inclusions. However, the inferred effect was within the limits of error for analyses of individual inclusions, and these workers were not able to replicate or resolve any effects.

II. RESULTS

We have found that TiO⁺ forms a stable and intense ion beam with an ion yield of $\sim 10^{-4}$ with Ta₂O₅ as a matrix and using thermal ionization techniques. Samples of 2×10^{-6} g of Ti gave ion beams of 2×10^{-11} A for ⁴⁸Ti¹⁶O⁺. Comparison of results obtained for TiO⁺ and Ti⁺ (see Table 1) shows the precision of oxide data (labeled o) to be much better than for the metal (e) on terrestrial normal, since TiO⁺/Ti⁺ ~ 20 . No evidence of spectral interferences could be detected in the TiO⁺ or Ti⁺ mass region under conditions of data acquisition. We found no significant interference from Cu⁺, Zn⁺, VO⁺, CaF⁺, TiF⁺, ScO⁺, K⁺, Ca⁺, or V⁺. The isotopic composition of Ti was calculated from the TiO⁺ spectrum assuming ¹⁶O:¹⁷O:¹⁸O = 1:0.0003708:0.002045 (Nier 1950). The ratio ¹⁸O/¹⁶O was determined during one TiO⁺ analysis by measurement of the ion beams at masses 68 and 66 and yielded 0.00203, in reasonable agreement with the assumed value. For all experiments the raw measured ratios of I_{62}/I_{64} were plotted against I_{66}/I_{64} and were found to lie on a fractionation line of slope -1.05 ± 0.02 . This shows that there is no evidence for changes in ¹⁸O/¹⁶O in a run or between runs of the

¹ Division Contribution No. 3426 (346).

TABLE 1
 TITANIUM ISOTOPIC COMPOSITIONS*

SAMPLE ^b	FARADAY CUP DATA		
	$\epsilon(47, 48)$	$\epsilon(49, 48)$	$\epsilon(50, 48)$
Terrestrial Samples			
TiO ₂ normal:			
1 e LI.....	-26±29	-13±30	0±30
2 e LIII.....	0±10	-2±10	-20±20
3 e LIII.....	-9±20	-3±20	-20±20
4 e LI.....	-10±30	+16±20	+12±20
5 e LI.....	+9±10	-6±10	+14±15
6 o LI.....	+0.5±0.8	+0.3±1.0	+0.5±1.0
7 o LIII.....	+1±1.6	-0.1±1.1	+0.4±2.0
8 o LI.....	-0.1±1.0	-0.9±1.1	-1.0±1.0
9 o LI.....	-1.2±1.0	-1.2±1.1	0.0±1.0
10 o LI.....	+0.1±1.0	+0.3±1.0	-0.4±0.9
10 e LI.....	-4±30	-28±30	+13±30
11 o LI.....	-0.3±1.0	+0.3±1.1	-0.4±0.7
12 o LI.....	+0±0.8	+0.9±1.1	+0.2±0.7
13 o LI.....	+0.5±1.0	+0.5±1.1	-1.5±1.6
BCR-1 o LI.....	+2.0±2.6	+0.0±2.4	-0.2±2.0
Lunar Sample			
75055 o LI.....	+0.3±2.0	-2.9±2.0	-1.6±2.0
Allende Samples			
Total o LIII.....	-0.7±1.6	+1.6±1.1	+1.4±1.3
Ca-Al-Ti Inclusions:			
EK-1-4-1 o LIII..	+14.4±2.5	+16.7±4.4	+35.4±7.0
(I) o LI.....	+12.1±2.1	+16.6±2.5	+34.9±2.9
o LI ^c	+12.9±6.5	+23±11	+43±10
o LI.....	+11.3±3.4	+21.4±4.0	+36.3±4.0
(II) o LIII..	+12.6±3.0	+19.9±2.9	+38.3±3.0
Mean.....	+12.7±1.6	+18.8±2.2	+36.9±2.4
C-1 o LI.....	+4.9±1.0	-6.1±1.0	-50.4±0.9
(I) o LI.....	+5.2±1.1	-7.5±1.3	-51.5±2.0
e LI ^d	-45±10
e LI ^d	-56±8
(II) o LIII..	+6.0±2.0	-8.4±3.0	-53.2±3.0
Mean.....	+5.2±0.8	-7.0±1.0	-51.2±1.1
EGG-1 o LI.....	-2.9±0.9	-4.6±1.2	+6.4±0.9
EGG-3 o LI.....	-3.8±1.0	-6.1±1.2	+6.5±1.0
o LI.....	-3.1±1.1	-5.4±1.0	+7.7±2.0
ELECTRON MULTIPLIER DATA ^e			
SAMPLE	$\epsilon(47, 49)$	$\epsilon(48/49)$	$\epsilon(50, 49)$
TiO ₂ normal e LI...	-8±11	-9±10	+17±15
C-1 e LI.....	+13±12	-35±16
e LI.....	+0±8	-37±8

* $\epsilon(i, j) = [(^{i}\text{Ti}/^{j}\text{Ti})_{\text{CORR}} / (^{i}\text{Ti}/^{j}\text{Ti})_N - 1] \times 10^4$; N = normal; CORR = measured ratio (M), corrected to a standard state for an effective fractionation factor α (per m.u.) for ($^{46}\text{Ti}/^{48}\text{Ti}$) as determined by ($^{46}\text{Ti}/^{48}\text{Ti}$)_M / ($^{46}\text{Ti}/^{48}\text{Ti}$)_N = $(1 + \alpha)^2$. The normal Ti composition used is ($^{46}\text{Ti}/^{48}\text{Ti}$)_N = 0.108548, ($^{47}\text{Ti}/^{48}\text{Ti}$)_N = 0.099315 ± 0.000005, ($^{49}\text{Ti}/^{48}\text{Ti}$)_N = 0.074463 ± 0.000004, ($^{50}\text{Ti}/^{48}\text{Ti}$)_N = 0.072422 ± 0.000004 (2 σ grand mean uncertainties). This normal composition is the grand mean determined from TiO⁺ analysis of TiO₂ normal (J&M, spectrographically pure). All error estimates are 2 σ (mean) per analysis.

^b e = Ti⁺ and o = TiO⁺ ion beams; LI or LIII = Lunatic I or III spectrometer.

^c Sample passed twice through chemical procedure.

^d No ^{47}Ti or ^{49}Ti data obtained.

^e Data normalized to ($^{46}\text{Ti}/^{48}\text{Ti}$)_N. ^{48}Ti data were not obtained at high ion beam intensities. See McCulloch and Wasserburg (1978a) for transformation of ϵ_{ij} for a change of index isotope and normalization.

same sample. In determining Ti ratios the only large correction for oxygen isotopes occurs at mass 66 ($^{50}\text{Ti}^{16}\text{O} + ^{48}\text{Ti}^{18}\text{O} + ^{49}\text{Ti}^{17}\text{O}$). The isotopic abundances for a terrestrial standard are shown in Table 1 and show a typical precision of $\pm 1 \epsilon$ (1 ϵ unit is 1 part in 10^4) 2 σ_{mean} for an individual experiment. Data were obtained on two instruments and found to be in good agreement and in accord with the grand average for terrestrial Ti as reported by Heydegger, Foster, and Compston (1979). In addition to the standard, a terrestrial basalt, a lunar basalt, and a sample of bulk Allende meteorite were analyzed. All these materials show a Ti isotopic composition indistinguishable from the standard to within 2 ϵ . Enriched standards made of normal Ti mixed with ^{47}Ti and ^{49}Ti were prepared and analyzed. Table 2 compares mass-spectrometrically measured values with the known gravimetric values and shows that effects at the level of 12 ϵ are quantitatively measured and that effects are detectable at $\sim 3 \epsilon$.

Measurements were made on two FUN inclusions, C-1 and EK-1-4-1, from Allende. The remaining world reserves of EK-1-4-1 are small so that the material available is very restricted. Pyroxenes rich in Ti ($\sim 8\%$ Ti) weighing $\sim 10^{-4}$ g were picked and analyzed after chemical separation of Ti (sample I). Aliquots of sample I were analyzed on the Lunatic I and III spectrometers. The results are in excellent agreement and show the Ti to be distinctly anomalous. The pattern of the anomalies for normalization at ^{46}Ti and ^{48}Ti is shown in Figure 1a. The chemical separation was repeated on a part of the previously separated Ti fraction and the results confirmed (see Table 1, note C). An additional analysis on a separately prepared sample of pyroxene (II) confirms these results. Fassaitic pyroxene (5×10^{-4} g) was handpicked from C-1 and analyzed (sample I). The results show a large negative anomaly at ^{50}Ti of -51 ϵ , a negative anomaly at ^{49}Ti , and a positive anomaly at ^{47}Ti . An additional analysis done on a separately prepared pyroxene (II) replicates the data on the first C-1 sample. To firmly establish the existence of effects in C-1, measurements were made of Ti⁺ as well as TiO⁺. Because of the much smaller Ti⁺ ion beam, data were taken both with the Faraday cup and with an electron multiplier. The precision of the Ti⁺ data is a factor of 5-10 lower than obtained on TiO⁺. The multiplier data using the Ti⁺ beam are shown in Table 1 (bottom lines) for the terrestrial standard and for C-1. These data quantitatively confirm the results on ^{50}Ti for C-1. To test whether Ti in more "typical"

 TABLE 2
 TITANIUM ENRICHED STANDARDS*

	$\epsilon(47, 48)$	$\epsilon(49, 48)$	$\epsilon(50, 48)$
Gravimetric—I.....	11.5	11.5	0.0
Measured—I.....	11.0±1.0	10.0±1.5	0.8±1.4
Gravimetric—II.....	3.7	3.7	0.0
Measured—II.....	3.7±0.6	3.1±1.0	1.3±1.3

* Deviations in parts in 10^4 (see Table 1).

Ca-Al inclusions shows evidence of effects, pyroxenes from large, coarse-grained inclusions were analyzed. These samples (EGG-1, EGG-3) had been found to contain ^{26}Mg excesses in phases with high Al/Mg which were inferred to result from ^{26}Al decay. They also showed evidence for small excesses in ^{48}Ca (Niederer and Papanastassiou 1979). The results show clear non-linear effects at ^{47}Ti , ^{49}Ti , and ^{50}Ti for both samples but at levels considerably smaller than for the two FUN samples.

III. DISCUSSION

The isotopic abundances of Ti from titaniferous pyroxenes in Ca-Al-Ti-rich inclusions in the Allende meteorite are found to be distinctly different from that in terrestrial and lunar materials. Using a normalization to ^{46}Ti and ^{48}Ti to correct for isotopic mass fractionation effects, a complex set of isotopic anomalies is observed at masses 47, 49, and 50. Anomalies are present at the level of +35 and -51 ϵu at mass 50 in the FUN samples EK-1-4-1 and C-1, respectively; smaller but well-resolved effects are also found in two

other Allende inclusions. This indicates that Ti isotopic anomalies are endemic in this type of material. Titanium is thus the only other measured element which shows widespread isotopically anomalous compositions similar to the ubiquitous anomalous oxygen discovered by Clayton, Grossman, and Mayeda (1973). Whether there is a quantitative correlation between the Ti and O anomalies remains to be seen. For EK-1-4-1 and C-1 the signs of the effects for Ti and the number of nuclei required to cause the effects are similar to those found for ^{48}Ca .

In discussing the patterns shown in Figure 1, it is useful to consider two simple models for reference. Model I is the case where exotic material (E) of a uniform isotopic composition is added to average solar material (N). In this case, for isotopes $M_1, M_1 + 1$, etc. (labeled 1, 2, etc.), the observed deviations ϵ_{jk} of isotope j relative to isotope k are given by

$$\epsilon_{jk} \times 10^{-4} = [(w_j^* z_E / w_j z_N) - (w_k^* z_E / w_k z_N) - (j - k)\alpha], \quad (1)$$

where w_j^* are the fractional atomic abundances of exotic (*) nuclei of the element ($w_j^* = N_j^* / \sum_i N_i^*$); z_E is the total number of exotic nuclei added; N_j^* is the number of exotic nuclei of species j ; and w_j and z_N are the fractional isotopic abundances of normal solar material and the total number of normal nuclei, respectively. The discrimination factor per mass unit is α , which in general is not known for any given experiment on nonnormal material. Since no data are available on absolute ratios to the required precision, a convenient pair of isotopes (u, v) is used for normalization. This gives $\epsilon_{uv} \equiv 0$ for all results of this type and, from equation (1), yields a relationship between α and $(w_u^* / w_u - w_v^* / w_v)$. If all data are arbitrarily normalized to, say, isotopes 1 and 3 (such as 46 and 48), then $\epsilon_{31} \equiv 0$ and $\alpha = (w_3^* / w_3 - w_1^* / w_1) z_E / 2 z_N$, which reduces equation (1) to the form $\epsilon_{j1} = z_E q_{j1}$, where q_{j1} is the value of ϵ_{j1} for $z_E = 1$. Thus all patterns resulting from addition to normal (two components N and E) must scale by a factor z_E ($z_E \geq 0$) for all isotopes and ϵ_{j1} cannot change sign for different samples (Fig. 2a).

Model II is the case where protosolar material with uniform initial abundance I has exotic material (E) of isotopically uniform abundance added to it. This results in normal material being a mixture of I and E components. The number of exotic nuclei required to comprise "normal" composition is \bar{z}_E with relative abundance w_j^* . Let the number of initial undiluted nuclei be z_I with relative abundances w_j^0 . Then

$$\epsilon_{jk} \times 10^{-4} = [(z_E - \bar{z}_E) / z_I] (w_j^* / w_j^0 - w_k^* / w_k^0) - (j - k)\alpha. \quad (2)$$

If we again arbitrarily normalize to isotopes 1 and 3, $\epsilon_{31} \equiv 0$ for all samples. We may choose any sample with $z_E < \bar{z}_E$ as an end member, say, (o) to explain all samples with a larger value of z_E . This yields $\epsilon_{j1} = -[(z_E - \bar{z}_E) / \bar{z}_E] \epsilon_{j1}^0$, which requires that, for any sample, ϵ_{j1} values are a scale factor times ϵ_{j1}^0 of

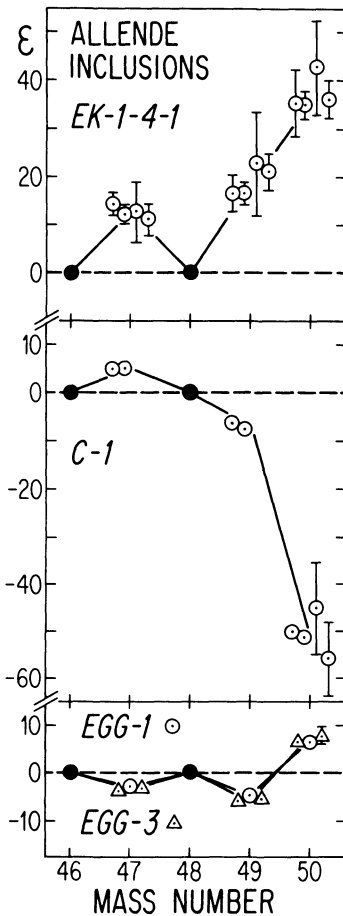


FIG. 1.— ϵ_{ij} values in parts in 10^4 , normalized to $(^{46}\text{Ti}/^{48}\text{Ti})_N$, see Table 1. Replicate analyses are shown spread out near the respective mass number. Top: FUN inclusion EK-1-4-1. Middle: FUN inclusion C-1. Bottom: small but distinctive anomalies in EGG-1 and EGG-3. These data require at least three nucleosynthetic components.

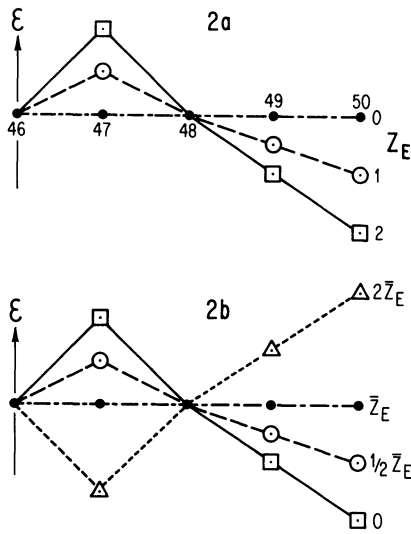


FIG. 2.—Schematic diagram showing abundance variations ϵ_{ij} relative to a reference standard with arbitrary normalization to masses 46 and 48. (a) Model I: addition of an exotic component to the reference standard; $z_E = 0, 1, 2$ corresponds to no addition and additions of 1, 2 units. (b) Model II: addition of exotic material to an initial state with $z_E = 0$. To make up normal $z_E = \bar{z}_E$. Additions with $z_E > \bar{z}_E$ change the sign of ϵ_{ij} relative to ϵ_{ij}^0 .

the chosen end member and all ϵ_{ij} simultaneously change sign as a function of z_E . From inspection of Figure 1 and consideration of the above rules, it may be seen that the Ti data cannot be explained by either Model I or Model II. For example, if C-1 were the least contaminated starting material, then the other samples (including normal) cannot be related to it by addition. The same conclusion holds if we assume that EGG-3, normal, and EK-1-4-1 represent two-component mixtures. We conclude that there are at least three distinct nucleosynthetic components of Ti present in the samples studied, and that the materials preserved in Allende inclusions are representative of incomplete mixtures from a wide variety of nuclear processes.

The general pattern for EK-1-4-1 for Ti appears to indicate excesses at all unshielded isotopes and follows the anomaly pattern found for Ba, Nd, and Sm (McCulloch and Wasserburg 1978a, b; Lugmair, Marti, and Scheinin 1978) as well as excesses of ^{42}Ca and ^{48}Ca (Lee, Papanastassiou, and Wasserburg 1978). The results on C-1 strongly point to a deficiency at ^{50}Ti which is in accord with the observations of deficiencies in ^{48}Ca and ^{135}Ba . However, there is evidence in Sr and Sm for isotopic mixtures in these inclusions which are not readily related to such correlation (Papanastassiou and Wasserburg 1978; McCulloch and Wasserburg 1978a, b). In addition, we see that not all the Ti abundance patterns are compatible with different proportions of shielded and unshielded isotopes analogous to standard “r” and “s” mixtures.

The data for Ca in C-1, EK-1-4-1, and HAL show

that no substantial effects exist at the rare isotope ^{46}Ca , although large effects are present in the more abundant ^{48}Ca and small effects in ^{42}Ca . It follows that the Ca and Ti effects cannot be due to a standard r-process in which stable nuclei result from decay of very neutron-rich isobars far off the line of beta stability. The generic mini-r-process of neutron bombardment, assuming a seed of solar abundances proposed by Truran and Cameron (1978) to explain the observed excesses of unshielded nuclei at large atomic number (Ba, Nd, Sm) in EK-1-4-1, needs to be explored in a more detailed manner to judge effects at Ca and Ti. An ad hoc hypothesis that ^{46}Ca has a very large neutron capture cross section [$>50 \sigma(^{48}\text{Ca})$] under these conditions is difficult to justify. From the study by Howard *et al.* (1972), which is the most extensive analysis of normal Ca and Ti production in explosive carbon burning using a reaction network, it appears that (n, γ) , (p, γ) , and (p, n) reactions on ^{40}Ca and ^{38}Ar play a key role. These authors find that absolute and relative Ti isotopic abundances are very sensitive to temperature and also calculate large overabundances of ^{46}Ca and ^{47}Ti which are not observed. Cameron (1979) has discussed the production of Ca and Ti for solar abundances with consideration of the problem of ^{46}Ca and points out that one of the most effective ways that neighboring isotopes can have enormously different abundances is when there is an approach to nuclear equilibrium. He concludes that neutron-rich silicon burning may be responsible for ^{46}Ca , ^{48}Ca , and ^{50}Ti production in solar proportions. It is clear that quasi-equilibrium or neutron-rich silicon burning can produce ^{48}Ca and ^{50}Ti without excessive amounts of ^{46}Ca . In contrast, calculations of detailed “kinetic” models involving n, p, α reactions on seed nuclei, such as those done by Howard *et al.* (1972), are found to grossly overproduce ^{46}Ca . It is possible that the mechanisms for quasi-equilibrium production of nuclides in the general neighborhood of the iron peak (Ca, Ti, V, Cr) require reconsideration in terms of both observed anomalies and normal abundances. The diversity of isotopic anomalies due to differing nuclear processes observed in Allende inclusions indicates mixing of material from very different stellar sites. This suggests that the observed anomalies are residues of much larger isotopic heterogeneities which must have originally been present in the protosolar nebula over small distances.

We acknowledge our ignorance of the detailed nuclear astrophysical processes which produced titanium. We thank the National Science Foundation, the National Aeronautics and Space Administration, and the Swiss National Science Foundation for supporting our efforts to explore these mysteries. Our colleagues Fouad Tera and Thomas Kaiser generously shared their deep knowledge of Ti chemistry with us. W. A. Fowler’s long-term interest in the iron peak has been useful in keeping us directed toward a state of quasi-equilibrium. We have profited substantially from discussions of nucleosynthesis with A. G. W. Cameron.

REFERENCES

- Bodansky, D., Clayton, D. D., and Fowler, W. A. 1968, *Ap. J. Suppl.*, **16**, 299.
- Cameron, A. G. W. 1979, *Ap. J. (Letters)*, **230**, L53.
- Clayton, R. N., Grossman, L., and Mayeda, T. K. 1973, *Science*, **182**, 485.
- Heydegger, H. R., Foster, J. J., and Compston, W. 1979, *Nature*, **278**, 704.
- Howard, W. M., Arnett, W. D., Clayton, D. D., and Woosley, S. E. 1972, *Ap. J.*, **175**, 201.
- Lee, T., Papanastassiou, D. A., and Wasserburg, G. J. 1978, *Ap. J. (Letters)*, **220**, L21.
- Lee, T., Russell, W. A., and Wasserburg, G. J. 1979, *Ap. J. (Letters)*, **228**, L93.
- Lugmair, G. W., Marti, K., and Scheinin, N. B. 1978, Abstracts—*Lunar and Planetary Science IX* (Houston: Lunar and Planet. Institute), p. 672.
- McCulloch, M. T., and Wasserburg, G. J. 1978a, *Ap. J. (Letters)*, **220**, L15.
- . 1978b, *Geophys. Res. Letters*, **5**, 599.
- Michaud, G., and Fowler, W. A. 1972, *Ap. J.*, **173**, 157.
- Niederer, F. R., and Papanastassiou, D. A. 1979, Abstracts—*Lunar and Planetary Science X* (Houston: Lunar and Planet. Institute), p. 913.
- Nier, A. O. 1950, *Phys. Rev.*, **77**, 789.
- Papanastassiou, D. A., and Wasserburg, G. J. 1978, *Geophys. Res. Letters*, **5**, 595.
- Truran, J. W., and Cameron, A. G. W. 1978, *Ap. J.*, **219**, 226.

F. R. NIEDERER, D. A. PAPANASTASSIOU, and G. J. WASSERBURG: The Lunatic Asylum, Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125