

# GENERAL ATOMIC

## DIVISION OF GENERAL DYNAMICS

GA-6999

ABUNDANCES OF Na, Sc, Cr, Mn, Fe, Co, AND Cu IN CHONDRULES;  
Na, Mn, AND Cu IN METEORITES; AND In IN METEORITIC  
AND TERRESTRIAL MATTER

QUARTERLY PROGRESS REPORT  
FOR THE PERIOD ENDING FEBRUARY 28, 1966

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DIVISION OF  
**GENERAL DYNAMICS**

JOHN JAY HOPKINS LABORATORY FOR PURE AND APPLIED SCIENCE  
P.O. BOX 608, SAN DIEGO, CALIFORNIA 92112

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Work done by:

R. A. Schmitt  
R. H. Smith

Report written by:

R. A. Schmitt

February 28, 1966

PREVIOUS REPORTS IN THIS SERIES

- GA-4782 - September, October, November, 1963
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- GA-5303 - March, April, May, 1964
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- GA-6414 - March, April, May, 1965
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- GA-6893 - September, October, November, 1965

This progress report covers the contract period from December 1, 1965, through February 28, 1966, under Contract NASw-843.

During this quarter, a manuscript entitled "Chainpur-like Chondrites, Possible Primitive Precursors of Ordinary L-Group Chondrites," by R. A. Schmitt, G. G. Goles, and R. H. Smith was prepared for submission to an appropriate journal.

Two invited lectures on "Meteorite Analysis" were presented by R. A. Schmitt at the Nineteenth Annual Louisiana State University Symposium on Modern Methods of Analytical Chemistry, Baton Rouge, Louisiana, January 24-27, 1966.

Abundances of seven elements--Na, Sc, Cr, Mn, Fe, Co, and Cu--were determined by instrumental neutron activation analysis (INAA) in 20 individual chondrules and in five troilite pieces separated from Cherokee Springs, a Soko-Banjitic chondrite (Table 1). Collation and interpretation of the presently determined abundances with previously established values for other chondrules<sup>(1)</sup> will be included in a future paper on chondrule abundances.

Average amounts of 0.3% Na, <3% Sc, <0.5% Cr, 4% Mn, 13% Co, and ~8% Cu of that found in whole chondrites have been found in five troilite pieces from Cherokee Springs (Table 1). Both Mn and Co have narrow dispersions of 6% to 7%, indicating equilibration of Mn and Co between the troilite, silicate, and metallic phases. Note that the amount of Fe determined by INAA (65.9 ±2.1%) approximately overlaps the theoretical amount 63.5% for the stoichiometric quantity of Fe in FeS. Since troilite represents ~5% of the overall mineral content in these meteorites, the troilitic contributions of Mn, Co, Cu, and the other four elements to the overall chondritic abundances are negligible.

From data on Na in troilite, upper limits may be calculated for silicate inclusions in the troilite. With an average of 20 ppm Na in troilite, or <20/6900 ppm Na in whole-rock Soko-Banjites, ≈0.3% of silicate may have been occluded in the troilitic specimens used for analysis. For Mn, therefore, the average Mn in the troilite due to possible silicate inclusions should be <(0.3%)(2500 ppm Mn in whole-rock Soko-Banjites) ≈10 ppm. But since 101 ±6 ppm Mn was observed in the troilite, at least 90% of the troilitic Mn must be indigenous, perhaps as the mineral alabandite. It is assumed that equal fractions of silicate minerals, such as plagioclase, pyroxene, and olivine, may be occluded in the overall silicate inclusion. The observed partition coefficient for

Table 1  
 ABUNDANCES OF Na, Sc, Cr, Mn, Fe, Co, AND Cu IN CHONDRULES OF  
 CHEROKEE SPRINGS (SOKO-BANJITIC CHONDRITE) DETERMINED BY INAA

Chondrule	Mass (mg)	Na (ppm)	Sc (ppm) <sup>a</sup>	Cr (ppm) <sup>a</sup>	Mn (ppm)	Fe (%)	Co (ppm)	Cu (ppm) <sup>b</sup>
1	1.95	8030±160	16.6±0.3	2260±50	2790±60	13.2±0.4	104±5	23±8
2	2.08	6750±130	11.1±0.3	970±20	2900±60	15.0±0.4	31±5	12±6
3	2.53	8170±160	3.9±0.3	6270±120	2900±60	15.5±0.4	120±10	10±6
4	2.81	7480±150	12.7±0.4	1880±40	2790±60	12.8±0.4	26±5	19±6
5	2.87	7350±200	11.9±0.3	1050±20	2740±60	14.7±0.3	76±4	19±6
6	3.10	7820±150	14.2±0.3	1230±30	2800±60	14.1±0.3	51±4	13±5
7	4.02	5900±120	10.9±0.3	1240±30	2790±60	16.7±0.5	140±10	30±6
8	6.09	7150±140	10.8±0.3	1910±40	2660±50	15.9±0.5	140±5	24±5
9	6.14	8420±160	3.7±0.2	12000±240	2280±40	16.1±0.4	220±10	41±6
10	7.43	6950±140	10.8±0.3	2750±50	2630±60	17.2±0.4	62±3	36±5
11	7.71	6660±120	12.7±0.3	1390±30	2650±50	14.1±0.3	81±3	24±6
12	7.79	7180±140	16.2±0.3	2900±60	2530±50	13.4±0.3	120±10	36±6
13	9.12	8050±160	18.3±0.4	1830±40	2490±50	13.9±0.3	170±10	33±8
14	9.13	6840±120	11.0±0.2	1280±30	2670±50	16.4±0.3	99±3	16±5
15	11.30	5650±100	10.0±0.2	4870±100	2700±50	18.3±0.3	160±10	29±6
16	12.26	7780±150	3.5±0.2	6190±120	2750±50	17.5±0.3	68±4	11±5
17	15.7	7930±160	10.2±0.3	2530±50	2510±50	15.6±0.3	270±10	50±7(D) <sup>c</sup>
18	38.9	5120±100	6.0±0.2	6020±120	2590±60	16.4±0.5	150±10	26±3(D)
19	46.6	5380±100	3.1±0.2	5230±100	2610±60	18.7±0.5	70±5	19±4(D)
20	70.9	7920±160	13.6±0.3	1840±40	2000±30	17.3±0.4	350±10	43±10(D)
Average					2640±150			
Troilited								
1	3.11	6±2	<0.23	<23	93±2	64.9±1.2	58±3	14.5±0.8(D)
2	3.89	34±3	<0.19	<21	102±2	67.3±1.3	54±3	105±2(D)(out)
3	6.56	24±2	<0.22	<19	95±2	66.7±1.3	53±3	4.5±1.0(D)
4	11.18		<0.17	<18	107±2	68.9±1.3	63±3	4.0±0.3
5	22.4		<0.16	<16	109±2	61.7±1.3	63±3	8.1±0.2(D)
Average			<0.19	<19	101±6	65.9±2.1	58±4	8±4

<sup>a</sup>No Cr and Sc lines observed in troilites. Upper limits were calculated by multiplying 3 times the standard deviation of total counts in channels of Cr and Sc peak positions (99% confidence level).

<sup>b</sup>Cu was counted via coincidence counts (CC) of 0.51-Mev annihilation  $\gamma$ 's of 12.8-hr Cu<sup>64</sup> using two 2-in. by 2-in. NaI crystals and two SCA with 0.46- to 0.56-Mev windows. The CC was used with a  $\tau$  of 0.3  $\mu$ sec, i. e.,  $2\tau = 0.6 \mu$ sec.

<sup>c</sup>(D) stands for the average value of two abundance determinations separated by a decay of one to two half-lives.

<sup>d</sup>Some may be from one large piece.

Mn between silicates and sulfide phases in the Cherokee Springs chondrites is  $\sim 25$ . Note that Mn has also been equilibrated in the chondrules to the same degree, i. e., with  $\pm 6\%$  dispersion. The observed Mn dispersion of  $6\%$  must be real and does not reflect the analytical error of  $2\%$  in Mn abundance determinations. The above Mn correlations suggest that abundance determinations of certain trace elements will be most helpful in unraveling the past histories of the constituent meteoritic minerals. Further work on minerals in collaboration with G. G. Goles (University of California at San Diego) is in progress.

The partition coefficient of Co between metal and sulfide phases may be similarly calculated. Assuming 460 ppm Co in the overall Cherokee Springs chondrite<sup>(2)</sup> and that the preponderance of Co resides in the metallic phase (assumed to be  $1\%$ ), the partition coefficient of Co between the metallic and sulfide phases is calculated by  $460/0.01/58 \approx 800$ .

In the preparation of an extensive manuscript<sup>(2)</sup> on elemental abundances, it became clear that elemental abundances which were first determined by INAA approximately 3 years ago should be redetermined and, also, that Cu should be redetermined in all  $\sim 150$  meteorites by our fast  $\gamma$ - $\gamma$  coincidence technique. When we first introduced the INAA technique in the multi-elemental analyses of siliceous matter some 3 years ago, we determined abundances by using the observed peak heights above the Compton continuum, as plotted out by the Moseley X-Y plotter. Furthermore, the standards used for some of the early analyses had larger volumes and, therefore, had large correction factors due to geometry differences. New and old abundance values are given in Table 2 for those meteorites for which values were redetermined during this quarter. Many of the old Na values and some of the old Mn values differed from the new values by  $\sim 10\%$ . Some of the old Na, Mn, and Cu values were determined by the accurate calculation method now used, i. e., total peak area with Compton continuum subtracted, as read off a printer tape.

The average Cu abundances in the ordinary chondrites as determined from the old data in Table 2 is  $\approx 60$  ppm, whereas the average obtained from the  $\gamma$ - $\gamma$  coincidence technique is  $\approx 90$  ppm. The latter average shows excellent agreement with radiochemical activation work.<sup>(2)</sup> Apparently in the old INAA of Cu, we oversubtracted for the  $\text{Na}^{24}$  contribution in the 0.51-MeV annihilation peak.

We are now formulating a computer program which will compute correlation coefficients of all pairs of elements weighted according to chondritic mass and to the inverse square of the standard deviation. This program will be used on all the previous chondrule abundances which by now number  $>2000$  individual elemental abundances.

Table 2  
 ABUNDANCES OF Na, Mn, AND Cu IN METEORITES DETERMINED BY INAA

Type of Meteorite	Mass (gm)	Na (ppm)		Mn (ppm)		Cu <sup>a</sup> (ppm)	
		New	Old	New	Old	New	Old
<u>Type III-A</u> Karoonda-C(-)	0.376	4430±250		1290±30		92±8	
<u>High Fe Group</u>							
Alessandria	0.220	4610±180	5890±100	2100±40	2120±80	132±26	50±20
Allegan-B	0.452	4990±100	5350±110	2000±60	2430±150	52±15	101±17
Archie	0.285	5330±200	6110±120	2280±46	2200±40	63±19	49±17
Beardsley-A	0.233	5310±100	5770±120	2900±90	2530±120	106±13	<120
Beardsley-B	0.329	5260±100	5000±300	2200±70	2350±120	111±12	-----
Beaver Creek	0.358	5030±200	5980±120	2170±40	2130±90	148±15	66±17
Bremerwörde	0.258	5940±240	6700±150	2440±40	2380±90	122±17	50±20
Castalia	0.354	5480±220	6500±130	2270±40	2250±90	89±14	46±18
Ehole	0.429	5310±200	6150±120	2240±40	2490±140	60±17	59±18
Kilbourn	0.440	5350±210	6230±120	2210±40	2180±90	95±12	67±17
Ochansk-A	0.285	6050±120	6190±120	1860±60	2400±120	83±11	50±40
Ochansk-B	0.358	5830±240	-----	2300±40	-----	71±15	-----
Pantar (II-dark) A	0.399	5180±200	6250±120	2120±40	2550±150	95±12	70±20
Pantar (II-dark) B	0.411	6040±120	6180±120	2300±70	2760±180	57±11	65±19
Pantar (II-lt) A	0.265	6180±240	6460±120	2340±50	2530±150	94±21	50±20
Pantar (II-lt) B	0.368	5490±100	6090±120	2220±70	2740±140	73±14	99±8
Pultusk	0.304	5720±120	6180±120	2350±70	2470±180	81±22	61±19
<u>Low Fe Group</u>							
Ausson	0.311	6400±240	6900±150	2570±50	2420±50	91±18	50±20
Barratta	0.385	6400±120	6600±120	2510±70	2530±170	56±9	60±30
Bath Furnace	0.426	6040±240	6640±130	2490±50	2310±90	82±12	30±20
Baxter	0.330	6950±280	7600±150	2530±50	2590±50	76±16	40±20
Bjurböle	0.217	6150±120	6980±150	2260±70	2860±140	112±14	100±40
Farmington	0.304	4840±50	5460±110	2210±70	2250±90	92±10	60±50
Harleton	0.301	7000±280	7350±150	2520±50	3000±300	70±14	60±20
Holbrook	0.302	6730±140	5970±120	2580±80	2870±150	80±13	-----
Leedey	0.291	6650±130	5790±120	2440±70	2730±70	118±11	-----
McKinney	0.256	5840±120	5420±120	2300±70	2850±150	134±12	-----
Mocs	0.417	5550±220	6110±120	2270±40	2150±120	136±14	63±18
Paragould	0.419	6650±240	7300±140	2550±50	2880±140	113±11	60±20
Peace River	0.276	6340±120	7050±140	2490±70	2760±160	99±25	51±7
St. Michel	0.219	7110±150	7500±300	2520±70	2640±130	87±11	<130
Walters-A	0.336	6480±260	6560±130	2580±50	2540±120	108±12	50±20

Table 2--(continued)

Type of Meteorite	Mass (gm)	Na (ppm)		Mn (ppm)		Cu <sup>a</sup> (ppm)	
		New	Old	New	Old	New	Old
<u>Soko-Banjites</u>							
Albareto	0.337	6260±120	7050±140	2510±70	2880±80	88±11	40±20
Ensisheim	0.218	5380±210	6200±200	2230±40	2440±130	117±19	70±40
Jelica	0.273	6340±240	7000±300	2590±50	2470±40	67±17	85±19
Lake Labyrinth	0.401	6530±260	7140±140	2640±50	2880±150	65±12	<110
Vavilovka	0.311	6920±140	6100±300	2490±70	3010±150	64±11	-----
<u>Enstatites</u>							
St. Marks	0.333	5630±110	5530±120	1570±50	2100±120	220±20(D) <sup>b</sup>	-----
<u>Ca-poor (Aubrites)</u>							
Bishopville-A	0.424	6440±260	6560±120	2420±50	2550±100	11±6	<35
Bishopville-B	0.460	9950±400	9900±200	870±20	800±30	7±8	<10
Cumberland Falls-A	0.228	280±10	220±20	870±20	860±30	1±6	6±2
Pesyanoë	0.484	2610±50	3410±60	1020±30	1040±30	12±4	15±5
<u>Ca-poor (Ureilites)</u>							
Novo Urei	0.333	300±20	520±30	2860±90	3050±60	12±4	9±1
<u>Ca-rich (Eucrites)</u>							
Juvinas	0.252	2800±60	2520±130	3970±120	4600±200	8±6	-----
Moore County	0.226	3070±60	3020±150	3450±100	3230±150	7±9	-----
Stannern	0.444	3780±80	3380±160	3970±120	4300±200	20±5	-----
Kapoeta (Howardites)	0.235	1620±50	1720±80	3910±120	2840±140	6±5	-----
Petersburg	0.241	2840±90	3000±150	3790±110	3590±160	6±6	-----
<u>Pallasites (Olivines)</u>							
Marjalati	0.492	58±14	-----	2160±40	-----	8±2	-----
Salta	0.263	52±19	-----	2120±40	-----	6±2	-----
<u>Mesosiderites</u>							
Estherville (silicate phase)	0.388	1630±40	-----	3460±120	-----	43±12	-----
<u>Special</u>							
Pine River (silicate phase of octahedrite)	0.414	5510±110	-----	1320±50	-----	81±8	-----

<sup>a</sup>Cu was counted via coincidence counts (CC) of the 0.51-Mev annihilation  $\gamma$ 's of 12.8-hr Cu<sup>64</sup>, using two 2-in. by 2-in. NaI crystals and two SCA with 0.46- to 0.56-Mev windows. The CC was used with a  $\tau$  of 0.3  $\mu$ sec, i. e.,  $2\tau = 0.6 \mu$ sec.

<sup>b</sup>(D) stands for the average value of two abundance determinations separated by a decay of two half-lives.



Greenland<sup>(3)</sup> recently reported In abundances for carbonaceous chondrites that were a factor of  $\sim 10$  greater than the atomic abundances suggested by Urey.<sup>(4)</sup> The average atomic abundance value of Cd, the element preceding In, as determined by us<sup>(5)</sup> was 1.8 Cd/10<sup>6</sup> Si atoms. This value agreed within a factor of two with the value of 0.9 Cd/10<sup>6</sup> Si atoms suggested by Urey.<sup>(4)</sup> It immediately became obvious that either In behaved very peculiarly in carbonaceous and other chondrites compared with the behavior of other trace elements like Cd, Hg, Tl, Pb, and Bi, or the In values determined by Greenland were inaccurate.

Akaiwa,<sup>(6)</sup> also using radiochemical neutron activation analysis, has determined Se, Te, and In abundances in three carbonaceous and one enstatitic chondrite. Since his values for In abundances were more in accord with those suggested by Urey,<sup>(4)</sup> we decided to analyze a few identical carbonaceous chondrites from pieces analyzed by Greenland and Akaiwa. Those previously analyzed by Greenland were obtained from G. G. Goles (University of California at San Diego) and those analyzed by Akaiwa were obtained from E. Anders (University of Chicago). The In values we found are listed in Table 3.

The radiochemical activation method used by us follows the procedure used by Schindewolf and Wahlgren<sup>(7)</sup> with slight modifications. In brief, we irradiate about 0.25 g of meteoritic or terrestrial powdered specimens and 2.048  $\mu\text{g}$  of In in 2 ml of solution in separate irradiation capsules. These capsules are placed in the rotating rack of the General Atomic TRIGA reactor for 0.5 hr at a thermal-neutron flux of  $\approx 2 \times 10^{12} \text{ cm}^{-2} \text{ sec}^{-1}$ . After irradiation the specimen and In carrier are fused with Na<sub>2</sub>O<sub>2</sub>. Decontamination consists of In bromide complex extraction into ether and a PdS step. The final precipitate of In<sub>2</sub>S<sub>3</sub> is weighed for chemical yield, and the 54-min In<sup>116m</sup> is beta counted by a Sharp Lowbeta counter and NaI scintillation spectrometer.

To test our procedure, we irradiated the ordinary chondrite Modoc spiked with 0.17 ppm In and also an unspiked piece of Modoc. Using the radiochemical method described above, we found  $0.17 \pm 0.01$  ppm In in the spiked specimen and  $0.0003 \pm 0.0001$  ppm In in the unspiked piece of Modoc. We then determined the In abundances in some of the carbonaceous chondrites (Table 3) and corroborated the values previously determined by Akaiwa and also by Smales and Mapper.<sup>(8)</sup> For example, in the Type I carbonaceous chondrite Orgueil, we found  $0.071 \pm 0.007$  ppm in two different pieces; Akaiwa reported  $0.12 \pm 0.01$  ppm and Smales and Mapper reported 0.082 ppm. For Mighei, we found  $0.064 \pm 0.006$  ppm, Akaiwa found  $0.050 \pm 0.004$  ppm, and Smales and Mapper found 0.049 ppm.

For Lancé, we found  $0.025 \pm 0.003$  ppm, Akaiwa reported  $0.031 \pm 0.001$  ppm, and Smales and Mapper reported 0.025 ppm. For Abee, we found

Table 3  
 INDIUM ABUNDANCES IN METEORITIC AND TERRESTRIAL MATTER  
 DETERMINED BY NEUTRON ACTIVATION ANALYSIS

Type	Specimen	In (ppm) <sup>a</sup>	In Atoms/ 10 <sup>6</sup> Si Atoms
Chondrites Type I	Orgueil <sup>b</sup>	0.064±0.006	0.17±0.02
	Orgueil <sup>c</sup>	0.080±0.008	
Type II	Mighei <sup>b</sup>	0.064±0.006	0.12±0.01
Type III-A	Lancé <sup>c</sup>	0.025±0.003	0.039±0.004
Type III-B	Chainpur	0.074±0.007	0.10±0.01
	Mezō-Madaras	0.013±0.001	0.017±0.002
Enstatites	Abee <sup>b</sup>	0.13±0.01	0.13±0.05
	Abee <sup>c</sup>	0.056±0.005	
Ordinary	Leedey (L)	0.0003±0.0001	0.0004±0.0002
	Modoc (L)	0.0003±0.0001	
	Holbrook (L)	0.0006±0.0001	
	Allegan (H)	0.0001±0.00003	
	Richardton (H)	0.0002±0.00005	
	Beardsley (H)	0.0021±0.0002	
Achondrites (Euclrites)	Juvinas	0.0016±0.0002	0.0017±0.0002
Terrestrial	40-North American composite shales <sup>d</sup>	0.070±0.007	
	36-European Paleozoic composite shales <sup>e</sup>	0.048±0.005	
	85-Granite composite, <60% SiO <sub>2</sub> <sup>d</sup>	0.083±0.008	
	191-Granite composite, 60% to 70% SiO <sub>2</sub> <sup>d</sup>	0.067±0.006	
	213-Granite composite, >70% SiO <sub>2</sub> <sup>d</sup>	0.057±0.006	

<sup>a</sup>For Types I, II, III-A, III-B, and enstatitic chondrites and the composite shales and granites, the 54-min In<sup>116m</sup> activity was measured by both beta counter and scintillation spectrometers. For the ordinary chondrites and achondrites, only beta decay measurements could be made by using a Sharp Lowbeta counter.

<sup>b</sup>Obtained from E. Anders.

<sup>c</sup>Obtained from G. G. Goles.

<sup>d</sup>Obtained from L. Haskin.

<sup>e</sup>Obtained from A. G. Herrmann.

0.093  $\pm$  0.037 ppm (the average in two pieces), Akaiwa found 0.13  $\pm$  0.02 ppm, and Smales and Mapper found 0.056 ppm. The above agreement is excellent for a trace element in the tens of ppb level of concentration, and we may conclude that the previous In values reported by Greenland<sup>(3)</sup> are definitely in error.

It immediately became obvious that a systematic study of In over the entire meteoritic and terrestrial spectra should be undertaken for a number of reasons. First, from the upper limits of In abundances in ordinary chondrites estimated by Schindewolf and Wahlgren,<sup>(8)</sup> In has been severely depleted in ordinary chondrites by  $\sim$ 70 compared with the average in carbonaceous chondrites. Second, since abundances of Cd (the preceding element which is also depleted ( $\sim$ 20) in ordinary chondrites) have been measured accurately by radiochemical activation analyses, the abundances of these two elements would anchor the  $N\sigma$  curve used in nucleosynthetic theory in the midrange of stable elements. Third, the element In is ideally suited for radiochemical activation analysis because of its convenient short half life; ideal beta and gamma-ray energies; and high sensitivity--down to a realistic  $\sim$ 0.00001 ppm under the present sample size, available neutron flux, and radiochemical separation times.

Schindewolf and Wahlgren<sup>(8)</sup> were only able to establish an upper limit of 0.001 ppm In in ordinary chondrites because of their high beta counter background of 65 cpm compared with our background of 0.3 cpm and their lower neutron flux of  $10^{11}$  cm<sup>-2</sup> sec<sup>-1</sup> compared with our flux of  $2 \times 10^{12}$  cm<sup>-2</sup> sec<sup>-1</sup>. From Table 3, the average In value observed in five ordinary chondrites is 0.0003  $\pm$  0.00017 ppm. Beardsley is anomalously high at 0.0021  $\pm$  0.002 ppm. For the ordinary chondrites, the initial observed beta counting rates (taken approximately 2.5 hr after the end of irradiation) varied from 10 to 50 cpm above background. Converting the mass abundances to atomic abundances (column 4 of Table 3), we note that In has been depleted in ordinary chondrites by  $\sim$ 250 compared with Type II carbonaceous chondrites or with Type III-B Chainpur. This value agrees with the depletion of Tl, an element in the same periodic group.

Since the depletion factor of In exceeds that of Cd by an order of magnitude, a study of In over the entire meteoritic spectrum should be most enlightening. We plan to analyze for In in all of the meteoritic classes, and all the data and their interpretation will be presented in a forthcoming journal paper.

For an overall understanding of In in the solar system, we have also begun to survey In in some composite terrestrial specimens (Table 3). Since many of the previous In terrestrial analyses are quite inaccurate, this radiochemical neutron activation analysis on composite specimens should firmly establish data for future studies on the geochemistry of In.

Other terrestrial specimens will include typical and composite basalts, ultramafic rocks, and proxenitic rocks kindly obtained from A. E. J. Engel, G. G. Goles, and L. Haskin. Interpretation of this terrestrial data will be included in the forthcoming manuscript on In abundances.

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Los Angeles  
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Arizona State University  
Tempe, Arizona 85281

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