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Bismuth contents of chondrites

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Abstract—A neutron activation technique has been developed for determination of the bismuth concentrations in C-, H-, L- and LL-group chondrites. The technique was tested by duplicate analyses of eight standard rocks and a single synthetic sample. The results obtained for standards AGV-1, BCR-1, DTS-1, G-2, GSP-1 and PCC-1 are the first reported. Our analyses of 14 carbonaceous and 5 equilibrated ordinary chondrite samples have confirmed that Bi is indeed a "strongly-depleted" element in meteorites. The mean Bi abundances in carbonaceous chondrites are 143, 71 and 37 atoms/10^9Si atoms for groups C1, C2 and C3, respectively, which relative to C1 yield ratios of: C1: C2: C3 = 1·00: 0·50: 0·26—nearly the same as those predicted by a two-component model. In 12 unequilibrated ordinary chondrites (UOC), the Bi contents generally decrease exponentially with increasing equilibration of the silicate phases although there are apparent exceptions to this trend for chondrites having highly unequilibrated silicates. The Bi concentrations in the UOC correlate well with those of carbon and primordial Ar, Kr and Xe determined by others in these same meteorites.

INTRODUCTION

DESPITE the enormous amount of research that has been conducted in recent years on elemental abundances in meteorites, Bi is one of the few elements whose abundance has not been well established. This is particularly surprising in view of the twofold importance of Bi to cosmochemistry: it is the heaviest stable element, hence has special significance in nucleosynthesis; and it is highly volatile, so that its abundance provides clues to the temperature history of meteorites. Thus, the establishment of its content in chondrites is important in understanding the processes that resulted in the formation of the meteoritic parent bodies.

Prior to this study, the Bi contents (or limits) in ten chondrites and two achondrites (Johnstown and Nuevo Laredo) had been measured (EHMANN and HUIZENGA, 1959; REED *et al.*, 1960; REED, 1963). In terms of the chemical–petrologic classification of VAN SCHMUS and WOOD (1967) the chondrites studied previously included replicate samples of: one C1; one C2; seven equilibrated ordinary chondrites—four H5, two L6, and one LL6; and one E4. The results of these studies clearly demonstrate that the extreme Bi contents of chondrites differ by a factor of more than a thousand and, in equilibrated ordinary chondrites at least, the Bi concentrations are quite low—on the order of a few ppb. These previous results also indicate that the Bi contents of chondrites depend on

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chondritic type and decrease in the order carbonaceous–enstatite–equilibrated ordinary chondrites. In detail, though, some results are puzzling. These include the C2/C1 Bi abundance ratio (Reed *et al.*, 1960) and extremely variable amounts of Bi in the equilibrated ordinary chondrites (Ehmann and Huizenga, 1959; Reed *et al.*, 1960; Reed, 1963).

In view of these facts, we decided to measure the Bi contents in a larger number of chondrites. In choosing the samples to be studied we decided to concentrate upon carbonaceous and unequilibrated ordinary chondrites as examples of "primitive" meteorites, and to include only a few equilibrated ordinary chondrites for comparison. This study was undertaken in conjunction with a broader study of other trace element contents in these same meteorites by an adaptation of neutron activation analysis (Laul, Case, Lipschutz, Pelly, Schmidt-Bleek and Wechter, in preparation). In this paper we report on the Bi contents in 31 samples including 27 different chondrites together with a preliminary interpretation of the data. A more complete discussion will be made in concert with the results of our broader study.

Experimental

In view of the generally low Bi contents in chondrites, neutron activation appeared to be the most suitable method. Our attempts to use previously-described radiochemical purification techniques for Bi proved unsuccessful since we could neither reproducibly separate Po^{210} for α-counting (Ehmann and Huizenga, 1959) nor obtain radiochemically-pure Bi^{210} using the scheme of Reed *et al.* (1960). Accordingly we were forced to devise another procedure which we tested by analyzing standard rocks and a synthetic sample (Table 1). This procedure was then used to determine the Bi contents of the chondrites listed in the Appendix and in Tables 2 and 3. These chondrites were all received as relatively large fragments except for Ivuna [B], which was a powdered sample collected when the specimen that yielded Ivuna [A] was cut in Tanzania (see Appendix for the sources and identification numbers of these samples). All samples were prepared for irradiation as described elsewhere (Laul *et al.*, 1969). In general the sample weights ranged from 0·7–1·4 g except for the Ivuna samples, Clovis #1 and Mezö-Madaras where the weights ranged from 0·3 to 0·5 g.

The monitors were prepared in batches of eight. To simulate the geometry of the samples and to minimize any effects due to self-shielding, monitor "beds" of 100–200 mg of MgO powder (Mallinckrodt reagent grade, previously analyzed by us to assure its low Bi content) were weighed into pre-cleaned quartz irradiation vials. The monitor solutions were prepared freshly for each batch by appropriate dilution of a previously standardized carrier solution (10 mg Bi/ml). A 100 λ aliquot (20 μg) of the monitor solution was pipetted onto the prepared "bed". The monitor vials were dried for 4–6 days at 65°C and sealed. The synthetic sample was prepared by "doping" 1-g of MgO powder with μg to mg quantities of all elements that we studied, including 20 μg of Bi. After preparation, this synthetic sample was treated exactly as the standards and chondrites.

Each irradiation (initially two, later three samples per monitor) was performed in the thermal column of the Argonne CP 5 Reactor at a flux of $\sim 8 \times 10^{12}$ thermal neutrons/cm^2 sec for 6 days. After irradiation the samples were dissolved in the presence of 100 mg of inactive Bi carrier and were processed as described elsewhere (Laul *et al.*, 1969) to remove specific gamma-ray emitters. The Bi-containing acid–sulfide precipitate was obtained by addition of thioacetamide to the solution remaining after the samples were extracted with diethyl ether and distilled in the presence of HBr–H_2SO_4.

Radiochemical purification

After this initial decontamination, the sulfide was processed extensively to assure its radiochemical purity. The basic procedure used was that developed by Prestwood (1963) for the

separation of Bi from mixed fission products. This procedure was, however, modified extensively for our purposes:

(a) The acid–sulfide precipitate was dissolved in conc. HCl and the solution boiled to remove H_2S. This solution was diluted to 20 ml with 6 N HCl and leaded onto a 36 ml Dowex AG 1 × 8 (100–200 mesh) anion exchange column. The column was washed successively with 20 ml 6 N HCl, 75 ml 0·5 N HCl and 50 ml H_2O (EHMANN and HUIZENGA, 1959) and the Bi fraction eluted with 125 ml 1 M H_2SO_4 (STRELOW and BOTHMA, 1967).

(b) To the effluent was added 10 ml 1 M thioacetamide and after digestion at 80°C Bi_2S_3 was precipitated and the supernate discarded.

(c) The Bi_2S_3 was dissolved in 10 ml conc. HCl and the solution evaporated nearly to dryness. BiOCl was precipitated by addition of H_2O and the supernate discarded.

(d) The BiOCl was dissolved in 2 ml conc. HCl and diluted to about 20 ml. After addition of 5 drops of Ag^+ carrier (25 mg/ml), an AgCl scavenge was performed and the filtrate collected.

(e) $Bi(OH)_3$ was precipitated with 5 ml conc. NH_4OH and the supernate discarded.

(f) The $Bi(OH)_3$ was dissolved in 2 ml conc. HCl and 5 drops each of Al, Fe, Cu, As, Se, Mo, Cd, In, Sn, Sb, Te, Ir and Hg holdback carriers (~10 mg/ml) in nitrate or chloride form were added. After evaporation to dryness, the residue was taken up in 25 ml of 6 N HCl and extracted with 25 ml of hexone. The organic layer was discarded. After addition of 1–2 g NaI to the aqueous phase, BiI_3 was extracted into 25 ml of hexone and the aqueous layer discarded. Following one wash with 25 ml 6 N HCl containing 1 g NaI, Bi^{3+} was extracted from the organic layer with 25 ml 6 N HCl containing 1 g $NaNO_2$. The organic phase was discarded.

(g) $Bi(OH)_3$ was precipitated with 5 ml conc. NH_4OH, washed once with H_2O, and both supernate and wash were discarded. The precipitate was dissolved in 3 ml conc. HNO_3, diluted to ~20 ml and 1 g Na_3PO_4 was added. After boiling, the $BiPO_4$ precipitate was washed once with H_2O and the supernate and wash discarded.

(h) The $BiPO_4$ was dissolved in 5 ml conc. HCl and 10 ml of 1 M thioacetamide was added to precipitate Bi_2S_3. The precipitate was washed with 25 ml conc. NH_4OH to remove soluble basic-sulfides and supernate and wash were discarded.

(i) Steps (c)–(g) were repeated except that no hold-back carriers were added in the repetition of step (f).

(j) $BiPO_4$ was dissolved with 2 ml conc. HCl, diluted to 10 ml and $Bi(OH)_3$ was precipitated by addition of 6 N NaOH. The supernate was discarded.

(k) $Bi(OH)_3$ was dissolved in 2 ml conc. HCl and, after dilution, the BiOCl precipitate was washed once with H_2O and the supernate and wash were discarded. The BiOCl precipitate was filtered onto a pre-weighed glass-fiber filter circle, washed with H_2O and ethanol, and dried at 110°C for 10 min. After cooling for 10 min, the precipitate was weighed and mounted for counting.

In nearly all of our experiments, we obtained chemical yields of 20–40%. For PCC-1 [A], AGV-1 [A] and Warrenton, however, we obtained chemical yields on the order of ~5%. Each BiOCl precipitate was counted for 10–15 min with a Ge(Li) detector and 1024-channel analyzer system in an attempt to detect gamma-emitting impurities. Since we found no evidence for such contaminants and the decay of the samples followed the known 5·01 day half-life of Bi^{210g} (LEDERER *et al.*, 1967) for at least 5 half-lives, we decided not to recycle all samples to constant specific activity. We were encouraged to make this decision after recycling two early samples (AGV-1 [A] and BCR-1 [A]). After application of the self-absorption correction the specific activities of the recycled samples agreed with the original specific activities to within 1%.

We did not find it necessary to process the flux monitors as exhaustively as the samples. After irradiation, the opened vial was placed in a 40 ml centrifuge tube containing 10 ml 6 N HCl and 50 mg each of Bi^{3+} and Tl^{3+} inert carriers. After heating to dissolve the MgO "bed", the solution and several 6 N HCl washes were placed in a 100 ml volumetric flask and the solution was diluted with H_2O. A 5-ml aliquot of this solution was then added to a centrifuge tube containing 5 ml of Bi^{3+} carrier solution (10 mg/ml). This solution was evaporated nearly to dryness, diluted to 20 ml with 6 N HCl and further processed as in steps (a)–(c), (e), (f, omitting the hold-back carriers), (g), (j) and (k). The chemical yields for the monitors ranged, in general, from 50–80%.

Counting and data analysis

The BiOCl samples (3·08 cm^2 area) were placed onto stainless steel counting discs and covered with mylar film (1·79 mg/cm^2). The samples were counted with a Beckmann–Sharp Low-beta II low background proportional counter. Normally, four different samples were counted, then a background, for 200 min each. However, 500-min counts were taken for low-activity samples with initial activities comparable to the 0·65 cpm typical background count-rate. The initial counting of the Bi samples was made 4–5 days after the end of irradiation and the activities were followed for at least 5 half-lives to assure that they decayed with the proper Bi^{210g} half-life. Only in the cases of G-1 [A] and DTS-1 [A] was there any significant evidence for a contaminant decaying with a half-life of other than 5·01 days. We used an average background, obtained by summing all of the individual background counts accumulated during counting of a sample, to calculate the net Bi^{210g} activity in the sample. These average backgrounds represented 2500–5000 min of counting time and ranged from 0·61 $\pm$ 0·02 to 0·71 $\pm$ 0·02 cpm. We observed no unusual background fluctuations during our study.

The raw data were processed using a CDC-6500 computer and a decay curve analysis program (Cumming, 1963) assuming both two-component and one-component systems. In all cases except for G-1 [A] and DTS-1 [A] we used the one-component output after comparative consideration of it and the two-component output for goodness-of-fit and number of discarded points. In general the time-zero net count rates for each output pair agreed to within 3% indicating the radiochemical purity of the samples. For each set of samples in a given irradiation, the net Bi^{210g} count rates at time-zero were corrected for self-absorption relative to the monitor in that irradiation. This empirical correction was seldom as much as 5% and never more than 15%.

Results and Discussion

The results on the standard rock samples are listed in Table 1. For these, the precision for the duplicate runs seems quite reasonable except for G-1 [A] and PCC-1 [A]. The former appeared to be heavily contaminated with some long-lived radioactivity which may have affected our Bi result considerably and the latter had an extremely low chemical yield. Thus we regard these results with

Table 1. Bismuth contents of U.S.G.S. standard rocks and synthetic sample

Standard	Bismuth concentration (ppb) A	B	mean*
AGV-1	56·1†	56·7	56·4 $\pm$ 0·4
BCR-1	46·4	47·0	46·7 $\pm$ 0·4
DTS-1	4·8‡	4·7	4·8 $\pm$ 0·1
G-1	76·2‡	46·3	46
G-2	35·9	39·3	37·6 $\pm$ 2·5
GSP-1	36·4	37·1	36·8 $\pm$ 0·5
PCC-1	14·6†	8·0	8
W-1	44·0	43·1	43·5 $\pm$ 0·5
"Doped" MgO	19·8 μg§		20·0 μg

* As noted in the text the errors listed are the estimated standard errors of the mean. Fleischer (1969) has not recommended any Bi values or magnitudes for standards G-1 and W-1. For the remaining standards Flanagan (1969) has listed upper limits of 500 ppb.

† These samples had very low chemical yields (~5%) and the results may be unreliable. We have retained the value for AGV-1 [A] because of its agreement with that of AGV-1 [B].

‡ The decay curves of those samples indicated two-component systems. The contamination was serious only in G-1 [A] whose value is disregarded.

§ From separate experiments on untreated MgO, the Bi contamination in the MgO "bed" was 0·005 μg, which is negligible compared to the amount of Bi added.

considerable reservation. The data from the remaining 6 sample-pairs may be used to estimate the precision of our technique when applied to homogeneous standards. For each pair we calculated the standard error of the mean in the normal fashion from the best estimate of the population variance which was, in turn, obtained from the sample variance after application of Bessel's correction. The estimated relative standard errors of the means ranged from 0·7 to 6·7% and in 5 of the 6 cases were 2% or less.

Table 2. Bismuth contents in carbonaceous chondrites

Meteorite	Type	Bi contents	
		(ppb)	(atoms/10^9Si atoms*)
Ivuna [A]	C1	106	134
Ivuna [B]†	C1	126	159
Orgueil [A]	C1	110‡	139
Mean§	C1	114 ± 7	143 ± 10
Cold Bokkeveld	C2	65·4	68·4
Mighei	C2	79·4‡	81·6
Murray [A]	C2	62·1	61·9
Murray [B]	C2	70·7	70·5
Mean§	C2	69 ± 5	71 ± 5
Grosnaja	C3 [V]	68·3	61·1
Vigarano	C3 [V]	51·0	44·0
Mean§	C3 [V]	60 ± 13	53 ± 11
Felix [A]	C3 [O]	38·5	32·4
Felix [B]	C3 [O]	42·8	36·0
Lancé	C3 [O]	48·9	42·0
Ornans	C3 [O]	23·8	20·4
Warrenton	C3 [O]	31‖	26‖
Mean§	C3 [O]	37 ± 5	31 ± 4
Mean§	C3	43 ± 6	37 ± 5

* Si contents taken from MASON (1963).

† This consisted of saw cuttings collected in Tanzania (Appendix).

‡ REED *et al.* (1960) reported Bi concentrations in Orgueil and Mighei of 130 and 180 ppb respectively.

‖ The chemical yield for this sample was quite low (~5%). Despite this, we have included the Bi result for Warrenton in the C3 [O] and C3 means because of its similarity to results obtained from other C3 [O] chondrites.

§ The uncertainty listed for each group mean is the estimated standard error of the mean.

For heterogeneous samples, such as chondrites, the estimated standard errors of the means would be expected to be much larger. Indeed, this is the case since duplicate samples of Ivuna, Murray and Felix yield estimated relative standard errors of the means of 12%, 10% and 23% respectively (Table 2). If we assume that all Cl, C2 and C3 chondrites represent samples of homogeneous populations, these estimated errors are 6, 7 and 14% respectively. However, there is reason to doubt this assumption for C3 chondrites (LAUL *et al.*, in preparation). Thus, at the 95% confidence level the precision of our measurements on heterogeneous samples of homogeneous populations may be estimated at 14%. In the case of the ordinary chondrites our intent was to conduct as broad a survey as possible in the time available. Thus unfortunately we were unable to carry out replicate analyses and cannot estimate the precision of our measurements.

Were there reliable or recommended values for the Bi contents of these standards, we could assess the accuracy of our measurements. Unfortunately this is not the case. The older standards (G-1 and W-1) have no recommended Bi value (Fleischer, 1969) while the newer ones have only an upper limit of <500 ppb reported (Flanagan, 1969). In all cases the Bi contents measured lie well below this detection limit. The single analysis of the synthetic sample (Table 1) cannot be used to obtain a statistically meaningful estimate of the accuracy of our measurements. However, the agreement of our results with the known Bi content of this sample provides some evidence for our accuracy.

Carbonaceous chondrites

Our values for the Bi concentrations and atomic abundances in the carbonaceous chondrites are listed in Table 2. The Bi concentrations in two of these, Orgueil and Mighei, had been measured previously by Reed *et al.* (1960). Their result on Orgueil is somewhat higher than any of our Cl analyses but this is not particularly disturbing. Their Mighei result, on the other hand, is distinctly higher than any of our results on other C2 chondrites or, for that matter, Cl chondrites. This alone causes us to regard the Mighei Bi result of Reed *et al.* (1960) with some suspicion. There is also some additional internal evidence which lends considerable support to our results.

From previous studies (Ehmann and Huizenga, 1959; Reed *et al.*, 1960; Reed, 1963) Anders (1964) observed that the Bi abundances in ordinary chondrites were 10–1000 times lower than that in Orgueil and concluded that Bi is "strongly-depleted" in ordinary chondrites. Our results are certainly in accord with this conclusion. The Bi abundances that we obtained from the equilibrated ordinary chondrites range from 1 to 12 atoms/10^9 Si atoms (Table 3) corresponding to a "depletion-factor" of 10–100 relative to the Cl results (Table 2). Based on his conclusion that Bi is a "strongly-depleted" element, Anders (1964) predicted that the Bi mean abundance ratios (relative to Cl) of the carbonaceous chondrites would be C1:C2:C3 = 1·00:0·55:0·32.

Our results (Table 2) verify this prediction. The mean Bi abundance of the three C1 samples is 143 $\pm$ 10 or 148 $\pm$ 9 atoms/10^9 Si atoms if the Orgueil result of Reed *et al.* (1960) is included. The four C2 samples yield a Bi abundance of 71 $\pm$ 5 atoms/10^9 Si atoms. For the C3 chondrites, several mean abundances may be computed. If we assume that these meteorites are of a single group, the Bi abundance of the seven samples studied is 43 $\pm$ 6 atoms/10^9 Si atoms. On the basis of mineralogic and petrographic studies, Van Schmus (1969) has suggested that the C3 chondrites consist of two groups, denoted as Ornans (abbreviated here as C3 [O]) and Vigarano (C3 [V]) subtypes. Of these, we studied five (including a duplicate) and two representatives, respectively, and these yield mean Bi abundances of 31 $\pm$ 4 and 53 $\pm$ 11 atoms/10^9 Si atoms. It is noteworthy that the C3 [V] samples had higher Bi abundances than the C3 [O] samples. While possibly coincidental, these results tend to support Van Schmus' (1969) suggestion and may indicate a chemical compositional difference between the two sub-types. These results then lead to Bi abundance ratios relative to C1 chondrites of C1:C2:C3 = 1·0:0·50:0·26, or C1:C2:C3 [V]:C3 [O] = 1·00:0·50:0·37:0·22, which are quite

Table 3. Analyses of equilibrated and unequilibrated ordinary chondrites

Meteorite*	Type†	PMD in olivine†	Carbon content %	Bi contents ppb	Bi contents atom/10^9 this work	Bi contents atom/10^9 atoms‡
Sharps	H3	37	0·95[a]	88·6	71·5	
Bremervörde	H3	15	0·22[b]	24·9	18·9	
Prairie Dog Creek	H3	6·9	0·35[b]	7·2	5·6[g]	
Clovis #1	H3	5·6	0·22[b]	4·6	3·7	
Fayetteville [light]	H	—		7·8	6·1[d,g]	
Fayetteville [dark]	H	—		10·9	8·6[d,g]	
Plainview	H5	—		15·4[h]	12·1[e]	
Krymka	(L)3	45	0·27[b]	17·0	12·1	
Mezö-Madaras	(L)3	28	0·46[b]	123	88·8	
Khohar	L3	18	0·32[b]	31·0	22·5	
Barratta	L4	4·2	0·085[b]	1·58	1·11	
Holbrook	L6	—	0·06[c]	2·34[i]	1·68[e]	
Bruderheim	L6	—	0·040[b]	1·4	1·0[f]	
Ngawi	(LL)3	40	0·39[b]	23·6	16·7	
Chainpur	(LL)3	32	0·44[b]	65·0	45·7	
Parnallee	(LL)3	19	0·19[b]	11·7	8·1	
Hamlet	LL(3,4)	3·5	0·16[b]	6·5	4·5	

* Meteorites listed in italics are finds; all others are observed falls.

† All data from VAN SCHMUS and WOOD (1967) except for Fayetteville (HEY, 1966). Parentheses are placed around those classifications that may be uncertain (VAN SCHMUS and WOOD, 1967).

‡ All PMD values and the Si data from DODD *et al.* (1967) unless otherwise noted.

[a] Jarosewich, unpublished analysis listed in DODD *et al.* (1967).

[b] MOORE and LEWIS (1967).

[c] MASON and WIIK (1961).

[d] MASON (1965).

[e] WING (1964).

[f] Average of analyses reported by DUKE *et al.* (1961) and BAADSGAARD *et al.* (1961).

[g] Average Si analysis for group.

[h] Replicate samples of this meteorite have previously yielded Bi concentrations of 3·0, 3·8 and 4·1 ppb (EHMANN and HUIZENGA, 1959).

[i] Replicate samples of this meteorite have previously yielded Bi concentrations of 2·1 ppb (EHMANN and HUIZENGA, 1959) and 1·7, 2·6 and 7·6 ppb (REED *et al.*, 1960).

similar to those predicted by ANDERS (1964, 1968) and LARIMER and ANDERS (1967) on the basis of a two-component model.

Having now established that the Bi contents of the carbonaceous chondrites vary with chondritic type it is appropriate that we consider the question of the "cosmic abundance" of Bi. Since it is generally accepted that C1 chondrites constitute the closest approximation to unaltered cosmic material, it seems likely that the Bi cosmic abundance is $0{\cdot}143 \pm 0{\cdot}010$ atoms/10^6 Si atoms [or $0{\cdot}148 \pm 0{\cdot}009$ atoms/10^6 Si atoms, including the Orgueil value of REED *et al.* (1960)]. This value is virtually identical to that adopted by SUESS and UREY (1956) [based, in turn, on the value adopted by NODDACK and NODDACK (1934)]. The revised Bi abundance value adopted by CAMERON (1968), which is based on the single Orgueil result of REED *et al.* (1960), should therefore be reduced slightly to 0·14–0·15 atoms/10^6 Si atoms in view of our results.

Ordinary chondrites

From the results in Table 3 it appears at first glance that the Bi contents of the equilibrated H-group chondrites may be about 5 times higher than those of the equilibrated L-group chondrites. This difference may well be fortuitous, however,

in view of the small number of samples analyzed. The Bi concentration ranges reported previously (EHMANN and HUIZENGA, 1959; REED *et al.*, 1960; REED, 1963) for equilibrated H-, L- and LL-chondrites are about the same and vary in the extreme cases by about a factor of 10^2 (Table 4). Indeed, for at least one L6 chondrite alone (Modoc) the extreme concentrations in 7 replicates vary by about the same factor (EHMANN and HUIZENGA, 1959; REED *et al.*, 1960). Part, if not all, of this variation may be due to sample inhomogeneity although at concentrations of ~1 ppb, experimental difficulties may play a significant role. In view of these variations it would clearly be improper to calculate arithmetic means for the Bi contents in ordinary chondrites. Based on all available data the geometric mean Bi contents in the equilibrated H- and L-groups are 2·5 and 1·3 ppb or 2·0 and 1·0 atoms/10^9 Si atoms respectively (Table 4). In the case of the

Table 4. Bismuth contents in ordinary chondrites

Chondritic group	Equilibrated			Unequilibrated		
	Range* (ppb)	Geometric means ppb	(atoms/10^9 Si atoms)	Range* (ppb)	Geometric means (ppb)	(atoms/10^9 Si atoms)
H	0·18–15(20)	2·5	2·0	4·6–89(4)	16	13
L	0·07–7·6(13)	1·3	1·0	1·6–120(4)	18	13
LL	0·55–1·0(2)	0·7	0·5	6·5–65(4)	19	14
All	0·07–15(35)	1·9	1·4	1·6–120(12)	18	14

* Data from this study, EHMANN and HUIZENGA (1959), REED *et al.* (1960) and REED (1963). The numbers in parentheses are the number of samples, not meteorites, analyzed of each group.

LL-group, only 2 samples have been studied. Thus, the Bi means for this group (0·7 ppb or 0·5 atoms/10^9 Si atoms) carry little statistical weight. Many further measurements will be required before firm conclusions can be drawn on possible group differences in the Bi contents of equilibrated ordinary chondrites. In this connection, we note that the dark phase of Fayetteville appears to have a Bi concentration 40% higher than that in the light. The only similar chondrite studied previously is Pantar in which the Bi concentration was reported to be 5–6 times higher in the dark phase than in the light (REED, 1963). We will not speculate upon the reasons for these differences until we have further information on the contents of other trace elements in the light and dark phases of Fayetteville.

It is well established that, among the ordinary chondrites, there exists a small number of unequilibrated ordinary chondrites (UOC) in which the silicates are chemically inhomogeneous (DODD and VAN SCHMUS, 1965; DODD *et al.*, 1967). Based on these inhomogeneities in the UOC, DODD *et al.* (1967) have established a semi-quantitative disequilibrium scale expressed as "percent mean deviation" of the Fe^{2+} in the olivine (PMD). Despite considerable efforts there is no consensus for the origin of these UOC. DODD (1969) has reviewed, in detail, the results of those studies pertinent to the origin of the UOC and, indeed, all chondrites, and has critically evaluated the rival theories which attempt to explain their origin. It seems that much further data must be obtained if ever the genesis of these chondrites is to be understood. One important point which is unsettled is whether the relationship of the unequilibrated H-, L- and LL-chondrites to each other is

more important than their respective group relationships to the equilibrated chondrites. For much of the discussion which follows we will assume the former relationship to be the more important although both will be considered.

Within this framework then, let us now specifically consider the Bi data of the H-, L- and LL-chondrites (Table 3). In two cases (Sharps, Mezö-Madaras), the Bi concentrations approach those of the C1 chondrites although, even for these two, the abundances are markedly lower. In the remaining UOC the abundances are lower by as much as 10^2, extending to the range of the equilibrated ordinary chondrites. This suggests the possibility that the Bi contents in equilibrated ordinary chondrites are progressively depleted with increasing petrologic type. From our data and those of EHMANN and HUIZENGA (1959), REED *et al.* (1960) and REED (1963), there appears to be no certain trend in this direction. Of course this tentative conclusion is based on relatively few analyses and may be changed when more type 4–6 samples are studied. The geometric mean Bi contents in the unequilibrated H-, L- and LL-chondrites are quite similar (Table 4)—16, 18 and 19 ppb or 13, 13 and 14 atoms/10^9 Si atoms, respectively. Insofar as the meteorites that we studied are representative of the unequilibrated ordinary chondrites these results indicate the lack of a marked dependence of mean Bi content upon chondritic class.

The Bi abundance data (Table 3) are plotted in Fig. 1 vs. the degree of equilibration of the olivine. A striking feature of Fig. 1 is the monotonic decrease in Bi abundance within each group with decreasing PMD (or increasing equilibration), suggesting that whatever process was responsible for equilibration was also reponsible for the decrease in the content of Bi. This general trend might be expected to result from processes similar to those postulated by DODD *et al.* (1967), i.e. progressive metamorphism, or LARIMER and ANDERS (1967), i.e. accumulation at different temperatures. What is unexpected, however, is the violation of this monotonic trend in the cases of the least equilibrated member of each chondritic group (Fig. 1). If we assume that the remaining chondrites of each group represent discrete evolutionary sequences (the dotted lines in Fig. 1), then the chondrites having the highest PMD values of each group appear to be considerably underabundant in Bi. Alternatively, if we assume a single evolutionary sequence for all UOC (the solid line in Fig. 1), the same conclusion holds. Can it be that these trends result from the omission of Sharps, Krymka and Ngawi in calculating the lines in Fig. 1? If these are included the least-squares line for the UOC as a group has a less steep slope but, even so, both Krymka and Ngawi remain underabundant in Bi. Furthermore, the least-squares line for the H-group UOC can hardly be shifted so as to include Sharps. It seems therefore that our observation is valid and that these three meteorites are distinctly underabundant in Bi. This observation appears equally inconsistent with the genetic models of DODD *et al.* (1967) or LARIMER and ANDERS (1967). It could be made consistent with either by the adoption of *ad hoc* assumptions the nature of which need not be discussed here.

It seems clear from Fig. 1 that our working hypothesis of an exponential relationship between the Bi contents and degree of equilibration of the UOC satisfies the empirical observations for all UOC except Sharps, Krymka and Ngawi. It must not be assumed however that this simple empirical relationship has any

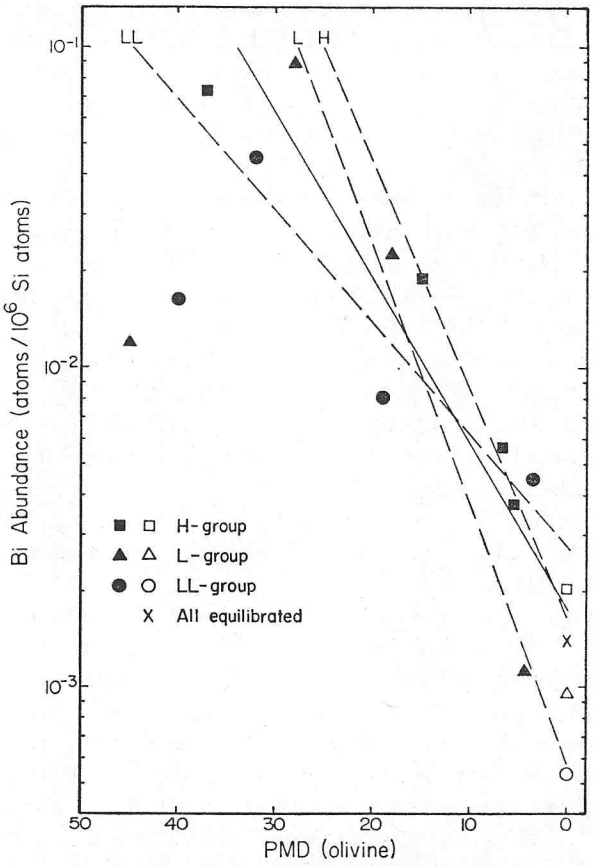


Fig. 1. Bismuth abundances versus the percent mean deviation (PMD) of olivine in ordinary chondrites. The closed symbols indicate individual unequilibrated ordinary chondrite analyses and the open symbols indicate geometric mean Bi abundances in the equilibrated ordinary chondrite groups. The geometric mean abundance for all equilibrated ordinary chondrites is indicated by "X". Except for the most unequilibrated member of each chondritic group, the Bi concentrations appear to decrease exponentially with PMD. Least-squares lines are shown for: (a) each chondritic group separately (dashed lines); (b) the UOC as a group (solid line). For the calculations, the chondrite having the highest PMD of each group was omitted since these meteorites appear to be distinctly underabundant in Bi (see text).

theoretical basis at the moment or can be extrapolated beyond the bounds indicated in Fig. 1. Indeed if such extrapolations are made to the extremes two paradoxical situations arise. The first of these is that extrapolation of the H- and L- group lines to PMD > 30 and the LL-group line to PMD > 50 would indicate Bi abundances in excess of those in C1 chondrites—a very unlikely prospect. In highly unequilibrated ordinary chondrites, the relationship between Bi and disequilibrium must be more complex than is indicated by our working hypothesis and, indeed, we have already noted Bi abundances to be low in such meteorites. The second paradox is that the Bi abundances in members of each group of

equilibrated ordinary chondrites (i.e. at zero PMD) would be expected to be quite similar when, in fact, they are not. In order to account for this, it seems obvious that after the PMD parameter ceases to be a measure of equilibration other processes must occur to redistribute Bi or cause its loss in equilibrated ordinary chondrites. Thus, in the remainder of this discussion, where we refer to the "nearly exponential" depletion of Bi with decreasing PMD or increasing equilibration it must be understood that we are describing a phenomenon and not implying any particular process.

With respect to Fig. 1, we may note some speculative but nonetheless interesting observations. When the lines for the H- and L-group UOC are extrapolated to zero PMD (Fig. 1), the respective Bi abundances are within 20% and 40% of the means calculated for equilibrated chondrites of these groups (Table 4). In the case of the LL-group the agreement is not good since the zero-PMD intercept is 6 times higher than the mean Bi abundance in equilibrated LL-group chondrites. The least-squares line for the LL-group UOC is much less steep than those of the H- and L-groups primarily because of the Hamlet datum. Can it be that the PMD datum for this chondrite is in error? If so, then the zero-PMD intercept of a line through the Chainpur and Parnallee points is within 20% of the mean Bi abundance of the equilibrated LL-group. We are reluctant to speculate further upon this since a straight line can always be drawn through 2 points and the equilibrated LL-group mean represents only 2 analyses. We note however that assuming a single evolutionary sequence for all UOC, the zero-PMD intercept is within 30% of the mean Bi abundance for all equilibrated ordinary chondrites. It may be that these seeming agreements are fortuitous and it would be well were the PMD values reexamined (DODD, personal communication).

Returning to less speculative matters it is interesting that carbon shows the same overall pattern as Bi—i.e. nearly exponential, progressive depletion with decreasing PMD, except for the least equilibrated chondrites, in which carbon is underabundant (Table 3; see also Fig. 14 of DODD, 1969). We would therefore expect a mutual correlation between the Bi and C concentrations in the UOC and this is indeed observed (Fig. 2), suggesting the influence of some process in common. It is worthwhile noting that the overall abundance trends for Bi alone (Fig. 1) or C alone (Fig. 14; DODD, 1969) are duplicated when one plots the Bi/C ratios vs. PMD for the UOC.

It seems scarcely possible that the Bi–C correlation (Fig. 2) represents the elements' proportional volatilization in some critical temperature region if one considers the primordial gas contents of the UOC (e.g. HEYMANN and MAZOR, 1968; ZÄHRINGER, 1968). In Fig. 3 we have plotted the primordial Ar^{36} content vs. Bi for the UOC. Despite the scatter in the noble gas data, there appears to be a good correlation between the concentrations of primordial Ar^{36} and Bi. While there seem to be correlations of Bi with primordial Kr^{84} and Xe^{132} as well, these are less striking than the one evident in Fig. 3 because of the smaller variation in the Kr^{84} and Xe^{132} contents of UOC. In connection with these correlations it seems rather surprising that the overall Bi concentrations in the UOC decrease at a far more rapid rate than do the noble gas concentrations (a factor of 10^2 for Bi compared with factors of 10 for Ar^{36} or 3–4 for Kr^{84} and Xe^{132}). It is also noteworthy

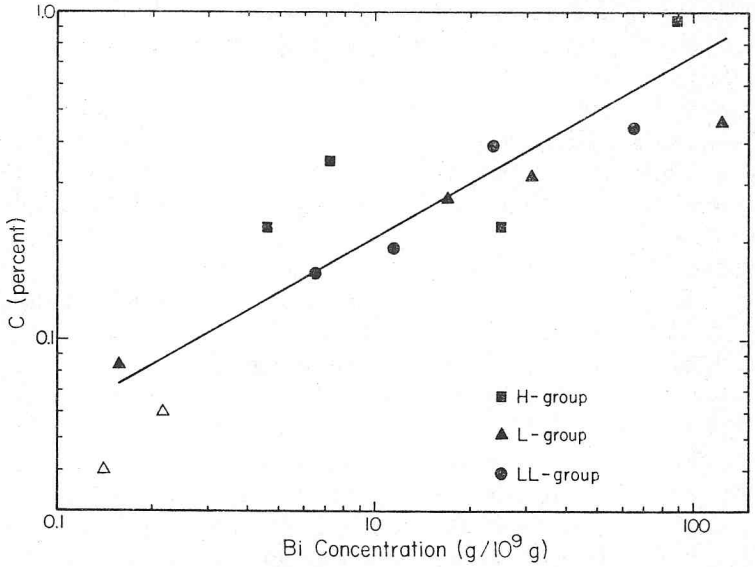


Fig. 2. Correlation between the bismuth and carbon contents of the ordinary chondrites. The solid line is calculated by least-squares analysis of all UOC data. The open symbols indicate data for equilibrated chondrites (L6).

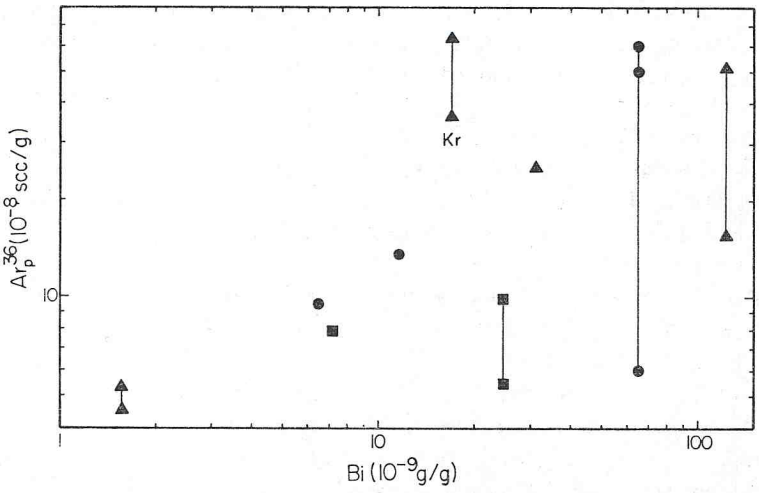


Fig. 3. Primordial Ar^{36} concentrations vs. Bi concentrations in UOC. Despite the scatter in the noble gas data (HEYMANN and MAZOR, 1968; ZÄHRINGER, 1968) the data seem well correlated. When Kr^{84} and Xe^{132} are plotted vs. Bi, similar correlations are observed. Krymka (Kr) seems to be an exception to these correlations in that in all three cases it is underabundant in Bi (or overabundant in primordial noble gases).

that with respect to the Ar^{36}, Kr^{84} and Xe^{132} concentrations, the only chondrite whose Bi content is clearly aberrant (e.g. Fig. 3) is Krymka, the L-group chondrite having the highest PMD.* Yet, the Bi contents of the UOC (including Krymka, Ngawi and Sharps) are consistent with their C contents (Fig. 2). Since both Bi and C can scarcely be more volatile than Ar, Kr and Xe, it seems that the trends evident in Figs. 1–3 cannot be the result of late volatilization losses. Instead these trends must be the result of some primordial process(es), the nature of which seems quite nebulous at this time.

Conclusions

Based on this survey of the Bi contents in 31 samples of carbonaceous and equilibrated and unequilibrated ordinary chondrites, a number of apparently significant observations may be made. These observations are:

(a) Bismuth is confirmed to be a "strongly-depleted" element (Anders, 1964).

(b) The mean Bi abundance ratios in the carbonaceous chondrites relative to that of C1 are practically identical to those predicted by Anders (1964). This, in turn, supports his hypothesis that the carbonaceous chondrites are mixtures of two components, (i.e. chondrules and matrix) which are, respectively, depleted and undepleted with reference to a number of trace elements of various geochemical behavior.

(c) The true cosmic abundance of Bi is 0·14–0·15 atoms/10^6 Si atoms based on our C1 analyses.

(d) The Bi contents of the unequilibrated ordinary chondrites are intermediate between those of the carbonaceous and equilibrated ordinary chondrites. There is a nearly exponential progressive decrease in the Bi contents of unequilibrated ordinary chondrites with the degree of equilibration except for the most unequilibrated H-, L- and LL-chondrites, in which Bi appears distinctly underabundant.

(e) The Bi contents of the unequilibrated ordinary chondrites correlate very well with carbon. The concentrations of the primordial gases Ar^{36}, Kr^{84} and Xe^{132} also correlate with Bi in most of these chondrites. The distinct exception appears to be Krymka, the only highly unequilibrated ordinary chondrite for which both Bi and rare gas data are available.

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* The Ar^{36}, Kr^{82} and Xe^{132} contents of Sharps and Ngawi, the most unequilibrated H- and LL- group chondrites that we studied, have not been reported. We would expect that when these are measured, both Ngawi and, to a lesser extent, Sharps will also be aberrant with respect to the Bi-noble gas correlations.

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Appendix—Sources and Sample Numbers of Meteorites Studied

1. R. S. Clarke Jr.; U.S. National Museum; Washington, D. C. *Clovis* (USNM-2170), *Felix* [B] (USNM-235), *Hamlet* (USNM-3455), *Ivuna* [A] (USNM-2478), *Ivuna* [B] (USNM-2478), *Krymka* (USNM-2488), *Murray* [A] (USNM-2122), *Murray* [B] (USNM-1519), *Ngawi* (USNM-2962), *Prairie Dog Creek* (USNM-1115), *Sharps* (USNM-640).
2. R. E. Folinsbee; University of Alberta; Canada *Bruderheim* (B-93).
3. P. K. Kuroda; University of Arkansas; Fayetteville, Ark. *Fayetteville.*
4. C. B. Moore; Arizona State University; Tempe, Ariz. *Chainpur* (ASU-424-1), *Holbrook* (ASU-452), *Khohar* (ASU-623-1), *Plainview* (ASU-92-423).
5. E. Olsen; Field Museum of Natural History; Chicago, Ill. *Barratta* (Me-1464), *Bremervörde* (Me-1758), *Cold Bokkeveld* (Me-1738), *Felix* [A] (Me-1330), *Grosnaja* (Me-1732), *Lancé* (Me-589), *Mezö-Madaras* (Me-1607), *Mighei* (Me-1456), *Orgueil* [A] (Me-509), *Ornans* (Me-1766), *Parnallee* (Me-437), *Vigarano* (Me-732), *Warrenton* (Me-1720).