Earth and Planetary Science Letters, 29 (1976) 302–308

[6]

THE ABUNDANCES OF ZIRCONIUM AND HAFNIUM IN THE SOLAR SYSTEM

R. GANAPATHY, GRACE M. PAPIA and LAWRENCE GROSSMAN [1]

Department of the Geophysical Sciences, The University of Chicago, Chicago, Ill. (USA)

Received September 12, 1975
Revised version received December 4, 1975

The concentrations of zirconium and hafnium have been determined in Orgueil, Murchison, Allende, Bruderheim and Alais by RNAA. The mean Zr/Hf weight ratio in the first four of these meteorites is 31.3 ± 2.2 indicating no major fractionation of Zr from Hf. Alais contains anomalously high amounts of many refractory lithophile elements, including Zr and Hf. Orgueil contains 3.1 ppm Zr and 0.11 ppm Hf, corresponding to 9.0 and 0.16 atoms, respectively, relative to 10^6 Si atoms.

1. Introduction

It is widely accepted that, of all matter so far studied, Cl chondrites are most representative of the mean composition of the total condensable matter of the solar system [1–3]. The solar system abundances of all but the most volatile elements are thus readily obtainable through precise measurements of their concentrations in this class of meteorites. Because of analytical difficulties [4], however, considerable uncertainty still surrounds the abundances of Zr and Hf. In the course of our investigations into the condensation characteristics of refractory elements [5,6], it became important to know the abundances of Zr and Hf to a high degree of accuracy in order to ascertain if they had fractionated from one another. We therefore decided to determine their concentrations in several meteorites.

2. Experimental

Three separate irradiations were performed. Rock standards and meteorite specimens analysed in each are described in Table 1. No areas of fusion crust were sampled. In the first irradiation, two well-analysed rock standards were used in order to eliminate any possible source of error connected with the preparation and processing of chemically prepared standards. For Zr, we used the NBS Flint clay 97a, 0.063 ± 0.003% ZrO_2, and for Hf, the standard pot of Perlman and Asaro [7], 6.23 ± 0.44 ppm.

Samples and standards were irradiated for five days at a thermal neutron flux of 2×10^{13} n cm^{-2} sec^{-1} in the CP-5 reactor at Argonne National Laboratory. After irradiation, separate carriers for Zr and Hf were added and the samples and standards were processed by conventional radiochemical methods similar to those used by Keays et al. [8] with the exceptions that nickel crucibles were used and Ce^{4+} was not added. After removal of rare earth fluorides from the rare earth fraction, Zr and Hf were precipitated as $Ba(Zr,Hf)F_6$ and then as $(Zr,Hf)(OH)_4$. At this stage, special attention was paid to removal of Eu through repeated LaF_3 precipitations. Finally, Zr and Hf were precipitated together as the tetramandelate and counted on a high-resolution Ge(Li) detector [6].

Gamma-ray spectra from the samples and standards indicated no extraneous contaminants. In particular, no ^{152}Eu activity was detected in any of our spectra. This is important because the ^{152}Eu/^{154}Eu activity ratio is ~21 and ^{154}Eu, having γ-ray peaks at 723.3 and 756.8 keV, is a potentially serious interference with ^{95}Zr whose peaks are at 724.4 and 756.9 keV. We

[1] Also Enrico Fermi Institute.

TABLE 1

Concentrations of Zr, Hf and U in meteorites and rock standards (ppm)

Meteorite	Type	Irradiation	Description	Source	Zr *	Hf	U	Zr/Hf
Orgueil	CI	1	60 mg, chunks	FMNH[1] Me 509	3.1 ± 0.1	0.11	–	28.2
		3	64 mg, chunks	FMNH Me 509	3.0 ± 0.2	–	–	
Murchison	C2	1	61 mg, powder	FMNH Me 2640	4.6 ± 0.2	0.14	–	32.9
Allende	C3	1	52 mg, powder	USNM[2] Split 23, Position 5	5.9 ± 0.2	0.19	–	31.1
Bruderheim	L6	1	128 mg, chunk	FMNH Me 2476	6.6 ± 0.1	0.20	–	33.0
						Mean		31.3 ± 2.2
Alais	CI	1	40 mg, chunks	FMNH Me 1486	173 ± 1	2.28	–	75.9
Rock standard								
NBS Flint clay		1	62 mg, powder	NBS	≡466[3]	15.4	–	30.3
		3	63 mg, powder	NBS	465 ± 19	–	6.58	30.2
Standard Pot		1	36 mg, powder	Asaro	214 ± 3	≡6.23[4]	–	34.3
		3	71 mg, powder	Asaro	215 ± 3	–	≡4.82[4]	34.5
BCR-1		3	58 mg, powder	USGS	173 ± 2	4.98[6]	≡1.74[5]	34.7

[1] Field Museum of Natural History.
[2] U.S. National Museum.
[3] National Bureau of Standards Certificate.
[4] Perlman and Asaro [7].
[5] Flanagan [10].
[6] Grossman and Ganapathy [6].
* Uncertainties quoted represent 1σ counting statistics only.

conclude that our Zr data are free of interference from Eu.

Rather than simply assuming that the Zr and Hf gravimetric yields were identical, we verified both of their chemical yields in a second irradiation. Because the maximum difference observed between the gravimetric and reactivation yields was only 5.9% (relative), we conclude that no major fractionation of Zr from Hf took place in our chemical procedure.

Ehmann and Chyi [4] have warned about the problem of Zr and Hf contamination by use of glassware used in previous analyses. Laboratory contamination of our samples is thought to be negligible since these were the first samples processed in our newly built laboratory and our glassware had never been used previously.

The third irradiation was designed primarily to check the Zr abundance in the Flint clay standard used in the first irradiation since the NBS certified value was obtained by spectrophotometry. The weight loss of specpure ZrO_2 on ignition to 1000°C was found to be only 0.13%, indicating no water of hydration. Consequently, 12.24 mg of this material were weighed into a quartz tube and used as a primary standard. Irradiated along with the Flint clay and ZrO_2 were samples of BCR-1, the standard pot and an additional sample of Orgueil. After irradiation, Zr carrier was added to all but the primary standard. Thermal neutron-induced fission of 1 μg of U produces ^{95}Zr activity equivalent to 7.087 μg of Zr. In order to determine the concentration of U in the Flint clay, Ba carrier was added to it and to the standard pot whose U concentration is 4.82 ± 0.44 ppm [7]. No Hf carrier was added, Hf was not determined and Zr gravimetric yields were not verified by re-irradiation in this series of analyses. Aside from these differences, Zr was determined in the same way as in the first irradiation and U was determined radiochemically through its fission product ^{140}Ba. The primary Zr standard was counted in identical geometry to the samples but without any chemical processing. No ^{152}Eu activity was seen in the spectrum of the primary standard and the activity ratio of the two ^{95}Zr photopeaks in it was within counting statistics of that in the chemically purified samples, indicating no interference from ^{154}Eu.

3. Discussion

3.1. Accuracy and precision

Analytical data for all rock standards and meteorites are given in Table 1. The U content of the Flint clay is 6.58 ± 0.05 ppm and accounts for 9.1% of its ^{95}Zr activity. After correction for this fission contribution, the Zr content of the Flint clay was found to be 465 ± 19 ppm compared to the primary ZrO_2 standard. This measurement is in exceptional agreement with the NBS certified value which corresponds to 466 ± 22 ppm Zr, justifying our use of the Flint clay as a standard in the first irradiation. Our fission-corrected value for the Zr content of BCR-1 is 173 ± 2 ppm. As always, however, direct comparison of this determination with literature data is hampered by a wide range of literature values, from 110 to 270 ppm [9]. The average of the XRF measurements in [9] is 177 ppm and Flanagan [10] quotes a "magnitude" of 190 ppm.

Based on the data for the standard pot, the reproducibility of the Zr data is excellent. After correcting for fission with the U content determined in [7], its Zr content was found to be 215 ± 3 ppm and 214 ± 3 ppm in two separate irradiations.

For the meteorite samples, errors due to counting statistics vary from 1 to 6% for ^{95}Zr and from 0.2 to 0.8% for ^{181}Hf. The high chondritic Zr/U ratio would lead to a fission contribution of only 1–2% to the ^{95}Zr activity. Consequently, no fission corrections were applied to the meteorite data. Taking into account all known sources of error, including uncertainties due to counting statistics and in the determinations of the yields, we estimate that our Zr and Hf concentrations are accurate to within 10%. Replicate Zr analyses of Orgueil, done in separate irradiations, are indistinguishable from one another, agreeing to within 3%.

3.2. Comparison of meteorite data with previous measurements

The Hf values for Allende and Bruderheim in Table 1 are higher than those of Ehmann and Rebagay [11] by 18–19%. Relative to the Ehmann and Chyi [4] Orgueil and Murchison data, our measurements are again higher, this time by 8–10%. Our Hf data are always within the stated analytical uncertainties of the values in these two papers from the Ehmann group although there is an indication of systematic differences between our two laboratories and perhaps between the two sets of Hf data from the Ehmann group. A more recent redetermination of Hf in Allende by the Ehmann group [12], however, is in much better agreement with our Allende value.

Our meteoritic Zr data are compared with other recent determinations in Table 2. Our carbonaceous chondrite data are consistently lower, meteorite for meteorite, than the data of the Ehmann group. The differences between our two laboratories, however, are seen to be greater for the earlier papers of the Ehmann group than for the later ones as they have progressively revised their data in a downward direction. The 1970 Allende and Orgueil data in [11] are factors of 2.2 and 3.0 higher, respectively, than in this work. The 1974 values for Murchison and Orgueil [4] are 35% and 68% higher, respectively, than here while the 1975 Allende concentration [12] is only 8% higher than ours. The most recent determinations of Zr in Orgueil and Murchison by the Ehmann group [4] are not within the stated analytical errors of our data. Their most recent Allende datum is in agreement with ours. Our value for the L-group chondrite Bruderheim is higher than that in [11] by 29% but the two values are barely within error of one another.

Also seen in Table 2 are the data of Palme [13]. The lower of his two Zr abundances in Orgueil agrees with the data in this work and the higher one is within error of the Ehmann and Chyi [4] data but not of our values. The Murray determination of Palme [13] is in agreement with that of Ehmann and Rebagay [11].

3.3. Consistency of the data

Recent work in cosmochemistry [5,6,14] suggests that the highly refractory elements were incorporated into the different classes of chondrites in a single component in which they occurred in cosmic proportion to one another. These models lead to the prediction that the Zr/Hf ratio should be nearly constant in all classes of chondrites. Excluding our data for Alais from this discussion for the time being, the mean Zr/Hf weight

TABLE 2

Comparison of recent Zr determinations in meteorites (ppm)

Meteorite	Ehmann and Rebagay, 1970 [11] (±15–20%)	Ehmann and Chyi, 1974 [4] (±10%)	Ehmann et al., 1975 [12] (±5–10%)	Palme, 1974 [13] (±12–20%)	This work (±10%)
Orgueil	10, 8.7	5.4, 4.7, 5.3, 5.5		3.65, 4.3	3.1, 3.0
Ivuna	8.6				
Murchison		6.4, 5.9			4.6
Murray	4.9, 5.5			5.5	
Allende	10, 11, 11, 12, 14, 17		6.8, 6.0		5.9
Karoonda	11, 9.3, 8.3	7.8, 8.1			
Bruderheim	5.1				6.6
Chainpur	7.0	6.4, 6.7			

ratio for the meteorites studied here (Table 1) is 31.3, with a standard deviation of 7.0%. The relative constancy of this ratio in these representatives of four different meteorite classes is in agreement with theoretical predictions [5] and analytical data for many other refractory lithophile elements [15]. For the same classes of meteorites, we note that the Ehmann group has reported a wide range of Zr/Hf ratios, from 25 to 81.

Further, the compilation of Van Schmus and Hayes [16] shows that the atomic abundances of Ca, Al and Ti relative to Si are 40%, 32% and 38% higher, respectively, in Allende than in Orgueil and that this refractory element enrichment is a general feature of Vigarano-type C3 chondrites. Table 3 shows atomic abundances of Zr and Hf relative to Si determined in this work. These refractories are seen to be enriched in Allende relative to Orgueil by 27% and 15%, respectively, suggestive of the findings in [16] for other refractories. We believe that our data thus pass an important test of internal consistency.

3.4. Previous Zr data

Setser and Ehmann [17] reported 92 ppm Zr in W-1 and Ehmann and Chyi [4] reported 107 ppm. Both of these values are within 15% of the recommended values of 100 ppm [18] and 105 ppm [10]. In retracting the Setser and Ehmann [17] meteoritic Zr data, Ehmann and Rebagay [11] attributed the high values in the previous work principally to Eu interference but suggested that this effect resulted in a less significant error in the higher Zr abundance terrestrial rocks. In view of the fact that the Zr/Eu ratio in W-1 is essentially the same as in chondrites (95 vs. 81), it is

TABLE 3

Atomic abundances of Zr and Hf relative to Si = 10^6 in the meteorite samples analysed in this work

Meteorite	Type	Si(wt.%)	Zr	Hf	Zr/Hf
Orgueil	C1	10.64 [26]	8.97	0.163	55.0
Orgueil	C1		8.68	–	
Murchison	C2	13.39 [27]	10.58	0.165	64.1
Allende	C3	16.00 [28]	11.35	0.187	60.7
Bruderheim	L6	18.7 [29]	10.87	0.168	64.7
		Mean	10.44	0.171	61.1
Alais	C1	9.71 [26]	549	3.69	149

difficult to understand why the W-1 Zr data in [4] have changed so little since 1964 while their chondritic Zr abundances have fallen by a factor of 8. Perhaps interference was not the cause of the high values in [17], particularly since Setser and Ehmann [17] determined that the half-lives of their photopeaks matched those of ^{95}Zr to within 1%.

Ehmann and Chyi [4] stated that their new meteoritic abundances are consistent with their previous Zr data for the same meteorites [11]. The only exception to this was their Orgueil data for which they suspected that their earlier sample was contaminated. Yet, Table 2 shows that their old Orgueil value was in good agreement with the Ivuna value in [11] while the new Orgueil value is now 40% lower than Ivuna. Thus, either both Ivuna and Orgueil were contaminated such that similar Zr contents resulted coincidentally or some of the Ehmann and Rebagay [11] data are systematically too high. Indeed, other evidence exists that the latter may be the case. The only other meteorites analysed in both [4] and [11] are Karoonda and Chainpur. As pointed out by Ehmann and Chyi [4], the Zr content reported for each of these meteorites in [4] is within error of its value in [11]. As seen in Table 2, however, for both meteorites, every value reported in [4] is lower than every value in [11]. Also, the updated Allende determination in [12] is again lower than in [11].

It appears that the abundances of Zr and Hf in the solar system, based on the data presented here for Orgueil, are 9.0 and 0.16 atoms, respectively, per 10^6 Si atoms. At the same time, it is recommended that these values be confirmed by several other laboratories

3.5. Previous estimates of the solar system abundances of Zr and Hf

In Table 4, we compare our Cl values for Zr and Hf with the estimates of other workers. Ehmann and Rebagay [11] determined the abundances of Zr and Hf in Orgueil and Ivuna and found a Zr/Hf atomic ratio of 55. In compiling his table of the abundances of the elements in the solar system, Cameron [2] adopted the mean of the Cl data summarized by Ehmann and Rebagay [19] for Zr. He considered the Cl Hf data of Ehmann and Rebagay [11] to be too high and computed the Hf abundance by dividing the Ehmann and Rebagay [11] Zr data by "the average chondritic Zr/Hf ratio". This weight ratio appears to be consistent with the Zr/Hf atomic ratio of Cameron [20], 124, which was adopted from the Suess and Urey [21] value which, in turn, is heavily dependent on the work of Von Hevesy and Würstlin [22,23].

Suess and Zeh [24] also considered the Ehmann and Rebagay [19] Cl Hf value to be too high because its resulting cosmic abundance is unusually high compared to its neighboring elements. Suess and Zeh [24] suspected that the Zr figure in [19] is also overabundant by the same factor because they felt that these data exhibited the "well-known abundance ratio of Zr to Hf". Consequently, they adopted the Ehmann and Rebagay [19] Zr and Hf concentrations in C2 chon-

TABLE 4

Comparison of estimates of the abundances of Zr and Hf in the solar system

Estimate	Concentration * in Cl chondrites			Atomic abundance relative to Si = 10^6		
	Zr (ppm)	Hf (ppm)	Zr/Hf weight ratio	Zr	Hf	Zr/Hf atomic ratio
Ehmann and Rebagay [11]	*9.0*	*0.32*	28	26	0.47	55
Cameron [2]	9.0	0.14	63	28	0.21	124
Suess and Zeh [24] **				13	0.22	59
Ehmann and Chyi [4]	*5.2*	*0.10*	52	15	0.15	100
Wänke et al. [25]	*4.1*	0.14	30	12	0.21	57
This work	*3.1*	*0.11*	28	9	0.16	55

* Italicized values are analytical determinations.

** Based on data for C2 chondrites.

drites for their abundance table because they are lower than the Cl data in [19] by a factor of 2.1 and the Zr/Hf ratio is nearly the same in both, 28 vs. 31.

As a result of their redetermination of Zr and Hf in Orgueil by a newer technique, Ehmann and Chyi [4] recommended the values 5.2 ± 0.5 ppm Zr and 0.10 ± 0.01 ppm Hf, corresponding to a Zr/Hf atomic ratio of 100. In so doing, the Ehmann group lowered their previous Zr value by more than 40% and their Hf value by more than a factor of three. The only other recent Zr determination in Cl's is that by Palme [13] as reported in Wänke et al. [25]. He obtained 4.1 ppm Zr in Orgueil and Wänke et al. computed the Hf content by dividing his Zr concentration by a Zr/Hf weight ratio of 30. This choice of the Zr/Hf ratio seems to have been influenced by Suess and Zeh [24] and the resulting Zr value is 21% lower than the Ehmann and Chyi [4] value. The agreement between the derived Hf values in [25] and [2] is seen to be fortuitous. Wänke et al. [25] began with a Zr value lower than that used by Cameron [2] by slightly more than a factor of two and divided it by a Zr/Hf ratio which was also lower than his by a similar factor. The Hf concentration reported for Orgueil in the present study confirms the value reported by Ehmann and Chyi [4] but our Zr value, like that of Palme [13], suggests a still lower abundance than theirs. It is again fortuitous that our Zr/Hf ratio agrees with that of Ehmann and Rebagay [11] because both our Zr and our Hf concentrations are a factor of three lower than in that study.

3.6. Alais

Our determinations of the Zr and Hf concentrations in the Cl Alais have been purposely ignored in the previous discussion. These elements are enormously enriched in our Alais sample compared to Orgueil, a factor of 54 for Zr and 21 for Hf. The resulting Zr/Hf ratio is much higher than in our other four meteorites. These are not the only refractory lithophile elements which have been found to be enriched in Alais. Grossman and Ganapathy [6] showed by INAA that another sample of this meteorite, also from the Field Museum, is enriched by factors of 21, 16, 1.8 and 10–80 in Ta, Hf, Sc and rare earths, respectively, relative to Orgueil. In addition, they observed that the siderophiles and the volatile lithophiles Na and Mn are depleted in that sample by factors of 2–4. We do not understand what caused this complex enrichment and depletion pattern but it is clear that samples of Alais from the Field Museum should be used with caution in measurements of the cosmic abundances.

Acknowledgments

This research was supported by funds from the National Aeronautics and Space Administration through grant NGR 14-001-249.

References

1 E. Anders, How well do we know "cosmic" abundances?, Geochim. Cosmochim. Acta 35 (1971) 516.
2 A.G.W. Cameron, Abundances of the elements in the solar system, Space Sci. Rev. 15 (1973) 121.
3 U. Krähenbühl, J.W. Morgan, R. Ganapathy and E. Anders, Abundance of 17 trace elements in carbonaceous chondrites, Geochim. Cosmochim. Acta 37 (1973) 1353.
4 W.D. Ehmann and L.L. Chyi, Zirconium and hafnium in meteorites, Earth Planet. Sci. Lett. 21 (1974) 230.
5 L. Grossman, Refractory trace elements in Ca–Al-rich inclusions in the Allende meteorite, Geochim. Cosmochim. Acta 37 (1973) 1119.
6 L. Grossman and R. Ganapathy, Trace elements in the Allende meteorite, 1. Coarse-grained, Ca-rich inclusions, Geochim. Cosmochim. Acta (1976) in press.
7 I. Perlman and F. Asaro, Pottery analysis by neutron activation, Archaeometry 11 (1969) 21.
8 R.R. Keays, R. Ganapathy, J.C. Laul, U. Krähenbühl and J.W. Morgan, The simultaneous determination of 20 trace elements in terrestrial, lunar and meteoritic material by radiochemical neutron activation analysis, Anal. Chim. Acta 72 (1974) 1.
9 F.J. Flanagan, U.S. Geological Survey standards, II. First compilation of data for the new U.S.G.S. rocks, Geochim. Cosmochim. Acta 33 (1969) 81.
10 F.J. Flanagan, 1972 values for international geochemical reference samples, Geochim. Cosmochim. Acta 37 (1973) 1189.
11 W.D. Ehmann and T.V. Rebagay, Zirconium and hafnium in meteorites by activation analysis, Geochim. Cosmochim. Acta 34 (1970) 649.
12 W.D. Ehmann, L.L. Chyi, A.N. Garg, B.R. Hawke, M-S. Ma, M.D. Miller, W.D. James Jr. and R.A. Pacer, Chemical studies of the lunar regolith with emphasis on zirconium and hafnium, Proc. 6th Lunar Sci. Conf. (1975) 1345.
13 H. Palme, Zerstörungsfreie Bestimmung einiger Spurenelemente in Mond- und Meteoritenproben mit 14 MeV-Neutronen, in: Analyse extraterrestrischen Materials, W. Kiesl and H. Malissa Jun., eds. (Springer-Verlag, New York, N.Y., 1974) 147.

14 J.W. Larimer and E. Anders, Chemical fractionations in meteorites, III. Major element fractionations in chondrites, Geochim. Cosmochim. Acta 34 (1970) 367.

15 L.H. Ahrens and H. von Michaelis, The composition of stony meteorites, III. Some inter-element relationships, Earth Planet. Sci. Lett. 5 (1969) 395.

16 W.R. van Schmus and J.M. Hayes, Chemical and petrographic correlations among carbonaceous chondrites, Geochim. Cosmochim. Acta 38 (1974) 47.

17 J.L. Setser and W.D. Ehmann, Zirconium and hafnium abundances in meteorites, tektites, and terrestrial materials, Geochim. Cosmochim. Acta 28 (1964) 769.

18 M. Fleischer, U.S. Geological Survey standards, I. Additional data on rocks G-1 and W-1, 1965–1967, Geochim. Cosmochim. Acta 33 (1969) 65.

19 W.D. Ehmann and T.V. Rebagay, Zirconium (40) and hafnium (72), in: Handbook of Elemental Abundances in Meteorites, B. Mason, ed. (Gordon and Breach, New York, N.Y., 1971) 307.

20 A.G.W. Cameron, A revised table of abundances of the elements, Astrophys. J. 129 (1959) 676.

21 H.E. Suess and H.C. Urey, Abundances of the elements, Rev. Mod. Phys. 28 (1956) 53.

22 G. von Hevesy and K. Würstlin, Über das Häufigkeitsverhältnis Zirkonium/Hafnium und Niob/Tantal, Z. Physik. Chem. 139 (1928) 605.

23 G. von Hevesy and K. Würstlin, Die Häufigkeit des Zirkoniums, Z. Anorg. Allgem. Chem. 216 (1934) 305.

24 H.E. Suess and H.D. Zeh, The abundances of the heavy elements, Astrophys. Space Sci. 23 (1973) 173.

25 H. Wänke, H. Baddenhausen, H. Palme and B. Spettel, On the chemistry of the Allende inclusions and their origin as high-temperature condensates, Earth Planet. Sci. Lett. 23 (1974) 1.

26 H.B. Wiik, On regular discontinuities in the composition of meteorites, Commentat. Phys.-Math., Soc. Sci. Fenn. 34 (1969) 135.

27 E. Jarosewich, Chemical analysis of the Murchison meteorite, Meteoritics 6 (1971) 49.

28 R.S. Clarke Jr., E. Jarosewich, B. Mason, J. Nelen, M. Gómez and J.R. Hyde, The Allende, Mexico, meteorite shower, Smithsonian Contrib. Earth Sci. 5 (1970).

29 C.B. Moore, Silicon (14), in: Handbook of Elemental Abundances in Meteorites, B. Mason, ed. (Gordon and Breach, New York, N.Y., 1971) 125.