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The composition of CI chondrites and their contents of chlorine and bromine: Results from instrumental neutron activation analysis

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Abstract–Between 1973 and 1994, 15 samples of CI chondrites were analyzed by neutron activation analysis at the Max-Planck-Institute for Chemistry, Department of Cosmochemistry in Mainz, Germany. The analyses comprise nine Orgueil samples and three samples of Ivuna, two of Alais and one of Tonk. Samples came from various sources and had masses between 5 and 600 mg. Most data are published here for the first time. The results for the nine Orgueil samples demonstrate the essentially homogeneous chemical composition of Orgueil at a level of a few milligrams. The analytical results of Ivuna, Alais, and Tonk agree, with only few exceptions, with the results of Orgueil analyses. All samples agree within ±3% in their contents of Sc, Ir, Cr, Fe, Co, Zn, and Se. The elements Sc and Ir represent the refractory component; Cr, Fe, and Co the main component; and Zn and Se the volatile component. Thus, in all CI chondrites there are essentially the same fractions of the fundamental cosmochemical components. The essentially identical chemical composition of all samples shows that their water contents are constant at about 20 ± 5 wt%. There is excellent agreement between the data listed here with data reported in the relevant literature. There is no doubt that the CI composition is a well-defined entity, which is thought to represent the non-gaseous compositions of the solar nebula and the photosphere of the Sun. In addition, we conclude that the recently proposed new CI chondritic chlorine and Br values are too low, when compared to earlier measurements.

INTRODUCTION

The composition of CI chondrites is widely used as a standard for the chemical composition of the average bulk solar system, for elements heavier than O and excluding rare gases. Thus, it is not surprising that the elemental composition of CI chondrites has been repeatedly determined since the early 1960s in order to refine our knowledge of the elemental concentrations in the solar system. Nine meteorites are known that belong to the group of CI1 chondrites, among these are five falls and four finds. Yet, published data compilations rely mostly on measurements of samples from one fall, Orgueil, which is the largest and most accessible member of this group. Here we report a full data set of four CI meteorites analyzed by instrumental neutron activation analysis (INAA) including nine Orgueil samples and three samples from Ivuna, two from Alais and one from a Tonk sample.

In a recent paper in *Nature*, Clay et al. (2017) revised the abundances of the halogens in CI chondrites by large factors relative to earlier estimates (Palme et al. 2014). Their chlorine and Br abundances for CI chondrites were lowered by factors of 6.05 and 17.3, respectively, and they suggest an iodine CI abundance lower by a factor of 9.3 compared to earlier estimates. (Since we are discussing the concentration of chlorine in CI chondrites we will use throughout the paper the full name of the element chlorine instead of the chemical abbreviation Cl to avoid confusion between the element chlorine and CI meteorites.) The basis for these revisions is the measurement of concentrations of chlorine, Br, and I in CI carbonaceous chondrites, applying a new analytical technique. Here we demonstrate that the revised abundances for chlorine and Br cannot be reliable. This issue is important, because CI concentrations are used for estimating average solar system abundances, based on the excellent agreement of CI data with elemental abundances in the Sun obtained by absorption line spectroscopy of the solar photosphere (see Palme et al. 2014). The CI data are often used in modeling the composition and accretion history of Earth and other planetary bodies. A review of the abundance determinations of the halogens in chondritic meteorites and in the Sun is published by Lodders and Fegley (2021).

We report here on the determination of the chlorine and Br contents of CI meteorites by INAA of bulk meteorite samples. Thus, the two elements will be discussed within the framework of a large number of other elements determined in the same samples with the INAA procedure. Some of these data were used in papers of the Mainz Cosmochemistry group either as normalization values in elemental plots or as end members in mixing models (e.g., Wänke et al. 1974; Palme et al. 1978; Wänke and Dreibus 1979). In an earlier compilation the average of the analyses of six Orgueil samples was reported, but no individual results were given (Palme and Beer 1993; Spettel et al. 1993). Part of the data were also included in setting up CI abundance tables (e.g., Palme and Beer 1993; Lodders et al. 2009; Palme et al. 2014). Since the full data set for the 15 CI chondrite samples was never published, we present here the complete chemical analyses of CI chondrites obtained with neutron activation techniques. This set includes all bulk analyses of CI chondrites performed at the Department of Cosmochemistry in the Max-Planck-Institute of Chemistry (MPI) in Mainz, Germany, between 1973 and 1994.

Another aspect of this work is to find out to what extent CI chondrites are chemically homogeneous. With INAA, some elements (Na, Sc, Cr, Mn, Fe, and Ir) can be accurately analyzed. If abundance variations are smaller than indicated by analytical uncertainties, homogeneous distribution on the scale of sample sizes can be assumed. Most of the analyzed samples have masses in the range of a few hundred milligrams. One analyzed sample, however, has a mass of only 5 mg. Heterogeneity on a milligram scale would be evident from the analysis of this sample.

Dreibus et al. (1977, 1979) reported data on halogens by pyrohydrolysis of neutron irradiated samples. The results of these analyses are somewhat lower than those of the nondestructive neutron activation analyses presented here. As pyrohydrolysis involves chemical processing, we do not consider these data here. We restrict the discussion of the halogens to the results of nondestructive analyses by instrumental neutron activation.

The data of a single, radiochemically processed Orgueil sample are included for completeness.

MATERIALS AND METHODS

The Orgueil samples come from different sources. ORG-1 and ORG-2 as well as ORG-6 to ORG-9 were from materials of the Mainz MPI meteorite collection, which is on permanent loan to the Senckenberg Forschungsinstitut and Natural History Museum in Frankfurt. While ORG-1, ORG-2, ORG-8, and ORG-9 were aliquots from larger, powdered samples, ORG-6 and ORG-7 were small chips. ORG-3 is from an Orgueil sample bought from a meteorite dealer. ORG-4 was a sample from the Smithsonian Institution in Washington given to us through Kurt Fredriksson (Smithsonian Institution, Washington). ORG-5 is from the meteorite collection of the Natural History Museum in Vienna, given to us by Gero Kurat (Natural History Museum, Vienna).

IVUNA-1, IVUNA-2, ALAIS-2, and Tonk are fragments obtained from Addi Bischoff in Münster (see Endreß and Bischoff 1996). IVUNA-3 and ALAIS-1 are samples from the Mainz MPI meteorite collection.

All samples were irradiated in the TRIGA reactor of the University of Mainz. Procedures are described in Wänke et al. (1977). A large number of meteorites and lunar samples have been analyzed in exactly the same way. Samples were positioned in the carousel of the TRIGA reactor and irradiated for 6 h with a neutron flux of 7×10^{11} n cm^{-2} s. The neutron flux is so low that samples are not measurably heated. The integral neutron dose was varied by less than 20% during the 21 yr time span of analyses, from 1973 to 1994. Carefully prepared standards of Au (epithermal neutrons) and of Mn (thermal neutrons) were used to monitor the neutron flux in each irradiation. Before irradiation samples were, at most, mechanically treated either to produce powder aliquots or to split them into smaller fragments. In particular, they were not heated before analysis. Samples were irradiated in polyethylene capsules. Initially, samples were counted in the same vials in which they were irradiated. After we learned that there is a very small amount of Br in the containers, we transferred samples to new unirradiated capsules for counting from 1992 onward. The amount of Br in the polyethylene capsules was so small that it would, in no case, have affected the Br results of even the smallest Orgueil sample. The counting with Ge(Li)-detectors was done at various times after irradiation and took about 2 months in total. Data reduction was done with specially designed software and final results with appropriate averaging of multiple countings were obtained 3–4 months after irradiation. For each sample analyzed a one-page result sheet was produced.

One sample (ORG-1) was, in addition, analyzed by radiochemical neutron activation analysis (RNAA) using procedures described by Wänke et al. (1970). This provided concentrations of Cu, Ge, Pd, In, Cs, REE, W, and Au. ORG-3, ORG-4, and Ivuna-1 were irradiated with 14 MeV neutrons from a deuterium accelerator before thermal neutron activation analysis, as described by Teschke and Wänke (1974), allowing the nondestructive determination of the concentrations of O, Mg, Al, Si, and Fe. Samples ORG-8, IVUNA-2, IVUNA-3, ALAIS-2, and TONK analyzed after 1992 received an additional short 3 min of irradiation in the TRIGA reactor of the University of Mainz providing data for Mg, Al, Ca, and V.

RESULTS

The analytical results for nine Orgueil samples are given in Table 1. In Table 2, results of the analyses of three Ivuna samples, two samples from Alais and one from Tonk are shown. The year of analysis and the masses (mg) analyzed are given for all samples. In Tables 1 and 2, uncertainties are listed as standard deviation in % for each analysis. Many years of experience with neutron activation analysis showed that the uncertainties introduced by element standards, neutron flux variations, and counting geometries are certainly less than 3%. Larger uncertainties are the result of poor counting statistics, i.e., uncertainties in Tables 1 and 2 above 3% reflect uncertainties in counting statistics. An uncertainty of 3% is assigned to analyses with a statistical uncertainty of better than 3% due to sufficiently high counting rates. These uncertainties are upper limits. They reflect the accuracy of analysis, estimated from many element standards routinely analyzed over the years and from comparisons with results from other laboratories (e.g., Palme and Beer 1993; Spettel et al. 1993; Lodders et al. 2009).

The element Fe was determined in ORG-3, ORG-4, and Ivuna-1 with INAA and with fast neutron activation analysis. Both procedures gave, within error limits, the same results.

The data for Tonk were published earlier by Endreß et al. (1994). A later short irradiation of 3 min yielded additional data for Al, Mg, V, and Ca, not listed in Endreß et al. (1994) and thus published here for the first time.

In Table 3, we have listed the average results of the Orgueil, Ivuna, and Alais analyses. The uncertainties for Orgueil are calculated from concentration variations of the nine individual samples. These data are compared to the CI data of Kallemeyn and Wasson (1981), the Orgueil data of Barrat et al. (2012), and the CI reference values of Palme et al. (2014).

DISCUSSION

In the following section we will discuss the elements in the sequence in which they are listed in Tables 1 and 2 and displayed in Figs. 1 and 2. The halogens chlorine and Br will be discussed separately.

Oxygen

There are only few determinations of the total oxygen content of CI meteorites. Ehmann (1971) lists 46.0 wt% O for CI meteorites obtained with 14 MeV neutron activation analysis. The three determinations of the bulk O content listed here were done with the same technique in Mainz and give similar results, 46.45% and 47.39% for two Orgueil samples and 46.66% for a single Ivuna sample (see Teschke and Wänke 1974). The close coherence of the bulk O data is remarkable. Assuming major and minor elements are bound in simple oxides (e.g., FeO, Al_2O_3, CaO, MnO, etc.), Orgueil requires about 24% oxygen (or about 25% if all Fe is Fe^{3+}). This leaves 22% of the bulk O content to be bound to H, C, and S. The dominant O-bearing compound is certainly oxygen bound in $(OH)^-$ components of phyllosilicates. Wiik (1956) determined 19.89% of water for Orgueil and 18.68% for Ivuna. The water reported by Wiik (1956) is the total oxidized hydrogen, involving the water bound as $(OH)^-$ in minerals and the water formed by combustion of organic compounds. King et al. (2015) obtained 18.7% water for Orgueil and 18.3% for Ivuna. Their estimate is based on the measured mass loss by heating the meteorites to temperatures between 200 and 800 °C. These estimates amount to about 16.6–17.7 wt% O bound in water. Any larger variations in the water content of CI chondrites would significantly change the bulk O concentration. Thus the constancy of measured oxygen in Orgueil and Ivuna by INAA (Tables 1 and 2) indicates that CI chondrites, in general, have about the same amount of water.

Independent evidence for a constant water content of CI chondrites is also provided by the rather constant concentrations of other elements in CI chondrites. For example, the average Cr content of the 15 CI samples analyzed is 2614 ± 73 ppm. Twelve samples have Cr contents deviating by less than 3% from the average value (see below). If the above cited water content of some 20 wt% would be as low as 15 wt% in another CI sample, the Cr content of that sample would be higher by 5% than the average value. Another example is the average Ir content of the 15 samples, which is 467 ± 13 ppb, 11 samples differ from the average by less than 2%, and 13 samples by less than 3%. The somewhat unusual ALAIS-2 sample differs by 7% in Ir and the 5 mg Orgueil sample by 5%. Variations of

Table 1. Chemical composition of Orgueil samples analyzed by neutron activation in Mainz from 1973 to 1993.

		ORG-1		ORG-2		ORG-3		ORG-4		ORG-5		ORG-6		ORG-7		ORG-8		ORG-9	
Year of analysis		1973		1974		1975		1980		1980		1988		1992		1992		1993	
Weight in mg		483.5	SD	515.7	SD	600.4	SD	163.1	SD	150.1	SD	5.28	SD	216.8	SD	206.0	SD	25.73	SD
O	%					46.45	3	47.39	3										
Na	ppm	4960	3	4990	3	5100	3	5940	3	5120	3	4260	3	4985	3	4900	3	5180	3
Mg	wt%					9.41	3	9.43	3							9.9	3		
Al	wt%					0.81	7	0.83	6							0.9	3		
Si	wt%					10.65	3	10.8	2										
Cl	ppm	560	10			560	20	560	10	560	10			620	24	580	15	760	25
K	ppm	450	10	570	10	530	10	546	5	605	5	546	8	545	5	545	4	575	6
Sc	ppm	5.95	3	5.89	3	5.94	3	5.93	3	6.22	3	5.74	4	5.91	3	5.81	3	5.87	3
Ca	wt%							1.04	20	1.06	15	0.85	41	0.98	30	0.81	8	0.7	25
Ti	wt%															0.052	25		
V	ppm															50.9	4		
Cr	ppm	2730	3	2640	3	2600	3	2620	3	2670	3	2490	3	2675	3	2650	3	2610	5
Mn	ppm	1830	3	1820	3	1820	3	2026	3	1925	3	1540	3	1780	3	1830	3	1850	3
Fe	wt%	17.83	3	18.48	3	18.41	3	18.38	3	18.99	3	18.30	3	18.58	3	18.36	3	18.86	3
Co	ppm	508	2	504	3	492	3	514	3	549	3	529	4	488	3	511	3	520	3
Ni	ppm	10,600	5	11,000	5	10,700	5	11,400	4	11,280	5	12600	5	11100	4	11900	4	12,000	4
Cu	ppm	108						115	15	133	15	<150		110	30	160	25	160	30
Zn	ppm	350	5	310	10	380	10	322	5	330	5	341	6	324	4	320	4	343	4
Ga	ppm	8.3	5	9.4	10	9.5	15	9.29	5	8.72	5	9.52	7	10.6	5	10.6	5	9.8	8
Ge	ppm	36.5	10																
As	ppm	2.23	5	1.5	10	1.5	15	1.74	5	1.77	5	1.73	6	1.78	5	1.75	4	1.76	6
Se	ppm	17	5	18.9	5	18.8	5	21	3	20.7	3	21.9	7	22	3	21.2	5	22.4	3
Br	ppm	2.6	5			2.95	5	2.64	3	3.31	4	1.97	8	2.62	6	3.41	5	1.935	7.4
Mo	ppm							1	25					1.1	30	1.3	25	0.91	20
Ru	ppm	0.5	15					0.61	25	0.69	15			0.75	25	0.68	20	0.97	20
Pd	ppm	0.36	15																
In	ppm	0.063	10																
Sb	ppm							0.14	20	0.14	25	0.16	20	0.12	15	0.15	10	0.16	15
Cs	ppm	0.17	10			0.17	20	0.18	15	0.19	20			<0.25		<0.25		<0.3	
La	ppm	0.38	5	0.49	5	0.264	8	0.23	10	0.54	10	0.26	20	0.247	7	0.454	6	0.22	15
Ce	ppm	0.76	10					0.71	15	0.73	25			0.64	20	0.67	20		
Nd	ppm							0.5	30										
Sm	ppm	0.133	5	0.17	10	0.154	5	0.157	3	0.163	5	0.151	7	0.15	4	0.155	4	0.139	3
Eu	ppm	0.05	5	0.054	10	0.056	10	0.057	5	0.057	5	0.056	20	0.055	15	0.057	25	0.059	20
Gd	ppm	0.2	10																
Tb	ppm	0.021	15					0.04	20	0.044	20			0.038	35	0.039	25		
Dy	ppm	0.22	5			0.26	40	0.25	20	0.26	20			<0.4		0.32	35	0.26	25
Ho	ppm	0.04	10																
Er	ppm	0.16	10																
Tm	ppm							0.027	15										
Yb	ppm	0.13	5			0.14	30	0.17	7	0.19	10	0.13	30	0.16	16	0.172	15	0.156	15

Table 1. *Continued*. Chemical composition of Orgueil samples analyzed by neutron activation in Mainz from 1973 to 1993.

		ORG-1		ORG-2		ORG-3		ORG-4		ORG-5		ORG-6		ORG-7		ORG-8		ORG-9	
Year of analysis		1973		1974		1975		1980		1980		1988		1992		1992		1993	
Weight in mg		483.5	SD	515.7	SD	600.4	SD	163.1	SD	150.1	SD	5.28	SD	216.8	SD	206.0	SD	25.73	SD
Lu	ppm	0.022	5					0.022	10	0.027	10			0.025	15	0.025	15	0.027	25
Hf	ppm							0.11	25	0.114	15			0.11	25	0.13	16	0.11	40
Ta	ppm													0.016	25	0.011	40		
W	ppm	0.089	10					<0.12						<0.14		<0.2			
Re	ppm	0.0406	5					0.045	15	0.0465	15			0.036	30	0.041	25	0.038	15
Os	ppm	0.46	10			0.49	20	0.53	15	0.61	15			0.503	12	0.498	8	0.54	12
Ir	ppm	0.457	2	0.475	2	0.474	2	0.47	3	0.479	3	0.491	5	0.475	3	0.458	3	0.476	3
Pt	ppm	1.05	10											2.4	40	1.3	25		
Au	ppm	0.14	2	0.146	2	0.14	3	0.155	3	0.149	3	0.133	4	0.172	3	0.148	3	0.154	3
Hg	ppm	180	5	240	5	5.3	10	170	5	196	3			140	4	190	4	4.6	10

SD, standard deviation in %.

Table 2. Chemical composition of Ivuna, Alais, and Tonk analyzed in Mainz between 1978 and 1994.

		IVUNA-1		IVUNA-2		IVUNA-3		ALAIS-1		ALAIS-2		TONK	
Year of analysis		1978		1994		1994		1980		1994		1994	
Weight mg		185.6	SD	70.83	SD	6.46	SD	unk.	SD	77.68	SD	41.41	SD
O	wt%	46.66	3										
Na	ppm	5780	3	5160	3	7720	3	5250	3	4370	3	5660	3
Mg	wt%	9.56	3	9.29	3	9.61	4			9.14	4	10.21	3
Al	wt%	0.88	5	0.76	4	0.75	4			0.61	4	0.79	5
Si	wt%	10.71	3										
Cl	ppm	635	20	430	35	690	25	710	15			510	25
K	ppm	380	15	360	7	1030	4	555	5	560	5	510	7
Ca	wt%	0.74	15	0.60	15	0.60	25	0.94	20	2.82	6	0.60	15
Sc	ppm	6.13	3	5.79	3	5.70	3	5.93	3	5.30	3	6.03	3
V	ppm			51.7	4	69.5	5			44.8	5	55.7	4
Cr	ppm	2630	3	2570	3	2570	3	2620	3	2440	3	2690	3
Mn	ppm	1900	3	1850	3	1290	3	2220	3	5040	3	1400	3
Fe	wt%	18.22	3	18.18	3	17.73	3	18.03	3	17.02	3	18.35	3
Co	ppm	499	3	484	3	454	3	501	3	490	3	332	3
Ni	ppm	11,300	4	11,500	4	10,800	4	11,460	5	11,600	4	7960	3
Cu	ppm			140	30	250	25	148	15	130	25	130	35
Zn	ppm	335	10	316	5	320	7	342	5	321	5	280	4
Ga	ppm	9.80	10	9.92	7	10.1	10	9.90	5	8.50	7	10.3	10
As	ppm	1.6	10	1.65	7	1.63	7	1.92	7	1.58	4	1.95	4
Se	ppm	21.1	5	21.7	5	21.4	7	20.8	5	20.6	4	21.2	5
Br	ppm	5.00	3	5.06	4	6.99	5	3.81	5	4.97	5	9.0	10
Mo	ppm					0.95	35	0.80	40	0.95	35	1.5	30
Ru	ppm	0.92	40	0.56	30			0.54	35	0.63	20	0.94	25
Sb	ppm	0.12	20	0.13	10	0.132	20	0.14	40	0.14	10	0.12	15
Cs	ppm	0.068	30	0.18	35			0.17	15				
La	ppm	0.24	10	0.21	15	0.19	25	0.24	15	0.24	15	0.22	20
Sm	ppm	0.15	10	0.148	7	0.140	4	0.143	5	0.149	4	0.150	4
Eu	ppm	0.059	10	0.056	15	0.056	20	0.057	10	0.055	15	0.053	20
Tb	ppm	0.032	25					0.037	40				
Dy	ppm	0.23	30	0.30	25			0.24	30	0.30	35	0.20	20
Yb	ppm	0.19	15	0.17	15	0.13	20	0.17	30	0.16	10	0.16	15
Lu	ppm	0.026	15	0.029	20	0.025	35	0.023	15	0.025	20	0.024	25
Hf	ppm	0.14	30	0.12	25			0.14	40	0.13	20	0.12	35
Re	ppm			0.045	15					0.036	20	0.055	30
Os	ppm	0.43	15	0.58	10	0.66	20	0.56	15	0.48	10	0.50	15
Ir	ppm	0.473	3	0.461	3	0.465	3	0.458	3	0.434	4	0.461	3
Pt	ppm			1.0	25							1.2	25
Au	ppm	0.149	3	0.143	3	0.123	4	0.146	3	0.149	3	0.0862	3
Hg	ppm	1.0	20	2.4	15			0.31	10	13	10	19	7

SD, standard deviation in %. unk., mass of sample ALAIS-1 is unknown.

water contents of ±5 wt% would show up in systematic variations of Sc, Cr, Fe, Co, and Ir at a level of 5% or more, that is, concentrations of all elements should deviate from the mean in the same direction. This is, however, not the case for the majority of the data reported in Tables 1 and 2.

The important conclusion is that the water content of CI chondrites is essentially constant. This is true for individual samples of a single meteorite as well as for all analyzed CI chondrites.

Sodium contents are more variable in CI meteorites than analytical uncertainties indicate. This clearly reflects inhomogeneous distribution of Na in CI chondrites on a scale of 100 mg. Other carbonaceous chondrites (see Palme et al. 1988) show similar variations in Na and other alkali elements. In CI chondrites the solubility of Na in water may lead to some redistribution. Nevertheless, all Na data are within the ±20% limit as indicated in Figs. 1 and 2. Only the 6.46 mg sample of IVUNA-3 (7730 ppm) has

Table 3. Average of Orgueil, Ivuna, and Alais and comparison with literature data.

		N	Orgueil average	SD	Ivuna average	Alais average	K&W (1981)	Barrat et al. (2012)	Palme et al. (2014)
O	wt%	2	46.92		46.66				45.9
Na	ppm	9	5048	8.0	6220	4810	4730	4800	4962
Mg	wt%	3	9.58	2.4	9.49	9.14	9.75	9.42	9.54
Al	wt%	3	0.85	4.6	0.80	0.61	0.88	0.792	0.84
Si	wt%	2	10.73		10.71				10.70
Cl	ppm	7	600	11.4	585	710			698
K	ppm	9	546	7.3	590	558	568	550	546
Ca	wt%	6	0.91	14.4	0.65	1.88	0.973	0.84	0.91
Ti	wt%	1	0.052					0.044	0.045
Sc	ppm	9	5.92	2.1	5.87	5.62	5.81	5.85	5.81
V	ppm	1	50.9		60.6	44.8	57.0	52.4	54.6
Cr	ppm	9	2632	2.4	2590	2530	2650	2630	2623
Mn	ppm	9	1825	6.7	1680	3630	1990	1910	1916
Fe	wt%	9	18.47	1.7	18.04	17.53	18.30	19.52	18.66
Co	ppm	9	513	3.4	479	496	515	519	513
Ni	ppm	9	11,398	5.4	11,200	11,530	10,600	11,300	10,910
Cu	ppm	6	131	16.8	195	139		127	133
Zn	ppm	9	336	5.9	324	332	316	303	309
Ga	ppm	9	9.53	7.5	9.92	9.20	9.90	9.48	9.62
Ge	ppm	1	36.5				35		32.6
As	ppm	9	1.75	11.4	1.62	1.75	1.90		1.74
Se	ppm	9	20.43	8.4	21.4	20.7	21.50		20.30
Br	ppm	8	2.68	19.0	5.68	4.39	3.70		3.26
Mo	ppm	4	1.08	13.5	0.95	0.88			0.96
Ru	ppm	6	0.700	20.5	0.74	0.59	0.719		0.69
Pd	ppm	1	0.36						0.56
In	ppm	1	0.063				0.087		0.078
Sb	ppm	6	0.145	9.5	0.13	0.14	0.14		0.145
Cs	ppm	4	0.178	4.7	0.12	0.17		0.189	0.188
La	ppm	9	0.343	34.3	0.21	0.24	0.230	0.235	0.2412
Ce	ppm	5	0.702	6.1				0.600	0.6194
Pr	ppm	1	0.084					0.091	0.0939
Nd	ppm	1	0.50					0.464	0.4737
Sm	ppm	9	0.152	7.0	0.146	0.146	0.137	0.153	0.1536
Eu	ppm	9	0.056	4.3	0.057	0.056	0.0580	0.0586	0.05883
Gd	ppm	1	0.20			0.180		0.2060	0.2069
Tb	ppm	5	0.036	21.9	0.032	0.037		0.0375	0.03797
Dy	ppm	6	0.262	11.3	0.27	0.27		0.254	0.2558
Ho	ppm	1	0.040					0.0566	0.05644
Er	ppm	1	0.160					0.1660	0.165
Tm	ppm	1	0.027					0.0262	0.02609
Yb	ppm	8	0.156	12.9	0.16	0.17	0.167	0.168	0.1687
Lu	ppm	6	0.025	8.3	0.027	0.024	0.0240	0.0246	0.0250
Hf	ppm	5	0.115	6.8	0.13	0.14		0.107	0.1065
Ta	ppm	2	0.014					0.0148	0.0150
W	ppm	1	0.089					0.110	0.0960
Re	ppm	6	0.041	8.9	0.045	0.036			0.0400
Os	ppm	7	0.519	8.6	0.56	0.52	0.490		0.495
Ir	ppm	9	0.473	2.1	0.466	0.446	0.456		0.469
Pt	ppm	3	1.583	37.0	1.0				0.9250
Au	ppm	9	0.149	7.15	0.138	0.148	0.154		0.148
Hg	ppm	8	141	60	1.7	6.66			0.35

N, number of Orgueil samples averaged; SD, standard deviations in % are given only for means of three and more analyses and reflect variations of individual Orgueil samples. For SD of means with $N \le 2$, see Table 1. K&W (1981), Kallemeyn and Wasson (1981).

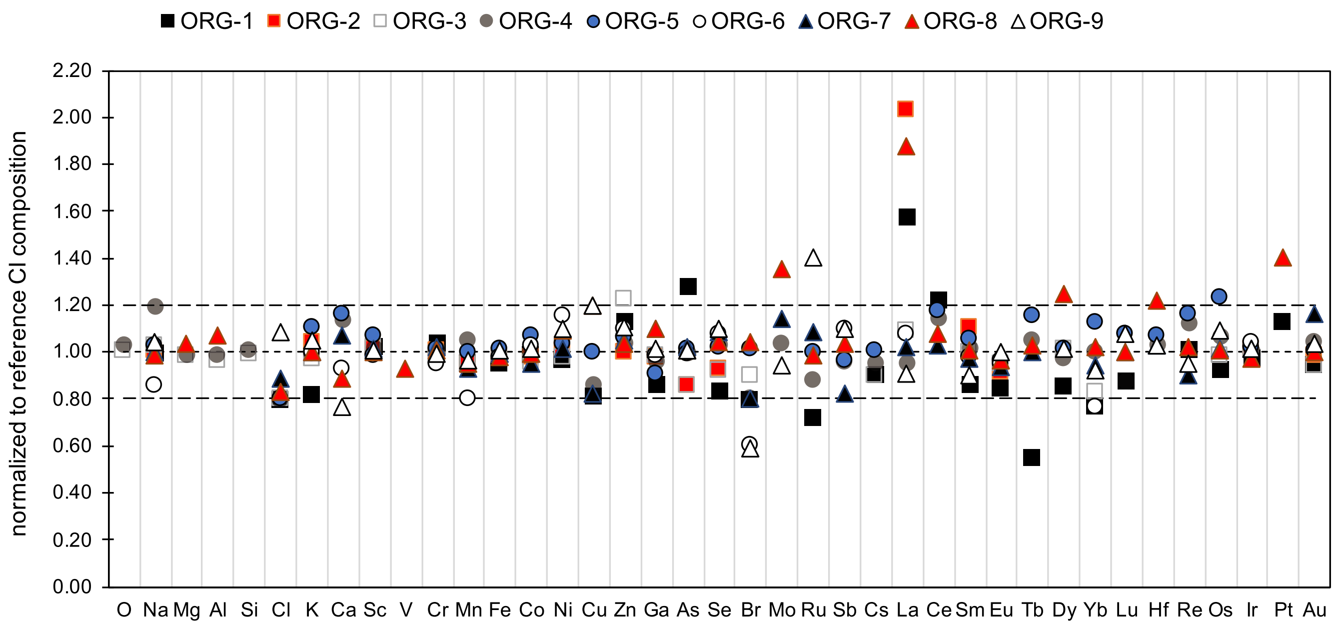

Fig. 1. The chemical composition of 9 Orgueil samples analyzed at the Department of Cosmochemistry in Mainz between 1973 and 1993 (see Table 1). Samples have masses from 5.28 to 515.7 mg. Data are normalized to the average CI composition from Palme et al. (2014) listed in the last column of Table 3. Most elements plot within a ±20% limit. High La in three Orgueil samples and a low concentration of Ca in ORG-9 are real and may reflect mobilization of these elements. Variations in chlorine and Br reflect inhomogeneous distribution of halogens (see text). Apparently, high concentrations of As, Mo, Ru, and Pt as well as low concentration of Tb result from higher analytical uncertainties, due to poor counting statistics (see standard deviations in Table 1). The concentrations of Sc, Cr, Fe, Co, and Ir agree within ±10%, and reflect the chemical homogeneity of Orgueil for these values on a mg scale. These element concentrations can be analyzed by INAA with high precision. Sodium and Mn belong to the same category, but show a larger spread. It is remarkable that the 5.28 mg sample ORG-6 does not show major deviations in chemistry from average CI values. (Color figure can be viewed at wileyonlinelibrary.com.)

a significantly higher Na content. The 5 mg Orgueil (ORG-6) sample has the lowest Na content (4360 ppm). Barrat et al. (2012) report similar variations in Na in their Orgueil samples with masses of 0.6–1 g.

Morlock et al. (2006) described Orgueil and the other CI meteorites as breccias with large local compositional variations. They found differences in Na contents by a factor of more than 10, much larger than observed here. The size of the clasts analyzed by Morlock et al. (2006) was around 100 µm, which converts to masses in the µg range, whereas our samples have masses in the mg range. In general, milligram samples show small variations in chemistry, compared to µg samples with much larger variability in chemistry.

Magnesium was analyzed with short TRIGA irradiations (3 min) and, in some of the earlier samples, with fast neutron activation analysis. The results of analyses of three Orgueil and three Ivuna and one Alais samples agree with Barrat et al. (2012) and Kallemeyn and Wasson (1981). The Tonk sample has slightly lower Mg contents (Table 3).

Silicon

The Si data of Orgueil and Ivuna were obtained with fast neutron activation analysis. The results agree perfectly with the Si value listed by Palme et al. (2014) in their compilation of CI chondrites, which are based on a larger set of data. The importance of the Mg and Si data is the well-defined Si/Mg ratio of 1.12 (weight ratio), with an estimated uncertainty of about ±4%. The corresponding Si/Mg wt. ratio in the solar photosphere is 1.053 ± 10%, according to the most recent paper (Asplund et al. 2021) well within the uncertainty of the meteoritic ratio but significantly lower than the ratio given in Scott et al. (2015). A recent paper by Lodders (2020) lists two values for this ratio 1.03 and 1.21, for 1D and 3D solar model atmospheres and different NLTE (non-local thermodynamic equilibrium) corrections.

Potassium

In Orgueil samples K is similarly variable as Na. Figure 3 is a K versus Na plot of CI chondrites. Most

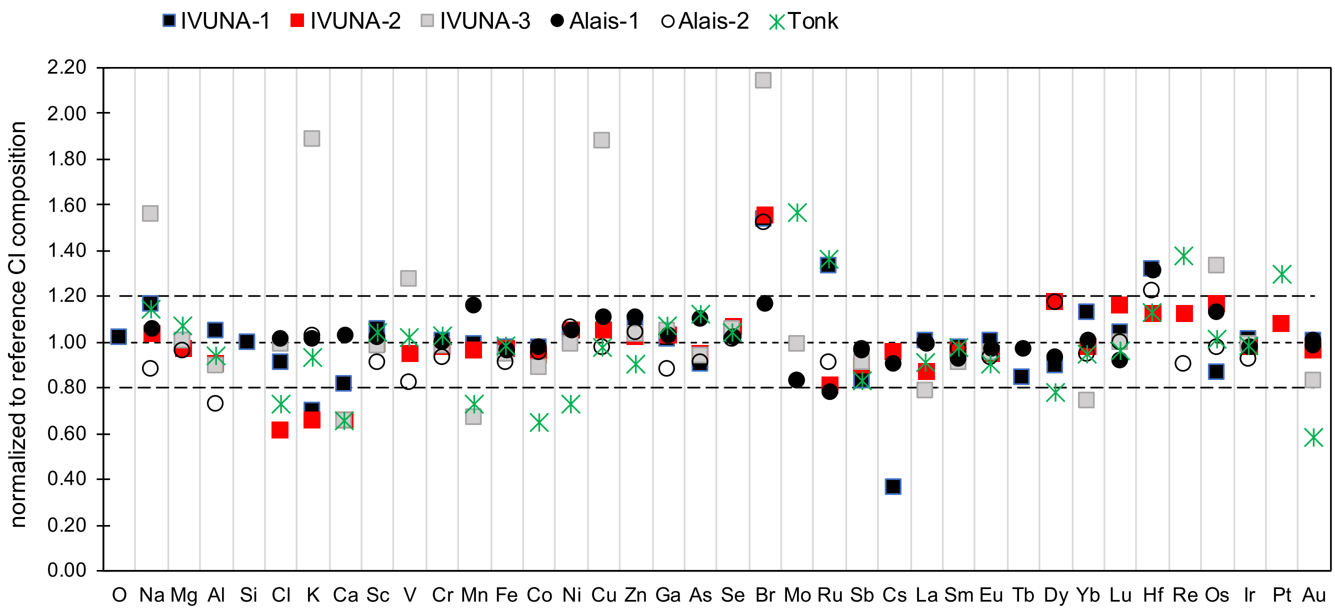

Fig. 2. Comparison of data from three samples of Ivuna, two samples of Alais and one sample of Tonk (Table 2). Data are normalized to the average CI composition from Palme et al. (2014), which is listed in the last column of Table 3. The compositional spread is somewhat larger than in Fig. 1. Sample ALAIS-2 is very high in Ca (off scale). Sample IVUNA-3 has high Na, K, and Br outside statistical uncertainties. Sample IVUNA-2 has low chlorine, high Br, and low K and Ca. The normalized concentrations of Sc, Cr, Fe, Co, Se, Zn, and Ir are very similar to each other, like in the Orgueil subsamples (see Fig. 1). Exceptions to this are Co and Fe concentrations of the TONK sample. The apparently high Mo, Ru, and Hf concentrations of TONK have no significance, because of poor counting statistics. (Color figure can be viewed at wileyonlinelibrary.com.)

Orgueil samples (full symbols) form a comparatively small cluster, although the variations exceed analytical uncertainties. Samples of this work are somewhat higher in Na than the four samples of Kallemeyn and Wasson (1981). The Barrat et al. (2012) Orgueil samples show some correlation of K and Na: one sample has very low Na and K and another sample has high Na and K. The low Na sample is also low in Rb and Cs, similar to the low Na sample of Braukmüller et al. (2018). The alkali elements seem to fractionate together. The Jarosewich (1990) sample is at the higher end of Na contents. In general, Na seems to be more variable than K, although a standard related bias in Na between our data and the Kallemeyn and Wasson (1981) data cannot be excluded. But it is also possible that the Orgueil samples analyzed by Kallemeyn and Wasson (1981) were from a single split, somewhat lower in Na than the average, while samples analyzed by Barrat et al. (2012) and those reported here sampled different parts of Orgueil. The variations in Na and K of non-Orgueil samples (open symbols) are larger than in Orgueil samples of this study, perhaps because of generally smaller sample sizes of non-Orgueil samples.

The three bulk CI estimates from Anders and Grevesse (1989), Lodders et al. (2009), and Palme et al. (2014) are all very similar. The CI data in these compilations contain many more data than plotted in Fig. 3. In particular, the Anders and Grevesse (1989) compilation has not considered any of the data shown in this plot, because all data of Fig. 3 were obtained after publication of the Anders and Grevesse (1989) compilation. Thus the mean Na content of CI chondrites is close to 5000 ppm and the mean K content is 550 ppm, which gives a mean Na/K ratio of 9.1 with an estimated uncertainty of better than 10%. The CI ratio by Palme et al. (2014) is 9.1, Barrat et al. (2012) report 8.7, and Kallemeyn and Wasson (1981) determined a Na/K ratio of 8.3 (Table 3). Ivuna is somewhat more variable, with high K and Na contents in the 6.48 mg sample and an Na/K ratio of 7.4, which is low compared to the other two Ivuna samples with Na/K ratios of 14.3 and 15.2, respectively. The higher variability of alkalis and also halogens (see below) could be caused by aqueous alteration as suggested by Endreß and Bischoff (1996).

The solar Na/K ratio is 8.3 ± 0.8 according to the recent compilation by Asplund et al. (2021), well within the combined error bars of solar and meteoritic abundances.

Calcium and Titanium

Both elements are not particularly suitable for INAA, as can been seen from the uncertainties reported in Tables 1 and 2. Ivuna samples are systematically low in Ca, one sample of Alais and the Tonk sample are

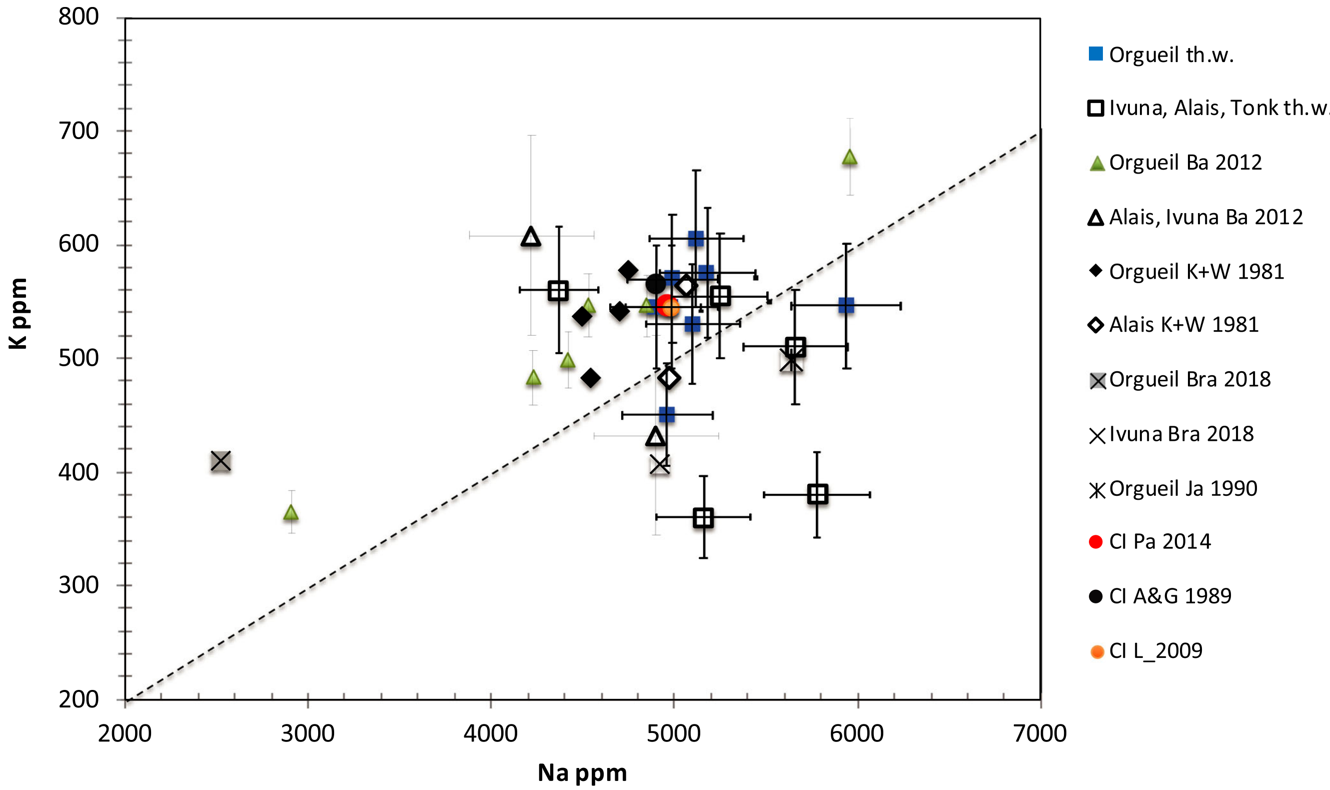

Fig. 3. K versus Na plot for CI chondrites. Orgueil—full symbols; other CI chondrites, Ivuna, Alais, and Tonk—open symbols; bulk CI estimates—full circles. Sources of data: th.w.—this work; Ba 2012—Barrat et al. (2012); K + W 1981—Kallemeyn and Wasson (1981); Bra 2018—Braukmüller et al. (2018); Ja 1990—Jarosewich (1990); Pa 2014—Palme et al. (2014); A&G 1989—Anders and Grevesse (1989); L_2009—Lodders et al. (2009). Error bars are only for samples with analytical results reported in this work. For simplicity we used ±10% for K and ±5 for Na. The stippled line indicates a Na/K ratio of 10. See text for details. (Color figure can be viewed at wileyonlinelibrary.com.)

also low in Ca. Morlock et al. (2006) found a very large variability in their bulk analyses, presumably because of carbonate formation, which separates Ca from Al (see also Brearley 2006). Both elements are refractory and occur together in silicates. The high Ca in ALAIS-2 of 2.82 wt% is remarkable (out of scale in Fig. 2). The same sample has an unusually high Mn content. This suggests a high content of carbonates, including breunnerite (Mn-carbonate). The formation of carbonates can be dated with the Mn-Cr-chronometer. The ages obtained are 3–4 million years after solar system formation (Hoppe et al. 2007; Visser et al. [2020] and literature therein) and may date the aqueous alteration of CI chondrites occasionally leading to the formation of larger carbonates.

Titanium was determined in one Orgueil sample only with poor accuracy, but within the limits of literature values.

Scandium

This element can be precisely determined with INAA. The mean Sc concentration of nine Orgueil samples is 5.92 ± 2.1% (Table 1; Fig. 1). Other CI chondrites have similar Sc concentrations, except for one ALAIS-2 sample with 5.3 ppm that has a high carbonate content (see Ca). Barrat et al. (2012) report a mean Sc in Orgueil of 5.80 ppm and Kallemeyn and Wasson (1981) find 5.81 ppm. The constancy of absolute Sc concentrations in four different CI chondrites analyzed here confirms earlier remarks on oxygen. All analyzed CI chondrites have similar water contents. Not only are there no major variations in the water content among CI chondrites, but also milligram samples of Orgueil have the same water content. Even the 5.28 mg sample (ORG-6 in Table 1) has an Sc content of 5.74 ppm, only 3% below the average. If this difference were real it could be achieved by a variation in water content from 20% to 17%.

Vanadium

The two V analyses of one Orgueil and one Tonk sample agree within error bars with the CI value (Palme et al. 2014). One Ivuna sample is too high and the Alais sample too low compared to the mean V content of CI chondrites.

Chromium, Manganese, Iron, Cobalt, and Nickel

These elements can be analyzed by INAA with high precision, similar to Sc, as can be seen from the small error bars for these elements in Tables 1 and 2. In the Orgueil samples all analyses of Cr, Mn, Fe, Co, and Ni are within ±20% of the average CI value, in most cases within ±10%. The same is true for the other CI meteorites, except for the more variable Mn contents, which probably reflect the uneven distribution of carbonates, the main carrier of Mn in CI chondrites (Morlock et al. 2006). Figure 4 shows the CI-normalized abundances of Sc, Fe, Cr, and Zn in the various CI chondrite samples of Orgueil, Ivuna, Alais, and Tonk, which agree within error to ±10% with their respective reference CI values (Palme et al. 2014). Sample ALAIS-2 has systematically lower concentrations of these elements, most likely due to dilution by a high fraction of carbonates, as indicated by excess Mn (5040 ppm) in this sample (Table 2). Cobalt and Ni show a similar behavior as Sc, Fe, Cr, and Zn in individual samples. Only the Tonk sample has slightly lower Co and Ni.

From Fig. 4, it is obvious that based on the data presented here one could define a slightly lower Fe content for CI chondrites than 18.66% estimated by Palme et al. (2014). The Orgueil data presented here give an Fe content of 18.47 ± 0.3 wt%. By including Ivuna and Tonk a lower value would be obtained. Kallemeyn and Wasson (1981) find an average of 18.30% Fe for CI chondrites, Anders and Grevesse (1989) report an average Fe content of 18.50% for Orgueil and 19.04% for average CI. In this case the non-Orgueil samples would increase the average CI Fe content, contrary to our finding. Braukmüller et al. (2018) report 19.25% Fe for Orgueil and 18.23% Fe for Ivuna, lower for Ivuna than for Orgueil. Barrat et al. (2012) obtained an average of 19.39% Fe in their Orgueil samples, while Jarosewich (1990) lists an Fe content of 18.85% for Orgueil. The estimate for Fe in CI chondrites by Palme et al. (2014) is 18.66%, in agreement with Wolf and Palme (2001) who find 18.69% Fe. Thus there still appears some uncertainty regarding the "true" average Orgueil and CI Fe contents. But it is clear from the analyses presented here that Fe contents of various Orgueil samples are surprisingly uniform with variations below ±2%.

For Cr concentrations there is a similar constancy, except that Kallemeyn and Wasson (1981) and Barrat et al. (2012) now agree with the data reported here (Table 3; Fig. 3). The Ivuna Cr concentration of Braukmüller et al. (2018) is also similar. Their Cr in Orgueil is slightly higher.

A similar situation is found for Co and Ni, where the Braukmüller et al. (2018) data also fit with the concentrations in Table 3. The average Fe/Ni ratio of all samples except Tonk is 16.7 ± 0.8, essentially CI-chondritic (17.1), when based on Palme et al. (2014). The average Ni/Co ratio (except Tonk) is with 22.6 ± 1.1 also chondritic (21.3) within uncertainties in all samples. The chondritic ratios among Fe, Co, and Ni implies that all three elements were added to the CI components as fully condensed metals and were later oxidized.

Copper and Zinc

The Cu data reported here have large uncertainties. The Orgueil and Alais data fit with the Barrat et al. (2012) data. The high average Ivuna value of Cu is caused by the high Cu concentration of IVUNA-3. Braukmüller et al. (2018) find similar concentrations of Cu (136 and 146 ppm) and Zn (321 and 337 ppm) in Ivuna and Orgueil. King et al. (2020) report 125 and 138 ppm Cu for two Ivuna samples, within the range of other CI chondrites. Somewhat higher Zn in comparison to the CI value (Palme et al. 2014) in Fig. 4 suggests a minor uncertainty of the Zn CI chondrite value.

Gallium and Arsenic

The Ga data are within error limits identical in all samples. The lowest Ga content is found for the somewhat unusual sample ALAIS-2, with a concentration 15% below the CI value of Palme et al. (2014). Gallium data agree with the data of other laboratories (Table 3), except for the Ga content of Ivuna determined by Braukmüller et al. (2018), which is slightly lower. The same is observed for As data which for most samples are identical within error limits. ALAIS-1 and Tonk have somewhat elevated abundances.

Selenium

The element Se is of special interest, because it is a proxy for sulfur. Dreibus et al. (1995) found an average S/Se ratio of 2540 for CI chondrites and an average ratio of 2560 ± 150 for a number of carbonaceous chondrites. The Se data in Tables 1 and 2 are very constant with a mean of 20.74 ± 1.4. A closer look at Tables 1 and 2 shows that the Se analyses until 1975 are systematically lower than later Se analyses, which is probably the result of using new and more precise standards after 1975. Excluding the three Orgueil analyses from 1973, 1974, and 1975, we calculate an average of 21.32 ± 0.52 ppm Se from CI data listed in Tables 1 and 2. These constant Se contents reflect constant S contents to within a few percent. Even the

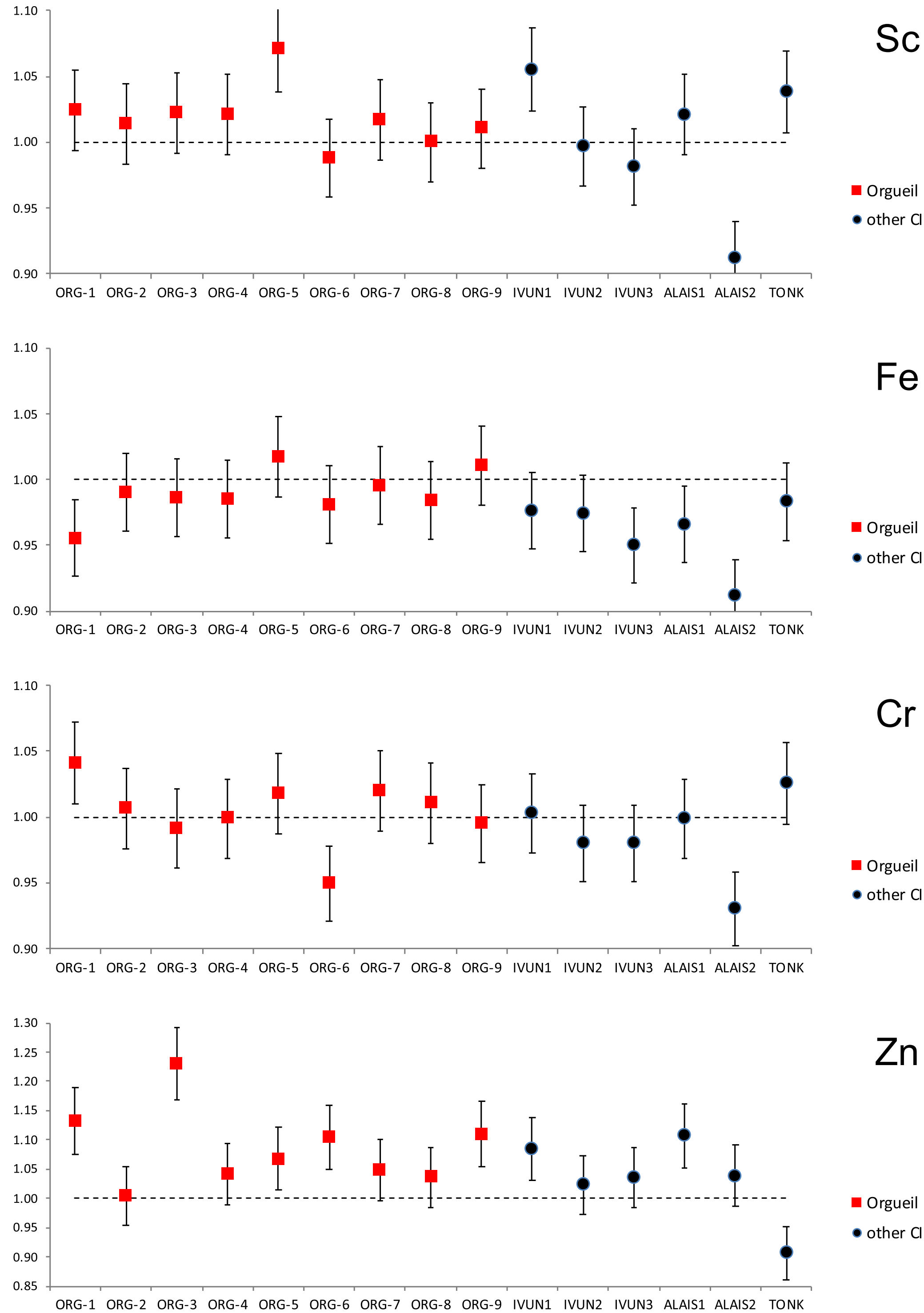

Fig. 4. CI-normalized abundances of Sc (refractory), Fe, Cr (major component), and Zn (volatile) in various samples of Orgueil, Ivuna, Alais, and Tonk with error bars. The normalized concentrations of Sc, Fe, Cr, and Zn are identical within error bars, except for the ALAIS2 sample, which is lower in Sc, Fe, and Cr, but still within 10% of the mean. The figure demonstrates that Orgueil is homogeneous in compatible refractory as well as in volatile elements. The three other CI chondrites are compositionally very similar to Orgueil. There is a small systematic bias of Fe (too low) and Zn (too high) compared to the average CI composition from Palme et al. (2014). (Color figure can be viewed at wileyonlinelibrary.com.)

5 mg ORG-6 sample and the 6 mg IVUNA-3 sample have "normal" Se contents (see also Figs. 1 and 2) and thus supposedly also constant S contents. This is also in agreement with the Orgueil Se content of 21.5 ppm reported by Kallemeyn and Wasson (1981). The mean Se content of 21.32 ppm transforms to an S content of 5.41%, close to the average CI S content of 5.35% listed in Palme et al. (2014) or 5.36% listed in Lodders (2020). A constant S content in all samples analyzed (except in the three "early" Orgueil analyses) is an important indicator that volatiles are homogeneously distributed in Orgueil and that other CI chondrites have the same fraction of volatiles as Orgueil.

Molybdenum, Ruthenium, Palladium, Antimony, and Cesium

Analyses of these elements with INAA can only be done with poor counting statistics implying fairly large uncertainties. Any statement regarding the homogeneity of Orgueil or the constancy of these elements in other CI chondrites involves these uncertainties. The Pd content in ORG-1 was determined by radiochemistry.

Rare Earth Elements

INAA is not the best method for analyzing rare Earth elements (REE) in chondrites. Only La, Sm, Eu, Yb, and Lu can be determined with reasonable accuracy and Ce and Lu with lesser accuracy. The problem with INAA is that an excellent analysis requires not only a reasonably high number of atoms but also a high neutron cross section, an easy to register γ-energy, and a convenient half life of the excited nuclei by absorption of a neutron. Thus, in INAA, the quality of detection of an element is not proportional to the number of atoms of a specific element.

Nevertheless, REE patterns of Orgueil samples and the other CI chondrites are basically chondritic, with the exception of three Orgueil samples, which are high in La and slightly enriched in Ce (Fig. 1). These enrichments are real. Light REE enrichments of CI samples are occasionally found in published analyses of Orgueil and Ivuna (Barrat et al. 2012; Dauphas and Pourmand 2015). The enriched samples ORG-1, ORG-2, and ORG-8 from our data set show no anomalies in Ca, excluding unusually high fractions of phosphates and carbonates as sources of light REE. The reason for the light REE enrichments in CI samples is unclear.

Hafnium and Tantalum

The few data for Hf and Ta have high counting errors. Within counting errors, they agree with more precisely determined abundances compiled in Palme et al. (2014).

Tungsten

The only analysis of W in ORG-1 was done with RNAA. It fits within analytical uncertainty with the value given by Palme et al. (2014), where the CI abundance of W is discussed in more detail.

Rhenium, Osmium, Iridium, Platinum, and Gold

These are all highly siderophile elements with very high metal/silicate partition coefficients. The elements Re and Pt can only be determined with limited accuracy (except for ORG-1 with radiochemistry for Re), Os is a bit more precise, Au is sufficiently accurate at the chondritic level, and Ir is extremely sensitive for INAA. The Os/Re and Os/Ir ratios in our suite of CI chondrites are within the average CI ratios of 12.38 and 1.06, respectively (Palme et al. 2014). The Ir contents are all very close to the CI value of 469 ppb. It should, however, be mentioned that there is a tendency for lower Ir concentrations in CI chondrites in more recent analyses. Braukmüller et al. (2018) find 409 ppb in Ivuna and 428 ppb in Orgueil. Horan et al. (2003) report 455.6 and 432.3 ppb for Orgueil and 406.0 and 428.2 ppb for Ivuna, while Fischer-Gödde et al. (2010) determined 435, 418, and 412 ppb Ir in Orgueil and 422 and 405 ppb in Ivuna.

All these data involved chemical dissolution of CI chondrites. In contrast, earlier nondestructive analyses with INAA or radiochemistry gave higher Ir concentrations. Krähenbühl et al. (1973) report 514 ± 25 ppb Ir for average CI, based on Orgueil and Ivuna analyses. Kallemeyn and Wasson (1981) reported 490 ppb Ir for CI chondrites, based on INAA. Anders and Grevesse (1989) list 481 ppb Ir as mean for average CI chondrites and 474 ppb for Orgueil analyses, averaging 27 single analyses, most of them presumably done by INAA or radiochemistry. It is possible that low Ir contents of newer analyses are caused by incomplete dissolution of samples. Some of the Ir may be contained in noble metal nuggets, which are difficult to dissolve. In this case, absolute abundances of noble metals will be lowered, while ratios among noble metals will not be affected.

The well-defined concentrations of Sc and Ir, which can be obtained with INAA, allow us to define a precise Sc/Ir ratio, which is important as it reflects the ratio of refractory lithophile to refractory siderophile elements. The average Orgueil ratio is 12.52 ± 0.36, close to the average CI ratio of 12.39 listed by Palme et al. (2014). The Ivuna, Alais, and Tonk data closely fit with this ratio. Thus, the refractory siderophile and refractory lithophile elements occur in the same ratios in small and large samples of CI chondrites.

The abundances of Au, a moderately volatile and siderophile element, are more variable, beyond analytical uncertainties. The concentrations of Au are more susceptible to aqueous alteration and thus easier to mobilize than Sc and Ir.

Mercury

The Hg data show the largest variability of all data, from 240 ppm in ORG-2 to 0.31 ppm in ALAIS-2. We emphasize here that the element Hg can be reliably analyzed with INAA. Ebihara et al. (1998) claim that there is an interference on the 279 KeV γ-line of ^{203}Hg with a half-life of 203 days by ^{75}Se with a half-life of 119.64 days. This interference cannot have affected our data, because the Se concentrations are uniform in all CI samples, as discussed above. If the decay of ^{75}Se had affected the Hg-measurements it would have produced the same level of Hg in all cases. This could not be more than the lowest Hg content of 0.38 ppm in ALAIS-2. Large variabilities of Hg in Orgueil are not unusual (see also Anders and Grevesse 1989). Variable Hg contents seem to extend to other CI chondrites, Tonk has 19 ppm Hg and ALAIS-2 0.31 ppm. Other authors also find large variabilities in Hg contents of CI meteorites (e.g., Meier et al. 2016). It is not clear if the measured Hg contents are contamination or reflect real abundance variations. Ultimately, isotopic studies will have to resolve this issue.

THE ABUNDANCES OF CHLORINE AND BROMINE IN CI CHONDRITES

Using INAA allows us to determine chlorine concentrations with moderate precision, because of poor counting statistics of the radioactive ^{38}Cl with a half-life of only 36 min. Nevertheless, we have obtained chlorine abundance data in six samples of Orgueil, three samples of Ivuna, and one sample of Alais and Tonk, each with a statistical error of 10–25%, except for IVUNA-3 with 35%. The mean Orgueil chlorine content is 600 ppm compared to 585 ppm for the mean Ivuna chlorine content and one Alais sample and Tonk with 710 and 510 ppm, respectively. These concentrations compare well with estimates of 717 ppm reported by Lodders and Fegley (2021). Clay et al. (2017), however, report 115 $\pm$ 36 ppm chlorine for Orgueil, about a factor of 5 below our measured chlorine contents. Our INAA analyses are non-destructive, that is, no chemical procedures were applied (i.e., samples were not dissolved). We have analyzed samples of different origin (from a meteorite dealer and from four large institutional meteorite collections: Mainz, Paris, Smithsonian Institution, Vienna) and samples have variable masses. In addition to chlorine and Br, we also analyzed a large number of major, minor, and trace elements, as described above and from these results, there is no doubt that our samples have typical bulk CI chondrite composition. Furthermore, chlorine abundances agree with earlier data by other authors (see compilation by Lodders and Fegley 2021). These agreements imply that the chlorine value for Orgueil obtained by Clay et al. (2017) is too low, and possibly an artefact caused by the chosen analytical method.

Bromine shows a similar behavior as chlorine. But with INAA, Br is easier to analyze. The precision is, in most cases, below 10%. Eight Orgueil samples yield a mean of 2.68 $\pm$ 0.51 ppm. The uncertainty is more than twice the uncertainty of a single Br analysis, which indicates that Br variations in Orgueil are real and reflect inhomogeneous distribution of Br in CI chondrites, although only ORG-3 and ORG-6 are below the 20% limit of the CI value of Palme et al. (2014). The Ivuna samples are higher in Br than Orgueil. Lodders and Fegley (2021) made the same observation in their compilation of Br data, 3.34 $\pm$ 0.34 ppm for Orgueil and 4.96 $\pm$ 0.60 ppm for Ivuna. Earlier compilations by Anders and Ebihara (1982) also reported higher Br contents in Ivuna and Alais compared to Orgueil. The significance of this observation is unclear. The Tonk sample is with 9.01 ppm, very high in Br, while the chlorine content of Tonk is within the compositional range of other CI chondrites.

Older radiochemical neutron activation analyses give similar results for chlorine and Br in CI chondrites. For example, Goles et al. (1967) obtained 773 ppm chlorine for three Orgueil samples and one Ivuna sample, and 3.56 ppm Br for three Orgueil samples and again a higher Br content of 5.1 ppm for Ivuna. Dreibus et al. (1979) also analyzed chondrites with neutron activation analysis combined with chemical separation by pyrohydrolysis. Their results for chlorine in Orgueil and Ivuna were 698 and 678 ppm, respectively, and for Br 2.51 ppm in Orgueil and 3.91 ppm in Ivuna. The INAA Br data presented here do not require any chemistry and there is no possibility for losses during chemical procedures. Nevertheless radiochemical procedures in combination with neutron activation analysis give similar results. The reader is also referred to the compilation of chondrite data by Lodders and Fegley (2021). The low CI concentrations of chlorine (115 ppm) and Br (0.189 ppm) suggested in Clay et al. (2017) appear unrealistic when compared to all other chlorine and Br determinations of CI

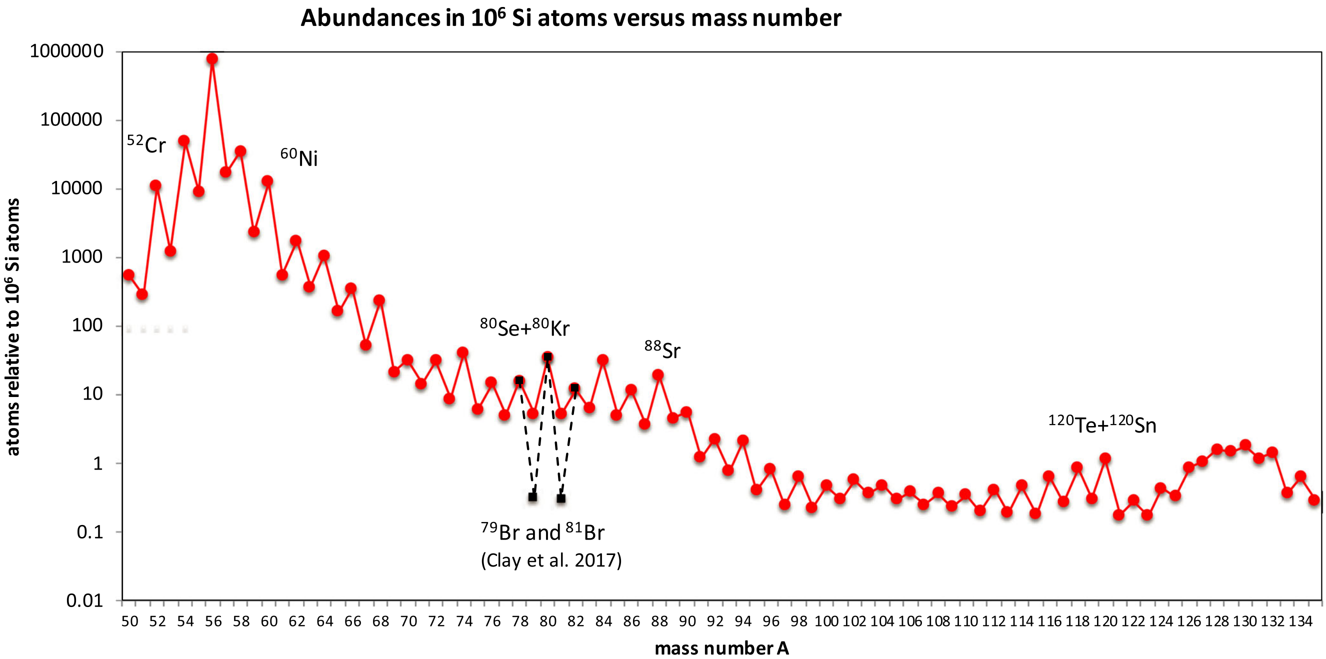

Fig. 5. Abundances versus mass number (normalized to Si = 10^6 atoms) derived from CI chondrite composition. Uneven mass numbers form a smooth curve. The Br abundances used so far (e.g., Palme et al. 2014) and recalculated for masses of ^{79}Br and ^{81}Br fit well into this pattern (red symbols). Replacing previously determined values with those recently suggested by Clay et al. (2017), indicated by black symbols and black dashed lines, destroys the smoothness of that pattern. All isotopic data were taken from Palme and Beer (1993). (Color figure can be viewed at wileyonlinelibrary.com.)

chondrites, and therefore should not be used as representing solar abundances.

A comparison between the meteoritic chlorine and Br data with the solar photospheric data is not possible, because there are no suitable lines for calculating solar photospheric abundances (Lodders and Fegley 2021). But abundance versus mass number plots also indicate that the non-INAA Br data are much too low.

Figure 5 shows a diagram of elemental abundances normalized to 10^6 atoms of Si versus mass number from mass 50–134. The generally higher abundances of even masses are apparent. Even and odd mass numbers, separately, plot along more or less smooth curves, with odd mass numbers forming a considerably smoother curve than even mass numbers. Historically, these so-called abundance rules, established by Suess (1947) postulating a smooth dependence of isotopic abundances on mass number A, especially of odd-A nuclei, played an important role in estimating unknown abundances and/or for detecting fractionation effects. Later, this rule was modified and supplemented by two additional rules (Suess and Zeh 1973). Today, this is considered an empirical rule that is rarely violated. It would nevertheless be very strange if only the Br data should be outliers, especially since older INAA Br data (Palme and Beer 1993) fit the empirical abundance rule.

SUMMARY

1. We have presented the results of INAA of 15 samples of CI chondrites: Orgueil (9), Ivuna (3), Alais (2), and Tonk (1). Analyses were done in the Cosmochemistry Department of the Max-Planck-Institute for Chemistry in Mainz between 1973 and 1994. Most of the data are published here for the first time.
2. Elements that can be determined with high accuracy by using INAA and that are diagnostic of distinct cosmochemical groups have the same concentrations in all 15 samples, with very few exceptions. Scandium is representative of refractory lithophile elements (e.g., Al, Ca, Ti), Ir is a typical refractory siderophile element (e.g., Re, Os), Fe and Cr represent the major undepleted component of silicates and metallic iron, and Zn stands for volatile elements. In addition, Se, a proxy for S, is constant in all samples to within a few percent, confirming the same volatile element abundances in all CI samples. Thus all Orgueil samples and Ivuna, Alais, and Tonk have the same mix of cosmochemical components.
3. The constant Fe/Ni/Co ratios of Orgueil, Ivuna, and Alais samples (only Tonk deviates somewhat) indicate that these elements were initially present in an FeNi-alloy, which was introduced with FeNi-metal in these three CI meteorites.

4. The extremely small variations in the absolute concentrations of the well-determined elements constrains the variation in the water content in samples of a single CI chondrite and among CI chondrites to 20 ± 5% wt%.
5. The chemical homogeneity holds for milligram samples. One 5.26 mg Orgueil sample and a 6.46 mg Ivuna sample have the same element abundance patterns as the general pattern defined by other CI samples.
6. On the scale of a few milligrams CI chondrites are chemically homogeneous, with very few exceptions, such as Na, Ca, Mn, and Au.
7. Although the two halogens chlorine and Br have statistical uncertainties of 20% and 5%, respectively, they are fairly constant in CI chondrites and the results agree with older data compiled by Lodders and Fegley (2021). The significantly lower halogen concentrations for CI chondrites suggested by Clay et al. (2017) are inconsistent with all other measurements.

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