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The absolute abundance of the chromium isotopes in some
secondary minerals*

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Abstract-Isotopic assays have been made on the chromium in samples from fourteen different chrominiferous minerals from different geographic and meteoritic sources. The results of the assays indicate that it is not possible to unequivocally state that variations in isotopic composition have been observed.

INTRODUCTION

Previous studies (FLESCH, SVEC, STALEY, 1960) have shown that the abundances of the chromium isotopes do not vary in chromite ores obtained from different sources throughout the world. That work has been extended to include chromium from other chrominiferous minerals as well as meteoritic sources. Table 1 describes fourteen mineral specimens used in this study.

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Table 1. Source of minerals used in this study

Sample number	Mineral	Location of deposit	Remarks
1	Kammererite ^a	Deer Creek, Wyoming, USA	chrom chlorite
2	Fuchsite ^a	Silver Leaf Mine, Manitoba, Canada	chrom mica
3	Uvarovite ^a	Oxford, Quebec, Canada	chrom garnet
4	Mariposite ^a	Clavero County, California, USA	chrom mica
5	Chrome Diopside ^a	Outakumpa Mine, Outakumpa, Finland	
6	Miloschite ^a	Ely, Nevada, USA	chrom kaolinite
7	Alexandrolite ^a	Tulare County, California, USA	chrom, clay-like mineral
8	Avalite ^a	Mt. Avala, Belgrade, Yugoslavia	chrom clay-like mineral
9	Merumite ^b	Merume River, British Guiana	Cr ₂ O ₃ · H ₂ O mixed with other chrom minerals
10	Crocoite ^a	Beresov Mine, Sverdlovsk, Siberia	
11	Crocoite ^c	New Caledonia	very good crystals
12	Crocoite ^d	Mt. Dundas, Tasmania	very good crystals
13	Chromite ^e	Miller meteorite, Arkansas, USA	chromite first separated from remainder of sample
14	---- ^e	Holbrook meteorite, Arizona, USA	whole sample used

The minerals were collected with the cooperation and assistance of:

^a Smithsonian Institute, United States National Museum. Samples designated according to national collection, 1 (93908), 2 (97637), 3 (C-2724), 5 (106659), 8 (R-4386), 10 (44367).

^b United States Geological Survey.

^c Los Angeles County Museum.

^d Iowa State University Geology Department.

^e The American Museum of Natural History.

EXPERIMENTAL

The chromium was separated from the minerals as lead chromate by adding Pb^{++} to the acidified and filtered leachings of a sodium peroxide fusion of the mineral. Either nitric or glacial acetic acid was employed to acidify the resulting strongly basic solutions. The lead chromate was mixed with cobalt trifluoride and chromyl fluoride, CrO_2F_2 , was vacuum distilled from the solid-solid mixture at 550°C . Except for minor modifications, this preparation of chromyl fluoride, the use of it to determine the relative abundances of the chromium isotopes mass spectrometrically, and the mass spectrometer used in the determination were the same as those fully described in the previous work.

Previously, relative ion currents were determined by recording ten spectrograms made by scanning the 120-124 mass range in alternate directions. Each pair of consecutive spectrograms was then averaged to give nine observations of the relative ion currents. The method used in this work involved alternate measurements of the ion currents at masses 120 and 122 until each ion current had been recorded six times. This gave effectively eleven scans of masses 120-122 in alternate directions. Each pair of consecutive spectrograms was averaged and ten mass 120 vs. mass 122 ion-current ratios were calculated. In a similar manner ten ion-current ratios each were determined for mass 123 vs. mass 122 and mass 124 vs. mass 122. These ratios were thus the relative intensities of the masses 120, 123 and 124 ion currents when the intensity of the mass 122 ion current was taken as unity. The method

described was counted as ten individual observations of the relative ion currents. Corrections for the effusive gas flow and oxygen isotopes were applied to these data and the abundances of the chromium isotopes determined. The procedure was repeated at least once for each sample. This method of alternately measuring two ion currents and operating on these measurements to arrive at ion-current ratios does not give results as precise as those which can be obtained with a dual collector instrument, but the standard deviation of individual measurements were reduced to about one half that obtained for data from single peak spectrograms of the 120-124 mass range.

A second viscous leak with adjustable orifice was added to the mass spectrometer inlet manifold so that the relative abundances of the chromium isotopes in an unknown sample could be rapidly compared to those in a carefully assayed reference sample. All the samples were thus compared to a single reference sample and assay errors due to day-to-day instrumental fluctuations were greatly reduced. This is particularly important for measurements made when the mass spectrometer is not behaving according to optimum operation characteristics.

The results of the isotopic assays of the chromium in the minerals corresponding to those in Table 1 are given in Table 2. It can be seen that the uncertainty of the individual means ($\sigma/\sqrt{n}$) calculated for each assay is much smaller than the uncertainty in the mean based on the thirteen means. This indicates that the isotopic composition of chromium is probably not the same for all the minerals. However, the variations are so small that they approach the precision of the present measurements

Table 2. Isotope abundance determinations of the chromium minerals

(isotope abundance, atom percent)

Sample number	Observations, (n)	Isotopes											
		mean	50 σ $\times 10^3$	$\sigma/\sqrt{n}$ $\times 10^3$	mean	52 σ $\times 10^3$	$\sigma/\sqrt{n}$ $\times 10^3$	mean	53 σ $\times 10^3$	$\sigma/\sqrt{n}$ $\times 10^3$	mean	54 σ $\times 10^3$	$\sigma/\sqrt{n}$
1	20	4.366	5.6	1.2	83.752	14.4	3.2	9.508	5.9	1.3	2.375	4.3	0.9
2	20	4.360	4.6	1.0	83.765	12.7	2.8	9.501	5.0	1.1	2.376	4.4	1.0
3	40	4.354	4.7	0.8	83.772	8.0	1.3	9.501	5.3	0.8	2.373	2.8	0.4
4	20	4.360	4.1	0.9	83.749	8.8	1.9	9.506	7.0	1.5	2.384	4.9	1.1
5	20	4.362	8.8	1.9	83.761	8.2	1.8	9.503	11.8	2.6	2.374	3.2	0.7
6	30	4.344	2.9	0.5	83.757	7.6	1.4	9.518	5.7	1.0	2.381	1.9	0.3
7	50	4.364	7.3	1.0	83.772	3.8	0.5	9.497	6.0	0.8	2.367	3.1	0.4
8	30	4.353	3.6	0.6	83.740	7.4	1.3	9.520	5.0	0.9	2.386	2.3	0.4
9	30	4.349	3.9	0.7	83.750	9.8	1.8	9.520	6.9	1.2	2.381	4.7	0.8
10	20	4.351	3.0	0.7	83.756	8.1	1.8	9.505	6.4	1.4	2.378	3.3	0.7
11	30	4.360	10.7	1.9	83.762	19.8	3.6	9.506	11.2	2.0	2.372	9.0	1.6
12	110	4.347	4.5	0.5	83.765	8.8	0.9	9.512	5.8	0.6	2.375	3.6	0.4
13	50	4.359	6.7	0.9	83.760	16.5	2.3	9.504	11.9	1.7	2.377	4.4	0.6
14	30	4.411	10.7	1.9	83.562	23.4	4.2	9.511	13.0	2.3	2.516	16.5	3.0
Number of means			σ_m			σ_m			σ_m		σ_m		
47 ^a		4.357	4.9		83.760	8.6		9.508	7.2		2.375	4.9	

^a All data except those for sample #14.

in magnitude, thus no meaningful confidence level can be placed upon any of the observed particular differences. If the samples are divided into groups of similar types, the clay-like minerals, miloschite, alexandrolite and avalite, show a wider fluctuation in assay values than any other group. Presumably more natural separation processes might be expected in the formation of these minerals and the variations may have some significance if greater experimental precision could be achieved for the small variations observed even here.

The data for sample 14 from the Holbrook Meteorite are certainly different from those of the others, but there are reasons to doubt their validity. The limited size of the original sample and the relative small proportion of chromium present (0.31 per cent) made application of the present method difficult. Only a small amount of lead chromate was prepared and no attempts were made to check for possible interfering substances present in the original sample which may not have been separated from the chromium. Small ion currents due to some unknown species were actually observed at mass positions adjacent to the 120 - 124 range expected for CrO_2F_2 . That similar ion currents did not exist within the 120 - 124 range is a tenuous assumption and it is impossible to accurately assess the affect on the observed results. These results are reported here primarily to indicate that something of interest may be present in the Holbrook meteorite but it would require a larger sample than was available for this work to resolve the problem.

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REFERENCES

FLESCHE G. D., SVEC H. J. and STALEY H. G. (1960) The absolute abundance of the chromium isotopes in chromite. Geochim Et Cosmochim Acta 20, 300.

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