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DETERMINATION OF METALLIC IRON, NICKEL AND COBALT IN METEORITES

RIASSUNTO. — È stato sviluppato un metodo elettrochimico per la determinazione del ferro, nichel e cobalto metallici nelle meteoriti. Le fasi metalliche sono state selettivamente disciolte e gli elementi metallici in esse presenti sono stati quindi determinati nella soluzione mediante assorbimento atomico. Questo metodo è stato utilizzato per analizzare miscele di una lega di Fe-Ni con polveri del meteorite di Allende per simulare il contenuto metallico delle condriti tipo H, L e LL. È stata altresì analizzata una condrite naturale LL.

ABSTRACT. — An electrochemical method has been developed for the determination of metallic iron, nickel and cobalt in meteorites. The metallic phases are efficiently dissolved away from other mineral phases, and the elements of the metal phases are then determined by Atomic Absorption Spectroscopy. This method was used to analyze mixtures of an iron-nickel alloy with Allende meteorite powders to simulate the metallic content of H, L and LL chondrites; furthermore an LL chondrite was also analyzed.

Introduction

The analysis of chondritic meteorites poses a special problem not associated with normal silicate analysis, due to the presence of metallic and sulfide phases using the classical chemical methods. It is difficult to determine accurately the distribution of iron, nickel and cobalt in each of the phases present in meteorites. The distribution of these elements is of great interest in the classification of the chondrites by the metallic iron/total iron ratio and because of genetic implications. The methods now in use for the determination of the metallic content in meteorites do not give satisfactory results. These methods are subject to various difficulties:

- a) when physical methods are used (i.e. magnetic separation method) metallic phases are contaminated by sulphides and silicates. In fact, the metal is often mixed with the sulphides or distributed in fine particles as inclusions among the silicates;
- b) when chemical methods are used the metallic phases are only partially extracted, especially when they contain a large amount of nickel, as shown by experimental data (table 1);
- c) there is partial hydrolysis of the dissolved iron at a given pH of the extracting

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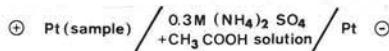
- solution. The critical value of the pH where the hydrolysis of the iron is initiated, is a function of the $C_{Fe^{+3}}$ in solution;
- d) the solubilities in the various extracting solutions of the different phases found in meteorites are incompletely known (JAROSEWICH, 1966);
- e) when the mercuric-chloride, ammonium-chloride system is used, an excessive length of time (about 100 hours) is required for the metal extraction to take place (EASTON and LOVERING, 1963).

An electrolytic corrosion of iron meteorites (which separates their non metallic portions) was described by TACKETT et al. (1966). These authors found that at currents of 0.5 amp. or less, only the iron appeared to stay in solution, while the nickel ended up as a metallic sludge at the bottom of the anode compartment. Furthermore the dissolved metals are hydrolyzed by the use of a neutral solution ($pH = 5$) and an uncontrolled voltage.

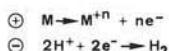
To overcome the difficulties listed above we propose a voltage-controlled (potentiostatic) method in which the metal of the crushed chondritic meteorites is dissolved in an acid solution ($pH \approx 3.6$).

Principle of the method

The method is based on the anodic dissolution of the metals in an electrochemical cell as given below:



The processes that take place are:



Because the sample is composed of mineral grains of various electrical conductivities, good contact between the metallic grains and the platinum anode is necessary to improve the efficiency of the dissolution. The best conditions can be obtained by varying the agitation rate of the solution.

Experimental

Reference samples

- 1) Extrapure « Ventron » iron powder, -325 mesh, and iron-nickel alloy powder, -325 mesh, having a 58:42 iron/nickel ratio.
- 2) A purified natural mixture of pyrrhotite ($\sim 80\%$) and pentlandite ($\sim 20\%$).
- 3) An Allende meteorite powder, supplied by the Smithsonian Institution (spit 20 position 4).

Results and discussion

The electrochemical method was tested against the copper-sulfate (HABASHY, 1961) and the $\text{HgCl}_2\text{-NH}_4\text{Cl}$ (FREIDHAM, 1888) procedures. These methods, as well as the KCuCl_3 method (RIOTT, 1941; HUGHES and HANNAKER, 1978 a, 1978 b), are based on the oxidation of the metal by another couple having a lower standard redox potential (LATTIMER, 1952). While complete extraction by these methods

TABLE 1

Show the results obtained by using the various extraction methods for pure metallic iron and for an iron-nickel alloy. It is possible to see that the $\text{HgCl}_2\text{-NH}_4\text{Cl}$ and the « new copper sulphate » methods do not give satisfactory results for nickeliferous alloys

METHOD	SOLUTION	INITIAL pH OF SOLUTION	EXTRACTION TIME h	METALLIC SAMPLE COMPOSITION %	TOTAL DISSOLVED METALS %	IRON IN DISSOLVED METALS %	NICKEL IN DISSOLVED METALS %
H.G.HABASHY	CuSO_4^+ metallic Hg	3.5	1	Fe:100	100	100	-
M.G.HABASHY	CuSO_4^+ metallic Hg	3.5	5	Fe:58-Ni:42	38	66	34
C.FRIEDHEIM	$\text{HgCl}_2\text{-NH}_4\text{Cl}$	4.3	100	Fe:100	100	100	-
C.FRIEDHEIM	$\text{HgCl}_2\text{-NH}_4\text{Cl}$	4.3	100	Fe:58-Ni:42	50	76	24
T.C.HUGHES AND P.HANNAKER	KCuCl_3 + D-Tartaric acid + CH_3COOH	4.3	24	Fe:58-Ni:42	85	59	41
THIS METHOD	$(\text{NH}_4)_2\text{SO}_4$ $+ \text{CH}_3\text{COOH}$	3.6	4	Fe:58-Ni:42	100	58	42

is attained when the metal is pure iron, dissolution is incomplete when the sample is an iron-nickel alloy (table 1). Further, the Ni/Fe ratio in the resulting solution is lower than its ratio in the alloy and is probably due to a passivation phenomena. The better results reported by HUGHES and HANNAKER (1978 a) are probably due to the low nickel content (1-10 %) of their analized alloys, in a true meteorite where taenite is also present (having up to 65 % of Ni), the dissolution of the metal using their method would be incomplete.

With the aim of evaluating the reliability of an electrochemical procedure, the following points had to be verified:

- 1) the complete dissolution of the metallic phases,
- 2) the insolubility of other iron-bearing mineral phases, and
- 3) the stability of the metallic ions both in solution and during their determination.

To prevent hydrolysis of the iron, the Fe^{+3} concentration in solution ($\text{pH} \sim 3.7$) must be kept at values low enough to avoid precipitation of ferric hydroxide. In our system, a high $\text{Fe}^{+2}/\text{Fe}^{+3}$ ratio in the solution was controlled by the Eh fixed

Sample crushing

The meteorite specimen is cleared, removing all its fusion crust, and about 1-2 grams is cut off. The sample is then carefully broken into small pieces and crushed finely (-200 mesh) in an alundum mortar by normal techniques (keeping the sample at near liquid air temperature). Further details about crushing techniques are given in EASTON and LOVERING (1963).

Analytical method

Fifty milligrams of a finely crushed meteoritic sample (-200 mesh) is placed in a platinum dish. Add about seventy milliliters of a 0.3 M solution of reagent grade $(\text{NH}_4)_2\text{SO}_4$, acidified with CH_3COOH to pH 3.6.

The anodic dissolution of the metals is obtained by keeping the platinum dish at a constant potential of +0.55 volts, which is controlled by a potentiostat (such

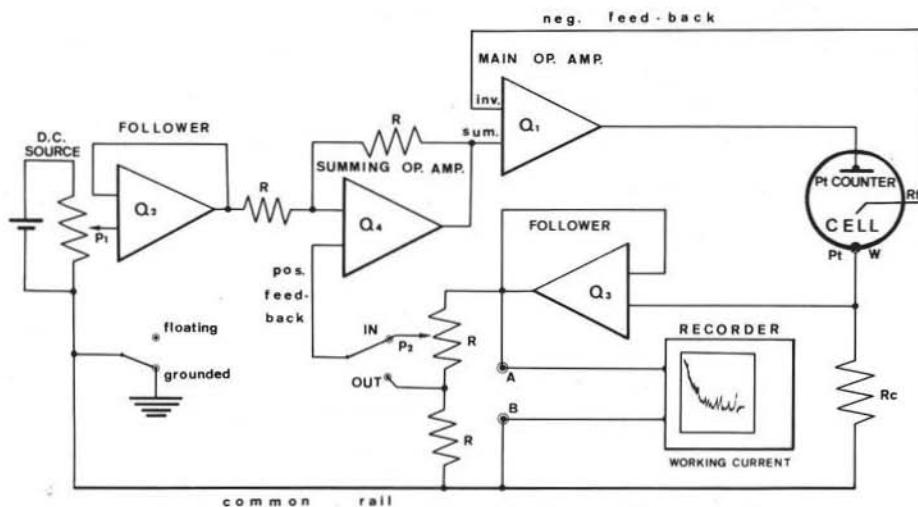


Fig. 1. — The potentiostatic circuit used for the anodic dissolution of metals. The voltage drop across the R_e resistor drives the operational amplifier Q_3 which supplies the common-mode-output at the terminals A and B (working current). In order to keep the working electrode at the same voltage drop across R_e is compensated by a positive feed-back picked up via a divider $R-R$ at the output of Q_3 .

as AMEL-551) having a saturated calomel reference electrode and a large-surface Pt counter electrode (fig. 1).

The solution is continuously agitated at room temperature in an oxygen-free atmosphere such as nitrogen, and the pH value must be periodically tested and adjusted to the initial value by adding acetic acid. Three to six hours are allowed to complete the dissolution of the metal. The solution is then filtered, acidified with HCl, brought to a volume of 100 ml. and each element is determined with an Atomic Absorption Spectrometer. Because of its low concentration, cobalt is determined by the method of standard addition.

by the potentiostat. The low Eh of the solution also prevents the oxidation of Fe^{+2} to Fe^{+3} in ferromagnesium silicates (CARROL, 1970).

The electrochemical method was used on mixtures of pyrrhotite and pentlandite, neither of which were soluble. STASCHUCK (1972) reported the stability of synthetic pyrrhotites as limited to low Eh values when the pH ranges between 3.5 and 4.0. The insolubility of these minerals during these experiments is probably related to the kinetics of their dissolution.

TABLE 2

Reports the results obtained using the anodic dissolution method for the determination of the metallic phases in some samples simulating the mineralogical composition of the H, L and LL chondrites. The extracted metal is also expressed in terms of its percentage in the bulk composition of the samples

SIMULATED ROCK	WEIGHT OF METAL* IN 50 mg OF SAMPLE	WEIGHT OF EXTRACTED METAL	EXTRACTED METAL METALLIC CONTENT OF SAMPLE	METAL IN THE WHOLE ROCK	
				% present	% extracted
H chondrite	1	7.5	7.51	100.1	average
	2	7.5	7.39	98.5	99.1
	3	7.5	7.40	98.7	
L chondrite	4	3.5	3.48	99.7	average
	5	3.5	3.45	98.7	99.4
	6	3.5	3.49	99.8	
LL chondrite	7	1.0	0.98	98.0	average
	8	1.0	1.01	101.0	99.3
	9	1.0	0.99	99.0	

* These values were obtained adding to an iron-nickel alloy (42 % Ni) the metal content of the Allende meteorite (0.2 %).

TABLE 3
*Metallic content in the Piancaldoli meteorite (LL chondrite)
determined by the electrochemical method*

$$\begin{array}{lll} \text{Fe}^\circ = 2.40\% & \text{Co}^\circ = 0.02\% & \text{Ni}_{\text{tot}} = 1.00\% \\ \text{Ni}^\circ = 0.40\% & \text{Fe}_{\text{tot}} = 19.73\% & \text{Co}_{\text{tot}} = 0.05\% \end{array}$$

We then prepared nine samples by mixing a metallic iron-nickel alloy with the Allende meteorite powders to simulate the metallic contents of H, L and LL chondrites. As expected, the current versus time variation curves obtained during dissolution were exponential.

The results of the analysis of these mixtures is given in table 2. The data show good agreement between the determined extractable metals and the metallic content of the original samples. The method was used to determine the metallic content in the Piancaldoli meteorite (table 3), and the results are in very good agreement with the modal analysis of metal phases carried out at the quantimet.

The electrochemical method selectively dissolves the metallic phases without dissolving other iron-bearing minerals. Oxidation occurs whenever a metallic grain comes in contact with the Pt dish. Because of higher current intensities, samples of higher metallic content do not require a much longer dissolution time. The method is particularly suited to the determination of metallic Fe, Ni and Co in meteorites.

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