Neutron Activation Analysis
of Fluid Inclusions for Copper, Manganese, and Zinc

Gerald K. Czamanske*
Edwin Roedder
Forrest C. Burns
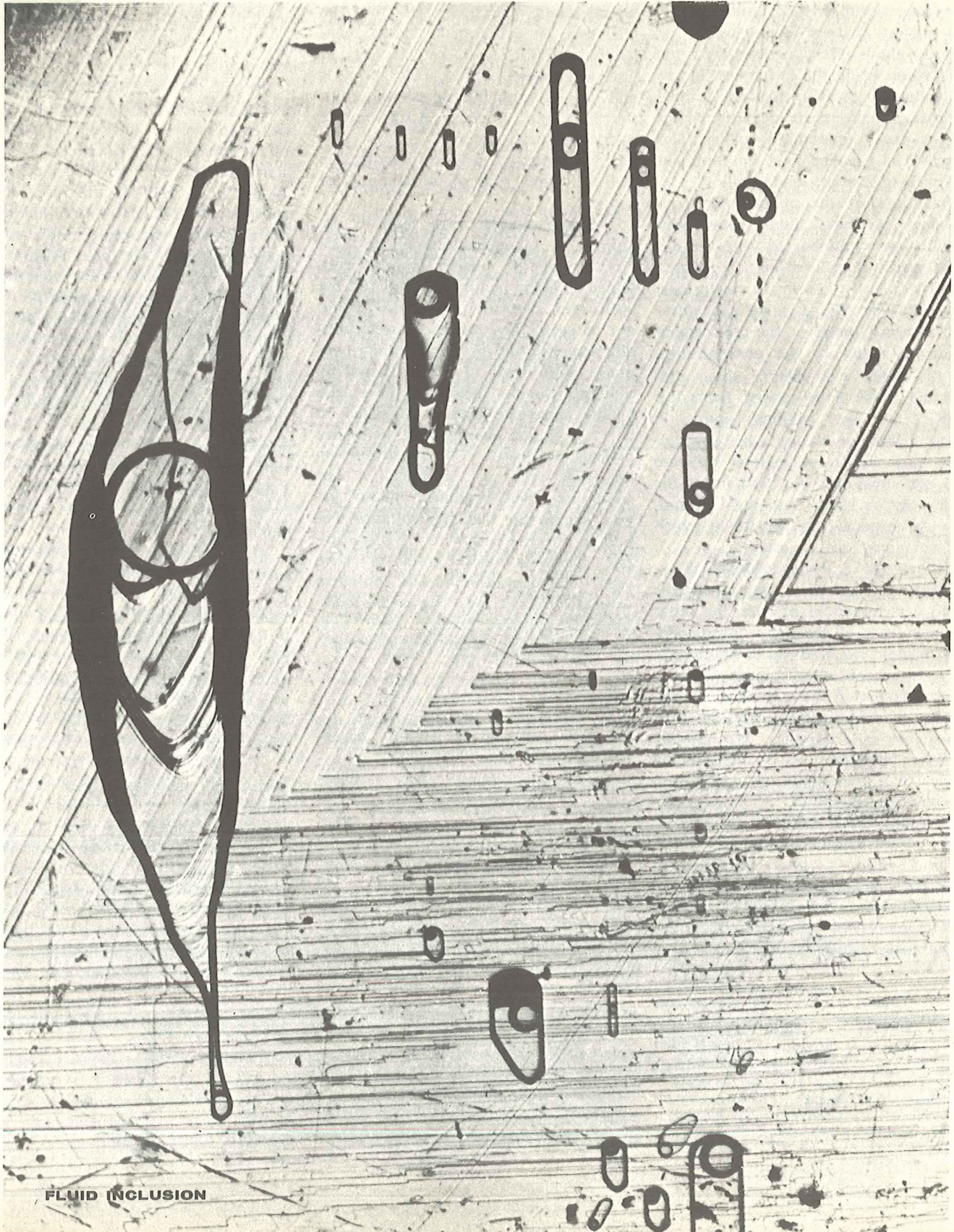
FLUID INCLUSION

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Abstract. *Microgram quantities of copper, manganese, and zinc, corresponding to concentrations greater than 100 parts per million, were found in milligram quantities of primary inclusion fluid extracted from samples of quartz and fluorite from two types of ore deposits. The results indicate that neutron activation is a useful analytical method for studying the content of heavy metal in fluid inclusions.*

Studies of microscopic fluid inclusions that occur in many minerals (*1, 2*) suggest that in some cases the trapped fluids are identical with the fluid from which the host mineral was precipitated. Such inclusions, termed "primary," have received particular attention from economic geologists interested in the chemical environment and mechanisms of ore deposition. Determinations of the major ionic constituents of these fluids have been feasible for a number of years (*1–3*).

Of special interest is the heavy (ore) metal content of primary inclusions, for it may be related to the concentration of heavy metals in the ore-forming fluid. Estimates of the concentration of the metal elements in these ore-forming fluids have ranged from less than 1 part per million (ppm), in saline brines, to that of a metallic sulfide melt. A recent indirect estimate (*4*) sets limits of 1 to 1000 ppm on the concentration range that might reasonably be expected in the fluids which formed many ore deposits.

Difficulties in the procedures of extraction and analysis have precluded valid determinations of even the order of magnitude of the heavy metal content of inclusion fluids up to the present time, but recent developments in technique (*5*) permit the extraction of relatively uncontaminated inclusion fluid from very small samples. We now describe a feasibility test for determining trace metal contents in such inclusions by neutron activation.

Samples were selected to provide high concentrations of undoubted primary inclusions, with a minimum of possible contaminants. Two different minerals from two different geologic environments were chosen to make this preliminary study more meaningful.

Liquid was extracted from: (i) euhedral white quartz crystals from the OH vein, an epithermal, slightly manganiferous Pb-Zn-Cu-Ag deposit at Creede, Mineral County, Colorado (*6*); and (ii) euhedral fluorite crystals from the Hill mine, Cave-in-Rock fluorite district, Hardin County, Illinois (*5*). The latter district contains considerable lead and zinc, plus minor amounts of copper.

The two samples were carefully examined at magnifications up to 125. Crystals of the quartz samples contained so many inclusions (1 to 10^{-9} mg each) that parts of the interiors could not be seen. The inclusions were zonally arranged and primary, mainly two-phase, with about 12 percent vapor by volume. Similar inclusions, in a pale yellow sphalerite crystal deposited in part contemporaneously with the quartz crystals, are shown in the illustration on the front cover of this issue. A few small inclusions contained mainly vapor, suggesting that the solution was boiling during entrapment. No precipitated daughter mineral grains (*4*) were seen. The sample of fluorite contained several large (2 mg) two-phase inclusions of negative crystal shape, with 5 percent vapor, occurring along cubic

growth planes in perfectly clear, pale to dark purple fluorite. [For a photomicrograph of similar inclusions, see (*2*) and cover photograph]. There were no daughter mineral grains. Three plainly visible opaque solid inclusions, about 5 μg each, were eliminated with a microsandblast unit. Thousands of tiny two-phase primary inclusions of yellow-brown oil were not removed; they occurred along numerous cubic growth planes and averaged about 0.001 μg each. There were no other visible imperfections.

The samples were reduced in size by sawing and were then ground and sandblasted to remove all visible impurities and to concentrate the inclusions. The quartz sample was further treated by boiling in an HCl-HF mixture. Both samples were boiled in room-temperature acetone at reduced pressure to remove immersion oils used during microscopy and were then repeatedly boiled in hot water at reduced pressure to fill all sandblasting pits and any invisible cracks prior to electrolysis. There were no visible cracks. The wet samples were transferred to Pyrex U-tubes and cleaned electrolytically for 18 (quartz sample) and 7 (fluorite sample) days, with eight changes of high purity water. Only during the first 2 days of this cleaning was there evidence of removal of soluble, ionizable impurities.

After drying at 110° and 80°C, respectively, the samples (17 g of quartz; 4 g of fluorite) were placed in clean stainless steel tubes (type 304, closed at one end with fluxless Heliarc welding) and crushed while under high vacuum in a system designed to obtain the weight of the water released (*5, 7*). The crushed samples (mostly < 3 mm) were leached three times (contact time, 1 minute each) with 10- to 20-ml portions of deionized water on a low-contamination, acid-washed asbestos filter, and then once with 20 ml of 10 percent HNO_3 at room temperature. Each portion was used to rinse the stainless sample tube before it was used to leach the sample. The electrical conductivity of the water leaches was determined in a 1-ml Pyrex cell

Table 1. Copper, manganese, and zinc contents of reagent blanks.

Metal	Water (μg/ml)	10% HNO_3 (μg/ml)
Cu	0.0015*	0.0100*
Mn	0.0008	0.0016
Zn	0.0073*	0.0160*

* Average of two determinations.

Table 2. Leachable copper, manganese, and zinc from inclusions in Creede, Colorado quartz and southern Illinois fluorite.

Metal	Water leach (μg)	Concn. in inclusion fluid* (μg/ml)	Acid leach (μg)	Concn. in inclusion fluid† (μg/ml)
Quartz sample (24.5 mg of fluid extracted)‡				
Cu	1.4	60	2.0	140
Mn	15.3	620	1.7	690
Zn	10.1	410	22.4	1330
Fluorite sample (4.87 mg of fluid extracted)‡				
Cu	0.71	150	43.8	9100
Mn	1.6	330	0.60	450
Zn	2.8	570	50.1	10,900

* Calculated on the basis of water leach data. † Calculated on the basis of the combined water and acid leach data. For each calculated concentration it is assumed that all of the metal had been present in solution in the fluid within the inclusions. ‡ The weight of the fluid extracted was calculated from the amount of water found by analysis (23.3 mg in the quartz sample and 3.65 mg in the fluorite sample) with a correction for dissolved salts known to be present (5 and 25 percent by weight, respectively) (see *5* and *6*).

Table 3. Semiquantitative spectrographic analyses of mineral fragment residues (*11*).

Metal	Quartz (ppm)	Fluorite (ppm)
Cu	50	< 30
Mn	20	1
Zn	200	< 100

with bare platinum electrodes. In each case the conductivity of the third leach was found to be approximately 10 percent of that of the first, indicating essentially complete leaching. The three leaches were acidified with HNO_3 to a pH of less than 2 and then combined. Blanks of water and acid were taken through the extraction procedure, except for contact with the stainless tubes.

Microscopic examination showed that all the large inclusions had been opened, but most of the tiny ones had not. A number of grains less than 90 μ in diameter, almost certainly pyrite and chlorite, could be seen inside the quartz fragments.

The sample leaches and blanks were transferred to high-density polyethylene test tubes for evaporation to smaller volume. Each fluid sample was irradiated with Cu, Mn, and Zn comparators in 2-dram polyethylene vials for 30 minutes at a slow neutron flux of 2×10^{12} neutrons per square centimeter per second. The irradiations were made in the Ordnance Materials Reactor at the Watertown Arsenal, Watertown, Mass.

Induced 12.9-hr Cu^{64}, 2.8-hr Mn^{56}, and 57-min Zn^{69} activities were measured. The metals were separated by a strongly basic Dowex 1×8 anion exchange column (7 mm by 7 cm; 100 to 200 mesh; flow rate, 0.4 ml/min) according to procedures established by Kraus and Moore [8]. Manganese was eluted with $6M$ HCl, copper with $1M$ HCl, and zinc with $0.005M$ HCl. It was necessary to further purify the Mn fraction from Na-contamination by adding sodium hold-back carrier and precipitating the manganese as MnO_2. This step was performed three times in order to remove the Na^{24} activity.

Determinations of the Cu and Mn contents were made by gamma counting on a multichannel analyzer and comparing the integrated counts under the photopeaks. Zinc was determined by beta counting the dried Zn fraction. Checks of radiochemical purity were provided by total gamma-ray spectra for Cu^{64} and Mn^{56}, and by half-life for Zn^{69}. Chemical yields were not determined, but on the basis of preliminary tracer experimentation with the columns, and continual monitoring during each separation, sample loss greater than 10 percent is considered improbable.

The analytical results obtained are presented in Tables 1 and 2. The estimated maximum uncertainty of these measurements is 20 percent. On the basis of the data in Table 1, correc-

tions not exceeding 10 percent have been applied to the raw data to give the figures of Table 2.

In view of the limited data presently available, interpretation of these results must be made with great caution. Since some of the results are unexpectedly high, the following suggested sources for the heavy metals found are evaluated briefly.

Natural sources in inclusions: (i) in solution, evaporates to a water-soluble form; (ii) in solution, evaporates to an acid-soluble form; (iii) visible daughter mineral grains, acid-soluble; and (iv) invisible films or dust of daughter minerals, acid-soluble. *Natural sources in host minerals:* (v) solid inclusions of chalcopyrite and sphalerite; (vi) solid inclusions of oxidation products; and (vii) integral part of host mineral structure. *External sources (introduced):* (viii) leaching of stainless steel tubes; (ix) other containers, water, acid, and reagents; and (x) accidental contamination.

The simplest interpretation is that the water leach values represent source (i) and the acid leach values source (ii). On the basis of microscopy, source (iii) is nil for the fluorite sample and probably nil for the quartz sample. Source (iv) would seem to be inadequate, as the required ore mineral film thicknesses ($> 1 \mu$) or dust concentrations (3 to 6 mg/cm^2) would be visible. For the quartz sample, source (v) is very possible, in view of the microscopy and the occurrence with sphalerite and chalcopyrite. However, leaching experiments on sphalerite and chalcopyrite, from the same vein, indicated rates of solution three or more orders of magnitude too low to explain the results obtained. Analysis of the residue (Table 3) also shows that such mineral grains cannot be present in large amounts. The fluorite sample had no "large" solid inclusions, and many thousands of small ones ($< 10 \mu$) would have to have dissolved to explain the high Cu and Zn acid leach values.

Analysis of the residue (Table 3) and a determination of the maximum rates of solution under the conditions used indicate that less than 1.5 μg of Zn could come from this source, plus source (vii). Source (vi) seems unlikely as a contributor for the quartz sample. It would require both water- and acid-soluble minerals to be enclosed in the quartz, and hence immune to electrolytic cleaning, and yet to be almost completely exposed to the

leaching after coarse crushing. Source (vi) is even more unlikely for the fluorite sample, because the amount of zinc and copper found on acid leaching would require the equivalent of a grain of basic sulfate nearly 0.5 mm in diameter for each metal—far more than would remain unobserved. Leaching tests on the stainless tubes indicate that source (viii) contributed less than 10 percent contamination to the acid leaches. The very low values for the blanks (Table 1) indicate that the total contribution from all sources listed under (ix) must be small. Source (x) can never be fully evaluated, except by additional determinations. The unlikely possibility of contamination by brass from the vacuum line was shown to be completely unrealistic by studies of the rates of solution of brass chips. Simultaneous contamination of one sample (the fluorite) with similar amounts of Cu and Zn also seems unlikely.

It may be suggested that minimum values for the metal concentrations in the ore fluid are given by the water leach data (Table 2, column 3) and that the combined metal contents of the acid and water leaches (Table 2, column 5) give maximum values. Further application of activation analysis to the study of fluid inclusions should eventually allow definite conclusions to be reached regarding the various contributions to the detected heavy metal content and may alter the tentative suggestions offered here [9, 10].

GERALD K. CZAMANSKE*
Department of Geology and Geophysics, Massachusetts Institute of Technology, Cambridge 39
EDWIN ROEDDER
U.S. Geological Survey, Washington 25, D.C.
FORREST C. BURNS
Watertown Arsenal, Watertown 72, Massachusetts

References and Notes

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8. K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.* 75, 1460 (1953).
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10. The paper by D. E. White *et al.* [*Science* **139**, 919 (1963)] provides an interesting comparison to the results presented here.
11. Analysis by C. L. Waring, U.S. Geological Survey.
   * Present address: Department of Geology, University of Washington, Seattle 5.