

GALLIUM IV. OCCURRENCE OF GALLIUM IN ZINC MINERALS¹

JACOB PAPISH AND CHESTER B. STILSON,
Cornell University, Department of Chemistry.

INTRODUCTORY

Gallium was discovered by Boisbaudran² in 1875 as a result of a chemical examination of zinc blende from Pierre-la-Fitte, Valley of Argeles in the Pyrenees. In a later publication Boisbaudran³ announced that blendes from Schwarzenberg, Bensberg, Asturias, Mandesse and Sweden also contained gallium, while a blende from Vieille-Montagne did not contain it. Cornwall⁴ found that gallium was present in blendes from Pierre-la-Fitte; Santander, Spain; Friedensville and Phoenixville, Pennsylvania; Joplin, Missouri; Warren, New Hampshire and Ellenville, New York; and that specimens of blende from Roxbury, Connecticut, and from Mine Hill, New Jersey, did not contain this element. Bartlett⁵ stated, in a manner not very convincing, that he had obtained a test for gallium in some low grade sulphurets from the Iron Silver Mine of Leadville, Colorado. Hartley and Ramage⁶ reported the presence of gallium in blendes from Pierre-la-Fitte; Bensberg; Santander; Alston Moor, Cumberland; Tipperary, Ireland; Zellerfeld, Saxony; Chemnitz, Hungary; Matlock, Derbyshire; Rio Tuerto, Spain; and Laxey, Isle of Man; and not in blendes from Freiberg, Saxony, and from Ravenswood, Queensland, Australia. Rimatori⁷ examined blendes from Bena de Padru, Montevecchio, Nassau, Nieddoris, Argentiera della Nurra, Rio Ollorchi, Rosas, and Riu Planu Castangais, and found that those from Montevecchio and Bena de Padru contained gallium. Urbain⁸ reported that of the sixty-four blende specimens examined by him five did not

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² Boisbaudran, *Compt. rend.*, **81**, 493 (1875).

³ Boisbaudran, *Ibid.*, **82**, 1098 (1876).

⁴ Cornwall, *Amer. Chem. Jour.*, **2**, 44 (1880).

⁵ Bartlett, *Jour. Soc. Chem. Ind.*, **8**, 896 (1889).

⁶ Hartley and Ramage, *Jour. Chem. Soc.*, **71**, 533 (1897).

⁷ Rimatori, *Atti. d. Reale Accad. d. Lincei*, Series 5, **13**, 1, 277 (1904).

⁸ Urbain, *Compt. rend.*, **149**, 602 (1909).

show spectral lines of gallium. He named five localities from which the galliferous blendes came: Webb City, Missouri; Stolberg, near Aix la Chapelle; European Turkey; Raibl, Carinthia; and Mexico. Cerdan⁹ examined sixty-eight samples of Spanish blende and found gallium in sixty of them. Hillebrand and Scherrer¹⁰ reported gallium in sulphides from Sunset, and Frisco, Idaho; Missouri, and Australia.

Cornwall¹¹ reported that he found no gallium in specimens of calamine from Friedensville, Pennsylvania, and Sterling, New Jersey, as well as in a sample of zincite from Franklin Furnace, New Jersey.

METHOD OF ANALYSIS

As far as it can be ascertained from recorded data the investigators just referred to depended upon spectroscopic methods for identifying gallium. The method most generally employed was the one in which the high-voltage spark was the means of spectral excitation. Hillebrand and Scherrer¹² made use of the carbon arc. The spark which was undoubtedly of the low-wattage type has drawbacks which made impossible the detection of very small traces of gallium in some of the zinc minerals.¹³ In the present work the arc method of excitation was employed for the detection of gallium. This method, which was described in the first article of this series,¹⁴ consisted in placing a small quantity of the pulverized zinc mineral between electrodes of artificial graphite, passing the arc discharge, and photographing the spectrum with the aid of a quartz spectrograph of the Littrow auto-collimating type. The spectral lines $\lambda\lambda 4172.0$ and 4033.0 served to establish the identity of gallium. These lines are of high sensitivity and they lie in a range where interference caused by lines of other elements is not very serious. This is especially true of $\lambda 4172.0$, since $\lambda 4033.0$ is overlapped by spectral lines of manganese and iron, commonly associated with zinc in minerals. But even $\lambda 4172.0$ was found at times inadequate. When graphite electrodes are used for the production of the arc in air, cyanogen bands are unavoidably

⁹ Cerdan, *Anal. Fis. Quim.*, **12**, 80 (1914).

¹⁰ Hillebrand and Scherrer, *Jour. Ind. and Eng. Chem.*, **8**, 225 (1916).

¹¹ *Loc. cit.*

¹² *Loc. cit.*

¹³ Papish and Kennard, "The High-Wattage Spark in Spectral Chemical Analysis." (*Not published*).

¹⁴ Papish and Holt, *Jour. Phys. Chem.*, **32**, 142 (1928).

present in the spectrograms; and $\lambda 4172.0$ lies within one of these bands. If this line of gallium is of low intensity it will be drowned, so to speak, in the brilliance of the cyanogen band, and as a result minute traces of gallium in zinc minerals will not be detected. To remedy this, recourse was made to silver electrodes whenever a spectrographic examination with the aid of graphite electrodes did not reveal the presence of gallium. The silver electrodes were admirably suited to this purpose: they were free from gallium and they gave no background of continuous spectrum in the range of $\lambda 4172.0$.

RESULTS

In the tables containing results of the present investigation "v" is used to designate that the spectral line was plainly visible, "f" that it was faint and "vf" very faint. Designation was omitted when the spectral line could not be detected because of interference of lines of other elements. This applies in very many cases to $\lambda 4033.0$, which, as already mentioned, is overlapped by spectral lines of manganese and iron.

SPHALERITE. Eighty specimens of sphalerite were examined for the presence of gallium and the results are recorded in Table I. As seen from this table all of them contained gallium. Sphalerite No. 52 was associated with dolomite, No. 64 with fluorite and quartz, and No. 73 with magnetite. Sphalerite No. 35 was a fossil shell variety occurring in Tully limestone at Moravia, New York.

TABLE I
GALLIUM LINES IN SPECTROGRAMS OF SPHALERITE

Sphalerite No.	Place of Origin	$\lambda\lambda$	
		4172.0	4033.0
1	Sullivan Mine, Kimberley, British Columbia	vf	
2	Lucky Jim Mine, Sandon-Kaslo, British Columbia	vf	
3	Bell Mine, Beavertell, British Columbia	vf	
4	Prosperity Mine, Marmot River, British Columbia	vf	
5	Mohawk Mine, New Hazelton, British Columbia	vf	
6	Geneva Lake Mine, Geneva Lake, Ontario	f	
7	Montauban, Quebec	f	
8	Quyong, Quebec	f	
9	Mexico	v	
10	Nogales, North Mexico	vf	
11	California	v	
12	Central City, Colorado	f	

TABLE I (Cont.)
GALLIUM LINES IN SPECTROGRAMS OF SPHALERITE

Sphalerite No.	Place of Origin	$\lambda\lambda$	
		4172.0	4033.0
13	Kokomo, Colorado	v	
14	Nevadaville, Colorado	f	
15	Moyer Mine, Leadville, Colorado	f	
16	Glacier Lake, near Boulder, Colorado	vf	
17	Jo Reynolds Mine, Idaho Springs, Colorado	f	
18	Roxbury, Connecticut	f	
19	Success Mine, Wallace, Idaho	vf	
20	Dubuque, Iowa	v	
21	Near Baxter Springs, Kansas	f	
22	Near Baxter Springs, Kansas	v	
23	Marion, Kentucky	v	
24	Ottawa County, Oklahoma	v	v
25	Rockport, Mass.	f	
26	Trout Mt. Mine, Missoula County, Montana	vf	
27	Joplin, Missouri	v	f
28	Joplin, Missouri	v	v
29	Webb City, Missouri	v	
30	Freiberg, Nevada	v	
31	Franklin Furnace, New Jersey	vf	
32	Kelly, New Mexico	v	
33	Hanover, New Mexico	vf	
34	Edwards, New York	f	f
35	Moravia, New York	v	
36	Niagara Falls, New York	v	
37	Rochester, New York	f	
38	Rossie, New York	v	
39	Tiffin, Ohio	f	
40	Centerville, Pennsylvania	v	
41	Mt. Joy, Lancaster County, Pennsylvania	v	
42	Wheatley Mines, near Friedensville, Pennsylvania	v	v
43	Ridgebury P. O., Pennsylvania	v	
44	Beaver County, Utah	v	
45	Judge Mine, Utah	v	
46	Austinville, Virginia	vf	
47	Bonsack, Virginia	v	
48	Bonsack, Virginia	f	
49	Wisconsin	v	
50	Raibl, Carinthia	f	
51	Při'bram, Bohemia	v	
52	Bleistadt, Bohemia	f	
53	Alston, Cumberland, England	v	
54	Cumberland, England	f	

TABLE I (Cont.)
GALLIUM LINES IN SPECTROGRAMS OF SPHALERITE

Sphalerite No.	Place of Origin	$\lambda\lambda$	
		4172.05	4033.01
55	Cumberland, England	v	
56	Cornwall, England	vf	
57	Schauenslund, Baden	vf	
58	Bodenmais, Bavaria	vf	
59	Kaiser Wilhelm Shaft, Clausthal, Germany	f	
60	Neudorf, Germany	f	
61	Prussia	f	
62	Steeffe Sea, Silesia	f	f
63	Freiberg, Saxony	vf	
64	St. Christopher Mine, Schwarzenberg, Saxony	vf	
65	Schwarzenberg, Saxony	f	
66	Schwarzenberg, Saxony	v	
67	Eschborich Mine, Moresnet, Belgium	f	
68	Chemnitz, Saxony	v	
69	Kapnik, Hungary	v	
70	Bottino, Tuscany, Italy	vf	
71	Felsö-bánya, Roumania	f	f
72	Rodnon, Transylvania	f	
73	Picos De Europa, Santander, Spain	vf	
74	Binnenthal, Switzerland	f	
75	Yechigo, Japan	f	
76	Zeekan, Tasmania	f	
77	Tzumb, Southwest Africa	v	
78	Pierre-la-Fitte, Pyrenees	v	
79	Montserrat, near Pasma, Bolivia	v	v
80	Braubach-on-Rhine	vf	

CALAMINE. The spectrographic test was applied to ten samples of calamine. These samples came from the following localities: Leadville, Colorado; Elkhorn, Montana; Joplin, Missouri; Branby, Missouri; Wentworth, Missouri; Ogdensburg, New Jersey; Organ Mountains, Dona Ana County, New Mexico; Friedensville, Pennsylvania; Bleiberg, Carinthia; Santander, Spain; La Duchessa, Sardinia, and Malfidano, Sardinia.

In all cases the gallium lines $\lambda\lambda 4172.0$ and 4033.0 could not be detected.

SMITHSONITE. Two specimens of this mineral, one from Marion, Kentucky, and one from Cerro Gordo District, Inyo County, California, were subjected to arc excitation. The spectrograms in both cases did not contain gallium lines.

ZINCITE. The zincite examined came from Franklin Furnace, New Jersey. The gallium lines were not visible in its spectrogram.

HYDROZINCITE. Nine specimens of hydrozincite were examined. The localities from which they came are as follows: Cerro Gordo District, Inyo Co., California; Hickory Cave Mine, Marion Kentucky; Ely, Nevada; Good Springs, Lincoln County, Nevada; Deming, New Mexico; Bethlehem, Pennsylvania; Raibl, Carinthia; Bleiberg, Carinthia; and Malfidano, Iglesias, Sardinia. In all cases the gallium lines in question were absent.

GAHNITE. Five specimens of this mineral from as many different localities were examined and the results are recorded in Table II. Gahnite No. 1 was associated with pyrites.

TABLE II
GALLIUM LINES IN SPECTROGRAMS OF GAHNITE

Gahnite No.	Place of Origin	$\lambda\lambda$	
		4172.0	4033.0
1	Charlemont, Mass.	f	
2	Franklin Furnace, New Jersey	v	
3	Bodenmais, Bavaria	v	
4	Fahlun, Sweden	v	
5	Orijarri, Finland	v	

HOPEITE. Hopeite from Franklin Furnace, New Jersey, on spectrographic examination was found to be galliferous: In its spectrogram $\lambda 4172.0$ was faintly visible and $\lambda 4033.0$ very faintly visible.

PARAHOPEITE. A specimen of this mineral from the H. B. Mine, Salmo, British Columbia, upon spectrographic examination gave the following results: $\lambda 4172.0$, faint, and $\lambda 4033.0$, very faint.

ADAMITE. A specimen of adamite from Cap Garonne, Dept. du Var, France, showed the gallium line $\lambda 4172.0$ distinctly; $\lambda 4033.0$ was not visible because of interference of lines of other elements. Another specimen from Laurium, Greece, showed $\lambda 4172.0$ faintly.

GOSLARITE. Two specimens of this mineral were examined spectrographically and no gallium lines were observed. The specimens came from Butte, Montana, and from Goslar, Harz, Germany.

HODGKINSONITE from Parker Mine, New Jersey, showed no gallium lines.

HARDYSTONITE. The specimen examined came from Franklin Furnace, New Jersey. The spectrogram did not contain the lines of gallium.

CLINOHEDRITE from Franklin Furnace, New Jersey, showed no gallium lines on spectrographic examination.

SUMMARY

The arc spectrographic method for the detection of gallium was applied to a number of zinc minerals with the following results:

All specimens of sphalerite, eighty in number, were found to be galliferous. The same is true of five specimens of gahnite, one specimen of hopeite, one of parahopeite and two specimens of adamite.

Gallium lines were absent in the spectrograms obtained from ten specimens of calamine, two of smithsonite, one specimen of zincite, nine specimens of hydrozincite, two of goslarite, and one specimen each of hodgkinsonite, hardystonite and clinohedrite.