Frankdicksonite, BaF₂, a New Mineral from Nevada

Arthur S. Radtke,

*U.S. Geological Survey,
Menlo Park, California 94025*

and Gordon E. Brown

*Department of Geology, Stanford University,
Stanford, California 94305*

Abstract

Frankdicksonite, BaF_2, occurs in small quartz veinlets in the Carlin gold deposit, Eureka County, Nevada. It is of hydrothermal origin, and the only closely associated mineral is quartz. The mineral crystallizes with the fluorite structure, with space group $Fm3m$, $a = 6.1964 \pm 0.0002$ Å, and $V = 237.91 \pm 0.03$ Å³. Strongest X-ray powder diffraction lines and their relative intensities are 3.581 (100), 2.191 (56), and 1.870 (47). Chemical analysis by electron microprobe gave Ba 77.98, Sr 0.24, F 21.41, sum 99.63 wt percent; spectrographic analysis showed Si 0.02, Al <0.002, Fe <0.001, Mg 0.0015, Ca <0.001, Ba Major, Cu <0.0007, Sr 0.5. Formula unit $Ba_{0.995}Sr_{0.005}F_2$. $Z = 4$. Frankdicksonite occurs as small transparent euhedral crystals which are vitreous in luster, show $\{100\}$ growth faces, and perfect $\{111\}$ cleavage. Vickers hardness on $\{111\}$ cleavage faces varied from 88–94 kg/mm² and averaged 90 (10 determinations). Density measured is 4.89 ± 0.01, calculated density is 4.885 g cm⁻³. The mineral is isotropic with index of refraction $n = 1.475 \pm 0.001$ measured in sodium light at 20°C. Under electron bombardment the mineral shows a strong medium-blue cathodo-luminescence. The name frankdicksonite is in honor of Dr. Frank W. Dickson, Professor of Geochemistry, Stanford University.

Introduction

During a detailed geologic study of disseminated gold ores at the Carlin deposit, Eureka County, Nevada, samples of small quartz veinlets, collected in 1970 by Radtke for stable isotope and fluid inclusion studies, were found to contain small amounts of a mineral which resembled fluorite in appearance. Although fluorite is associated with quartz veinlets in the deposit, several samples collected at two locations in the East Pit area were found to contain small crystals of barium fluoride, BaF_2, spatially separated from fluorite.

The mineral is named in honor of our friend and colleague Dr. Frank W. Dickson, Professor of Geochemistry, Department of Geology, Stanford University, in recognition of his contributions in the fields of geology and geochemistry of low-temperature ore deposits. The mineral name, frankdicksonite, and designation as a new mineral were approved by the Commission of New Minerals and Mineral Names, IMA, in May 1974.

Synthetic BaF_2 was among the AX_2 compounds studied by Goldschmidt and co-workers between 1919 and 1920. Goldschmidt's discovery that AX_2 compounds with radius ratio (r_A/r_X) greater than 0.732 crystallize with the fluorite structure led to his now famous radius ratio principle of crystal chemistry (Goldschmidt, 1958). The radius ratio, $r_{Ba}/r_F = 1.08$, is well above this value, and synthetic BaF_2 crystallizes with the fluorite $A^{VIII}X^{IV}_2$ structure (see Davey, 1922; Brock, Oftedaland, and Pabst, 1929).

The possible existence of natural BaF_2 was suggested by Fleischer (1970). Because of the high solubility of BaF_2 relative to that of the corresponding Ba-sulfate, -phosphate, and -carbonate, Fleischer postulated that BaF_2 was not likely to occur associated with these phases. The mineral associations observed for frankdicksonite are consistent with Fleischer's suggestion.

Occurrence

Frankdicksonite occurs in quartz veinlets collected from two locations in the East Pit of the
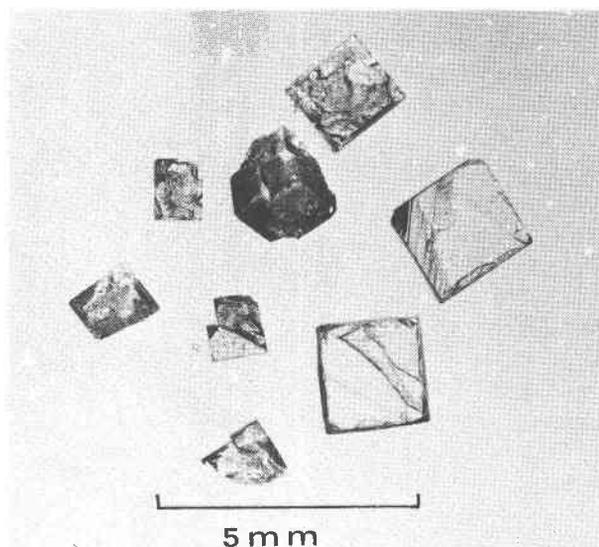
FIG. 1. Crystals of frankdicksonite from the Carlin gold deposit.

Carlin gold deposit. The first locality is on the 6420 bench, approximate elevation 6425 feet, mine coordinates 23,050 N, 20,100 E. At this location small shattered grains of frankdicksonite up to about 2 mm in diameter occur in a small quartz veinlet about 5 cm wide which follows a north-striking high-angle fault. No other minerals were identified in the quartz veinlet at this location; however, approximately 5 meters higher, small amounts of pyrite and gold are associated with the quartz. Wallrocks in this part of the deposit are silicified, carbonaceous, arsenic-rich, high-grade gold-bearing limestones of the Roberts Mountains Formation. The second location is also in the East Pit on the 6320 bench, approximate elevation 6325 feet, mine coordinates 23,800 N, 20,750 E. At this occurrence frankdicksonite crystals up to 4 mm in diameter are encased by quartz in a small veinlet which follows the contact between an altered dacite or latite dike and heavily silicified limestone of the Roberts Mountains Formation. Although no other primary hydrothermal minerals are associated with the quartz and frankdicksonite in this location, small amounts of fluorite are present about 5 meters lower in the veinlet. Details of the geology of the mine area and the two locations where frankdicksonite was found are included in the geologic map of the Carlin deposit (Radtke, 1973).

Physical and Optical Properties

Frankdicksonite from the Carlin mine occurs as small discrete euhedral crystals ranging from 0.1 mm to 4 mm in diameter. Representative grains of the mineral are shown in Figure 1. The crystals are transparent, have vitreous luster, and show only $\{100\}$ growth forms and perfect $\{111\}$ cleavage. Vickers hardness on $\{111\}$ cleavage faces determined with a Leitz hardness indentor using a 100-gram load ranged from 88 to 94 and averaged 90 kg/mm^2 (10 determinations), which falls close to 95 kg/mm^2 measured for synthetic BaF_2 by Chernevskaya (1966). This average converted to Mohs' hardness scale is approximately 2.5. The density measured with a Berman balance is 4.89 ± 0.01 based on three determinations at 20°C in CCl_4, which compares well with the calculated density of 4.885 g cm^{-3}, computed using the empirical formula unit reported in Table 2, $Z = 4$, and the measured cell edge.

The mineral is isotropic and the index of refraction, measured in sodium light by the immersion method at 20°C, is $n = 1.475 \pm 0.001$. This corresponds well with the value for the index of refraction of synthetic BaF_2 of $n = 1.474$ reported by Wulff and Heigl (1931). When exposed to a 15 kV electron beam on the electron microprobe, our samples of frankdicksonite showed a strong medium-blue cathodoluminescence.

X-ray Crystallography

Tentative identification of BaF_2 was accomplished using powder diffraction techniques; a comparison of d-spacings and intensity ratios between synthetic BaF_2 (XPDF Card #4-4052: Swanson and Tatge, 1953) and our sample shows no significant differences. The d-spacings and intensity ratios reported in Table 1 were obtained from slow, continuous scans (½° 2θ/min) on a Norelco diffractometer employing Ni-filtered Cu-radiation and a scintillation detector. Two separate powder mounts were prepared and run using semiconductor-grade silicon metal ($a = 5.43903 \pm 0.00008$ Å) and synthetic spinel (MgAl$_2$O$_4$; $a = 8.0828 \pm 0.0005$ Å) respectively, as internal standards. Twenty-two unique 2θ values from these scans (including $K\beta$ lines for the *400,331,531,711,* and *731* reflections and omitting the $K\alpha$ lines for the *444* and *640* reflections) were used in a least-squares cell parameter refinement which yielded $a = 6.1964 \pm 0.0002$ Å and $V = 237.91 \pm 0.03$ Å^3. As a further check of structure

type, several cleavage fragments were examined using the Precession technique and $MoK\alpha$ radiation. Zero and upper level photographs display systematic presences (hkl:h,k,l all odd or all even) and rotational symmetry consistent with the space group of fluorite, $Fm3m$, and intensities consistent with the fluorite structure (see Chernevskaya and Ananeva, 1966). Although the possibility of a non-cubic form of BaF_2 exists (Ott, 1926), our data are entirely consistent with cubic symmetry. The one perfect cleavage was confirmed as {111}. The observed Ba-F distance (2.683 Å) compares reasonably well with the sum of Shannon and Prewitt (1969) radii ($r_{Ba}VIII + r_F IV = 2.73$ Å). The difference in Mohs' hardness between fluorite (H = 4) and frankdicksonite (H $\cong$ 2.5) is consistent with the 0.319 Å difference between Ca-F and Ba-F bond lengths.

Chemical Composition

Several crystals of frankdicksonite were chemically analyzed using the Applied Research Laboratory EMX-SM electron microprobe in the Department of Geology, Stanford University. Qualitative spectral scans run on seven grains showed only barium, strontium, and fluorine to be present in detectable amounts. Three grains were chosen for quantitative analysis, and five spots on each grain were analyzed for these elements. Analytical con-

TABLE 2. Microprobe Analysis of Frankdicksonite

| Sample No. | Weight Percent | | | |
	Ba	Sr	F	Σ
1	77.93	0.23	21.38	99.54
2	78.12	0.26	21.34	99.72
3	77.90	0.24	21.51	99.65
Avg.	77.98	0.24	21.41	99.63

Empirical formula unit = $Ba_{0.995}Sr_{0.005}F_{1.998}$

Idealized formula unit = $Ba_{0.995}Sr_{0.005}F_2$

ditions used for the analyses were: (1) barium, $L\alpha$ characteristic line, LiF crystal, 15 kV, synthetic BaF_2 standard; (2) strontium, $L\alpha_1$ characteristic line, PET crystal, 15 kV, synthetic SrF_2 standard; and (3) fluorine, $K\alpha$ characteristic line, RAP crystal, 15 kV, synthetic BaF_2 standard. Results of the quantitative chemical analyses are shown in Table 2. Because of the similarity between the standards used and the mineral analyzed, no matrix correction factors were applied to the analyses.

Although calcium was not detected in the preliminary wavelength scans, a quantitative analysis for calcium was carried out using the $CaK\alpha$ characteristic line and the LiF crystal. Calcium was not detected and, if present in the mineral, is less than the calculated limit of detection for the microprobe (<0.015 wt percent).

Hand-picked fragments from several crystals were combined and analyzed for minor constituents using the standard semiquantitative spectrographic technique of the U.S. Geological Survey. Data from this analysis are presented in Table 3.

Empirical cell contents of $4[Ba_{0.995}Sr_{0.005}F_{1.998}]$ were determined by normalizing with respect to measured density and unit cell volume.

TABLE 1. Comparison of Powder Diffraction Data for Synthetic CaF_2, Synthetic BaF_2, and Frankdicksonite

| hkl | Synthetic CaF_2* | | Synthetic BaF_2** | | Frankdicksonite | | |
	d(Å)	I/I_1	d(Å)	I/I_1	d_{obs}(Å)	d_{calc}(Å)	I/I_1†
111	3.153	94	3.579	100	3.581	3.577	100
200	---	---	3.100	30	3.099	3.098	21
220	1.931	100	2.193	79	2.191	2.191	56
311	1.647	35	1.870	51	1.870	1.868	47
222	---	---	1.790	3	1.789	1.789	4
400	1.366	12	1.550	6	1.550	1.549	4
331	1.253	10	1.423	13	1.422	1.422	20
420	---	---	1.386	6	1.386	1.386	9
422	1.1150	16	1.266	14	1.266	1.265	20
511	1.0512	7	1.193	6	1.193	1.192	11
440	0.9657	5	1.096	2	1.095	1.095	3
531	0.9233	7	1.048	6	1.047	1.047	14
600	0.9105	1	1.033	<1	1.033	1.033	3
620	0.8637	9	0.9803	2	0.9799	0.9797	2
533	0.8330	3	0.9455	1	0.9449	0.9449	1
622	---	---	0.9347	3	0.9341	0.9341	3
444	---	---	0.8948	1	--- ††	---	---
711	---	---	0.8682	4	0.8677	0.8677	5
640	---	---	0.8599	1	--- ††	---	---
642	---	---	0.8285	5	0.8279	0.8280	5
731	---	---	0.8072	6	0.8067	0.8067	6

*XPDF Card No. 4-0864, Swanson and Tatge (1953).

**XPDF Card No. 4-0452, Swanson and Tatge (1953).

†Intensities measured by integration of peak areas.

††Not observed.

TABLE 3. Semiquantitative Spectrographic Analysis of Frankdicksonite

Element	Wt percent	Element	Wt percent
Si	0.02	Ca	<0.0015
Al	<0.002	Ba	>20
Fe	<0.001	Cu	<0.0007
Mg	0.0015	Sr	0.5

[Sought but not found: Ag, As, Au, B, Be, Bi , Cd, Ce, Co, Cr, Eu, Ga, Ge, Hf, In, K, La, Li, Mo, Mn, Na, Nb, Ni, P, Pb, Pd, Pt, Re, Sb, Sc, Sn, Ta, Te, Th, Ti, Tl, U, V, W, Y, Yb, Zn, Zr. Analyst: Chris Heropoulos, U.S. Geol. Survey, Menlo Park, Calif.]

Paragenesis

The chemical history of the Carlin gold deposit is complex, and a detailed description of the entire sequence is beyond the scope of this paper. The fact that a mineral with the apparent high solubility of frankdicksonite was deposited from the hydrothermal ore solution and survived being dissolved out merits a short discussion of the implications of its presence. The solubility of BaF_2 in water is much greater than that of CaF_2; values given by Weast (1970) for these compounds are 1.2 gm/kgm at 25°C and 0.017 gm/kgm at 26°C, respectively.

The ore solution responsible for the Carlin deposit transported significant amounts of barium in addition to silica, gold, pyrite, and a variety of other sulfides (Radtke and Scheiner, 1970). Most of the barium in the deposit is in the form of barite which apparently formed when barium (Ba^{2+}) in the ore solution combined with sulfate formed by the oxidation of sulfide minerals in the host rocks. There is no association between barite and frankdicksonite in the ore deposit. Locally, small veinlets of quartz formed where the ore solutions were trapped in open fractures or along contacts between limestone and igneous dikes. Although fluorite is scattered randomly throughout these veinlets, both localities where frankdicksonite is present have certain features in common; fluorite is absent and the contact of the wallrock against the veinlets lacks calcite and dolomite. In one location the limestone against the veinlets has been replaced inwardly by silica to form jasperoid; in the other location, the limestone on one side shows this same feature and the other wall of the veinlet is an igneous dike. Therefore, we assume that where frankdicksonite formed, the solution was low in calcium and saturated with respect to BaF_2, and that no additional calcium reached the site because the wallrock either lacked calcium or was armored by jasperoid. These assumptions are consistent with findings that frankdicksonite contains less than 15 ppm calcium (Table 3).

All the grains of frankdicksonite which were found were completely encased in quartz. This feature was apparently responsible for the persistence of the mineral in spite of its high solubility. Field relationships indicate these small quartz veinlets which contain small scattered amounts of pyrite, gold, and fluorite, and locally contain frankdicksonite, formed during the main phase of hydrothermal activity.

References

BROCH, E., I. OFTEDALAND, AND A. PABST (1929) Neubestimmung der Gitterkonstanten von KF, CsCl, and BaF₂. Z. Physik Chem. Leipzig, **B3**, 209–214.

CHERNEVSKAYA, E. G. (1966) Hardness of mixed single crystals of CaF₂ type. Optiko-Mekhan. Prom. **33**, 51–52.

———, AND G. V. ANANEVA (1966) Structure of CaF₂, SrF₂, and BaF₂ two component mixed crystals. Fiz. Tverd. Tela, **8**, 216–219.

DAVEY, W. P. (1922) The absolute sizes of certain monovalent and bivalent ions. Phys. Rev. **19**, 248–252.

FLEISCHER, MICHAEL (1970) Some possible new minerals not yet found. Mineral. Rec. Fall 1970, 121–123.

GOLDSCHMIDT, V. M. (1958) Geochemistry. Oxford Press, England, 730 pp.

OTT, H. (1926) Die Strukturen von MnO, MnS, AgF, NiS, SnI₄, SrCl₂, BaF₂; Präzisionsmessungen einiger Alkalihalogenide. Z. Kristallogr. **63**, 222–230.

RADTKE, A. S. (1973) Preliminary geologic map of the Carlin gold mine, Eureka County, Nevada. U.S. Geol. Surv. Misc. Field Studies Map, **MF-534**, Scale 1:4800.

———, AND B. J. SCHEINER (1970) Studies of hydrothermal gold deposition (I). Carlin gold deposit, Nevada: The role of carbonaceous materials in gold deposition. Econ. Geol. **65**, 87–102.

SHANNON, R. D., AND C. T. PREWITT (1969) Effective ionic radii in oxides and fluorides. Acta Crystallogr. **B25**, 925–946.

SWANSON, H. E., AND E. TATGE (1953) Standard X-ray diffraction powder patterns. Nat. Bur. Stand. Circ. **539**, **1**, 95 pp.

WEAST, ROBERT C. (1970) Handbook of Chemistry and Physics, 51st Edition, 1970–1971, Section B. Chemical Rubber Co., Cleveland, Ohio, 245 p.

WULFF, PETER, AND ALOIS HEIGL (1931) Refraktometrische Messungen auf Kristallen. Z. Kristallogr. **77**, 84–121.