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CONSTRAINTS ON THE GENESIS OF YELLOW FLUORITE IN HYDROTHERMAL BARITE–FLUORITE VEINS OF THE ERZGEBIRGE, EASTERN GERMANY: EVIDENCE FROM OPTICAL ABSORPTION SPECTROSCOPY, RARE-EARTH-ELEMENT DATA, AND FLUID-INCLUSION INVESTIGATIONS

Michael TRINKLER

Alpha Geoservice, Talstraße 31, 09627 Bobritzsch, OT Niederbobritzsch, Germany

Thomas MONECKE[§]

Geological Survey of Canada, Natural Resources Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada

Rainer THOMAS

GeoForschungsZentrum Potsdam, Telegrafenberg B120, D–14473 Potsdam, Germany

Abstract

The optical absorption spectra of yellow fluorite crystals from hydrothermal barite–fluorite veins of the Erzgebirge, eastern Germany, are characterized by a broad absorption band with a peak at 433 nm that shows a subtle vibronic structure. The optical absorption behavior of the crystals is attributed to the presence of O_3^- centers in the structure; the O_3 molecules were incorporated during crystallization. The presence of the O_3^- centers implies that a very specific chemical reaction must have taken place during crystallization, under particular physicochemical conditions. Thermal stability constraints of the yellow coloration suggest that the fluorite formed at low to moderate temperatures (below 250 to 400°C), which agrees with homogenization temperatures determined on fluid inclusions entrapped in the crystals (below 150°C). The crystals have a middle-rare-earth-element-enriched signature. The depletion of the light rare-earth elements in the fluorite-forming fluids was caused by the precipitation of Ce-rich phases prior to the formation of fluorite, whereas the incorporation of the heavy rare-earth elements into fluorite was suppressed by the formation of carbonate complexes in the hydrothermal fluids. Fluid-inclusion data show that fluorite formation occurred in a comparably stagnant environment typified by the mixing of fluids of different salinity and composition, namely a highly saline, $CaCl_2$- and NaCl-rich brine that contained some Na_2SO_4, Na_2CO_3, $NaHCO_3$, $CaSO_4$, and $SrSO_4$, as well as a NaCl-dominated fluid of distinctly lower salinity. Fluorite precipitation from the cooling hydrothermal fluids occurred in a relatively reducing environment under near-neutral conditions. We propose a chemical reaction that may have led to the formation of O_3^- centers in the structure, and that may also explain the formation of the yellow coloration of fluorite in other hydrothermal systems. In particular, fluorite precipitation in some Mississippi-Valley-type deposits apparently occurred under very similar environmental conditions.

Keywords: optical absorption spectroscopy, rare-earth elements, fluid-inclusion data, fluorite, hydrothermal vein deposits, Erzgebirge, Germany.

Sommaire

Les spectres d'absorption optique de cristaux de fluorite jaune provenant de veines hydrothermales à barite–fluorite dans la chaîne Erzgebirge, dans l'est de l'Allemagne, montrent une absorption floue ayant un maximum à 433 nm et une structure vibronique subtile. Le comportement en absorption optique des cristaux serait attribuable à la présence de centres O_3^- dans la structure; les molécules O_3 auraient été incorporées lors de la cristallisation. La présence de centres O_3^- implique qu'une réaction très spécifique doit avoir eu lieu lors de la formation, sous conditions physicochimiques particulières. Les contraintes de stabilité thermique de la coloration jaune font penser que la fluorite s'est formée à températures faibles ou modérées (sous 250 à 400°C), ce qui concorde avec les températures d'homogénéisation des inclusions fluides piégées dans les cristaux (inférieures à 150°C). Les cristaux font preuve d'enrichissement en terres rares intermédiaires. L'apauvrissement des terres rares légères dans la phase fluide formant la fluorite aurait été causé par la précipitation précoce de phases riches en Ce avant la formation de la fluorite, tandis que l'incorporation des terres rares lourdes était due à la formation de complexes carbonatés dans la phase fluide.

[§] *E-mail address*: tmonecke@nrcan.gc.ca

D'après les données sur les inclusions fluides, la fluorite se serait formée dans un milieu relativement stagnant où a pu se faire un mélange de phases fluides de salinité et de composition différentes; un était fortement salin, une saumure riche en $CaCl_2$ et NaCl contenant aussi Na_2SO_4, Na_2CO_3, $NaHCO_3$, $CaSO_4$, et $SrSO_4$, et l'autre, un fluide contenant NaCl mais de plus faible salinité. La précipitation de la fluorite à partir de la phase fluide en se refroidissant a eu lieu dans un mileu relativement réducteur et près de la neutralité. Nous proposons une réaction chimique qui pourrait expliquer la formation des centres O_3^- dans la structure, et aussi de la coloration jaune de la fluorite d'autres systèmes hydrothermaux. En particulier, la précipitation de la fluorite à certains gisements de type Mississippi Valley se serait déroulée dans un milieu très semblable.

(Traduit par la Rédaction)

Mots-clés: spectroscopie de l'absorption optique, terres rares, données sur les inclusions fluides, fluorite, gisements en veines hydrothermales, Erzgebirge, Allemagne.

INTRODUCTION

Naturally occurring fluorite exhibits a wide range of colors. Particularly common are pale green, green, yellow, bluish green, grayish, violet, bluish violet, brown, and rose crystals. It has been known for several decades that these different colors are related to the defect structure and trace-element content of fluorite (Przibram 1952, 1953, Bill *et al.* 1967, Braithwaite *et al.* 1973, Leckebusch *et al.* 1974). Several authors have established that the physicochemical environment of fluorite formation represents an important control on the real structural properties of natural fluorite and, therefore, ultimately dictates the color of this mineral (Krasilshchykova *et al.* 1974, Bill & Calas 1978, Trinkler 1997). In particular, the optical absorption and trace-element contents of rose, brown, pale green, green, and violet fluorite samples have been studied extensively to constrain the origin and evolution of the mineralizing hydrothermal fluids in granite-related rare-metal deposits (Krasilshchykova *et al.* 1986, Trinkler *et al.* 1993, Höhndorf *et al.* 1994, Morozov *et al.* 1996, Monecke *et al.* 2000, 2002, Kempe *et al.* 2002).

In contrast to other color varieties, little currently is known on the physicochemical conditions required for the formation of yellow fluorite. Despite several attempts, the yellow variety of fluorite has not yet been successfully synthesized in experimental studies (Bill & Mareda 1975, Bill 1979, 1982, pers. commun., 2004). The occurrence of yellow crystals in nature is restricted to only a few types of hydrothermal mineralization, implying a direct genetic control on the deposition of this color variety. Yellow fluorite is particularly common in post-Variscan hydrothermal barite–fluorite veins occurring in the Variscan orogenic belt of central and western Europe. For instance, this type of fluorite has been described from the Massif Central in southern France (Bill & Calas 1978, Hubert *et al.* 1982, Lhégu *et al.* 1982, Jébrak *et al.* 1985, Munoz *et al.* 1999) and the Erzgebirge in eastern Germany (Baumann 1994a, Bau & Dulski 1995, Kuschka 1996, 1997). In addition to hydrothermal barite–fluorite veins, yellow fluorite is an abundant gangue mineral in some Mississippi-Valley-type (MVT) deposits. The occurrence of this color variety has, for instance, been documented from deposits of the Pennine Orefield in England (Dunham 1937, 1983, Sawkins 1966, Bau *et al.* 2003), the Illinois–Kentucky fluorspar district in the United States (Hall & Friedman 1963, Cunningham & Heyl 1980, Heyl 1983, Richardson & Pinckney 1984, Spry *et al.* 1990, Chesley *et al.* 1994, Spry & Fuhrmann 1994), and the MVT deposits of northwestern Ohio in the United States (Carlson 1983).

In the present contribution, we attempt to constrain the physicochemical environment required for the formation of yellow fluorite by combining the results of optical absorption spectroscopic investigations and rare-earth-element (REE) analyses with fluid-inclusion data. We focus on fluorite crystals collected from hydrothermal barite–fluorite veins occurring in the Erzgebirge, eastern Germany. We show that all samples investigated share certain spectral and trace-element characteristics that are directly related to the growth conditions of yellow fluorite in the hydrothermal environment. On the basis of these results, we propose a mechanism that may account for the yellow coloration of the fluorite crystals, and discuss the implications for the understanding of ore-forming processes involving the deposition of yellow fluorite.

GEOLOGICAL SETTING

The Erzgebirge is exposed at the border region between Saxony and Czech Republic, at the northwestern margin of the Bohemian Massif. The Erzgebirge represents a NE–SW-trending antiformal structure that forms part of the Saxothuringian Zone of the Variscan fold belt. It comprises a core of gneiss and mica schist that is surrounded by a mantle of phyllite and slate (Fig. 1). The metamorphic basement rocks of the Erzgebirge have Proterozoic to Paleozoic protolith ages. Metamorphism occurred in the early Carboniferous as a consequence of crustal thickening during the early Variscan orogeny (Kröner & Willner 1998, Mingram 1998, Tichomirowa *et al.* 2001).

In the Late Carboniferous and Early Permian, rhyodacitic to rhyolitic lavas and lamprophyric dikes were emplaced. However, these rocks are subordinate in volume compared to the large masses of granite that were intruded in the crust at shallow levels, forming multiphase plutons of various sizes and compositions. The Erzgebirge granites appear to have intruded the surrounding country-rock during two main events (Breiter *et al.* 1991, 1999, Tischendorf & Förster 1994). Radiometric dating suggests that these events occurred at 330 Ma and 280 to 290 Ma, respectively (Nasdala *et al.* 1998, Kempe *et al.* 1999b, Kempe 2003). The emplacement of the younger and compositionally more evolved granites was associated with the formation of world-class Sn–W and hydrothermal U deposits (Štemprok & Šulcek 1969, Schuppan *et al.* 1994, Štemprok *et al.* 1994, Baumann *et al.* 2000).

Subsequent to the emplacement of these younger granites, a period of hydrothermal activity resulted in the formation of complex systems of veins in the Erzgebirge and adjacent parts of the Variscan fold belt. The hydrothermal veins that formed during this period have been traditionally referred to as late Variscan in origin. The late Variscan hydrothermal vein-type deposits have been mined extensively, yielding a significant production of precious and base metals (Ag, Pb–Zn–Cu) over the centuries. A subsequent period of hydrothermal activity during the Mesozoic to Cenozoic resulted in the formation of post-Variscan systems of veins. These veins represent a highly specialized mineralization that possesses anomalous concentrations of certain combinations of elements (*e.g.*, Ba–Sr, Bi–Co–Ni–As–Ag, Ge–Hg, Fe–Mn). The relative age relationships and mineral associations of the late and post-Variscan systems of veins have been studied by numerous authors, including

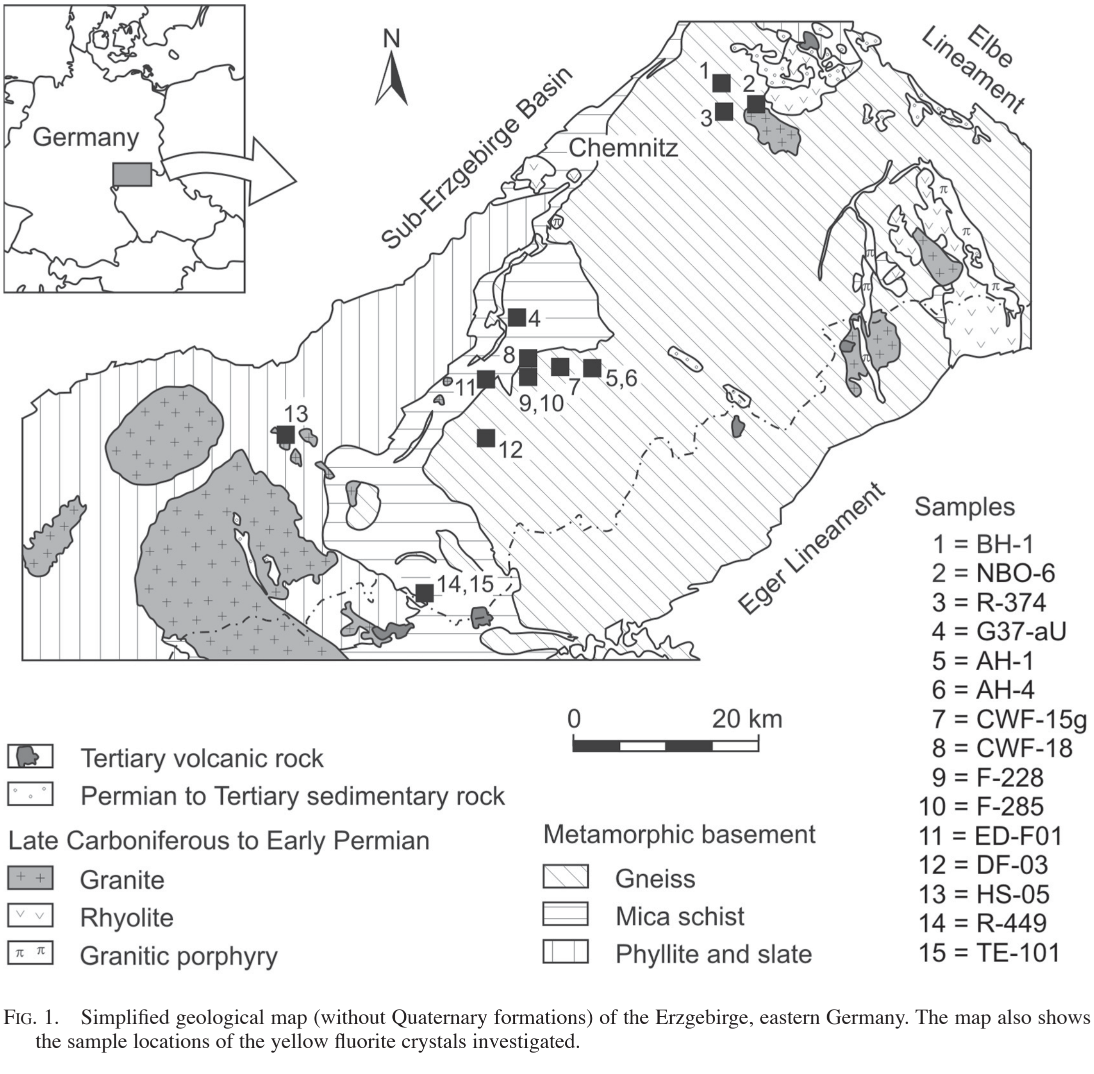

FIG. 1. Simplified geological map (without Quaternary formations) of the Erzgebirge, eastern Germany. The map also shows the sample locations of the yellow fluorite crystals investigated.

Seifert *et al.* (1992), Baumann (1994a, b), Kuschka (1996, 1997), and Baumann *et al.* (2000).

The yellow fluorite samples investigated in the present study were collected from post-Variscan hydrothermal veins that largely consist of barite, fluorite, and some quartz. Careful textural investigations of the hydrothermal veins reveal that the white to slightly reddish barite was deposited typically prior to the fluorite, whereas the formation of quartz postdates the precipitation of the fluorite. The hydrothermal barite–fluorite veins also contain sulfides that appear to have precipitated essentially contemporaneously with, and slightly after, the barite (Kuschka 1996, 1997). However, yellow fluorite also hosts small inclusions of sulfides such as pyrite, chalcopyrite, galena, and emplectite (Reissmann 1993, Trinkler 1997). Although carbonates are commonly absent in the hydrothermal barite–fluorite veins, younger carbonates are locally present.

MATERIALS AND METHODS

The present study is based on fifteen samples of yellow fluorite that were collected from the major occurrences of hydrothermal fluorite–barite veins in the Erzgebirge (Table 1). These occurrences belong to different mining districts in the eastern, central, and western Erzgebirge (Fig. 1). Based on this selection of samples, it should be possible to identify optical absorption, trace-element, and fluid-inclusion attributes that are universal for yellow fluorite from the Erzgebirge.

Initially, the yellow fluorite samples were crushed, and transparent cleavage splinters lacking optical heterogeneity were hand-picked under a binocular microscope (20× magnification). Fragments that were approximately 2 to 5 mm in thickness were selected for the spectroscopic investigations. The cleavage splinters were mounted into equidimensional apertures that were cut into black cardboard paper. Optical absorption spectra of the yellow fluorite fragments were then recorded on a Carl Zeiss Jena SPECORD M 400 at Alpha Geoservice. The spectra were collected at room temperature in the UV–VIS region (200 to 900 nm) using a step width of 1.0 nm, a measurement time of 2 nm/s, and a slit width of 1 nm. Although the cleavage surfaces of the fragments used were mostly parallel, the cleavage splinters were placed immediately in front of the optical window of the photomultiplier to minimize intensity loss by optical scattering of the samples. The investigations were conducted at conditions similar to those described by Trinkler *et al.* (1993).

The REE concentrations of the samples were determined by inductively coupled plasma – mass spectrometry (ICP–MS) at the GeoForschungsZentrum Potsdam. The fluorite samples were hand-picked under a binocular microscope (20× magnification) and then powdered by hand in an agate mortar. The powders (~50 to 250 mg) were decomposed with 10 mL of 8% $AlCl_3$ solution for 2 h at 70°C in a shaking water-bath. After cooling, the sample solutions were filtered into 50 mL volumetric flasks and made up to a volume with 0.5 M HCl to stabilize the REE in solution (Robinson *et al.* 1999, Yu *et al.* 2000, Dulski 2001). Before analysis, the solutions were diluted 1:10 (resulting in a final dilution-factor of 2000), and Ru and Re were added as internal standards to compensate for instrumental drift. The ICP–MS analyses were carried out by external calibration using a Perkin–Elmer – Sciex Elan Model 5000A. The random errors of the analytical method were determined by repeated decomposition and analysis of

TABLE 1. SAMPLE LOCATIONS AND DESCRIPTIONS OF YELLOW FLUORITE CRYSTALS COLLECTED IN THE ERZGEBIRGE, EASTERN GERMANY

Sample	Sample location	Fluorite color	Sulfide incl.
BH-1	Beihilfe mine, Halsbrücke, near Freiberg	Yellow	Pyrite, galena
NBO-6	Granite quarry at Naundorf, near Freiberg	Pale yellow to yellowish	Pyrite
R-374	Reiche Zeche mine, Freiberg	Yellowish	Pyrite, galena
G37-aU	Grießbach, near Zschopau	Yellow	Chalcopyrite
AH-1	Vater Abraham shaft, Lauta, near Marienberg	Yellow	Chalcopyrite
AH-4	Vater Abraham shaft, Lauta, near Marienberg	Dark yellow	Chalcopyrite
CWF-15g	Palmbaum shaft, Gehringswalde near Marienberg	Yellow	Pyrite
CWF-18	Barite adit at Brandbach, near Warmbad, Wolkenstein	Yellow	-
F-228	Armer Leute Bergfreund shaft, Zeisigstein, near Wolkenstein	Yellow	Pyrite
F-285	Armer Leute Bergfreund shaft, Zeisigstein, near Wolkenstein	Yellow	Chalcopyrite
ED-F01	Ehrenfriedersdorf Sn mine, Ehrenfriedersdorf	Light yellow to pale yellow	Chalcopyrite
DF-03	Gneiss quarry at Dörfel, near Annaberg	Light yellow	Pyrite
HS-05	Shaft 38, Schlema, near Schneeberg	Honey yellow	-
R-449	Pöhla-Tellerhäuser U mine, Pöhla, near Schwarzenberg	Yellow	Chalcopyrite
TE-101	Pöhla-Tellerhäuser U mine, Pöhla, near Schwarzenberg	Light yellow	-

an in-house fluorite reference material. The precision was found to be usually better than 5% for all elements analyzed. The analytical accuracy was checked by comparing data obtained on the same in-house reference material dissolved with HF + $HClO_4$ and analyzed by ICP–MS and inductively coupled plasma – atomic emission spectroscopy (ICP–AES) in other laboratories. The results agree well; deviations by more than 5% have been observed for some REE, however (Bau & Dulski 1995). Additional details on the analytical method used are given by Dulski (1994).

Small thick-section chips with a thickness of 300 μm and doubly polished with 0.25 μm diamond spray were prepared from the fluorite samples for the fluid-inclusion investigations. Microthermometric measurements on primary fluid inclusions were conducted using a calibrated LINKAM THMS 600 heating and freezing stage, together with a TMS92 temperature programmer and a LNP2 cooling system mounted on an Olympus microscope (600× magnification using a ULWD CD Plan 40/0.5 objective). The stage was calibrated with synthetic fluid inclusions of known density and composition and various melting-point standards like indium, tin, lead, and potassium dichromate. All measurements were performed under argon. The standard deviation of the measured temperature depends on the absolute temperature and is in every case better than ±2.5°C for temperatures exceeding 100°C and ≤0.2°C for cryometric measurements at temperatures below 20°C. The computer package FLUIDS by Bakker (2003) and Bakker & Brown (2003) was used for the analysis of the fluid-inclusion data and for the calculation of properties of the bulk fluid.

Observed daughter and gas phases contained in the fluid inclusions were determined on the basis of diagnostic Raman bands. Confocal Raman spectroscopy was conducted at the GeoForschungsZentrum Potsdam using a Dilor XY Laser Raman Triple 800 mm spectrometer equipped with an Olympus optical microscope and a long-working-distance 80× objective. The 488 nm line of a Coherent Innova 70–3 Argon laser (power of 450 mW) was used for sample excitation. The confocal pinhole size was 150 μm in diameter. The spectra were recorded with a Peltier-cooled CCD detector. Each spectrum was collected five times with a counting time of 50 s for each accumulation.

RESULTS

The optical absorption spectra of the yellow fluorite samples are shown in Figure 2. The spectroscopic investigations revealed that the fluorite crystals are typified by a strong absorption band in the ultraviolet region. The position of the band varies among the samples, but is typically located at 200 to 230 nm. Figure 2 illustrates that some samples are typified by an additional weak absorption at 306 nm. In the visible region, the fluorite samples show a strong absorption band centered at 433 nm that possesses a distinct vibronic structure. Several spectra exhibit an additional low-energy band near 578 nm.

The REE concentrations of the samples are compiled in Table 2. The corresponding normalized REE patterns are given in Figure 3. Normalization was performed to the chondrite data given by Anders & Grevesse (1989). The patterns of the yellow fluorite samples investigated exhibit a depletion of the light rare-earth elements (LREE). In the samples from the Freiberg mining district, eastern Erzgebirge, the normalized concentrations of the LREE decrease from La to Nd and increase from Nd to Gd (Fig. 3a). In contrast, the normalized concentrations of the LREE in the samples from the central and western Erzgebirge increase steadily from La to Gd. The ratio La_n/Gd_n of the samples from the Freiberg mining district varies between 0.5 and 0.8, whereas the other samples show a value ranging from 0.1 to 0.6. All normalized REE patterns are enriched in the middle rare-earth elements (MREE). Maximum normalized contents can be observed for Gd or Tb. The heavy rare-earth elements (HREE) are strongly depleted in all samples, and their normalized concentrations define a straight-line relationship (Fig. 3). The ratio Gd_n/Yb_n varies between 2.1 and 10.1.

The normalized REE patterns of the fluorite samples lack an analytically significant Ce anomaly (Fig. 3). The calculated Ce/Ce^* values range from only 0.9 to 1.0. In contrast, Eu commonly plots away from the trend defined by the neighboring REE. We found a positive Eu anomaly for the samples collected in the Freiberg mining district, eastern Erzgebirge (Fig. 3a). The Eu/Eu^* value in these samples ranges from 1.3 to 1.8. Samples collected from other parts of the Erzgebirge exhibit a negative Eu anomaly, with a Eu/Eu^* value between 0.6 and 1.0 (Table 2).

The samples of yellow fluorite mostly contain two-phase liquid-rich fluid inclusions with an apparently consistent ratio of liquid to vapor. In some cases, the inclusions contain small crystals of daughter minerals, mostly calcite, anhydrite, and celestine. Eutectic melting temperatures around –52°C suggest that the entrapped highly saline liquid can be modeled by the system H_2O–NaCl–$CaCl_2$. During heating of these inclusions, the composition of the inclusion system develops along the cotectic curve separating the ice + liquid and hydrohalite + liquid fields as hydrohalite breaks down and ice melts. In Table 3, we give the composition of the inclusion liquid as calculated from the melting temperatures (T_m hydrohalite and T_m ice). We also list the homogenization temperatures and the data on the low-temperature phase behavior of the model system H_2O–NaCl–$CaCl_2$. The temperatures of homogenization represent minimum temperatures of entrapment. However, because it can be assumed that the fluorite crystallized in a quasi-open system, these temperatures are regarded to represent the temperatures of fluorite formation.

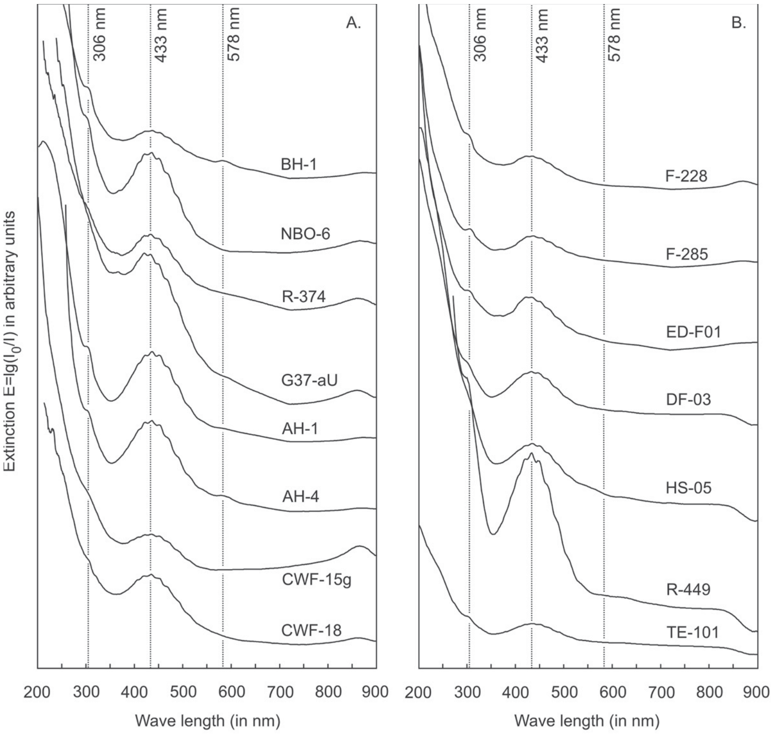

FIG. 2. Optical absorption spectra in the UV–VIS region (200 to 900 nm) of the yellow fluorite crystals. The spectra are normalized to a sample thickness of one millimeter. Note the subtle vibronic structure of the band centered at 433 nm.

DISCUSSION

Optical absorption spectroscopy revealed that all crystals of yellow fluorite investigated are typified by a broad absorption band centered at 433 nm. Bill (1982) has shown that this absorption band is caused by the presence of O_3^- centers in the structure; they substitute for pairs of neighboring F^- ions. The optical absorption spectra collected in the present study (Fig. 2) also show the vibronic structure documented by previous authors (Bill & von der Osten 1976, Mitra 1981, Bill 1982). In addition to the O_3^- center, the yellow fluorite crystals from the hydrothermal barite–fluorite veins seem to contain O_2^- centers, known to produce the optical absorption band at 230 nm (Bill & Calas 1978, Bill 1979).

Bill & Mareda (1975) as well as Bill (1979) showed that the incorporation of O_3^- and O_2^- molecular ions into the structure of yellow fluorite is typically accompanied by substitutional Na^+, presumably providing charge compensation for the monovalent molecular ions. Bulk samples of yellow fluorite indeed contain elevated contents of Na when compared to rose, green, or blue color varieties (Bill & Mareda 1975, Bill & Calas 1978, Möller & Dulski 1985). Although the Na content of the fluorite crystals from the hydrothermal barite–fluorite veins of the Erzgebirge was not determined in the present study, we can assume that Na^+ required for the charge balance of O_3^- and O_2^- was readily accessible during fluorite precipitation. The fluid-inclusion data collected as a part of the present study, as well as the results of previous investigations (Thomas 1979, Thomas & Tischendorf 1988, Klemm 1994a, b) indicate that the fluorite-forming hydrothermal fluids were, as a rule, highly saline (> 10 equiv. wt.% NaCl) and dominated by $CaCl_2$ and NaCl, with minor Na_2SO_4, Na_2CO_3, $NaHCO_3$, $CaSO_4$, and $SrSO_4$.

Experimental investigations have established that the yellow color related to the O_3^- center is reversibly destroyed by heating to temperatures of about 250°C, presumably due to a change in the valence state of the yellow center, whereas irreversible destruction is achieved at temperatures exceeding 350 to 400°C (Bill *et al.* 1967, Calas *et al.* 1972, Mitra 1981, Bill 1982, pers. commun., 2004, Trinkler 1997). Assuming that the O_3^- center is primary (see below), we must conclude that fluorite crystallization in the hydrothermal barite–fluorite veins occurred at temperatures below the

TABLE 2. REE AND Y DATA ON YELLOW FLUORITE CRYSTALS FROM HYDROTHERMAL BARITE–FLUORITE VEINS FROM THE ERZGEBIRGE, EASTERN GERMANY

	BH-1	NBO-06	R-374	G-37aU	AH-1	AH-4	CWF-15g	CWF-18	F-228	F-285	ED-F01	DF-03	HS-05	R-449	TE-101
Y ppm	337	271	196	185	157	210	173	173	195	130	89.8	213	177	176	154
La	16.4	14.2	16.6	5.41	6.79	5.77	1.33	12.2	14.3	2.92	1.12	6.59	4.09	4.02	2.51
Ce	39.8	25.7	35.5	17.2	26.2	20.3	4.48	32.8	39.6	12.6	4.86	16.9	9.92	14.6	9.50
Pr	6.20	3.48	5.04	3.07	5.36	4.20	0.96	5.55	6.59	2.98	1.23	2.85	1.64	2.85	2.15
Nd	30.7	16.0	26.0	18.3	32.0	25.7	6.99	29.8	33.5	20.8	9.43	15.1	10.2	17.3	14.2
Sm	15.0	9.22	11.1	10.2	17.5	15.6	7.22	12.8	16.7	18.3	8.72	8.65	9.19	10.7	12.5
Eu	8.68	7.49	6.00	4.55	5.25	4.37	2.51	3.28	4.54	4.07	1.97	2.34	4.50	3.03	3.36
Gd	25.9	18.4	18.3	17.7	22.1	25.6	15.5	18.7	24.4	26.6	13.6	17.3	22.0	20.1	25.1
Tb	5.10	3.57	2.00	2.95	3.11	3.38	2.87	3.23	4.64	3.76	1.77	3.16	2.86	3.30	3.84
Dy	28.0	20.8	14.8	15.2	13.0	14.9	14.4	16.2	22.4	15.4	7.91	18.2	13.7	16.7	17.4
Ho	4.73	3.67	2.60	2.58	1.85	2.18	2.14	2.50	3.34	2.13	1.14	3.26	2.16	2.53	2.45
Er	12.1	9.23	6.40	6.23	3.96	4.74	4.88	5.65	7.76	4.92	2.54	7.81	4.20	5.84	5.07
Tm	1.57	1.16	0.92	0.66	0.43	0.54	0.55	0.62	0.91	0.54	0.30	0.92	0.42	0.70	0.58
Yb	10.1	6.36	4.85	3.85	2.44	2.73	2.92	3.27	5.53	3.06	1.64	4.88	1.80	4.18	3.07
Lu	1.21	0.74	0.61	0.44	0.28	0.34	0.33	0.37	0.64	0.35	0.19	0.61	0.19	0.50	0.38
La_n/Gd_n	0.53	0.65	0.76	0.26	0.26	0.19	0.07	0.55	0.49	0.09	0.07	0.32	0.16	0.17	0.08
Gd_n/Yb_n	2.12	2.39	3.12	3.80	7.49	7.75	4.39	4.73	3.65	7.19	6.85	2.93	10.10	3.97	6.76
Ce/Ce^*	0.95	0.88	0.93	1.01	1.04	0.99	0.95	0.96	0.98	1.02	0.99	0.93	0.92	1.03	0.98
Eu/Eu^*	1.34	1.75	1.28	1.03	0.81	0.66	0.72	0.64	0.68	0.56	0.55	0.58	0.96	0.63	0.58

Notes: The normalization is based on the C1 chondrite data given by Anders & Grevesse (1989). The Ce anomaly is defined as $Ce/Ce^* = Ce_n / \sqrt{La_n \times Pr_n}$, and the Eu anomaly is given by $Eu/Eu^* = Eu_n / \sqrt{Sm_n \times Gd_n}$.

TABLE 3. FLUID-INCLUSION DATA OF YELLOW FLUORITE CRYSTALS FROM HYDROTHERMAL BARITE–FLUORITE VEINS OF THE ERZGEBIRGE, EASTERN GERMANY

Sample	T_h °C	*n*	T_m Hhl °C	T_m ice °C	NaCl wt.%	$CaCl_2$ wt.%	Na/Ca	Daughter phases, vapor composition (Raman spectroscopy)
BH-1	119 ± 1	10	-25.1	-22.2	20.6	3.1	0.94	calcite, celestine, anhydrite (<1 vol.%); vapor bubble: $X(CO_2) \leq 0.002$, $X(N_2) = 0.819$, $X(CH_4) = 0.179$ (on water-free basis)
NBO-6	125 ± 1	10	-27.3	-17.2	7.8	11.7	0.09	
R-374	121 ± 1	10	-47.3	-22.3	1.5	20.3	0.01	
G37-aU	88 ± 1	10	-20.7	-7.7	11.5	0.0	-	
AH-1	134 ± 3	25	-45.4	-8.6	1.0	11.8	0.01	hematite, CO_2 in vapor bubble
AH-4	106 ± 5	10	-45.4	-11.6	1.2	14.2	0.01	
CWF-15g	99 ± 7	9	-46.7	-8.2	0.9	11.5	0.01	
	129 ± 3	10	-46.7	-8.7	0.9	12.0	0.01	
CWF-18	≤ 40		n.d.	n.d.	-	-	-	
F-228	111 ± 3	15	-29.7	-21.7	6.1	15.9	0.05	celestine (≤1 vol.%), anhydrite (≤1 vol.%); CO_2 in vapor bubble
F-285	90 ± 2	10	-29.9	-11.4	4.1	11.2	0.05	CO_2 in vapor bubble
ED-F01	114 ± 3	15	-40.6	-12.0	1.8	14.0	0.02	vapor bubble: $X(CO_2) = 0.557$, $X(N_2) = 0.407$, $X(CH_4) = 0.036$ (on water-free basis)
DF-03	112 ± 3	10	-45.3	-14.1	1.4	15.9	0.01	
HS-05	no were measurements possible							
R-449	129 ± 7	15	-35.2	-26.6	4.1	20.0	0.03	
TE-101	102 ± 1	11	-46.0	-23.0	1.7	20.5	0.01	

Notes: T_h temperature of homogenization (to the liquid phase); T_m temperature of ice melting (hydrohalite, ice); n.d.: not detected; n: number of inclusions studied; Hhl: hydrohalite.

stability limit of the yellow coloration. Primary two-phase fluid inclusions contained in the yellow fluorite crystals from the hydrothermal barite–fluorite veins of the Erzgebirge homogenize at temperatures below 150°C, indicating that the yellow fluorite may have formed at temperatures significantly below the stability limit of the yellow coloration.

The presence of sulfide inclusions in yellow fluorite crystals (Reissmann 1993, Trinkler 1997) is indicative for the presence of sulfide or polysulfide species in the fluorite-forming hydrothermal fluids. Measurements with a sulfide-sensitive electrode confirmed that S^{2-} is indeed a significant component of fluid inclusions entrapped in quartz of the hydrothermal barite–fluorite veins of the Erzgebirge (Klemm 1994b). The attachment of primary fluid inclusions to galena crystals located on growth zones in yellow fluorite crystals from Halsbrücke in the Freiberg mining district represents a further indication for the abundant presence of sulfide species in the hydrothermal fluids (R. Thomas, unpubl. data). These observations collectively indicate that fluorite crystallization took place in a relatively reducing environment.

Because the physicochemical environment of fluorite formation represents a prime control on the REE geochemistry of this mineral (Marchand *et al*. 1976, Grappin *et al*. 1979), additional constraints on the origin of the yellow fluorite can be derived from the trace-element data. Figure 4 shows the concentrations of Ce plotted against the Gd contents of a wide range of fluorite samples having different colors. Owing to the pronounced enrichment of the MREE, the samples of yellow fluorite investigated here have Ce/Gd values below unity and plot in the lower portion of the diagram. The plot illustrates that the yellow fluorite crystals exhibit only limited compositional variations, implying that a very specific process of REE fractionation took place during the formation of the hydrothermal barite–fluorite veins.

Similar MREE-enriched patterns have also been reported for mineral precipitates from hydrothermal systems that lack fluorite as a major gangue mineral

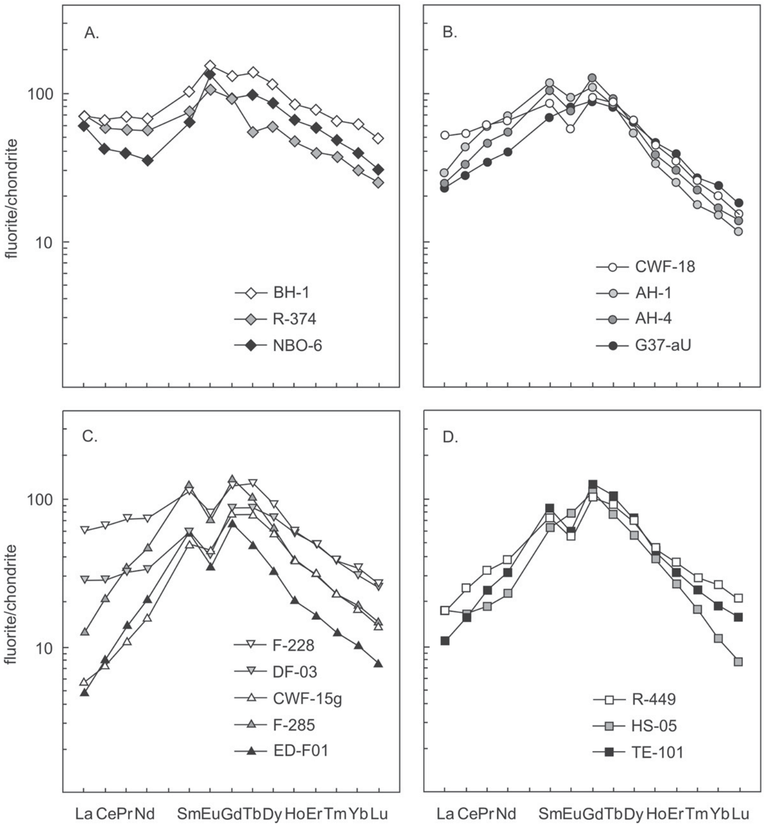

FIG. 3. Chondrite-normalized REE patterns of the yellow fluorite crystals. Normalization was performed using the chondrite data given by Anders & Grevesse (1989). Note that all samples are typified by patterns that are enriched in the MREE.

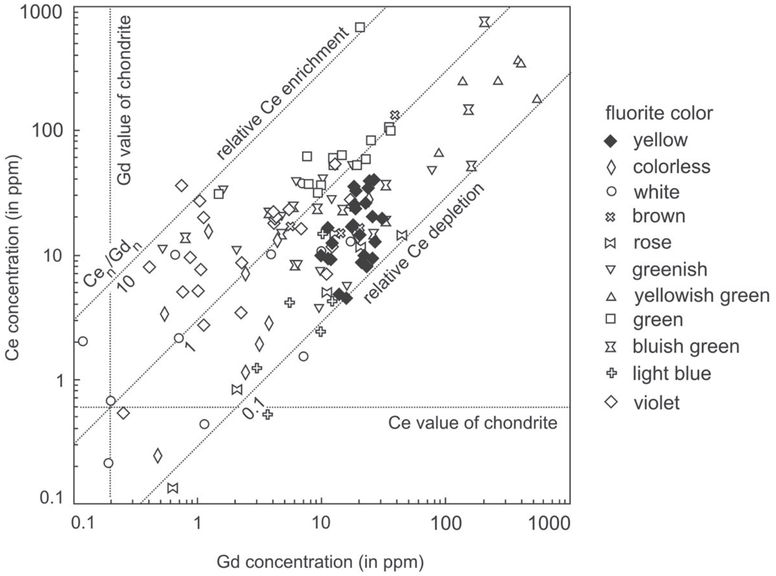

FIG. 4. Scatter diagram displaying the concentration of Ce plotted against the Gd content for fluorite samples of different colors. Note that yellow fluorite samples from hydrothermal barite–fluorite veins exhibit comparably restricted compositions.

(Kempe & Oberthür 1997, Ghaderi *et al.* 1999, Kempe *et al.* 1999a, Brugger *et al.* 2000, Wagner & Erzinger 2001, Yang *et al.* 2001). Therefore, processes of element fractionation resulting in this type of REE patterns are not limited to the environment of yellow fluorite formation.

A model for the formation of MREE-enriched patterns has been proposed by Kempe *et al.* (1999a). These authors suggested that the MREE enrichment of scheelite in the Muruntau and Myutenbai gold deposits in Uzbekistan is caused by a fractionation of the REE between hydrothermal precipitates forming at different times during the evolution of the fluid phase. They proposed that early-formed minerals, such as Ce-rich phases, preferentially incorporated the LREE. The MREE were concentrated in main-stage hydrothermal precipitates such as scheelite, whereas the HREE were enriched in late carbonate minerals. Because of the abundant occurrence of carbonate minerals in the gold deposits, Kempe *et al.* (1999a) suggested that the formation of REE carbonate complexes in the hydrothermal fluids may have contributed to the formation of MREE-enriched patterns of scheelite. The carbonate complexes may have stabilized the HREE in the hydrothermal fluids and, therefore, inhibited their incorporation into main-stage scheelite. Consequently, late hydrothermal precipitates like carbonates were enriched in the HREE. This assumption is supported by the fact that the stability of REE carbonate complexes increases with increasing atomic number (Luo & Byrne 2004) and is in agreement with the results of other REE studies on carbonate-rich systems (Graf 1984, Bau 1991, Bau & Möller 1992), as well as with general considerations of REE behavior (Möller *et al.* 1998). Scheelite occurring in the gold deposits of the Kalgoorlie–Norseman region in Australia was also found to exhibit a pronounced enrichment in the MREE, whereas associated calcite is typified by high concentrations of the HREE (Ghaderi *et al.* 1999). Additional support for the model of Kempe *et al.* (1999a) comes from a study on Alpine-type fissure veins occurring in the Rhenish Massif of Germany. Wagner & Erzinger (2001) established that apatite contained in these veins shows a MREE-enriched pattern, whereas late calcite was found to be strongly enriched in the HREE. The results of these studies support the above assumption that MREE-enriched patterns occur in main-stage minerals precipitated in hydrothermal systems in which the evolution of the fluid involved the formation of early LREE-enriched phases and late HREE-enriched carbonates.

It seems likely that the model proposed by Kempe *et al.* (1999a) can also be applied in the case of the yellow fluorite investigated in the present contribution. Gas chromatographic analyses of fluid inclusions entrapped in the various minerals constituting the hydrothermal barite–fluorite veins of the Erzgebirge have shown that CO_2, CH_4, and N_2 were the principal gaseous species in the hydrothermal fluids (Klemm 1994b). Although the HCO_3^- content of fluid inclusions is typically below the limit of detection of the titrimetric method used, Klemm (1994a) recorded maximum HCO_3^- concentrations of approximately 50 g/L for fluid inclusions hosted by barite from the Freiberg mining district. Daughter crystals of nahcolite ($NaHCO_3$), up to 2 vol.%, have commonly been observed in primary fluid inclusions entrapped in crystals of yellow fluorite of the hydrothermal barite–fluorite veins of the Erzgebirge, which equals to a HCO_3^- concentration of 38 g/L. Daughter crystals of calcite are comparably rare (Thomas 1979). These results imply that carbonate species represented an important component of the hydrothermal fluids forming the barite–fluorite veins, although precipitation of carbonates did not occur contemporaneously with the formation of the yellow fluorite. The precipitation of calcite was probably inhibited by the near-neutral nature of the hydrothermal fluids.

Close inspection of the normalized REE patterns reveals that samples of yellow fluorite taken from different hydrothermal barite–fluorite veins exhibit some significant variations in the relative depletion of the LREE, whereas the depletion of the HREE is apparently more uniform (Fig. 3). This observation can potentially be explained by variable depletion of the LREE during the proposed early process of REE fractionation that involved the formation of LREE-enriched phases. However, it is also possible that this depletion is caused by mixing processes in the hydrothermal system. The hydrothermal fluids, depleted in the LREE as a consequence of the formation of early LREE-enriched phases, may have mixed with a second fluid that was characterized by a LREE-enriched signature similar to that in most crustal rocks. Model calculations show that the kink observable in the REE patterns of the fluorite samples from the Freiberg mining district (Fig. 3a) can be obtained by the mixing of two fluids having a signature that is LREE-depleted and LREE-enriched, respectively. The behavior of the HREE was not significantly affected by such a mixing process because of the relatively low concentrations of these elements in the admixed LREE-rich fluid.

A model of fluid mixing is supported by the results of fluid-inclusion studies. Thomas (1979) has shown that fluorite and associated minerals of the hydrothermal barite–fluorite veins of the Erzgebirge commonly host a second type of fluid inclusions in addition to the above-mentioned highly saline fluid that is dominated by $CaCl_2$ and NaCl. This second type of fluid inclusion was found to be characterized by NaCl-dominant fluids of distinctly lower salinity. Thomas (1979) suggested that fluid mixing did not always result in the entrapment of two distinct types of fluid-inclusion populations, but is also manifested by variations in the salinity of the highly saline fluid inclusions, as observed for the yellow fluorite samples investigated in the present study. Two distinct types of fluid inclusions occur in aggregates of polycrystalline fluorite in the hydrothermal barite–fluorite veins that precipitated rapidly under turbulent conditions, whereas only one type of fluid inclusion is present in fluorite that crystallized in a stagnant environment, as evidenced by the large sizes of the crystals (up to several centimeters) and mostly excellent appearance. The aggregates of polycrystalline fluorite exhibit no characteristic optical absorption at 433 nm (Trinkler 1997).

On the basis of fluid-inclusion evidence, we conclude that mineral precipitation in the hydrothermal barite–fluorite veins occurred in an environment characterized by the mixing of fluids from two different sources. Thomas (1979) proposed that the highly saline, $CaCl_2$- and NaCl-rich fluid containing some minor Na_2SO_4, Na_2CO_3, $NaHCO_3$, $CaSO_4$, and $SrSO_4$ represents formation water, similar to modern oil-field brines. The origin of the NaCl-dominant, fluorine-bearing fluid of lower salinity is unresolved, but such a fluid may have been derived from a deeper, possibly magmatic source.

Further information on the origin of the hydrothermal fluids can be drawn from the occurrence of Eu anomalies in the chondrite-normalized REE pattern of the yellow crystals (Fig. 3). The formation of divalent Eu represents the reason for the fractionation of this element from the neighboring REE, which occur only in the trivalent state. Europium occurs predominantly in the divalent state in a relatively reducing environment or at temperatures exceeding approximately 250°C (Sverjensky 1984, Bau 1991, Bau & Möller 1992). Because the fluid-inclusion data indicate a lower temperature of fluorite formation, fractionation of Eu from the neighboring elements is unlikely to have taken place during fluorite crystallization. The hydrothermal fluids thus went through a high-temperature stage and cooled during the fluid evolution prior to fluorite crystallization.

The discussion of the trace-element data and fluid-inclusion evidence shows that the yellow fluorite formed in a very specific environment. These specifics may have played an important role in the development of the yellow coloration of the fluorite if a secondary origin of the O_3^- center can be ruled out.

Several authors have proposed that O_2^- centers in alkali halides are of secondary origin, *i.e.*, that these defects may form within the structure of already existing crystals. In particular, Rolfe *et al.* (1961) have found that O_2^- centers may develop in OH^--doped alkali halides in response to irradiation by ionizing radiation (Meistrich 1968, Cywiński & Damm 1982). Radiolysis of OH^- ions has been proposed to result in the production of interstitial hydrogen atoms and O^- ions (Kerkhoff 1960) whereby transient O_2^{2-} centers can form (Cywiński & Damm 1982). Subsequently, a more stable O_2^- defect may originate from the release of an electron from the O_2^{2-} center or, alternatively, from the trapping of a free hole (Cywiński & Damm 1982). A secondary origin of the O_2^- centers in fluorite causing the optical absorption band at 230 nm (Fig. 2) can thus not be ruled out. In contrast, extensive experimental studies employing irradiation by ionizing radiation at various conditions failed to produce O_3^- centers in fluorite that cause the absorption band at 433 nm (H. Bill, pers. commun., 2004). Therefore, it has long been proposed that the yellow color of fluorite is primary, *i.e.*, developed at the time of fluorite precipitation (Calas *et al.* 1972, Bill & Mareda 1975).

Optical absorption measurements on barite associated with the yellow fluorite crystals studied in the present contribution show that O_3^- defects also are present (M. Trinkler, unpubl. data). This observation implies that the O_3^- center is primary because it is difficult to envisage that similar secondary processes may have led to the formation of O_3^- defects in the very different structures of barite and fluorite. It seems more likely that a specific chemical reaction took place during the formation of barite and fluorite that led to a primary incorporation of O_3 aggregates in both minerals, which ultimately transform to O_3^- centers in the host structures by charge transfers.

It has been known for a long time (Panayeff 1909) that undisturbed alkaline and carbonate-bearing solutions containing Ce^{3+} are able to form cerium peroxide compounds. These compounds possibly decompose during the crystallization of fluorite, allowing O_3 to be incorporated into the growing crystals. For instance, it appears possible that a chemical reaction such as

$$Ce_2[O_3 / (CO_3)_3]{\bullet}4Na_2CO_3 + H_2O \Rightarrow O_3{\bullet}Na^+_{\text{fluorite}} + Ce_2(CO_3)_3 + OH^- + 3Na_2CO_3 + NaHCO_3$$

took place during the formation of the yellow fluorite crystals. According to the equation, the cerium-peroxide-bearing compound contained in the hydrothermal fluids decomposes into O_3 and Na^+ at the surfaces of the growing crystals. An O_3^- center is subsequently formed by charge transfer. The resulting O_3^- center in the fluorite structure replaces two neighboring F^- ions, whereby charge compensation is achieved by substitutional Na^+. The O_3^- center is stabilized by the crystal field of the fluorite structure (Julg & Ozias 1985). Subsequent to the decomposition of the cerium-peroxide-bearing compound at the crystal surface, Ce^{3+} occurs as a carbonate species that cannot be readily included into the growing crystal of fluorite. However, it can act as a catalyst and locally promote the production of additional O_3 aggregates, especially if new carbonate-bearing fluids are provided to the site of fluorite precipitation. The proposed chemical reaction of cerium peroxidation requires a relatively reducing environment because oxidation of Ce to the tetravalent state would inhibit the reaction. Taking into account that the evidence from fluid inclusions and trace elements support the assumption that the hydrothermal fluids were highly saline and apparently rich in carbonate species, the proposed mechanism (or a similar chemical reaction) represents a reasonable explanation for a primary origin of the yellow color in fluorite from hydrothermal barite–fluorite veins of the Erzgebirge. However, ultimate verification must await hydrothermal growth experiments that will show whether yellow fluorite can be indeed synthesized under the given environmental conditions.

The mechanism suggested above may also be responsible for the yellow coloration of hydrothermal fluorite that crystallized under comparable environmental circumstances in other deposits. In particular, we envisage that the yellow coloration of fluorite contained in hydrothermal barite–fluorite veins of the Massif Central of France formed by a similar process. Yellow fluorite from these veins shows a broad absorption band at 433 nm also (Calas & Touray 1972, Calas *et al.* 1972, Bill & von der Osten 1976, Bill & Calas 1978) and is also typified by pronounced enrichments of the MREE (Jébrak *et al.* 1985). Calas *et al.* (1972) and Lhégu *et al.* (1982) showed that yellow fluorite from the Massif Central precipitated from hydrothermal fluids that also are highly saline (14 to 20 equiv. wt.% NaCl) at low to moderate temperatures (homogenization temperatures between 80 and 150°C).

The physicochemical conditions of fluorite formation in many MVT deposits are broadly comparable to those responsible for the fluorite formation in the hydrothermal barite–fluorite veins of the Erzgebirge. Studies of fluid inclusions contained in yellow fluorite have shown that the hydrothermal fluids forming MVT deposits were also moderately hot (homogenization temperatures below 200°C), highly saline (>15 equiv. wt.% NaCl), and rich in NaCl and $CaCl_2$ (Hall & Friedman 1963, Sawkins 1966, Cunningham & Heyl 1980, Richardson & Pinckney 1984, Spry *et al.* 1990, Spry & Fuhrmann 1994). In many cases, fluid inclusions hosted by fluorite and associated minerals contain hydrocarbons, implying that mineral precipitation in MVT deposits occurred in a relatively reducing environment (Freas 1961, Hall & Friedman 1963, Cunningham & Heyl 1980, Richardson & Pinckney 1984, Souissi *et al.* 1997, González-Partida *et al.* 2003, Guillaume *et al.* 2003). Moreover, chalcopyrite inclusions have been reported to occur in yellow fluorite from the Illinois–Kentucky fluorspar district in the United States (Richardson & Pinckney 1984). Figure 5 shows the optical absorption spectrum and the normalized REE pattern of a crystal of yellow fluorite from the Victory mine, Cave-in-Rock District, Illinois. The broad band at 433 nm indicates that the color of the fluorite specimen is related to the presence of O_3^- centers in the crystal structure. The REE pattern of the sample is comparable to those sampled in the Erzgebirge. A similar enrichment of the MREE has also been documented for yellow fluorite from the Illinois–Kentucky fluorspar district in the United States by Burruss *et al.* (1992) and Chesley *et al.* (1994).

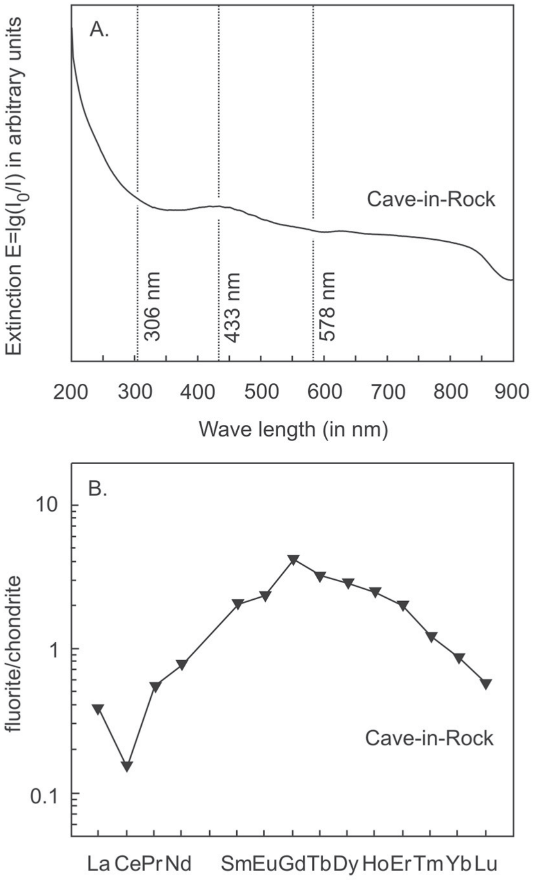

FIG. 5. Optical absorption spectrum and chondrite-normalized REE plot of yellow fluorite from the Victory mine, Cave-in-Rock district, Illinois. Note that the absorption spectrum shows a broad band peaking at 433 nm. The normalized REE pattern is enriched in the MREE.

CONCLUSIONS

The present investigations show that the yellow coloration of fluorite contained in hydrothermal barite–fluorite veins from the Erzgebirge, eastern Germany, is caused by the presence of O_3^- centers in the fluorite structure. We propose that these defects are of primary origin. Based on experimental findings of earlier authors, a possible reaction involving the autoperoxidation of trivalent cerium may well lead to the development of O_3^- centers in the fluorite. Because yellow fluorite occurs only in a limited number of hydrothermal deposits, it is likely that the proposed chemical reaction occurs only under physicochemical conditions that are rarely realized in nature.

On the basis of a combination of geological background information, the results of trace-element investigations and fluid-inclusion data, the physicochemical environment required for the formation of yellow fluorite has been constrained. We propose that fluorite crystallization took place in a relatively stagnant environment that was characterized by the mixing of two fluids differing in salinity and chemical composition. The presence of carbonate species in the fluorite-forming hydrothermal fluids is considered to be a prerequisite for the formation of the yellow fluorite coloration. The yellow coloration only developed because the fluorite crystals formed at low to moderate temperatures (homogenization temperatures below 150°C, stability limit of yellow coloration at 250 to 400°C) in a relatively reducing and near-neutral environment.

The present study supports the findings of previous authors that the color of hydrothermal fluorite can, in general, be related to the physicochemical environment of fluorite precipitation. The recognition of color varieties and paragenetic sequences, therefore, represents an important basis for genetic studies on fluorite-bearing ore deposits. Because the color of this mineral is easily recognizable during field studies, this property of hydrothermal fluorite may be used to select representative samples for subsequent analytical investigations, such as fluid-inclusion work, trace-element analyses, and isotopic studies.

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