Nd, Pb, and Sr Isotope Systematics of Fluorite at the Amba Dongar Carbonatite Complex, India: Evidence for Hydrothermal and Crustal Fluid Mixing

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Abstract

The Cretaceous Amba Dongar Complex contains one of the largest fluorite deposits (11.6 million tons at 30 wt % CaF_2) associated with any carbonatite. Fluorite mineralization postdates carbonatite emplacement and takes the form of replacement hydrothermal veins concentrated at the carbonatite-country rock contact.

Sr isotope ratios from the Amba Dongar fluorites reveal large isotopic variations that can only be attributed to reaction between a carbonatite-derived, F-rich fluid and continental crust (or crustal-derived fluid). The extremely variable initial $^{87}Sr/^{86}Sr$ ratios (0.70910–0.71729) are intermediate between those of the carbonatites (0.70549–0.70628) and the host Bagh sandstones (0.75359–0.78274); they correlate negatively with Sr abundances. Sr isotope ratios from intrasample fluorites show large isotopic variations (0.70910–0.71425) that cover almost the entire range of values found for all of the fluorites measured from Amba Dongar. The Pb isotope ratios from the fluorites are also variable and differ from those of the country rocks. Compared to the carbonatites, most contain similar $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ ratios but more radiogenic $^{206}Pb/^{204}Pb$ values. Galena and pyrite coeval with fluorite mineralization have Pb isotope ratios which overlap those from most of the fluorites, but which are isotopically distinct from one another. In contrast, initial $^{143}Nd/^{144}Nd$ isotope ratios from most of the fluorites are relatively uniform (0.51240–0.51247), quite different to those from the surrounding Bagh sandstones (0.51122–0.51149), but similar to those from the carbonatites (0.51248–0.51253).

The new isotopic results are partly consistent with a model for fluorite deposition involving interaction between ground waters within the surrounding country rocks and an F-rich, carbonatite-derived fluid (Deans and Powell, 1968). The variation in the Sr isotope composition for the fluorites suggests that certain physiochemical parameters of the mineralizing fluids were changing with time of deposition.

Introduction

IN RECENT years, fluorite mineralization associated with igneous rocks has received considerable attention because of the possible association with economic concentrations of Be, Mo, Sn, and U (Burt and Sheridan, 1980; Rytuba, 1981; Westra and Keith, 1981; Barton et al., 1982; Burt et al., 1982). Economic fluorite deposits associated with carbonatite complexes (Mariano, 1989) include Amba Dongar, India (11.6 Mt of 30 wt % CaF_2), Okorusu, Namibia (7–10 Mt of 35 wt % CaF_2), Mato Preto, Brazil (4.8 Mt of 58 wt % CaF_2), and Tchivira Quilengues, Angola (unestimated reserves). The important roles of halogens (F and Cl), which exsolve in fluids from the late stages of carbonatite magma differentiation, include: (1) lowering of carbonatite melt liquidus temperatures (Jago and Gittins, 1991), (2) formation of fenite zones (metasomatically altered country rocks, Gittins et al., 1990), and (3) production of large fluorite deposits (Edgar and Arima, 1985; Bailey and Hampton, 1990).

Fluorite mineralization associated with carbonatite complexes usually occurs as infillings in solution cavities or voids in brecciated country rocks (Mariano, 1989). The deposits at Amba Dongar, Okorusu, and Tchivira Quilengues occur as either hydrothermal overprints or infillings in the adjacent fenites at the contact between the carbonatite and the host rocks (Mariano, 1989). Economic concentrations of fluorite associated with carbonatite complexes have been mainly attributed to late-stage hydrothermal activity, and this model is supported by the low homogenization temperatures (100°–

150°C) shown by fluid inclusion studies on fluorites from the Amba Dongar and Okorusu carbonatite complexes (Roedder, 1973).

Previous isotopic investigations of fluorite deposits, related to different types of magmatism, have shown that Sr isotope ratios can serve as useful tracers of fluid sources in hydrothermal systems (e.g., Deans and Powell, 1968; Kesler, 1977; Norman and Landis, 1983; Ruiz et al., 1985; Canals and Cardellach, 1993; Galindo et al., 1994). Recent Nd isotope studies (e.g., Halliday et al., 1990) and Sm-Nd dating of hydrothermal fluorite mineralization (e.g., Chesley et al., 1991, 1994) have shown that the Nd initial ratios reflect the composition of the ore fluids and provide reliable ages for ore formation.

This study focuses on the Nd, Pb, and Sr isotope analyses of hydrothermal fluorite from the main deposit at Amba Dongar, located on the northern side of the calciocarbonatite ring (Fig. 1). This is the first detailed radiogenic isotopic investigation of fluorite mineralization associated with any carbonatite complex, and these Pb isotope ratios are the first documented from fluorites. Specimens consist mainly of coarse-grained fluorite, either of a single variety (e.g., yellow—sample AMDO-104B, or black—sample AMDO-108), or intermixed fluorite of different colors (e.g., AMDO-100). Textural evidence from samples which contain both carbonatite and fluorite clearly show that fluorite deposition was later than carbonatite formation. All of the fluorite samples used in this study were taken from either cavities or crosscutting veins that replaced the host ferrocarbonatite. On the basis of Nd, Pb, and Sr isotope ratios from the fluorites associated with the Amba Dongar carbonatite complex, we attempt to determine the origin and evolution of the ore-forming fluids.

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Geology

The Cretaceous (~60 Ma, Deans et al., 1973) Amba Dongar carbonatite complex is located in west-central India at the northern extremity of the Deccan flood basalts and forms part of the Chotta Udaipur carbonatite-alkalic district associated with the Narmada rift (Fig. 1; Viladkar, 1981). The Amba Dongar carbonatite intrudes the Cretaceous Bagh limestones and sandstones, Eocene Deccan basalts, and underlying Precambrian basement rocks of the Dharwar series, which are not exposed at Amba Dongar but are present in the northern region of the Chotta Udaipur alkalic province (Viladkar, 1981). The geology of Amba Dongar is shown in Figure 1. An innermost ring of carbonatite breccia rimmed by calciocarbonatite is intruded by plugs and dikes of ferrocarbonatite and cored by basalt.

Fluorite mineralization

Mining of the major fluorite deposit, located on the north side of the ring dike complex within fenitized (metasomatically altered) country rocks (Fig. 1), started in 1970 by the Gujarat Mineral Development Corporation and is ongoing. Fluorite is found mainly in large hydrothermal veins which clearly postdate and replace calcio- and ferrocarbonatite (Viladkar and Wimmenauer, 1992) and also occurs as a disseminated magmatic mineral.

Fluorspar mineralization at Amba Dongar is commonly confined to brecciated and sheared Cretaceous Bagh sandstones that make up the surrounding rocks. Unfenitized Bagh sandstone consists dominantly of quartz (rounded to subrounded grains), a minor amount of feldspar, and trace amounts of biotite, muscovite, and hornblende (Gwalani et al., 1990). Major element analysis of unfenitized Bagh sandstone (Sukheswala and Viladkar, 1981) confirms the quartz-rich nature, with 96.78 wt percent SiO_2, 1.05 wt percent Fe_2O_3, and 0.51 wt percent Al_2O_3. The hydrothermal fluorite can occur as either widespread disseminations in brecciated host rocks, vugs of varying dimensions (a few centimeters to 0.7 m), and fracture fillings which in places are more than 3 m wide. Vugs are commonly lined by aggregates of fluorite cubes set in a fine-grained matrix of fluorite. Many zones of mineralization are themselves brecciated and carry relict fragments of host rocks. Fluorite found in veins may be associated and intergrown with barite, chalcopyrite, dickite, galena, and pyrite (Srivastava and Karkare, 1989); in some cases it is coated with quartz, Fe oxide, and Mn oxides (Viladkar and Wimmenauer, 1992).

The hydrothermal fluorite at Amba Dongar can be grouped into earlier (violet, light blue, green) and later (colorless and yellow) varieties (Deans et al., 1973). Color zonation and crustification, commonly observed in the cavities, indicate that the violet and blue varieties were precipitated earlier than the yellow or green. Unlike many of the stratiform hydrothermal fluorite deposits which preserve the entire sequence of fluorite paragenesis over great distances (e.g., Cave-in-Rock; Richardson and Pinckney, 1984, Richardson et al., 1988), individual fluorite veins at Amba Dongar in general do not contain all of the fluorite varieties observed in the deposit. The early hydrothermal fluorites (violet and blue) have low abundances of Sr (212–864 ppm), high Y

(100–300 ppm; Deans et al., 1973). Homogenization temperatures from 32 fluid inclusions (Roedder, 1973) range from 150° to 161°C. The average salinity of the fluid inclusions from the early hydrothermal fluorites is 1.8 wt percent NaCl. The later colorless and yellow hydrothermal fluorites contain higher Sr (~1,000–1,500 ppm) and lower Y (100 ppm) contents; fluid inclusions ($n = 11$) have lower salinities (0.8 wt % NaCl) and slightly lower homogenization temperatures (112°–118°C; Roedder, 1973). The homogenization temperatures (112°–160°C) determined from fluid inclusion data show a range similar to those documented from other major fluorite deposits, e.g. Cave-in-Rock, Illinois (115°–151°C; Richardson and Pinckney, 1984).

Analytical Methods

Fluorite samples (0.10–0.15 g) were dissolved in a multistage acid procedure involving concentrated H_2SO_4 and HCl acid (Richardson and Blenkinsop, 1989). Analytical procedures for Nd and Sr are similar to those described in Bell et al. (1987). Two sandstone samples were dissolved in an $HF-HNO_3$ mixture for approximately 48 h at a minimum temperature of 170°C. Carbonate samples were dissolved in an $HCl-HNO_3$ mixture under pressure for at least 24 h. Pb was separated in HBr and HCl using a two column anion ion-exchange technique. Details are given in Simonetti et al. (1995). Nd and Sr blanks are ~0.5 ng; those for Pb range from 0.2 to 1.5 ng. Nd, Pb, Rb Sm, Sr, and U concentrations (Tables 1 and 2) were determined by isotope dilution using ^{145}Nd, ^{87}Rb, ^{149}Sm, and ^{84}Sr spikes, and a mixed $^{206}Pb-^{233}U-^{235}U$ spike. Nd and Sr were analyzed using a double Re filament technique, and all isotope ratios were measured on a Finnigan-MAT 261 multicollector solid source mass spectrometer, operated in the static mode. Samples for Pb isotope analyses were run on a single Re filament using silica gel and phosphoric acid. Reproducibility of isotopic ratios for samples and standards are given in Tables 1 and 2.

Results

Nd, Pb, and Sr isotope results were obtained from the Amba Dongar fluorites and two samples, one fine grained and the other coarse grained, of unfenitized Bagh sandstone (AMDO-117). The data are given in Tables 1 and 2 and shown in Figures 2, 3, and 4. On the basis of their Rb and Sr contents (Table 1), the calculated $^{87}Rb/^{86}Sr$ ratios for the fluorites are low (<0.002), and therefore present-day $^{87}Sr/^{86}Sr$ isotope ratios are considered good approximations to the initial ratios that existed at the time of fluorite mineralization. Although the $^{147}Sm/^{144}Nd$ ratios for the fluorites are variable (0.189–0.517), the corrections to present-day $^{143}Nd/^{144}Nd$ isotope ratios (Table 1) are small because the complex only dates at 60 Ma. Unlike the Sm-Nd study of fluorites from the Illinois-Kentucky fluorite district (Chesley et al., 1994), the $^{147}Sm/^{144}Nd$ ratios for the fluorites from Amba Dongar do not correlate with color. In addition, although fluorite mineralization has been dated using the Sm-Nd isochron method (e.g., Chesley et al., 1991, 1994), a similar plot using the Amba Dongar fluorite data shows much scatter and does not provide any useful information regarding the age of fluorite deposition.

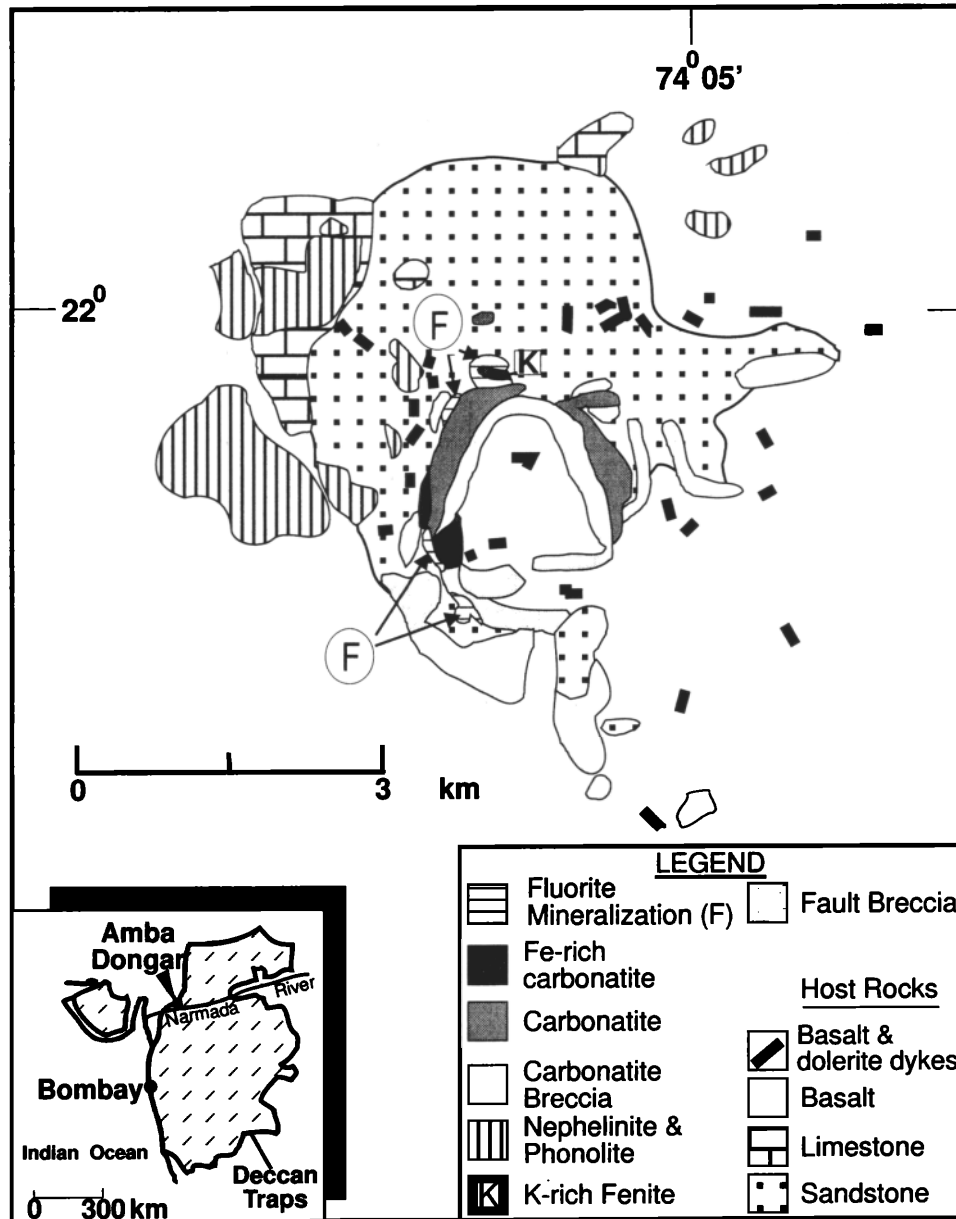Initial $^{87}Sr/^{86}Sr$ isotope ratios from the fluorites are highly

FIG. 1. Geologic map of the Amba Dongar carbonatite complex (modified after Viladkar, 1981). Inset shows geographic location of the Amba Dongar complex at the northern extremity of the Deccan flood basalts and within the Narmada rift valley.

variable (0.70910–0.71729) and are negatively correlated with Sr contents (Fig. 2). Figure 2 shows that the Sr isotope ratios from the fluorites lie between those from the Amba Dongar carbonatites (Simonetti et al., 1995) and those from the surrounding Bagh sandstone (Table 1). The Sr isotope ratios and Sr contents from the Amba Dongar fluorites (Table 1) are similar to those determined earlier by Deans and Powell (1968), although the analytical uncertainty of 0.14 percent associated with their Sr isotope compositions is much greater than the value of 0.003 percent (2σ level) quoted in this paper (see Table 1). In general, the early violet and light blue fluorites show higher $^{87}Sr/^{86}Sr$ isotope values than do the later colorless and yellow varieties (Fig. 2).

Sr isotope data from four intermixed varieties of fluorite (colorless, purple, light blue, and yellow) from the same hand specimen (AMDO-100) show that the fluorites are isotopically heterogeneous and span almost the entire range of Sr isotope compositions shown by all other fluorites. The data from AMDO-100 are shown in Figure 2. This is an important finding and significantly different from Sr isotope results from other hydrothermal fluorite deposits, such as the barite-fluorite veins of the Catalonian Coastal Ranges (Canals and Cardellach, 1993), which show that the barite and different fluorite varieties from a given vein deposit all have similar Sr isotope ratios. The Sr isotope results from the Amba Dongar intrasample fluorites, sampled at a hand specimen scale, sug-

TABLE 1. Nd and Sr Isotope Data from Amba Dongar Fluorites and the Bagh Sandstone

Sample no.	Rb (ppm)	Sr (ppm)	$^{87}Sr/^{86}Sr$ initial	Nd (ppm)	Sm (ppm)	$^{143}Nd/^{144}Nd$ measured	$^{143}Nd/^{144}Nd$ initial
Fluorites							
Amdo-100 purple	0.05	635	0.71132	2.73	2.33	0.51262	0.51242
Amdo-100 light blue	0.11	864	0.71098	3.79	2.33	0.51255	0.51240
Amdo-100 colorless	0.37	330	0.71425	4.30	3.12	0.51255	0.51238
Amdo-100 yellow	6.90	1524	0.70909	2.42	1.06	0.51245	0.51235
			0.70910+			0.51238	0.51228+
Amdo-104b yellow	0.18	1579	0.70985	6.56	2.41	0.51253	0.51244
Amdo-108 black	0.17	1006	0.70994	18.82	7.85	0.51256	0.51246
Amdo-111 purple	0.12	212	0.71729	5.96	2.09	0.51255	0.51247
Amdo-111 FG	0.05	1009	0.71139	4.37	3.22	0.51260	0.51243
F-3 purple	0.18	386	0.71213	3.53	1.32	0.51253	0.51244
			0.71215+			0.51253	0.51244+
F-3 light blue	0.02	408	0.71257	5.36	1.67	0.51253	0.51246
F-1 colorless	0.08	1342	0.71027	—	—	—	—
Sandstone							
Amdo-117C	76.4	59.4	0.75359	3.92	0.62	0.51126	0.51122
Amdo-117F	135.9	62.8	0.78274	5.03	0.84	0.51153	0.51149

Isotope results normalized to $^{146}Nd/^{144}Nd = 0.7219$ and $^{86}Sr/^{88}Sr = 0.1194$; NBS 987 Sr standard $= 0.71025 \pm 0.00002$, La Jolla Nd standard $= 0.51186 \pm 0.00002$, and BCR-1 $^{143}Nd/^{144}Nd = 0.51266 \pm 0.00002$; uncertainties are given at the 2σ level; uncertainty of Nd and Sr abundances, determined by isotope dilution (details in Bell et al., 1987), is $\pm0.5\%$; concentrations of Nd and Sm in BCR-1 were determined at 28.52 ppm and 6.48 ppm, respectively; (—) = not determined; + = duplicate analysis, initial ratios for duplicate analysis were calculated assuming a Sm/Nd ratio to that of the first analysis

gest that the fluid responsible for the fluorite mineralization underwent rapid chemical changes.

Unlike the Sr isotope ratios, the initial $^{143}Nd/^{144}Nd$ isotope ratios from the Amba Dongar fluorites are similar to one another (0.51235–0.51247) and show no correlation with Nd abundances (2.4–18.8 ppm, Table 1). This suggests that Nd was derived from a single source throughout the entire time that fluorite was being precipitated. Compared to the initial Nd isotope ratios from the carbonatites (avg 0.51250; Simonetti et al., 1995), those from the fluorites have slightly lower initial Nd isotope ratios (avg 0.51243).

The Nd and Sr isotope data from the Amba Dongar fluorites and carbonatites are plotted in Figure 3. Both the carbonatite (Simonetti et al., 1995) and fluorite data plot in the lower right quadrant. Data that fall in the lower right quadrant of Figure 3 indicate derivation from a source with a time-integrated, high Rb/Sr and Nd/Sm ratios relative to primitive earth models, such as melts generated from a large ion lithophile-enriched mantle source (e.g., old metasomatic event), mantle-derived melts contaminated by continental crust, or rocks of continental crust.

Chondrite-normalized REE patterns (Fig. 5) for some of

TABLE 2. Pb Isotope Data from Amba Dongar Fluorites, Sulfides, and the Bagh Sandstone

Sample no.	U (ppm)	Pb (ppm)	Measured			Initial	
			$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$	$^{208}Pb/^{204}Pb$	$^{206}Pb/^{204}Pb$	$^{207}Pb/^{204}Pb$
Fluorites							
Amdo-100 purple	—	2.2	19.87	15.77	40.32		
Amdo-100 light blue	—	2.0	19.88	15.78	40.30		
Amdo-100 colorless	—	1.1	19.86	15.77	40.30		
Amdo-100 yellow	—	0.1	18.60	15.62	38.30		
			18.51+	15.65+	38.40+		
Amdo-104b yellow	—	4.5	19.82	15.79	40.35		
Amdo-108 black	—	9.6	19.28	15.72	39.81		
Amdo-111 purple	0.6	1.3	19.35	15.81	39.86	19.08	15.80
Amdo-111 FG	0.2	439	19.95	15.89	40.76	19.95	15.80
F-3 purple	0.5	12.5	17.48	15.56	37.37	17.46	15.56
F-3 light blue	—	0.8	19.73	15.76	40.15		
Sulfides							
Amdo-111 galena	—	—	19.86	15.83	40.53		
Amdo-111 pyrite	—	—	19.35	15.86	40.29		
Bagh sandstone							
Amdo-117C	3.0	13.3	17.84	15.76	38.59	17.71	15.76
			17.78+	15.76+	38.53+		
Amdo-117F	5.8	16.7	17.74	15.75	38.54	17.54	15.74

Reproducibility of Pb isotope ratios is 0.1% at the 2σ level; an average fractionation factor of 0.1% per mass unit was applied to all measured ratios based on analyses of NBS 982; (—) = not determined; + = duplicate analysis
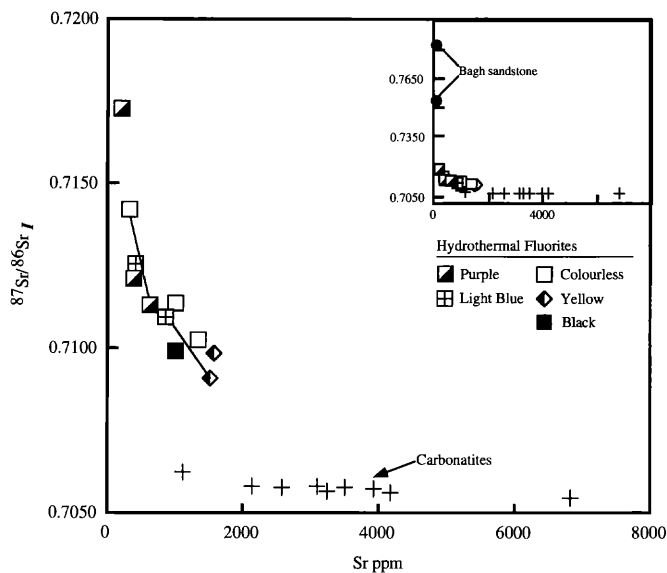
FIG. 2. Initial $^{87}Sr/^{86}Sr$ isotope ratios vs. Sr (ppm) for the Amba Dongar fluorites and carbonatites (Simonetti et al., 1995). Solid line connects intra-sample fluorite varieties. Inset shows highly radiogenic Sr isotope ratios for the two Bagh sandstone samples.

the different fluorites, using the data given in Viladkar and Wimmenauer (1992), differ markedly from those of the carbonatites. A direct comparison between the isotopic data obtained here and the REE data shown in Figure 5 (Viladkar and Wimmenauer, 1992), however, is not entirely valid since different samples were used in the two studies. In addition, it is impossible to say whether the positive Yb anomalies shown by the carbonatite, fluorites, and sandstone are significant or an artifact from the method of analysis (Viladkar and Wimmenauer, 1992).

The fluorites analyzed by Viladkar and Wimmenauer
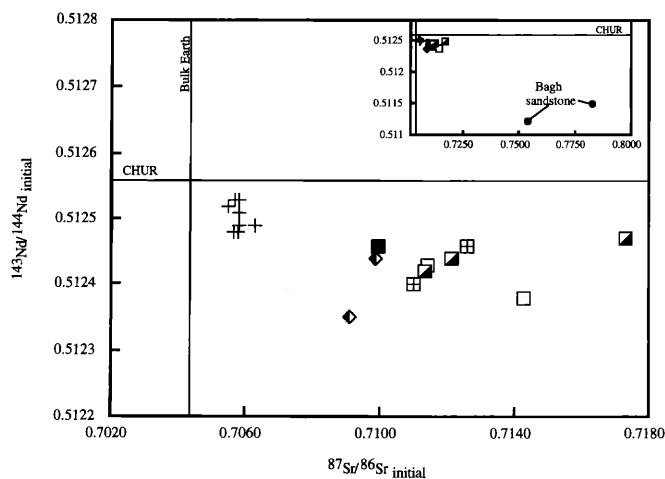
FIG. 3. Initial $^{143}Nd/^{144}Nd$ vs. $^{87}Sr/^{86}Sr$ isotope ratios for Amba Dongar fluorites and carbonatites (Simonetti et al., 1995). CHUR (chondritic uniform reservoir) and bulk earth values are corrected for Rb ($^{87}Rb/^{86}Sr = 0.083$) and Sm ($^{147}Sm/^{144}Nd = 0.1967$) decay from present-day values of 0.512638 and 0.7045, respectively, to 60 Ma. Symbols as in Figure 2. The inset shows the much lower Nd isotope ratios for the Bagh sandstone compared to those from the carbonatites and fluorites.
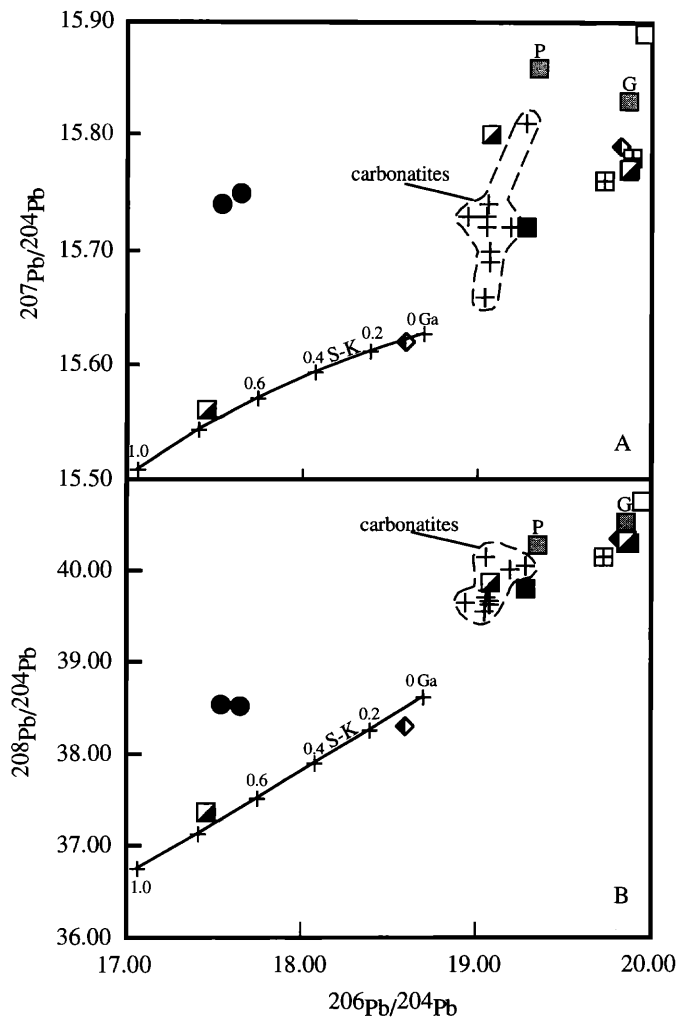

FIG. 4. Present-day Pb isotope ratios for Amba Dongar carbonatites (Simonetti et al., 1995) and fluorites. G = galena, P = pyrite, S/K = Stacey-Kramers (1975) Pb evolution curve. A. $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$. B. $^{208}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$. Symbols as in Figure 2.

(1992) have identical REE patterns to one another with almost horizontal slopes, which differ significantly from the steeply negative, chondrite-normalized REE patterns from the carbonatites (Fig. 5). One of the more interesting features to emerge from Figure 5 is that both carbonatites and fluorites have similar chondrite-normalized Yb and Lu values. Included in Figure 5 is the chondrite-normalized data from a single sample of unfenitized Bagh sandstone (Viladkar and Dulski, 1986). The fluorites and the sandstone have similar light REE values, but the sandstone has much lower values for the heavy REE. The patterns for the fluorites in Figure 5 suggest either that the light REE partition preferentially into the melt rather than in the fluid, or that at the time of exsolution of the F-rich fluid, the magma was depleted in the light REE but enriched in the heavy REE. A late-stage light REE-depleted, F-rich fluid may have resulted from the crystallization of light REE-bearing minerals, such as apatite, calcite or dolomite (Hornig, 1988), and pyrochlore (Hogarth, 1989), which are known to occur in the Amba Dongar carbonatite (Viladkar and Wimmenauer, 1992).
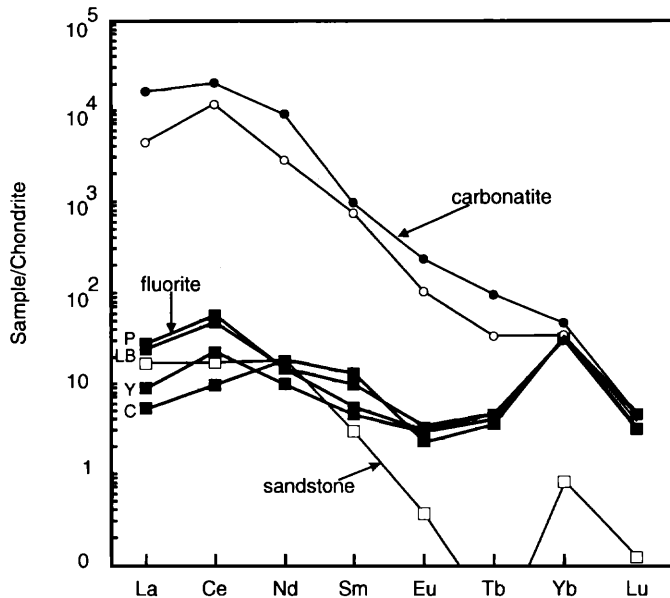
FIG. 5. Chondrite-normalized REE plot for Amba Dongar carbonatites, fluorites, and the Bagh sandstone. Solid circle = ferrocarbonatite (data from Viladkar and Dulski, 1986); open circle = calciocarbonatite (data from Viladkar and Dulski, 1986); open square = Bagh sandstone (data from Viladkar and Dulski, 1986, except for Nd and Sm values obtained from this study). REE data from Viladkar and Dulski (1986) was determined by neutron activation. Solid square = fluorites: P = purple, LB = light blue, Y = yellow, C = colorless. Chondrite values from McDonough and Frey (1989).

Isotopic ratios from the two samples of Bagh sandstone, one coarse grained (AMDO-117C) and the other fine grained (AMDO-117F), also plot within the enriched quadrant of Figure 3 (inset) but at much higher initial Sr (0.78274 and 0.75359) and significantly lower initial Nd (0.51149 and 0.51122) isotope ratios than the fluorites. The variation of about 4.0 percent in the $^{87}Sr/^{86}Sr$ isotope ratios obtained from the two Bagh sandstone samples is significantly greater than the typical 0.005 percent reproducibility shown by the duplicate analyses of the Amba Dongar fluorites (Table 1). The large variations in Nd and Sr isotope ratios, shown by the Bagh sandstone samples, simply reflect mineralogical inhomogeneity between the two samples.

The Pb isotope ratios from the fluorite samples (Table 2) are considered initial values because of the age of the complex and the low U concentrations (0.2–0.6 ppm) determined from three fluorite samples (AMDO-111FG = Fluorite adjacent to Galena, F-3 purple, and AMDO-111 purple). Pb isotope ratios from the fluorites, as well as the Pb isotope field defined by the Amba Dongar carbonatite data (Simonetti et al., 1995), are shown in Figure 4. The large spread in $^{207}Pb/^{204}Pb$ isotope ratios shown by the carbonatites (Fig. 4) has been attributed to low-temperature, meteoric water alteration which affected predominantly the ferrocarbonatites (Simonetti et al., 1995). Figure 4A shows that most of the fluorite samples and carbonatites plot to the right and above the Stacey-Kramers (1975) Pb evolution curve (which defines the model evolution of Pb isotope composition in the continental crust), and most of the fluorites fall to the right of the carbonatite field. Three of the four fluorite varieties from sample

AMDO-100 have identical Pb isotope ratios (Table 2) and therefore are in isotopic equilibrium. The yellow fluorite sample from AMDO-100, as well as sample F-3 (purple), have Pb isotope ratios much lower than those of any of the other fluorites, and these plot close to the Stacey-Kramers (1975) Pb evolution curve, at positions that correspond to ages of approximately 100 and 800 Ma, respectively. We attach no real significance to the model Pb ages of 100 and 800 Ma. The Pb isotope ratios from the Bagh sandstone samples are similar to one another and plot to the left of the carbonatite field, well above the Stacey-Kramers (1975) Pb evolution curve.

Sulfide minerals, such as chalcopyrite and pyrite, are common in carbonatite complexes (Hogarth, 1989), with the Precambrian Phalaborwa complex (South Africa) containing the largest concentration of sulfides (predominantly chalcopyrite) associated with any carbonatite occurrence (Mariano, 1989). Galena and pyrite occur at Amba Dongar and are disseminated in both the fluorite deposits and the carbonatite. The Pb isotope ratios from a galena and pyrite associated with the fluorite mineralization at Amba Dongar also plot to the right of the carbonatite field (Fig. 4) and are similar to those from the fluorites (Table 2, Fig. 4). These ratios are considered close to initial values, because galena and pyrite contain either no or little U (Doe, 1970). A colorless fluorite (AMDO-111FG), taken from the same vein as the galena, has a high Pb abundance (439 ppm) and Pb isotope ratios that are more radiogenic (Fig. 4), indicating that the galena and associated colorless fluorite did not coprecipitate from the same fluid. The gross similarity of the Pb isotope ratios of the galena and pyrite, and those from the fluorites suggests a source for Pb that was quite different from that of the carbonatite magma. The lack of correlation between the Pb and initial $^{87}Sr/^{86}Sr$ isotope ratios for the Amba Dongar fluorites argues for an independent evolution of Pb and Sr in the mineralizing fluids.

Discussion

Source of fluorine

At Amba Dongar, the most likely source of the fluorine is the carbonatite itself because disseminated fluorite is found within the Amba Dongar calciocarbonatites (Viladkar and Wimmenauer, 1992). Deans and Powell (1968) also concluded that the fluorine responsible for the Amba Dongar fluorite deposits was almost certainly derived from residual hydrothermal solutions escaping from the solidifying carbonatite magma. Fluorite is also common in many other carbonatites, including the natrocarbonatite lavas from the 1988 eruption of the active carbonatite volcano of Oldoinyo Lengai (Tanzania) that contain up to 5 wt percent fluorine (Keller and Krafft, 1990). Experimental results show that at a pressure of 1 kbar about 8 wt percent fluorine is soluble in liquids of $CaCO_3$-Na_2CO_3 before fluorite is stabilized (Jago and Gittins, 1991). A carbonatite magma with high fluorine content (~8 wt %) will consequently undergo extreme crystal fractionation due to a depressed liquidus temperature and then expel F-rich fluids following water saturation during the later stages of carbonatite magma differentiation (Gittins, 1989).

According to Richardson and Holland (1979), fluorite deposition can occur when a Ca^+-F^--saturated fluid either (1)

cools (the drop in temperature may be as small as 5°–10°C) and/or undergoes changes in chemistry, (2) mixes with another fluid of completely different chemistry, (3) experiences a large change in pressure (at least 1 kbar), or (4) interacts with wall rocks. Changes in pH or Eh do not affect fluorite solubility in the fluid phase (Richardson and Holland, 1979). The large variation in Pb and Sr isotope ratios shown by the hydrothermal fluorites at Amba Dongar is indicative of open-system behavior, such as two-component fluid mixing or fluid-crust interaction.

Fluid mixing-crustal interaction

Deans and Powell (1968) proposed that fluorite deposition occurred only when F-rich fluids encountered calcareous ground waters which had permeated the surrounding Bagh limestones and sandstones. This model is consistent with the occurrence of major fluorite deposits at the contact between the Bagh sandstone and carbonatite ring structure (Fig. 1) and is also supported by the low salinities and low homogenization temperatures obtained from the fluid inclusions of the Amba Dongar fluorites (Roedder, 1973). In more recent isotopic studies of some hydrothermal fluorite vein deposits associated with slightly older granitic magmatism (e.g., Canals and Cardellach, 1993; Galindo et al., 1994), two-component fluid mixing, between a crustal-derived fluid and seawater, has been advocated as the mechanism responsible for the mineralization.

The highly radiogenic Sr isotope ratios (~0.71100–0.71700) from the early hydrothermal fluorites are significantly different from those of the carbonatite and suggest that during the early stages of fluorite deposition, the Sr incorporated into the purple and blue fluorite varieties was mainly derived from a more radiogenic source than the carbonatite.

The reaction that controls fluorite deposition at Amba Dongar, which involves calcareous ground water interacting with an F-rich fluid, may be analogous to the limestone replacement reaction believed to be responsible for the generation of the Manto fluorite deposits in Mexico (Kesler, 1977): $2F^- + 2H_2O + CaCO_3 \rightarrow CaF_2 + HCO_3^- + OH^-$. The position of the fluorite deposits at the contact between the carbonatite and the surrounding country rocks suggests that fluorite deposition occurred in response to an increase in the Ca content, and perhaps changes in salinity and temperature of the fluid, as suggested by Kesler (1977) and Helgeson (1969). For example, only 5 to 500 ppm fluorine is required to cause fluorite deposition for a fluid with a temperature of 150°C, pH in the range of 6 to 8, and HCO_3^- activity in the range of 30 to 2,000 ppm (Kesler, 1977).

In order to model the Sr isotope ratios from the fluorites using two-component mixing, which has ground water as one of its end members, the values for two unknown parameters have to be estimated: the Sr isotope composition and the Sr content of the ground water during the time of fluorite mineralization. Present-day ground waters typically contain very low concentrations (<1 ppm) of Sr, although this value is dependent on many factors, such as the age of the basin in question as well as the composition, Sr content, and permeability of the host rocks. Assuming dissolution of all Ca- and Sr-bearing phases from the Bagh sandstone, the ground wa-
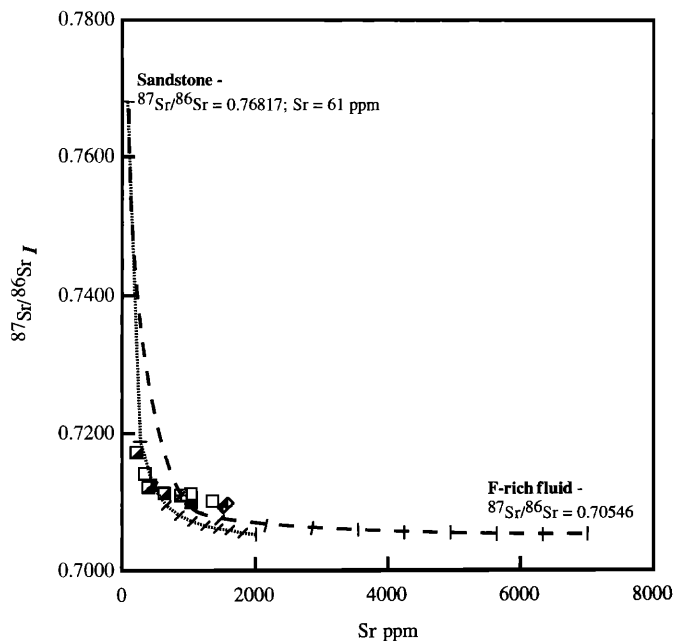

FIG. 6.   Initial $^{87}Sr/^{86}Sr$ ratios vs. Sr (ppm) for Amba Dongar fluorites. Also shown are two dotted lines which represent the extreme position of binary mixing curves between the Bagh sandstone and carbonatite-derived fluid with variable Sr contents (2,000–7,000 ppm). See text for details. Slash marks along binary mixing lines are at 10 percent intervals. Symbols as in Figure 2.

ters surrounding the carbonatite body at the time of fluid mineralization would have contained approximately 60 ppm Sr (Table 1), an $^{87}Sr/^{86}Sr$ isotope ratio between 0.75359 and 0.78274 (Table 1), and 3,600 ppm Ca based on a sample of unfenitized sandstone (Sukheswala and Viladkar, 1981). An additional source of Ca and Sr are small limestone deposits interbedded with the sandstone.

The negative correlation between Sr isotope ratios and Sr content shown in Figure 2 can be attributed to a binary mixing process between an F-rich end member with high Sr contents (>1,600 ppm) and an $^{87}Sr/^{86}Sr$ isotope ratio of ~0.7055 (i.e., F-rich fluid exsolved from differentiating carbonatite magma), and a second end member containing a lower Sr content and higher Sr isotope ratio (i.e., Bagh sandstone or ground water in equilibrium with the sandstone). Although the fluids are probably at low temperature, a high fluorine content will most certainly produce a highly reactive fluid capable of dissolving most Sr-bearing phases within the surrounding Bagh limestones and sandstones. The two curves, shown in Figure 6, mark the outermost limits of a series of binary mixing curves calculated using the data from unfenitized Bagh sandstone (average initial $^{87}Sr/^{86}Sr$ and Sr content of 0.76817 and 61 ppm, respectively), and an F-rich carbonatite-derived fluid with an Sr isotope ratio of 0.70546 (equivalent to the most primitive carbonatite sample; Simonetti et al., 1995) and variable Sr contents (2,000–7,000 ppm). With the exception of the curve involving an Sr content of 7,000 ppm (for the carbonatite-derived fluid), the other binary mixing curves provide a reasonable fit to the distribution of the fluorite data, especially to the data for those fluorites that contain <1,000 ppm Sr (Fig. 6). The binary mixing calcula-

tions also show that the Sr in the Amba Dongar fluorites is predominantly from a crustal source, with an estimated ground-water (sandstone)/carbonatite ratio in the mixture ranging between 7:3 to 9:1.

The $\delta^{18}O$ values (13.73–24.67‰) for ferrocarbonatites from Amba Dongar, which were emplaced just prior to fluorite mineralization, are much higher than those for primary magmatic carbonates (6–10‰, Keller and Hoefs, 1995). These heavy $\delta^{18}O$ isotope ratios for the ferrocarbonatites have been attributed to low-temperature interaction with meteoric water (Simonetti et al., 1995) and support the involvement of the latter in the formation of the fluorite deposits. Involvement of meteoric water was an important factor in the formation of the fluorite deposits within the Illinois-Kentucky fluorspar district (e.g., Richardson et al., 1988; Ruiz et al., 1988), in the vicinity of Hicks dome, which has been proposed as an upper expression of carbonatitic activity (Mariano, 1989).

Some inconsistencies exist, however, with respect to the ground-water and carbonatite-derived fluid mixing model:

1. The decrease in $^{87}Sr/^{86}Sr$ ratios of the fluorites with time of deposition opposes to a trend that would be intuitively expected from a process involving simple binary mixing between an F-rich, carbonatite-derived fluid and country rock and/or meteoric water. The temporal variation for the Sr isotope ratios from fluorites at Cave-in-Rock, Illinois (Ruiz et al., 1988), is one example where the influence of meteoric water is recorded during the later stages of mineralization.

2. The relatively constant Nd isotope ratios from the fluorites and their similarity to those from the carbonatites (Simonetti et al., 1995) suggest a minimal contribution of the REE from the surrounding sandstones. Although the fluorites and sandstone contain similar Nd contents (Table 1) and light REE chondrite-normalized values (Fig. 5), the initial $^{143}Nd/^{144}Nd$ isotope ratios from the fluorites show that their Nd was dominantly of magmatic origin and not scavenged from the surrounding sandstone. The REE in the sandstone are probably held in trace amounts of detrital accessory minerals such as zircon (Gwalani et al., 1990) which are not as easily dissolved by the F-rich carbonatite-derived fluid as are other mineral phases.

3. The relatively high Pb isotope ratios for most of the Amba Dongar fluorites are inconsistent with a model involving simple binary mixing between F-rich, carbonatite-derived fluid and sandstone, if the isotope ratios of the Bagh sandstone analyzed (Table 2) are representative of the unit as a whole. This may not be the case, however, because the two samples of Bagh sandstone show considerable Nd, Sr (Table 1), and to some extent, Pb ($^{206}Pb/^{204}Pb$) isotope heterogeneity (Table 2). The less radiogenic $^{206}Pb/^{204}Pb$ isotope ratios (18.60 and 17.46) from fluorite samples AMDO-100 yellow and F-3 purple, however, suggest that the some of the fluorite-forming fluid may have interacted with Bagh sandstone containing a Pb isotope composition similar to that shown in Table 2 ($^{206}Pb/^{204}Pb$ = 17.54–17.71).

The difficulties involving a two-component fluid mixing model suggests a more complex history of fluorite formation involving other important parameters which control fluorite deposition, such as temperature (Richardson and Pinckney, 1984). Recently, Plumlee and Goldhaber (1992) produced a series of chemical reaction path models which simulated cooling of the probable ore fluid. The model showed this to be an important control in the precipitation of ore and gangue minerals. In addition, Chesley et al. (1994) also proposed that cooling of the hydrothermal fluid was the principal factor which controlled fluorite deposition at Cave-in-Rock (Illinois-Kentucky fluorspar district). It is possible, therefore, that with progressive fluorite deposition at Amba Dongar, cooling of the hydrothermal fluid promoted fluorite precipitation and limited the fluid's involvement with the surrounding meteoric water. This would explain the decreasing $^{87}Sr/^{86}Sr$ ratios (i.e., decreasing component of crustal-derived Sr) with progressive fluorite deposition from the early violet and blue to later yellow and colorless varieties.

Alternative explanations for the origin of the higher Pb isotope ratios from most of the Amba Dongar fluorites include either the involvement of an additional, more radiogenic source, or selective leaching of less resistant minerals containing radiogenic Pb isotope ratios (due to high U/Pb ratios), such as biotite, muscovite, and hornblende which are also present in the Bagh sandstone (Gwalani et al., 1990).

Model for fluorite deposition at Amba Dongar

Our preferred model for fluorite deposition at Amba Dongar involves interaction between an F-rich carbonatite-derived fluid and ground waters present in the surrounding Bagh sandstone at the time of fluorite mineralization (Deans and Powell, 1968). The drop in salinities (from 1.8–0.8 wt % NaCl) and homogenization temperatures (from 150°–112°C) from fluid inclusions (Roedder, 1973) of early to late fluorites support a model involving a cooling, F-rich, carbonatite-derived fluid mixing with meteoric water during formation of the Amba Dongar hydrothermal fluorites. The low salinities of the fluorite fluid inclusions supports the important ground-water contribution to the fluorite mineralization at Amba Dongar. Although the late-stage fluorites have lower Sr isotope ratios than the early varieties, their $^{87}Sr/^{86}Sr$ isotope values remain significantly higher than those of the carbonatites (Simonetti et al., 1995), suggesting that one of the prerequisites for fluorite deposition at Amba Dongar was crustal interaction. In addition, the facts that most carbonatite-related fluorite deposits occur at the carbonatite-country rock contact and that the country rocks are themselves replaced by fluorite provide further evidence for such an interpretation. This interpretation is also consistent with the Sr isotope results from some other fluorite deposits related to igneous complexes (e.g., Canals and Cardellach, 1993; Galindo et al., 1994), which show that the Sr isotope composition of the fluorite is always higher than that of the proposed associated magmatic end member.

Conclusions

Most of the fluorites from Amba Dongar contain similar Nd but more radiogenic Pb and Sr isotope ratios than does the carbonatite, indicating open-system behavior during the evolution of the carbonatite-derived, hydrothermal fluid. The Sr isotope ratios from the fluorites indicate interaction between an F-rich, carbonatite-derived fluid with an isotopic composition similar to that of the carbonatites, and a more radiogenic source, such as upper crust. The intrasample Pb

and Sr isotope variations indicate changes in fluid isotopic composition during deposition, and such large intrasample variations are attributed by us to equilibration of a single carbonatite-derived fluid in response to cooling and interaction with ground waters associated with the Bagh sandstone at the time of fluorite mineralization. The close genetic association between the carbonatite magma and the exsolved F-rich fluid is supported by their similar Nd isotope ratios and similar heavy REE chondrite-normalized ratios.

The Pb isotope ratios from the fluorites show that they are quite different from the values shown by the carbonatites, and significantly different from those from the Bagh sandstone. Most of the Pb isotope ratios are more radiogenic than those of the carbonatites, but similar to those of galena and pyrite. The Pb isotope data place additional constraints on the evolution of the mineralizing fluid, suggesting that the fluid interacted either with crustal material that was not Bagh sandstone or with minerals from the sandstone with much higher U/Pb ratios than those of the whole rocks. Our findings from the Nd, Sr, and Pb isotope data point to a complex evolutionary history for the mineralizing solutions that involved ongoing interactions between a cooling F-rich fluid, derived from the carbonatite melt, and the continental crust.

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