# Age, Sr- and Nd-Isotope Systematics, and Origin of Two Fluorite Lodes, Sierras Pampeanas, Argentina[1]

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## Abstract

Fluorite mineralization at the La Nueva and Bubu mines yields Sm-Nd ages of 131 ± 22 and 117 ± 26 Ma, respectively. Thus, the mineralization most probably is related to a late Gondwanian (Lower Cretaceous) extensional and magmatic event that affected the Sierras Pampeanas basement during the opening of the Atlantic Ocean. Hydrothermal fluids involved in the formation of the fluorite probably were of meteoric origin, their isotopic composition (Sr and Nd) resulting largely from the incongruent dissolution of feldspars in the host porphyritic granites.

## Introduction

THE SIERRAS PAMPEANAS are blocks of pre-Andean basement exposed in central and northwestern Argentina. They consist of Paleozoic granitoids and medium- to high-grade metamorphic rocks, mostly schists and gneisses, that supposedly are of Upper Precambrian to Lower Paleozoic age (Linares and Latorre, 1969; Cingolani and Varela, 1975).

Fluorite veins of economic interest are relatively common in the Sierras Pampeanas west and south of the city of Córdoba; in some cases they are being mined at present. Despite previous studies of the geology and mineralogy of these lodes, uncertainties remain concerning their age and the source of the ore-forming hydrothermal fluids. The suggested ages range from Late Paleozoic—i.e., possibly related to the host granitoids (Angeleli et al., 1980)—to Late Tertiary (González Díaz, 1972).

The recent application of Sm-Nd systematics to the study of fluorite in hydrothermal veins, when combined with Sr-isotope geochemistry, represents a powerful technique for determining the age of the mineralization and for constraining the source and subsequent history of the mineralizing fluids involved (Halliday et al.,

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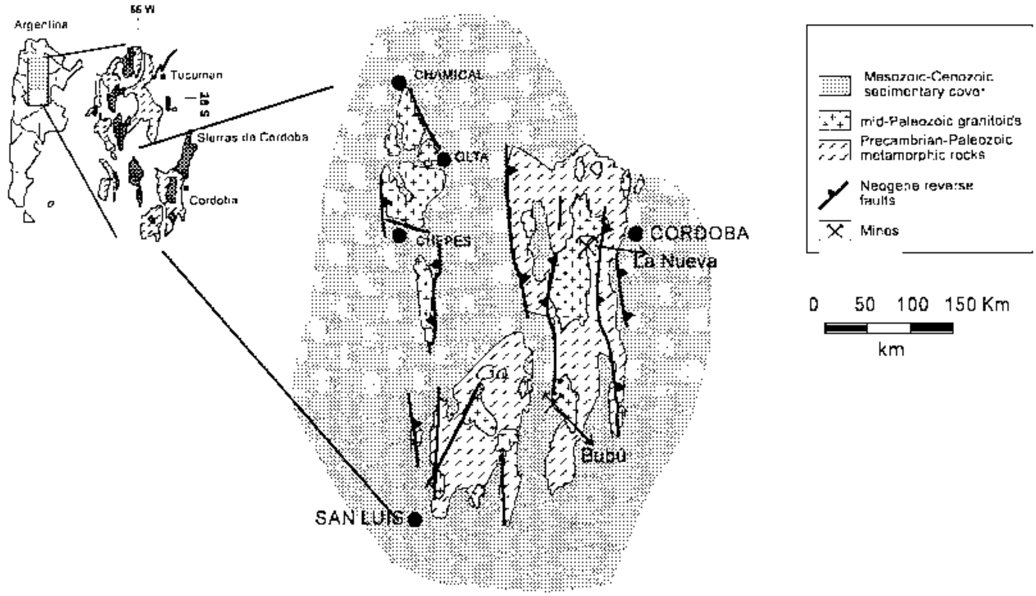

FIG. 1. Geological sketch map of the Sierras Pampeanas, showing the location of the two mines studied.

1986, 1990; Darbyshire and Shepherd, 1990; Chesley et al., 1991; Galindo et al., 1994; Höhndorf et al., 1994; Nagler et al., 1995). In this paper we provide Sm-Nd ages of fluorites from two sites in Córdoba province—La Nueva mine (31°27′ S, 64°36′ W), ~14 km west of Villa Carlos Paz, and Bubu mine (32°36′ S, 64°57′ W), in the Sierra de Comechingones (Fig. 1).

## Geological Setting

The La Nueva mine is located near the border of the large S-type granitic batholith of Achala. Veins occur on both sides of the granitoid contact with the metamorphic rocks. The Bubu mine is located within the broadly comparable Cerro Aspero batholith, not far from its southeastern contact with the metamorphic envelope (Fig. 1).

The Achala and Cerro Aspero batholiths belong to the G2 group of granitoids of the Sierras Pampeanas, which are middle Paleozoic in age (Rapela et al., 1992). A whole-rock Rb-Sr isochron age of 358 ± 9 Ma, i.e., Late Devonian–Early Carboniferous, was obtained for part of the Achala batholith by Rapela et al. (1991). Porphyritic biotite (± muscovite) monzogranites are the main petrographic type, followed in importance by two-mica leucogranites (Rapela et al., 1992). These granitoids have high contents of large-ion lithophile elements, as well as of P and Ti. Initial $^{87}$Sr/$^{86}$Sr ratios also are high (typically >0.712), suggesting derivation of the magmas by crustal anatexis. W and U hydrothermal deposits and complex pegmatites rich in Li, Be, Nb, Ta, and U are common within these batholiths.

Fluorite is a rare accessory mineral in the monzogranites, as well as in association with beryl in greisenized zones in the two-mica leucogranites. It also is a gangue mineral in high-temperature wolframite veins. However, most of the fluorite in the area of the Achala and Cerro Aspero batholiths is in discordant veins, which often are located close to the contacts with the enclosing metamorphic rocks. On a regional scale, the fluorite veins are the easternmost manifestation of a ~400 km wide belt of fluorite deposits that extends westward to the boundary of the Andes and that is related to first-order tectonic lineaments (Magliola Mundet, 1990). The mines studied in this paper form part of the Larca-Bubu metallogenic subdistrict, which is a part of the larger Sierras Pampeanas–Precordillera district (Menoyo and Brodtkorb, 1975).

The fluorite veins form an *en echelon* swarm, with trends close to N100°E and dips of 70°N

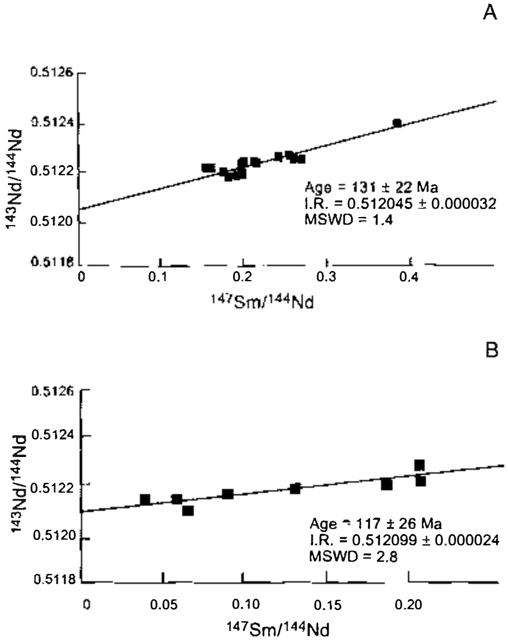

FIG. 2. Sm-Nd isochrons from fluorites. A. La Nueva mine. B. Bubu mine.

at La Nueva, whereas at Bubu the veins are subvertical with a dominant direction of N35° to 50°E (Fig. 2). The thickness of the veins is variable, but usually is <2 m; length along strike ranges from a few meters to several hundred meters. The main veins often branch off into smaller subparallel veins. The septa between veins consist of strongly brecciated host rocks that show intense silicification.

The veins consist of banded fluorite and chalcedony. Some pyrite (either older or younger than fluorite) in late fractures and traces of U-minerals also can be found. The fluorite is fibrous to columnar (with the long axis perpendicular to the banding) or sometimes cubic. Individual layers of fluorite are 1 mm to 10 cm thick and display a remarkable color variation—black; light and dark purple; and, to a lesser extent, amber, green, and colorless. At La Nueva, precipitation would appear to be from black → purple → yellow. The position of the green fluorite is not obvious. Repeated zonation often is found, suggesting that infilling of the fractures occurred in pulses.

The fluorite lodes were formed at shallow depths (<2 km) and at temperatures of 215° to 300° C (Coniglio, 1992). These conditions are common elsewhere in fluorite veins of the unconformity-related type (Dill and Nielsen, 1987; Rowan et al., 1996).

## Isotope Geochemistry

Fluorite samples of different colors from the two mines were analyzed for isotopic composition (Sr and Nd, and Sm/Nd ratio) by mass-spectrometric isotope dilution. The analytical methods and data-reduction issues involved are described in Galindo et al. (1994). In some cases, samples were taken from different-colored bands in the same hand specimen. In total, 16 samples were analyzed from La Nueva and 8 from Bubu (Table 1). In three samples from La Nueva, Rb and Sr also were determined; all the samples have low $^{87}$Rb/$^{86}$Sr ratios (0.007 to 0.036), indicating that only a small age correction was necessary to obtain the initial $^{87}$Rb/$^{86}$Sr ratio from the measured ratio. The rest of the samples were corrected using a value of 0.02 that was assumed for this purpose. Errors ($2\sigma$ level) are assumed to be 0.1% in Sm/Nd and 0.006% in $^{143}$Nd/$^{144}$Nd ratios.

Sm-Nd isochron plots are shown in Figure 2. For La Nueva, the $^{147}$Sm/$^{144}$Nd ratio varies from 0.154 to 0.385, and the data points define an isochron (MSWD = 1.4) with an age of 131 ± 22 Ma and an initial $^{143}$Nd/$^{144}$Nd ratio of 0.51204 ± 0.00003. The corresponding $\epsilon$Nd values at 130 Ma are −7.8 to −8.8. Initial $^{87}$Sr/$^{86}$Sr ratios vary from 0.722 to 0.727 and appear to fall into two groups with mean values close to 0.723 and 0.726. This may reflect a color difference (the first group is mainly black and yellow, the second purple and green), but there is no comparable variation in Nd. The results for the Bubu mine display more scatter and yield an isochron of 117 ± 26 Ma (MSWD = 2.8). The corresponding initial $^{143}$Nd/$^{144}$Nd ratio is 0.51210 ± 0.00002, and $\epsilon$Nd$_t$ values range from −7.0 to −8.3. The spread of $^{147}$Sm/$^{144}$Nd (0.042 to 0.204) is less than at La Nueva. If the two sets of Sm-Nd data are combined, the result (MSWD = 3.6) is 104 ± 13 Ma. The Sr-isotope composition also is distinctively less radiogenic than at La Nueva ($^{87}$Sr/$^{86}$Sr = 0.717 to 0.722, with most values near 0.721).

TABLE 1. Rb/Sr and Sm/Nd Data of Fluorites from La Nueva and Bubu Mines

| Sample[1] | Sm, ppm | Nd, ppm | $^{147}Sm/^{144}Nd$ | % s.d. | $^{143}Nd/^{144}Nd$ | % s.d. | $^{143}Nd/^{144}Nd$ | $\epsilon Nd_{131}$ | Rb, ppm | Sr, ppm | $^{87}Rb/^{86}Sr$ | $^{87}Sr/^{86}Sr$ | $^{87}Sr/^{86}Sr_{131}$ | $\epsilon Sr_{131}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| La Nueva mine | | | | | | | | | | | | | | |
| 175-1b | 1.708 | 6.705 | 0.1540 | 0.1 | 0.512201 | 0.003 | 0.512069 | -7.9 | | | 0.020 | 0.723520 | 0.723483 | 272 |
| 176-2b | 1.642 | 6.184 | 0.1605 | 0.1 | 0.512211 | 0.003 | 0.512073 | -7.8 | | | 0.020 | 0.722321 | 0.722284 | 255 |
| 177-1y | 5.506 | 8.651 | 0.3847 | 0.1 | 0.512394 | 0.003 | 0.512064 | -7.9 | 0.22 | 52.0 | 0.013 | 0.726406 | 0.726383 | 313 |
| 178-2y | 3.128 | 8.943 | 0.2114 | 0.1 | 0.512239 | 0.003 | 0.512058 | -8.1 | | | 0.020 | 0.722681 | 0.722644 | 260 |
| 179-3y | 1.553 | 4.730 | 0.1985 | 0.1 | 0.512228 | 0.003 | 0.512058 | -8.1 | | | 0.020 | 0.723357 | 0.723320 | 269 |
| 180-1c | 3.589 | 8.076 | 0.2686 | 0.1 | 0.512251 | 0.003 | 0.512021 | -8.8 | | | 0.020 | 0.723300 | 0.723263 | 269 |
| 181-2c | 1.516 | 4.800 | 0.1909 | 0.1 | 0.512185 | 0.003 | 0.512021 | -8.8 | 0.12 | 50.5 | 0.007 | 0.726303 | 0.726291 | 312 |
| 182-1g | 8.240 | 25.087 | 0.1985 | 0.1 | 0.512203 | 0.003 | 0.512033 | -8.6 | 0.93 | 77.3 | 0.036 | 0.726765 | 0.726698 | 317 |
| 183-2g | 8.329 | 25.618 | 0.1965 | 0.1 | 0.512205 | 0.003 | 0.512037 | -8.5 | | | 0.020 | 0.726371 | 0.726334 | 312 |
| 184-1p | 4.444 | 11.153 | 0.2409 | 0.1 | 0.512259 | 0.003 | 0.512053 | -8.2 | | | 0.020 | 0.726848 | 0.726811 | 319 |
| 185-2p | 8.491 | 23.916 | 0.2146 | 0.1 | 0.512236 | 0.003 | 0.512052 | -8.2 | | | 0.020 | 0.726462 | 0.726425 | 313 |
| LN3-1 | 1.448 | 4.855 | 0.1803 | 0.1 | 0.512174 | 0.003 | 0.512019 | -8.8 | | | 0.020 | 0.724156 | 0.724119 | 281 |
| LN3-2 | 1.741 | 6.047 | 0.1740 | 0.1 | 0.512198 | 0.003 | 0.512049 | -8.2 | | | 0.020 | 0.725304 | 0.725267 | 297 |
| LN3-3 | 0.961 | 2.249 | 0.2583 | 0.1 | 0.512250 | 0.003 | 0.512029 | -8.6 | | | 0.020 | 0.725836 | 0.725799 | 305 |
| LN3-6 | 3.040 | 7.247 | 0.2536 | 0.1 | 0.512267 | 0.003 | 0.512050 | -8.2 | | | 0.020 | 0.726574 | 0.726537 | 315 |
| LN4-1 | 9.657 | 29.645 | 0.1969 | 0.1 | 0.512211 | 0.003 | 0.512042 | -8.4 | | | 0.020 | 0.726617 | 0.726580 | 316 |
| Bubu mine | | | | | | | | | | | | | | |
| 1-c | 0.510 | 4.786 | 0.0644 | 0.1 | 0.512111 | 0.003 | 0.512062 | -8.3 | | | 0.020 | 0.720016 | 0.7199827 | 222 |
| 2-1y | 0.069 | 0.993 | 0.0422 | 0.1 | 0.512150 | 0.003 | 0.512118 | -7.3 | | | 0.020 | 0.720913 | 0.7208797 | 235 |
| 3-2y | 0.223 | 2.338 | 0.0577 | 0.1 | 0.512153 | 0.003 | 0.512109 | -7.4 | | | 0.020 | 0.720916 | 0.7208827 | 235 |
| 4-g | 13.671 | 40.483 | 0.2041 | 0.1 | 0.512247 | 0.003 | 0.512091 | -7.8 | | | 0.020 | 0.720615 | 0.7205817 | 230 |
| 5-w | 1.034 | 3.383 | 0.1847 | 0.1 | 0.512211 | 0.003 | 0.512070 | -8.2 | | | 0.020 | 0.722130 | 0.7220967 | 252 |
| 6-1p | 0.107 | 0.317 | 0.2036 | 0.1 | 0.512288 | 0.003 | 0.512132 | -7.0 | | | 0.020 | 0.716807 | 0.7167737 | 176 |
| 7-r | 1.768 | 12.163 | 0.0879 | 0.1 | 0.512174 | 0.003 | 0.512107 | -7.5 | | | 0.020 | 0.720925 | 0.7208917 | 235 |
| 8-2p | 3.544 | 16.542 | 0.1295 | 0.1 | 0.512208 | 0.003 | 0.512109 | 7.4 | | | 0.020 | 0.720909 | 0.7208757 | 234 |

[1] Lowercase letters in sample designations refer to fluorite colors: b = black; y = yellow; c = colorless; g = green; p = purple; w = white; r = pink.

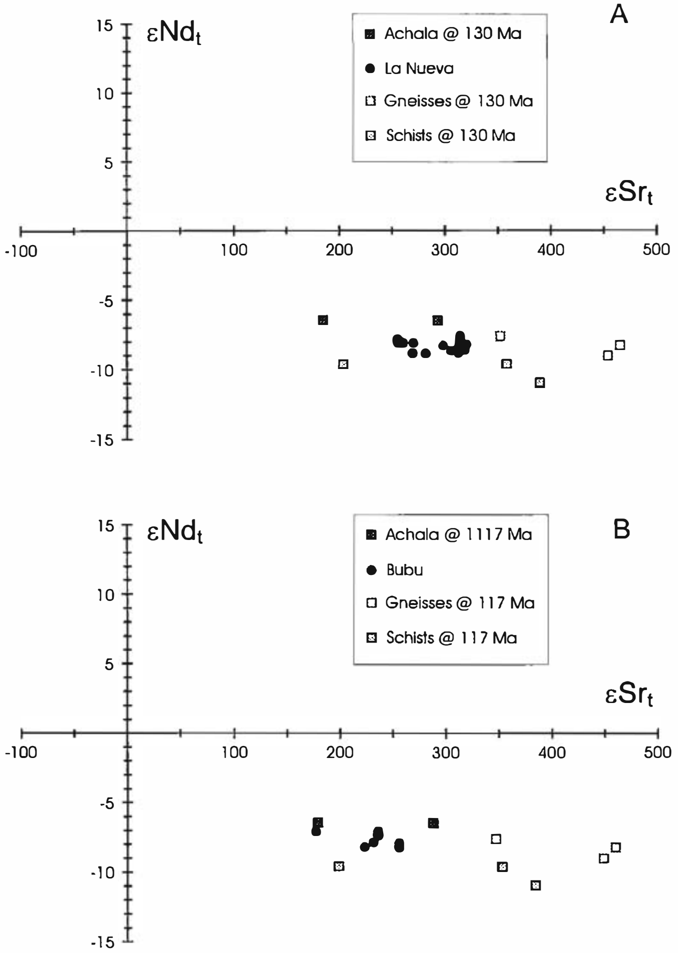

FIG. 3. $\epsilon Nd_t$-$\epsilon Sr_t$ plots of fluorites and regional rocks: Achala porphyritic monzogranites and metamorphic rocks (unpubl. data). A. La Nueva mine. B. Bubu mine.

## Discussion and Conclusions

The isochron relationships obtained do not result in very precise ages because of the small range of $^{143}Nd/^{144}Nd$ ratios. Nevertheless, the similarity of the two results indicates that they record a formation event that was almost certainly Early Cretaceous in age—within the limits of error the stratigraphic range is Upper Jurassic to Middle Cretaceous. This rules out the possibility of any genetic association with the magmatic stage of the Achala and Cerro Aspero batholiths, which host the lodes.

However, Early Cretaceous emplacement is readily related to brittle deformation of the basement rocks of the Sierras Pampeanas under regional extensional conditions (e.g., Ciciarelli, 1984). Concomitant eruption of alkali basalt took place along the La Punilla and La Calera faults (Kay and Ramos, 1996). K-Ar ages of 112 ± 6 Ma and 128 ± 5 Ma have been quoted for this volcanism in the Sierra de los Condores and Pungo area (Gordillo and Lencinas, 1976). Similarly, K-Ar ages from 120 ± 2 Ma to 130 ± 6 Ma are recorded by Gonzalez and Kawashita (1972), in the area south of Los Condores and Almafuerte. Trachybasalt dikes with equivalent K-Ar ages also have been recognized by Stipanicic and Linares (1975), and it is noteworthy that these follow trends that are similar to those of the fluorite veins. The thermal anomaly represented by the alkali volcanism could well have resulted in high-level convective circulation of the hot (>300° C) hydrothermal fluids that deposited the fluorites. This Mesozoic tectonothermal event also can be correlated with the Argentinian late-Gondwanic event defined by Rapela and Llambias (1997).

Isotope geochemistry may be used to constrain the source of Sr and Nd in the hydrothermal fluids. The Nd-isotope composition of the fluorites at the time of formation (Table 1) is quite similar in both mines ($\epsilon$Nd = –7.4 to –8.8 at La Nueva, and –7.4 to –8.3 at Bubu), and is less radiogenic than that of the Achala porphyritic granites at the same age (two available samples of the latter yield $\epsilon Nd_{130}$ values of –6.5 and –6.9 [unpubl. data]). This suggests that a source of neodymium other than the granites was involved. In this respect, most available $\epsilon Nd_{130}$ signatures of metamorphic rocks from different areas of the Sierras de Córdoba (unpubl. data) are lower than –9, with a mean value at ~–10 (Fig. 3). However, the $^{87}Sr/^{86}Sr$ composition of the fluorites is almost bracketed by that of the porphyritic granites ($\epsilon$Sr = 176 to 317 and 151 to 291, respectively), whereas the metamorphic rocks generally display $\epsilon Sr_{130}$ values higher than 350 (Fig. 3). This suggests that most of the Sr in the fluid was contributed by the granites and is supported by evidence of pervasive hydrothermal alteration found at the selvages of the veins.

On a $\epsilon$Nd-$\epsilon$Sr diagram (Fig. 3), fluorites plot between the porphyritic granitoids and the metamorphic rocks from different areas of the Sierras de Córdoba (unpubl. data), suggesting that the isotopic composition of the fluorites might be explained by the mixing of a granitic and a metamorphic component in the fluid. However, a more realistic interpretation arises if fluid/rock interaction is considered in terms of whole-rock–fluid disequilibrium, i.e., if the dissolution behavior of the host-rock minerals during the hydrothermal alteration is taken into account (Galindo et al., 1994). The incongruent dissolution of feldspars during phyllic alteration (quartz + sericite + chlorite) probably is the main process controlling the isotopic composition of the circulating hot fluid. As these minerals contain most of the Sr in the rocks, the composition of the circulating hydrothermal fluid will be progressively modified to match that of the granite. The low Sm/Nd ratios of feldspars relative to accessory minerals such as apatite, zircon, and sphene (Hanson, 1980), along with mass-balance considerations, could explain the low $\epsilon$Nd values of the fluorites relative to those of the granites. Most of the rare-earth elements contained in accessory minerals and biotite probably are retained despite chloritization (Alderton et al., 1980) and therefore do not contribute to a large extent to the fluid composition. This also can explain the homogeneity of the initial $^{143}Nd/^{144}Nd$ suggested by the isochrons. The slight differences in isotopic composition between deposits located in the two mines, especially in initial $^{87}Sr/^{86}Sr$ ratios, could indicate that they were formed from discrete high-level convection systems with locally controlled compositions.

There is no direct evidence indicating the ultimate source of the fluids prior to their high-level equilibration. The fluids could have been derived from water of mantle origin associated with the Cretaceous alkali volcanism or, perhaps more likely, they may have formed from meteoric water that percolated into the circulating system or convection cell.

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