27. R. A. Robie, B. S. Hemingway, J. R. Fisher, *U.S. Geol. Surv. Bull. 1452* (1978).
28. D. M. Jenkins, *Contrib. Mineral. Petrol.* **88**, 332 (1984).
29. L. Grossman, A. Hashimoto, R. Hinton, *Meteoritics* **21**, 379 (1986).
30. K. Tomeoka and P. R. Buseck, *Nature* **299**, 326 (1982).
31. B. Dominik *et al.*, *Proc. Lunar Planet. Sci. Conf.* **9**, 1249 (1978).
32. R. G. Prinn and B. Fegley, in *Origin and Evolution of Planetary and Satellite Atmospheres*, S. Atreya, J. Pollack, M. Matthews, Eds. (Univ. of Arizona Press, Tucson, 1989), pp. 78–136.
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Samarium-Neodymium Direct Dating of Fluorite Mineralization

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The direct dating of many styles of hydrothermal mineralization has proved difficult, limiting understanding of the geological processes that lead to crustal fluid flow and the formation of major ore deposits. The hydrothermal mineral fluorite (CaF_2) displays large variations in rare earth element (REE) abundance and samarium/neodymium ratios within a single vein. Samarium-neodymium dating of fluorite from the classic granite-hosted tin deposits of southwest England demonstrates its use as a precise chronometer of mineralization. The concentrations of light rare earth elements (LREEs) in the fluorites are highly variable and suggest the coeval precipitation of an LREE-rich phase as the most likely cause of the extreme variation in samarium/neodymium ratios.

MANY HYDROTHERMAL ORE DEPOSITS lack minerals that are suitable for isotopic dating. The most readily applicable techniques, such as U-Pb dating of pitchblende and K-Ar dating of sericite, are compromised by susceptibility to continuous or episodic chemical and thermal disturbances associated with hydrothermal activity along fracture systems. Furthermore, isotopic techniques used to date ore deposition commonly utilize alteration products, gangue minerals, or fluids that may not be coeval with ore-forming minerals. We need to be able to date mineralization directly and accurately in order to understand fully the many different products of crustal fluid flow, such as Mississippi Valley Type (MVT) deposits (*1*). Similarly, because it has not been possible to resolve the age of specific stages of ore deposition, most researchers have commonly concluded that granite-related hydrothermal mineralization is concurrent with or immediately follows magma emplacement ($<10^6$ years) (*2, 3*), whereas it has recently been demonstrated that mineralization can postdate the host granite by as much as 3 million to 25 million years (*4–6*).

Fluorites display highly variable rare earth element (REE) patterns, the causes of which are poorly understood (*7–10*). In this report, we demonstrate that the large range of Sm/Nd ratios in fluorite from southwest England permits the determination of high-precision Sm-Nd isochron ages. This technique allows the accurate dating of a variety of ore deposits and thus the timing of major fluid movements in the crust that have hitherto proved undatable with the use of other geochronological methods.

The Cornish Sn deposits are a classical, although complex, example of granite-related hydrothermal mineralization (*11–13*). Mineralization is spatially related to the Cornubian batholith, a series of peraluminous biotite-muscovite granites, intruded into polydeformed sedimentary and volcanic rocks of Devonian and Carboniferous age, at 280 to 290 Ma (million years ago) (*5*). The plutons are intruded by medium- to fine-grained granitic or aplitic dikes and, locally, by late-stage Li-rich or topaz-bearing granites. The final stage of magmatism, 270 to 280 Ma (*5*), is represented by a series of fine-grained, felsic dikes crosscutting the major plutons.

Mineralization is expressed as multiple, steeply dipping veins that cut both the granites and the country rocks and has been broadly classified into three main stages: (i) stage 1, early Sn- and W-bearing pegmatite deposits and Sn-bearing, greisen-bordered veins with fluid-inclusion homogenization temperatures (T_h) of 300° to 500°C, (ii) stage 2, polymetallic (Cu, Pb, Zn, Sn) quartz veins with T_h of 200° to 380°C, and (iii) stage 3, late polymetallic (Cu, Pb, Zn, Ag) sulfide veins, locally termed "crosscourses," with T_h of 105° to 180°C (*14–17*). Stage 2 veins represent the major episode of Sn and Cu mineralization. The classic mineralogical zoning and structures of these ore bodies, together with their apparent spatial relationships with the granites, has led to the traditional view that this stage of mineralization was directly linked to plutonism. The fluid inclusions analyzed from stage 3 crosscourse mineralization are similar in composition to Na-Ca-Cl–rich deep sedimentary brines and are probably from a younger regional event, unrelated to the intrusion of the Cornubian batholith (*16*).

Fluorite samples analyzed in this study were collected at the Wheal Jane and South Crofty mines in the vicinity of the Carnmenellis pluton (*11, 18*). Mineralization at the Wheal Jane Mine is hosted by Upper Devonian slate, and shale of the Mylor Formation and biotite-muscovite granite are not exposed in the mine or recorded in drill core. At South Crofty, however, similar mineralization crosscuts both the granite and the Mylor Formation. Samples from the South Crofty Mine were collected only from granite-hosted veins because of limited mine access.

Sm and Nd concentrations for fluorites and spatially associated hydrothermal alteration products from the Wheal Jane and South Crofty mines vary over more than two orders of magnitude (Table 1). The $^{147}Sm/^{144}Nd$ ratios range from 0.12 to 0.95 and have a spread of as much as 0.12 to 0.37 within a single hand specimen. In the fluorite from the South Crofty, stage 2, Sn-bearing polymetallic veins there is a clear relation between the intensity of the color, Sm and Nd concentrations, and Sm/Nd ratios (Table 1).

Sm-Nd isotopic data for fluorites from the Sn-bearing polymetallic veins at South Crofty and Wheal Jane define precise isochrons (Fig. 1, A and B). Data for chloritic hydrothermal alteration products and crosscourse fluorites plot below these isochrons and have been excluded from the regressions. The data for South Crofty fluorites yield a slope corresponding to an age of 259 ± 7 Ma (2σ) and an intercept of 0.51197 [initial ϵ_{Nd} (deviation in parts per 10^4 from coeval bulk earth) = -6.5 ± 0.2]; the mean square of weighted deviates (MSWD) is 1.0 (Fig. 1B). The Wheal Jane fluorites define a slope corresponding to an age of 266 ± 3 Ma (2σ) and an intercept of

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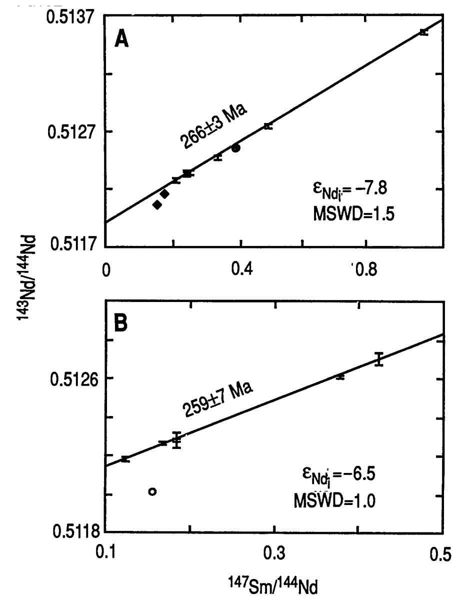

Fig. 1. Sm-Nd isochrons for the (**A**) Wheal Jane and (**B**) South Crofty mines. Fluorites from stage-2 veins are plotted as 2σ mean error bars. Other symbols are as follows: filled diamonds, crosscourse fluorites; filled circle, mixed fluorite and chloritic alteration; open circle, chloritic alteration; see text for explanation.

0.51190 (initial ϵ_{Nd} = −7.8 ± 0.2); the MSWD is 1.5 (Fig. 1A). The absence of nonanalytical scatter in the data (indicated by the low MSWD) and the overlapping ages, despite the different initial ϵ_{Nd} values and the large variation in REE abundance, are consistent with the idea that the initial isotopic compositions of the fluorites defining each isochron were uniform.

The Sm-Nd isochron ages obtained for the two mines overlap within error and are significantly younger than the Rb-Sr age (290 ± 2 Ma) determined for the Carnmenellis pluton (*5*). These data support the hypothesis that main-stage polymetallic mineralization at South Crofty and Wheal Jane postdates emplacement of the Carnmenellis pluton by at least 20 million years (*4, 5, 15*). This relation suggests that mineralization may be genetically linked to later intrusive activity.

The initial ϵ_{Nd} values for the regressed isochrons from South Crofty and Wheal Jane are significantly different (−6.5 ± 0.2 and −7.8 ± 0.2, respectively). The fluorite samples analyzed from the South Crofty Mine are hosted completely within granite, whereas veins at the Wheal Jane Mine are hosted within the Upper Devonian Mylor Formation. Calculated ϵ_{Nd} values for the Carnmenellis pluton at 260 Ma are −6.7 to −7.5 and for the sedimentary rocks are −10 to −12 (*19*). These data suggest that the REEs in the fluids at South Crofty were derived from the granite or a related source. The initial ϵ_{Nd} values of the fluids at Wheal Jane may have been lowered as a result of incorporation of REE from the sedimentary rocks, but clearly most of the Nd was derived from the granite. The Sm-Nd data for the crosscourse fluorite mineralization and hydrothermal alteration products plot well below the isochron defined by stage 2 polymetallic mineralization (Fig. 1, A and B). Because calculated ϵ_{Nd} values do not intersect those of the granite at any time, the Nd in the crosscourse fluids was most likely derived from different sources. There is abundant evidence that the major polymetallic stage 2 veins have been hydrothermally altered during such later regional events (*4, 15*). This rejuvenation evidently did not disturb the Sm-Nd systems in the stage 2 fluorites; thus this approach can potentially be used in areas of complex alteration histories.

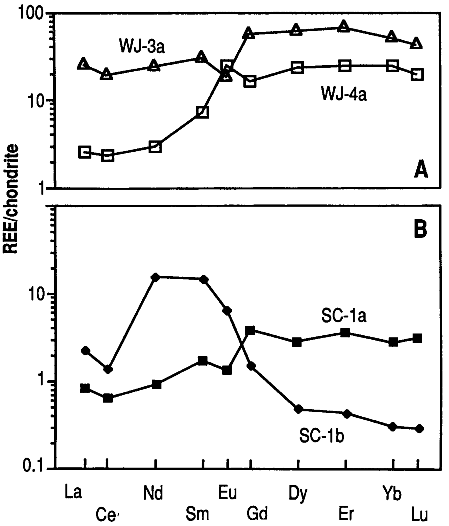

Fig. 2. Chondrite-normalized REE patterns for fluorite, determined by isotope dilution, from the (**A**) Wheal Jane and (**B**) South Crofty mines. The REE abundances from the Leedy chondrite (*28*) were used for normalization.

In order to understand the causes of the large variations in Sm/Nd ratios, it is necessary to study the spectrum of REE concentrations in these samples. Chondrite-normalized REE diagrams for fluorite from both South Crofty and Wheal Jane reveal large fractionations in the light REE (Fig. 2, A and B). Fluorite with higher LREE concentrations and lower Sm/Nd ratios is paragenetically earlier than fluorite with lower LREE concentrations and higher Sm/Nd ratios. All samples have negative Ce anomalies. Pronounced Ce anomalies reported for other minerals in igneous and metamorphic rocks have generally been attributed to seawater alteration of the source or concurrent crystallization of LREE-rich phases, such as monazite, which preferentially accumulate Ce and La (*20*). The minor kinking in the patterns of the heavy rare earth elements (HREE) for the South Crofty samples is similar to those of other minerals found in fluid-rich environments (*21*). The observed Eu anomalies are both negative and positive and are not uniformly associated with either the LREE-rich or LREE-depleted patterns. Thermodynamic calculations suggest that at elevated temperatures (>250°C) Eu^{2+} should be dominant over Eu^{3+} (*22*) and may substitute more readily for Ca^{2+} than trivalent REEs. Leaching of Eu from feldspars in the host rock during fluid circulation may also lead to positive Eu anomalies

Table 1. Sm-Nd isotopic analyses (*25–27*) for fluorites and alteration minerals from Cornwall, England. F, fluorite; Ch, chloritic alteration; W, white; C, clear; LG, light green; DG, dark green; P, purple; *, crosscourse.

Sample	Mineral	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{143}Nd/^{144}Nd$	±2σ
			Wheal Jane			
WJ-1a	LG-F	15.6	28.5	0.3313	0.512464	± 10
WJ-1b	C-F	9.04	5.79	0.9453	0.513544	± 10
WJ-2	C-F	6.19	17.7	0.2115	0.512269	± 20
WJ-3a	LG-F	7.23	17.9	0.2442	0.512331	± 10
WJ-3b	W,C-F	5.60	13.4	0.2519	0.512335	± 10
WJ-3c	LG-F	5.43	13.5	0.2439	0.512321	± 10
WJ-4a	P-F	1.69	2.11	0.4835	0.512734	± 10
WJ-4b	F and Ch	0.950	1.47	0.3901	0.512553	± 10
WJ-5*	P-F	2.10	7.90	0.1569	0.512055	± 10
WJ-6*	P-F	2.22	7.52	0.1786	0.512149	± 10
			South Crofty			
SC-1a	W-F	0.407	0.654	0.3772	0.512609	± 10
SC-1b	W-F	3.42	11.3	0.1836	0.512277	± 10
SC-1c	LG-F	5.47	19.7	0.1676	0.512263	± 10
SC-1d	DG-F	53.5	260	0.1243	0.512180	± 10
SC-1e	DG-F	58.9	288	0.1234	0.512180	± 10
SC-2a	LG-F	1.22	3.99	0.1847	0.512279	± 30
SC-2b	W-F	1.71	2.45	0.4225	0.512704	± 47
SC-2c	Ch	0.800	3.07	0.1571	0.512003	± 10

and variable abundances. The HREE patterns are relatively flat, and, although the overall abundance changes, the patterns remain similar within an individual mine. However, in South Crofty the HREE are apparently concentrated in the later fluids, whereas at Wheal Jane the converse is true, the explanation of which is currently unclear.

The variation in REE patterns cannot be attributable to a mixing of fluids from different sources in the vein systems because this would result in variable initial ϵ_{Nd} values. It is also difficult to envisage why the HREEs should maintain such consistent patterns if mixing is responsible for changes in the LREEs. Leaching of uraninite or other HREE-rich minerals would not only fractionate the REEs but would also increase the relative abundance of all HREEs in the mineralizing fluid. Similarly, leaching of LREE-enriched phases, such as monazite, could not produce the depletion in the LREEs observed in the paragenetically later fluorite.

These relations lead us to conclude that the most likely mechanism for producing the observed change in the Sm-Nd composition of the fluid is the coeval precipitation of an unidentified LREE-enriched phase, analogous to monazite, in the hydrothermal system. The dramatic crossover in the REE element patterns is good evidence for the importance of such a process at South Crofty. The extent to which such a model can be extended to account for the Sm-Nd fractionation observed in many other kinds of fluorite-bearing mineralization (*7, 9, 23, 24*), such as MVT deposits, is uncertain.

Regardless of the exact mechanism, REE fractionation in fluorites is commonly observed. The large range in Sm/Nd ratios, the low uncertainty in age, and resistance to late hydrothermal effects render the Sm-Nd dating technique a powerful geochronometer even for relatively young mineralization.

REFERENCES AND NOTES

1. W. C. Kelly, J. M. Sharp, D. E. White, *Geology* **11**, 309 (1983).
2. B. J. Skinner, in *Geochemistry of Hydrothermal Ore Deposits*, H. L. Barnes, Ed. (Wiley, New York, ed. 2, 1979), p. 10.
3. L. M. Cathles, *Econ. Geol. 75 Anniv. Vol.* (1981), p. 424.
4. A. N. Halliday, *Econ. Geol.* **75**, 752 (1980).
5. D. P. F. Darbyshire and T. J. Shepherd, *J. Geol. Soc. London* **142**, 1159 (1985); J. T. Chesley, unpublished data.
6. L. W. Snee, J. F. Sutter, W. C. Kelly, *Econ. Geol.* **83**, 335 (1988).
7. P. Möller, P. P. Parekh, H. J. Schneider, *Miner. Deposita* **11**, 111 (1976).
8. P. Bratter *et al.*, *Erzmetall* **25**, 389 (1972).
9. A. N. Halliday, T. J. Shepherd, A. P. Dickin, J. T. Chesley, *Nature* **344**, 54 (1990); J. T. Chesley, A. N. Halliday, T. J. Shepherd, R. C. Scrivener, paper presented at the 7th International Conference on Geochronology, Cosmochronology, and Isotope Geology, 24 to 29 September 1990, Canberra, Australia.
10. I. V. Chernyshev, V. A. Troitsky, D. Z. Zhuralev, paper presented at the 6th International Conference on Geochronology, Cosmochronology, and Isotope Geology, 30 June to 4 July 1986, Cambridge, United Kingdom; *Terra Cognita* **6**, 226 (1986).
11. H. G. Dines, *Mem. Geol. Surv. G.B.* **1**, 1 (1956); *ibid.* **2**, 509 (1956).
12. M. Stone and C. S. Exley, in *High Heat Production (HHP) Granites, Hydrothermal Circulation, and Ore Genesis* (Institution of Mining and Metallurgy, London, 1985), pp. 571–593.
13. N. J. Jackson, J. Willis-Richards, D. A. C. Manning, M. S. Sams, *Econ. Geol.* **84**, 1101 (1989).
14. N. J. Jackson, J. Moore, A. H. Rankin, *J. Geol. Soc. London* **134**, 343 (1977).
15. N. J. Jackson, A. N. Halliday, S. M. F. Shepard, J. G. Mitchell, in *Metallization Associated with Acid Magmatism*, A. M. Evans, Ed. (Wiley, Chichester, 1982), pp 137–179.
16. T. J. Shepherd, M. F. Miller, R. C. Scrivener, D. P. F. Darbyshire, in *High Heat Production (HHP) Granites, Hydrothermal Circulation, and Ore Genesis* (Institution of Mining and Metallurgy, London, 1985), pp. 345–364; T. J. Shepherd and R. C. Scrivener, *Ussher Soc. Proc.* **6**, 491 (1987).
17. R. C. Scrivener, T. J. Shepherd, N. Garrioch, *Ussher Soc. Proc.* **6**, 412 (1986).
18. K. F. G. Hosking, *Trans. R. Soc. Cornwall* **18**, 309 (1962).
19. D. P. F. Darbyshire and T. J. Shepherd, paper presented at the 7th International Conference on Geochronology, Cosmochronology, and Isotope Geology, 24 to 29 September 1990, Canberra, Australia; D. P. F. Darbyshire, unpublished data.
20. H. Puchelt and R. Emmermann, *Earth Planet. Sci. Lett.* **31**, 279 (1976).
21. A. Masuda and Y. Ikeuchi, *Geochem. J*, **13**, 19 (1979).
22. D. A. Sverjensky, *Econ. Geol.* **79**, 23 (1984).
23. T. J. Shepherd, D. P. F. Darbyshire, G. R. Moore, D. A. Greenwood, *Bull. Bur. Mech. Gites Min.* **2**, 371 (1982).
24. J. T. Chesley, unpublished data.
25. Standard ion-exchange procedures were used to separate the REEs (*26*). All concentration measurements were performed by isotope dilution at the University of Michigan on a VG sector mass spectrometer (*26*). An average $^{143}Nd/^{144}Nd$ ratio of 0.511862 ± 10 was obtained for the La Jolla standard. Ages were calculated with model 1 regressions on Isoplot (*27*). The decay constant λ $^{147}Sm = 6.54 \times 10^{-12}$ year^{-1} was used for age calculations. We calculated the ϵ_{Nd} values using present-day values for bulk earth of $^{143}Nd/^{144}Nd = 0.512636$ and $^{147}Sm/^{144}Nd = 0.1967$.
26. A. N. Halliday *et al.*, *Earth Planet. Sci. Lett.* **94**, 274 (1989).
27. K. R. Ludwig, *U.S. Geol. Surv. Open File Rep. 88-557* (rev. 1990).
28. A. Masuda, N. Nakamura, T. Tanaka, *Geochim. Cosmochim. Acta* **37**, 239 (1973).
29. We thank M. Owen, P. Gribble, and S. Speed of Carnon Consolidated Limited for access to the South Crofty and Wheal Jane mines and for geologic expertise during sample collection. S. Nakai provided expertise during REE analysis. We thank T. J. Shepherd, W. C. Kelly, S. F. Kesler, K. Mezger, J. R. O'Neil, and D. P. F. Darbyshire for discussion and critical review of the original manuscript. Research was supported by National Science Foundation grants EAR 8616061, 8804072, and 9004413 to A.N.H. This paper is published with the approval of the Director of the British Geological Survey (Natural Environment Research Council).

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A Calcium-Dependent Protein Kinase with a Regulatory Domain Similar to Calmodulin

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Calcium can function as a second messenger through stimulation of calcium-dependent protein kinases. A protein kinase that requires calcium but not calmodulin or phospholipids for activity has been purified from soybean. The kinase itself binds calcium with high affinity. A complementary DNA clone for this kinase has been identified; it encodes a protein with a predicted molecular mass of 57,175 daltons. This protein contains a catalytic domain similar to that of calmodulin-dependent kinases and a calmodulin-like region with four calcium binding domains (EF hands). The predicted structure of this kinase explains its direct regulation via calcium binding and establishes it as a prototype for a new family of calcium-regulated protein kinases.

IN PLANTS, FREE CALCIUM (Ca^{2+}) HAS been implicated as a second messenger in diverse processes including cytoplasmic streaming and signal transduction (*1*). Increased concentrations of intracellular Ca^{2+} have been shown to regulate stomatal closure (*2*). In animals, Ca^{2+} can regulate signal transduction pathways by activating protein kinases dependent on Ca^{2+} and calmodulin (Ca^{2+}/calmodulin) (*3*). Calmodulin is present in plant cells (*4*) and some evidence that plant cells also contain Ca^{2+}/calmodulin-dependent kinase activity has been presented (*5*). However, a Ca^{2+}-dependent serine-threonine protein kinase has been purified from soybean (*Glycine max* L. cv Wayne) that does not require calmodulin. This Ca^{2+}-dependent protein kinase (CDPK) shows half-maximal stimulation at 2 μM Ca^{2+} and the enzyme itself contains a high affinity Ca^{2+} binding site or sites (*6, 7*).

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