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PRELIMINARY NOTE

Dissolution of Fluorite (CaF_2) for Isotope Geochemistry

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SUMMARY

Due to the chemical similarities among Ca, Sr and the rare-earth elements, fluorite (CaF_2), a accessory mineral that occurs in ore deposits, igneous, hydrothermal and metamorphic rocks, can be used to monitor genetic processes in these settings. Using a quantitative, low blank, H_2SO_4-based dissolution technique, we analysed fluorite from the East Kemptville tin mine, Nova Scotia, Canada. An exceptionally wide variation in initial $^{87}Sr/^{86}Sr$ ratio (0.71342 - 0.77495), and Sr (30 - 1370 ppm) and Rb (1 - 13 ppm) contents resulted, probably due to fluid interaction after ore formation.

Fluorite (CaF_2) is a common accessory mineral that occurs in igneous, hydrothermal and metamorphic rocks and many types of ore deposits. Radioisotope geochemistry is used to clarify the genetic processes responsible for the formation and alteration of these rocks. Due to the chemical coherence

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of Ca, Sr and the rare-earth elements (REE), fluorite is bound to become more important as it can be used to monitor these important elements in many geological settings. In particular, the isotopic composition of Sr and Nd can be used to monitor primary source composition, fluid mixing paths and chemical processes. Fluorite was generally thought to contain minor amounts of the radioactive parent element Rb, so the measured strontium isotopic ratio was considered to be a valid approximation of the initial ^{87}Sr/^{86}Sr ratio. However, this assumption is not always valid (Table 1).

Perhaps because fluorite is difficult to dissolve, this potentially useful mineral has not been widely utilized. Using the following H_2SO_4-based

TABLE 1

Rb-Sr data: fluorite from the East Kemptville mine, Nova Scotia.

SAMPLE	Rb	Sr	87Rb/86Sr	---87Sr/86Sr---	
	ppm	ppm	atomic	atomic	
				*	#
EKS19	13.0	1420	0.03	0.71354	0.71342
EKS69	2.05	34.3	0.17	0.71641	0.71560
EKS49	5.99	52.0	0.33	0.71996	0.71840
EKS65	2.45	1370	0.01	0.72320	0.72318
EKAD4	6.44	548	0.03	0.77511	0.77495
E2710	2.71	582	0.01	0.74986	0.74980
EKS42	9.32	358	0.08	0.72344	0.72309
EK433		29.9		0.76012	
EKCC1	1.24	279	0.01	0.72514	0.72508
EKCC2	0.818	72.9	0.03	0.72269	0.72254

* present-day strontium isotopic ratio

\# initial strontium isotopic ratio

(calculated from present-day ratio and time since crystallization of host granitic rocks - 330 million years) dissolution technique, we analysed fluorite from the East Kemptville tin mine, Nova Scotia, Canada [1,2]. This fluorite has a wide variation in initial $^{87}Sr/^{86}Sr$ ratio (0.71342 -0.77495), and Sr (30 - 1370 ppm) and Rb (1 - 13 ppm) contents (Table 1).

We dissolved fluorite by placing 50 - 100 mg of fluorite, 1 - 2 mls of Ultrex H_2SO_4 (18M) and 0.1 ml Ultrex HNO_3 (16M) in a 100 ml Teflon wide-mouthed evaporating dish. This mixture was held at 150°C until the digestion was complete (several hours) and the fluorite was converted to a white slurry. More H_2SO_4 was added if required. When dissolution was complete, the temperature was increased to 220°C to evaporate about half of the remaining H_2SO_4. The dish was cooled and 2 - 7 ml of distilled 2.5M HCl was added to the acid dropwise to minimize the strong exothermic reaction and avoid sample loss. After the white precipitate dissolved (1 - 12 hrs), the temperature was increased to about 220°C to evaporate the excess HCl and H_2SO_4. When fuming was complete, the evaporating dish was immediately removed from the hot-plate. Further baking made the residue very difficult to dissolve subsequently.

The sample was taken back into solution using warm water and split into three aliquots. One portion was retained for future Sm-Nd analyses. The others were individually spiked for Rb or Sr using artificially-enriched isotopes obtained from the Oak Ridge National Laboratory. The aliquots were then processed using standard ion-exchange techniques. Aliquots were spiked separately to eliminate the possible interference of ^{87}Rb (from the Rb spike) in the ^{87}Sr signal during mass spectrometric analyses.

Isotopic analyses were obtained using a Finnigan-MAT 261 multicollector solid-source mass spectrometer at Carleton University. At the 1 sigma level, analytical precision was 0.3% and 0.8% for Sr and Rb concentrations respectively, 0.85% for $^{87}Rb/^{86}Sr$ and 0.002% for $^{87}Sr/^{86}Sr$. The blank for the entire procedure outlined above contained 0.25 ng Rb and 2 ng Sr. The average $^{87}Sr/^{86}Sr$ ratio for 40 analyses of the National Bureau of Standards Sr standard NBS987 was 0.71023 $\pm$ 0.00003 over a three year period.

Using this technique, we have successfully analysed fluorite from the fluorine-rich East Kemptville mine and related granitic rocks [2,3]. The results are being used to monitor variations in the initial strontium ratio and Rb and Sr concentrations in the ore-forming fluids temporally and spatially throughout the deposit. A subset of the East Kemptville data (Table 1) illustrates the wide ranges encountered in fluorite sampled from the ore and several vein sets. The Rb contents of East Kemptville fluorite are 4 - 10 times higher that the five other published spiked analyses [5,6] which range from 0.58 - 3 ppm. These high contents reflect the Rb-rich environment of the East Kemptville deposit. The variation in Sr content of East Kemptville fluorite (30 - 1370 ppm) is similar to that previously reported elsewhere for spiked analyses [5,6]. However, because there are so few spiked analyses reported, it is difficult to say if such a range in Sr content in the fluorite from one deposit is unusual.

Typically, planetary rocks have strontium initial ratios that range from 0.699 (*e.g.* the basaltic achondritic meteorite Juvinas [7]) to 0.731 (*e.g.* F, B, P-enriched Macusani obsidian, Peru [8]). The variation in strontium initial ratios from East Kemptville fluorite is at least double this range. A survey of the available literature suggests that the isotopic composition of fluorite can correlate with that of sedimentary rocks [9], associated igneous rocks [10,11] or mixtures of fluids from several sources [4,5,11,12]. Our preliminary interpretation is that the variation in the East Kemptville fluorite data is related to the interaction of an unusually F-rich aqueous fluid with the host leucomonzogranite and overlying clastic metasedimentary rocks. Rb and Sr were added at different times to this fluid [2,3].

Addition of ^{87}Sr *via* the radioactive decay of ^{87}Rb could substantially alter the ^{87}Sr/^{86}Sr ratio of fluorite formed hundreds of millions of years ago. For this reason, we recommend that the Rb content of fluorites should always be measured, especially for those fluorites associated with highly differentiated Rb-rich granites or rhyolites. Furthermore, fluorite formed in granitic or hydrothermal environments can be depleted in light REE [13,14] and thus have relatively high Sm/Nd ratios. These fluorites could have enough variation in Sm/Nd to be dated by the Sm/Nd method.

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1 J.M. Richardson, in: R.P. Taylor and D.F. Strong (eds) 'Recent Advances in the Geology of Granite Related Mineral Deposits' Canadian Institute of Mining and Metallurgy, Montreal, Quebec, Special Volume 39 (l988) p. 265.
2 J.M. Richardson, Genesis of the East Kemptville greisen-hosted tin deposit, Davis Lake complex, Southwestern Nova Scotia. Unpublished PhD thesis, Carleton University, Ottawa, Ontario, Canada (l988) 293p.
3 J.M. Richardson, J. Blenkinsop, and K. Bell, Contrib. Min. Pet., (in press).
4 M.C. Metz, D.G. Brookins, Rosenberg, P.E. and R.E. Zartman, Econ. Geol., 80 (1985) 394.
5 P. Horn, H. Kohler and D. Muller-Sohnius, Chem. Geol. (Iso. Geol. Sect.), 58 (1986) 259.
6 A.P. Dickin, C.M. Rice and R.S. Harmon, Econ. Geol., 81 (l986) 904.
7 C.J. Allegre, J.L. Birck, S. Fourcade and M.P. Semet, Science, 187 (l975) 436.
8 M. Pichavant, J.V. Herrera, S. Boulier, L. Briqueu, J.L. Joron, M. Juteau, L. Marin, A. Michard, S.M.F. Sheppard, M. Treuil, and M. Vernet, in B.O. Mysen (ed.) 'Magmatic Processes: Physicochemical Principles' Special Publication #1, The Geochemical Society, University Park, Pennsylvania (l987) p. 359.
9 J. Ruiz, S.E. Kesler, S.E. and L.M. Jones, Econ. Geol., 80 (1985) 33.
10 N.B.W. Harris, A.E.R.O. Mohammed and M.Z. Shaddah, Geol. Mag., 120 (1983) 115.
11 K.M. Kessen, M.S. Woodruff and N.K. Grant, Econ. Geol., 76 (1981) 913.
12 D.I. Norman and G.P. Landis, Econ. Geol., 78 (1983) 451.
13 G.K. Muecke, and D.B. Clarke, Can. Min., 19 (1981) 133.
14 V. Ekambaran, D.G. Brookins, P.E. Rosenberg and K.M. Emanuel, Chem. Geol., (1986) 319.