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FLORENCITE: A FIRST OCCURRENCE IN CANADA

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ABSTRACT

Colorless to greyish florencite, with formula $Al_3(Ce_{0.54}La_{0.27}Nd_{0.11}Sm_{0.04}Ca_{0.04})(PO_4)_2(OH)_6$, occurs as millimetre-sized porphyrotopic rhombehedra in fossiliferous shales of the Late Precambrian Little Dal Group in the Mackenzie Mountains, Northwest Territories. Physical properties determined are: H∼6, good {001} cleavage, specific gravity 3.54 (3.69 calc.), uniaxial (+), ω 1.702, ϵ 1.715 (±0.002), a 6.99, c 16.25 Å (±0.01 Å). The sedimentary fabric and the similar rare-earth distribution in the host shale and in the florencite indicate that the mineral has formed authigenically. Florencite may be a more common authigenic constituent of Precambrian shales than suspected; its presence may permit the isotopic dating of the rocks by the Sm–Nd method.

Keywords: florencite, Northwest Territories, Little Dal Group, rare earths.

SOMMAIRE

Une florencite incolore à grisâtre, de formule $Al_3(Ce_{0.54}La_{0.27}Nd_{0.11}Sm_{0.04}Ca_{0.04})(PO_4)_2(OH)_6$ se rencontre sous forme de rhomboèdres porphyrotopiques de dimension millimétrique, dans un schiste argileux fossilifère du Groupe Little Dal d'âge Précambrien récent, dans les Monts Mackenzie (Territoires du Nord-Ouest). La florencite montre les propriétés suivantes: dureté ∼6; clivage {001} bon; densité 3.54 (calc. 3.69), uniaxe (+), ω 1.702, ϵ 1.715 (±0.002), a 6.99, c 16.25 Å (± 0.01 Å). Le contexte sédimentaire et la similitude entre la distribution des terres rares dans le schiste argileux et dans la florencite indiquent que le minéral est de cristallisation authigène. La florencite pourrait être plus fréquente qu'on ne l'admet généralement comme composant authigène des schistes argileux du Précambrien; sa présence pourrait permettre la datation isotopique de ces roches par la méthode Sm–Nd.

Mots-clés: florencite, Territoires du Nord-Ouest, Groupe Little Dal, terres rares.

INTRODUCTION

Florencite, a rare-earth phosphate of the crandallite group, has been reported as an accessory mineral in mica schists, in sands, as a placer mineral, in pegmatites and carbonatites as well as in vein deposits associated with alkaline intrusions. Florencite is known from Europe, Asia, Africa, South America and also from North America, where it has been described from Virginia (Mitchell & Geitgey 1968) and California (Milton & Bastron 1971). More recently, Lefebvre & Gasparrini (1980) described florencite from the Zairian Copper Belt and reviewed the available data concerning the mineral. The first Canadian discovery, in the Mackenzie Mountains, is unusual in that the florencite occurs as millimetre-sized, porphyrotopic crystals in shales. It is of particular interest not only because of its rarity and unusual crystallinity, but also because of its potential application to isotopic dating of the host sedimentary rocks by the relatively new Sm–Nd method.

FLORENCITE LOCALITY

Specimens were found in the Backbone Ranges of the Mackenzie Mountains, on a small northeast-facing spur of rusty-weathering black shale, below an escarpment of stromatolitic dolostones, at 63°50′20″ N, 127°33′55″ W and at an elevation of approximately 1770 m (Fig. 1). The locality is in the northwestern corner of the 1:250,000 Wrigley Lake sheet (N.T.S. 95M) and also appears on the geological map of the same name included in Gabrielse *et al.* (1973, Map 1315A). The locality is close to cross-section A–B on that map, just west of the point where it intersects the outcrop trace of the Plateau Thrust.

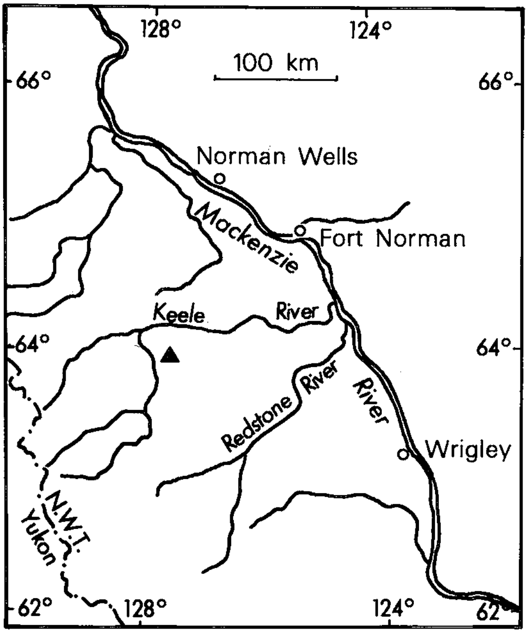

FIG. 1. Location map. Triangle shows position of florencite occurrence.

Geological Setting

The florencite occurs in an allochthonous sequence of Late Precambrian sedimentary rocks (Fig. 2A) that underlies the Backbone Ranges and that has been thrust northeastward over a Paleozoic assemblage along the Plateau Thrust (Gabrielse *et al.* 1973, Map 1315A). Florencite is present in the upper half of the "rusty shale subunit" of the Little Dal Group (Aitken 1977, Hofmann & Aitken 1979). This unit is comprised predominantly of rusty weathering black shales that are pyritic and phosphatic and that carry megafossils similar to *Chuaria* and *Tawuia* found previously in the somewhat older "basinal sequence" of the Little Dal Group (Hofmann & Aitken 1979).

Mineralogy

The millimetre-sized, colorless to greyish crystals, identified as florencite by X-ray diffraction, were collected by the second author in thin, slab-like specimens of black, rusty weathering shale. The florencite occurs as porphyrotopic crystals, protruding from the bedding plane surface of the shale specimen, where they have developed with a density of approximately 5 crystals *per* square centimetre (Figs. 2B, 2C). The florencite horizon from which crystals were extracted for study is less than 1 mm thick. The mineral was also observed and identified in several other specimens from the shale sequence. However, in these, the crystals occur much more sporadically than shown in Figures 2B and 2C. It is probable that the mineral occurs in varying abundance throughout the shale sequence.

The mineral occurs as well-formed elongate rhombohedra up to 2 mm in length; the typical crystal in the specimen studied is 0.3 x 1 mm in size. Small crystals are colorless, whereas larger ones are greyish with a greasy lustre or may be darkened owing to the inclusion of shale material. Physical and optical properties are as follows: hardness ~6, good {001} cleavage, uniaxial positive with ω 1.702 and ϵ 1.715 ($\pm$0.002). The specific gravity of 3.54, estimated by floating crystals in Clerici solution diluted with water, is somewhat lower than the calculated value 3.69, presumably because of included shale material. Microscopic examination using immersion oil indicates that the crystals commonly contain inclusions of shale material. Some crystals show thinly spaced (<0.01 mm) striations suggestive of polysynthetic twinning.

The shale matrix is made up of quartz and sericite ($2M_1$ muscovite) with only trace amounts of chlorite. Heavy-liquid separation of the shale yielded a small amount (~1%) of submillimetre-size lumps or pellets made up of goethite, minor maghemite and occasional specks of iron sulfide, probably pyrite.

Because of its excellent cristallinity, the Canadian florencite yields a more complete powder pattern (Table 1) than florencite from other localities (Lefebvre & Gasparrini 1980). Indexing the powder pattern using the data of Lefebvre & Gasparrini yields *a* 6.99, *c* 16.25 Å ($\pm$0.01 Å), virtually identical to the cell dimensions of the Zaire florencite (*a* 6.987, *c* 16.248 Å).

Results of microprobe analyses of 10 grains of florencite are given in Table 2. The analyses were done by C. Gasparrini and M. Gorton using the energy-dispersion technique and data-reduction procedures as outlined in Lefebvre & Gasparrini (1980). Calculation of the mineral formula on an anhydrous basis of 22 oxygens (Table 2) leads to relatively good stoichiometric proportions if SiO_2 is ignored. Inclusion of SiO_2 in the calculations yields lower, nonstoichiometric ratios, suggesting that the SiO_2 reported in the analyses results from quartz inclusions in the mineral.

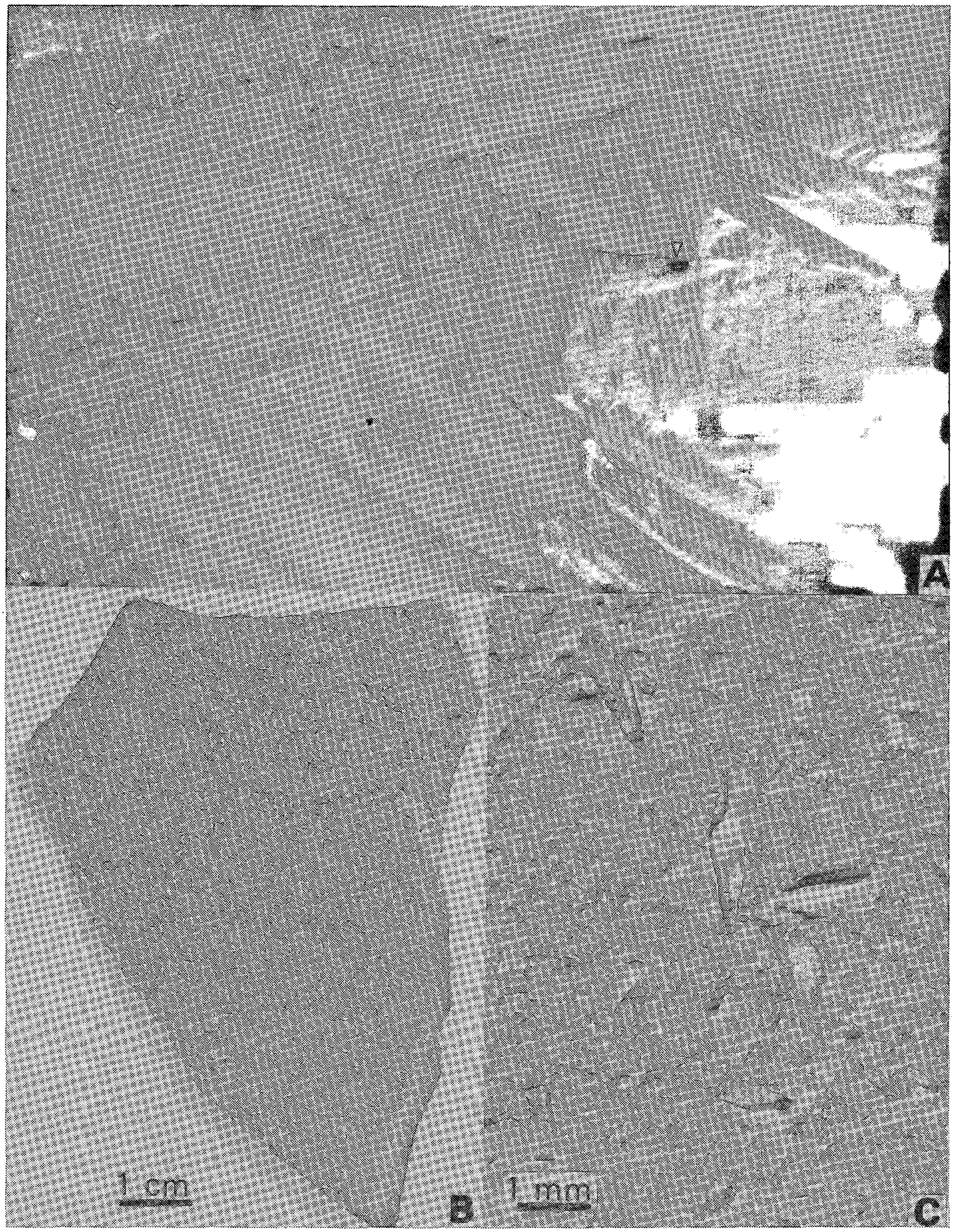

FIG. 2. Florencite occurrence in the shale from the Backbone Ranges, Mackenzie Mountains, N.W.T. (A) View looking west to section of Little Dal Group. Florencite locality (triangle) is in rusty-weathering black shale unit below cliff-forming carbonates. (B) Hand specimen of rusty-weathering black shale, showing abundant millimetre-size crystals of euhedral florencite. Cat. no. 61536, National Mineral Collection of Canada. (C) Enlarged view of cluster of florencite crystals, showing well-developed rhombohedral faces.

TABLE 1. POWDER X-RAY-DIFFRACTION DATA OF FLORENCITE

1			2			3		
d meas.	I	hkℓ	d meas.	I	hkℓ	d meas.	I	hkℓ
5.65	80	101	5.67	90	101	5.68	90	101
5.42	5	003	-	-	-	-	-	-
4.85	5	012	-	-	-	-	-	-
3.48	60	110	3.49	70	110	3.51	70	110
3.36	15	104	3.37	10	104	-	-	-
2.93	100	113	2.93	100	113	2.94	100	113
2.83	15	015	2.86	20	015	2.85	20	015
2.71	15	006	2.743	20	-	2.718	20	006
2.42	20	024	-	-	-	2.423	30	024
2.26	10	211	-	-	-	2.254	10	211
2.202	25	122	2.208	10	122	-	-	-
2.170	40	107	2.171	80	107	2.181	65	107
2.139	10	116	-	-	-	-	-	-
1.990	10	214	-	-	-	1.983	35	214
1.927	5	018	-	-	-	-	-	-
1.886	40	303	1.884	70	303	1.884	60	303
1.868	5	125	-	-	-	-	-	-
1.742	30	220	1.743	70	220	1.743	45	220
1.685	10	208	-	-	-	1.678	10	208
1.661	5	223	-	-	-	-	-	-
1.627	10	217	-	-	-	1.619	20	306
1.604	10	119	1.601	70	-	-	-	-
1.570	5	10·10	-	-	-	-	-	-
1.486	15	042	1.487	20	042	1.487	20	042
1.466	15	226	1.467	20	226	1.467	20	226
1.433	20	01·11	1.435	20	01.11	1.434	20	01.11
1.415	5	404	1.418	10	404	1.419	15	404
1.379	5	045	-	-	-	-	-	-
1.358	10	137	1.358	10	137	1.355	10	00.12
1.345	10	309	1.334	10	-	1.343	10	309
1.316	5	324	1.313	10	324	1.321	10	410
1.280	15	413	1.281	50	413	1.282	25	413
1.260	5	11·12	-	-	-	1.262	10	11.12
1.184	10	146	1.190	70	327	1.187	20	416
1.163	5	330	-	-	-	1.163	20	330
1.137	5	333	-	-	-	-	-	-
1.127	5	422	-	-	-	-	-	-
1.107	5	244	-	-	-	-	-	-
1.097	10	20·14	-	-	-	-	-	-

1. Florencite, this study; camera 114.5 mm, Cu $K\alpha$ radiation, average of two samples. 2. Florencite, Zaire (Lefebvre & Gasparrini 1980). 3. Florencite, Diamantina (Lefebvre & Gasparrini 1980).

The Mackenzie Mountains florencite is not appreciably zoned, for it deviates only slightly from its average formula $Al_3(Ce_{0.54}La_{0.27}Nd_{0.11}Sm_{0.04}Ca_{0.04})(PO_4)_2(OH)_6$. Cerium is the dominant rare earth, as in most specimens of florencite, followed by lanthanum, neodymium and samarium, a sequence that parallels the rare-earth distribution in shales (Haskin & Schmitt 1967). The La/Ce and Sm/Ce ratios of the Canadian florencite, 0.495 and 0.079, respectively, are almost identical to the ratios of these elements in shales (0.51, 0.09: Haskin & Schmitt 1967). The Nd/Ce ratio of the florencite is, however, significantly lower than the corresponding ratio in shales (0.21 *versus* 0.48).

The chemical composition of the florencite-bearing shale and the trace-element contents of four shale specimens from the mineral locality are given in Table 3, together with the rare-earth contents in the composite of North American shales given by Haskin & Schmitt (19....7). The trace-element analyses were done by J.N. Ludden and C. Gariépy using neutron-activation methods. The rare-earth data listed in Table 3 are shown on a chondrite-normalized basis in Figure 3. Normalization was carried out with respect to the Leedy chondrite values divided by 1.2 (Masuda *et al.* 1973). Except for a weak but persistent negative europium anomaly, which may reflect the source area of the shale or may be attributable to its Proterozoic makeup (Taylor & McLennan 1981), the florencite-bearing shales yield rare-earth patterns typical of shales. These patterns are closely similar to that of the composite of North American shales (Haskin & Schmitt 1967). In fact, the average total rare-earth content in the four specimens analyzed is virtually identical with that of the composite of North American shales (167.44 *versus* 168.28 ppm; Table 3). The total rare-earths and the rare-earth patterns of specimens H–0 to H–4 do not seem obviously dependent on whether florencite is present or absent in the shale. This, together with the similar La/Ce and Sm/Ce ratios in the florencite and in its host shales, indicates that the florencite has formed authigenically from small amounts of P_2O_5 available in the shales. The Canadian discovery invites interesting speculation about possible occurrences of florencite in other Precambrian shale sequences. Indeed, the normal, relatively low P_2O_5 contents of the analyzed specimens and the typical, strong enrichment of the light rare-earths in shales (Haskin & Schmitt 1967) suggest that florencite may be a more common authigenic constituent of shales than has been suspected. This possibility should be kept in mind when studying Precambrian shales, for authigenic florencite would make these rocks amenable to isotopic dating by the relatively new Sm–Nd method.

Acknowledgements

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TABLE 2. MICROPROBE ANALYSES OF FLORENCITE FROM THE MACKENZIE MOUNTAINS, N.W.T.

Al_2O_3	30.56	30.69	30.86	30.53	29.97	30.76	29.93	28.97	28.67	25.11	
SiO_2	0.0	0.37	0.71	0.78	1.34	1.58	4.10	5.84	8.28	15.09	
P_2O_5	28.12	28.31	27.66	28.01	28.48	28.07	27.90	27.27	26.22	23.92	
CaO	0.54	0.49	0.55	0.53	0.45	0.50	0.47	0.30	0.54	0.32	
La_2O_3	8.72	7.76	9.94	8.04	9.19	10.18	9.93	6.85	8.16	8.04	
Ce_2O_3	17.97	18.42	17.46	18.07	18.30	18.02	18.58	19.29	16.65	15.11	
Pr_2O_3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
Nd_2O_3	3.36	4.87	3.22	4.55	4.51	3.09	3.55	4.90	3.10	2.63	
Sm_2O_3	2.07	1.68	1.08	1.55	1.55	1.20	1.38	1.56	1.41	1.32	
TOTAL	91.34	92.59	91.48	92.06	93.79	93.40	95.84	94.98	93.03	91.54	
	Calculated formulas on the basis of 22(O), i.e., $R_2O_3 \cdot 3Al_2O_3 \cdot (P_2O_5)_2$										
											Av.
Al	5.990	5.999	6.104	6.019	5.879	6.033	5.992	5.909	6.050	5.900	5.99
Si	-	-	-	-	-	-	-	-	-	-	-
P	3.961	3.976	3.930	3.967	4.013	3.955	4.012	3.995	3.971	4.042	3.98
Ca	0.096	0.087	0.099	0.095	0.080	0.089	0.086	0.055	0.103	0.068	0.086
La	0.542	0.480	0.623	0.503	0.572	0.632	0.630	0.443	0.544	0.599	0.557
Ce	1.093	1.118	1.073	1.108	1.116	1.098	1.155	1.222	1.091	1.104	1.118
Nd	0.199	0.289	0.193	0.271	0.268	0.184	0.215	0.302	0.198	0.187	0.231
Sm	0.118	0.096	0.062	0.088	0.088	0.068	0.080	0.093	0.086	0.091	0.087
ΣR.E.	2.048	2.070	2.050	2.065	2.124	2.071	2.166	2.113	2.020	2.044	2.079

Average formula $Al_3(Ce_{.54}La_{.27}Nd_{.11}Sm_{.04}Ca_{.04})(PO_4)_2(OH)_6$

Analysts: C. Gasparrini and M. Gorton

TABLE 3. CHEMICAL COMPOSITION OF FLORENCITE-BEARING SHALES

Spec. n°	H-1[1] %		H-0[2] ppm	H-1[2] ppm	H-2[2] ppm	H-4[2] ppm	NA[3] ppm
SiO_2	63.25	La	40.80	24.25	30.12	48.32	39
Al_2O_3	19.50	Ce	99.52	56.84	62.96	109.44	76
Fe_2O_3	5.49	Nd	45.39	22.36	25.54	47.77	37
CaO	0.05	Sm	8.47	4.53	4.80	8.33	7.0
Na_2O	0.01	Eu	1.57	0.81	0.60	1.50	2.0
K_2O	5.55	Tb	1.35	0.77	0.79	1.10	1.3
MgO	0.46	Ho	1.50	1.21	1.16	1.62	1.40
TiO_2	0.99	Tm	0.61	0.45	0.52	-	0.58
P_2O_5[4]	0.05-0.8	Yb	3.96	3.45	3.47	3.48	3.4
L.I.	4.64	Lu	0.58	0.48	0.49	0.50	0.60
Tot.	99.99	Sc	15.61	19.71	17.78	17.94	
		Cr	59.5	77.5	83.2	82.0	
		Hf	5.55	5.18	6.86	5.82	
		Ta	1.19	1.30	2.23	1.26	
		Th	12.39	13.69	12.38	15.01	
		U	2.76	2.41	2.35	2.04	
		ΣRE	203.75	115.5	130.45	22.26	168.28

(1) Analyst: V. Kubat, Ecole Polytechnique
(2) Analyst: J.N. Ludden and C. Gariépy, Université de Montréal
(3) Composite of North American Shales, Haskin & Schmitt (1967, 238)
(4) Range determined on three speciments
H-0: shale matrix of the florencite-rich specimen shown on Fig. 2A, B after extracting the florencite with heavy liquids.
H-1, H-2: shales containing occasional macroscopic florencite crystals
H-4: shale without macroscopic florencite.

as-yet-unidentified crystals were collected while the section was under investigation for the presence of Precambrian fossils. Pouliot later identified the crystals as florencite. Electron-microprobe analyses quoted in this paper were done by C. Gasparrini & M. Gorton of Minmet Scientific Ltd., Toronto. The trace-element analyses of the florencite-bearing shale were done by J.N. Ludden & C. Gariépy at the geochemical laboratory of the Université de Montréal. Financial support for this study by the Natural Sciences and Engineering Research Council of Canada (grants A6101 to Pouliot and A7484 to Hofmann) is gratefully acknowledged. We thank Guy Perrault and two anonymous reviewers for critically reading the manuscript.

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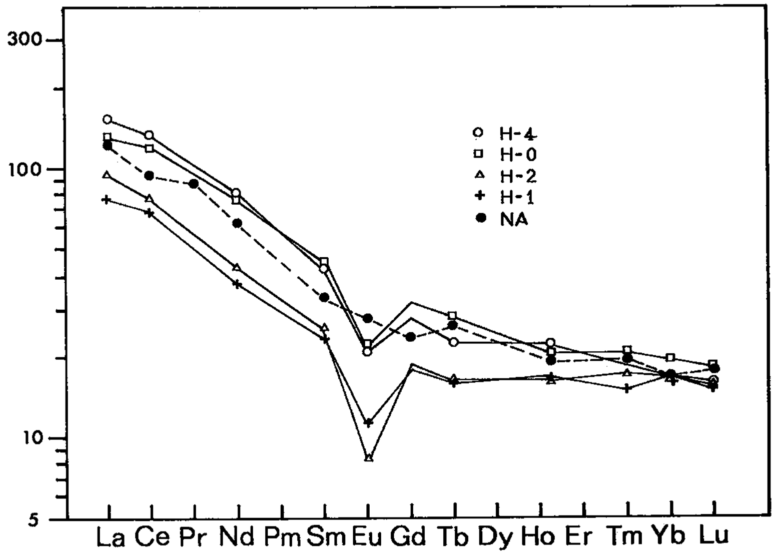

FIG. 3. Chondrite-normalized rare-earth distribution in florencite-bearing shales and in the composite of North American shales (NA; Haskin & Schmitt 1967).

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