

Churchite and Florencite (Nd) from Sausalito, California

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Rare earth phosphate minerals occur in association with manganese oxides slightly over half a mile south of Sausalito, Marin County, California, at the base of a roadcut on the north side of the lateral to Highway 101. Churchite (weinschenkite)¹ was first found here by Leo Rosenhahn of San Anselmo and identified by E. B. Gross, then of the California Division of Mines.

The minerals are found in the weathering zone on fracture surfaces in a chert unit of the Jurassic and Cretaceous Franciscan formation that consists of alternating beds of radiolarian chert, 5 to 10 cm thick, and shale, 1 or 2 cm thick. A basalt unit of the Franciscan crops out about a hundred meters away. The minerals occur near a fault (Fig. 1), which probably favored downward percolation of ground water. Before excavation the occurrence was probably 5 or 10 meters below ground level on a steep hillside. Clay minerals, hematite, and lithiophorite are the most abundant minerals on the fracture surfaces; todorokite and the two rare earth minerals churchite and florencite are moderately abundant.

Lithiophorite occurs as dark-brown or black botryoidal crusts up to several millimeters thick, composed of very thin shells. The X-ray diffraction pattern is almost identical with pattern 3 of Fleischer and Faust (1963). A spectrographic analysis is given in table 1. Despite the name and the accepted formula $(Al, Li)MnO_2(OH)_2$ of lithiophorite (Wadsley, 1952), the low content of lithium is not unusual. Lithiophorite from some occurrences contains only trace amounts of lithium. Copper, barium and other elements perhaps fill the role, assigned by Wadsley to lithium, of expanding the bond lengths in the $(Al)(OH)_6$ octahedra some 3 percent over normal Al-OH bond lengths, allowing a match to the $Mn(OH)_6$ octa-



Figure 1. Rare earth mineral locality in chert of the Franciscan Formation near Sausalito, California. Photograph by J. Schlocker.

¹Churchite was discovered in Cornwall in 1865. Only qualitative tests for the rare earth elements were made, and the mineral was assumed to be a cerium mineral. Weinschenkite was described from Bavaria in 1922, where it was found in such abundance that miners used it for Christmas tree "snow." In 1952 analysis of type material showed churchite to be an yttrium mineral identical with weinschenkite. Both names have continued in use, reflecting a difference of opinion as to whether or not the deficiencies in the original characterization of churchite justify setting aside priority. In connection with this report a decision was requested from the Commission on New Minerals and Mineral Names of the International Mineralogical Association, and it has ruled by a majority vote in favor of churchite.

Table 1. Semiquantitative spectrographic analysis of lithiophorite¹

Mn	major	Li 700 ppm (Li ₂ O 0.32%)
Al	5 %	Be 15
Cu	>2	Sc 50
Si	2	Ti 200
Fe	2	Cr 5
Ba	2	Co 70
Ni	0.5	Sr 30
Zn	0.5	Nb 10
Ca	0.2	Mo 30
Na	0.15	La 100
Mg	0.15	Nd 300
V	0.15	Gd 150
Y	0.1	Dy 200
		Ho 30
		Yb 70

Chris Heropoulos, analyst. Li₂O by atomic absorption spectrophotometry, H. N. Elsheimer, analyst.

¹ Values in left column all percent, those in right column parts per million.

hedra in the adjacent layers. The cobalt content of the Sausalito lithiophorite is surprisingly low; other analyses show one or two percent cobalt, on the same order of abundance as nickel.

Todorokite (Na, Ca, K, Mn⁺²) (Mn + ⁺, Mg)₆O₁₂ · 3H₂O occurs as soft dark-brown nodular aggregates with a bronzy luster, composed of platy crystals too small for satisfactory optical measurements. X-ray diffraction yielded four lines at the spacings of the stronger lines of todorokite, together with strong quartz lines, perhaps resulting from a fine skeletal intergrowth of the two minerals, as at some other occurrences. Nodules of todorokite are closely associated with the rare earth minerals; some are perched on churchite crusts.

Churchite (YPO₄ · 2H₂O), a structural isotype of gypsum (CaSO₄ · 2H₂O), occurs as snowy white crusts and tufts composed of radiating needles just resolvable with the hand lens. Florencite [RE Al₃(PO₄)₂(OH)₆] occurs as moderate-brown pulverulent earthy material in which individual crystals cannot be distinguished with the microscope. The two minerals are usually but not invariably associated; a crust of churchite commonly rests on a base of florencite. The X-ray diffraction pattern of the churchite matches existing standards; the pattern obtained from the florencite is indeterminate within the plumbogummite group.

Churchite is now known from over a dozen localities. All are in the weathering zone; at least half are in association with manganese and iron oxides. Florencite is generally a primary mineral found in pegmatites, carbonatites, or metamorphic rocks, but it occurs along

with churchite in the weathering zone of the Burley pegmatite, Virginia (Mitchell and Geitgey, 1968). A third hydrous rare earth phosphate, rhabdophane, occurs at the Burley pegmatite and in an iron-manganese oxide deposit at Salisbury, Connecticut (Hildebrand, Carron, and Rose, 1957), but has not been found at Sausalito.

At three or four churchite occurrences there is an obvious source of rare earths, for example at Krasnoyarsk, Siberia (Noneshnikova, 1960) where churchite replaced xenotime, or the Burley pegmatite, which contains large masses of perrierite. At most of the occurrences, however, the primary source seems to be the trace amounts dispersed in ordinary rock or soil. At Sausalito the rare earths are presumably derived mostly from the shale, which has a normal low total content of rare earths and a normal Ce/Nd+La ratio (table 3). The mineral association at Sausalito and other localities suggests that absorption of rare earths on colloidal manganese oxides was an important step in the formative process, as proposed for a churchite occurrence at Kelly Bank, Virginia, by Milton, Murata, and Knechtel (1944) and supported by the experiments of Belousov and Kolobov (1965). Crystallization of the churchite and florencite was presumably a later event, probably coincident with recrystallization of the manganese oxides.

For the Kelly Bank occurrence, Milton, Murata, and Knechtel (1944) postulated that the primary concentra-

Table 3. Semiquantitative spectrographic analyses of rocks from Sausalito lateral.

	Chert	Shale	Basalt
Y	n.d.	.007%	.003 %
La	n.d.	.010	n.d.
Ce	n.d.	.020	n.d.
Nd	n.d.	.015	n.d.
Yb	n.d.	.0007	.0003

n.d. - not detected; Helen Worthing, analyst.

tion of rare earths, before adsorption on the manganese oxides, was a biogeochemical extraction, particularly by chestnut and hickory trees. Robinson, Bastron, and Murata (1958) found that hickory leaves can contain four or five times as much rare earths as the soil on which the tree grows. At the Sausalito locality it is undetermined whether concentration involved a biogeochemical stage. There are at present no broad-leaved trees; the flora consists of grass, low brush, and annuals.

Spectrographic analyses (table 2 and Fig. 2) show the usual predominance of rare earth elements of even atomic number. Yttrium and the heavier rare earths are concentrated in the churchite and the lighter rare earths in florencite. This can be attributed to the effect of the smaller ionic radii of the heavier rare earth elements and

Table 2. Semiquantitative spectrographic analyses of churchite and florencite.

	Churchite (percent)	Florencite (percent)
Y	>20	1.5
La	(<0.03)	2
Ce	0.2	0.5
Pr	(<0.1)	0.7
Nd	(<0.07)	3.
Sm	1.5	1.
Eu	1.	0.7
Gd	1.	1.5
Tb	1.5.	(<0.1)
Dy	7	0.7
Ho	1.5	0.1
Er	5.	0.2
Tm	1.	0.01
Yb	5.	0.05
Lu	0.5	(<0.015)
P	>10	10
Ba	0.2	7
Sr	0.02	0.7
Ca	1.5	1.
Fe	0.3	10.
Mn	1.5	7.
Mg	1.5	0.3
Ti	--	0.7
Cu	0.5	0.5

Rare earths were not found at detection limits given in parentheses. Si, Al, K not looked for. Harry Bastron, analyst.

yttrium. Structural sites occupied by these elements in churchite have an eight-fold coordination, whereas those in florencite are slightly larger, with a nine-fold coordination (Strunz, 1966). A sample of Kelly Bank, Virginia, churchite was analyzed at the same time and showed a composition almost identical with the Sausalito mineral.

All florencites that have been analyzed heretofore are the species florencite-(Ce), following Levinson's (1966) system of nomenclature in terms of the dominant rare earth element, and have ratios of Ce/Nd+La of about 1:1, normal for most cerium group minerals. The Sausalito mineral is a barian variety of the species florencite-(Nd). The unusual Ce/Nd+La ratio of 1:10 is comparable to the 1:100 ratio in the rhabdophane-(Nd) from Salisbury (Hildebrand, Carron, and Rose, 1957). The anomalously low content of cerium in the florencite indicates that during at least one stage of the process cerium failed to follow its sister elements. Cerium alone among the rare earths can be oxidized in nature to the quadrivalent state and, as Robinson, Bastron, and Murata (1958) pointed out, the transition takes place within the range of Eh and pH found in soils. Quadrivalent cer-

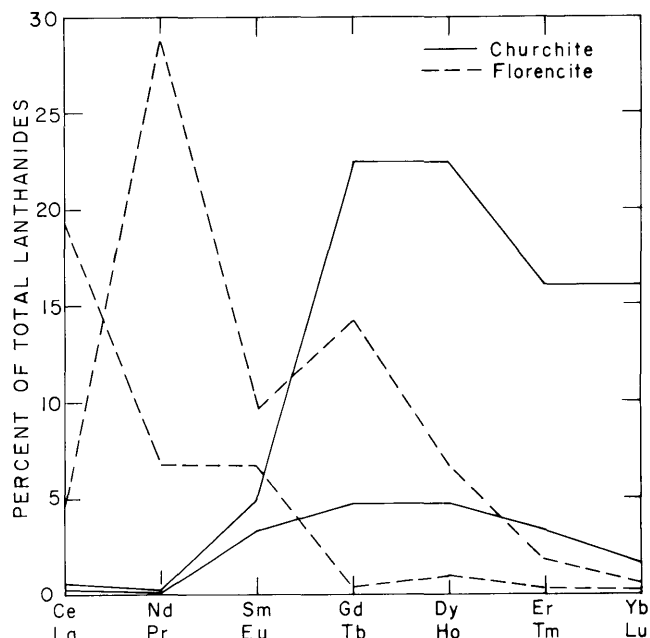


Figure 2. Distribution of rare earth elements in churchite and florencite. Upper and lower curves are for elements of even and odd atomic number, respectively.

ium is in general less soluble and will not be transported with other rare earths. It is significant that the florencite from the Burley pegmatite, which formed by oxidation in place, shows little if any loss of cerium relative to its predecessor perrierite, even though a small amount of secondary cerianite (CeO₂) also formed.

Churchite is undoubtedly a much commoner mineral than realized. Any powdery white mineral associated with supergene manganese oxides should be suspected as churchite and if confirmed, the much less noticeable florencite and rhabdophane should be looked for.

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