

Present-day deposition of lepidolite from thermal waters in Yellowstone National Park¹

KEITH E. BARGAR, MELVIN H. BEESON, ROBERT O. FOURNIER,
AND L. J. PATRICK MUFFLER

U.S. Geological Survey, Menlo Park, California

Abstract

Lepidolite found at depths of 23.8 to 28.5 meters in core from a drill hole near Ojo Caliente hot spring in Lower Geyser Basin, Yellowstone National Park, appears to be precipitating at 130° to 140°C from water of the presently active geothermal system. This water has a very high fluorine content and an extraordinarily high ratio of lithium to potassium.

Introduction

In the course of a systematic mineralogic study of hydrothermal alteration of glacial sediments and rhyolite in core from U.S.G.S. drill hole Y-3, Yellowstone National Park, lepidolite was discovered and shown to have been precipitated from geothermal water at temperatures of 130° to 140°C. To the best of our knowledge, this is the first report of lepidolite from a low-temperature hydrothermal system or from a modern geothermal system. Previously, lepidolite has been found only in pegmatites, granites, aplites, and high-temperature veins (Deer, Howie, and Zussman, 1962).

Geologic Occurrence

Drill hole Y-3 is approximately 43 m north of Ojo Caliente hot spring on the west rim of Pocket Basin in Lower Geyser Basin, Yellowstone National Park (Muffler, White, and Truesdell, 1971, Figures 3 and 4). From the surface to a depth of 42.3 m the drill hole penetrated hydrothermally cemented conglomerate, sandstone, and siltstone of late Pleistocene age. Beneath these periglacial sediments is the Nez Perce Creek flow, a rhyolite lava extruded approximately 150,000 years ago (J. D. Obradovich, oral communication, October, 1972).

Lepidolite is found in Y-3 at depths of 23.8 to 28.5 m as linings and partial fillings (along with other hydrothermal minerals) of intergranular cavities of conglomerate and coarse-grained sandstone. Lepidolite occurs as polycrystalline mats displaying pearly luster; individual platy crystals range from

less than 0.01 mm to 0.04 mm across, with a few grains up to 0.1 mm. It is intergrown with hydrothermal quartz, pectolite, montmorillonite, and possibly albite. Hydrothermal analcime and pyrite occur in the same specimens as lepidolite, but were not observed in association with lepidolite. Hydrothermal calcite, fluorite, chalcedony, aegirine, and clinoptilolite also occur in the interval 23.8–28.5 m. Lepidolite occurs only in the coarse-grained sandstones and conglomerates, whereas clinoptilolite is restricted to the fine-grained sandstones and siltstones.

Because of its mode of occurrence and association with other hydrothermal minerals, lepidolite in Y-3 is considered to be of hydrothermal origin. Furthermore, the hydrothermal minerals of Y-3 appear to have been deposited by the fluids of the geothermal system still active at present (*cf* Honda and Muffler, 1970), probably at temperatures not much different from those measured during drilling.

Temperature of Formation

Temperatures of 132.4°C and 140.1°C were measured at depths of 24.3 and 31.2 m during pauses in drilling. Measurements were made with a maximum-reading mercury thermometer at least 16 hours after the termination of drill-water circulation at the end of an 8-hour drilling shift; they are considered to be a close approximation to pre-drilling ground temperatures (unpublished data of D. E. White, R. O. Fournier, L. J. P. Muffler, and A. H. Truesdell). The temperatures measured plot very close to the reference boiling-point curve for pure water under the hydrostatic pressure of a column of pure water everywhere at the boiling point (Muffler, White, and Truesdell, 1971, Figure 2).

¹ Publication authorized by the Director, U.S. Geological Survey.

Mineralogic Data

Lepidolite was first detected during routine X-ray diffraction studies of the Y-3 core. The small basal spacing relative to that of illite (a predictable hydrothermal mineral) prompted concentration of the mica by hand-picking, after which the mineral was identified as lepidolite. Table 1 shows X-ray diffraction data for two samples of lepidolite from Y-3, along with the X-ray diffraction data given by Munoz (1968, Table 3) for a synthetic polyolithionite.

A precise determination of the (005) spacing using the method of Guidotti (1966, p. 1782) gave 1.977 Å for lepidolite from 23.8 m and 1.974 Å for lepidolite from 28.3 m. Using Figure 6 of Munoz (1968), the basal spacings calculated from the (005) determinations give compositions along the

TABLE 1. X-ray Diffraction Data for Lepidolite from 23.8 m and 28.3 m in Y-3, Compared with Synthetic Polyolithionite (Munoz, 1968, Table 3)*

hkl	Synthetic polyolithionite		Y3-23.8 m		Y3-28.3 m	
	d (Å)	I	d (Å)	I	d (Å)	I
001	9.869	2	9.882	4.5	9.934	4
002	4.930	9	4.946	10	4.954	10
020	4.473	5	4.477	0.5	4.476	1
110, 110	4.438	3	≈ 4.43	0.5	4.437	0.5
111	4.302	4	4.307	0.5	4.302	0.5
021	4.078	3	≈ 4.08	0.5	4.086	0.5
111	3.821	3	≈ 3.82	0.5	3.829	0.5
112	3.589	10	3.593	0.5	3.601	1
022	3.311	10				
003	3.289	9	3.296	7	3.299	8
112	3.065	10	3.069	1	3.071	1.5
113	2.867	7	2.868	0.5	2.872	1
023	2.651	5	2.654	0.5	2.656	0.5
201, 130, 130	2.580	7	2.580	0.5	2.583	1
131, 200, 200	2.552	5	2.554	0.5	2.554	1
004, 113	2.470	2	2.470	0.5	2.471	0.5
131	2.441	2	-	-	≈ 2.45	0.5
132	2.372	5	2.374	0.5	2.376	1
040, 221	2.239	2	≈ 2.24	0.5	2.240	0.5
203, 220, 220	2.217	2	≈ 2.22	0.5	≈ 2.22	0.5
041	2.186	2	≈ 2.19	0.5	2.189	0.5
222	≈ 2.15	1	≈ 2.16	0.5	≈ 2.15	0.5
133	2.125	3	2.126	0.5	2.119	0.5
221	≈ 2.09	1	≈ 2.09	0.5	≈ 2.10	0.5
005	1.974	9	1.977	4.5	1.974	6
133	1.944	2	≈ 1.95	0.5	1.947	0.5
224	≈ 1.79	1	-	-	-	-
205, 223	≈ 1.72	1	-	-	-	-
134, 115	≈ 1.71	1	-	-	1.708	0.5
006, 135	1.641	4	≈ 1.64	0.5	≈ 1.64	0.5
313	≈ 1.61	0.5	-	-	-	-
243	≈ 1.58	1	-	-	-	-
152	≈ 1.57	1	-	-	≈ 1.57	0.5
153, 242	≈ 1.54	0.5	-	-	-	-
314	≈ 1.51	-	-	-	-	-
060, 331	1.497	4	≈ 1.50	0.5	≈ 1.50	0.5

*Y-3 data corrected for quartz internal standard. Intensity on arbitrary scale using peak heights.

polyolithionite-muscovite join of $Pl_{88}Ms_{12}$ and $Pl_{98}Ms_{02}$, respectively.

Examination in immersion oil under a petrographic microscope shows the lepidolite to have perfect {001} cleavage, parallel extinction, and an α' index of refraction of about 1.55.

Chemical Data

Lepidolite from 23.8 m was analyzed for all significant elements except Li, O, and H on an ARL EMX electron microprobe, using natural and synthetic mineral standards. All data were corrected for drift, background, matrix absorption, characteristic fluorescence, and atomic number effects (Beeson, 1967; Beaman and Isasi, 1970) (Table 2, column 1).

Spectrographic analysis of impure lepidolite from 28.3 m gave the results shown in Table 2, column 2. Thirty additional elements were looked for but not detected.

X-ray diffraction and optical examination of the spectrographically analyzed sample suggest about 34 percent impurities (mostly quartz, plagioclase, alkali feldspar, analcime, and pectolite). Recalculating the lithium spectrographic value for these impurities suggests that lepidolite contains about 3.5 percent Li or 7.5 percent Li_2O by weight.

The complete chemical analyses of the lepidolite can be approximated by combining the microprobe data expressed as oxides with the Li_2O value calculated from the quantitative spectrographic analyses, and making reasonable assumptions for H_2O^+ (see footnote to Table 2). Even with the addition of Li_2O and H_2O^+ , however, the oxide total is significantly short of 100 percent (Table 2, column 3). Inasmuch as the microprobe values are reproducible, and since no additional major elements appeared in the quantitative spectrographic analyses, the low total is considered to be the result of the small grain size effect² (Page, Calk, and Carr, 1968).

The chemical data have been recalculated to ions per unit formula (Table 2, column 4) using the computer program of Jackson, Stevens, and Bowen (1967) based on the formula $K_2(Li, Al)_{5-6}[Si_{6-7}Al_{2-3}O_{20}](OH, F)_4$. Comparison of the recalculated chemical data (Table 2, column 4) with

² The size of the lepidolite grains in the sample that was analyzed with the microprobe was later determined to lie in the lower size range, 4 to 10 μ . Furthermore, only those grains presenting an edge were selected for analysis to insure that the electron beam would not be penetrating a very thin lepidolite tablet.

Figures 25 to 28 of Foster (1960) corroborates the X-ray data in indicating that the lepidolite from Y-3 is a polyolithionite.

Water Composition

Two major water-producing zones were penetrated in the Y-3 drill hole at depths of approximately 28 and 88 meters. Lepidolite occurs in and just above the more shallow zone, which according to unpublished data of D. E. White, R. O. Fournier, L. J. P. Muffler, and A. H. Truesdell is a fissure carrying boiling water from the deep aquifer (88 m) up to Ojo Caliente hot spring.

Water from the 88 m aquifer was sampled in Y-3 without loss of steam and analyzed (see Table 3, column 1). The results may be compared with the composition of water from Ojo Caliente spring

TABLE 2. Analyses of Lepidolite from Y-3[†]

	1	2 ^{††}	3	4 ^{†††}
Si	26.3	>10	SiO ₂ 56.3	Si 8.01
Al	5.8	8*	Al ₂ O ₃ 10.9	Al 0.0
Fe	.39	1.5	Fe ₂ O ₃ .56	Al 1.83
Mn	.02	.01	MnO .02	Fe ³⁺ 0.06
Mg	.01	.07	MgO .02	Mn 0.002
Sr	.03		SrO .03	Mg 0.004
Li		2.3*	Li ₂ O 7.5	Li 4.29
Na	.14	3.	Na ₂ O .19	
K	8.7	>5	K ₂ O 10.5	Sr 0.003
Rb	.08	.16*	Rb ₂ O .09	Na 0.05
Cs	.01	.0005*	Cs ₂ O .01	K 1.91
F	7.7		F 7.7	Rb 0.008
			H ₂ O ⁺ .56	Cs 0.001
Ca				F 3.47
Ti	.15			OH 0.53
Ba	.02		Total 94.4	
Be	.0002			
Cr	.0003			
Cu	.00015			
La	.007			
Nb	.003			
Pb	.0015			
Sr	.003			
V	.005			
Y	.002			
Zr	.02			
Ga	.001			
Ge	.01			
Yb	.0002			

[†]Column 1: Electron microprobe analyses by M. H. Beeson (precision ± 3% of amount present for major elements and ± 10% for minor elements). The analysis is a composite of analyses made on 3 different days, and only those values which could be reasonably reproduced are reported. Column 2: Spectrographic analyses by Harry Bastron (sample contains ~ 34% impurities). Values marked by asterisk are quantitative determinations with overall accuracy of ± 15%. Other values are semiquantitative determinations of lesser accuracy. Column 3: Microprobe data and Li spectrographic value (corrected for impurities) recalculated to oxide percent.

^{††}Looked for but not detected: Ag, As, Au, B, Bi, Cd, Co, Mo, Ni, Pd, Pt, Sb, Sc, Sn, Te, U, W, Zn, P, Ce, Hf, In, Re, Ta, Th, Tl, Pr, Nd, Sm, Eu.

^{†††}Number of ions on the basis of 24 (O, OH, F).

^{††††}Based upon the assumption that F plus OH equals 4.00. (Estimate is in agreement with Foster, 1960, Figure 30).

TABLE 3. Composition of Waters (in parts per million)*

	(1) Y-3 drill hole	(2)** Spring water	(3) Ojo Caliente spring
pH	8.12	--	8.31
SiO ₂	--	--	230
Al	--	--	1.0
Fe	0.1	0.12	0.18
Ca	1.26	1.48	1.1
Mg	0.02	.02	.02
Na	270	318	317
K	11	13	9.2
Li	3.5	4.1	4.5
HCO ₃ [†]	177	208	249
SO ₄	19.1	22.5	27
Cl	278	327	331
F	30	35	33
B	3.6	4.2	4.0
Σ cations (m. equiv.)	12.55	14.70	14.74
Σ anions (m. equiv.)	12.52	14.66	15.44
Atomic Li/K	1.8	1.8	2.8
Atomic Cl/F	5.0	5.0	5.4

*Roberta Barnes, analyst.

**Calculated composition assuming 14.5 percent loss of steam.

[†]Includes both HCO₃⁻ and CO₃⁻ recalculated to HCO₃⁻.

(Table 3, column 3). Although both waters are very dilute, it is apparent that water from Ojo Caliente is slightly more concentrated than that sampled from the 88 meter aquifer in Y-3. We believe that the differences are due in part to loss of steam and in part to reaction with the wallrock during ascent of the water. We conclude that the water which deposited the lepidolite from 23.8 to 28.5 m was intermediate in composition between the water sampled from the 88 m aquifer and Ojo Caliente spring.

Taking the silica content of Ojo Caliente as 230 ppm, and assuming adiabatic cooling, a reservoir temperature of 176° ± 3°C may be estimated by the method of Fournier and Rowe (1966). This temperature is in excellent agreement with the measured aquifer temperature of 174°C. Therefore, it appears that an assumption of adiabatic cooling is good, and that about 15.0 percent steam separated from the deep water by the time it emerged in Ojo Caliente spring. We then can calculate from column 1 an ideal composition of Ojo Caliente water, assuming neither reaction with the wallrock nor precipitation of dissolved constituents during ascent from the 88 m aquifer. The result is shown in Table 3, column 2. A comparison of columns 2 and 3 in Table 3 shows that significant loss of potassium and a probable loss of calcium occurred during ascent

of the solution. In contrast, within analytical error there was no loss or gain of sodium, chloride, or fluoride. Unfortunately, the precision of the lithium analyses is only about ± 0.3 ppm³ and, therefore, the difference in lithium between column 2 and column 3 is not significant.

Two aspects of the water composition deserve special notice; the waters are relatively rich both in lithium and fluoride. Although the absolute quantity of lithium (3.5 to 4.5 ppm) is not great, the atomic ratio Li/K is extraordinarily high, ranging from about 1.8 in the well water to about 2.8 in the spring water. The absolute fluoride concentration (30 to 33 ppm) is remarkably high compared to all other neutral to slightly alkaline ground waters (.1-24 ppm; White, Hem, and Waring, 1963), and the atomic ratio Cl/F is low (about 5) compared to most other known geothermal waters (White, Hem, and Waring, 1963; Mahon, 1964; Ellis, 1967). Although the lepidolite is forming from a relatively dilute water solution, this water is anomalously rich in lithium and fluoride, the two chemical constituents necessary for the formation of lepidolite.

References

- BEAMAN, D. R., AND J. A. ISASI (1970) A critical examination of computer programs used in electron microprobe analysis. *Anal. Chem.* **42**, 1540-1568.
- BEESON, M. H. (1967) A computer program for processing electron microprobe data. *U. S. Geol. Surv. Open-File Rep.* 40 pp.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock Forming Minerals. Vol. 3, Sheet Silicates.* Longmans, Green, and Co., Ltd., London, England, 270 pp.
- ELLIS, A. J. (1967) The chemistry of some explored geothermal systems. In, H. L. Barnes, Ed., *Geochemistry of Hydrothermal Ore Deposits.* Holt, Rinehart and Winston, Inc., New York, pp. 465-514.
- FOSTER, M. D. (1960) Interpretation of the composition of lithium micas. *U. S. Geol. Surv. Prof. Pap.* **354-E**, 115-147.
- FOURNIER, R. O., AND J. J. ROWE (1966) Estimation of underground temperatures from the silica content of water from hot springs and wet steam wells. *Amer. J. Sci.* **264**, 685-697.
- GUIDOTTI, C. V. (1966) Variations of the basal spacing of muscovite in sillimanite-bearing pelitic schists of North-western Maine. *Amer. Mineral.* **51**, 1778-1786.
- HONDA, S., AND L. J. P. MUFFLER (1970) Hydrothermal alteration in core from research drill hole Y-1, Upper Geyser Basin, Yellowstone National Park, Wyoming. *Amer. Mineral.* **55**, 1714-1737.
- JACKSON, E. D., R. E. STEVENS, AND R. W. BOWEN (1967) A computer-based procedure for deriving mineral formulas from mineral analyses. *U. S. Geol. Surv. Prof. Pap.* **575-C**, 23-31.
- MAHON, W. A. J. (1964) Fluorine in the natural thermal waters of New Zealand. *New Zealand J. Sci.* **7**, 3-28.
- MUFFLER, L. J. P., D. E. WHITE, AND A. H. TRUESDELL (1971) Hydrothermal explosion craters in Yellowstone National Park. *Geo. Soc. Amer. Bull.* **82**, 723-740.
- MUNOZ, J. L. (1968) Physical properties of synthetic lepidolites. *Amer. Mineral.* **53**, 1490-1512.
- PAGE, N. J., L. C. CALK, AND M. H. CARR (1968) Problems of small-particle analysis with the electron microprobe. *U. S. Geol. Surv. Prof. Pap.* **600-C**, 31-37.
- WHITE, D. E., J. D. HEM, AND G. A. WARING (1963) Chemical composition of subsurface waters. In, *Data of geochemistry.* *U. S. Geol. Surv. Prof. Pap.* **440-F**, 67 pp.

³ The waters were analyzed before lepidolite was recognized as an alteration product. Therefore, lithium was determined in a routine manner without special effort to obtain greater than usual analytical precision and accuracy.