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PRECIPITATION OF LAUMONTITE WITH QUARTZ, THENARDITE, AND GYPSUM AT SESPE HOT SPRINGS, WESTERN TRANSVERSE RANGES, CALIFORNIA[1]

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Abstract—Well-crystallized laumontite has been found for the first time precipitating naturally at the earth's surface at temperatures of 89° to 43°C as a component of gray to white coatings and efflorescences on exterior surface and as precipitates on interior fractures of stones and blocks lining Hot Springs Creek immediately downstream from Sespe Hot Springs, Ventura County, California. X-ray powder diffraction, scanning electron microscope (SEM), and electron microprobe analyses show thenardite to be the dominant phase in the exterior coatings, in association with minor microcrystalline (<50 μm) laumontite and gypsum. Macrocrystalline (>1 mm) laumontite is the dominant phase in interior fracture coatings and is associated with quartz, potassium feldspar, and gypsum. Trace amounts of smectite(?), halite, a mercury sulfide, an iron sulfide, an iron-bearing mineral (possibly an oxide or carbonate), and a copper mineral are also present. Zeolites other than laumontite have not been seen, and carbonate minerals are either entirely or nearly absent. SEM textures indicate nonreactive intergrowths of laumontite, quartz, potassium feldspar, and gypsum. Unbroken laumontite crystals are generally euhedral or have skeletal growth characteristics and exhibit sharp, fresh, non-corroded faces, edges, and corners.

The water issuing from the hottest and largest spring is 89°C, has a pH of 7.74, 1200 mg/liter total dissolved solids, and contains Na^+, Cl^-, SO_4^{2-}, and H_4SiO_4 as the dominant dissolved species. Computations indicate that the water is supersaturated with respect to laumontite, quartz, chlorite, and prehnite and is slightly undersaturated with respect to calcite and noncrystalline silica. Water-dominated water–rock interaction is indicated by isotopic analyses. The δO^{18} composition expectable on the basis of the -81‰ δD composition is -11.38‰ instead of the -9.5‰ actually found (all referred to SMOW). The water chemistry suggests that the subsurface water source may have a temperature of 125°–135°C. This temperature range, together with the regionally low geothermal gradient, implies that the source is probably 3550 to 3900 m beneath the springs in fractured and permeable Mesozoic and older plutonites and gneisses.

The discovery of laumontite crystallizing at atmospheric pressure and 43°C (or lower) provides important insight into the processes responsible for burial diagenetic laumontite and a valuable perspective on the zeolite metamorphic facies.

Key Words—Diagenesis, Efflorescence, Hot spring, Isotope analysis, Laumontite, Water, Zeolite.

INTRODUCTION

Laumontite was discovered in 1980 at Sespe Hot Springs, Ventura County, California, as macroscopic to submicroscopic crystals associated with neocrystalline quartz, sulfate minerals, and several other minor phases. The mineral occurs in gray to white coatings on exterior surfaces and as precipitates in cracks of stones in contact with waters of the spring-fed stream in Hot Springs Canyon. Virtually all studies of laumontite and its mineral associations are based on products of subsurface processes, resulting from either shallow hydrothermal or deeper diagenetic and metamorphic reactions. Most of those studies are based on relict products exposed to view by erosion and which are manifestly inactive. Even in the few areas where noneroded subsurface occurrences have been studied in detail, uncertainty about whether the diagenetic phases are relict or are products of currently active processes invites debate (Castaño and Sparks, 1974; Merino, 1975; McCulloh *et al.*, 1978, pp. 31–33). Added to this uncertainty are the inherent difficulties of obtaining trustworthy estimates of *in situ* temperatures and pressures in deep boreholes and the related problem of collecting undisturbed samples of formation fluids. Interpretations of the physical and chemical significance of the mineral products in terms of subsurface processes are thus weakened even under the best of conditions.

Laumontite is difficult to synthesize in laboratory experiments (Liou, 1971a, 1971b, pp. 384–385, 387) because of the apparent sluggishness of the reactions and the ". . . extreme difficulty of nucleating and growing laumontite" (Liou, 1971b, p. 387). Successful synthesis was achieved only by the ". . . decomposition of natural wairakite in the presence of natural laumontite and either H_2O (very slow reaction) or 0.25 N NaCl (slow reaction) solution" and then only at fluid pressures and

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temperatures exceeding 1000 bars and 250°C (Liou, 1971b, Table 6). The conditions apparently required for laboratory synthesis are well beyond the range encountered in most deep boreholes. They are applicable only in the most deeply eroded sedimentary terranes and are therefore not suitable for interpreting most laumontite occurrences.

At Pauzhetka, Kamchatka, "silica gels" are naturally deposited in hot springs and associated streams. Such gels accumulate also in heating radiators that utilize the hot geothermal waters (Lebedev and Gorokhova, 1968). Electron microscopy and X-ray diffraction analysis of microcrystalline phases separated from gels from the radiators reveal minute crystals identified as "adularia" and "laumontite." These same minerals are said to occur in well cores from beneath the area as secondary minerals in hydrothermally altered dacite tuff at depths of 30–250 m, where NaCl solutions vaporize at temperatures of 100°–190°C (Averyev *et al.*, 1962; Rusinov, 1965). Critical reexamination of the published X-ray powder diffraction data of Lebedev and Gorokhova (1968) suggests that the identification of part of the crystallites as "adularia" may be in error and raises questions about other aspects of the work, even though laumontite does appear to be present.

Barnes *et al.* (1978) studied eleven warm springs on South Island, New Zealand. All of the springs are associated either with faults or deeply cut valleys. All of the waters are supersaturated with respect to laumontite and are dilute to extremely dilute in terms of total dissolved species. Noncrystalline siliceous gels occur as precipitates at two of the springs, and Barnes *et al.* (1978) speculated that the gels might be laumontite precursors. The temperatures of the waters of the two springs precipitating the gel coatings are 52° and 55°C, whereas the range of temperatures for all eleven springs of their study is 40° to 65°C. No laumontite or other zeolite was recognized as a precipitate from waters of any of the springs studied.

Therefore, any surface occurrence of laumontite where the mineral may be currently precipitating is of extraordinary interest. Despite numerous documented occurrences of laumontite (and wairakite) at relatively shallow depths in geothermal systems, the only occurrence thus far recognized of well-crystallized laumontite precipitating naturally under surface conditions is the one described here.

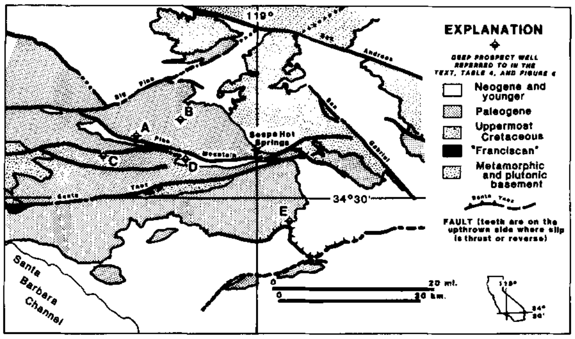

Figure 1. Generalized geologic map of part of the northwestern Transverse Ranges, California, showing the location of Sespe Hot Springs in relation to the major faults, the distribution of the principal rock groupings, and the locations of abandoned deep prospect wells mentioned in the text.

GEOLOGIC SETTING OF SESPE HOT SPRINGS

Sespe Hot Springs is located in the western Transverse Ranges province of southern California (Figure 1), within a region of rugged coastal mountains near the eastern end of the Santa Ynez Mountains at 34°35.7′N lat. and 118°59.9′W long. The Tertiary strata that constitute much of the western Transverse Ranges (Nagle and Parker, 1971; Chipping, 1972) were deposited in an elongate depositional basin which became disrupted and attenuated by several now east-trending faults during and after deposition (Dickinson, 1969; Nilsen and Clarke, 1975). Near Sespe Hot Springs, the local base of the sedimentary section has been bared by erosion along the northeast wall of a 900-m deep canyon occupied by Hot Springs Creek. Fossiliferous lenticular beds of marine mudstone of lower or middle Eocene age lie immediately above basal arkosic sandstone and conglomerate. Although Merrill (1954) suggested that the contact is a fault of large displacement, the field evidence suggests, as Givens (1974, Figures 3 and 6) showed, that the Eocene beds are in unconformable and only locally faulted contact with the gneisses and granitic rocks to the northeast. Eocene beds near the contact strike northwest and dip 25°–60° southwesterly. Aeromagnetic data suggest that the sediment/basement rock interface dips to the southwest to where it intersects the Pine Mountain fault.

The Sespe Hot Springs issue from fractures along or very close to the basal contact at about 845 m above sea level. Four distinct springs issue from restricted fracture openings in steeply dipping, massive, and thoroughly indurated conglomerate and sandstone along the northeastern wall of the canyon. Two additional separate areas of seeping and steaming ground are distinguishable along the northeastern edge of the alluviated canyon floor. The combined flow of the group of springs and seeps has been estimated at 470 liters/min (Renner *et al.*, 1975), and the temperature of the hottest spring is 88°–90°C (Waring, 1915, p. 66; Stearns *et al.*, 1937, p. 125). The temperature of water flowing from the coldest (and the highest and smallest) spring is 34°–36°C.

Torrential runoff after exceptionally heavy rains during the winters of 1969, 1979, and 1980 left the floor of the canyon of Hot Springs Creek gullied, nearly bare, and strewn with boulders. Upstream from the springs,

Table 1. Chemical compositions of hot spring waters.

	California	New Zealand	
	Sespe Hot Springs	Cow Stream	Lake Summer
Temperature (°C)	89	52	55
pH	7.74	8.44	9.01
Ca^{2+}	22	1.5	1.1
Mg^{2+}	0.11	0.02	0.01
Sr^{2+}	—	0.12	0.06
Na^{+}	330	189	97
K^{+}	14	3.5	1.3
Li^{+}	0.76	0.78	0.20
Mn^{2+}	0.00	0.00	0.00
Fe^{2+}	0.00	0.00	0.00
Cl^{-}	290	117	4.2
F^{-}	12.0	7.2	7.0
SO_4^{2-}	292	62	19
HCO_3^{-}	70	259	189
CO_3^{2-}	0.29	5.96	16.7
SiO_2(aq)	91	70	59
H_3BO_3(aq)	74.4	46	17.0
NH_3(aq)	0.6	2.0	6.0
H_2S(aq)	2.5	21	5.8
Al	0.019	0.010	0.008
Al^{3+}	1×10^{-19}	5.0×10^{-20}	1.0×10^{-22}
pCO_2	2.3×10^{-3}	1.1×10^{-3}	2.2×10^{-4}
Rb^{+}	—	0.011	0.004
Ca^{2+}	—	0.004	0.004

Concentrations are in mg/liter except for Al^{3+} which is given in molality, and pCO_2 which is given in atmospheres.

Hot Springs Creek is normally a small perennial freshwater stream. The steady outflow from the springs is not only hot but also somewhat mineralized, so that for a few hundred meters downstream from the springs the boulders and gravel of the stream bank are partially and unevenly coated above the water level by white to light gray precipitates and efflorescences. The temperature of the flowing water where coatings occur is 89° to 34°C. Blue-green algae flourish in the clear, hot stream, except in the immediate vicinity of the hottest spring, where small amounts of hydrogen sulfide bubble forth. The vicinity of the springs is without travertine, siliceous sinter, or a tufa apron. The very localized, partial, and uneven coatings are the only precipitates visible and are the sources of the laumontite and other minerals.

METHODS

Water samples from the hottest of Sespe Hot Springs were collected and analyzed in accordance with the procedures recommended by Presser and Barnes (1974), involving field determination of pH, alkalinity, sulfide, and ammonia, and filtration, alumina extraction, and acidification. The thermal water was collected in 1977 by R. H. Mariner and W. C. Evans and analyzed by T. S. Presser.

The precipitates, crusts, efflorescences, and crystalline coatings present in and along the banks of Hot Springs Creek were systematically examined and selectively sampled from the hottest spring to a point downstream of the coolest spring where the water temperature is 34°C. Hand lens examination of the precipitates reveals a variety of hard and apparently noncrystalline to powdery white crystalline coatings on exterior rock surfaces in contact with the water but projecting above water level, plus coarser and obviously crystalline coatings on incipient fractures in such rocks. These different precipitates were studied by routine optical petrography, X-ray powder diffraction (XRD), scanning electron microscopy (SEM), and electron microprobe techniques. Powders for XRD analysis were sedimented onto glass slides, and diffractograms were prepared using a Picker diffractometer and Ni-filtered CuKα radiation. SEM examination was carried out on samples prepared with a gold-sputter coating using an ISI Super IIIA system equipped with a PGT 1000 energy-dispersive X-ray attachment.

The chemical composition of individual laumontite crystals was analyzed on an ARL-EMX microprobe, utilizing a 15-kV excitation potential at 0.010 μA. Both natural and synthetic standards were used in combination. Oxide proportions were obtained by C. E. Meyer after correction using a modified online data-reduction program (Yakowitz *et al.*, 1973).

Reaction states were calculated using the equation $\Delta G_R = RT \ln(Q/K)$, where ΔG_R is the Gibbs free energy difference between the actual state of the reaction and the equilibrium state, R is the gas constant, T is the absolute temperature, Q is the reaction quotient, and K is the equilibrium constant. Details of the calculations may be found in Kharaka and Barnes (1973).

RESULTS

The water of Sespe Hot Springs is dilute and deficient in carbonate species. The largest and hottest of the springs yields water at 89°C containing 1200 mg/liter of the dissolved substances shown in Table 1. Measured pH is 7.74. Reaction states for the water with respect to selected minerals (Kharaka and Barnes, 1973) are shown in Table 2. For comparison, equivalent analyses and reaction states are shown in Tables 1 and 2 for two New Zealand springs previously suspected of precipitating a laumontite precursor.

Minute, needle-like, colorless crystals are sparingly present and barely detectable by hand lens examination of white to gray, amorphous- to powdery-appearing exterior coatings on a variety of stones in contact with both air and hot-spring water. More obvious, but much rarer, are macroscopic, colorless to white, stubby prismatic to acicular, crystals of the same mineral lining cracks and fractures in transported blocks and stones of gneiss, granite, sandstone, and mudstone. Such crystals are as much as 4 mm long and occur preferentially in the parts of the fractured blocks that project above water. Both the minute exterior needles and the

Table 2. Calculated reaction states of Sespe Hot Springs and New Zealand hot-springs waters.

	California	New Zealand	
Mineral	Sespe Hot Springs Juncal Arkose	Cow Stream Torless Group graywacke	Lake Sumner Torless Group graywacke
Low albite	−1.22	0.17	−1.6
High albite	−2.39	−1.1	−2.9
Analcime	−3.89	−2.8	−4.1
Calcite	−0.004	−0.45	−0.015
Magnesium chlorite	6.34	5.6	9.2
Fluorite	0.57	−1.6	−1.8
Laumontite	3.14	3.8	1.7
Muscovite	6.55	8.9	4.6
Anorthite	−3.57	−3.3	−4.7
Prehnite	0.15	−1.4	−1.4
Quartz	0.56	0.92	0.54
Wairakite	−2.85	−3.2	−5.2
Silica gel	−0.95	−0.73	−1.1
Beta-cristobalite	−0.84	−0.60	−0.96

Reaction states indicated for water from Sespe Hot Springs with respect to minerals composing representative arkose of Eocene age. Equivalent data from New Zealand hot springs are presented for comparison. Results are in kilocalories. Positive values indicate supersaturation and negative values undersaturation, respectively. Uncertainties in G_R are maximum (+10% error in analyzed constituents, −0.02 pH error, and −10% errors in concentrations of solutes and +0.02 pH unit). Equivalent data from New Zealand hot springs are in part after Barnes *et al.* (1978, Table 5).

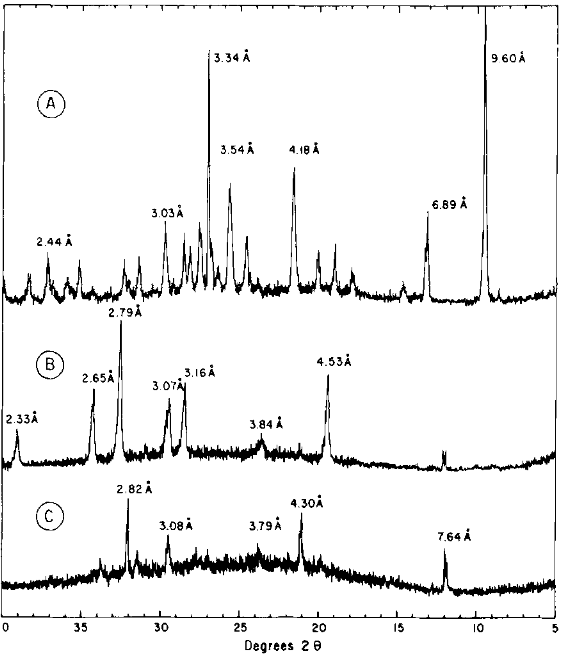

Figure 2. X-ray powder diffraction patterns of precipitates collected from Hot Springs Creek at Sespe Hot Springs; (A) laumontite, (B) thenardite, (C) gypsum. Indicated d-spacings are those that are critically diagnostic for each mineral. Ni-filtered, CuKα radiation; scan rate 2°2θ/min; chart speed 1 inch/min.

coarser fracture-linings occur at the outlet of the main spring on the east side of Hot Springs Creek where water temperature is about 89°C. Well-crystallized fracture coatings occur in growth positions (relative to the present stream level) downstream from the main spring to points where the temperature of the flowing water is 62°C, below which the stream-water composition is complicated by both cold and hot tributary sources. Minute laumontite needles have been identified in coatings where the stream temperature is as low as 43°C. The very finely crystalline nature of the exterior coatings and efflorescences, and the fact that three or more minerals are generally present, necessitated using XRD analysis and SEM (combined with energy dispersive X-ray analyses) to identify laumontite, thenardite, gypsum, quartz, potassium feldspar, and minute amounts of smectite(?). Other phases seen in trace amounts in some samples are halite, a mercury sulfide, an iron sulfide, and an iron-bearing mineral that is possibly an oxide or carbonate. Representative XRD patterns of laumontite, thenardite, and gypsum are shown in Figure 2.

In addition to aiding in the identification of both major and minor minerals, SEM studies also provided textural evidence regarding the stability of the principal minerals. Unbroken, coarsely crystalline laumontite that coats fractures exhibits both euhedral and skeletal growth forms with sharp, noncorroded crystal faces and edges (Figure 3A and 3B). Laumontite in external coatings forms minute (<50 μm) euhedral prisms associated intimately with thenardite and rare gypsum (Figure 3C), whereas laumontite in fractures is intimately associated with neo-formed quartz (Figure 3D), rare gypsum (Figure 3E), and potassium feldspar (Figure 3F). The only occurrences of macroscopic laumontite recognized thus far are from fractures in stones that are in contact with hot-spring waters. The euhedral laumontite prisms that occur in thenardite-rich external coatings (Figure 3C) are clearly a product of the sulfate-bearing water. SEM textures indicate nonreactive intergrowths of laumontite, quartz, potassium feldspar, and gypsum. Gypsum is not a common companion of subsurface laumontite. SEM analyses also show that neither carbonate minerals nor zeolites other than laumontite are present, an observation that is important to the understanding of the origin and paragenesis of laumontite elsewhere. The chemical characteristics of the water are compatible with the mineral paragenesis. Calculations (Table 2) indicate that the water is supersaturated with respect to laumontite and quartz and slightly undersaturated with respect to calcite.

Chemical compositions determined by electron microprobe analyses of selected large crystals partly coating a fracture in a gneiss block are given in Table 3. Analyses of the core and rim of a single crystal suggest

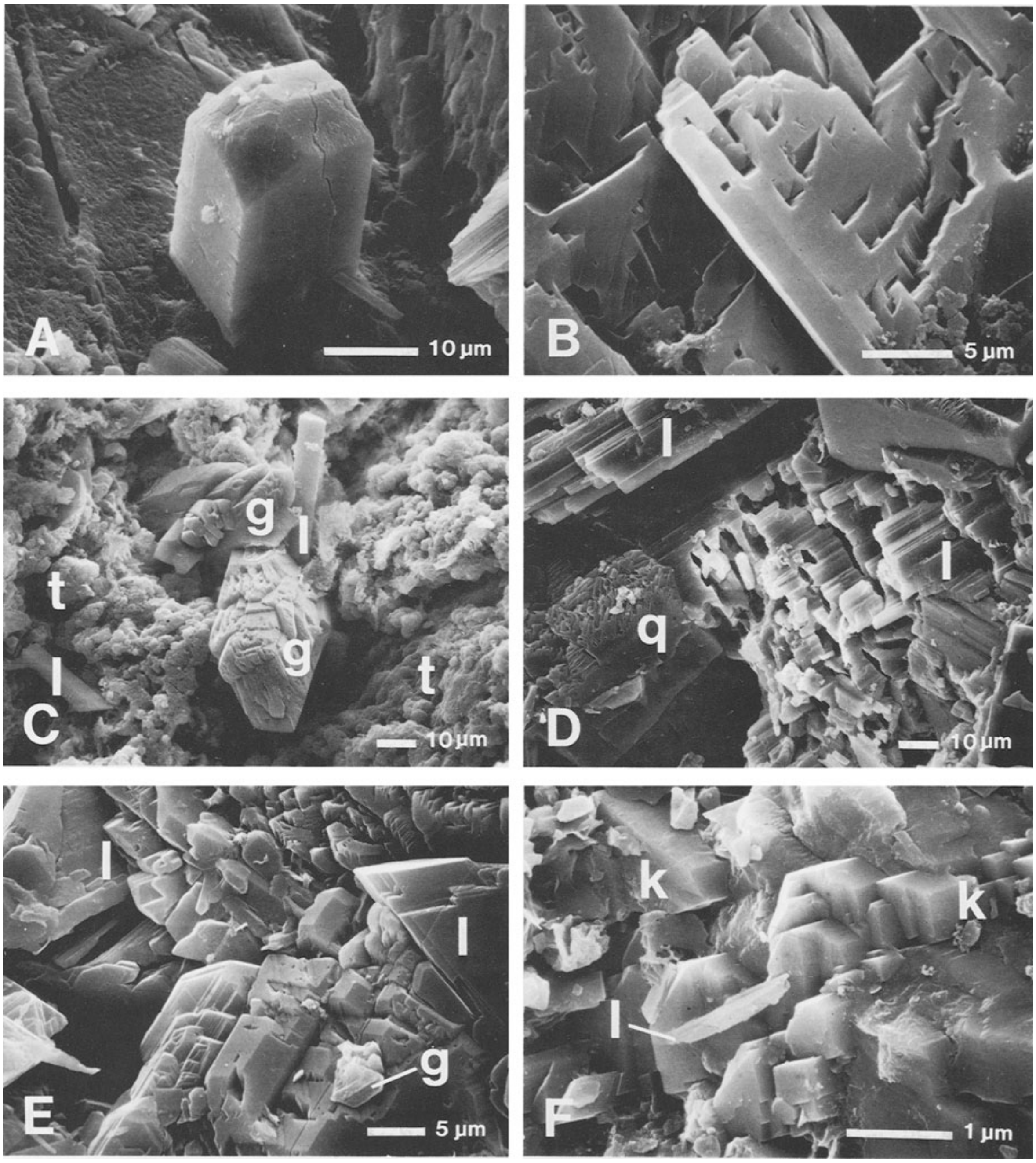

Figure 3. Scanning electron micrographs of minerals composing precipitates from Hot Springs Creek at Sespe Hot Springs, California. Euhedral laumontite crystallites (A) and skeletal laumontite in a growth mode (B), both from a coating of a fracture in a cobble of gneiss. Figure C shows laumontite prisms (l) intergrown with stubby, twinned gypsum (g) and thenardite coating the exterior of one cobble of gneiss. Figures D, E, and F show associations of laumontite (l) with newly-formed quartz (q), a gypsum microlite (g), and potassium feldspar (k), respectively.

that the rim may contain more K and Na but less Ca than the core. The more calcic core presumably represents the older and more stable laumontite and suggests the existence of a chemical potential gradient within the crystal. Compositions are also given in Table 3 for a burial-metamorphic laumontite and a near-surface and a deeper geothermal laumontite (Coombs, 1952; Seki *et al.*, 1969, Table 4c; Petrova, 1970, Table 4). The highest contents of both Na_2O and K_2O occur in the metamorphic laumontite.

Table 3. Compositions of laumontite from Sespe Hot Springs, California, and other sites and of siliceous deposits from warm springs in New Zealand and Pauzhetka, Kamchatka.

	Laumontite						Siliceous deposits		
	Sespe Hot Springs[1]			New Zealand[2]	Japan[3]	Kamchatka[4]	New Zealand[5]		Pauzhetka, Kamchatka[6]
Oxide	av.	core	rim	metamorphic	hydrothermal		(a)	(b)	
SiO_2	50.58	50.09	51.60	50.63	50.97	51.56	86	86	67.05
Al_2O_3	22.01	21.75	21.96	22.07	21.50	20.15	6	6	15.33
Fe_2O_3	0.01	0.00	0.01	0.73	0.10	0.16	—	—	—
MgO	0.003	0.00	0.00	0.40	tr.	0.00	2	2	1.48
CaO	11.51	11.60	11.26	10.72	12.22	13.48	3	3	3.41
Na_2O	0.17	0.15	0.27	1.08	0.28	0.57	3	4	1.48
K_2O	0.25	0.27	0.34	0.45	0.10	0.12	—	—	4.03

[1] Laumontite from hottest spring (water temperature about 89°C). C. E. Meyer, analyst.

[2] Otama, Southland, New Zealand burial metamorphic (outcrop) (Coombs, 1952, Table III, no. 1).

[3] Katayama geothermal area, dacite tuff from borehole core at 108.4 m and 171.5°C (Seki *et al.*, 1969, Table 4 and Figure 4).

[4] Paratunka geothermal area borehole GK-1, vein at 1164 m (Petrova, 1970, Table 4).

[5] Approximate compositions of siliceous gels from Lake Sumner (a) and Cow Stream (b) hot springs, New Zealand (after Barnes *et al.*, 1978, Table 4).

[6] Composition (after subtraction of iron and normalization to 100%) of siliceous gel containing microcrystalline laumontite and "adularia" (Lebedev and Gorokhova, 1968, Table 1).

Isotopic analyses of water from Sespe Hot Springs indicate that water-rock reaction was substantial and water dominated. The delta deuterium composition is −81‰, and the δO^{18} composition is −9.5‰, both referred to SMOW. Local meteoric water composition lies on the line defined by

$$\delta D = 8\delta O^{18} + 10$$

(Craig, 1953). The δO^{18} composition expected on the basis of the deuterium composition is −11.38‰, contrasted with the −9.5‰ actually found. The −2‰ difference results from isotopic exchange between water and rock. The excess of O^{18} in the oxygen of the hot-spring water is comparable to shifts observed in some other geothermal waters (Panichi and Gonfiantini, 1978, Figure 1; White *et al.*, 1973, Figure 1), indicating derivation from isotopically heavy silicates of plutonic or deep metamorphic origin.

DISCUSSION

Many thick geosynclinal sedimentary sequences have undergone partial low-grade regional burial alteration or "metamorphism" (Kossovskaya and Shutov, 1958; Zen, 1974; Zen and Thompson, 1974), some of them in the zeolite facies (of Coombs *et al.*, 1959; Coombs, 1960; Coombs, 1971; Boles and Coombs, 1977; Ghent, 1979). Laumontite (with quartz), an index mineral to the zeolite facies, commonly occurs in plagioclase-rich arkose and volcanogenic sandstones as pore-filling cement or partial replacement of detrital plagioclase grains, lithic volcanic grains, biotite, and hornblende and as fracture linings or veinlets. Laumontite occurs in suitable host rocks in many late Mesozoic and Tertiary sedimentary basins of both the Pacific margin (Hoare *et al.*, 1964; McCulloh and Stewart, 1979), and other tectonically active or volcanic regions (Otalara, 1964; Stalder, 1979). It is a distinctive indicator of changes produced in mineralogically immature clastic rocks that have been buried and heated in the presence of abundant dilute pore waters at above average geothermal gradients. Subsurface occurrences suggest that laumontite crystallization is controlled by both temperature and fluid pressure and is limited by both pore-fluid and host-rock compositions, and they suggest that crystallization can occur at all depths from near the surface to greater than 7 km. Locally steep alteration fronts are definable at intermediate depths and mappable where control is sufficient (McCulloh *et al.*, 1978, Figures 2 and 7).

Laumontite is present in the western Transverse Ranges in some Paleogene strata. Its presence has been previously noted (Madsen and Murata, 1970; Helmold, 1979) but with few supporting details. Evidence for laumontite alteration was sought but not found in rocks younger than early Miocene anywhere within the extremely thick Neogene fill of the Ventura basin south of the Topatopa Mountains (American Association of Petroleum Geologists, 1956; Nagle and Parker, 1971, Figure 12), even in samples from wells as deep as 5.7 km. The presently very low geothermal gradients prevalent throughout the eastern part of the sedimentary basin, including the uplifted and eroded parts in the Topatopa Mountains, are too low to permit such regional alteration. Important middle Tertiary changes in regional thermal regime are implied.

Outcrops of Eocene arkosic sandstones near Sespe Hot Springs are composed mostly of quartz, plagioclase, and potassium feldspar with relatively minor

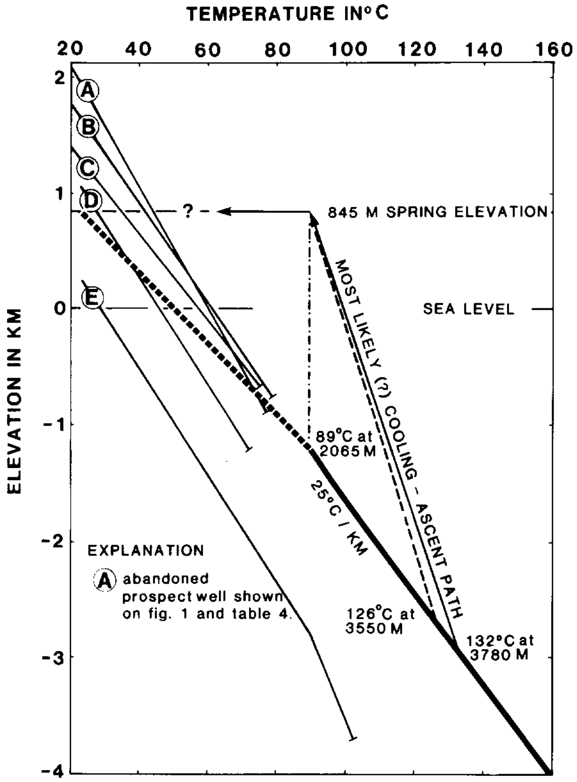

Figure 4. Subsurface temperatures vs. depth from abandoned prospect wells drilled in the Pine Mountain–Topatopa Mountains region of the western Transverse Ranges, California. Locations of wells are shown in Figure 1.

amounts of biotite, muscovite, and chlorite. Some feldspar grains are sericitized, and carbonate is present both as replacements and pore fillings. Volcanic detritus is scarce and consists mostly of well-rounded resistant porphyry clasts. Tuffaceous detritus is volumetrically so unimportant that it cannot play a significant role in the origin of the hot springs solutes. Thus laumontite is not necessarily an alteration product of volcanogenic sediments as has been suggested for some other occurrences. No laumontite has been found in surface or subsurface Eocene rocks north of the Pine Mountain fault.

The temperature of the water from which laumontite is crystallizing is 89°C to 43°C. Most of the precipitates, including laumontite, occur above water level in or on stones in contact with water. Evaporative concentration aided by capillary-solution transport evidently plays an important role in the crystallization process.

The high temperature of the water issuing from Sespe Hot Springs is difficult to explain. Insufficient data are available to assess accurately the geothermal gradient in the area within a few kilometers of the springs. The nearest deep wells drilled in search of petroleum are located 16 to 26 km northwest, west, and south of the springs (Figure 1 and Table 4). In the absence of pertinent data closer to the springs, temperatures measured in these wells during well-logging operations were used to estimate the subsurface thermal conditions. Procedures outlined elsewhere (Bostick *et al.*, 1978, pp. 74–75; McCulloh and Beyer, 1979) were used to calculate the corrections required to compensate for the cooling effect of drilling operations on subsurface temperatures. No attempt was made to correct for the quasi-static distortions produced by the extreme surface topography. Instead, the approximate geothermal gradients are plotted in Figure 4 relative to the surface elevation of each wellhead. The geothermal gradient in the Sespe Hot Springs region apparently is not unusually high. A gradient not higher than 0.032°C/m might characterize the region west of the hot springs between the surface and about −1220 m, and an even lower gradient of 0.025°C/m probably exists at greater depths.

Both the chemical compositions and the isotopic compositions of hot-spring water (and gas) have been used to estimate the subsurface temperatures of source aquifers (Fournier *et al.*, 1974). Applying such estimation techniques to the Sespe Hot Springs water leads to a family of only slightly divergent results. An estimate of 132°C is based on the dissolved silica content, assuming subsurface equilibrium with quartz (Fournier and Rowe, 1966; Fournier, 1977). An estimate of 126°C results from calculations based on the "Na-K-Ca geothermometer" (Fournier and Truesdell, 1973, 1974), assuming a value of ⅓ for their "β." Substantially higher and lower temperatures result from calculations based on other data and assumptions; for example, 110°C on the basis of the sulfate-water isotope geothermometer (Brook *et al.*, 1979, Table 6, n. 61).

Assuming that the geothermal gradient beneath and west of Sespe Hot Springs is as described in Figure 4, the source of the 89°C water flowing from the largest spring would necessarily be 2065 m (or more) below the spring if heat was not lost from the water during its ascent. Under the same assumptions, a reservoir temperature of 112°C is permissible only if the water ascends from 2990 m (or more) and undergoes a corresponding heat loss and temperature drop. A reservoir temperature of 135°C is permissible only if the source is ≤3895 m below the springs. From these considerations alone, it is evident that the springs are fed by an unusual hot water system, and that the laumontite crystallizing at the springs is a highly localized occurrence.

Nothing is known directly about the nature of the rocks at depth beneath the springs, beyond the fact that the thermal water issues from fracture openings very close to the steeply dipping unconformity between the base of the Eocene ("Capay Stage" of Clark and Vokes, 1936) sequence and an extensive massif of plutonites and gneisses. The nearest outcrops of pre-Eocene sedimentary rocks are less than 10 km southwest of Sespe Hot Springs and consist of about 1500 m of clastic Cretaceous and Paleocene strata whose base is unexposed (Rust, 1966). However, these rocks are southwest of the Santa Ynez fault and probably were separated from the site of the springs by about 45 km prior to left-lateral strike-slip fault movements (McCulloh, 1981). North of the Santa Ynez fault, the nearest pre-Eocene sedimentary rocks are uppermost Cretaceous and Paleocene strata penetrated in the bottom part of an abandoned prospect hole drilled to 2035 m by the Ohio Oil Co. about 31 km west of the springs (Table 4 and Vedder *et al.*, 1973). The full thickness of Cretaceous and possibly older strata beneath the bottom of this hole is not known, but as much as 3000 m has been estimated (Nagle and Parker, 1971, Figure 4), partly because 4600 m of these strata crop out 16 km farther west (47 km west of Sespe Hot Springs).

Hidden Cretaceous and (or) Paleocene strata may possibly abut the basement rocks beneath the Hot Springs across an old fault overlapped and concealed by the unconformable base of the middle Eocene strata. If so, their gravimetric expression is unimpressive (Hanna *et al.*, 1974). Regional paleogeographic reconstructions suggest that the thickness of any strata older than middle Eocene does not exceed 1000 m (Nagle and Parker, 1971), an estimate that is in keeping with maximum-thickness estimates based on preliminary interpretations of aeromagnetic data.

All available evidence suggests that the thermal waters issuing from Sespe Hot Springs rise from reservoirs at depths of 3000–4000 m. Yet, the geologic and geophysical data suggest that less than 1000 m of sedimentary rocks vertically underlie the site of the springs. If the source of the water lies within the thicker mass of sedimentary rocks to the west, the fluid must rise very rapidly through a laterally very extended permeable conduit. If the source of the water is directly beneath the springs, a permeable zone of fracturing must extend to great depth within the basement rock massif southwest of the San Gabriel fault zone (Crowell, 1975).

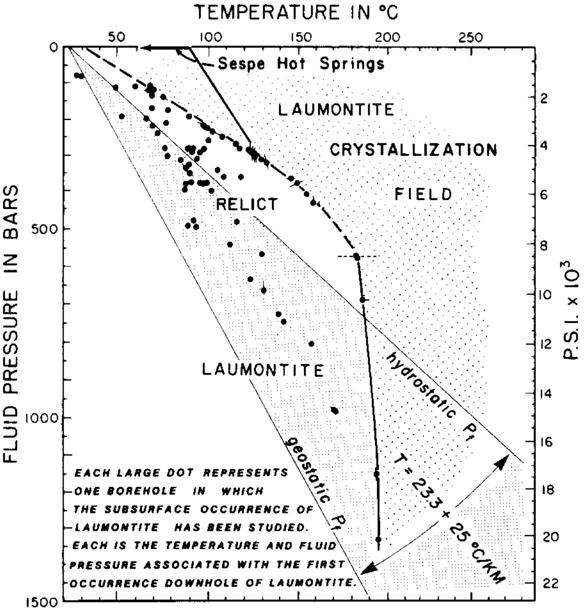

Figure 5. Crystallization temperatures of laumontite at Sespe Hot Springs in relation to the temperature and fluid pressure field of crystallization of subsurface laumontite as established by McCulloh and Stewart (1979).

CONCLUSIONS AND COMMENTARY

Everything about the crystallization of laumontite at Sespe Hot Springs is consistent with interpretations that were reached previously from studies of subsurface laumontite from deep wells drilled in actively subsiding Neogene sedimentary basins on the Pacific margin (McCulloh *et al.*, 1978, Figure 6; McCulloh and Stewart, 1979). Laumontite evidently can crystallize at any depth between the surface and 6700 m wherever the appropriate combination of temperature, fluid pres-

Table 4. Approximate geothermal gradients of abandoned wells.[1]

Letter desig- nation Figures 1 and 4	Operator	Lease and well number	Location[2]	Year drilled	Elevations and (total depth) (m)	Temperature gradient (°C/km)
A	Standard Oil Co. of Calif. (Chevron USA, Inc.)	Hattie Russell No. 1	Sec. 11, T6N R23W	1950	2074 (2971)	1.8
B	Intex (Tesoro)	"U.S.L."No. 1-35	Sec. 35, T6N R22W	1967	1756 (2514)	2.1
C	Ohio Oil Co. (Marathon Oil Co.)	I.M.R. Gov't. No. 1	Sec. 30, T6N R23W	1955	1376 (2035)	2.5
D	Riddle and Gottlieb	"U.S.L." No. 25-1	Sec. 25, T6N R22W	1969	1058 (2283)	2.0
E	Western Gulf Oil Co.	Ivers-Van Trees No. 1	Sec. 1, T4N R20W	1956	246 (4000)	2.0 to 3048 m 1.2 at depths >3048 m

[1] Temperatures measured while logging (suitably adjusted for the thermal disturbances caused by drilling).

[2] California, San Bernardino Baseline and Meridian.

sure, and composition are met and mineralogically immature, permeable, and porous rocks have interacted sufficiently with interstitial water having exceptionally low pCO_2. A particular occurrence of laumontite thus has no distinguishing depth significance and is not interpretable in terms of temperature or pressure of crystallization unless information is independently available concerning some associated depth-dependent factor. Figure 5 shows the temperature range through which laumontite is known to crystallize at Sespe Hot Springs plotted in relation to the temperature-fluid pressure field of subsurface laumontite crystallization as established by McCulloh and Stewart (1979).

Laumontite can crystallize directly from solutions of appropriate composition. Derivation from some precursor zeolite mineral, such as stilbite or heulandite, is not required. The concept of a depth zonation of zeolitic minerals in burial diagenesis (Miyashiro and Shido, 1970) is, therefore, not necessarily valid with respect to the mineral laumontite. However, where other zeolites, such as clinoptilolite, heulandite, and stilbite, are present in a burial succession, they are prime candidates for replacement or reaction to form laumontite providing the conditions required for crystallization of the calcium zeolite are otherwise met.

The data from Sespe Hot Springs provide a guide for the design of hydrothermal experiments aimed toward the laboratory synthesis of laumontite and the experimental verification of the multiple controls on its crystallization (temperature, fluid pressure, fluid composition, pCO_2) that seem evident from subsurface observations. Far from being sluggish, the reactions involved in the crystallization of laumontite appear to occur rapidly and with great facility where all of the demands of the mineral are met.

The petrogenetic grid portraying the low-temperature, low-pressure field of burial diagenesis and deep-burial metamorphism is now in need of important revisions. The laumontite subfacies of the zeolite metamorphic facies (Coombs, 1971; Boles and Coombs, 1977) gains new meaning through the findings at Sespe Hot Springs in combination with those from deep Neogene basins. The boundary of the T-P_f field of apparently stable crystallization of laumontite with quartz (Figure 5) obliquely transects the petrogenetic grid in such a way that it carries a potential for use as a low-temperature geothermometer-geobarometer for quantitative evaluation of other low-temperature diagenetic phases and reactions, most of which seemingly proceed at slower rates.

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Резюме—Хорошо-выкристаллизированный лаумонтит был найден первый раз натурально осажденным на поверхности земли при температуре 89° до 43°C как компонент серых до белых покрытий и эфлоресценции на внешних поверхностях и как осадки во внутренных трещинах камней и блоков, залегающих Ручей Гейзера непосредственно по течению реки от Сеспе Гейзера, Вентура Область, Калифорния. Анализ при помощи рентгеновской порошковой дифракции, сканирующего микроскопа (SEM) и электронного микроанализатора показал, что тенардит является главной фазой во внешних покрытиях вместе с небольшим количеством микрокристаллического (<50 μм) лаумонтита и гипса. Макрокристаллический (>1 мм) лаумонтит является главной фазой во внутренних покрытиях трещин и связан с кварцем, калиевым фельдшпатом, и гипсом. Следы смектита(?), галита, сульфида ртути, сульфида железа (возможно окиси или карбоната), и медного минерала тоже присутствуют. Другие цеолиты, чем лаумонтит, не присутствуют. SEM текстуры показывают нереактивные прорастания лаумонтита, кварца, калиевого фельдшпата и гипса. Неразбитые кристаллы лаумонтита обычно являются евэдрическими или имеют характеристики скелетного взроста и проявляют острые, свежие, нескородированные грани, краи и углы.

Вода из самого горячего и самого большого гейзера о температуре 43°C имеет pH равное 7,74 и 1200 мг/литр растворенных твердых тел, а Na$^+$, Cl$^-$, SO$_4^{2-}$, и H$_4$SiO$_4$ являются главными растворенными веществами. Вычисления указывают на то, что вода перенасыщена по отношению к лаумонтиту, кварцу и прегниту и немного ненасыщена относительно кальцита и некристаллического кремнезема. Изотопный анализ указывает на вододоминирующие взаимодействие воды с породой. Состав δO^{18}, ожидаемый на основе −81‰ δD состава, есть −11,38‰ вместо −9,5‰, найденного в действительности (все относится к SMOW). Химический состав воды указывает на то, что подповерхностные источники воды могут иметь температуру 125°–135°C. Этот диапазон температур вместе с местным низким геотермальным градиентом указывает на то, что источник находится, вероятно, 3550 до 3900 м под гейзером, в трещиноватом и проницаемом мезозойском уровне и более древних плутонитах и гнейсах.

Открытия лаумонтита, кристаллизирующегося при атмосферическом давлении и температуре 62°C (или меньшей) дает возможность лучше понимать процессы, ответственные за глубинный диагенетический лаумонтит, и дает ценную перспективу на метаморфические цеолитовые преобразования. [E.C.]

Resümee—Gut kristallisierter Laumontit wurde zum ersten Mal als natürliche Ausfällung an der Erdoberfläche bei Temperaturen von 89° bis 43°C als eine Komponente in grauen bis weißen Oberzügen und Ausblühungen auf Oberflächen und als Ausfällungen auf inneren Bruchflächen von Steinen und Blöcken gefunden, die den Hot Springs Creek unmittelbar unterhalb von Sespe Hot Springs, Ventura County, Kalifornien, begrenzen. Röntgenpulverdiffraktometer-, rasterelektronenmikroskopische (SEM) und Mikrosonden-Untersuchungen zeigen, daß Thenardit in den äußeren Überzügen die häufigste Phase ist zusammen mit geringen Mengen von mikrokristallinem (<50 μm) Laumontit und Gips. Makrokristalliner (>1 mm) Laumontit ist die überwiegende Phase in den Überzügen auf inneren Kluftflächen zusammen mit Quarz, Kalifeldspat und Gips. Geringe Mengen von Smektit(?), Steinsalz, einem Quecksilbersulfid, einem Eisensulfid, einem eisenhaltigen Mineral (möglicherweise ein Oxid oder Karbonat), und einem Kupfermineral sind ebenfalls vorhanden. Andere Zeolithe außer Laumontit wurden nicht beobachtet. Karbonatminerale fehlen entweder vollständig oder nahezu. SEM-Texturen deuten auf eine nicht durch Reaktion bedingte Verwachsung von Laumontit, Quarz, Kalifeldspat, und Gips hin. Unzerbrochene Laumontitkristalle sind im allgemeinen idiomorph oder zeigen Skelettwachstum und haben scharfe, frische, nichtkorrodierte Flächen, Kanten, und Ecken.

Das Wasser von der heißesten und größten Quelle hat eine Temperatur von 43°C, einen pH von 7,74, 1200 mg/liter gelöste Feststoffe und enthält vor allem Na$^+$, Cl$^-$, SO$_4^{2-}$, und H$_4$SiO$_4$. Berechnungen deuten darauf hin, daß das Wasser im Hinblick auf Laumontit, Quarz, Chlorit, und Prehnit übersättigt ist, während es im Hinblick auf Calcit und nichtkristallinem SiO$_2$ leicht untersättigt ist. Wasserdominierte Wasser-Gestein-Wechselwirkungen werden durch die Isotopenanalyse angezeigt. Die δO^{18}-Zusammensetzung, die aufgrund der −81‰ δD-Zusammensetzung zu erwarten war, beträgt −11,38‰ anstatt der −9,5‰, die tatsächlich gefunden wurden (bezogen auf SMOW). Die Wasserzusammensetzung deutet darauf hin, daß das unterirdische Wasserreservoir eine Temperatur von 125° bis 135°C haben kann. Dieser Temperaturbereich zusammen mit dem niedrigen geothermischen Gradienten in dieser Gegend bedeuten, daß das Reservoir wahrscheinlich 3550 bis 3900 m unter den Quellen in zerbrochenen und durchlässigen mesozoischen und älteren Plutoniten und Gneisen liegt.

Die Beobachtung von Laumontit, der bei Atmosphärendruck und 62°C (oder niedriger) kristallisiert, liefert wertvolle Einblicke in die Prozesse, die für die diagenetische Bildung von Laumontit verantwortlich sind, und wertvolle Hinweise für die metamorphe Zeolithfazies. [U.W.]

Résumé—Pour la première fois, la laumonite bien cristallisée a été trouvée précipitant naturellement à la surface de la terre à des températures de 89°C à 43°C, en tant que composant de couches grises et blanches et d'efflorescences sur les surfaces externes de pierres et de blocs le long de Hot Springs Creek et directement en aval de Sespe Hot Springs, Ventura, California, et en tant que précipités sur les fractures intérieures de ces mêmes pierres et blocs. La diffraction poudrée aux rayons-X, le microscope électronique à transmission (SEM) et des analyses de microprobe d'électrons montrent que la thénardite est la phase dominante dans les couches extérieures, en association avec de la laumonite et du gypse microcristallins mineurs (<50 μm). La laumonite macrocristalline (>1 mm) est la phase dominante dans les couches de fractures intérieures et est associée avec du quartz, du feldspar potassique, et du gypse. De petites quantités de smectite(?), de l'halite, un sulfide de mercure, un sulfide de fer, un minéral contenant du fer (possiblement un oxide ou un carbonate) et un minéral de cuivre, sont également présents. Des zéolites autre que la laumonite n'ont pas été observées et les minéraux carbonates sont soit complètement, ou presqu'absents. Les textures SEM indiquent des intercroissances non-réactives de laumonite, de quartz, de feldspar potassique, et de gypse. Les cristaux de laumonite non-brisés sont généralement euhédraux ou ont des caractéristiques de croissance squelettique, et exhibent des faces, des bords, et des coins tranchants, frais et non-corrodés.

L'eau provenant de la source la plus grande et la plus chaude a 43°C, a un pH de 7,74, a 1200 mg/litre de solides dissolus au total, et contient Na^+, Cl^-, SO_4^{2-}, et H_4SiO_4 comme espèces dissolues dominantes. Des computations idiquent que l'eau est supersaturée respectivement à la laumonite, le quartz, la chlorite, et la prehnite, et est un peu sous-saturée respectivement au calcite et à la silice non-cristalline. Les interactions dominées par l'eau entre l'eau et la roche sont indiquées par des analyses isotopiques. La composition δO^{18} à laquelle on pourrait s'attendre basé sur la composition $-81‰$ δD est $-11{,}38‰$, au lieu de $-9{,}5‰$ trouvée (toutes referrées à SMOW). La qualité chimique de l'eau suggère que la source d'eau souterraine pourrait avoir une température de 125°–135°C. Cette gamme de températures, avec le gradient géothermal bas de la région, implique que la source est probablement à 3550 à 3900 m sous les sources dans des plutonites et des gneiss mésozoiques fracturées et perméables. La découverte de laumonite cristallisant à la surface à pression atmosphérique et à 62°C (ou à une température plus basse) fournit une vue importante des procédés responsables pour la laumonite diagénétique souterraine et une perspective précieuse du facies métamorphique de zéolite. [D.J.]