HYDROTHERMAL EPIDOTE FORMED IN THE SALTON SEA GEOTHERMAL SYSTEM, CALIFORNIA[1]

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Abstract

Epidote is being formed as a hydrothermal metamorphic product in metasediments in the Salton Sea geothermal system. One of the two analyzed epidotes has a composition of 32 mole percent $Ca_2Fe_3Si_3O_{12}(OH)$ and occurs with chlorite, hematite, pyrite, quartz, albite, and K-feldspar. The second epidote has a composition of 20 mole percent $Ca_2Fe_3Si_3O_{12}(OH)$ and occurs with iron-bearing tremolite, quartz, and pyrite. Both epidotes formed at temperatures of approximately 320°C and under 125–145 atm hydrostatic pressure. Variation in oxygen fugacity is the mechanism most likely to account for the different epidote compositions and mineral associations.

Introduction

The purpose of this paper is to record significant data obtained from the study of two epidotes from the Salton Sea geothermal system, southeastern California, and to present evidence that these epidotes are products of the hydrothermal metamorphism presently taking place.

The occurrence of epidote in hot-spring systems in Iceland, New Zealand, and Kamchatka, USSR was summarized by White and Sigvaldason (1963). Rusinov restudied the epidote in boreholes at Pauzhetka Springs, Kamchatka, and concluded that this epidote was clastic and unrelated to hydrothermal alteration except for "isolated instances of possible microrecrystallization of epidote in cavities" (Rusinov, 1966, p. 737). Steiner (1966) presented textural criteria for the hydrothermal origin of epidote at Wairakei, New Zealand. Epidote of hydrothermal metamorphic origin from the Salton Sea geothermal system was first described by White, Anderson, and Grubbs (1963).

Geologic Setting

The Salton Sea geothermal system is entirely within Pliocene and Quaternary sediments of the Colorado River delta at the north end of the Gulf of California. At the time of deposition, these detrital sediments were sand, silts, and clays made up of quartz, calcite, dolomite, plagioclase, K-feldspar, montmorillonite, illite, and kaolinite (Muffler and Doe, 1968). At measured temperatures as high as 360°C these sediments are being transformed to low-grade metamorphic rocks of the greenschist facies (Muffler and White, unpublished data). Iron-rich epidote

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is a common product of this metamorphism at temperatures greater than approximately 290 to 310°C and at depths greater than approximately 3,000 feet (915 meters). Muffler and White conclude that the metamorphic parageneses of the Salton Sea geothermal system reflect the present thermal environment and not some higher temperature regime of the past.

PETROLOGY

The epidotes described in this paper occur in core samples recovered from deep exploratory wells near the center of the geothermal field. W823-4,296 is from a depth of 4,296 feet (1, 310 meters) in I.I.D. No. 2 well. W747h is from a depth of 4,920 feet (1,500 meters) in I.I.D. No. 1 well. Graphs of temperatures within the wells after drilling (Helgeson, 1968) indicate a temperature of approximately 320°C for both samples.

W823-4,296 is a medium-grained metasandstone of even grain size (Fig. 1). The mineral assemblage is epidote, quartz, tremolite (with approximately 15 percent ferroactinolite molecule as determined by indices of refraction using the curves of Deer, Howie, and Zussman, 1963, p. 257), and pyrite. Traces of calcite, K-feldspar, plagioclase, zircon, sphene, and apatite were detected in the course of mechanical separation of
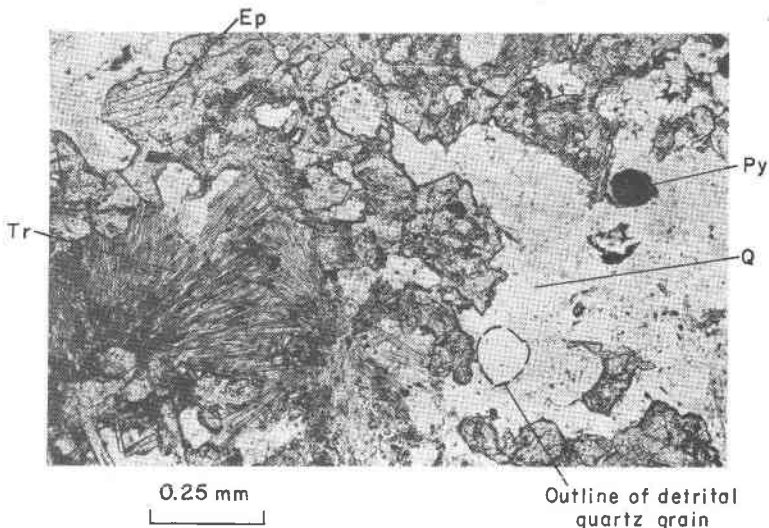

FIG. 1. Photomicrograph of metasandstone W823-4,296 from I.I.D. No. 2 well, Salton Sea geothermal field. Ep, epidote. Tr, tremolite. Py, pyrite. Q, quartz. Relict detrital form of quartz grain indicated by dashed line.
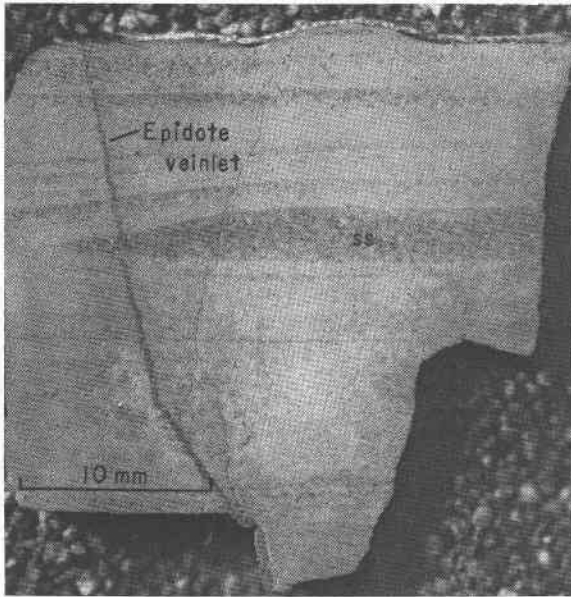
FIG. 2. Veinlet of epidote cutting metasiltstone with lenses of metasandstone in W747h, I.I.D. No. 1 well, Salton Sea geothermal field. Disseminated idioblastic crystals of epidote and pyrite occur throughout the sample and are concentrated in the metasandstone lenses (ss).

epidote from the other minerals; we found no hematite, magnetite, pyrrhotite or graphite. The grains are idioblastic, and only quartz shows relict detrital forms. Porosity is high and may well be secondary porosity produced during hydrothermal metamorphism by removal of material. Epidote is disseminated as sharply bounded idioblastic crystals throughout the rock. The epidote is relatively free of mineral inclusions but contains abundant fluid inclusions.

W747h is a metasiltstone with interbedded lenses of poorly sorted fine-grained metasandstone (Fig. 2). The mineral assemblage is chlorite, epidote, quartz, pyrite, hematite, and albite. The rock also contains traces of sphene, K-feldspar (detrital?), and relict detrital plagioclase (as calcic as labradorite) which is probably metastable. Epidote occurs as disseminated idioblastic crystals and as one thin veinlet (Fig. 2). Fluid inclusions are sporadic in the epidote.

Modal petrographic analyses indicate approximately 34 percent epidote in W823–4,296 and 14 percent in W747h. Metasandstone at other depths in I.I.D. No. 1 well contains up to 72 percent epidote.

Textural criteria indicate that the epidote in both samples formed by hydrothermal metamorphism rather than being original clastic grains. The epidote veinlet of Figure 2 is unequivocal. In addition, the disseminated epidote in both samples in idioblastic, shows no detrital or relict detrital forms, and in each sample is of uniform composition (excluding minor zoning variation). The distribution of epidote is related neither to the exotic metavolcanic sand grains that occur sporadically in the samples nor to sedimentary structures. Locally, the epidote is more abundant in sediments of coarser grain size; we interpret this correlation as being due to greater ease of access of hydrothermal fluid in the sandstones.

Epidote does occur sporadically in the unmetamorphosed sediments of the Colorado River delta in the Salton Trough (Mufler and Doe, 1968). This clastic epidote, however, occurs only in trace quantities ($<<1\%$) and is a low-Fe (clinozoisite) epidote, in contrast to the hydrothermal epidote, which is high in Fe.

MINERALOGY

Epidote was separated from W823-4,296 and W747h using gravity and magnetic techniques on several size fractions of the crushed samples. Final purification was accomplished on material between 88 and 30 microns in diameter using density-adjusted Clerici solution and a Frantz magnetic separator. At front and side tilts of 15°, W823-4,296 epidote was concentrated between 0.5 and 0.6 amp, and W747h epidote between 0.39 and 0.43 amp. Optical and X-ray diffraction examination of the purified fractions showed less than 1 percent impurities (primarily quartz inclusions) in both samples. In addition, W823-4,296 contained approximately 1 percent fluid inclusions.

Zoning was prominently developed in a few grains of W747h and in about one half of the grains of W823-4,296. In W823-4,296 compositional variation between zones (as estimated from index of refraction measurements, occurred primarily in a thin marginal zone.

Splits of the purified fractions were analyzed (Table 1) using wet chemical methods as described by Peck (1964). Ions per formula were calculated using the computer-based procedure of Jackson, Stevens, and Bowen (1967). These calculations show the analyses of both epidotes to be high in Si and low in OH compared with the ideal formula Ca_2 $(Fe^{3+}, Al)_3Si_3O_{12}(OH)$. The high Si is probably due to quartz contamination of the analyzed separate. The low OH may represent analytical error. The extraction of total water in silicates is extremely difficult, and we cannot insure complete liberation of water by the fusion with a lead oxide-lead chromate flux.

TABLE 1. CHEMICAL ANALYSES, UNIT-CELL PARAMETERS, AND OPTICAL DATA
FOR TWO HYDROTHERMAL EPIDOTES FROM THE SALTON SEA GEOTHERMAL
FIELD, IMPERIAL COUNTY, CALIFORNIA

Chemical Analysis[a]	W747h	W823–4,296
SiO_2	38.2	39.1
Al_2O_3	21.6	25.4
Fe_2O_3	15.9	10.1
FeO	.20	.17
MnO	.39	.18
CaO	22.2	23.2
H_2O^+	1.4	1.6
H_2O^-	.03	.00
Total	99.89	99.75

Number of ions on the basis of 13(O, OH)

	W747h		W823–4,296	
Si	3.073	} 3.07	3.081	} 3.08
Al	—		—	
Al	2.048	} 3.01	2.359	} 2.96
Fe^{3+}	.963		.599	
Fe^{2+}	.014		.011	
Mn	.027	} 1.96	.012	} 1.98
Ca	1.914		1.959	
OH	.767		.841	

Spectrographic analysis for minor elements[b]

	W747h	W823–4,296
B	0.004	0.013
Ba	.0004	.0006
Be	.0003	.0001
Cr	.0008	.0024
Cu	.0026	.0020
Ga	.0040	.0028
Ge	.003	—
La	.005	.005
Mg	.022	.065
Mn	.26	.13
Na	—	.03
Ni	<.0006	<.0006
Pb	.002	.002
Sc	.0010	.0010
Sr	.16	.12
Ti	.044	.090
V	.0055	.030
Y	.004	.004
Yb	.0003	.0002
Zr	<.002	.004

Unit-cell parameters

a, Å	$8.91 \pm .001$	$8.89 \pm .001$
b, Å	$5.64 \pm .001$	$5.62 \pm .001$
c, Å	$10.18 \pm .003$	$10.16 \pm .001$
vol., Å³	462.10	458.92
β	115°29′	115°25′
$\Delta 2\theta CuK\alpha_1$ $(020_{Ep} - 111_{Si})$	3.23°	3.40°

Optical data[c]

α	1.740 ± 0.002	1.719 ± 0.002
β	1.762 ± 0.002	1.736 ± 0.002
γ	1.781 ± 0.002	1.748 ± 0.002
$2V\alpha$	$70° \pm 4°$	$85° \pm 4°$
$\alpha \wedge Z$	$5 - 10°$	5°
Dispersion	Strong r>v	Moderate r>v
Pleochroism: α	Pale yellow	
β	Pale yellow green	None
γ	Yellow green	
Zoning	Observed in some grains	Common
Color of mineral grains in sunlight	Dark yellow green	Yellow green

[a] Analyzed by Marcelyn Cremer.

[b] Analyzed by R. E. Mays and Chris Heropoulos, U. S. Geological Survey.
Overall accuracy is ± 15 percent except near the limits of detection where only one digit is reported.
Looked for but not found: Ag, As, Au, Bi, Cd, Ce, Co, Ge, Hf, Hg, In, K, Li, Mo, Nb, P, Pd, Pt, Re, Sb, Sn, Ta, Te, Th, Tl, U, W, Zn, Pr, Nd, Sm, Eu.

[c] Refractive indices measured in Na light; $2V$ measured on universal stage in plane light.

Samples were prepared for X-ray study by hand grinding, adding powdered silicon, and mounting in an aluminum cell pack modified according to Niskanen's method (1964) for random grain orientation. X-ray diffraction data were obtained on a Norelco unit using a high intensity Cu tube, focusing monochromator, no β filter and a scintillation counter. Settings were 35 kv, 35 ma, 1/4°/minute goniometer speed and 1/4 in./minute chart speed. Measured epidote peak positions were cor-

rected against the silicon peak positions, and the corrected data were used to calculate cell dimensions by a least-squares computer refinement (Evans, Appleman, and Handwerker, 1963).

The cell dimensions and chemical data thus obtained for W823-4,296 fit closely the curves of Myer (1965, p. 83; 1966, p. 376). For W747h, the fit is not good for the individual cell dimensions, although the volume agrees closely with Myer's curve. The position of the 020 epidote peak (relative to silicon 111 peak) of W747h fits Myer's curve somewhat better than W823-4,296.

Indices of refraction of the central, slightly zoned parts of epidote crystals of W823-4,296 (Table 1) correlate well with the chemical data using the curves (Fig. 3) of Deer, Howie, and Zussman (1962, p. 203). The thin marginal zone observed on some crystals gave indices as high as $\alpha = 1.723$, $\beta = 1.745$, and $\gamma = 1.757$ (about 26 percent pistacite molecule on the determinative curves of Deer, Howie, and Zussman).

The indices of epidote from W747h plot above the determinative curves of Deer, Howie, and Zussman (1962, p. 203). However, several of their data points at the iron-rich end of the epidote series also are well above the curves as drawn. The curves perhaps should be redrawn with appreciably more curvature at the iron-rich end.

Discussion

Both analyzed epidotes are rich in iron. W747h contains 32 mol percent iron end member ($Ca_2Fe_3Si_3O_{12}(OH)$), and W823-4,296 contains 20 mol percent iron end member.

In addition, the two epidotes occur in different associations. W747h occurs with hematite and with chlorite of $Fe/Fe+Mg = 0.321$ (Muffler and White, unpublished data), but with no amphibole. W823-4,296 occurs with iron-bearing tremolite (17 percent ferroactinolite molecule) but with no chlorite or hematite. Pyrite occurs in both samples, but is more abundant in W747h.

Differences in temperature and pressure at the time of formation are unlikely to account for these differences in composition and assemblage. The temperature-depth data of Helgeson (1968) indicate temperatures of about 320°C at the depths from which the core samples came. Hydrostatic pressures interpolated for the appropriate depths from the data of Helgeson (1968) are approximately 143 atm for W747h and 127 atm for W823-4, 296.

Strens (1965) has proposed that a miscibility gap exists between clinozoisite and epidote, and the data of Holdaway (1965) on epidote from metamorphic rocks of the Klamath Mountains also suggest a miscibility gap. Brown (1967) however, found that many epidotes from the green-

schist facies of eastern Otago fall in the range occupied by the solvus deduced by Strens (1965, Fig. 2). Epidote W823-4,296, formed at approximately 320°C in the Salton Sea geothermal system, contains 20 mol percent $Ca_2Fe_3Si_3O_{12}(OH)$ and falls well within Strens' deduced miscibility gap at this temperature.

The available chemical analyses of brines from I.I.D. No. 1 and I.I.D. No. 2 make it difficult to ascribe the differing epidote compositions and assemblages to different concentrations of components in the brine. In all respects, the analyzed brines are nearly identical (Table 2). These

TABLE 2. MAJOR DISSOLVED CONSTITUENTS, PARTS PER MILLION, IN BRINES IN
I.I.D. No. 1 AND I.I.D. No. 2 WELLS, SALTON SEA GEOTHERMAL FIELD

	I.I.D. No. 1[a]	I.I.D. No. 2[b]
SiO_2	400	400
Fe	2,090	2,000
Al	41	—
Mn	1,560	1,370
Ca	28,000	28,800
Mg	54	10
Na	50,400	53,000
K	17,500	16,500
Cl	155,000	155,000
HCO_3	>150	690
pH	— 5.2	4.64

[a] White (1968) Table 1.

[b] Helgeson (1968) Table 1. HCO_3 recalculated from 500 ppm total CO_2 given by Helgeson. pH calculated for 300° C. Al not reported.

analyzed brines, however, are samples of produced fluid taken at the well head. They best represent the composition of the brines in the reservoir zones in which the epidotes occurred, but in neither well can one be sure that the analyzed brines came from the exact depths at which the epidotes occurred. Accordingly, one cannot preclude the possibility of formation fluids of differing composition than the analyzed fluids. Indeed, assuming equilibrium between each mineral assemblage and its corresponding fluid phase, some significant compositional differences between the fluid phases are implicit.

Possibly the controlling variable in the fluid is the fugacity of oxygen. Differing values of f_{O_2} would be expected to affect the Fe^{2+}/Fe^{3+} ratio in the fluid, but because almost all iron in solution is ferrous, such variations would be well below analytical sensitivity. In addition, one cannot guarantee that the Fe^{2+}/Fe^{3+} ratio in an analyzed sample is the

same as when collected, and any differences in Fe^{2+}/Fe^{3+} among brines from different beds within the production zone would be homogenized during eruption.

Inasmuch as epidote is an iron-bearing mineral, the fugacity of oxygen would be expected to influence both epidote stability and composition. In a qualitative sense, high f_{O_2} should promote the growth of high-iron epidote, for almost all the iron in the epidote structure is in the ferric state. Experimental data on the stability and composition of epidote as a function of f_{O_2}, however, are lacking.

The fugacity of oxygen is undoubtedly an important variable in determining the stability of the other iron-bearing minerals in the Salton Sea drill core. The hematite-magnetite buffer as a function of f_{O_2} is well known at 800 to 1,000°C, and has been extrapolated to lower temperatures (Eugster and Wones, 1962). Ernst (1966) showed that oxygen fugacities in excess of the magnetite+quartz+fayalite buffer greatly reduce the stability of ferroactinolite (which makes up 17 percent of the iron-bearing tremolite of W823-4,296). Hellner, Hinrichsen, and Seifert (1965, p. 160) state that the 14 Å chlorite field in the join $Mg_5Al_2Si_3O_{10}$(OH)$_8$-$Fe_5Al_2Si_3O_{10}$(OH)$_8$ at 300°C to 700°C expands strongly to the iron-rich side with increasing oxygen pressure.

Brown's study of rocks of the greenschist facies in eastern Otago, New Zealand, also points up the possible importance of f_{O_2} in determining the composition of epidote. His Figure 6 shows that all epidotes from the quartzo-feldspathic schists studied fall between 12 and 21 percent $Ca_2Fe_3Si_3O_{12}$(OH). These quartzo-feldspathic schists commonly contain graphite, a mineral that indicates low f_{O_2} during metamorphism (Miyashiro, 1964). Brown's data, however, do not permit an unequivocal corresponding correlation of high f_{O_2} with high-iron epidote, perhaps owing to the effect of other variables such as the activity of water or the activity of iron.

Our suggested correlation of high-iron epidote with relatively high f_{O_2} is compatible with the data of Ernst (1964, p. 1636–1637, 1647). Six epidotes from the blueschist facies rocks in Japan contain approximately 33 mol percent $Ca_2Fe_3Si_3O_{12}$(OH). Ernst infers a relatively elevated f_{O_2} for these rocks from the absence of graphite and from the presence of hematite or magnetite in five of the six samples.

Despite some ambiguities in precise interpretation, the studies of Brown (1967) and of Ernst (1964) are compatible with our conclusion from the Salton Sea geothermal system. The fugacity of oxygen appears to be an important variable in determining the composition of metamorphic epidote, and epidote of intermediate composition appears to

be stable at relatively low temperature (300–400°C) under conditions of relatively low f_{O_2}.

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