MASTER

TOPICAL REPORT

**PETROLOGY, GEOCHRONOLOGY, AND
CHEMICAL EVOLUTION OF THE
TWIN PEAKS RHYOLITE DOMES, UTAH**

By

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Petrology, Geochronology, and Chemical
Evolution of the Twin Peaks Rhyolite Domes, Utah

by

H. R. Crecraft, W. P. Nash, and S. H. Evans, Jr.

ABSTRACT

Two distinct sequences of silicic volcanism at the Twin Peaks volcanic field, Millard County, Utah, spanned periods from $2.74 \pm .10$ to $2.54 \pm .09$ m.y. and $2.43 \pm .08$ to $2.35 \pm .08$ m.y., and produced a total exposed volume of 4 km^3 of rhyolites and volcanoclastics. Wet chemical, x-ray fluorescence, microprobe, atomic absorption, and neutron activation methods have been employed to obtain a wide range of chemical data on whole rock and mineral separate samples. Calculated distribution coefficients are comparable to previously published values for high silica rocks. Each sequence is characterized by a systematic trend from $<72\%$ to $>76\% \text{SiO}_2$. Accompanying this increase in SiO_2 over time are increases in Rb, Y, Sb, Cs, U, Th, HREE and decreases in Mg, Co, Fe, Sr, Ba, and LREE. Decreases in temperature and f_{O_2} and an increase in $f_{\text{H}_2\text{O}}$ are also indicated. These trends are very similar to gradients observed in ash flow tuffs erupted instantaneously from compositionally zoned magma chambers. Chemical evolution at Twin Peaks was dominated by the same mechanisms of liquid state differentiation which produce the compositional zonation in larger silicic magma chambers.

Using the chemical differences between two samples erupted from the late stage, stratified magma of the early sequence as a model of liquid state differentiation at Twin Peaks, the relative effects of crystal settling and liquid state differentiation have been estimated

for each sequence. Crystal settling was of only minor significance in the evolution of the early sequence and was responsible for only several percent of the total chemical variation. In the later sequence, crystal settling was the dominant agent initially. Settling velocities and chemical variations indicate settling of 10% sanidine, 3% plagioclase, 2.5% augite, 1% magnetite, and .025% zircon, before liquid state differentiation became the dominant effect later in the sequence.

The effects of gravity, pressure, thermal, and compositional gradients on the distribution of components are calculated. Observed gradients of most major components, including H_2O , agree in direction to those predicted by the gravitational field alone, but are far greater in magnitude. The density gradient due to the compositional gradient is sufficient to arrest thermal convection. A pressure gradient also predicts an upward increase in X_{H_2O} but not f_{H_2O} . The dominant effect on the distribution of major components is the thermal gradient. By considering crystal-liquid equilibria in a subliquidus system, and treating enthalpies of fusion and crystallization as heats of transfer, simple steady state thermodynamic theory predicts very large gradients in the directions observed for all major and volatile components. The effect of a water gradient is shown to produce a parallel SiO_2 gradient. The changes in liquid structure as a result of major component gradients probably determine trace element distributions.

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INTRODUCTION

Large scale pyroclastic eruptions represent rapidly quenched voluminous samples tapped in one brief moment from the upper portion of silicic magma chambers. Gradients in the chemistry, mineralogy, and intensive parameters have been observed in various pyroclastic sequences and have been used to deduce the physio-chemical regimes within the upper portion of silicic magma chambers immediately prior to eruption for the Bishop Tuff, Ca., (Hildreth, 1977, 1979), Bandelier Tuff, N.M. (Smith, 1979), rhyolites of the Coso Range, Ca. (Bacon, 1979), and elsewhere. A consistent model is emerging and indicates that the upper portions of large silicic magma chambers consist of a nonconvecting zone in which silica and volatiles increase and total phenocryst content declines upwards with a decrease in temperature and pressure. Accompanying these gradients are other characteristic gradients in major and trace components, which for the most part are remarkably consistent from one region to another. This study is an effort to determine 1) whether the processes responsible for the development of these chemical and mineralogical gradients are operative in a small scale silicic system in which no voluminous pyroclastic eruption occurred, 2) the extent to which such processes control its overall evolution, and 3) the mechanisms by which these processes do control chemical distributions.

The total exposed volume of silicic volcanics in the Twin Peaks,

Utah field is 4 km³, and consists of crystalline rhyolites and pyroclastic material. There may be as much as 8 km³ of additional pyroclastic material buried in the subsurface. Whole rock and mineral data, calculated intensive parameters, and potassium-argon dating provide constraints on the chemical evolution of the Twin Peaks magmas, and permit the determination of the relative effect and timing of the various mechanisms which contribute to the overall evolution of the Twin Peaks system throughout its history.

GEOLOGY

Introduction

The Twin Peaks area lies in the southern portion of the Black Rock Desert graben, near the eastern margin of the Basin and Range province in west-central Utah. This region is characterized by late Cenozoic extension (Cook et al., 1971; Stewart, 1971) and present day high seismicity (Smith and Sbar, 1973; Olson, 1976). Episodic basalt-rhyolite volcanism related to Basin and Range tectonism was initiated in this region 20 m.y. ago and has continued into the Holocene (Rowley, et al., 1979).

The late Pliocene-early Pleistocene silicic volcanics in the Twin Peaks area were described by Haugh (1978), who proposed that the distribution of volcanics was related to ring dike fissures associated with a trap door Glencoe-type cauldron collapse. Carrier (1979) undertook a gravity and heat flow study of the area and concluded that little or no subsidence had actually occurred. Present day heat flow values (96 mW/m²) are near typical background for the Basin and Range.

Locally associated basalts have been studied by Clark (1977), Hoover (1974), Best and Brimhall (1974) and Condie and Barsky (1972). Local lacustrine limestones were described by Clark (1977) and Zimmerman (1961).

Geology of Twin Peaks Area

Silicic volcanism in the Twin Peaks area spanned a period from

Fig. 1: Generalized Geologic Map of the Twin
Peaks Area, Millard County, Utah

2.74 to 2.35 m.y., and is the oldest dated volcanism within the immediate region. This volcanic activity produced a series of flows, domes, and volcanoclastic deposits whose distribution is shown in Fig. 1. No voluminous ash deposits characteristic of large scale caldera collapse are exposed in the Twin Peaks field. However, small volume welded and non-welded ash flow deposits occur in the Cudahy Mine Unit of the Twin Peaks field; within and to the south of the area volcanic ash has been found interbedded in fluvial and lacustrine deposits of the area which appear to be contemporaneous with the rhyolitic volcanism. This sedimentary sequence is late Pliocene to early Pleistocene in age (Clark, 1977) and is confined to the local region of basalt-rhyolite volcanism:

The structural relationship of the fluvial and lacustrine environments to the rhyolitic volcanism is unknown. The occurrence of a hundred meter section of predominantly limestone within the area suggests an appreciable amount of subsidence with respect to the water level during its deposition. Drill hole logs (Carrier, 1979) confirm the presence of a greater than 100 meter sequence of lacustrine sediment elsewhere in the immediate area. The possibility of appreciable caldera subsidence is indicated by the existence of a buried tuff chemically related to the Twin Peaks rhyolites which was encountered in a drill hole ten kilometers south of any exposed silicic volcanic in the Twin Peaks area. A substantially larger eruptive volume than has been previously recognized (Carrier, 1979; Haugh, 1978) is probable based on this finding, and suggests that there might have been a greater degree of subsidence of the roof block

than indicated by geophysical studies. The restricted occurrence of these sedimentary sequences raise the intriguing question as to whether they are related to a cauldron lake. At present, this question remains unanswered.

Although Clark (1977) considered the basalts in the area to be considerably younger than the rhyolites, basalt on the southwest slope of South Twin Peak is included as fragments within the rhyolite, indicating that basaltic activity commenced prior to the emplacement of South Twin Peak, the youngest rhyolite in the area.

Only three dates have been obtained on basalts in the area: 2.0 m.y. at Black Point (Clark, 1977), and .97 and .92 m.y. for the Black Rock flow (Condie and Barsky, 1972). On the basis of flow morphology, Clark argues that all other basalts in the area are younger than those dated. The fluvial and lacustrine deposits were contemporaneous with some of the basalt flows, which lie both stratigraphically above and below the limestones.

A north-south trending anticlinal arch which postdates the silicic volcanism runs through the Twin Peaks area, uplifting and tilting basalts and limestones, most prominently just to the east of South Twin Peak. The sedimentary sequence is well exposed in the core of this anticline where it is capped by younger basalts.

FIELD RELATIONS AND PETROGRAPHY

The silicic volcanic rocks in the Twin Peaks area show a variety of textural compositions ranging from felsite, obsidian, and volcanoclastics in the Cudahy Mine Unit, to crystalline rhyolite which comprises the rest of the field. Sample numbers, unit names, and locations are given in Table 1 and modal analyses are given in Table 2.

Coyote Hills Rhyolite

Coyote Hills rhyolite (samples 12 and 15) occurs in the southwest portion of the Coyote Hills, with smaller extrusives found on the north and south-west sides of North Twin Peak. One cubic kilometer of this unit is exposed.

This unit is essentially devoid of quartz phenocrysts. Plagioclase is the dominant phenocryst comprising at times greater than ten percent of the rock by volume. It is zoned and ranges from one up to two millimeters in length. Some of the larger phenocrysts contain abundant crystallite inclusions. Sanidine, in contrast, occurs only as microphenocrysts, and rarely exceeds .5 millimeters in length.

The mafic minerals in this unit are augite and hypersthene, although Haugh (1978) has reported fayalite in addition to these. Pyroxenes are generally euhedral, range from .2 to .8 mm in length, and commonly occur in cumulophyric aggregates with oxides and

Table 1: Sample numbers and locations

<u>Sample Number</u>	<u>Unit</u>	<u>Location</u>
2	C.M.U.	Black Point
4	N.T.P.	Northeast side of North Twin Peak
5	C.H.	North side of North Twin Peak
6	N.T.P.	North side of North Twin Peak
8	S.T.P.	Southeast side of South Twin Peak
9	C.M.U.	East of South Twin Peak
12	C.H.	Southeast of Coyote Hills
15	C.H.	West side of Coyote Hills
18	C.M.U.	Cudahy Mine, Coyote Hills
19	C.M.U.	South of Cudahy Mine
20	M.D.	Mid Dome
30	NTP	North side of North Twin Peak
CORE	C.M.U.(?)	3 km South of Burnt Mountain

Abbreviations:

C.H.	Coyote Hills Rhyolite
C.M.U.	Cudahy Mine Unit
S.T.P.	South Twin Peak Rhyolite
N.T.P.	North Twin Peak Rhyolite
M.D.	Mid Dome Rhyolite

Table 2. Twin Peaks Rhyolite Modal Compositions
(volume %)

[illegible]

frequently plagioclase.

Groundmass comprises 84% of the rock by volume and consists predominantly of plagioclase with subsidiary amounts of quartz, sanidine, oxides, and accessory zircon.

North Twin Peak Rhyolite

The North Twin Peak rhyolite (samples 4 and 6) comprises most of North Twin Peaks and has a total exposed volume of .4 cubic kilometers. This unit exhibits pronounced chemical and mineralogical variety. Samples 4 and 6, (Figure 1), span the observed mineralogical variation of twelve samples of North Twin Peak rhyolite studied in thin section. They represent, respectively, the least and most mafic extremes of this unit.

Rounded quartz grains up to eight millimeters are present in sample 6 and up to three millimeters in 4. Though smaller, quartz is considerably more abundant in 4. Plagioclase is again the most abundant phenocryst, comprising up to seventeen percent in sample 6. Plagioclase is generally strongly zoned (Figure 9) and occurs in individual grains up to five millimeters in length, as well as in composite aggregates, some of which are believed to be xenolithic. Very large sanidine up to 30 millimeters in length occur in this unit. In thin section, it has resorbed edges, and sometimes contains plagioclase inclusions. Sanidine in graphic intergrowth with quartz is common.

Biotite is the sole mafic mineral in the less mafic portions. Biotite is generally rimmed with oxides and is commonly associated with

sphene. Where found along with pyroxene in more mafic portions, biotite shows alteration to oxides. Clinopyroxene and rare orthopyroxene are usually .1 to .2 millimeters in length, but may be as large as one millimeter. They are often surrounded by reaction rims and are sometimes entirely replaced by amphibole. Pyroxenes and biotite are often found in the aggregates, both with and without plagioclase.

Coarse grained groundmass comprises about seventy percent of the unit by volume. It is composed of quartz and feldspar grains commonly .1 millimeter or longer, with accessory oxides, apatite, sphene, and zircon.

Mid Dome Rhyolite

The very small hill located half way between North and South Twin Peaks is designated the Mid Dome Rhyolite (Sample 20). Its total exposed volume is about 7×10^{-4} cubic kilometers. Petrographically, it is similar to the less mafic portions of the North Twin Peak rhyolite (Sample 4).

South Twin Peak Rhyolite

South Twin Peak rhyolite (Sample 8) comprises the .3 cubic kilometers of South Twin Peak. Total phenocryst content ranges from less than three percent by volume along the northern margins of the peak, to twenty percent higher up the northern slope and along the southwestern margin. Quartz occurs as rounded grains up to four millimeters in length. Plagioclase occurs as individual grains, generally one millimeter or less, and in aggregates similar to those

in North Twin Peak rhyolite. It generally exhibits slight zoning. Sanidine occurs as large grains up to five millimeters in length. Biotite is the only mafic mineral, and appears very fresh.

The groundmass is composed of fine grained (.01 to .05 mm) quartz, sanidine, plagioclase, oxides, and accessory zircon. Hematite in the groundmass gives this unit a characteristic red hue in hand specimen.

Cudahy Mine Unit

The Cudahy Mine Unit has an exposed volume of 2 cubic kilometers, and is the most silicic unit exposed in the Twin Peaks area. It is found in the central and northern portions of the Coyote Hills, east of South Twin Peak, and in a small exposure north of Black Point. Although only samples from one member of this unit, as described by Haugh (1978), have been chemically analyzed in this study, Haugh states that all members are chemically indistinguishable.

The early Felsite/Obsidian member occurs at Black Point, east of South Twin Peak, and in the Coyote Hills. This member was sampled and analyzed at all three locations. Obsidian "apache tears" from east of South Twin Peak (Sample 9) contain rare sanidine, plagioclase, and oxide phenocrysts set in a glass matrix with well developed flow layering. Samples of obsidian near the Cudahy Mine (Samples 18 and 19) were devoid of phenocrysts in thin section, although a single quartz grain was found in an "apache tear" sample nearby. Heavy mineral separates from a large volume of obsidian yielded biotite and another, undetermined, heavy mineral.

The felsite from north of Black Point (Sample 2), which is chemically similar to the obsidians, contains sanidine, plagioclase, quartz and red biotite in a devitrified matrix, which shows relict flow layering. Included in the matrix are spherulites and lithophysae with vapor phase quartz and sanidine.

In addition to the tuffs described by Haugh (1978), a tuff was encountered in a core from a hole drilled by Chevron Resources Company about ten kilometers south of South Twin Peak (see Fig. 1). The tuff was encountered at a depth of thirty meters and the sample was taken at 110 meters. The tuff is chemically coherent with, and is believed to be cogenetic with, the Twin Peak rhyolites. It is however more highly evolved in its chemistry than the Early Felsite/Obsidian samples analyzed. On the basis of its overall chemical coherence with the Twin Peaks volcanics and its degree of chemical evolution, it is believed to be a highly evolved member of the Cudahy Mine unit, or a separate but closely related unit.

GEOCHRONOLOGY

Potassium-argon dates for the Twin Peaks volcanics were determined on sanidines from rhyolite and on whole rock samples for obsidian; the results are presented in Table 3.

The Coyote Hills rhyolite was the first unit erupted in the area at $2.74 \pm .10$ m.y. This unit is petrographically the most mafic and is believed to represent the primitive Twin Peaks magma. Next to be erupted were the high silica volcanics of the Cudahy Mine Unit. Three obsidian samples have yielded dates at $2.63 \pm .10$, $2.54 \pm .09$ and $2.43 \pm .08$ m.y. These samples are chemically very similar, however, and are here included in a single unit, probably emplaced within a short time period. Two samples from the North Twin Peak rhyolite have yielded ages of $2.35 \pm .08$ and $2.43 \pm .08$ m.y. Apparently following the North Twin Peak rhyolite closely in time, was the high silica South Twin Peak rhyolite. This unit has been dated at $2.35 \pm .08$ m.y. and is believed to be the youngest rhyolite in the area.

Table 3. Potassium-argon age dates for the Twin Peaks Volcanic Center

Sample	Unit	Age (m.y.)
4	North Twin Peak	2.35±.08
8	South Twin Peak	2.35±.08
9	Cudahy Mine	2.63±.10
15	Coyote Hills	2.74±.10
18	Cudahy Mine	2.54±.09
19	Cudahy Mine	2.43±.12
30	North Twin Peak	2.43±.08

Additional age dates:

Lipman et al. (1977)	Cudahy Mine	2.38±0.15
	South Twin Peak	2.33±0.12

Leudke and Smith

(1978)	Cudahy Mine	2.28±0.08
	South Twin Peak	2.41±0.14

* Note: Dates of Leudke and Smith recalculated using new constants for comparison with other dates in table.

WHOLE ROCK CHEMISTRY

Major Elements

Major elements were determined by wet chemical methods described by Carmichael et al. (1968) except for F, which was analyzed by specific ion electrode, and the alkalis, analyzed by flame photometry following a lithium metaborate fusion (Shapiro, 1975).

Major element analyses and CIPW norms are given in Table 4. The rocks are very close to alumina saturation. Normative corundum, which appears in most of the norms, disappears when CO_2 and F are neglected due to the liberation of Ca from calcite and fluorite to form additional anorthite.

When element concentrations are plotted against time, a chemical trend towards more highly evolved rocks is seen to occur between Coyote Hills and Cudahy Mine (early trend) and between North Twin Peak and South Twin Peak (later trend) with a major reversal occurring between the two. SiO_2 and FeO are plotted against age in Fig. 2, in which they show this pattern, characteristic of most of the major and trace elements.

Major elements are plotted in Fig. 3 against rubidium. Rubidium has been selected because it 1) is determined with good precision, 2) has a low crystal/liquid distribution coefficient and would be concentrated in residual liquids produced by crystal fractionation, and 3) it is enriched in highly evolved silicic liquids by liquid

Table 4. Whole Rock Major Element Analyses and CIPW Norms of Twin Peaks Rhyolites.

Sample	2	4	5	6	8	9	12
SiO ₂	75.26	73.83	71.58	71.91	76.18	75.24	71.62
TiO ₂	0.06	0.30	0.30	0.41	0.08	0.09	0.41
Al ₂ O ₃	13.05	13.04	12.73	13.53	12.30	12.88	13.30
Fe ₂ O ₃	0.89	0.77	2.10	1.35	0.81	0.29	1.31
FeO	0.08	1.19	0.48	0.93	0.40	0.62	1.26
MnO	0.06	0.02	0.03	0.03	0.01	0.05	0.05
MgO	0.08	0.34	0.44	0.50	0.16	0.07	0.50
CaO	0.72	1.30	2.00	1.50	0.89	0.72	1.80
Na ₂ O	3.96	3.70	3.25	3.96	3.20	3.67	3.48
K ₂ O	5.26	4.72	4.38	4.97	5.18	5.31	5.24
P ₂ O ₅	0.08	0.09	0.10	0.14	0.02	0.01	0.11
H ₂ O ⁺	0.09	0.49	0.63	0.17	0.11	0.03	0.08
H ₂ O ⁻	0.02	0.04	0.03	0.02	0.01	0.05	0.01
F	0.16	0.21	0.10	0.05	0.14	0.76	0.15
CO ₂	0.00	0.02	0.95	0.00	0.05	0.01	0.24
Sum	99.77	100.06	100.10	99.47	99.54	99.80	99.56
-O=F	0.07	0.09	0.04	0.02	0.06	0.32	0.06
Total	99.70	99.97	100.06	99.45	99.48	99.48	99.50
Q	31.15	31.31	30.14	26.70	36.20	33.07	27.84
c	0.14	0.22	0.49	0.00	0.33	1.10	0.00
or	31.08	27.89	31.79	29.37	30.61	31.38	30.96
ab	33.51	31.31	27.50	33.51	27.08	31.05	29.45
an	1.90	4.43	2.93	4.47	3.00	0.00	5.20
di-wo	0.00	0.00	0.00	0.88	0.00	0.00	0.34
di-en	0.00	0.00	0.00	0.76	0.00	0.00	0.21
di-fs	0.00	0.00	0.00	0.00	0.00	0.00	0.11
hy-en	0.20	0.85	1.10	0.48	0.40	0.17	1.03
hy-fs	0.00	1.09	0.00	0.00	0.00	0.84	0.54
mt	0.28	1.12	0.78	1.91	1.09	0.42	1.90
il	0.11	0.57	0.57	0.78	0.15	0.17	0.78
hm	0.70	0.00	1.57	0.03	0.06	0.00	0.00
ap	0.19	0.21	0.24	0.33	0.05	0.02	0.26
fr	0.32	0.42	0.20	0.09	0.29	0.98	0.30
cc	0.00	0.05	2.16	0.00	0.11	0.00	0.55

Table 4. Whole Rock Major Element and CIPW Norms of Twin Peaks Rhyolite (continued)

Sample	15	18	19	20	30	core
SiO ₂	70.92	75.67	75.86	74.99	72.73	76.59
TiO ₂	0.47	0.12	0.11	0.26	0.40	0.04
Al ₂ O ₃	13.47	12.94	12.86	12.97	12.93	12.11
Fe ₂ O ₃	1.17	0.22	0.21	1.06	1.62	0.62
FeO	1.53	0.65	0.66	0.24	1.10	0.18
MnO	0.05	0.04	0.05	0.00	0.08	0.03
MgO	0.53	0.08	0.07	0.20	0.65	0.07
CaO	2.09	0.72	0.74	1.20	1.35	0.35
Na ₂ O	3.50	3.99	3.93	2.95	2.95	4.02
K ₂ O	5.19	4.90	4.96	4.93	5.55	4.41
P ₂ O ₅	0.12	0.02	0.02	0.05	0.13	0.02
H ₂ O ⁺	0.55	0.30	0.35	0.35	-	0.34
H ₂ O ⁻	0.01	0.04	0.04	0.06	-	0.06
F	0.15	0.22	0.20	0.14	0.14	0.42
CO ₂	0.44	0.00	0.00	0.16	0.01	0.00
Sum	100.19	99.9	100.06	99.56	99.64	99.38
-O=F	0.06	0.09	0.08	0.06	0.06	0.18
Total	100.13	99.81	99.98	99.50	99.58	99.08
Q	26.80	32.36	32.57	37.04	31.21	36.22
c	0.00	0.38	0.26	1.41	0.31	0.72
or	30.67	28.96	29.31	29.13	32.80	26.06
ab	29.62	33.76	33.25	24.96	24.96	34.02
an	5.72	1.90	2.08	3.73	4.80	0.00
di-wo	0.17	0.00	0.00	0.00	0.00	0.00
di-en	0.09	0.00	0.00	0.00	0.00	0.00
di-fs	0.08	0.00	0.00	0.00	0.00	0.00
hy-en	1.23	0.20	0.17	0.50	1.62	0.17
hy-fs	1.08	0.89	0.95	0.00	0.17	0.00
mt	1.70	0.32	0.30	0.02	2.35	0.56
il	0.89	0.23	0.21	0.49	0.76	0.08
hm	0.00	0.00	0.00	1.05	0.00	0.23
ap	0.28	0.02	0.05	0.12	0.31	0.05
fr	0.30	0.45	0.41	0.28	0.28	0.45
cc	1.00	0.00	0.00	0.36	0.02	0.00

Figure 2. Variations of whole rock SiO_2 and FeO with Potassium-Argon age. Two distinct sequences, each characterized by increasing SiO_2 and decreasing FeO , are evident. Most major and trace elements show similar systematic variations with time.

Figure 3. Major element concentrations in the Twin Peaks rhyolites versus rubidium. Open squares signify the early sequence; closed squares signify the late sequence. The two paths are generally parallel but noncoincident, indicating similar mechanisms of control over the two sequences for most elements. The alkalis, and to a lesser extent, Al_2O_3 , are notable exceptions.

state differentiation as described by Hildreth (1979).

The two intervals of differentiation are distinguished by the open squares (trend I) and the closed squares (trend II). The two separate paths are Coyote Hills - Cudahy Mine - Core for the early trend and North Twin Peak (samples 6 and 4) - Mid Dome - South Twin Peak for the later trend.

Conspicuously deviating from the latter trend is sample 30. Sample 30 is from a location very near sample 6 and closely resembles it petrographically. Chemically, however, it is quite anomalous and will be discussed more fully later. It is arbitrarily excluded from the present discussion.

For all the major elements except the alkalis (and to a lesser extent Al_2O_3), the two trends are nearly parallel to each other. The alkalis are apparently dominantly controlled by contrasting mechanisms in each sequence.

The whole rock samples are plotted on a Q-Ab-Or ternary in Fig. 4. Also shown are the minimum liquidus (piercing) points for this system at 1 kb water pressure with 3% and 5% anorthite (James and Hamilton, 1969) and at 1 and 5 kb water pressure and no anorthite (Tuttle and Bowen, 1958). One kilobar would be the approximate total pressure near the top of a magma chamber at the 3 km depth estimated by Carrier (1979) using gravity modeling, and is an upper limit for water pressure. If the effect of water on the liquidus relations of the anorthite bearing and anorthite free systems is similar, the piercing points would be expected to shift towards the quartz-orthoclase edge for lower water pressures.

Figure 4. Twin Peaks rhyolites in terms of normative quartz, albite, and orthoclase. Open squares signify the early sequence; closed circles signify the late sequence. Contrasting mechanisms are indicated by the differences between the two trends. Arrows indicate the directions in which liquids would proceed by crystallization of plagioclase (double arrow) and sanidine (single arrow). Crosses represent the minima at .5 and 1 kb water pressure (Tuttle and Bowen, 1958) and circles represent piercing points for 3% and 5% anorthite at 1 kb water pressure (James and Hamilton, 1969).

The path traced by the earlier interval of differentiation moves away from the Or apex and crosses the Ab-Or thermal trough with presumed decrease in temperature. The path is similar to that noted by Hildreth (1977, 1979) for the Bishop Tuff. It is not consistent with the path of a salic liquid controlled by crystal-liquid equilibria, and is believed to be due to the same liquid state differentiation mechanism postulated by Hildreth (1977, 1979), Shaw et al. (1976), and Smith (1979).

The samples from the later sequence (6, 4, 20, 8), in contrast, plot along a path that is at a high angle to the earlier sequence, and is more consistent with the path of a salic liquid, containing between three and four percent anorthite, which is controlled by feldspar-liquid equilibria. The arrows in Figure 4 indicate the direction the liquid would move with crystallization of the sanidine and plagioclase contained in each sample.

Trace Elements

Trace elements were analyzed primarily by instrumental neutron activation analysis (INAA) (Perlman and Asaro, 1969) and X-ray fluorescence (XRF). Results are given in Tables 5 and 6, respectively. In addition Li, Be, and Cu were determined by atomic absorption and S by a Leeco Sulfur analyzer (Table 6). Trace elements show large variations with La, Eu, Cs, Sr, and Ba each extending over an order of magnitude.

Trace elements are plotted against Rb in Fig. 5. Sr, La, Sc, Hf, Zr, and Eu decrease with increasing Rb whereas Ta, Th, U, Li, Be,

Lu, Pb, Y, and Nb generally increase. Many of the trace element variations can be resolved into the two differentiation trends and are distinguished by open squares for the early trend and closed squares for the late trend. The paths for most elements are again generally parallel indicating similar mechanisms of control on their concentrations. Specific differences, however (e.g., Lu, Mn, Y, and Nb), attest to there being other influences as well.

The rare earth elements (REE) for representative samples are plotted in Fig. 6. The more highly evolved rocks show a characteristic flattening (and even reversal for the core sample) of the slope and an increase in the europium anomaly.

The overall pattern of chemical changes for all the elements for which good whole rock data are available is best indicated by comparing the enrichment factors for the two sequences shown in Fig. 7. For each sequence the concentration of each element in the more evolved rock is divided by its concentration in the less evolved rock. Shown also for comparison are the enrichment factors for the Bishop Tuff, which reflect compositional differences due essentially to liquid state differentiation alone (Hildreth, 1977, 1979). Definite similarities and contrasts are apparent. Depletion in Mg, P, Ca, Ti, Fe, Sr, Zr and Ba, and enrichment in Rb, Y, Sb, and Cs seem to be characteristic of liquid state differentiation, and are observed in both sequences at Twin Peaks. In contrast, Mn and Nb are depleted over the second sequence, and Sc over both sequences, whereas all three are enriched in the more evolved Bishop Tuff samples. Also characteristic of liquid state differentiation seems to be the general

Table 5. Whole Rock Instrumental Neutron Activation Analyses
(values in ppm except where designated %)

	2	4	5	6
La	16.8±0.5	69.7±0.9	89.0±1.1	69.1±0.9
Ce	45.5±0.7	150.3±1.5	183.0±1.8	133.4±1.3
Nd	24.1±1.1	61.0±1.6	74.3±1.9	51.5±1.5
Sm	5.99±0.06	8.12±0.08	10.97±0.11	7.22±0.07
Eu	0.281±0.008	1.207±0.013	1.520±0.016	1.327±0.015
Tb	1.13±0.06	0.88±0.05	1.26±0.06	0.81±0.05
Dy	7.98±0.17	5.93±0.14	8.44±0.18	5.38±0.14
Yb	6.97±0.07	4.31±0.05	5.26±0.06	3.81±0.04
Lu	1.021±0.032	0.640±0.024	0.736±0.026	0.591±0.023
Sc	1.873±0.019	4.51±0.04	5.44±0.05	5.79±0.06
Th	28.15±0.28	18.16±0.18	15.43±0.15	16.73±0.17
U	6.69±0.07	2.41±0.04	1.52±0.03	1.69±0.03
Cs	3.39±0.07	2.05±0.08	1.80±0.08	0.56±0.07
Hf	4.94±0.07	6.76±0.09	8.46±0.10	9.64±0.11
Fe%	0.694±0.016	1.545±0.021	1.928±0.023	1.790±0.022
Rb	275±7	116±4	138±5	95±4
Ba	16	761±13	1402±18	1270±17
Ni	<7	<10	<9	<9
Cr	<2.2	2.7±0.7	<3.3	3.6±0.7
Sb	0.23±0.04	0.20±0.05	.12±0.14	0.08±0.04
Ti%	0.055±0.016	0.171±0.016	0.201±0.017	0.273±0.019
Mo	<4.3	<1.9	1.5±0.6	<1.2
Ta	2.981±.030	1.379±.014	1.368±.014	1.259±.013
Mn	394±8	110.1±2.2	211±4	177±3

Table 5. Whole Rock Instrumental Neutron Activation Analyses
(Continued)

	8	9	12	15
La	33.2±0.6	11.6±0.4	87.9±1.1	85.9±1.0
Ce	74.8±0.8	34.5±0.6	186.0±1.9	181.7±1.8
Nd	33.9±1.1	19.5±1.0	75.6±1.9	73.6±1.9
Sm	5.58±0.06	5.51±0.06	11.18±0.11	10.76±0.11
Eu	0.530±0.009	0.212±0.007	1.697±0.018	1.746±0.018
Tb	0.72±0.04	1.07±0.06	1.31±0.07	1.26±0.07
Dy	4.91±0.13	8.10±0.13	8.70±0.14	7.80±0.14
Yb	4.27±0.05	7.47±0.07	5.51±0.06	4.98±0.05
Lu	0.609±0.022	1.119±0.034	0.769±0.027	0.718±0.025
Sc	1.458±0.015	1.892±0.019	6.81±0.07	6.83±0.07
Th	21.49±0.21	28.35±0.28	15.39±0.15	15.10±0.15
U	3.73±0.04	5.98±0.06	2.36±0.04	2.29±0.04
Cs	1.90±0.06	5.11±0.09	1.18±0.09	1.09±0.24
Hf	4.44±0.07	5.06±9.97	9.62±0.11	8.93±0.11
Fe%	0.891±0.015	0.695±0.012	2.049±0.025	1.049±0.24
Rb	192±5	290±7	132±5	130±4
Ba	69±8	<7	1510±20	1520±20
Ni	<7	<7	<10	<10
Cr	<2.8	<1.4	3.7±0.7	<2.9
Sb	0.20±0.04	0.20±0.04	0.18±0.05	<0.18
Ti%	0.055±0.018	<0.05	0.240±0.015	0.224±0.016
Mo	7.9±0.9	3.4±0.9	2.8±0.7	3.3±0.7
Ta	1.836±0.18	2.570±0.1	1.574±0.16	1.297±.013
Mn	52.0±1.5	423±9	408±9	390±8

Table 5. Whole Rock Instrumental Neutron Activation Analyses
(Continued)

	18	19	20	Core
La	12.1±0.4	14.0±0.4	57.9±0.8	8.4±0.5
Ce	34.2±0.6	38.1±0.6	122.1±1.2	26.0±0.6
Nd	20.1±1.0	21.3±1.0	45.6±1.3	18.2±1.2
Sm	5.55±0.06	5.57±0.06	6.21±0.06	7.24±0.07
Eu	0.215±0.007	0.219±0.007	0.800±0.011	0.033±0.006
Tb	1.05±0.06	1.08±0.06	0.64±0.04	1.89±0.10
Dy	8.08±0.14	7.55±0.13	4.47±0.09	14.79±0.16
Yb	7.55±0.08	7.15±0.07	3.57±0.04	13.26±0.13
Lu	1.120±0.034	1.054±0.032	0.511±0.020	1.760±0.019
Sc	1.922±0.019	1.864±0.019	2.371±0.024	1.744±0.017
Th	28.54±0.29	27.79±0.28	23.10±0.23	36.07±0.36
U	7.07±0.07	6.65±0.07	2.71±0.04	7.68±0.08
Cs	5.34±0.08	4.94±0.08	1.59±0.07	11.89±0.17
Hf	4.89±0.07	5.03±0.07	5.55±0.08	6.81±0.09
Fe%	0.664±0.012	0.684±0.012	1.903±0.017	0.560±0.014
Rb	284±7	275±7	152±6	480±16
Ba	<8	<10	338±10	<14
Ni	<7	<13	<7	<9
Cr	<2.2	1.4±0.6	2.0±0.6	3.1±0.6
Sb	0.14±0.04	0.21±0.04	0.12±0.04	0.82±0.08
Ti%	<0.06	0.047±0.017	0.175±0.013	<0.05
Mo	3.2±0.8	4.3±0.9	4.5±0.7	<4.1
Ta	2.620±0.026	2.473±0.025	1.604±0.016	5.50±0.05
Mn	426±9	407±9	87.4±1.8	494±10

Table 6. Other Trace Element Analyses of
Twin Peaks Ryolites (values in ppm)

Sample no.	2	4	5	6	8	9	12
Nb ¹	34	19	25	18	13	38	26
Zr ¹	95	198	275	270	95	87	319
Y ¹	42	25	33	25	29	43	32
Sr ¹	21	190	143	240	48	10	170
Rb ¹	259	110	132	93	192	267	120
Pb ¹	36	12	17	9	31	42	24
Zn ¹	36	15	39	9	9	42	42
Li ²	36	29	20	19	37	74	25
Be ²	3.5	2.1	2.1	2.0	2.6	4.5	1.1
Cu ²	-	-	-	-	-	-	-
S ³	5	47	36	5	10	16	36

Sample no.	15	18	19	20	30	core
Nb ¹	28	41	34	19	21	66
Zr ¹	321	89	91	145	236	81
Y ¹	30	43	40	22	33	82
Sr ¹	197	9	10	141	156	4
Rb ¹	119	276	264	143	144	458
Pb ¹	24	43	45	26	20	44
Zn ¹	43	36	35	9	-	39
Li ²	22	-	68	24	-	105
Be ²	2.5	5.2	7.0	2.6	-	8.7
Cu ²	8.0	-	5.4	5.6	-	7.1
S ³	19	2	0	271	-	23

-
- 1 x-ray diffraction
2 atomic absorption
3 Leeco Sulfer analyzer

Figure 5. Concentrations of trace elements versus rubidium concentration in the Twin Peak rhyolites. Open squares are the early sequence and closed squares are the late sequence. The generally parallel paths indicate most elements have similar mechanisms of control in each sequence.

Figure 6. Chondrite normalized (Evensen et al., 1978) whole rock rare earth element neutron activation analyses. Samples 5 and 12 plot on the same line as sample 15, and samples 2, 9, and 19 plot on the same line as 18. More evolved rhyolites have flatter slopes and more pronounced europium anomalies.

Figure 7. Enrichment factors (concentrations in the most evolved rock divided by concentrations in the least evolved rock) for the early sequence, late sequence, and for comparison, the Bishop Tuff (Hildreth, 1977, 1979).

increase in enrichment (decrease in depletion) of the REE from the light to heavy. Both trends at Twin Peaks show this same behavior, but the crossover point between depleted and enriched elements is shifted to the right at Twin Peaks compared with Bishop Tuff, with the younger sequence at Twin Peaks showing a greater shift than the earlier. The antithetic behavior of Na and K, with Na enriched and K depleted, is observed in the Bishop Tuff suite and in the early Twin Peaks sequence. In the younger sequence, however, K is enriched and Na is depleted.

These comparisons suggest that liquid state differentiation as described by Hildreth (1977, 1979) is perhaps the dominant control on chemical differentiation, but that there are other factors which influence the chemistry as well, particularly in the second sequence. In the following discussion, the term "enriched" or "highly evolved" refers to those rhyolites that have undergone liquid state or other mechanisms of differentiation, and which are generally enriched in Si, Rb, and volatiles, and depleted in Fe, Ca, Mg, Sr, and Ba.

MINERALOGY

Of the major minerals, only plagioclase and sanidine are present in all units as phenocrysts. Quartz phenocrysts are found in all except the Coyote Hills rhyolites. Biotite is the most abundant mafic mineral and occurs in all units except Coyote Hills, where augite and orthopyroxene are found. Augite and traces of orthopyroxene are also present in portions of the North Twin Peak rhyolite body.

Magnetite, ilmenite, and zircon are present as accessories in all crystalline rhyolites, although no zircon was found in the Cudahy Mine Unit. Apatite and sphene were found only in the North Twin Peak rhyolite.

Quartz

One INAA analysis of quartz, from North Twin Peaks (Sample 4), is given in Table 7. Trace element concentrations are all very low; except for Fe, Ti, Na, Mn, and Ba, all detected concentrations were below one ppm. The rare earth elements are plotted in Fig. 8. The pronounced drop between La and Nd seems to be real. All other rare earths fall between .1 to .3 times chondrite values. The distinct dissimilarity in the REE patterns for quartz and whole rock analyses (c.f. Figs. 6 and 8) seems to rule out melt inclusions as the principal source of trace elements in the quartz.

Sanidine

Microprobe analyses for sanidine are given in Table 8 and are

Table 7. Quartz Neutron Activation Analyses

La	.89±.16
Ce	.76±.09
Nd	.052±.18
Sm	.0597±.0025
Eu	.0215±.0019
Tb	.0063±0.0015
Dy	.055±.006
Yb	.051±.004
Lu	.0116±.0022
Sc	.0091±.0010
Fe%	.43±.006
Th	.108±.005
U	.041±.002
Cs	.038±.010
Hf	.124±.007
Rb	1.07±.29
Ba	7.1±2.4
Ni	<2.4
Cr	.32±.06
Sb	<.06
Ti%	.0086±.0013
Mo	<.4
Ta	0.0090±0.0007
Na%	0.0470±.0009
Al%	<0.17
Mn	1.20±0.07
Co	0.131±0.019
W	<0.9

Figure 8. Rare earth element analysis of quartz from sample 4;
North Twin Peak.

Table 8. Microprobe Analyses of
Sanidine from Twin Peaks

Sample	2	4	5	6	8	12	15	20
Wt. % Oxides								
CaO	0.22	0.17	0.74	0.28	0.22	0.64	0.63	0.28
K ₂ O	11.9	9.16	9.33	7.91	11.8	9.41	9.39	11.4
Na ₂ O	3.32	5.30	4.64	5.68	3.36	4.27	4.36	3.67
BaO	0.10	0.17	1.10	1.87	0.03	2.00	1.88	0.14
Fe ₂ O ₃	0.10	0.13	0.20	0.22	0.11	0.23	0.24	0.12
Wt. % Components								
An	1.09	0.84	3.67	1.31	1.09	3.18	3.13	1.24
Or	70.2	54.1	55.1	46.8	69.9	55.6	55.5	67.5
Ab	28.1	44.9	39.3	48.1	28.1	36.1	36.7	31.1
Cn	0.24	0.42	2.69	4.58	0.07	4.90	4.60	0.34
Total	99.6	100.3	100.7	100.8	99.2	99.8	99.9	100.2
Recalculated Mole%								
An	1.08	0.82	3.65	1.32	1.08	3.28	3.20	1.22
Or	69.4	52.8	54.9	47.2	69.3	57.3	56.8	66.4
Ab	29.5	46.4	41.5	51.5	29.6	39.5	40.1	32.4

Figure 9. Microprobe analyses of Twin Peaks feldspars.

plotted in Fig. 9. Strong oscillatory zoning in the North Twin Peak sanidine ranges from Ab₄₀ to Ab₅₅. In both the Cudahy Mine felsite and South Twin Peak rhyolite, sanidine is moderately zoned and increases in Ab content towards the rim, from Ab₂₃ to Ab₃₃. For the entire Twin Peaks suite, average sanidine analyses range from Ab₅₃ in North Twin Peaks rhyolite to Ab₂₇ in the Cudahy mine felsite, and correlate well with the whole rock Rb content (Fig. 10).

Trace element concentrations determined by INAA and XRF are given in Tables 9 and 10. Due to the very small grain size of the sanidine in Coyote Hills rhyolite, pure separates for samples 12 and 15 could not be obtained for trace element analysis. Sanidine is very strongly enriched in Ba and Sr, and is slightly enriched in Rb and Pb relative to the host rock. Ba and Sr decrease, and Rb increases with increasing orthoclase content (Fig. 12), reflecting primarily the changes in the concentration in the liquid (Section VIII). Except for Eu, the REE are all strongly depleted relative to the whole rock concentrations, but otherwise are similar to the whole rock REE pattern (c.f. Figs. 6 and 11).

Plagioclase

Microprobe analyses for plagioclase are given in Table 11 and are plotted in Fig. 9. Plagioclase from the less evolved rocks are zoned from An₆₀ to An₃₁; zoning decreases in the more highly evolved units. Average anorthite contents of the plagioclase range from An₄₂ to An₂₇ and are plotted against the whole rock Rb in Fig. 12.

Trace element concentrations are given in Tables 10 and 12.

Figure 10. Sanidine composition versus host rock rubidium concentration.

Table 9. Sanidine Neutron Activation Analyses

	4	6	8	20
La	4.4±.5	6.0±.5	2.29±.36	3.7±.6
Ce	5.76±.26	6.90±.5	.9±.04	1.6±.5
Nd	1.6±.26	1.7±.5	.9±.04	1.6±.5
Sm	.183±.006	.221±.007	.108±.005	.132±.006
Eu	2.260±.023	2.548±.025	1.213±.013	1.876±.019
Tb	.012±.005	.034±.005	.010±.004	.010±.004
Dy	<.30	.38±.07	.19±.06	<.12
Yb	.111±.012	.114±.013	.105±.010	.106±.011
Lu	.029±.006	.015±.007	.014±.005	.018±.006
Sc	.090±.004	.087±.004	.018±.003	.032±.004
Fe%	.095±.004	.108±.004	.058±.003	.074±.004
Th	.355±.018	.456±.021	.335±.012	.405±.016
U	.087±.019	.118±.022	.129±.014	.103±.017
Cs	.252±.029	.226±.030	.203±.024	.414±.028
Hf	.120±.026	.16±.07	.228±.015	.219±.031
Rb	170±6	152±5	208±7	215±7
Ba	3372±50	4813±70	330±9	1696±28
Ni	5.5±2.0	4.8±1.3	4.7±1.8	<4
Cr	<.9	<1.5	<.8	<1.3
Sb	<.06	<.05	<.05	<.02
Ti%	<.05	<.08	<.07	<.05
Mo	<.7	<.9	1.05±.27	.96±.33
Ta	0.00142±0.0015	0.0231±0.0016	0.0177±0.0013	0.0200±0.0014
Na%	3.34±.007	4.09±0.01	2.29±0.04	2.74±0.05
Al%	9.71±0.16	10.2±0.2	9.84±0.21	9.74±0.17
Mn	<6	<7	<4	<5
Co	0.30±0.04	0.155±0.030	0.059±0.018	0.048±0.005
W	<2.2	6	<3.3	<4

Table 10. X-ray fluorescence analyses of feldspar (values in ppm)

Sample	4	6	8	12	20
Plagioclase					
Nb	1	1	1	-	-
Zr	7	25	33	18	28
Y	1	5	2	4	4
Sr	570	765	207	1190	532
Rb	5	9	5	7	8
Pb	11	13	12	13	15
Ti	62	83	53	137	60
Fe	1474	1852	1098	2482	1530
Zn	11	11	11	16	11
Sanidine					
Nb	-	-	-	-	9
Zr	2	4	5	-	5
Y	2	1	-	-	-
Sr	390	449	127	-	294
Rb	147	134	174	-	204
Pb	27	24	28	-	31
Ti	58	55	39	-	46
Fe	742	867	532	-	618
Zn	1	-	-	-	2

Figure 11. Rare earth element analyses of Twin Peaks feldspars.

Table 11. Microprobe Analyses of
Plagioclase from Twin Peaks

Sample No.	2	4	5	6	8	12	15	20
wt % oxides								
CaO	4.81	6.06	7.38	6.97	5.25	7.19	7.05	5.70
K ₂ O	1.14	1.06	.89	.73	1.25	1.27	1.18	1.12
Na ₂ O	8.22	7.53	6.82	7.10	7.85	6.68	6.77	7.67
BaO	0.01	0.03	0.12	0.06	0.01	0.16	0.14	0.02
Fe ₂ O ₃	0.41	0.29	0.38	0.33	0.19	0.36	0.41	0.26
wt% Compounds								
An	23.9	30.1	36.6	34.6	26.1	35.7	35.0	28.3
Or	6.73	6.29	5.25	4.34	7.41	7.51	6.97	6.61
Ab	69.6	63.7	57.7	60.1	66.4	56.5	57.3	64.9
Cn	0.02	0.07	0.29	0.15	0.02	0.39	0.34	0.05
Total	100.3	100.1	99.8	99.2	99.9	100.1	99.6	99.9
Recalculated Mole %								
An	22.9	28.9	35.5	33.7	25.1	34.6	34.1	27.3
Or	6.45	6.05	5.09	4.23	7.13	7.28	6.79	6.36
Ab	70.7	65.0	59.4	62.1	67.8	58.1	59.2	66.4

Figure 12. Plagioclase composition versus host rock rubidium content.

Rb (Whole Rock)

Table 12. Plagioclase Neutron Activation Analyses

	4	6	8
La	20.3±.6	27.5±.7	9.0±.5
Ce	28.5±.4	39.5±.5	14.89±.31
Nd	7.7±.5	12.4±.6	5.4±.5
Sm	.827±.009	1.329±.034	.740±.008
Eu	2.565±.026	3.392±.034	1.448±.014
Tb	.075±.006	.112±.007	.069±.006
Dy	.37±.06	.72±.06	.51±.06
Yb	.249±.011	.361±.013	.418±.012
Lu	.039±.006	.052±.008	.074±.007
Sc	.222±.005	.049±.005	.084±.004
Fe%	.195±.005	.212±.005	.143±.004
Th	.523±.015	.604±.017	1.604±.019
U	.109±.017	.191±.021	.455±.019
Cs	.170±.029	.096±.030	.226±.024
Hf	.366±.021	1.440±.028	1.069±.022
Rb	8.4±1.2	7.4±1.2	18.4±1.3
Ba	293±10	558±13	54±6
Ni	5.9±1.9	5.8±2.0	<5
Cr	<.6	<.7	<.7
Sb	<.06	<.06	<.06
Ti%	<.08	<.09	<.07
Mo	<.7	<.8	2.26±.36
Ta	0.0256±0.0014	0.0338±0.0015	0.0927±0.0018
Na%	5.24±0.10	5.64±0.11	5.37±0.11
Al%	11.6±0.2	12.9±0.3	11.3±0.3
Mn	16.6±2.3	9.0±2.3	17.5±2.1
Co	0.77±0.05	0.25±0.04	0.098±0.02
W	<2.7	<4	<3.2

Table 12. Plagioclase Neutron Activation Analyses (continued)

	12	15	20
La	34.7±.8	35.4±.8	18.3±.6
Ce	50.0±.6	52.4±.6	28.1±.4
Nd	15.2±.8	14.0±.8	8.1±.5
Sm	1.756±.018	1.724±.017	.870±.009
Eu	5.55±.06	5.12±.05	2.284±.023
Tb	.148±.009	.135±.009	.072±.006
Dy	.68±.05	.68±.06	.53±.10
Yb	.340±.015	.364±.015	.346±.012
Lu	.040±.008	.049±.008	.063±.007
Sc	.204±.006	.191±.006	.124±.004
Fe%	.271±.006	.264±.006	.177±.004
Th	.551±.020	.796±.021	1.186±.018
U	.144±.023	.171±.024	.330±.020
Cs	<.14	.110±.036	.060±.027
Hf	.510±.010	.555±.036	1.515±.027
Rb	11.2±1.5	24.2±1.8	7.0±1.1
Ba	1851±38	1863±39	238±28
Ni	6.8±2.5	9.0±2.4	5.2±1.7
Cr	<1.0	<.8	<.8
Sb	<.09	<.04	<.10
Ti%	<.07	<.07	<.08
Mo	<1.2	<1.3	1.16±.34
Ta	0.0665±0.0019	0.0380±0.0018	0.0442±0.0015
Na%	4.87±0.10	4.71±0.09	5.26±0.11
Al%	13.0±0.2	13.0±0.2	12.5±0.3
Mn	28.6±2.2	29.1±2.2	20.8±2.2
Co	0.58±0.05	0.27±0.04	0.168±0.031
W	<6	<3.0	<3.1

Plagioclase is very strongly enriched in Sr and less strongly in Ba relative to the host rock. In Fig. 12 they are seen to correlate well with the An content of the plagioclase. Fe and Zn are both enriched in plagioclase relative to sanidine.

The REE pattern (Fig. 11) shows a marked positive Eu anomaly in plagioclase, although it is not as pronounced as in sanidine. The other REE are enriched by nearly an order of magnitude relative to sanidine. With the exception of Eu, the plagioclase REE pattern also parallels the whole rock pattern.

Biotite

Microprobe analyses of biotites from North and South Twin Peaks and Mid Dome rhyolites are given in Table 13. Trace amounts of biotites also occur in the Cudahy Mine Unit but have not been analyzed. Several major elements for four biotites are plotted against whole rock Rb in Fig. 13. The elements correlate well with the whole rock Rb, but Si, Fe, F, and Mn in the biotite oppose the whole rock trends.

XRF and INAA analyses for trace elements are given in Tables 14 and 15. Rb, Cs, Ba, Sc, Mn, Nb, Ta, Zn, Ni, Cr, Co, and Mo are all significantly concentrated into biotite relative to the host rock. Both Sc and Nb are more enriched in the later biotites in opposition to the whole rock trends. The REE concentrations are plotted in Figure 14. South Twin Peak biotites are significantly enriched in all REE compared to the other biotites.

Table 13. Microprobe analyses of Biotite

	4	6	8	20
SiO ₂	38.7	39.5	36.4	37.4
TiO ₂	4.54	4.62	4.28	4.46
Al ₂ O ₃	12.1	11.6	12.1	12.6
FeO	13.7	13.4	24.6	19.7
MnO	.09	.05	.44	.66
MgO	15.5	15.8	8.84	11.6
CaO	.27	.03	.16	.09
BaO	.18	.26	.22	.24
K ₂ O	9.92	9.98	9.60	9.61
Na ₂ O	.67	.70	.45	.52
F	5.07	5.86	2.46	4.47
Cl	.12	.06	.17	.17
Sum	100.9	101.9	99.7	101.5
F,Cl=0	2.16	2.16	1.08	1.92
Total	98.7	99.7	98.6	99.6

Figure 13. Biotite composition versus host rock rubidium.

Table 14. Biotite XRF trace element analyses (values in ppm)

Sample	4	8	20
Nb	68	118	93
Zr	153	163	143
Y	30	30	30
Sr	24	15	21
Rb	320	424	294
Pb	14	17	2
Zn	165	351	413

Table 15. Biotite Neutron Activation Analyses.

	4	8	20
La	81.1±.9	459±5	41.5±.8
Ce	168.1±1.7	770±8	100.7±1.1
Nd	61.2±1.5	187±7	39.4±1.3
Sm	7.88±.08	23.05±.23	6.45±.07
Eu	.399±.012	1.67±.020	.223±.012
Tb	.71±.06	2.71±.15	.700±.024
Dy	4.23±.19	16.4±.6	4.49±.23
Yb	2.49±.04	12.72±.14	2.84±.04
Lu	.373±0.21	2.00±.07	.420±.022
Sc	19.50±.20	26.66±.27	30.9±.3
Fe%	10.90±.11	19.53±.2	14.69±.15
Th	4.93±.10	41.6±.4	16.23±.16
U	1.073±.030	4.46±.07	1.728±.034
Cs	7.96±.19	6.34±.21	3.10±.19
Hf	2.86±.08	36.3±.4	4.40±.08
Rb	375±13	404±.15	383±13
Ba	2471±38	1235±32	2049±35
Ni	32±10	252±15	<54
Cr	16.4±1.8	491±5	14.9±1.0
Sb	<.3	<.28	<0.4
Ti%	1.66±.06	1.953±.032	2.789±.028
Mo	3.3±.7	3.7±1.4	21.9±2.2
Ta	1.627±.016	3.51±.034	2.501±0.025
Na%	0.501±0.008	0.526±0.010	0.397±0.008
Al%	7.4±2	5.7±0.3	7.31±0.146
Mn	853±17	5123±102	4198±84
Co	48.0±.6	40.2±.5	47.1±0.6
W	1.7±.7	5.6±2.0	2.5±0.7

Figure 14. Rare earth element analyses of Twin Peaks biotites.

Orthopyroxene

Major element analyses for pyroxenes are listed in Table 16 and are plotted in Fig. 15. The two distinct groupings for orthopyroxene from North Twin Peaks (sample 6) are due to the scarcity of orthopyroxene; only three phenocrysts were analyzed, and they probably represent a continuous range rather than two discrete populations.

The orthopyroxene from North Twin Peaks shows greater compositional variability and is richer in Mg compared with that from Coyote Hills. The enstatite-ferrosilite projection of microprobe analyses for North Twin Peaks range from En₃₇ Fs₆₃ to En₅₈ Fs₄₂ and for Coyote Hills, from En₄₅ Fs₅₅ to En₅₉ Fs₄₁. Although some zoning was noted, the variability occurs primarily between individual phenocrysts rather than within them.

Trace element analyses of pyroxenes are given in Table 17. Sc, Mn, and Co are strongly concentrated in the orthopyroxenes relative to the host rock. The REE concentrations for both pyroxenes are plotted in Fig. 16. Whereas the whole rock REE pattern for Coyote Hills rhyolite shows only a slight Eu anomaly, a much more pronounced negative anomaly is present in both pyroxenes. Also, the slopes are considerably flatter than for the corresponding whole rock patterns (cf. Figs. 6 and 16).

Augite

Augite is enriched in Na, Al, Mn, Sc, and REE compared with orthopyroxenes (Tables 16 and 17). As with the orthopyroxenes, augite from North Twin Peak has greater compositional variability and is more Mg rich than augite from Coyote Hills (Fig. 15). Projected onto the.

Table 16. Microprobe Analyses of Pyroxene

Sample No.	6	12	15
Orthopyroxene			
SiO ₂	51.3	51.7	51.7
TiO ₂	.26	.19	.16
Al ₂ O ₃	.48	.85	.79
FeO	29.9	27.2	27.1
MnO	1.43	1.16	1.15
MgO	15.4	17.9	17.8
CaO	1.26	1.16	1.39
Na ₂ O	.02	.12	.09
	100.1	100.3	100.2
Clinopyroxene			
SiO ₂	52.2	51.8	51.8
TiO ₂	.32	.29	.29
Al ₂ O ₃	.70	1.38	1.28
FeO	13.5	14.9	14.3
MnO	.37	.62	.63
MgO	11.9	12.1	12.0
CaO	20.2	19.3	19.8
Na ₂ O	.55	.56	.54
	99.7	101.0	100.6

Figure 15. Microprobe analyses of Twin Peaks pyroxenes in terms of wollastonite, enstatite and ferrosilite.

PYROXENES

Table 17. Pyroxene Neutron Activation Analyses

	<u>Orthopyroxene</u>	
	12	15
La	58.6±1.0	66.8±.8
Ce	151.0±1.5	165.8±1.7
Nd	85.7±2.1	90.4±2.2
Sm	15.23±.15	15.93±1.6
Eu	.897±.017	.810±.016
Th	2.10±.05	2.18±.05
Dy	13.6±.6	12.8±.6
Yb	10.03±.10	10.84±.10
Lu	1.513±.030	1.60±.05
Sc	59.8±.6	60.6±.6
Fe%	21.06±.21	21.1±.2
Th	1.70±.09	2.24±.11
U	.282±.032	.388±.032
Cs	.90±.14	.47±.17
Hf	1.64±.09	1.87±.09
Rb	<34	<14
Ba	<55	<59
Ni	<49	<58
Cr	<5	<3
Sb	<.3	<.7
Ti%	.175±.037	<.32
Mo	<2.0	<1.9
Ta	0.187±0.005	0.238±0.005
Na%	0.077±0.016	0.154±0.016
Al%	<1.1	0.41±0.13
Mn	7646±153	7641±153
Co	60.2±0.6	60.8±0.7
W	<2.4	<5

Table 17. Pyroxene Neutron Activation Analyses (Continued)

	<u>Clinopyroxene</u>		
	6	12	15
La	103.1±3.3	61.9±1.4	68.2±2.2
Ce	330.9±3.3	201.9±2.0	234.5±2.3
Nd	224±4	157.1±3.4	164±4
Sm	47.1±1.1	36.1±.7	36.4±.8
Eu	3.162±.032	3.379±.034	3.301±.033
Th	7.63±.14	5.34±.10	5.72±.10
Dy	48.8±.5	34.8±.4	35.5±.4
Yb	33.61±.34	17.88±.18	18.30±.18
Lu	4.88±.30	2.37±.13	2.46±.13
Sc	145.5±1.5	170.5±1.7	169.7±1.7
Fe%	10.89±.11	10.19±.10	10.74±.11
Th	3.65±.17	1.38±.12	1.98±.14
U	<.8	<.4	<.6
Cs	<.9	<.7	<.7
Hf	8.82±.14	3.35±.12	4.73±.13
Rb	<58	<93	<91
Ba	<78	<66	<44
Ni	<87	<54	<107
Cr	<20	<19	<30
Sb	<.9	<10	<1.8
Ti%	.184±.025	.164±.027	.122±.030
Mo	<2.5	<2.1	<2.2
Ta	0.579±0.007	0.136±0.006	0.158±0.006
Na%	0.768±0.015	0.308±0.008	0.338±0.008
Al%	0.80±0.06	1.13±0.10	0.96±0.16
Mn	3383±67	4253±850	4293.86
Co	32.9±0.5	34.1±0.5	35.3±0.5
W	<2.0	<4	<4

Figure 16. Rare earth element analyses of Twin Peaks pyroxenes.

diopside-hedenbergite binary, augite from North Twin Peaks ranges from Di₆₇ Hd₃₃ to Di₄₇ Hd₅₃. Augite from Coyote Hills ranges from Di₆₂ Hd₃₈ to Di₄₇ Hd₅₃.

Except for Eu, the REE concentrations are greater in augite from North Twin Peak than from Coyote Hills (Fig. 16). This is in contrast with the whole rock REE concentrations, which are greater in the Coyote Hills rhyolite (Fig. 6).

Fe-Ti Oxides

Average microprobe analyses for titanomagnetite and ilmenite are given in Table 18. Unoxidized Fe-Ti oxides are very homogeneous within and between grains. Oxidation of both oxides was common in most of the rocks particularly in North Twin Peaks where no unoxidized magnetite was found. Ulvospinel content in titanomagnetite ranges systematically from 30.3 mole percent in South Twin Peak rhyolite to 46.9 mole percent in Coyote Hills rhyolite, as calculated according to the method of Carmichael (1967). Ilmenite ranges from 8.3 mole percent R₂O₃ in Coyote Hills to 9.4 percent in North Twin Peaks but does not exhibit any systematic trend.

Trace element compositions are tabulated in Table 19. The oxides concentrate a variety of elements. Ilmenite preferentially incorporates U, Th, Zn, Ta, Mn, Hf, and the REE, whereas titanomagnetite preferentially incorporates V, Mo, and Sc. Co is incorporated into both oxides about equally.

The rare earth elements are plotted in Fig. 17. Both oxides show a pronounced negative Eu anomaly although in the whole rock samples,

Table 18. Iron-Titanium Oxide Microprobe Analyses

	<u>Magnetite</u>			
	8	12	15	20
SiO ₂	.07	.16	.18	.04
TiO ₂	10.3	16.3	16.5	15.7
Al ₂ O ₃	.99	1.12	1.27	1.29
FeO(T)	81.9	78.2	77.5	78.5
MnO	.26	.78	.76	.75
MgO	.08	.17	.29	.25
CaO	.01	.05	.06	.03
Cr ₂ O ₃	.01	.02	.03	.02
V ₂ O ₃	.09	.20	.19	.21
ZnO	.08	.25	.25	.22
Total	93.8	97.2	97.0	97.1
% FeO	40.1	45.5	45.5	44.8
% Fe ₂ O ₃	46.5	36.3	35.6	37.5
Recalculated				
Total	98.5	100.8	100.6	100.8
Mole % USP	30.3	46.2	46.9	44.2
Mole % R ₂ O ₃	-	-	-	-

Table 18. Iron-Titanium Oxides Microprobe Analyses
(Continued)

	<u>Ilmenite</u>				
	6	8	12	15	20
SiO ₂	0.00	.07	.05	.07	.06
TiO ₂	48.0	48.3	48.8	48.7	48.6
Al ₂ O ₃	.01	.04	.03	.04	.05
FeO(T)	50.0	50.8	50.0	50.1	49.3
MnO	1.19	.73	1.20	1.06	1.05
MgO	.39	.17	.23	.34	.64
CaO	.02	.05	.05	.00	.04
Cr ₂ O ₃	.01	.00	.00	.01	.01
V ₂ O ₃	.06	.03	.05	.04	.04
ZnO	.09	.11	.05	.06	.08
Total	99.7	100.3	100.5	100.4	99.9
%FeO	41.1	42.3	42.2	42.1	41.4
%Fe ₂ O ₃	9.82	9.52	8.72	8.87	8.80
Recalculated					
Total	100.7	101.3	101.4	101.3	100.7
Mole % USP	-	-	-	-	-
Mole %R ₂ O ₃	9.36	9.05	8.29	8.42	8.40

Table 19. Iron-Titanium Oxides Neutron Activation Analyses

	<u>Magnetite</u>				<u>Ilmenite</u>
	6	12	15	6	
La	116.6±1.3	65.4±.9	76.7±1.1	429±1.3	
Ce	311.0±3.1	176.3±1.8	205.2±2.0	900±9	
Nd	151.0±3.0	104.1±2.4	118.8±2.6	325±6	
Sm	25.70±.25	19.02±.19	20.32±.20	39.1±1.2	
Eu	1.164±.012	.530±.019	.437±.018	1.379±.027	
Tb	2.79±1.5	2.16±.13	2.24±.13	3.83±.19	
Dy	17.62±.31	12.8±.4	13.2±.4	19.5±.6	
Yb	6.21±.07	4.93±.07	5.63±.07	11.87±.15	
Lu	.672±.032	.648±.032	.783±.034	1.66±.06	
Sc	3.41±.14	48.3±.5	52.8±.5	13.06±1.3	
Fe%	62.3±.6	56.9±.6	54.9±.3	34.9±.3	
Th	5.15±.07	1.37±.08	2.52±.11	122.3±1.2	
U	1.36±.04	.49±.04	1.14±.04	5.30±.16	
Cs	<.8	<.9	<.9	<.9	
Hf	8.65±.13	16.21±.19	24.67±.25	28.55±.19	
Rb	<22	<43	<25	<24	
Ba	<27	<34	<28	<28	
Ni	78±21	<52	<42	<54	
Cr	172±7	113±7	112±7	11±6	
Sb	<.5	<.8	<1.0	<.9	
Ti%	5.39±.05	8.67±.09	9.70±.10	26.1±.7	
Mo	7.9±.8	31.3±2.2	34.6±2.2	<4	
Ta	2.374±.023	3.975±.039	5.40±.04	108.3±1.1	
Na%	<.02	<.04	<.04	<.06	
Al%	<1.2	<2	<3	<6	
Mn	2237±45	5629±112	5259±105	8305±166	
Co	74.2±.9	82.1±1.0	87.2±1.0	73.2±.9	
W	4.5±1.0	<5	<5	<5	
V	1265±207	1230±208	1252±217	<800	
Zn	508±102	1600	1700	600	

Figure 17. Rare earth element analyses of Twin Peaks iron titanium oxides.

it is nearly absent. The REE contents are higher in titanomagnetite from North Twin Peaks than from Coyote Hills in contrast to the whole rock concentrations.

INTENSIVE PARAMETERS

Temperatures and oxygen fugacities are calculated from coexisting ilmenite and titanomagnetite by the method of Buddington and Lindsley (1964) and are listed in Table 20. Calculated temperatures for Coyote Hills rhyolite are 880° and 875°C, and the log fugacities of oxygen are -12.8 and -12.9. The temperature and f_{O_2} for the Mid Dome rhyolite are only very slightly lower (865°C and -13.1) although it is at least 300,000 years younger. A temperature of 775°C and log fugacity of -14.4 are calculated for the South Twin Peak rhyolite.

A cylindrical magma chamber 10 km wide, 3 1/2 km thick, and 3 km deep, as modeled by Carrier (1979), would be expected to cool within 50,000 years (Chapman, personal communication). This constraint requires the existence of a sustained heat source and/or multiple pulses of magma, which is consistent with the geochemical data.

The data listed in Table 20 are plotted in Figure 18 along with the fayalite-magnetite-quartz buffer curve. The Coyote Hills, Mid Dome, and South Twin Peak rhyolites plot increasingly above the FMQ buffer curve, consistent with other pyroxene and biotite bearing rhyolites (Carmichael, 1967).

Water fugacities for South Twin Peak and Mid Dome rhyolites were calculated using the reaction:

Table 20. Estimated Temperature, Fugacities, and Water Content

Sample No.	Unit	Age M.Y.	Fe-Ti Temp. °C	-Log f_{O_2}	f_{H_2O}	WT% H_2O
12	Coyote Hills		875	12.9		
15	Coyote Hills	2.74	880	12.8		
20	Mid Dome	2.43	865	13.1	162	1.3-1.2
8	South Twin Peak	2.35	775	14.4	550	3.0-2.6

Figure 18. Oxygen fugacity-temperature plot of Twin Peaks rhyolites.
Solid line is fayalite-magnetite-quartz buffer.

This reaction yields the relation (Hildreth, 1977):

$$\ln f_{\text{H}_2\text{O}} = \ln a_{\text{ann}}^{\text{bi}} + \frac{1}{2} \ln f_{\text{O}_2} - \ln a_{\text{Fe}_3\text{O}_4}^{\text{mt}} - \ln a_{\text{KAlSi}_3\text{O}_8}^{\text{san}} \\ + \frac{119,973}{T} + 5.66 + \frac{0.00903}{T} \quad (\text{P-1})$$

The activity of Fe_3O_4 is assumed to equal its mole fraction in titanomagnetite, and for annite, multi-site ideal ionic mixing is assumed. Sanidine activity was determined using data of Waldbaum and Thompson (1969).

The calculated water fugacities for the two units range from 162 to 550 bars and are given in Table 20. Water contents calculated by the method of Nicholls (1977) are also given in Table 20. Although the uncertainties in this method (see Hildreth, 1977) are large, the results are reasonable and indicate that the South Twin Peak magma was significantly enriched in water (2.6 - 3.0%) compared to the Mid Dome magma (1.2-1.3%).

Whether or not convection occurred in the evolved magmas is of importance in interpreting magmatic evolution. The existence of a thermal gradient would promote convection in a homogeneous magma chamber, but convection could be arrested if a compositional gradient developed, producing a sufficiently stabilizing density distribution. Because the rhyolites were tapped from an evolving system through time, no gradients in the magma chamber at any given point in its history were sampled directly (with the probable exception of the core and Cudahy Mine samples). It will be shown later (Section IX), however, that the changes developed through time are due largely to the same liquid state mechanisms resulting in pronounced gradients

found in the Bishop Tuff (Hildreth, 1977, 1979), the Bandelier tuff (Smith, 1979), in the Coso Range (Bacon, 1979), and also found to occur between the core and Cudahy Mine samples. It is hypothesized that the changes developed and observed over time due to liquid state phenomena, are similar to changes with depth in the evolved magmas. Since, as will be seen in Section IX, the evolution from the Mid Dome to South Twin Peak rhyolites is largely due to these liquid state mechanisms, we may determine whether or not the magma chamber was convecting just prior to the eruption of the South Twin Peak magma by comparing the South Twin Peak magma with the Mid Dome magma.

Convection occurs when the difference between the dimensionless thermal Rayleigh number Ra_T and compositional Rayleigh number Ra_X exceeds an effective Rayleigh number, Ra_e , which has the same role as the critical Rayleigh number, Ra_c , in ordinary convection (Turner, 1973; Shaw, 1974). For any reasonable geometry, this value is less than 10^3 (Rosenberger, 1979). If we consider only the effects of water on the density gradient, and model the Twin Peaks magma chamber as a cylinder of thickness l and radius r these parameters are then given by (Lighthill, 1953):

$$Ra_T = \frac{\alpha g \Delta T r^4}{l \kappa \nu} \quad \text{and} \quad Ra_X = \frac{\xi g \Delta X_W r^4}{l D \nu}$$

where $\alpha = 4 \times 10^{-5} \text{ deg K}^{-1}$ is the coefficient of thermal expansion, $\Delta T = 90^\circ$, $\kappa = 7 \times 10^{-3} \text{ cm}^2 \text{ s}^{-1}$ is the thermal diffusivity, $\nu = 10^7$ to $10^8 \text{ cm}^2 \text{ s}^{-1}$ is the kinematic viscosity, $\Delta X_W = .016$ is the difference in weight fraction of water, $\xi = -\frac{1}{\rho} \left(\frac{\delta \rho}{\delta X_W} \right)_{T,P=2}$, and $D = 5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$

(Karsten and Delaney, 1980) is the diffusivity of water. For these values, $Ra_T \ll Ra_\chi$, so that stagnation is predicted. In Section X it is shown that the gradients for all major components except K_2O greatly exceed those necessary for isothermal equilibrium in a gravitational field, and thus they contribute further to mechanical stability.

CRYSTAL-LIQUID PARTITIONING

The crystal-liquid distribution coefficient is defined as the ratio of concentrations of an element in the crystal phase to the liquid phase which are in equilibrium with each other. Natural crystallizing systems more closely approximate conditions of surface equilibrium (Albarede and Bottinga, 1972). In this case, the order and amount of crystallization may become significant when total phenocryst content exceeds several percent. Furthermore, the groundmass of all samples for which phenocrysts were analyzed was entirely devitrified so no direct determination of liquid compositions could be made. For these reasons, a program was developed to calculate distribution coefficients given an assumed crystallization sequence and assuming crystallization in a closed system from an initial liquid represented by the whole rock bulk composition. The mathematical model, program description and listing are given in the appendix.

Partitioning of many of the trace elements between liquid and crystalline phases were calculated assuming a crystallization sequence given generally by: magnetite, ilmenite; followed by pyroxene, biotite, plagioclase; and followed by quartz, sanidine. Overlap of crystallization was assumed but had only slight effect on the calculated results. Zircon was not considered because of its unknown abundances in the rocks; as a result, the calculated distribution

coefficients for Zr, and to a lesser extent Hf, are lower than the actual values.

The distribution coefficients are given in Table 21, and those for the rare earth elements are also plotted in Fig. 19 along with data from Hildreth (1977) for high silica rhyolites and from Arth (1976) for dacites and rhyodacites.

Both feldspars enrich Eu from 2 to 3.5 times relative to the Twin Peaks host liquids. The partitioning of the other REE between plagioclase and liquid decreases progressively from .29 to .39 for La to .05 to .12 in Lu, and parallels, but is less than plagioclase-liquid partitioning in the Bishop Tuff magma (Hildreth, 1977). Distribution coefficients for REE other than Eu are about an order of magnitude less for sanidine compared to plagioclase. They again parallel the range of values observed by Hildreth (1977) in the Bishop Tuff, but overlap or are only slightly lower (see Fig. 19).

Sanidine concentrates Ba three to six times over the liquid and also enriches Sr, Pb, and Rb. Plagioclase concentrates Sr very strongly, from three to ten times, and slightly concentrates Ba and Pb in some of the more mafic rhyolites. All other trace elements are depleted in both plagioclase and alkali feldspar with respect to host liquids. Depletion in almost all cases is greater than observed in the Bishop Tuff.

Distribution coefficients for biotites exhibit the largest range among all the phenocrysts at Twin Peaks. Partitioning of all the REE in the South Twin Peak biotites exceeds the values for the North Twin Peak biotites by approximately an order of magnitude. No discernible

Table 21. Crystal-Liquid Distribution Coefficients

	<u>Sanidine</u>			
	4	6	8	20
Rb	1.3	1.3	.98	1.3
Cs	.10	.32	.09	.20
Sr	2.7	3.2	3.2	3.5
Ba	4.2	3.4	5.9	7.5
Sc	.02	.03	.01	.01
Mn	-	-	-	-
Zn	-	-	-	-
Y	-	-	-	-
Zr	.01	.01	.05	.03
Nb	-	-	-	-
Hf	.01	.01	.05	.04
Ta	.001	.02	.01	.01
Pb	2.0	2.8	.82	1.0
Th	.02	.02	.01	.01
U	.03	.05	.04	.03
La	.05	.07	.06	.05
Ce	.03	.05	.03	.02
Nd	.02	.03	.02	.03
Sm	.02	.03	.01	.02
Eu	2.1	3.0	2.5	3.3
Tb	.01	.04	.01	.01
Dy	<.05	.07	.03	<.004
Yb	.02	.03	.02	.02
Lu	.03	.02	.02	.03

Table 21. Crystal-Liquid Distribution Coefficients
(Continued)

	<u>Plagioclase</u>					
	4	6	8	12	15	20
Rb	.07	.07	.09	.09	.19	.05
Cs	.08	.16	.12	<.12	.09	.04
Sr	3.5	4.0	4.6	8.7	10.5	4.7
Ba	.37	.41	.79	1.2	1.2	.71
Sc	.05	.01	.06	.04	.03	.05
Mn	.003	.08	.5	.10	.10	.36
Zn	.74	1.7	1.2	.40	.44	1.9
Y	.04	.18	.07	.12	.12	.18
Zr	.03	.08	.34	.05	.05	.19
Nb	-	-	-	-	-	-
Hf	.05	.14	.24	.05	.06	.33
Ta	.02	.03	.05	.04	.03	.04
Pb	.89	1.5	.38	.52	.51	.57
Th	.03	.03	.07	.03	.05	.05
U	.03	.10	.12	.06	.07	.12
La	.30	.38	.29	.38	.39	.31
Ce	.19	.29	.20	.26	.27	.22
Nd	.12	.24	.16	.20	.18	.17
Sm	.10	.19	.13	.16	.16	.14
Eu	2.3	3.2	2.8	3.5	3.4	3.3
Tb	.08	.15	.09	.11	.10	.11
Dy	.06	.15	.10	.08	.08	.11
Yb	.05	.10	.10	.06	.07	.09
Lu	.06	.09	.12	.05	.07	.12

Table 21. Crystal-Liquid Distribution Coefficients
(Continued)

	<u>Quartz</u>	<u>Biotite</u>		
	4	4	8	20
Rb	.01	3.0	2.0	2.5
Cs	.02	3.4	3.2	1.8
Sr	-	.13	.31	.15
Ba	-	3.0	18	6.2
Sc	.01	4.1	18	13
Mn	-	11.9	110	60
Zn	-	10.7	40	50
Y	-	1.0	.99	1.3
Zr	-	.65	1.7	.92
Nb	-	3.1	8.8	4.6
Hf	.01	.36	18	.92
Ta	.08	1.0	2.0	1.4
Pb	-	1.1	.53	.07
Th	.005	.24	1.2	.65
U	.09	-	1.2	.59
La	.01	1.1	14.7	.67
Ce	.004	1.1	10.1	.77
Nd	.001	.92	5.4	.80
Sm	.006	.87	4.0	.96
Eu	.02	.38	3.3	.35
Tb	.006	.71	3.6	.10
Dy	.007	.62	3.2	.91
Yb	.009	.49	2.9	.73
Lu	.01	.49	3.1	.76

Table 21. Crystal-Liquid Distribution Coefficients
(Continued)

	<u>Orthopyroxene</u>		6	<u>Augite</u>	
	12	15		12	15
Rb	-	-	-	-	-
Cs	.76	.40	-	-	-
Sr	-	-	-	-	-
Ba	-	-	-	-	-
Sc	10	12	25.1	30	30.6
Mn	25	27	17.1	14.2	14.9
Zn	-	-	-	-	-
Y	-	-	-	-	-
Zr	-	-	-	-	-
Nb	-	-	-	-	-
Hf	.17	.20	.91	.84	.50
Ta	.12	.19	.46	.09	.13
Pb	-	-	-	-	-
Th	.11	.14	.22	.09	.12
U	.11	.16	-	-	-
La	.65	.74	1.5	.68	.76
Ce	.79	.87	2.5	1.1	1.2
Nd	1.1	1.2	4.5	2.0	2.1
Sm	1.4	1.4	6.9	3.2	3.3
Eu	.56	.54	2.6	2.2	2.2
Tb	1.6	1.7	10.3	4.0	4.4
Dy	1.6	1.6	9.8	3.9	4.4
Yb	1.8	2.1	9.5	3.2	3.5
Lu	1.9	2.1	8.8	3.0	3.3

Table 21. Crystal-Liquid Distribution Coefficients
(Continued)

	<u>Magnetite</u>			<u>Ilmenite</u>
	6	12	15	6
Rb	-	-	-	-
Cs	-	-	-	-
Sr	-	-	-	-
Ba	-	-	-	-
Sc	4.6	7.4	8.0	2.3
Mn	13	16	15	49
Zn	64	48	52	75
Y	-	-	-	-
Zr	-	-	-	-
Nb	-	-	-	-
Hf	.90	1.7	2.8	3.0
Ta	7.9	5.6	13	20
Pb	-	-	-	-
Th	.31	.09	.17	7.3
U	.81	.21	.50	3.1
La	1.7	.74	.89	0.23
Ce	2.4	.99	1.1	6.8
Nd	3.0	1.3	1.6	6.3
Sm	3.5	1.7	1.9	5.5
Eu	1.2	.32	.25	1.0
Tb	3.5	1.7	1.8	4.8
Dy	3.3	1.5	1.7	3.6
Yb	1.6	.89	1.1	3.1
Lu	1.2	.84	1.1	2.1

Figure 19. Calculated crystal-liquid distribution coefficients of rare earth elements for analyzed crystal phases. Stipled area is for Twin Peaks, slashed areas for Bishop Tuff (Hildreth, 1977), and dashed line is for dacites and rhyodacites (Arth, 1976).

Eu anomaly is present in the partitioning of the South Twin Peak biotites, but a significant negative anomaly exists for the North Twin Peak and Mid Dome biotites. An overall decrease in partitioning from the light to heavy REE is apparent, ranging from 13 to 3 in the South Twin Peak biotites and from 1.0 to .5 in the North Twin Peak biotites. The calculated distribution coefficients for the Mid Dome biotite increase from .67 in La to 1.0 in Tb, and fall to .76 in Lu. The trend of decreasing biotite-liquid partitioning towards the heavy REE (HREE) which is observed for the Twin Peaks biotite is also evident in the Bishop Tuff biotite (Fig. 19) but contrasts with the slight increase recorded for biotites in dacitic liquids (Arth, 1976).

South Twin Peak biotite concentrates all trace elements analyzed except Rb and Zn significantly more than the North Twin Peak or Mid Dome biotites, and except for Sr and Pb, it is enriched in all trace elements relative to the liquid. Mn, Zn, Ta, Sc, and Ba in decreasing order are most strongly enriched, from 100 to 18 times. Distribution coefficients for the Bishop Tuff biotite are generally comparable with the Mid Dome and North Twin Peak biotites, but are greatly exceeded by the South Twin Peak biotite.

Both pyroxenes in the Twin Peaks magmas show a slight depletion in La of about .7 with respect to the liquid, and exhibit a progressive increase in enrichment towards the HREE, in contrast to the phases discussed so far. Augite enriches Lu more than three times whereas orthopyroxene enriches Lu about two times. Both show a negative Eu anomaly which is greater in orthopyroxene.

Comparison of the distribution coefficients for pyroxenes for the

three sets of data shown in Fig. 19 shows that the values for the Twin Peaks magmas are intermediate to the values for high silica and dacitic magmas. The increase in the distribution coefficients from La to Lu is similar to the pattern observed in dacites (Arth, 1976), but is in contrast to that noted by Hildreth (1977) for the pyroxenes in the Bishop Tuff. In terms of major element composition, the Twin Peaks and Bishop Tuff pyroxenes are very similar, so the crystal composition cannot be responsible for the opposing trends. The Coyote Hills magma was approximately 85° hotter, which is expected to decrease the distribution coefficients in the REE as a whole, and contained several percent less silica than the pyroxene-bearing Bishop Tuff magma. These differences can be expected to have an appreciable effect on the distribution coefficients. Nicholls and Harris (1980) have documented significant temperature and compositional effects in clinopyroxene partition coefficients for andesite and basalt host liquids. Inspection of the enrichment factors patterns for the Bishop Tuff and the Core/Cudahy Mine (Fig. 21), which represent changes due only to liquid state phenomena (see next section), indicates that the LREE are more compatible than HREE in the hotter, less silicic liquids. This difference in relative liquid compatibilities between the light and heavy REE probably accounts in part for the opposed trends of partitioning between La and Lu; all else being equivalent, the less compatible an element is in the liquid phase, the more it will tend to be enriched in the crystalline phase.

Other trace elements are also generally partitioned into the Twin Peaks pyroxenes less strongly than into the Bishop Tuff pyroxenes.

The pyroxenes most strongly enrich Sc, 30 times for augite and 10 times for orthopyroxene (vs 100 and 19 for the Bishop Tuff), and Mn, 14 times for augite and 26 times for orthopyroxenes (vs 30 and 55 for the Bishop Tuff) (Hildreth, 1977).

The REE distribution coefficients for magnetite in the Coyote Hills and North Twin Peak magmas show the same relation to the Bishop Tuff magnetites as the respective pyroxenes. The magnetite-liquid partitioning of La is about ten times lower for the Twin Peaks magnetites compared to the Bishop Tuff magnetite, but the values converge towards Lu. The contrast in magnetite compositions between the two systems, however, does not warrant any conclusions to be made on the relative liquid compatibilities for light and heavy REE. The Twin Peaks magnetites exhibit a modest enrichment exceeding three times the liquid concentrations for the middle REE, and decrease to about one towards La and Lu. A pronounced negative Eu anomaly is also evident. All other trace elements analyzed except U and Th are concentrated into magnetite. Zn shows the greatest degree of partitioning and exceeds 60 times.

Only one ilmenite, from North Twin Peak, was analyzed. It concentrates all REE to a greater degree than magnetite, from about six times for the LREE to four times in the HREE. Eu is again markedly less enriched than the other REE and is only slightly concentrated from the liquid. Zn, Mn, Ta, and Th are all strongly partitioned into ilmenite, from 75 times for Zn to 73 times for Th.

The distribution of the REE between quartz and the North Twin Peak magma is very unsystematic. Values decrease from .012 for La to

.001 for Nd, increase to a high of .02 for Eu, and then remain fairly constant for the HREE at about .01. The changes exhibited by the REE are large compared to the analytical precision and remain unaccounted for.

PETROGENESIS

Studies of large pyroclastic deposits have been concerned with the chemical and mineralogical gradients within the roof zones of large silicic magma chambers. Such studies look at a mature magma chamber at one instant in its history and observe the effects of the processes operative at that late stage in the magma chamber's evolution. In particular, the effects of liquid state differentiation which is operative in an apparently nonconvecting cupola are observed.

In contrast to these systems, the suite of rocks at Twin Peaks records the effects of processes operative throughout its history. The periodic eruption of rhyolites of each differentiation sequence records the changes that lead from an initial magma, which was probably relatively homogeneous and convecting, to the development of a highly evolved stagnant roof zone. In a system such as this, it would be expected that, in addition to liquid state differentiation, the effects of crystal settling and magma-wall rock interaction would also be apparent. These effects, insofar as they may be evaluated, are described in the following sections, and are then used to model the observed chemical changes evident in the Twin Peaks rhyolite suite.

Crystal Settling

Theoretical calculations indicate that crystal settling should be expected in the Twin Peaks magmas, and this effect can be recognized.

The effect of zircon settling on Zr and Hf concentrations, for example, is evident in the plot of Zr vs Hf in Figure 20. The line from sample 15 gives the path of changing liquid composition with the removal of zircon, and is close to the overall trend observed in the Twin Peaks suite. In contrast, rhyolites of the Bishop Tuff, in which crystal settling was negligible, exhibit little variation and no coherence between Zr and Hf. The coherence observed at Twin Peaks is therefore reasonably attributed to zircon settling.

Stokes crystal settling velocities for the North Twin Peaks and Coyote Hills magmas, using viscosities and densities calculated by the methods of Shaw (1972) and Bottinga and Weil (1970), are given in Table 22 for various water concentrations. Because of the chemical and mineralogical similarity, the 1.2 to 1.3 percent water content calculated for the Mid Dome magma may be close to the value for the North Twin Peak magma, but no estimate is available for the Coyote Hills magma. Aside from the uncertainty in the water content, to which settling velocities are extremely sensitive, variations in grain size introduce further uncertainties. The results nevertheless indicate the relative importance of settling for some of the minerals present and give ranges of magnitude for their absolute rates. The data indicate that crystal settling may have been significant, particularly for the feldspars in the North Twin Peaks magma. The entire exposed volume of the Twin Peaks volcanics would represent only the top fifty meters of the magma chamber as modeled by Carrier (1979), so that crystal settling lengths of that order of magnitude could cause appreciable effects.

Figure 20. Plot of Zr vs Hf for the Twin Peaks rhyolites. The line from sample 15 indicates the path of changing liquid composition with removal of zircon. Its near coincidence with the other rhyolites suggests that zircon settling is the primary control on these elements. In contrast, the Bishop Tuff rhyolites fall in the enclosed region and show little variation or coherence.

Table 22. Settling Velocities (meters/1000 yrs)

	<u>North Twin Peak</u>			<u>Coyote Hills</u>		
% H ₂ O	1	2	3	1	2	3
log η (poise)	7.82	6.91	6.15	8.21	7.24	6.41
density (gm/cm ³)	2.33	2.27	2.22	2.34	2.28	2.24
<u>Settling Velocities</u>						
Sanidine	62	635	4300	.06	.72	5.5
Plagioclase	4.5	43	280	.83	3.7	27
Pyroxene	1.0	8.3	50	-16	1.8	11
Magnetite	.67	5.5	32	.12	1.2	7.9
Zircon	.06	.5	3.0	.02	.23	1.6

The effects of settling of analyzed phenocrysts for the North Twin Peaks and Coyote Hills magmas are presented graphically in Fig. 21. The amounts of settling are arbitrary but reasonable amounts, and are seen to effect some elements significantly. Particularly effective are orthopyroxene for removing Mg, Sc, Mn, and Fe; augite for removing Mg, Ca, Sc, Mn, and Fe; magnetite for removing Ti, Mn, Fe, and Zn; plagioclase for removing Ca, Sr, Eu, Na, and Al; sanidine for removing Na, Al, K, Ba, Eu, Rb, Sr, and Pb; and zircon for removing Zr and Hf. The effects of zircon on the other elements, especially Lu, indicated in Fig. 21 are based on Rayleigh fractionation using distribution coefficients from Hildreth (1977) and may be excessively high for the Twin Peaks rhyolites, by analogy to his distribution coefficient for Hf compared to the Twin Peaks system.

The results presented in Fig. 21 will be referred to when discussing the role of crystal settling in the chemical evolution of the Twin Peaks magmas.

Magma-Wall Rock interaction

Magma-wall rock interactions are poorly understood and the effects uncertain. The study by Nielson et al. (1978) on the geology of the Roosevelt Hot Springs, 20 kilometers to the south, indicates that the basement rocks, into which the Twin Peaks magma probably intruded, are dominated by gneisses in which alkali feldspar, plagioclase, and quartz dominate. In terms of major components, these rocks are generally more mafic than the rhyolites themselves, so that direct assimilation cannot result in the trend towards more evolved

Figure 21. Enrichment factors plot showing effects of crystal settling for various phenocrysts in the Coyote Hills magma (early sequence) and North Twin Peak magma (late sequence).

rhyolites over time. The lack of trace element data precludes prediction of trace element behavior either by direct assimilation or crystal-liquid equilibrium distribution. It is very unlikely, however, that such interactions could deplete later magmas, for example, in Ba, Sr, Mg, LREE (but not HREE) so significantly.

Exchange of components, whether through a discrete vapor phase or through the liquid, is probably a far more reasonable mechanism. The study by Orville (1963) on alkali vapor exchange between alkali feldspars in a temperature gradient shows that such a mechanism can occur. In many ways the question concerning the effects of a thermal gradient within a magma chamber is the same as concerning the effects of a thermal gradient between a magma and the wall rock. It will be shown later in discussing the thermal gradient effect, that an increase in K and depletion in Na in a hotter region can be predicted. Since these are so easily mobilized in the presence of heated water, magma wall rock interaction would be expected to affect these elements most easily.

Liquid State Differentiation

Comparison of the enrichment factors between the least and most evolved rock of the Bishop Tuff (Hildreth, 1977, 1979) and between the core tuff and Cudahy Mine Unit (Fig. 22) indicates a very similar relationship between the two pairs of rocks. In both systems the crossover between depletion in the LREE and enrichment in the HREE occurs between Nd and Sm, and the degree of enrichment drops slightly after Dy. A sharp depletion in Eu is also characteristic in both

Figure 22. Enrichment factors plots for core/Cudahy Mine Unit (sample 18) and for Bishop Tuff (Hildreth, 1977). These two plots show a striking similarity and indicate a similar relationship between the two pairs of rocks.

systems.

With the exception of Sc, all the other elements exhibit parallel changes in these two systems. Ba and P concentrations show a pronounced decrease with increased enrichment, but are already at or below the detection limits in the Cudahy Mine Unit.

Because of the similarities in the chemical differentiation, the core sample is believed to bear the same relationship to the Cudahy Mine Unit as the most evolved rocks of the Bishop Tuff bear to the least evolved. That is, the core sample is interpreted to have been erupted from the uppermost portion of the magma chamber immediately preceeding the eruption of the deeper, slightly less enriched levels represented by the Cudahy Mine Unit. As with the Bishop Tuff enrichment factors, the enrichment factors for the changes between the core sample and Cudahy mine unit represent chemical gradients within the top of the magma chamber immediately prior to eruption. The scarcity of phenocrysts in the Cudahy Mine Unit rules out the effect of crystal settling as contributing to the chemical gradients. Furthermore, Hildreth (1977) effectively demonstrated that assimilation did not contribute to the chemical gradients in the Bishop Tuff magma chamber. If contamination by assimilation did occur, liquid state differentiation apparently occurred rapidly enough to prevent compositional gradients due to assimilation from building up. It may be assumed with reasonable confidence then, that the enrichment patterns in Fig. 22 are due to liquid state mechanisms alone.

The most characteristic effect of liquid state differentiation is the progressive change from greatest depletion in La to greatest

enrichment in Dy. No established mechanisms such as crystal settling or assimilation can account for this effect. For an enrichment pattern between two magmas, any difference in the enrichments of La and Dy is attributed to liquid-state differentiation, as defined by the core/Cudahy Mine enrichment pattern. Correspondingly, the relative difference between the enrichment factors of La and Dy is therefore used as the criterion to determine the extent of liquid state differentiation in an enrichment pattern. It would be expected, however, that the exact effects of liquid state differentiation would change with changes in pressure, temperature, and composition, so that the use of this model for liquid state differentiation in other Twin Peaks magmas is not strictly applicable. In particular, a smaller degree of depletion in Eu and a greater depletion in the other REE is inferred for the other Twin Peaks magmas when the effects of liquid state diffusion are normalized and compared to the core/Cudahy Mine model.

Whole Rock Chemical Evolution

The chemical changes which took place during each sequence of differentiation occurred over time and represent the combined effects of crystal settling, wall rock interaction, and liquid state differentiation.

The enrichment pattern between the Coyote Hills rhyolite and Cudahy Mine Unit is given in Fig. 23. If it is assumed that the effects of liquid state differentiation are independent of effects due to other phenomena such as crystal settling and wall rock reaction we

Figure 23. Enrichment factors plot representing chemical evolution in the early sequence. Top: Enrichment factors plot for Cudahy Mine Unit (sample 18)/Coyote Hills rhyolite (sample 12). Bottom: Enrichment factors plot for same, but after subtracting the effects of liquid state differentiation, as defined by the core/Cudahy Mine Unit enrichment pattern.

may add or subtract the effects of liquid state differentiation from the remaining effects. The changes calculated after subtracting the effects of liquid state differentiation (as defined by the core/Cudahy Mine enrichment pattern) are also plotted in Fig. 23. The remaining slight enrichment in Na, K, Ca, and Al, could be accounted for by a net assimilation of approximately 10% (of the magma mass) of a gneiss wall rock. It is questionable whether a cooling magma at or below the liquidus could supply the necessary heat of fusion to assimilate more feldspathic material than is removed by crystal settling. The longevity of this sequence (about 200,000 yrs) attests to there having been a sustained heat input, however, and the relatively slow settling rates for sanidine and plagioclase in the Coyote Hills magma (Table 22) may make this a viable explanation for the apparent enrichment in these components. Exchange with the wall rock, rather than assimilation, may also have been involved, but the effects of such a mechanism remain still uncertain.

Settling of less than two percent of the magma mass as orthopyroxene could account for the depletion in Mg and Mn, and an additional two percent removal of augite could account for the observed depletion in Sc (see Fig. 21). Settling velocities for pyroxenes in the Coyote Hills magma with one percent water (Table 22) were sufficient for the pyroxenes to have settled 30 meters over the 200,000 year period between eruptions, so that the amount of pyroxene removed would have been limited largely by the amount crystallized.

The depletion in Zr and most of the depletion in Hf may be accounted for by removal of .025% of the magma as zircon; and the

observed depletion in Sr can be explained by removal of less than 10% as plagioclase.

Neither crystal settling nor assimilation, however, can account for the 40% depletion exhibited by most of the REE. This apparent depletion is most reasonably attributed to differences in the effects of liquid state differentiation between the Coyote Hills and Cudahy Mine magmas and between the Cudahy Mine and core tuff model. This difference may well account for part or all of the apparent Eu enrichment, and other differences as well.

The chemical changes which occurred between the "primitive" North Twin Peak magma (sample 6) and the North Twin Peak (samples 4 and 30), and Mid Dome are displayed in Fig. 24.

The data available for sample 30 indicate that its relation to sample 6, near which it was located and to which it is petrographically very similar, is inconsistent with either crystal settling or liquid state differentiation. The enrichments in Mg, Fe, and Mn in 30 are not compatible with the other changes exhibited using either model. These differences may be due to some localized phenomenon, possibly due to local contamination by wall or roof rock.

The enrichment patterns for the rare earths between the North Twin Peak (6) rhyolite and the North Twin Peak (4) and Mid Dome (20) rhyolites are very flat, indicating little effect of liquid state differentiation on them. Their petrographic similarity and lack of substantial liquid state differentiation suggests that the three were erupted over a short time period. Nevertheless, the settling velocities shown in Table 22 indicate that even over a time period as

Figure 24. Enrichment factors plots representing the chemical changes in the first part of the late sequence. Plots indicate the evolution of the North Twin Peak magmas (samples 4 and 30) and Mid Dome magma (sample 20) from the North Twin Peak magma (sample 6).

short as 10,000 years, settling of plagioclase and especially of sanidine in the North Twin Peak magma could have been significant, even with as little as 1% water. Settling of augite and magnetite would also have been appreciable, particularly if the water content of the magma were slightly higher or the time period longer.

Any settling of augite would have had to have been paired with some liquid state differentiation to result in the flat enrichment pattern for the REE for North Twin Peak (4)/North Twin Peak (6) and Mid Dome/North Twin Peak (6) patterns.

In Fig. 25 is shown the effect of removing 2.5% augite, 10% sanidine, 3% plagioclase, 1% magnetite, and .025% zircon, and enough liquid state differentiation to offset the effect of augite settling on the REE. The correlation between this and the Mid Dome/North Twin Peak (6) enrichment pattern is quite good for most elements. Only Zn, Y, Hf, and Pb do not correlate in direction and most others correlate generally well in magnitude. The greater degree of depletion in Eu and the smaller degree for the other REE may again be due to a difference from the model in effect of liquid state differentiation, as may other differences as well. Overall error due to the error in the liquid state differentiation model is small, however, because of crystal settling as the dominant influence. The proportions used to model crystal settling were based upon their chemical effects rather than upon their relative settling velocities and abundances, but the proportions and absolute amounts are nevertheless reasonably consistent with the mineralogies and settling velocities for the magmas.

Figure 25. Enrichment factors plot of the model for the evolution from North Twin Peak (sample 6) magma to Mid Dome magma (sample 20). From an initial liquid equal in composition to sample 6, the derivative liquid is calculated by subtracting 10% sanidine, 2.5% augite, 3% plagioclase, 1% magnetite, .025% zircon, and liquid state differentiation sufficient to make the difference between the enrichment factors of La and Dy equal to the North Twin Peak/Mid Dome enrichment factors.

The variations from North Twin Peak (6) to North Twin Peak (4) rhyolites are similar as to the Mid Dome rhyolite, but are generally smaller in magnitude. The same mechanisms acting over a shorter period of time can account for the North Twin Peak (4)/North Twin Peak (6) enrichment pattern equally well.

The enrichment pattern for the evolution from the North Twin Peak (6) magma to the South Twin Peak magma is given in Fig. 26. The pronounced increase in enrichment across the REE indicates substantial differentiation in the liquid state. The crossover between depletion and enrichment, however, does not occur until after Dy; nearly all the REE are depleted. The remaining changes, after subtracting the effects of liquid state differentiation to account for the differences between La and Dy, are also shown in Fig. 26. The apparent enrichment in Eu is again most plausibly attributed to an excessively large depletion in Eu in the model. Otherwise, Fig. 26 does not deviate significantly from the enrichment patterns for the evolution of the Mid Dome and North Twin Peak (4) magmas, or from the model in Fig. 25. The most notable difference is the enrichment in K. With sanidine the dominant mineral settling, and with its high settling velocity (Table 22), a net increase in alkali feldspar by assimilation is very unlikely and would represent a significant change from earlier in the magmatic sequence in which little or no effects by assimilation were noted. Interaction with the wall rock due to a thermal gradient between the magma and wall rock, as will be discussed in the next section, may account for the residual enrichment (after accounting for liquid state effects) in K and depletion in Na observed in the South

Figure 26. Enrichment factors plot of chemical changes in the late sequence. Top: Plot represents chemical changes from the Mid Dome magma (sample 20) to South Twin Peak magma (sample 8). Bottom: Plot represents changes between same magmas after subtracting the effects of liquid state differentiation.

Twin Peak magma. This effect may also account for the enriched K and depleted Na evident in the enrichment patterns for North Twin Peak (4) and Mid Dome magmas relative to the model in Fig. 25.

The observed chemical changes with evolution of each sequence can be accounted for fairly well by the mechanisms of crystal settling, liquid state differentiation, and perhaps some limited form of wall rock interaction. Before probing some of the possible mechanisms of liquid state differentiation, there is one more process which may be involved in relating the two differentiation sequences at Twin Peaks.

Partial Melting

It is well recognized that the ultimate source of all magmas is the partial melting of deep rocks. The two sequences of differentiation overlap chemically to such a degree as to strongly suggest there being a common source. The question arises if that common source is directly related to zone of partial melting or if perhaps there is a large intermediate magma chamber from which the two initial magmas were tapped.

Lack of data on the trace element compositions of possible source rocks renders the prediction of partial melt compositions exceedingly speculative at best. The relative compositions between two melts derived from progressive partial melting of a common source, however, is independent of the actual trace element composition of the source rocks. Fig 27 shows the chemical relationship between the Coyote Hills and North Twin Peak (6) magmas. In order to test the hypothesis that these two magmas were derived directly from progressive melting

Figure 27. Enrichment factors plot for Coyote Hills/North Twin Peaks. These represent the primitive magmas of the first and second sequences respectively.

15/6

Figure 28. Enrichment factors plot representing chemical differences between two liquids formed by progressive batch melting of gabbro (top) granodiorite (middle), and tonalite (bottom) source rocks.

of a common source, the enrichment pattern in Fig. 27 may be compared with those in Fig. 28. These enrichment patterns represent the relative changes in trace element composition between an initial liquid at equilibrium with three rock types representing possible source rocks (Wyllie, 1977) and a second liquid produced by equilibrium batch melting of an additional 20% of the rock (Shaw, 1970).

Distribution coefficients calculated for the Coyote Hills and North Twin Peak magmas were used to model the partial melting. Although the absolute magnitudes would probably change; the relative magnitudes should be similar between the two contrasting regimes.

Comparison of the data for the partial melting models for gabbro, tonalite, and granodiorite does not suggest a close relationship between the two magmas and a common zone of partial melting. No mineral or assemblage of minerals known to the writer can account for the progressive enrichment in the first liquid of the middle REE, relative to La, Lu, and Eu. Furthermore, the enrichment in elements which are concentrated in mafic minerals (e.g. Mg, Ca, Sc, Mn, and Fe) in the first liquid would appear inconsistent with a progressive melting model. The pronounced enrichment in Mn and Zn, neither of which changes much over each sequence, is interesting to note but is unexplained. A long and complicated history from partial melting to the eventual eruption at the surface would be expected and is apparent.

POSSIBLE MECHANISMS OF LIQUID STATE DIFFERENTIATION

The occurrence and behavior of liquid state differentiation mechanisms seems to be widespread and similar in effect (Hildreth, 1977, 1979; Smith, 1979; Bacon, 1979; Luddington et al., 1979). There are various possible mechanisms: the gravitational field, thermal gradient, pressure gradient, and chemical gradient. All four and perhaps other mechanisms probably combine to produce the observed chemical trends attributed to liquid state differentiation. The effects of each of these are discussed below.

Gravity

If we consider the effect of the gravitational field alone upon the distribution of magmatic components, and neglect for now the temperature gradient, we may write for the potential of a component i:

$$d\mu_i = \left(\frac{\delta\mu_i}{\delta h}\right) dh + \left(\frac{\delta\mu_i}{\delta P}\right) dP + \left(\frac{\delta\mu_i}{\delta x_i}\right) dx_i$$

where h , P , and x_i are the height, pressure and mole fraction of i within the magma chamber. The first partial derivative is simply the change in energy per mole due to a change in height and is equal to $M_i g$ where M_i is the molal mass and g is the gravitational acceleration. The second partial derivative is equal to the partial molar volume $\bar{V}_i$. The pressure decreases with height and is determined by the density ρ of the liquid, so that $dP = -\rho g dh$. For ideal solutions, $\delta\mu_i/\delta x_i = RT/x_i$. Making these substitutions and assuming

gravitational equilibrium, we get:

$$d\mu_i = 0 = M_i g dh - \bar{V}_i \rho g dh + \frac{RT}{X_i} dx_i$$

and on rearranging:

$$\frac{1}{X_i} \frac{dX_i}{dh} = \frac{(\bar{V}_i P - M_i)g}{RT} \quad (1)$$

Equation 1 gives the gradient of component i with height in mole fraction per unit length, normalized to the mole fraction of component i .

Gradients were calculated using partial molar volume data of Bottinga and Weill (1970) for the oxides and of Burnham and Davis (1974) for water, and assume a temperature of 875°C and a density of 2.35, calculated for the Coyote Hills magma from the data of Bottinga and Weill (1970). Comparison of these data (Table 23) with the enrichment factors for liquid state diffusion in the Bishop Tuff (Fig. 7) indicate that the predicted direction of enrichment for every oxide except K_2O agrees with the observed directions. The magnitudes of the gradients, however, are small and only amount to a few mole percent per kilometer times the mole fraction of the component. The gravitational field is of only minor importance in the development of the observed gradients.

Pressure Gradient and H_2O

Data of Burnham and Davis (1971), based on detailed P-T-X data of water in albite melts, allow the calculation of the effect of pressure on the water fugacity in a magma. The set of curves in Fig. 29 shows

Table 23. Predicted Gradients Due to Gravitational Field

Oxide	$\bar{V}_i(\text{cm}^3/\text{mole})$	$\frac{dc}{dh}/X \left(\frac{\text{mole\%}}{\text{km}} / \text{mole fraction} \right)$
SiO_2	26.75	+0.28
Al_2O_3	37.69	-1.37
MgO	10.85	-1.52
CaO	16.85	-1.69
SrO	20.10	-5.79
FeO	12.3	-4.46
Na_2O	27.16	+0.19
K_2O	42.6	+0.61
H_2O	23.5	+3.82

Figure 29. Diagram showing the relationship between water fugacity, water content, and total pressure in a magma equal to Coyote Hills rhyolite (sample 15) in composition. At constant water fugacity, representing an equilibrium condition, water content increases with a decrease in total pressure.

WT % H₂O vs TOTAL PRESSURE

the relationship between the fugacity and weight fraction of water and the total pressure, calculated by the method of Nicholls (1977) for the Coyote Hills magma at 875°C. The curves represent the equilibrium distribution of water at various fugacities within a pressure gradient. If, for example, water is in equilibrium within the pressure gradient, and its fugacity is 250 bars throughout, at one kilobar pressure the water concentration is 1.6%, and at two kilobars it is 1.35%. The pressure gradient thus predicts an upwards enrichment in water, but its magnitude is too low to account for the increase from 1.3% water in the Mid Dome magma to 3% in the South Twin Peak magma. It also fails to explain the actual increase in water fugacity observed between the two magmas and as also observed in the Bishop Tuff magma chamber (Hildreth, 1977).

Thermal Gradient

Up to this point only effects in an isothermal system have been considered. A thermal gradient is probably the most significant driving force on the major components. In order to consider the effects of a thermal gradient, we must introduce a quantity Q^* called the heat of transfer. It is defined as the quantity of heat transferred with a mole of a substance from one region into another region at a different temperature, other than the heat content of the substance itself.

In order to visualize the nature of Q^* , consider two regions I and II (Fig. 30), each in equilibrium but held at different temperatures by contact with a reservoir, which are connected by a

Figure 30. Schematic diagram used to aid in the interpretation of the heat of transfer, Q^* . Regions I and II are each in internal equilibrium and fixed at different temperatures T_1 and T_2 . A thermal gradient exists across M which connects I and II. The heat of transfer Q_i^* ; may be viewed as the heat which must be absorbed by I from the reservoir R at the junction I-M, in order to maintain constant temperature in I when a mole of component i is transferred from I into M. This heat would have to be given off at the junction M-II when the mole of i leaves M and enters II, in order to maintain constant temperature in II. Thus, the total heat transferred with i equals the internal heat of i, H_i , plus the heat of transfer, or $H_i + Q^*$.

region M across which a thermal gradient exists. Upon a transfer of a component i from I through M into II, there is in general a heat effect as i enters M and the opposite effect as i leaves M and enters II. Thus, there is an additional component of heat transferred from I to II, due to the heat effect just described, and this is the heat of transfer Q^* . For example, if regions I and II consist of a pure vapor and M is a rubber membrane, this heat effect is the heat of solution of the gas in the membrane. Or, if M consists of a liquid phase and I and II consist of the vapor at the respective saturation pressures, the heat effect is due to the heat of condensation (see Hatsopoulos and Kennan, 1965, pp. 647-650 for a discussion of the latter example). Q^* may be interpreted as the heat flux in from a reservoir R (Fig. 30) at the junction which would be required in order to maintain a constant temperature when a mole of substance flows out of the quasistatic region I. In the second example above, it is easily seen that for a mole of vapor to pass from I into M, which consists of its condensed phase, it must condense. In order to maintain constant temperature in I, an amount of heat equal to H_i^V , where H_i^V is the molar heat of vaporization of i , must be absorbed by R at the junction to compensate for the heat liberated by condensation. Q^* , therefore is equal to $-H_i^V$. As i leaves M and enters II the opposite effect occurs as heat would need to be transferred from R to II to maintain a constant temperature in II. The total heat actually transferred from I to II in this example is the enthalpy of the component i itself, minus the heat of vaporization, $\bar{H} - H_i^V = \bar{H} + Q^*$.

The partial molar entropy S of a component in solution equals

$(H/T) - (\mu/T)$. Since the total enthalpy associated with the transfer is $\bar{H}+Q^*$, the change in entropy associated with the transfer is given

$$\begin{aligned} \text{by: } dS_{\text{irr}} &= S_2 - S_1 = \left(\frac{\bar{H}+Q^*}{T_2} - \frac{\mu_2}{T_2} \right) - \left(\frac{\bar{H}+Q^*}{T_1} - \frac{\mu_1}{T_1} \right) \\ &= \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} + (\bar{H}+Q^*) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned} \quad (2)$$

where μ_1 and μ_2 are the chemical potentials at T_1 and T_2 . For an infinitesimal change, Equation 2 becomes

$$dS_{\text{irr}} = -d \left(\frac{\mu}{T} \right) + (\bar{H}+Q^*) d \left(\frac{1}{T} \right) \quad (3)$$

Expansion of the first term in Equation 3 in terms of the variables $1/T$ and $\ln X$ gives:

$$dS_{\text{irr}} = - \left(\frac{\delta(\frac{\mu}{T})}{\delta(\frac{1}{T})} \right)_X d \left(\frac{1}{T} \right) - \left(\frac{\delta(\frac{\mu}{T})}{\delta \ln X} \right)_T d \ln X + (\bar{H} + Q^*) d \left(\frac{1}{T} \right) \quad (4)$$

The second term reduces to $R \frac{\delta \ln a}{\delta \ln X} d \ln X$, and the first term yields the following:

$$\left(\frac{\delta(\frac{\mu}{T})}{\delta(\frac{1}{T})} \right)_X = \mu + \frac{1}{T} \left(\frac{\delta \mu}{\delta(\frac{1}{T})} \right)_X = \mu - T \left(\frac{\delta \mu}{\delta T} \right)_X = \mu - T d\bar{S} = \bar{H}$$

Making these substitutions into (4) yields

$$dS_{\text{irr}} = -R \frac{\delta \ln a}{\delta \ln X} d \ln X + Q^* d \left(\frac{1}{T} \right) \quad (5)$$

In a steady state system, $dS_{\text{irr}} = 0$, so that (5) gives (Lewis and Randall, 1969; Equation 28-33, p. 460)

$$\frac{d \ln X}{dT} = - \frac{Q^*}{RT^2} \frac{\ln X}{\ln a}$$

Although this derivation is based on classical thermodynamics which strictly deals with equilibrium conditions only, the results have been verified for steady state systems by Onsager's relations. For a more rigorous derivation, see Hatsopoulos and Keenan (1965, Chapter 49) or Denbigh (1951).

Equation (6) states that a positive Q^* results in a spontaneous transfer of a component into a cooler region, and negative Q^* predicts the reverse. This is intuitively reasonable and simply states that in a thermal gradient, matter will flow in a direction such that the resulting heat of transfer flows from hot to cold.

Values for Q^* for components in silicate liquids are unknown. In a subliquidus system, however, it is an easy matter to calculate the heats of fusion or crystallization which result from the transfer of a component. These heat effects are large and probably greatly exceed the effects of transfer due to purely liquid phenomena.

To illustrate how heats of fusion can be identified as heats of transfer, consider the schematic diagram of a subliquidus magma in Fig. 31. We will consider the effect of a thermal gradient across the zone H and two lamina above and below H which are small enough to consider as being in equilibrium. We thus have a situation similar to that in Fig. 30 in which the zone M connecting two quasistatic regions is now H.

We will first consider the effect of a thermal gradient on water in the system $\text{NaAlSi}_3\text{O}_8\text{-H}_2\text{O}$. The zone H then contains a solution of liquid $\text{NaAlSi}_3\text{O}_8$ and H_2O and crystals of albite. We will assume $T =$

Figure 31. Schematic diagram of a magma chamber and subliquidus magma. Zone H corresponds to zone M in figure 29, and consists of an assemblage of liquid and crystal phases across which a temperature gradient exists. This zone connects two lamina above and below H which are thin enough to consider as being in internal equilibrium. These correspond to regions I and II in figure 29.

950°C and $P = 1$ kb. At this temperature and pressure, the water content in the liquid is fixed at 30 mole % (Burnham and Davis, 1974). A flow of one mole of water across h into H therefore causes the melting of 3.3 moles of albite, so in order to maintain isothermal conditions, 198 kJ of heat would have to be added at the junction h to compensate for the heat absorbed by melting (Robie et al., 1978). The heat of transfer is therefore $Q^* = 198$ kJ. Using this value and $a_{H_2O} = .6$ (Burnham and Davis, 1974), equation (6) yields:

$$\frac{d \ln X}{dT} = - .038$$

This gradient is equal to a twofold increase in H_2O with a decrease in temperature of only 20°. The thermal gradient therefore exerts a very strong upward potential on not only water, but all volatiles in general.

As a second simple example, we consider the system $NaAlSi_3O_8$ - $KAlSi_3O_8$ at 1 kb water pressure. At 900°C, sanidine of composition $Ab_{12}Or_{88}$ is in equilibrium with liquid of anhydrous composition $Ab_{42}Or_{58}$ (Bowen and Tuttle, 1950). With temperature and pressure fixed, this system has 0 degrees of freedom so that an addition of one mole of Ab to the liquid would result in the melting of 1.9 moles of the sanidine in order to preserve a constant liquid composition. Thus, the heat of fusion yields a heat of transfer for Ab of $Q^*_{Ab} = +118$ kJ, resulting in a very high potential for Ab to increase in the cooler region. In an analogous fashion, $Q^*_{Or} = -87$ kJ where the enthalpy of fusion for sanidine was calculated assuming ideal mixing and using data of Robie et al. (1978). Thus in this

simple example, the Or component would be driven to the hot end.

Using the ideas developed in the two previous examples, we are now ready to consider the effects of a thermal gradient on one of the Twin Peaks magmas. Specifically, we will consider the effect of a thermal gradient on the assemblage present in the South Twin Peak magma, since thermal diffusion was evidently in effect, and it has an assemblage of phenocrysts to work with. We shall concern ourselves only with the components SiO_2 , $\text{NaAlSi}_3\text{O}_8$, KAlSi_3O_8 , and $\text{CaAl}_2\text{Si}_2\text{O}_8$; that is, with the granite system. Plagioclase, sanidine, and quartz were all present as phenocrysts in the liquid, so that there are four phases. For a fixed temperature and pressure, the phase rule requires that the compositions of all phases are also fixed. Table 24 gives the compositions in terms of mole fractions of these components for the whole rock, quartz, sanidine, and plagioclase, and for the residual liquid calculated by subtraction of the phenocrysts from the whole rock composition according to their modal abundances. Because all phases are fixed in composition, it is possible to calculate the effects necessary to maintain constant phase compositions due to adding a mole of a component to this assemblage. In general, the possible effects are melting and/or crystallizing of any or all of the existing mineral phases. This must occur in such proportions that the net composition added to or removed from the liquid, due to the addition of the original component plus the resulting additions or subtractions due to melting or crystallizing of crystals, is equal to the original, fixed liquid composition.

In order to represent this relation mathematically, we must

Table 24.

Mole fraction of components in South Twin Peak phases.

i/j		1	2	3	4	
		<u>Whole Rock</u>	<u>Quartz</u>	<u>Sanidine</u>	<u>Plagioclase</u>	<u>Liquid</u>
SiO ₂	1	0.350	1.0	0.0	0.0	0.116
KAlSi ₃ O ₈	2	0.319	0.0	0.693	0.071	0.464
NaAlSi ₃ O ₈	3	0.300	0.0	0.296	0.678	0.385
CaAl ₂ Si ₂ O ₈	4	0.031	0.0	0.011	0.251	0.035

define the following terms: x_{ij} is the mole fraction of the i th component in the j th phase. These values are given in Table 24 along with the indices; P_{ij} is the proportion of the j th phase which will need to be added to the liquid (i.e. melted) when a mole of component i is initially added; A_{ik} is the number of moles of component i initially added. $A_{ik} = 1$ if $i = k$ or 0 if $i \neq k$. We may now express the relation, given previously, mathematically. Using these definitions, the proportions of phases added by melting which are necessary to maintain a constant composition with the addition of a mole of component i , are related by the following expression:

$$\begin{bmatrix} A_{i1} \\ A_{i2} \\ A_{i3} \\ A_{i4} \end{bmatrix} + P_{i1} \begin{bmatrix} x_{11} \\ x_{21} \\ x_{31} \\ x_{41} \end{bmatrix} + P_{i2} \begin{bmatrix} x_{12} \\ x_{22} \\ x_{32} \\ x_{42} \end{bmatrix} + P_{i3} \begin{bmatrix} x_{13} \\ x_{23} \\ x_{33} \\ x_{43} \end{bmatrix} = P_{i4} \begin{bmatrix} x_{14} \\ x_{24} \\ x_{34} \\ x_{44} \end{bmatrix} \quad (7)$$

Each vector represents the composition of a specific phase. The first vector represents the mole of component i initially added. The next three represent the compositions of the mineral phases which are added to the liquid (by melting) in the given proportions. The sum of these terms must equal some multiple, P_{i4} , of the liquid composition, which is represented by the right hand vector. The set of vector equations represented in equation (7) may be combined into a single matrix equation, given by

$$\begin{bmatrix} x_{11} & x_{12} & x_{13} & x_{14} \\ x_{21} & x_{22} & x_{23} & x_{24} \\ x_{31} & x_{32} & x_{33} & x_{34} \\ x_{41} & x_{42} & x_{43} & x_{44} \end{bmatrix} \begin{bmatrix} P_{i1} & P_{i2} & P_{i3} & P_{i4} \\ P_{12} & P_{22} & P_{32} & P_{42} \\ P_{13} & P_{23} & P_{33} & P_{43} \\ P_{14} & P_{24} & P_{34} & P_{44} \end{bmatrix} = - \begin{bmatrix} 1000 \\ 0100 \\ 0010 \\ 0001 \end{bmatrix} \quad (8)$$

in which the values for A_{ij} have been substituted. Substitution of the values for X_{ij} given in table 24 and solving equation (8) yields the solution matrix:

$$[P_{ji}] = \begin{bmatrix} \text{SiO}_2 & \text{KAlSi}_3\text{O}_8 & \text{NaAlSi}_3\text{O}_8 & \text{CaAl}_2\text{Si}_2\text{O}_8 \\ -1 & -0.40 & 1.01 & -2.61 \\ 0 & -3.66 & 5.72 & -14.40 \\ 0 & -0.31 & 0.96 & -6.49 \\ 0 & -3.35 & 8.68 & -22.50 \end{bmatrix} \begin{matrix} \text{quartz} \\ \text{sanidine} \\ \text{plagioclase} \\ \text{liquid} \end{matrix}$$

Thus, the effect of adding a mole of component SiO_2 ($i=1$) is represented by the vector

$$[P_{j1}] = \begin{bmatrix} -1 \\ 0 \\ 0 \\ 0 \end{bmatrix}$$

This says that if one mole of SiO_2 is added, then one mole of quartz is removed by crystallizing, no plagioclase or sanidine is added or removed, and the net amount of liquid added is zero. The resulting heat of transfer resulting from flow of one mole of SiO_2 into this zone is the negative value of the heat of fusion of SiO_2 (cristobalite) and is $Q^*_{\text{SiO}_2} = -8.2 \text{ kJ}$ (Robie et al, 1978).

The effect of adding one mole of KAlSi_3O_8 ($i=2$) is to crystallize 0.40 moles of quartz, 3.66 moles of sanidine, .31 moles of plagioclase, resulting in a net removal of 3.35 moles of the initial liquid to maintain the same final composition. Assuming a linear

relationship between mole fraction of components in the feldspars and their heats of fusion, data from Robie et al. (1978) yield a heat of transfer $Q^* = -246$ kJ. In similar fashion, the heat of transfer for one mole of $\text{NaAlSi}_3\text{O}_8$ is $Q^*\text{NaAlSi}_3\text{O}_8 = +418$ kJ, and for $\text{CaAl}_2\text{Si}_2\text{O}_8$, $Q^*\text{CaAl}_2\text{Si}_2\text{O}_8 = -1,319$ kJ. These values are all extremely large and the potentials exerted on these components by a thermal gradient across a zone equal in composition to the South Twin Peak magma is very large. These values predict a very strong depletion of $\text{CaAl}_2\text{Si}_2\text{O}_8$ and a smaller but still significant depletion in KAlSi_3O_8 in the cooler portions. A far smaller depletion in SiO_2 and a large enrichment in $\text{NaAlSi}_3\text{O}_8$ are also predicted. These components, however, cannot all be treated as independent and ideal solutes. With the very large potentials for KAlSi_3O_8 and $\text{CaAl}_2\text{Si}_2\text{O}_8$ to be driven downward, the net effect on SiO_2 may be that it is driven upwards despite a relatively small downward potential predicted when considering SiO_2 as an isolated component. In addition, it will be shown that a water gradient can exert a significant upward potential on SiO_2 , so the success of this simple model is still quite remarkable and can also be used to predict the very strong depletion in the mafic components in the cooler roof zone.

These relations would hold for any two regions of different temperature which are connected by the given assemblage. Thus, this model would predict a potential for this magma to incorporate K and give up Na to the cooler wall rock. As we saw earlier, there is some evidence that this did occur.

Any nonisothermal and non-convecting subliquidus magma should

exhibit these effects. In general, components that decrease the liquidus temperature of a magma should be driven into the cooler region. This model can thus explain the decrease in phenocryst content with decrease in temperature and the common occurrence of resorbed quartz and sanidine phenocrysts. The depletion of K in the cooler liquids, in which the sanidine is highest in K, clearly deviates from crystal-liquid equilibria relations and may also be explained by this model, since these effects occur only after crystal phases are present.

Chemical Gradients

The three driving forces for liquid state diffusion so far described may all influence the distribution of components in the magma, but the final distribution of any component depends upon the combined effect of each of these forces and also upon the effect of the resulting compositional gradients on the chemical potential of that component. The experiments of Watson (1976) on the partitioning of minor components between two coexisting immiscible liquids demonstrates the effectiveness of liquid composition on the distribution of minor components. Trace element enrichment patterns at Twin Peaks and elsewhere, however, indicate a far more complex behavior than in the simple anhydrous system of Watson, in which the partitioning coefficients were proportional to the cationic field strength (charge/radius).

The effect of an upward enrichment in water, which is predicted by all of the previous models, decreases the activity coefficient of

SiO_2 and thus promotes the upward enrichment of silica. Data from Tuttle and Bowen (1958) are plotted in Fig. 32 and show the relationship between SiO_2 and H_2O concentrations in the system SiO_2 -(50% Or + 50% Ab)- H_2O . The solid curves represent the concentration of SiO_2 in a liquid saturated with respect to both SiO_2 and H_2O for the two different pressures indicated. The abscissa gives the free energy of formation of quartz at 1 bar at various temperatures indicated by the dashed isotherms (Robie et al, 1978). Thus, point A represents a quartz and water saturated system in which the anhydrous liquid composition is 82.2 weight percent SiO_2 and the pressure is 981 bars. Under these conditions, the temperature is 840°C and the free energy of formation of the quartz is $G_{\text{fSiO}_2}^\circ = -712$ kJ per mole. The water content, determined by the method of Nicholls (1977), is 1.78 weight percent. Point B represents the system in which the quartz has the same free energy of formation, but the water pressure is 490 bars. The anhydrous SiO_2 content is in this case 81.2 weight percent and the calculated water content is 1.2%. Under these conditions, the temperature is slightly higher because of the slight effect of pressure on increasing $G_{\text{fSiO}_2}^\circ$ at a constant temperature. If we disregard this small pressure effect, points A and B would represent two systems in which SiO_2 is in mutual equilibrium. Thus in this example, an increase of only .6% H_2O results in a 1% increase in SiO_2 . That the increase in SiO_2 is due to an increase in water content rather than the decrease in total pressure can be inferred from data of Luth (1969) for the dry systems Q-Ab and Q-Or. In both cases for the quartz-liquid systems, an increase in pressure is

Figure 32. Diagram showing the relationship between SiO_2 content and Gibbs free energy (G_{SiO_2}) in a quartz-water saturated liquid in the SiO_2 -(50% $\text{NaAlSi}_3\text{O}_8$ -50% KAlSi_3O_8) system at 491 bars and 981 bars pressure. At the higher water pressure, corresponding to 1.78 wt% water (Nicholls, 1977) (point A), the concentration of SiO_2 is greater than at lower pressure, corresponding to 1.20% water (point B), for liquids in equilibrium with quartz of the same Gibbs free energy of formation. Because of the slight pressure effect on $G_f^{\text{SiO}_2}$, point B is at a slightly higher temperature which is indicated by the nearly vertical, dashed isotherms.

observed to increase the stability of quartz, whereas in the water saturated system, a decrease in pressure stabilizes quartz. This suggests that it is the decrease in water content rather than total pressure which stabilizes quartz.

The effect of chemical gradients is probably the most significant effect on the distribution of trace elements whose concentrations have little relation to the bulk extensive properties of the magma. The distribution of a trace element within a chemical gradient is similar to the distribution between two discrete phases (i.e., liquid and crystal) except that there is a continuous change in phases. In order to develop this idea, we assume the validity of Henry's law, given here by:

$$a_i = kx_i$$

where a_i is the activity of i , x_i is its mole fraction, and k_i is the Henry's law coefficient and is constant. Then, the potential of i is given by:

$$\mu_i = \mu_i^\circ + RT \ln k_i x_i$$

which yields:

$$k_i x_i = \exp[(\mu_i - \mu_i^\circ)/RT]$$

where μ_i° is the standard state potential of i . Differentiating with respect to x_i , we get:

$$k_i = \exp [(\mu_i - \mu_i^\circ)/RT] (1/RT) (\delta\mu_i/\delta x_i) \quad (9)$$

The distribution of i in equilibrium between two distinct portions A and B of the liquid is described by Nernst's Law:

$$D_i^{A/B} = \frac{X_i^A}{X_i^B} = \frac{K_i^B}{K_i^A} \quad (10)$$

Since at equilibrium, $\mu_i^A = \mu_i^B$ and μ_i° is dependent only upon the choice of standard states, substituting (9) into (10) yields:

$$D_i^{A/B} = \frac{K_i^B}{K_i^A} = \left(\frac{\delta\mu_i^B}{\delta X_i^B} \right) / \left(\frac{\delta\mu_i^A}{\delta X_i^A} \right)$$

Thus for a component i , the greater $\delta\mu_i/\delta X_i$ is in one region relative to another, the greater is the driving potential from the one to the other.

As a possible direct measure of $\delta\mu_i/\delta X_i$, the distribution coefficients between liquids of varying composition and a mineral of constant composition should reflect the change in $\delta\mu_i/\delta X_i$ with the liquid. Unfortunately, only quartz shows no compositional change with a change in liquid composition, and only one quartz analysis is available.

The difference in the partitioning of REE in very similar pyroxenes between the Bishop Tuff and Twin Peaks magma described in Section VIII may be partially due to a relatively greater increase in $\delta\mu/\delta X$ for the LREE with respect to the HREE in the more evolved Bishop Tuff magma. A greater increase in $\delta\mu/\delta X$ for the LREE in more evolved liquids is consistent with the relative depletion of the LREE in evolved liquids as indicated in enrichment patterns.

SUMMARY

Two distinct sequences of chemical evolution gave rise to a total exposed volume of 4 km³ of rhyolites and pyroclastic rocks in the Twin Peaks, Utah field. Each sequence is characterized by a trend from less silicic to more silicic rocks. The first sequence spanned a period of about 200,000 years, was controlled predominantly by liquid state differentiation, and culminated in small scale pyroclastic eruptions. The latter sequence spanned a shorter time, possibly as long as 100,000 years, and clearly exhibited crystal settling effects in addition to liquid state differentiation. Some magma-wall rock interaction is also indicated. Calculated distribution coefficients are similar to those determined for high silica rhyolites by Hildreth (1977), except for the less silicic magmas, for which distribution coefficients approach values given by Arth (1976) for rhyodacites.

Calculated temperature and water contents of the magma indicate that the late stage of the second sequence was non-convecting, and this is assumed to have been the case for the early sequence as well, by analogy to the later sequence and to other silicic magma systems. The chemical trends observed in each sequence are interpreted to have resulted from the evolution from a relatively homogeneous and convecting magma to one in which a steeply zoned non-convecting roof zone existed, similar to those suggested for larger silicic magma

chambers which have given rise to large scale pyroclastic eruptions. Due to the size, thermal input, and perhaps other factors, no large scale eruptions occurred at Twin Peaks.

The gravitational field, pressure gradient, and thermal gradient all affect the distribution of the major components in the upper magma chamber. The thermal gradient, however, exerts by far the most dominant effect. Theoretical calculations of the effects of a thermal gradient superposed on the South Twin Peak magma (simplified to the four components of the granite system, i.e. SiO_2 , KAlSi_3O_8 , $\text{NaAlSi}_3\text{O}_8$, $\text{CaAl}_2\text{Si}_2\text{O}_8$), predicts the observed enrichments and depletions of these components. Addition of a component to a subliquidus system will in general result in heat effects due to crystallization and/or fusion of crystal phases as the system returns to an equilibrium state, determined by the phase relations. This heat effect can be considered as the heat of transfer for a component entering into such a subliquidus system. Calculation of these heat effects demonstrate that a thermal gradient in the South Twin Peak magma exerted a very strong potential for chemical gradients to develop; these agree with the observed directions of gradients. In addition, this model predicts the pronounced depletion of the mafic components as well.

Chemical evolution at the Twin Peaks field was modified by recognizable crystal settling effects and possible wall rock reaction, but was dominated by liquid state differentiation. The effects of liquid state differentiation in this small volcanic system is remarkably consistent with the effects observed in the large scale magma chambers.

APPENDIX I

CALCULATION OF DISTRIBUTION COEFFICIENTS AND USE OF DISCO PROGRAM

Introduction

The crystal/liquid distribution coefficient for an element i and mineral j is given by

$$D_{ij/l} = C_{ij}/C_{i^l}$$

where l is the liquid phase, i and j are the indexes for the element and mineral respectively, and C_{ij} and C_{i^l} are the respective concentrations in each phase at equilibrium. Natural crystallizing systems, however, more closely approximate conditions of surface equilibrium (Neumann et al., 1954; Gast, 1968) so that for a finite amount of mineral j , the average C_{ij} does not give the concentration of i in j at equilibrium with the concentration in the liquid. This error increases with increasing phenocryst composition (Albarede and Bottinga, 1972). Further problems arise in determining distribution coefficients if no glass exists in the groundmass, as is the case with many of the Twin Peak rhyolites.

For these reasons a system of equations was developed which expresses the whole-rock normalized mineral concentrations, $C_{ij}/C_{i^{wr}}$, in terms of the $D_{ij/l}$. For a system of M minerals and for each element i , this system consists of M equations, for which M unknowns can be determined. The program DISCO was created to solve for the

distribution coefficients, given C_{ij}/C_{jwr} for each mineral j . For unanalyzed minerals, DISCO will also solve for the whole-rock normalized concentrations, given an assumed value for the distribution coefficient.

This program uses the subprogram NSIMEQ (Univac, 1970) to solve the system of nonlinear equations, using the Newton-Raphson method.

Inherent in any model for determining and using distribution coefficients is the assumption that the crystallizing system approximated a closed system, so that the whole rock concentrations equal the initial liquid concentrations.

The Algorithm

In a system in which several phases are crystallizing, a bulk distribution coefficient is defined by

$$B_i = \sum_j X_j D_{ij} / l \quad (11)$$

where X_j is the fraction of the j th mineral in the crystallizing mass. Under conditions of surface equilibrium, Gast (1968) has shown that the concentration of i in the liquid, C_i^l , is given by

$$C_i^l / C_i^0 = F \exp(B_i - 1) \quad (12)$$

F is the fraction of liquid in the system, and C_i^0 is the initial concentration of i in the liquid.

For the case in which crystallization takes place in different stages, involving different proportions and/or different crystal phases, the crystallization sequence can be tabulated as in Table 24. $F(K)$ is the fraction of liquid and $X(K, J)$ is the fraction of mineral J

at the crystallization sequence point (CSP) K:

The fraction of mineral J crystallized over the interval K-1 to K is given by

$$B(K,J) = \frac{X(K,J) - X(K-1,J)}{F(K-1) - F(K)} \quad (13)$$

Substituting (13) into (11) and making changes in notation, we get for the bulk distribution coefficient over the interval K-1 to K the following:

$$B(K,M2+1) = \sum_{J=1}^{M2} B(K,J) \cdot D(J) \quad (14)$$

where D(J) is the distribution coefficient of the element in question between the liquid and mineral J. M2 is equal to the number of minerals being considered. B(K,M2+1) designates the bulk distribution coefficient over the interval K-1 to K. B(K,J) designates the partial derivative of B(K,M2+1) with respect to the Jth mineral, and is defined in equation (13). Here, and in the following discussion, the index M2+1 has been omitted.

By making the appropriate changes in (12) for the interval K-1 to K of a crystallization sequence, we get

$$CL(K)/CL(K-1) = [F(K)/F(K-1)] \exp(B(K,M2+1)-1) \quad (15)$$

where CL(K) is the concentration in the liquid at CSP K. Setting CL(0)=1 (i.e., using whole rock normalized concentrations for CL(K)), it follows from (15) that

$$CL(K) = \prod_{n=1}^K CL(n)/CL(n-1) = \prod_{n=1}^K [F(n)/F(n-1)] \exp(B(n,M2+1)-1)$$

or for $CL(K-1)$

$$CL(K-1) = \prod_{n=0}^{K-1} [F(n)/F(n-1)] \exp(B(n, M2+1)-1) \quad (16)$$

where $F(-1) \equiv 1 = F(0)$.

The amount of an element removed from the liquid phase and added to the bulk solid phase (S), over the interval $K-1$ to K is given by

$$AMT(K, S) = CL(K-1) \cdot F(K-1) - CL(K) \cdot F(K). \quad (17)$$

Factoring out $CL(K-1) \cdot F(K-1)$ from each term and substituting (15) into (17) yields

$$AMT(K, S) = CL(K-1) \cdot F(K-1) [1 - (F(K)/F(K-1)) \exp(B(K, M2+1))] \quad (18)$$

We now define the function $FBL(K)$ by

$$FBL(K) = AMT(K, S)/CL(K-1) \quad (19)$$

Of the total amount of an element to enter the bulk solid phase over the interval $K-1$ to K , the fraction that enters a specific mineral J is proportional to $D(J)$, and to the fraction of J crystallized over that interval, given by $B(K, J)$. Furthermore, the sum of the amounts entering each mineral phase must equal the amount entering the bulk solid phase. Using these two relations and equation (14), we can define the following:

$$FMB(K, J)/AMT(K, S) = D(J) \cdot B(K, J)/B(K, M2+1) \quad (20)$$

Now, combining equations (16), (19), and (20), it can be seen that the amount of an element entering the mineral J over the interval $K-1$ to K is given by

$$AMT(K,J) = CL(K-1) \cdot FBL(K) \cdot FMB(K,J) \quad (21)$$

It follows that the average concentration of any element in J is

$$C(J) = \sum_{K=1}^{P2} (CL(K-1) \cdot FBL(K) \cdot FMB(K,J)) / X(P2,J) \quad (22)$$

where P2 is the number of intervals of crystallization.

Discussion

For each element, equation (22) defines an array of M2 equations, where M2 is the number of minerals considered. If a crystallization sequence table, such as is tabulated in Table 24, can be constructed (described below), and, if for each mineral, either the whole rock normalized concentration, T(J), is known, or the corresponding distribution coefficient is assigned an assumed value, the remaining unknowns can be solved. In order for NSIMEQ to solve the system of equations defined by DISCO, a "sufficiently close" estimate of the D(J)'s is required. For this system of equations the radius of convergence is infinite, and the T(J) values are used as initial estimates.

A negative value input for the concentration in a mineral indicates that its absolute value is assumed to be the correct distribution coefficient and that it is to be held fixed. This value enters into the bulk distribution coefficient calculation, but the number of equations solved by NSIMEQ is reduced by one for each negative value. After the other D(J)'s are solved, the concentrations for those minerals are determined by the forward calculation of the respective equations. The concentration in the final liquid is also

computed for each element by simple mass balance relations.

One can construct a crystallization sequence table by first determining the mode (in weight percent) of the rock being considered. One can then either assume modal crystallization, in which case $P2 = 1$, or determine a sequence of crystallization which results in the final mode, and which is constrained by petrographic and petrologic relations. An example is given in Table 25.

Execution of DISCO

DISCO is written for FORTRAN V, and must be compiled by the FOR compiler, which may be accessed from storage in the University of Utah Computer Center library. The required data file is given in Table 26.

Table 25. MODEL CRYSTALLIZATION SEQUENCE TABLE

CRYSTALLIZATION SEQUENCE PT (CSP)	LIQUID FRACTION	WEIGHT FRACTION OF MINERAL J					
		1	2	...	J	...	M2
0	$F(0) = 1$	0	0		0		0
1	$F(1)$	$X(1,1)$	$X(1,2)$	...	$X(1,J)$	...	$X(1,M2)$
2	$F(2)$	$X(2,1)$	$X(2,2)$	...	$X(2,J)$	...	$X(2,M2)$
.	.	.	.		.		.
.	.	.	.		.		.
.	.	.	.		.		.
K	$F(K)$	$X(K,1)$	$X(K,2)$	...	$X(K,J)$	...	$X(K,M2)$
.	.	.	.		.		.
.	.	.	.		.		.
.	.	.	.		.		.
P2	$F(P2)$	$X(P2,1)$	$X(P2,2)$		$X(P1,J)$	...	$X(P2,M2)$

Table 26. DATA INPUT FOR PROGRAM DISCO

CARD	INPUT
First	Title -- columns 1-80 (20A4)
Second	Mineral names -- up to 10 minerals (10A6)
Next 1 to 15	Element name -- columns 1-2 Whole rock concentration -- columns 7-12 Mineral concentrations, or negative of assumed distribution coefficient -- columns 13 - 72 (A2, 4X, 11F 6.2)
Next 1	Blank -- to indicate preceding card was for the last element in the data set
Next 1 to 8	Crystallization Sequence Table: 1 card per K; start with K=1 F(K) -- columns 1-6 X(K,J); J=1 up to 10 --columns 7-67 (11F 6.2)
Last	Blank

APPENDIX II: PROGRAM LISTING

```

    DIMENSION TITLE(20),D(31,10), MIN(11), ELT(31), P(10,1), Q(10,1),
    C ED(10), Z(10,11), CD(10), QD(10,1), IR(10), JC(10), X2(10),WR(30)
    C,WRK(3)
    COMMON P2,F(9), T(30,11), X(9,10) ,I ,IDX(10),FIXD(10),M2,C(10,11)
    DATA WRK/'WHOL', 'E RO', 'CK' '/'
    INTEGER P2, E2
    EXTERNAL JACOBI
    L=0
    NMAX=10
    ITMAX=100
    EPS1=.000001
    EPS3=.0005
    M1=1
    READ(5,102) (TITLE(I),I=1,20)
    WRITE(6,202) (TITLE(I),I=1,20)
    READ(5,100) (MIN(J),J=1,11)
    DO 10 J=1,11
    IF(MIN(J).EQ.' ') GO TO 12
10 CONTINUE
12 M2=J-1
    MIN(J)='LIQUID'
    M3=J
    WRITE(6,240)
    WRITE(6,245) (WRK(J), J=1,3), (MIN(J), J=1,M3)
    DO 20 I=1,31
    READ(5,110) ELT(I), WR(I), (D(I,J), J=1,M2)
    IF(ELT(I).EQ.' ') GO TO 22
    DO 21 J=1,M2
21 T(I,J)=D(I,J)/WR(I)
20 CONTINUE
22 E2=I-1
    DO 40 K=1,9
    READ(5,130) F(K), (X(K,J), J=1,M2)
    IF(F(K).EQ.0.) GO TO 42
40 CONTINUE

```

```

42 P2=K-1
   DO 65 I=1,E2
57 M=1
   N=1
   DO 50 J=1,M2
   IDX(J)=0
   IF(D(I,J).LE.0) GO TO 52
   ED(N)=T(I,J)
   N=N+1
   GO TO 50
52 FIXD(M)=-D(I,J)
   IDX(J)=1
   M=M+1
50 CONTINUE
   TOTAL=.0
   DO 17 J=1,M2
17 TOTAL=TOTAL+X(P2,J)*T(I,J)*(1-IDX(J))
   IF(TOTAL.LE.1.) GO TO 58
   WRITE(6,290)
   WRITE(6,292) ELT(I)
   GO TO 65
58 M6=N-1
   CALL NSIMEQ(JACOBI,P,QD,Z,NMAX,IR,JC,M6,M1,L,ITMAX,SI,DS,SF,EPSI,
C EPS2,EPS3,Q,ED,CD,X2,IERR1,IERR2)
   IF(IERR1.GT.-1) GO TO 81
   WRITE(6,301)
81 IF(IERR2.GT.-1) GO TO 59
   WRITE(6,302)
59 N=1
   M=1
   DO 62 J=1,M2
   D(I,J)=(1-IDX(J))*CD(N)-IDX(J)*FIXD(M)
   N=N+1-IDX(J)
62 M=M+IDX(J)
   T(I,M3)=WR(I)/F(P2)

```

```

      DO 85 J=1,M2
      T(I,J)=(T(I,J)-C(J,M3))*WR(I)
      T(I,M3)=T(I,M3)-X(P2,J)*T(I,J)/F(P2)
      IF(IDX(J) .EQ. 1) T(I,J) =-T(I,J)
85  CONTINUE
      WRITE(6,248)  ELT(I), WR(I), (T(I,J), J=1,M3)
65  CONTINUE
      WRITE(6,210)
      WRITE(6,220) (MIN(J), J=1,M2)
      DO 74 I=1,E2
74  WRITE(6,230) ELT(I),(D(I,J), J=1,M2)
      WRITE (6,250)
      WRITE (6,260) (MIN(J), J=1,M2)
      DO 90 K=1,P2
90  WRITE (6,270) F(K), (X(K,J), J=1,M2)
      STOP
100 FORMAT(11A6)
102 FORMAT(20A4)
110 FORMAT(A2,4X,11F6.0)
130 FORMAT(10F6.0)
202 FORMAT(1H1, 20X, 20A4)
210 FORMAT(1H0,///,20X,'DISTRIBUTION COEFFICIENTS (MINUS SIGN INDICATE
      CS FIXED COEFFICIENT)')
240 FORMAT (1H0,///,20X, 'TRACE ELEMENT CONCENTRATIONS (MINUS SIGN IND
      CATES CALCULATED VALUE)')
220 FORMAT(1H0,/,22X,11(A6,4X))
230 FORMAT(1H0,12X, A2, 2X,11F10.3)
245 FORMAT(1H0, /, 18X, 3A4, 11(4X, A5))
248 FORMAT(1H0, 12X, A2, F12.3, 11F10.3)
250 FORMAT(1H0,///,10X,'CRYSTALIZATION SEQUENCE')
260 FORMAT(11X,1HF, 10(2X,A6))
270 FORMAT(7X, F5.4, 10(2X, F6.4))
290 FORMAT(1H0, 10X, 'ERROR--CONCENTRATION OF      IN BULK SOLID EXCEEDS
      C WHOLE ROCK CONCENTRATION FOR GIVEN MODE')

```

```

292 FORMAT(1H+, 34X, A2)
301 FORMAT(1H0, 10X, 'ERROR RETURN: JACOBIAN MATRIX SINGULAR')
302 FORMAT(1H0, 10X, 'ERROR RETURN: NO. OF ITERATIONS EXCEEDED ITMAX')
END

```

```

SUBROUTINE JACOBI(C, NMAX, ED, M6, M1, CN)
  DIMENSION Q(10,1), D(10), CN(10,11), X1(10), CL(8,11), B(8,11),
  C FBL(8,11), FMB(10,11), ED(10)
  COMMON P2, F(9), T(30,11), X(9,10), I, IDX(10), FIXD(10), M2, C(10,11)
  INTEGER P2
  M3=M2+1
  M=1
  N=1
  DO 5 J=1, M2
    D(J)=IDX(J)*FIXD(M)+(1-IDX(J))*ED(N)
    N=N+1-IDX(J)
5  M=M+IDX(J)
  DO 90 J=1, M2
    F1=1
    F2=1
    C(J, M2+1)=0.
    FMB(J, M2+1)=0.
    CL(1, M2+1)=1.
    DO 10 N=1, M2
      X1(N)=0.
      C(J, N)=0.
10  CL(1, N)=0.
    DO 30 K=1, P2
      FMB(J, K)=0.
      IF(J.GT.1) GO TO 40
      B(K, M2+1)=0.
40

```



```

DO 20 N=1,M2
B(K,N)=(X(K,N)-X1(N))/(F1-F(K))
B(K,M2+1)=B(K,M2+1)+B(K,N)*D(N)
20 X1(N)=X(K,N)
FBL(K,M2+1)=(1.-( F(K)/F1)**P(K,M2+1))*F1
IF(K.EQ.1) GO TO 40
CL(K,M2+1)=CL(K-1, M2+1)*(F2-FPL(K-1, M2+1))/F1
40 IF(B(K,M2+1).EQ.0.) GO TO 42
FMB(J,M2+1)=D(J)*B(K,J)/B(K,M2+1)
42 C(J,M2+1)=C(J,M2+1)+FMB(J,M2+1)*CL(K,M2+1)*FBL(K,M2+1)
W=(FBL(K,M2+1)-F1)*ALOG(F(K)/F1)
DO 60 N=1,M2
M=0
IF(J.EQ.N) M=1
IF(J.GT.1) GO TO 55
FBL(K,N)=W*B(K,N)
IF(K.EQ.1) GO TO 55
CL(K,N)=(F2-FBL(K-1, M2+1))/(F1 )* CL(K-1,N)-CL(K-1, M2+1)
C *FPL(K-1, N)/F1
55 IF(B(K,M2+1).EQ.0.) GO TO 56
FMB(J,N)=B(K,J)*(B(K,M2+1)*M-D(J)*B(K,N))/B(K,M2+1)**2
56 T1=FMB(J,M2+1)*FBL(K,M2+1)*CL(K,N )
T2=FMB(J,M2+1)*FBL(K,N )*CL(K,M2+1)
T3=FMB(J,N )*FBL(K,M2+1)*CL(K,M2+1)
60 C(J,N)=C(J,N)+(T1+T2+T3)/X(P2,J)
IF(K.GT.1) F2=F(K-1)
30 F1=F(K)
90 C(J,M3)=T(I,J)-C(J,M3)/X(P2,J)
M=1
DO 110 J=1,M2
IF(IDX(J).EQ.1) GO TO 110
K=1

```

```
DO 105 N=1,M3  
IF(IDX(N) .EQ. 1) GO TO 105  
CN(M,K)=C(J,N)  
K=K+1  
105 CONTINUE  
M=M+1  
110 CONTINUE  
RETURN  
END
```

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