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Development and Application of A Mass Spectrometric
System to Study Volatile Components of Fluid Inclusions

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by

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ABSTRACT OF THE THESIS

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Master of Science

Graduate Program in Geological Sciences

University of California, Riverside, June, 1992

Professor Michael McKibben, Chairman

A quadrupole mass spectrometric system coupled with mechanical decrepitation was constructed and calibrated to study fluid inclusions from an active geothermal system. Fluid inclusions in Salton Sea Scientific Drilling Project (SSSDP) well cores and ejecta from flow tests were analyzed. Ion currents from selected mass/charge ratio numbers were measured for gases from ruptured inclusions in epidote, calcite, and hematite vein minerals from different depths.

Water, carbon dioxide, hydrogen sulfide, sulfur dioxide, and C1-C4+ hydrocarbons and free nitrogen were analyzed. Excess amounts of 32 AMU not attributable to hydrogen sulfide and sulfur dioxide were most probably

due to oxygen from post-decrepitation surface reactions and sulfur from sulfides and mercaptans. Variations in gas compositions indicate single-phase trapping of a variable composition fluid.

The differences between mass spectrometric analysis and direct flow test chemistry results can primarily be attributed to surface adsorptive effects during mass spectrometric analysis. If an amount of water 581 times that detected and an amount of carbon dioxide 57 times that detected are artificially added to the analysis results for an average hematite sample, reconciliation of ppm sulfur and carbon dioxide in the mass spectrometric analyses with flow test data is achieved, effectively calibrating the system for relative adsorption effects of water and carbon dioxide. Results for all minerals are summarized in the table below.

State 2-14 Salton Sea Scientific Drilling Project
Volatile Compositions (Mole Fractions)
581 x Water Loss Compensated
57 x CO₂ Loss Compensated

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.996	16.2	2.0	541.7	8.2	1.2
MAX	0.999	27.0	4.8	3514.2	11.3	3.6
AVG	0.999	19.6	2.9	1447.0	9.9	1.7
STD	0.001	2.4	0.7	781.0	0.8	0.5

28 AMU indicated in the above table is primarily nitrogen and hydrocarbons. The 32 AMU listed in the above table is not attributable directly to hydrogen sulfide and sulfur dioxide and is probably from oxygen

generated by surface reactions and sulfur from sulfides
and mercaptans.

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INTRODUCTION

When crystals grow or recrystallize in a fluid medium, irregularities in growth trap small portions of the mother liquor in the solid crystal. These pockets of trapped host fluid are known as primary fluid inclusions when trapped along crystal faces. Healing of fractures during crystal growth yields pseudo-secondary inclusions, while the healing of fractures in the presence of a later fluid medium after primary crystallization produces secondary inclusions. There may be more than one population of secondary inclusions within a single specimen (Barker and Smith, 1986).

Fluid inclusions can exhibit wide ranges in composition, showing extremes from inclusions that are practically 100% carbon dioxide in metamorphic rocks, to fluid inclusions from hydrothermal systems that are almost exclusively water. Generally, fluid inclusions are water solutions containing less than 10 wt% solutes, although the solute can range from greater than 50 wt% to practically 0 wt% (Roedder, 1984). Major nonvolatile components of the solutes are typically Na, K, Ca, Mg, Cl, SO₄, and lesser amounts of many other ions. Usually, Na and Cl are the most abundant ions.

Carbon dioxide, as a liquid or vapor phase, is not uncommon in fluid inclusions and may be the dominant phase (Roedder, 1984). Other volatile components can include the noble gases, hydrogen sulfide, ammonia, nitrogen, hydrocarbons, sulfur dioxide, and other less common components (Roedder, 1984).

Fluid inclusions seldom have dimensions larger than 1 mm, although larger examples (hundreds of milliliters in volume) are known. The most abundant type of inclusion is the two phase liquid and vapor kind, characterized by a low viscosity fluid, with a ratio of liquid to vapor at room temperature greater than unity. (Roedder, 1984). In any given mineral, there are characteristically 10 to 100 times as many inclusions in the 1-10 micron range than in the >10 micron range. Most geothermometric studies are based on inclusions in the 10-100 micron range (Roedder, 1984). In total volume, fluid inclusions seldom comprise greater than a few tenths of a percent of the mineral sample, even though the sheer number of inclusions can be quite large. For example, white quartz or calcite is white usually due to the presence of approximately a billion inclusions in each cubic centimeter of mineral (Roedder, 1984).

Fluid inclusions may also contain daughter minerals that precipitated from the mother liquor in the inclusion. Clathrates (in the case of fluid inclusions, frequently a carbon dioxide rich phase) may also form from the liquid in the fluid inclusion, and the interested reader is referred to Roedder (1984) for a more complete treatment.

Fluid inclusions can yield valuable data concerning the conditions of formation of a host mineral. Standard techniques (geothermometry) involve cooling and heating inclusions under a microscope to glean data pertaining to the temperature that the inclusions were trapped, as well as the salinity of the fluid phase. This science of geothermometry was initially developed by Sorby in 1858. The use of fluid inclusions as geothermometers is a result of differential shrinkage of the host mineral and the inclusion fluid, with the inclusion fluid having a coefficient of thermal expansion far greater than the mineral matrix. Thus, when the temperature of a fluid inclusion is dropped to surface conditions, the liquid shrinks much more than the confining mineral, commonly forming a vapor bubble within the inclusion. Geothermometry, when coupled with other observed data and appropriate thermodynamic correlations and

corrections can give estimates of the pressure and approximate average density of the fluid at trapping. Fluid density data are important as they are the primary driving force in the circulation of fluids (Roedder, 1984).

The wide compositional variations observed in gases from fluid inclusions (Graney et. al., 1991) have been correlated with the distribution of mineralization in the host hydrothermal system. In the case of gold, this may be directly related to the concentration of H_2S , as the metal is transported in the aqueous form of $Au(HS)_2^-$ (Henley, 1987). This underscores the potential utility of using experimentally determined gas contents from mineral samples as applied to gold exploration. Accurate knowledge of fluid inclusion volatile concentrations allows the determination of the thermal and chemical equilibria, as well as revealing episodes of boiling and gas loss and two-phase entrapment (Hedenquist, 1987). Use of volatile gas ratio geothermometers may allow the determination of true field temperatures during drilling, thus avoiding the problem associated with establishment of equilibrium temperature in the drill hole after the thermal shock of drilling (Sass et. al., 1988, Roedder and Howard, 1988). There are other examples of the interpretations

of fluid inclusion gas compositions, for which the interested reader is directed to Hedenquist (1987), or Henley (1987).

Todd (1956), and Zimmerman (1966) pioneered the analysis of fluid inclusion gas compositions by mass spectrometry. Zimmerman and Todd both used conventional magnetic mass spectrometers. Utilized here is a relatively newer technique, involving the mechanical decrepitation of inclusions and the subsequent quadrupole mass spectrometric analysis of the volatile contents. This system was constructed after initial models developed by other institutions (Kesler et. al., 1986; Barker and Smith, 1986; Norman and Sawkins, 1987)

The Salton Sea Scientific Drilling Project produced well core and flow test ejecta, which when coupled with fluid compositional data from flow tests, provide a unique opportunity to calibrate and test a mass spectrometer system for fluid inclusion gas analysis. Calibration has been accomplished by comparing analyses of the volatiles evolved during the crushing of a mineral containing fluid inclusions with the volatile composition indicated by the analysis of flow test fluids, assuming that the minerals grow from fluids similar in composition to the modern geothermal fluids.

SALTON SEA GEOTHERMAL SYSTEM

The Salton Sea geothermal system (SSGS) is located in southeast California, at the southeastern end of the Salton Sea (Fig. 1). The SSGS is one of several active geothermal systems located within the Salton Trough, an active rift zone. The Salton Trough is comprised of the Imperial Valley of southern California, U.S.A., and the Mexicali Valley of northern Baja California, Mexico.

The Salton Trough is the landward region of the transition between East Pacific Rise extensional tectonics and the strike-slip tectonics of the San Andreas fault system (Elders et al., 1972; Elders, 1979). Geothermally active environments have been formed within many of the isolated rhombochasms (extensional basins) that link sections of transform type faulting within the Salton Trough.

The northern portion (Imperial Valley) of the rift has been largely isolated from the marine waters of the Gulf of California for the past 4 million years by trans-axial sedimentation from the Colorado River (Merriam and Bandy, 1965; Elders, 1979; Van de Kamp 1973; Winker and Kidwell, 1986; Winker, 1987). Water entering the restricted Salton Basin since that time has escaped primarily by evaporation. Both this closed basin nature, and the evaporitic sedimentary and

Figure 1 Map of the Salton Trough

extensional environment of this geothermal field contribute to its unique high salinity character (Elders and Sass, 1988; Herzig et al., 1988; McKibben et al., 1988b).

Most of the sediment deposition has occurred during flooding stages of the Colorado River producing the Pliocene-Holocene Lake Cahuilla, which intermittently filled the Salton Basin (Waters, 1983). Lacustrine and intervening low-desert sheetflood and playa stages extensively reworked and redistributed sediments in this shallow basin (Herzig et al., 1988). Mafic and felsic igneous rocks locally intrude these sediments (Herzig and Elders, 1988). In areas of geothermal activity, the sediment pile has also undergone extensive hydrothermal metamorphism, producing the greenschist facies observed at depths below 900 meters in core from the Salton Sea Scientific Drilling Project (Herzig, et. al., 1988), and even amphibolite facies hornfelses at depths below 3000 meters (Cho et al., 1988).

Drill core from the SSSDP revealed eight mineralized vein sets or principal vertical fracture zones (VFZ) (Andes, 1987). The inclinations of these fracture zones are vertical to subvertical. VFZ 1, 3, 6, 7, and 8 are sulfide-carbonate dominated. VFZ4 is

oxide-carbonate dominated, and VFZ 2 and 5 are sulfide-carbonate dominated by abundant late stage oxides (Andes, 1987). In fracture zones 2, 4, and 5 a final phase of hematite mineralization was found. Only fracture zones with this late stage hematite mineralization are now open, implying that they are presently interacting with the geothermal fluids (Andes, 1987). Thermodynamic analysis of mineralogic results from studies of core from two other SSGS wells, Magmamax 2, and River Ranch 1, established that equilibrium exists between modern reservoir brines and the late stage hematite bearing assemblages (McKibben, 1979; McKibben and Elders, 1985).

Salton Sea geothermal system sulfide ore deposition apparently is constrained by the availability of hydrogen sulfide, which is generated by the hydrothermal reduction of evaporitic SO_4 (McKibben and Eldridge, 1989).

DRILLING SUMMARY AND FLOW TEST RESULTS

In 1984, the Department of Energy, the National Science Foundation, and the United States Geological Survey undertook the Salton Sea Scientific Drilling Project (SSDP) to investigate the Salton Sea hydrothermal system. Spud-in for the Salton Sea

Scientific Drilling Project well, State 2-14 (S2-14), took place on October 23, 1985, and in the next 160 days a depth of 10,564 feet (3,220 meters) was reached. Thirty-six spot cores were taken, with a total of approximately 725 feet (221 meters) recovered from the well (Harper and Rabb, 1986). Fluid samples for scientific study and estimates of productivity from zones at 6,120 feet (1865 meters) and 10,475 feet (3193 meters) were obtained from two flow tests (Tables 1 and 2). Ejecta (primarily spongy epidote, but also containing a minor amount of hematite and pyrite (Charles et. al., 1988)) from the flow test of the 6,120 foot flow zone served as the source of some of the samples studied for inclusion volatile components.

Table 1.
State 2-14 Flow Test Results

First Flow Test - December 1985
Estimated Flow Zone 6120 Feet

Approximate Duration (Hours)	Flow Rate (lb/hr)	Wellhead Temperature (degrees F)	Wellhead Pressure (psia)	Estimated * Enthalpy (BTU/lb)
4	600,000	400	215	400
12	80,000	460	455	400
2	430,000	410	235	400
9	150,000	460	465	400

* Based on James correlation with TDS correction
From Harper and Rabb, 1986.

The average reservoir temperature inferred from the first flow test data was approximately 305 C (Thompson and Fournier, 1988) , with a TDS of the reservoir fluid of 25.0 wt% (Thompson and Fournier, 1988). The calculated density of the pre-flashed reservoir fluid at 305 C and 1870 meters depth ranges from 0.998 (no thermal loss prior to sampling) to 1.0107 g/cc (10% thermal loss) (Thompson and Fournier, 1988).

Of the common cation geothermometers in use, the Na-K-Ca method suggests a temperature of 310 C, which is closest to the measured temperature of 305 C in the production horizon (Thompson and Fournier, 1988). Typical analyses of the SSGS brines produced from the vicinity of the 6120 foot flow zone (Table 2) indicates that the fluids are rich enough in metals to be considered ore-forming fluids (White et al., 1963; Skinner et al., 1967).

The fluids from the flow tests are Na-Ca-K chloride solutions having approximate molar cation ratios of 0.68:0.20:0.12, with high concentrations of various metals, and had a TDS level of approximately 26 wt% (Williams and McKibben, 1989).

The composition of the fluid from the first flow test (indicated by results of Williams and McKibben in Table 2) is assumed representative of the composition

that may have been trapped in the fluid inclusions in minerals found in the iron rich epidote ejecta. This assumption (drawn from conclusions of Caruso et. al., 1988) is based upon thermodynamic analysis of phase relations among vein filling minerals and aqueous solutions at depths near 1867 meters (the first flow test) and 300 C.

Table 2
S2-14 Flash Corrected Brine Analyses
Williams and McKibben Charles et. al.
(1988) (1989)

pH	5.4	5.3
Depth (meters)	1850-1890	1866
Na	53,000 ppm	57,250
Ca	27,400	29,900
K	16,700	18,920
Fe	1,560	1,560
Mn	1,450	1,400
SiO ₂	>461 (a)	774
Zn	518	580
Sr	411	450
B	257	296
Ba	203	200
Li	196	250
Mg	33	38
Pb	100	134
Cd	2.2	3.0
NH ₄ ⁺	333	268
Cl ⁻	151,000	157,600
Br ⁻	99	114
CO ₂	1,600 (b)	1,594
H ₂ S	15	3.71
H ₂	(c)	15.7
N ₂	(c)	17.3
CH ₄	(c)	32.5
SO ₄ ⁼	65	7.4

(a) Silica samples low due to precipitation prior to and during sampling.

(b) Volumetric analysis of total non-condensable gas.

(c) Not measured

SAMPLES USED

In this study, the minerals analyzed were calcites from core taken at 3017 and 3132 feet, epidote flow test ejecta, and hematite from core taken at 4681 feet.

Calcite from core samples that were analyzed for volatiles in this study came from or were proximal to VFZ2, which occurs at a depth of 913 - 922 meters. In VFZ2, the filling minerals are, in order of decreasing abundance, epidote, calcite, quartz, chalcopryrite, pyrite, hematite, sphalerite, and galena (Andes, 1987). The calcite in VFZ2 is typically found as large, anhedral to subhedral, extensively fractured masses. Fluid inclusion homogenization temperatures for this zone were found to cluster around 240 C, with salinities approaching 16 wt% (Andes, 1987).

Fluid inclusion studies (Andes, 1987) of calcite, sphalerite, and quartz in vertical fracture zones 1, 2, 3, 4, and 7 indicated that salinities of the mineralizing fluids increased with depth from 12 to 26 wt.% NaCl equivalent. Several of the transparent minerals in VFZ 5, 6, and 8 were examined but no fluid inclusions were found that could be used for data collection (Andes, 1987). In fluid inclusions from this zone and in SSSDP core in general, no daughter minerals or clathrates were observed (Roedder and Howard, 1988).

Hematite analyzed for volatiles in this study came from VFZ4, which occurs at a depth of 1415 - 1438 meters. Fracture filling minerals in this zone are, in order of decreasing abundance, epidote, calcite, hematite, pyrite, quartz, and chalcopyrite (Andes, 1987). In this zone, specular hematite displays radial, fan-like growth patterns in the open space of partially filled fractures, and occurs as a bladed network of grains in totally filled fractures. Fluid inclusion homogenization temperatures for this zone were found to be approximately 285 C and exhibited salinities approaching 22 wt% (Andes, 1987).

The epidote analyzed for volatiles in this study came from ejecta from the first flow test and were probably formed proximal to VFZ5, which extends from 1699 - 1670 meters. Vein filling minerals encountered in VFZ5 are, in order of decreasing abundance, epidote, chlorite, hematite, with subequal amounts of minor calcite, quartz, adularia, chalcopyrite and pyrite (Andes, 1987). In this VFZ, the epidote is present as both euhedral, acicular crystals and as more massive anhedral grains (Andes, 1987, Charles et. al., 1988). The actual samples that were analyzed for volatile contents were euhedral, acicular crystal groups of spongy epidote, with a very minor amount of chlorite,

pyrite, and hematite.

THEORY OF MASS SPECTROMETER OPERATION

In a quadrupole mass spectrometer, several discrete steps are involved in the measurement process. Initially, the sample gas must be introduced into an area where it is ionized by a thoriated iridium filament. This is accomplished by the principle of electron-impact ionization.

The mass spectrometer utilized in this study has an enclosed source that ensures that the sample gas has the greatest probability of coming into contact with electrons from the filament to become ionized. This higher sensitivity allows for smaller overall sample sizes than can be measured using an open source spectrometer.

After ionization, the charged species are accelerated in a potential field and directed toward an ion detector, in this case an electron multiplier.

Before reaching the electron multiplier, the accelerated ions are introduced into a section where radio frequency electromagnetic fields are applied. When coupled with a ramped DC voltage, selected mass/charge numbers are allowed to pass to the electron multiplier. A single ion that impinges on the multiplier surface initiates a shower of secondary

electrons that essentially "multiplies" the original ion current. These secondary charges are then measured at the collector of the electron multiplier. Electron multiplier amplification can be varied by adjusting the applied voltage and can easily exceed 1×10^6 .

EQUIPMENT DETAIL

Components of the fluid inclusion mass spectrometric system include the vacuum maintenance system, the crushing apparatus, the quadrupole mass spectrometer, a host computer, pressure measurement instrumentation, a two-zone automatic temperature controller, and ancillary piping and valving (Fig. 2).

The instrumentation utilizes a VG/Fisons SXP300 quadrupole mass spectrometer with an enclosed source and electron multiplier detector. A pulse counting option was available but was not utilized for this study. This system can analyze from 1-300 AMU (Atomic Mass Units). The spectrometer was interfaced to and controlled by a standard IBM AT compatible computer using control and data acquisition software supplied by Fisons instruments.

The enclosed source of the mass spectrometer was directly fed from a sapphire seat controlled leak valve. This ensured that all liberated gases traveled through the mass spectrometer source.

A custom vacuum sample crushing assembly modified from a bellows-sealed Nupro valve (Fig. 3) was designed to accomplish several purposes. The system was desired to have the smallest possible volume in order to maximize pressure rise for small volume inclusion analysis. A small surface area was required to minimize adsorption effects. Our design had to allow for filtration of the small dust size particles generated during crushing to prevent them from entering and fouling the precision leak valve. The design needed to provide for an efficient and complete crush of the mineral. It was also desired to incorporate the ability to backflush and clean the filtration system after each crush. Ideally, an acceptable system should require minimal dismantling of the crushing chamber to remove the old mineral sample and replace it with a new specimen for analysis.

The system was fabricated from stainless steel and utilized flanges with copper gaskets for high vacuum sealing. A stainless steel frit with filtration down to 0.5 micron was utilized for dust removal purposes.

Figure 2
System Schematic

Figure 3
Crushing Assembly Detail
(Approximately to scale)

A turbomolecular pump provided clean and rapid pumpdown of the sample inlet assembly immediately following sample introduction. Use of high vacuum components allowed rapid pump-down to mass spectrometer background pressures of approximately 1×10^{-8} Torr. External heating tapes reduced adsorption of water and gases on surfaces within the vacuum system. These tapes were automatically temperature controlled in two zones. One zone heated the sample crushing and controlled leak valve area, while the other zone heated the mass spectrometer and ion pumps. A nominal setpoint for both zones was 100 F (38 C).

After a mineral analysis, the system was bled to 1-2 psi above atmospheric pressure with helium, as it poses the least adsorption problem on surfaces (de Boer, 1968). During bleed up, the helium served to backflush the frit to remove trapped dust particles from the previous mineral analysis. Helium was allowed to flow during vacuuming and removal of the crushed mineral to prevent internal contact with air during cleaning.

SYSTEM PARAMETERS

For this set of analyses, the standard machine settings for the Fisons SXP-300 quadrupole mass spectrometer are listed in Table 3 .

The emission, electron energy, source potential, and ion polarity settings affected the operation of the ion source. These are all located on the main SXP control unit. The emission potentiometer set emission current which was displayed on the panel meter on the main SXP control unit. The electron energy potentiometer set the electron energy (filament potential to source potential) in the range of 1-100 volts. Adjustment of the ion energy potentiometer set the potential (relative to ground) of the ionization chamber. The range of this adjustment is 0-50 volts. The ion polarity switch set the positive/negative ion measurement mode, and the multiplier/Faraday cup detector modes.

Resolution was set to 5.00 to give standard resolution. The control action of this parameter was more significant at higher masses. Resolution adjustment actually varied the DC/RF ratio. The Delta M potentiometer varied the DC offset and was set to 50%. The Delta M control action was approximately uniform over the adjustment range. The pole bias ten-turn potentiometer varied the mean potential of the mass filter, so that ions were accelerated or slowed so as to optimize peak shape and sensitivity. The range of adjustment was -500 to +500 volts.

Table 3 - System Parameters
(actual machine settings)

Emission 0.14e-3 Amps
Electron Energy 5.2 (52 volts)
Source Potential 1.0 (10 volts)
Positive Ion Polarity
Electron Multiplier 2.5 (2500 Volts)
Pole Bias -1.8 red scale (-90 Volts)
Delta Mass 50%
Resolution 4.72

CALIBRATION

In order to determine the instrument response to unknown gas samples, calibration was accomplished with pure gases and gas mixtures.

When a gas molecule is ionized, it is common for a number of daughter ion fragmentation products to be produced. For example, when carbon dioxide is ionized, carbon monoxide and other fragments are created. The relative amounts of these daughter products depend somewhat upon specific system parameters. Mass fragmentation patterns for the pure gases of interest and their ionization sensitivities with respect to nitrogen (a recognized standard in mass spectrometry) must be determined.

Manometrically prepared gas mixtures were utilized to calibrate the system. This is more cost effective, and was thus chosen. One problem associated with this method is that anticipated levels of the condensable components are significantly different from those that

can be prepared. Water, for instance, is practically impossible to manometrically prepare as an accurate mixture at almost any level.

Simple equimolar mixtures of nitrogen with carbon dioxide, ammonia, hydrogen sulfide, sulfur dioxide, and methane were manometrically prepared on a vacuum system. These samples, as well as pure individual standard gases, were transferred to the mass spectrometric system and individually analyzed. Results were stored and used as standards for evaluation of later analyses.

Another option for system calibration was to crush synthetically prepared fluid inclusions. Synthetic inclusions could possibly be manufactured to have volatile levels close to those expected to be measured in some natural minerals, while other volatile levels may be virtually impossible to synthesize. Synthetic inclusions are also expensive and may be subject to post-trapping fluid compositional changes, and post-decrepitation reactions and surface effects.

Determination of mass fragmentation patterns are fundamental if one desires to sort out effects from the superposition of mass isobars from different parent components. Table 4 indicates mass corrected average

fragmentation patterns that were found for each pure gas.

Table 4 - System Fragmentation Factors

Component	Mass Number (Percentage of Principal Peak)			
	1	2	3	4
Water	18(100)	17(18.9)	16(0.7)	20(0.20)
Nitrogen	28(100)	14(1.29)	15(.0047)	----
Methane	16(100)	15(67.7)	14(8.5)	13(2.8)
Ammonia	17(100)	16(58.6)	15(2.5)	14(.15)
Carbon Dioxide	44(100)	28(7.47)	16(2.45)	12(0.3)
Hydrogen Sulfide	34(100)	32(48.0)	33(37.7)	----
Sulfur Dioxide	64(100)	48(63.5)	32(2.0)	16(0.4)

Table 5 indicates the ionization efficiencies that were found for the manometrically prepared mixtures of pure gases and nitrogen. Ionization efficiencies measure how efficiently a gas is ionized, mass filtered and detected with respect to nitrogen. If a sample gas ionized as easily as nitrogen (ionization efficiency with respect to nitrogen = 1.0), an equimolar mixture of it and nitrogen would give equal ion currents with regard to principal peaks (e.g., water). By the same principle, if a sample gas has an ionization efficiency of 0.50, an equimolar mixture of this gas with nitrogen would yield ion currents of 2:1 nitrogen to the sample gas (e.g., ammonia).

Table 5 - System Ionization Efficiencies

Component	Molar Ionization Efficiency (With respect to Nitrogen)
Ammonia	0.45
Carbon Dioxide	1.375
Hydrogen Sulfide	1.14
Sulfur Dioxide	1.23
Water	1.06
Argon	1.6
Methane	0.45
Oxygen	0.65

SAMPLE PREPARATION

Mineral samples may be contaminated by unwanted volatiles from a number of sources. In this study, the main source addressed was contamination of permeable well cores and ejecta by drilling fluids. Over 400 barrels of diesel fuel and 800 gallons of polymer (Harper and Rabb, 1986) were consumed during the drilling of State 2-14, and these components were in intimate contact with all of the cores and some of the ejecta from the flow tests. This type of contamination could manifest itself by giving high results for organics and reduced sulfur compounds (sulfides and mercaptans originally from hydrocarbons used in drilling mud), which may suggest an incorrect oxidation state for the system.

In order to remove organic contamination from drilling mud, the samples were first cleaned with acetonitrile (Alexandrovskaya et al., 1980). The mineral samples were immersed in acetonitrile, allowed to soak

for 3 days, decanted, soaked in fresh acetonitrile for another day, decanted, and soaked in fresh acetonitrile once again for another day. The solvent was then decanted and each sample was boiled in distilled water for 30 minutes 3 times, using fresh water with each boiling. After the final boiling, the water was decanted, the minerals washed a final time with distilled water, and then they were stored in a vacuum oven at approximately 1 PSIA and 60 degrees C until the mineral was sorted and selected for analysis. Minerals were stored in this fashion indefinitely.

The minerals were sorted under a binocular microscope to assure that a typical pure mineral phase had been selected and not an assemblage of two or more minerals. No attempt was made to classify the actual fluid inclusions present according to size or type prior to crushing. As a result, the analyses reported effectively represent a mixture of all inclusions that were present in the samples. Andes (1987), and Roedder and Howard (1988) describe the different types of inclusions that were found in the SSSDP core material.

DECREPITATION METHODS

Decrepitation of inclusions may be accomplished in a variety of ways. The simplest and most straightforward method is to mechanically crush the

host mineral under vacuum, thus releasing the volatile components trapped in the crushed inclusions. Problems associated with this method include adsorption and chemical reactions on freshly created mineral surfaces during crushing, and the inability to distinguish between multiple generation inclusion populations. This type of system has the lowest cost and does not have to collect data as fast as the thermal or laser decrepitation methods (discussed below) because the latter try to resolve individual inclusions. Mechanical decrepitation has the advantage of being carried out at low temperatures, which tends to minimize some of the chemical reactive effects that might occur at higher temperatures. Andrawes et. al. (1984) describe mechanical decrepitation methods as applied to a GC-MS (gas chromatograph - mass spectrometer) system to analyze gas compositions in fluid inclusions.

A more exotic and costly method to release the fluids for analysis is by thermal decrepitation (Barker and Smith, 1986; Norman and Sawkins, 1987; Guha et. al., 1990). In this method the inclusions are burst by increasing the temperature until the internal fluid pressure exceeds the confining strength of the mineral matrix. This system also has the disadvantage of adsorption and reaction on freshly created mineral

surfaces, but such effects would be less pronounced than in the mechanical decrepitation method, as the time that a species spends adsorbed on a surface decreases with temperature (de Boer, 1968). Effects from water retention by hydrated salts left behind after decrepitation, which can be significant for samples with high TDS, may be attenuated using thermal decrepitation. Using this method, if the mass spectrometer has sufficient sensitivity and the data acquisition system is fast enough, individual inclusion gas compositions may be resolved during analysis. A disadvantage here, as pointed out in the previous paragraph, is that the inclusion contents are released at higher temperatures, thus increasing the possibility of unwanted side reactions. Also, the amount of surface area produced relative to mechanical crushing may be considerably less.

Still higher on the cost and complexity scale is laser decrepitation which utilizes a laser to burst single specific inclusions. Such a system minimizes the creation of fresh mineral surfaces and may target exclusively an inclusion that was previously analyzed for trapping temperatures and pressures. A possible problem that may be associated with laser decrepitation is in localized extreme temperatures during

decrepitation that may promote unwanted side reactions of the inclusion components. Sommer et. al. (1985) provide a more complete treatment of laser decrepitation methods.

The system constructed for this study has the ability to be upgraded to accomplish both thermal and laser decrepitation in the future, financial and manpower considerations permitting.

CRUSHING PROCEDURES

Optimum grain sizes and amounts for the minerals depend upon the apparent inclusion volume density in the mineral to be analyzed. The following amounts of individual minerals that were loaded for an analysis are typical of SSDP minerals.

Two to three spongy epidote grains approximately 2-3 mm in size were ideal for the existing crushing apparatus.

Calcite crush results were improved when ten to fifteen smaller grains (<1 mm) were utilized in the analysis. Calcite was more varied as far as size consistency of crushes within the same sample, where volatiles released from initial crushes were far greater than those released from later crushes. As a result, best results were obtained when care was taken during crushing, utilizing a slower, more gradual

crushing action than that used for the epidote or hematite.

Crush results for hematite were also improved if smaller particles were utilized for analysis. Hematite is more malleable than the epidote or calcite, and care was taken not to overtighten the crushing stem during decrepitation. The apparent fluid inclusion mass percent in hematite appeared to be less than that encountered in the calcite and epidote samples. As a result, it was necessary to use more hematite per analysis to attain ion currents similar to those yielded from calcite and epidote samples.

During crushing, the ion currents displayed on the computer screen were closely monitored so as to avoid exceeding the measuring range (saturating) for any of the gases analyzed. Slow controlled crushes tended not to saturate the detector signal on channels as often, thus saving a sample material as well as the time required for the system to return to a reasonable background level before the next crush.

After crushing, the system was bled with helium, and the crushed mineral remnants were then vacuumed from the crushing chamber. At this point a new sample was introduced into the chamber and it was pumped down.

ADSORPTION PHENOMENA

Different volatile species travel at different effective velocities through any system. This effect is primarily due to differential adsorptive tendencies of the volatiles onto the metal surfaces, the filter frit, and freshly generated mineral surfaces.

The component with the highest heat of adsorption is retarded the most (de Boer, 1968) and thus travels with an effective velocity lower than a component with a lower heat of adsorption.

As described by de Boer (1968), different components can have quite different values for the heat of adsorption on various surfaces, and as a result, such values are quite application specific. Helium has values typically <100 cal/mole, and gases like argon, oxygen, and nitrogen exhibit values that range from 3.5-4 kcal/mole. Heats of adsorption for carbon dioxide on different surfaces can range from 3.5 to 8 kcal/mole. Ammonia has heats of adsorption on various surfaces of approximately 8 kcal/mole. Water has a heat of adsorption 10 kcal/mole or higher on different adsorbents. Values of 10-15 kcal/mole are typical for many gases consisting of heavier molecules (de Boer, 1968).

The most extreme example of adsorption is

chemisorption, where adsorption is also accompanied by a chemical association with evolution of a large amount of heat, typically >100 kcal/mole. An example of this would be the chemisorption of oxygen onto tungsten, with a measured heat of adsorption of 147 kcal/mole (de Boer, 1968). Chemisorption effects are discussed here only to give some relative values to the heats of adsorption that occur in nature.

The average time of adsorption t (de Boer, 1968) that a species spends on the surface in the adsorbed state is related to the heat of adsorption Q by the following equation:

$$t = p(\exp[Q/RT])$$

where p = oscillation period of the molecules in the adsorbed state

R = gas constant

T = absolute temperature

It can be shown that $p = h/kT$ (h = Planck's constant, k = Boltzmann constant, T = absolute temperature) for a molecule that upon adsorption has lost exactly one degree of freedom of translation, whilst at the same time retaining all its degrees of freedom of rotation and of internal vibration (de Boer, 1968). At room temperature, this translates to a value for p of approximately 1.6×10^{-13} second.

Using 1.6×10^{-13} second as the value for p , a heat

of adsorption of 4 kcal/mole yields an adsorption time of 1×10^{-10} second; a heat of adsorption of 10 kcal/mole gives an adsorption time of 3.2×10^{-6} second; and a heat of adsorption (chemisorption, discussed here to emphasize the exponential effect of adsorption energies on the time spent adsorbed on a surface) for oxygen on tungsten of 147 kcal/mole gives an adsorption time of $1 \times 10^{+95}$ seconds. Obviously, the higher the heat of adsorption, the more time that the species will need to flow through to the source of the mass spectrometer. Other factors can change the effective velocity that a species exhibits traveling through a system, such as mean free path and system geometry. de Boer (1968) presents a more thorough treatment of these effects.

If water alone were adsorbed on metal and freshly created mineral surfaces during an analysis, gas ratios of other volatile components would not change. Alternatively, if other components are adsorbed along with water during the process, the relative gas ratios involving those components will change. Species with greater tendency for adsorption on the surfaces will be delayed and/or depleted more than less adsorbed components. Consequently, the apparent gas ratios of the analyzed components will change.

THERMODYNAMICS OF SELECTED REACTIONS

When a high temperature, single-phase fluid inclusion is trapped at depth and later brought to surface temperature and pressure, a low pressure (significantly lower pressure than that encountered at trapping) vapor-phase bubble commonly forms. The lower pressures in an inclusion with such a vapor phase will favor reactions that have a positive volume change. Further lowering of pressure upon decrepitation will additionally favor such reactions.

Consider the vapor phase decomposition of ammonia to form nitrogen and hydrogen (a), and the vapor phase reaction of water and hydrogen sulfide to produce sulfur dioxide and hydrogen (b).

Reactions (a) and (b) are favored at lower pressures due to the net increases in mole number of products over reactants. Thermodynamically (Table 6), the ammonia decomposition reaction is not expected to significantly occur at 1 atmosphere or even at 1×10^{-9} atmosphere (the approximate base pressure at decrepitation). The sulfur dioxide formation reaction (b) is not readily anticipated at 1 bar and 298 K, but

would convert significant reactants to products (if not kinetically limited) at decrepitation pressures of 1×10^{-9} atmosphere.

Table 6
Log K For Selected Reactions

	298 K(1 BAR)	298 K(10^{-9} BAR)
Reaction (a)@	-19.90	-2.14
Reaction (b)@	-5.75	3.13
Reaction (c)@	-40	-32
Reaction (d)@	46.7	46.7
Reaction (e)*	19.6	-15.92
Reaction (f)*	-19.6	15.92

@ Calculated from data in Robie et. al., 1979

* Calculated from data in Shock and Helgeson, 1988

The vapor phase was the site that the reaction was assumed to take place for reactions (a) and (b). Realistically, it is not known where these reactions may be taking place, in the vapor bubble, in the brine, or on a mineral wall with adsorbed metals (Cu, Pt, Li, Ag, Au, etc..) acting as catalysts.

A series of reactions that may also produce SO_2 have been suggested by S. Kesler (M.A. McKibben, personal communication). These reactions involve post-trapping processes (before decrepitation) accompanying vapor bubble formation and hydrogen diffusion (c), (d), (e), as well as the reaction after decrepitation (f) :

Thermodynamically, reaction (c) is not anticipated to significantly occur at 298 K and 1 bar, while reactions (d) and (e) (298 K and 1 bar) and reaction (f) (298 K and 10^{-9} bar) are expected to convert significant reactants to products (Table 6).

The level of 32 AMU detected by mass spectrometric analysis not attributable to H₂S (hereafter called excess 32 AMU) is greater than the amounts that are attributed to oxygen as predicted by the (c) and (d) reactions (Graney et. al., 1991). When coupled with thermodynamic considerations, oxygen contributed from post-decrepitation surface reactions and other components that generate 32 AMU fragments upon ionization (carbon disulfide, mercaptans, etc.) must produce the excess 32 AMU signal.

DATA REDUCTION AND ANALYSIS

Data were typically recorded in the multiple ion monitoring mode. In this mode of operation, selected AMU's were sequentially scanned (by peak hopping) and the values were written directly to hard disk drive in real time. Table 7 lists commonly scanned mass/charge

ratio numbers, and the possible source species that produce the measured ion currents during an analysis.

Table 7 - Source Components for Observed Ion Currents

Mass Number	Peak Identification (Most prominent source species capitalized,*Parent peak (100%) for compound)
13	METHANE
14	NITROGEN , METHANE , Ammonia
15	METHANE, AMMONIA
16	WATER,Ammonia,*Methane,Carbon Dioxide,Oxygen
17	WATER,*Ammonia
18	*WATER
20	WATER, Argon
28	HYDROCARBONS (C2-C4),*NITROGEN , Carbon Dioxide
32	HYDROGEN SULFIDE, *Oxygen, Sulfides
33	HYDROGEN SULFIDE
34	*HYDROGEN SULFIDE
40	*ARGON
44	*CARBON DIOXIDE
64	*SULFUR DIOXIDE

Scan rates are affected by the gain ranges used for the components that were measured, the accuracy at which the levels were to be recorded, and the number of channels (mass numbers) that were selected.

After the data were written to the hard disk and backed up on diskettes, they were loaded into the POST-SOFT computer software supplied by Fisons instruments. The POSTSOFT software allowed integration of individual ion currents that were stored during analysis. Since the analysis time integrated was the same for all species within an analysis, the areas under peaks were

proportional to the amount of each ion (AMU) that reached the detector.

The data were coupled with fragmentation patterns generated from the analysis of pure gases during calibration (Table 4) to yield ternary plots that gave insight into mixtures that may be causing the observed results (Figures 4 - 9). When coupled with both fragmentation patterns and ionization efficiencies, these data also yielded estimates of the apparent mole fractions of the evolved (or at least detected) volatile components (Table 8).

RESULTS

Thirty eight mineral crushes were selected based upon the general quality of the respective analyses. For example, runs with saturated channels, or with exceptional noise were discarded. Raw data from these runs are listed in Appendix A.

After the quality criteria were met, of these thirty eight analyses, 8 were of calcite vein mineral from core taken at 3017 feet, 9 were of calcite vein minerals from core taken at 3132 feet, 13 were of hematite vein mineral from core taken at 4681 feet, and 8 were from spongy epidote ejecta generated during the first flow test at 6120 feet.

Ion currents were integrated, mass corrected

and loaded into a spreadsheet which generated a file format that allowed normalization and plotting on a ternary diagram.

To calculate a representative mole fraction for the different species, mass corrected integrated ion currents for 44 AMU, 34 AMU, and 64 AMU were ionization efficiency (Table 5) corrected in a spreadsheet. Fragmentation factors (Table 4) were then used to subtract overlapping signals from other secondary peaks (e.g., remove H₂S and SO₂ contribution to the 32 AMU peak), and to estimate the 18 AMU level from the raw integrated 16 AMU data. Individual areas were summed, and the individual areas were then divided into the sum to determine a weight fraction for the respective species. Thus (for O₂ sensitivity=0.65, nitrogen sensitivity=1.00, 18 AMU=H₂O):

$$18\text{AMU} = (16\text{AMU}(\text{raw}) - 44\text{AMU}(\text{raw}) * .0245) / [(1.06) * (0.007)]$$

$$\text{H}_2\text{S} = 34\text{AMU} = 34\text{AMU}(\text{raw}) / 1.14$$

$$32\text{AMU} = 32\text{AMU}(\text{raw}) - 34\text{AMU}(\text{raw}) * (0.48) \\ - 64\text{AMU}(\text{raw}) * (0.02)$$

$$28\text{AMU} = 28\text{AMU}(\text{raw}) - 44\text{AMU}(\text{raw}) * (0.00747)$$

$$\text{O}_2 = 44\text{AMU} = 44\text{AMU}(\text{raw}) / 1.375$$

$$\text{SO}_2 = 64\text{AMU} = 64\text{AMU}(\text{raw}) / 1.23$$

$$\text{SUMAREA} = (18\text{AMU} + 28\text{AMU} + 32\text{AMU} + 34\text{AMU} + 44\text{AMU} + 64\text{AMU})$$

$$\text{PPMSO}_2 = 1 \times 10 + 6 * 64\text{AMU} / \text{SUMAREA}$$

Utilizing the above procedure to calculate mole fractions for volatiles evolved during an average hematite analysis, carbon dioxide levels were about an order of magnitude higher than expected (879 ppm expected vs 8501 ppm average), and hydrogen sulfide levels were approximately 2.5 orders of magnitude over what was anticipated (10.6 ppm expected vs. 5433 ppm average). Excess 32 AMU not attributed to hydrogen sulfide and sulfur dioxide, here interpreted as oxygen and sulfur, were detected (1789 ppm average, no sensitivity correction available), as was 64 AMU (sulfur dioxide, 1127 ppm average), and 28 AMU (nitrogen and hydrocarbons, 12,201 ppm average, no sensitivity correction available). Calculated results for the mineral analyses are presented in Table 8. Also indicated are the minimum and maximum values and the average and standard deviation for the mole fractions in the volatile species for the different minerals, and average results for all mineral samples.

Absolute mole fractions shown in Table 8 may be in error due to water and (to a lesser extent) carbon dioxide retention. Retention of other volatiles is also expected, but to a significantly lesser extent. This volatile retention is due to surface adsorption on system surfaces and freshly created mineral

Table 8. Calculated Volatile Mole Fractions
No Compensation for Water Adsorption
No Compensation for CO2 Adsorption

Calcite 3017 feet

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.952	9309.5	1136.6	10301.6	5775.0	718.8
MAX	0.970	11027.3	2328.3	28971.9	6350.2	902.6
AVG	0.963	10015.5	1748.6	18604.4	6056.3	796.4
STD	0.005	519.5	358.1	5326.3	197.3	62.0

Calcite 3132 Feet

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.947	9119.2	1213.9	11005.4	5220.3	810.7
MAX	0.971	11213.3	2100.6	33514.8	5902.7	1219.0
AVG	0.960	10094.5	1615.6	22112.3	5555.7	926.6
STD	0.007	668.8	263.9	7268.3	229.7	128.5

Flow Zone Epidote

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.970	10224.8	1121.1	7006.5	4943.7	752.1
MAX	0.975	12485.1	1447.6	10462.2	5385.6	1023.8
AVG	0.972	11310.8	1295.7	9254.9	5232.5	943.5
STD	0.002	759.6	108.9	1123.4	127.3	84.8

Hematite 4681 Feet

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.966	9429.6	1147.0	5292.5	4658.2	691.1
MAX	0.974	15244.8	2715.3	12554.4	5974.0	2055.8
AVG	0.971	12201.2	1787.9	8501.3	5433.6	1126.6
STD	0.002	1363.2	390.9	2092.2	441.2	415.8

Total Samples S2-14

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.947	9119.2	1121.1	5292.5	4658.2	691.1
MAX	0.975	15244.8	2715.3	33514.8	6350.2	2055.8
AVG	0.967	11054.6	1635.2	14010.5	5551.3	971.2
STD	0.007	1352.5	365.1	7441.9	413.0	284.1

Table 9. Calculated Volatile Mole Fractions

Water Adsorption Loss = 581 x

CO2 Adsorption Loss = 57 x

Calcite 3017 Feet

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.997	16.7	2.0	1057.5	10.3	1.3
MAX	0.999	19.5	4.2	3024.1	11.3	1.6
AVG	0.998	17.8	3.1	1924.6	10.8	1.4
STD	0.001	0.9	0.6	561.2	0.3	0.1

Calcite 3132 Feet

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.996	16.2	2.1	1128.7	9.3	1.4
MAX	0.999	20.3	3.8	3514.2	10.5	2.2
AVG	0.998	18.0	2.9	2296.1	9.9	1.7
STD	0.001	1.2	0.5	770.2	0.4	0.2

Flow Zone Epidote

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.999	18.0	2.0	715.5	8.7	1.3
MAX	0.999	22.1	2.6	1072.6	9.5	1.8
AVG	0.999	20.0	2.3	948.2	9.2	1.7
STD	0.000	1.4	0.2	116.4	0.2	0.2

Hematite 4681 Feet

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.999	16.6	2.0	541.7	8.2	1.2
MAX	0.999	27.0	4.8	1293.2	10.6	3.6
AVG	0.999	21.6	3.2	872.1	9.6	2.0
STD	0.000	2.4	0.7	216.3	0.8	0.7

Total Samples S2-14

	Xw	PPM28	PPM32	PPMCO2	PPMH2S	PPMSO2
MIN	0.996	16.2	2.0	541.7	8.2	1.2
MAX	0.999	27.0	4.8	3514.2	11.3	3.6
AVG	0.999	19.6	2.9	1447.0	9.9	1.7
STD	0.001	2.4	0.7	781.0	0.8	0.5

surfaces, and from the retention of volatiles in hydrated salts of non-volatile components in the brine. Assuming that post-decrepitation adsorption of water and carbon dioxide are the major effects changing the observed volatile levels, the observed volatile levels may be reconciled to those observed in flow tests of the SSSDP well State 2-14 by artificially (by spreadsheet) adding water and CO₂ to the analysis. If an amount of water 581 times that which makes it to the detector for the average hematite analysis is artificially added, and an amount of CO₂ 57 times that which makes it to the detector is also added, results similar to flow test analyses are obtained (Table 9).

Crushed optical grade quartz at 110 C and 0.5 Torr can adsorb water at 0.120 ml(STP)/gm and CO₂ at 0.018 ml(STP)/gm (Barker and Torkelson, 1975). Adsorption levels for water and carbon dioxide on two different basalts (Barker and Torkelson, 1975) are similar to the values given for the optical grade quartz. Using these values as an approximate guide, water is adsorbed 6.67 times as much (molar basis, 110 C) as CO₂ on freshly crushed optical grade synthetic quartz. On a molar basis, our results at 38 C that compensate for CO₂ and H₂O losses to reconcile Williams and McKibben flow test (Table 2a) results (581x for water and 57x for CO₂

molar basis, $\text{H}_2\text{S} + \text{SO}_2 \times (34/64) = 10.6$ ppmv, CO_2 in volatiles = 879 ppmv) indicate that the water is adsorbed on our system and on freshly created mineral surfaces 10.1 times as much as CO_2 . The difference in these relative adsorption ratios may be from temperature, pressure, high salinity host fluids in our samples, and different surface effects.

Reconciliation of average hematite crush results with data from Charles et. al. (Table 2b) indicate it is necessary to add 2350x the water detected and 234x the CO_2 detected to arrive at the volatile levels suggested by their results. This yields a ratio of water to carbon dioxide adsorption of 10.04 for our analysis system and freshly created mineral surfaces for the Charles et. al. flow test data. Significantly higher reconciliation values are from the reduced H_2S level in the Charles et. al. flow test data.

The data shown in Figures 4 - 9 include individual analyses of sequential crushes of mineral fragments, analyses of different fragments from individual mineral samples, analyses of calcite fragments from different depths, and analyses of different host minerals. These plots do not have any compensation for adsorbed components, and indicate trends in the levels of the species detected.

It is important to understand that the detector ion current response to a mineral crush is affected by several factors. The originally trapped inclusion contents may be subject to post-trapping chemical changes resulting from fluid inclusion cooling and vapor bubble formation. The pressure drop at decrepitation may further alter the volatile composition of the fluid inclusion contents. Post-decrepitation processes such as adsorption and surface reactions, coupled with the potential reactions of gases during ionization will also alter fluid inclusion apparent volatile compositions. Obviously, a complete treatment of the factors affecting detector response is beyond the scope of this study.

As Figure 4 indicates, H₂S principal and daughter peaks (34,33,32 AMU), and oxygen and sulfur (32 AMU), plot in a very tight cluster, indicating good analytical reproducibility for a variety of mineral hosts and implying that these inclusions release upon crushing and subsequent analysis a mixture of hydrogen sulfide with excess 32 AMU (oxygen and sulfur).

The calibration point for pure hydrogen sulfide is indicated on the plot, along with the points for pure sulfur and oxygen (32 AMU corner).

**Figure 4 - Sample Reproducibility and
Hydrogen Sulfide Fragmentation
32(S & O2) vs 33(HS) vs 34(H2S)**

As Figure 5 and Table 9 indicate, calcites from 3017 feet depth exhibit the highest CO₂ (44 AMU) levels, with significant variation between successive individual analyses of single mineral chips. Both epidote and hematite samples from greater depth indicate measurably lower concentrations of CO₂. Essentially constant H₂O (16 AMU, a minor peak of water) : H₂S (34 AMU) ratios argue against phase separation (boiling or effervescence) during trapping as a mechanism for such CO₂ variability, as hydrogen sulfide and carbon dioxide would both be preferentially partitioned into the vapor phase by such a process.

In Figure 6, masses 34 (H₂S), 44 (CO₂), and 28 (nitrogen and hydrocarbons) are plotted, and indicate chemical differences in fluid inclusion volatile contents from different minerals.

Transients in aqueous CO₂ concentrations during precipitation of calcite in the reservoir could have been recorded (e.g. loss of aqueous CO₂ due to precipitation of calcite in the formation, so that calcite trapped progressively decreasing aqueous CO₂ concentrations). Calcites exhibited the highest values and widest ranges in CO₂ concentrations, while epidotes clustered with mid-range carbon dioxide concentrations with the least variation. Hematites had the lowest CO₂

Figure 5 - Carbon Dioxide Variations
16 (Water) vs 44 (CO₂) vs 34 (H₂S)

Figure 6 - Carbon Dioxide Variations
34(H₂S) vs 44(CO₂) vs 28(N₂ and Hydrocarbons)

44 AMU

● Pure CO₂

+ CALCITE 3017 FEET

△ CALCITE 3132 FEET

□ EPIDOTE FLOW ZONE

◇ HEMATITE 4681 FEET

Pure H₂S
10*34 AMU

N₂ & C₂-C₃ Hydrocarbons
28 AMU

values, exhibiting intermediate concentration variations. A very minor portion of the elevated CO₂ values in calcites may be from the destruction of the calcite crystalline structure during crushing (M.A. McKibben, personal communication).

The reaction of methane with water, forced by hydrogen diffusion, effectively could alter carbon dioxide levels in the inclusions as indicated by (g).

Figure 7 indicates that inclusions generate during analysis a mixture of H₂S, oxygen and monatomic sulfur, and somewhat variable SO₂ as shown by pure gas calibration points. Although sulfur dioxide (64 AMU) concentrations are low, hematite samples appear to be significantly more variable as well as SO₂ enriched. A possible source for the SO₂ enrichment and variation in the hematite samples may be from the oxidation of pyrite inclusions in the hematite host (M.A. McKibben, personal communication).

The equilibrium Log K value for the reaction of oxygen and hydrogen sulfide to produce sulfur dioxide and hydrogen is 47 at 298 K. This K value indicates that complete conversion of H₂S and oxygen is to be expected at room temperature, if no kinetic barriers exist.

Figure 7 - Sulfur Dioxide Variations
SO₂(64 AMU) vs O₂ and S(32 AMU) vs H₂S(34 AMU)

In the absence of kinetic barriers, the oxidation of H₂S by water at the conditions encountered at the low pressures following decrepitation and the thiosulfate mechanism as proposed by Kesler are the most probable sources of SO₂ that has been observed (reactions (b), (c), (d), (e), and (f) previously discussed in the thermodynamics section). This may also explain the elevated SO₂ levels in hematite, which may also be enhanced by the oxidation of pyrite inclusions in the hematite host.

Figure 8 summarizes the apparent host mineral control of CO₂ (44 AMU), H₂S (34 AMU), SO₂ (64 AMU) levels in analyzed fluid inclusions. Epidote samples have very reproducible compositions. Calcite samples, however show wide variability in CO₂ at nearly constant H₂S/SO₂ while hematite inclusion populations indicate variable SO₂ at constant CO₂/H₂S. The possible sources of CO₂ variations were discussed above.

Variable sulfur dioxide levels in hematite were observed. Changing SO₂ concentrations in the mother liquor may have been recorded during mineralization and explain the observed variations. As discussed previously, the SO₂ variations may also be enhanced by oxidation of pyrite inclusions in the hematite host.

In Figure 9, plotted points for pure methane,

Figure 8 - Mineral Control of
Inclusion Composition
10x64(SO₂) vs 44(CO₂) vs 34(H₂S)

Figure 9 - Hydrocarbon and Ammonia
Constraints
10x13(CH) vs 14(CH₂ & N) vs 15(NH & CH₃)

14 AMU

Nitrogen

- + CALCITE 3017 FEET
- △ CALCITE 3132 FEET
- EPIDOTE FLOW ZONE
- ◇ HEMATITE 4681 FEET

10*13 AMU

15 AMU

ethane and ammonia indicate that the mineral inclusion data points are most likely due to a mixture of hydrocarbons with negligible contributions from ammonia. The ethane cracking pattern plotted in this figure is typical and came from data supplied with the mass spectrometer software.

CONCLUSIONS

A low cost quadrupole mass spectrometer coupled with a custom crushing apparatus can provide reproducible determinations of fluid inclusion gas contents.

The adsorptive effects of metal and freshly created mineral surfaces and the retention of water by hydrated salt complexes significantly reduces detected water and carbon dioxide.

Calibration is attainable by reconciling the differences between mass spectrometric analysis and flow test results. For our system, reconciliation with Williams and McKibben flow test results indicated that only 1/582 of the water and 1/58 of the CO₂ evolved in an analysis is not adsorbed on system and freshly created mineral surfaces and subsequently reached the detector. Mass spectrometric analysis of SSSDP epidote ejecta volatiles by others will allow the ultimate calibration of their respective systems for

H₂O and CO₂.

Variable carbon dioxide levels indicate trapping of single-phase fluids of differing compositions, rather than trapping of two-phase boiling or effervescing fluids. This is evident from relatively constant ratios of CO₂ relative to other gases including hydrogen sulfide, nitrogen, and hydrocarbons.

Calcite samples typically contained the highest carbon dioxide levels with the widest variation, perhaps implying precipitation of the host mineral during a transient event in which variable CO₂ levels were generated and recorded in the inclusion.

Enhanced CO₂ levels in the calcite samples may have also been due to the destruction of the calcite crystalline structure during crushing, (M.A. McKibben, personal communication) but are expected to have a minimal effect on analysis results.

Formation of sulfur dioxide probably involves the post-trapping oxidation of hydrogen sulfide by water promoted by the low pressures encountered at decrepitation, and also as a result of the thiosulfate mechanism as proposed by S. Kesler. Enhanced SO₂ levels in hematite may be from the oxidation of pyrite inclusions in the hematite host mineral (M.A. McKibben, personal communication).

Levels of 32 AMU in excess of that expected from pure H₂S could be due to a mixture of oxygen and sulfur generated during the decrepitation and measurement process. The portion of the excess 32 AMU signal attributed to sulfur is most likely generated during the ionization of sulfides and mercaptans originally sourced in the inclusion fluids. Another possible source for the sulfides and mercaptans is from drilling mud contamination.

The hydrocarbons observed in the inclusions appear to be dominated by methane and C₂ - C₄ compounds. These are most likely pyrolysis products of organics leached from Salton basin sediments.

APPENDIX A

DATA

In the following data sets, the run information is listed first. The mineral type, run identification number, well, and depth. This is followed by the areas that were calculated for the respective channels, started by channel 2, and following to channel 64 (11 channels total). To reproduce the results as indicated in Tables 8 and 9, the H2S values should be multiplied by 2.2, the CO2 values should be multiplied by 1.4, and the SO2 values should be multiplied by 2.1 .

EXAMPLE :

CALCITE,91092103,s2-14,3017 feet

AMU 2 Area (Proportional to mass of m/z 2 measured)

AMU 13 Area

AMU 14 Area

AMU 15 Area

AMU 16 Area

AMU 28 Area

AMU 32 Area

AMU 33 Area

AMU 34 Area

AMU 44 Area

AMU 64 Area

CALCITE 91090906 S2-14 3017 FT

2.7142E-07

1.049E-07

5.198E-07

2.336E-06

3.404E-05

5.454E-05

2.402E-05

1.183E-05

.0000147

4.566E-05

.0000019

CALCITE 91090907 S2-14 3017 FT

1.8256E-07

9.580001E-08

2.462E-07

1.106E-06

1.6464E-05

2.566E-05

1.1124E-05

5.854E-06

6.834E-06

.0000353

9.388E-07

CALCITE 91090909 S2-14 3017 FT

1.492E-07
6.74E-08
2.478E-07
6.522E-07
1.0616E-05
1.5736E-05
6.474E-06
3.5136E-06
4.0826E-06
2.5162E-05
6.408E-07

CALCITE 91090910 S2-14 3017 FT

2.4316E-07
5.899E-08
4.1302E-07
1.1072E-06
2.0288E-05
3.119E-05
1.28944E-05
6.7604E-06
8.356001E-06
3.647E-05
1.1932E-06

CALCITE 91090911 S2-14 3017 FT

1.439E-07
5.866E-08
1.9006E-07
5.666E-07
1.017E-05
.0000151
6.86E-06
3.3136E-06
3.8652E-06
2.9892E-05
6.568E-07

CALCITE 91090912 S2-14 3017 FT

1.117E-07
5.9E-08
2.234E-07
5.198E-07

9.396E-06
1.538E-05
6.54E-06
3.064E-06
3.616E-06
3.326E-05
5.012E-07

CALCITE 91091002 S2-14 3017 FT

2.422E-07
9.84E-08
4.41E-07
1.1712E-06
2.264E-05
3.316E-05
1.3462E-05
7.922E-06
9.606E-06
5.106E-05
1.4096E-06

CALCITE 91091003 S2-14 3017 FT

4.48E-07
1.4174E-07
7.110001E-07
1.9408E-06
3.5388E-05
5.348E-05
2.193E-05
1.1816E-05
1.4174E-05
8.256E-05
2.408E-06

CALCITE 91091211 S2-14 3132 FT

2.846E-07
7.44E-08
3.982E-07
1.388E-06
2.274E-05
3.618E-05
1.2328E-05
6.725E-06
8.222001E-06
3.246E-05
1.824E-06

CALCITE 91091213 S2-14 3132 FT

1.53E-07
4.659E-08
2.602E-07
7.422E-07
.0000119
1.76364E-05
7.091E-06
4.0124E-06
4.7122E-06
2.5314E-05
.0000011

CALCITE 91091214 S2-14 3132 FT

1.7E-07
6.12E-08
2.654E-07
6.972E-07
1.3104E-05
2.114E-05
8.454E-06
4.286E-06
5.118E-06
3.008E-05
8.362E-07

CALCITE 91091303 S2-14 3132 FT

1.8752E-07
5.732E-08
4.57E-07
8.592E-07
1.5418E-05
2.1534E-05
9.5748E-06
4.9724E-06
5.7764E-06
3.1624E-05
1.156E-06

CALCITE 91091304 S2-14 3132 FT

2.388E-07
6.766001E-08
2.941E-07
1.0292E-06
1.736E-05
2.754E-05

1.0186E-05
5.236E-06
6.132E-06
4.594E-05
.0000012

CALCITE 91091305 S2-14 3132 FT

1.5104E-07
4.884E-08
2.72E-07
6.716E-07
1.2856E-05
2.052E-05
8.372E-06
4.176E-06
4.75E-06
4.568E-05
8.314E-07

CALCITE 91091306 S2-14 3132 FT

2.2402E-07
7.1776E-08
5.09E-07
1.1258E-06
2.1172E-05
3.204E-05
1.1928E-05
6.086E-06
7.664E-06
5.726E-05
1.2812E-06

CALCITE 91091307 S2-14 3132 FT

2.9128E-07
1.0776E-07
4.338E-07
1.2848E-06
2.667E-05
4.1624E-05
1.39878E-05
7.56E-06
8.878E-06
1.0202E-04
1.5654E-06

CALCITE 91091308 S2-14 3132 FT

3.036E-07
9.246E-08
5.392E-07
1.4044E-06
2.4498E-05
4.402E-05
1.4628E-05
7.206E-06
8.717999E-06
9.886799E-05
1.4262E-06

HEMATITE 91090505 S2-14 4681 FT

0
0
5.4186E-07
0
1.9164E-05
3.388E-05
1.1654E-05
6.7282E-06
7.6818E-06
1.8848E-05
1.7326E-06

HEMATITE 91090506 S2-14 4681 FT

0
0
2.088E-07
0
5.72E-06
1.007E-05
3.974E-06
1.834E-06
2.31E-06
9.29E-06
5.5E-07

HEMATITE 91090610 S2-14 4681 FT

3.506E-07
0
9.839999E-07
2.126E-06
.0000306
5.736E-05

1.6216E-05
9.266E-06
1.0864E-05
2.1498E-05
4.98E-06

HEMATITE 91090611 S2-14 4681 FT

1.31E-07
0
9.634E-07
8.438E-07
1.32844E-05
2.8586E-05
8.416E-06
4.207E-06
4.8956E-06
1.2826E-05
1.808E-06

HEMATITE 91090612 S2-14 4681 FT

1.98E-07
0
8.980001E-07
1.2854E-06
2.1102E-05
4.0032E-05
1.2202E-05
6.3458E-06
7.734E-06
1.8536E-05
.0000016

HEMATITE 91090613 S2-14 4681 FT

2.84E-07
0
8.482E-07
1.45076E-06
.000026
.0000442
1.464E-05
7.33E-06
8.900001E-06
2.0496E-05
3.332E-06

HEMATITE 91090614 S2-14 4681 FT

3.488E-07
0
9.59E-07
2.186E-06
2.602E-05
4.458001E-05
1.5478E-05
7.428E-06
8.918E-06
2.334E-05
2.392E-06

HEMATITE 91091203 S2-14 4681 FT

8.168E-08
6.18E-08
3.1294E-07
5.3136E-07
7.08E-06
1.1798E-05
4.866001E-06
2.3654E-06
2.856E-06
7.980401E-06
4.982E-07

HEMATITE 91091204 S2-14 4681 FT

6.332E-08
4.616E-08
2.3098E-07
4.654E-07
5.482E-06
8.438E-06
3.4252E-06
1.8606E-06
.0000022
6.546E-06
2.95E-07

HEMATITE 91091205 S2-14 4681 FT

8.41E-08
5.28E-08
2.887E-07
3.962E-07
4.624E-06
8.686E-06

3.304E-06
1.5908E-06
1.9026E-06
6.122E-06
2.8588E-07

HEMATITE 91091206 S2-14 4681 FT

7.6E-08
4.838E-08
3.114E-07
5.2E-07
5.772E-06
9.503999E-06
3.7232E-06
1.874E-06
.0000021
7.1708E-06
3.3868E-07

HEMATITE 91091207 S2-14 4681 FT

7.082E-08
4.702E-08
2.075E-07
5.562E-07
5.64E-06
9.72E-06
3.866E-06
1.757E-06
2.284E-06
8.530001E-06
3.644E-07

HEMATITE 91091209 S2-14 4681 FT

4.486E-08
1.812E-08
1.22E-07
1.966E-07
2.368E-06
3.266E-06
1.654E-06
6.49E-07
7.584E-07
.0000029
1.347E-07

EPIDOTE 91090604 S2-14 FLOW ZONE

0
0
7.300001
3.074E-06
4.554E-05
.0000774
2.518E-05
.0000146
1.676E-05
5.704E-05
3.08E-06

EPIDOTE 91090605 S2-14 FLOW ZONE

0
0
6.758E-07
1.9046E-06
3.302E-05
5.268E-05
1.846E-05
9.419E-06
1.181E-05
4.4898E-05
2.5744E-06

EPIDOTE 91090606 S2-14 FLOW ZONE

0
0
8.828E-07
2.698E-06
4.436E-05
7.526E-05
2.363E-05
.0000135
1.6126E-05
5.638E-05
3.2994E-06

EPIDOTE 91090607 S2-14 FLOW ZONE

0
0
1.106E-06
2.614E-06
3.702E-05
6.636E-05

2.112E-05
1.1652E-05
1.3724E-05
4.744E-05
2.949E-06

EPIDOTE 91090608 S2-14 FLOW ZONE

0
0
1.088E-06
2.4774E-06
3.872E-05
6.0782E-05
1.9976E-05
1.1496E-05
1.3166E-05
4.7488E-05
2.9334E-06

EPIDOTE 91090609 S2-14 FLOW ZONE

0
0
8.352E-07
2.232E-06
3.862E-05
6.658001E-05
2.188E-05
1.168E-05
.0000137
5.112E-05
3.01E-06

EPIDOTE 91091103 S2-14 FLOW ZONE

4.508E-07
1.02772E-07
6.772E-07
1.6808E-06
2.7492E-05
4.086E-05
1.515E-05
8.516E-06
1.00054E-05
2.532E-05
2.074E-06

EPIDOTE 91091104 S2-14 FLOW ZONE

1.41E-07
4.3776E-08
2.554E-07
6.2724E-07
9.839999E-06
1.448E-05
5.644001E-06
2.8836E-06
3.586E-06
1.009E-05
5.784E-07

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