

Mass spectrometric analysis of volatiles in fluid inclusions: aliquot calibration valve to simulate inclusion rupture

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Received 13 September 1995; accepted 2 April 1996

Abstract

Analysis of nano- to picomole quantities of gas released from microscopic fluid inclusions in minerals can be critical in determining details of the physical and chemical conditions under which mineral deposits formed. Such analyses can routinely be performed using quadrupole mass spectrometry of volatiles released by inclusion decrepitation as minerals are heated or crushed. However, steady-state calibration of mass spectrometric factors has proved inadequate to accurately quantify small amounts of inclusion gas mixtures analyzed under dynamic conditions. An on-line gas aliquot valve mass spectrometer calibrating system has been developed, using adaptation of an high-pressure liquid chromatography valve. By rapidly discharging controlled aliquots of standard gases or gas mixtures, dynamic calibrations simulate nearly all analytical parameters that affect volatiles released during mechanical rupture of fluid inclusions. Analytical sensitivity of the mass spectrometry system is non-linear in its dependence on partial pressure, an effect which could not be deduced using steady-state calibrations. After applying this additional correction, microsample measurements previously wildly in contrast with presumed trapping conditions now accurately reproduce fluid compositions known from geothermal well flow tests or bulk inclusion analyses.

1. Introduction

The growth of minerals in natural environments commonly allows surface irregularities to trap aliquots of the growth medium. Since the chemistry of this growth fluid is of critical importance to our understanding of geologic conditions under which such minerals formed (Giggenbach, 1980; Roedder, 1984; D'Amore and Truesdell, 1985; Hedenquist, 1986; Norman and Sawkins, 1987; Kesler, 1991; Landis and Hofstra, 1991), much attention has been directed toward quantification of fluid inclusion compositions as direct indicators of growth conditions.

Fluid inclusions, because of their small volumes,

are most commonly analyzed only for gross physical–chemical nature using non-destructive microthermometric techniques (Roedder, 1984, 1990). Bulk chemical analyses of inclusions in large amounts of mineral are also occasionally performed using gas chromatographic (Roedder, 1990; Takenouchi, 1991; Channer and Spooner, 1994) or cryogenic separation/mass spectrometric methods (Sommer et al., 1985; Norman and Sawkins, 1987; Landis and Hofstra, 1991; Norman and Musgrave, 1994). In recent years however, tremendous strides have been made in microanalysis of individual inclusions (or populations of small inclusions) by direct mass spectrometric techniques (Kesler, 1991).

Chemical analysis of minor volatile constituents

of 1–100- μm -diameter inclusions, containing only nano- to picomole quantities of species of interest, presents unique problems in extraction system and mass spectrometer calibration. The most sensitive mass spectrometric methods involve direct release of the inclusion contents into a scanning quadrupole or time-of-flight mass spectrometer, with quantification of the signal for each component of interest using a sensitive electron multiplier (EM) detector/amplifier (Barker and Smith, 1986; Landis and Hofstra, 1991; Barker and Underwood, 1992; Sloan, 1992; Williams and Taylor, 1996). Microanalytical techniques involve volatile release by rapid opening of inclusions under vacuum, and thus produce a dynamic gas transfer environment (Fig. 1). Release and pump-down of inclusion volatiles typically takes place over a period of microseconds (Barker and Smith, 1986; Barker and Underwood, 1992) when using high-temperature decrepitation, and seconds to minutes (Graney et al., 1991; Landis and Hofstra, 1991; Sloan, 1992; Williams and Taylor, 1996) using mechanical fracturing and gas transfer through a controlled leak. Under complex dynamic conditions, it appears wise to calibrate analytical system response under conditions which mimic the entire set of processes involved in analysis of bursting inclusions.

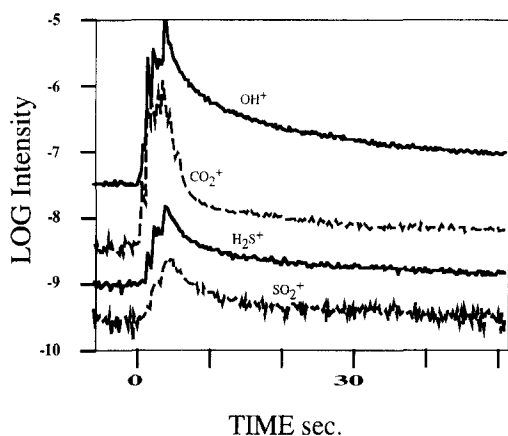


Fig. 1. Simplified multiple ion monitoring (MIM) ion intensity (*LOG Intens.*) vs. *TIME* plot of volatile release from natural fluid inclusions in quartz. Ion signals abruptly increase by several orders of magnitude (note individual inclusion sub-peaks) followed by a gradual return to background values. Traces represent OH^+ water fragment at 17 amu, H_2S^+ (34 amu), CO_2^+ (44 amu) and SO_2^+ (64 amu).

1.1. Previous work

1.1.1. Fluid inclusion volatile measurements

Bulk fluid inclusion sampling methods, in which large quantities of mineral are crushed or thermally decrepitated (Norman and Sawkins, 1987; Landis and Hofstra, 1991; Takenouchi, 1991; Norman and Musgrave, 1994), have been extensively used in investigations of hydrothermal ore bodies. Because of the large quantities of gas produced, the liberated condensible and non-condensable volatile fractions can be cryogenically separated, manometrically measured and then separately leaked under steady-state conditions into a mass spectrometer or gas chromatograph for quantification.

Natural mineral samples commonly contain multiple generations of fluid inclusions with radically differing compositions (Roedder, 1984, 1990). Unfortunately, such inclusion populations are combined in bulk analysis, with a consequent loss of valuable geochemical information. Microanalytical techniques are necessary to extract these details of chemically evolving mineral growth fluids. Direct mass spectrometric analysis of inclusion gases released by gradual mechanical crushing (Graney et al., 1991; Sloan, 1992; Williams et al., 1992; Williams and Taylor, 1996) or thermal decrepitation (Barker and Smith, 1986; Kesler et al., 1986; Norman and Sawkins, 1987; Guha et al., 1990; Landis and Hofstra, 1991; Barker and Underwood, 1992; Norman and Musgrave, 1994) have been performed in order to deduce the composition of small quantities of volatiles released from individual fluid inclusions. In microanalyses, gas adsorption on mineral and apparatus surfaces, as well as chemical (gas–gas or gas–surface) reactions are minimized by design of systems that facilitate rapid transfer of released volatiles directly into the mass spectrometer source (Barker and Smith, 1986; Guha et al., 1990; Graney et al., 1991; Landis and Hofstra, 1991; Barker and Underwood, 1992; Sloan, 1992; Williams and Taylor, 1996). The direct flow of volatiles released from inclusion decrepitation produces dynamic rather than steady-state conditions. Consequently, analyses record “bursts” of abrupt gas release provided by fracturing or decrepitation, and the somewhat more gradual pressure decrease as gases flow through the apparatus to the pumps (Fig. 1).

1.1.2. Mass spectrometer calibration

Ideally, all calibrations should be conducted under operating conditions identical to analyses, since source, analyzer and EM detector/amplifier mass-linearity, ion fragmentation, transmission efficiency and sensitivity vary somewhat with changes in instrument settings or mass spectrometer pressure. Comprehensive fluid inclusion analytical system calibrations must address a variety of factors involving gas release, transport and mass spectrometric processes:

(1) Dynamics of transport of different gases through the analytical system.

(2) Mass spectrometer source ionization characteristics (ion fragmentation patterns) for each species of interest.

(3) Sensitivity to each volatile species.

(4) Mass spectrometer source, ion filter, detector/amplifier linearity.

Although several papers have discussed details of steady-state (Norman and Sawkins, 1987; Landis and Hofstra, 1991; Sloan, 1992) and dynamic (Barker and Underwood, 1992) ion fragmentation and relative ion sensitivity calibrations, little has been discussed concerning additional calibrations of extraction, gas transport dynamics or mass spectrometric response linearity to complex gas mixtures over the wide pressure ranges produced by abrupt fluid release from inclusions.

1.1.2.1. Steady-state calibration. For ease and precision in calibration, fragmentation and sensitivity have typically (Norman and Sawkins, 1987; Landis and Hofstra, 1991; Barker and Underwood, 1992; Sloan, 1992) been measured using a large reservoir of standard gas (or gas mixture) leaked into the ion source through an adjustable valve. This steady-state flow condition provides nearly constant gas pressure from which highly reproducible mass spectrometric readings can be obtained. Calibrated parameters of fragmentation and relative sensitivity, can subsequently be combined by matrix methods (Landis and Hofstra, 1991) and utilized to deconvolve complicated spectra provided by natural samples.

Mass spectrometer response linearity calibrations have not been specifically discussed in fluid inclusion analytical literature, but experience (Sloan, 1992; Williams et al., 1992; Williams and Taylor, 1996;

this study) indicates that quantitative calibration over several orders of magnitude total and partial pressure utilizing steady-state methods is quite difficult.

1.1.2.2. Calibration under dynamic conditions. The published record concerning quantitative mass spectrometer calibration under dynamic conditions is limited to empirical comparisons of data, to known or presumed compositions of synthetic or natural inclusion populations (Barker and Underwood, 1992; Sloan, 1992; Williams et al., 1992). Using thermal decrepitation of minerals dominated by a single volatile, Barker and Underwood (1992) illustrate that dynamic measurements of ion fragmentation compare well with steady-state calibrations. Thermal dehydration of calcium hydroxide gave constraints on sensitivity (Barker and Smith, 1986), but this technique was unable to establish independent sensitivity calibrations for diverse gases, over wide pressure ranges. Using natural minerals from active geothermal systems of known fluid composition, Sloan (1992) and Williams et al. (1992) observed that despite similar dynamic and steady-state calibration factors for ion fragmentation and relative sensitivity, corrected fluid inclusion volatile analyses differed from presumed growth fluid compositions by orders of magnitude (SS^j, Table 1). Similar apparent errors in inclusion composition, most often anomalous low water content and high trace gas abundances, have been blamed on adsorption or the presence of gas-rich inclusion populations (Norman and Sawkins, 1987; Graney et al., 1991).

Sloan (1992) surmised that errors were due to preferential adsorption of certain gas phases, while Williams et al. (1992) attributed the error to inadequate calibration of dynamic aspects (including adsorption) of the analytical process. Relative rates of gas throughput in the Rapid Analysis of Total Fluid Inclusion Contents (RATFI_{NC}) mass spectrometer system (Sloan, 1992; Williams and Taylor, 1996; A.E. Williams, unpublished data), however, suggest that adsorption is an unlikely cause of observed errors, causing a change of focus to the present study of source, ion filter and EM detector/amplifier linearity.

Calibration under conditions which mimic the dynamic decrepitation process can alleviate many potential errors induced in single inclusion analysis

Table 1

Volatile ratio data for mineral growth fluids from Hansonburg Fluorite (FL), Broadlands BR-45 Quartz (BR) and Salton Sea State 2-14 Epidote (SS)

	CO ₂ /H ₂ O	H ₂ S/H ₂ O	N ₂ /H ₂ O	Ar/H ₂ O	He/H ₂ O
FL ^a	3.4×10^{-3}	5.3×10^{-4}	2.7×10^{-3}	4.0×10^{-5}	2.0×10^{-6}
FL ^a	1.8×10^{-3}	9.3×10^{-4}	2.6×10^{-3}	0.6×10^{-5}	2.0×10^{-6}
FL ^b	0.93×10^{-3}	1.1×10^{-4}	4.5×10^{-3} ^c	6.4×10^{-5}	1.6×10^{-6}
BR ^d	1.55×10^{-2}	5.3×10^{-3}			
BR ^d	1.57×10^{-2}	4.8×10^{-3}			
BR ^e	0.47×10^{-2}	6.0×10^{-5}			
BR ^b	1.34×10^{-2}	9.0×10^{-5}	1.1×10^{-3} ^c	1.6×10^{-5}	2.9×10^{-6}
SS ^f	7.9×10^{-4}	0.2×10^{-5}	1.4×10^{-5}		
SS ^f	8.7×10^{-4}	0.3×10^{-5}	1.5×10^{-5}		
SS ^g	9.1×10^{-4}	0.5×10^{-5}			
SS ^h	9.2×10^{-4}	0.5×10^{-5}			
SS ⁱ	8.8×10^{-4}	1.1×10^{-5}			
SS ⁱ	8.8×10^{-4}	0.7×10^{-5}			
SS ^j	95.2×10^{-4}	538×10^{-5}			
SS ^b	12.5×10^{-4}	1.05×10^{-5}	27.0×10^{-5} ^c	2.6×10^{-5}	

^a Bulk fluid inclusion data (Norman and Sawkins, 1987).

^b Fluid inclusion data, fully corrected average (this investigation).

^c 28-amu signal corrected for CO₂ fragment only.

^d Bulk fluid inclusion data (S. Takenouchi, from Hedenquist, pers. comm.).

^e Geothermal production fluid (Hedenquist, 1990).

^f Geothermal production fluid (Charles et al., 1988).

^g Geothermal production fluid (Michels, 1986).

^h Geothermal production fluid (McKibben et al., 1987).

ⁱ Geothermal production fluid (Williams and McKibben, 1989).

^j Fluid inclusion data, steady-state corrected average (Sloan, 1992).

methods. Although dynamic calibration can be performed using natural inclusions of known composition (Norman and Sawkins, 1987; Barker and Underwood, 1992; Sloan, 1992; Williams et al., 1992; this study), or with artificial inclusions or microcapillaries (Norman and Sawkins, 1987; Böhlke and Irwin, 1992), these techniques are limited, respectively, by the range of natural gas compositions available and the difficulty of producing artificial micro-standards.

2. Design of calibration and analysis system

This study describes development of an on-line, high-vacuum aliquot valve calibration device to repetitively dispense known quantities of gases or gas mixtures to the analytical system. This system is intended to directly calibrate the mass spectrometer under dynamic conditions, over a wide range in quantity and composition of gas.

The fluid inclusion analysis apparatus utilized in this study includes a mechanical decrepitation chamber with a maximum volume of 1 cm³ (CC, Fig. 2) constructed from an high-vacuum bellows valve modified to progressively apply pressure to 1–3-mm-diameter sample mineral grains. The chamber is easily disassembled to permit removal of crushed material and loading of fresh samples. This crushing chamber assembly mounts directly, via all metal high-vacuum flanges to an intermediate valved manifold and a Varian 951 conductance limiting valve (LV, Fig. 2) having a total volume of ~5 cm³ upstream of the mass spectrometer source. The intermediate manifold provides a valved port through which the chamber is evacuated after sample loading, and a connection to the calibration aliquot valve described below. The entire assembly is heated (typically 50–80°C) to discourage adsorption.

Downstream of the conductance limiting valve, the crushing assembly is connected to a ~30-cm³ volume including the enclosed source of a VG

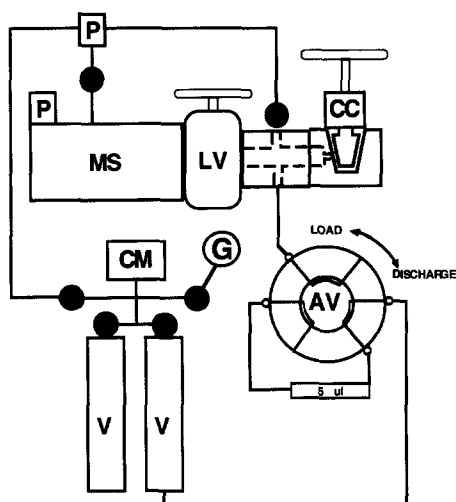


Fig. 2. Schematic representation of the fluid inclusion calibration, crushing, and analysis assembly described in the text. CC = sample crushing chamber; LV = leak valve to ion source; MS = mass spectrometer; P = vacuum pumps; G = calibration gas; CM = capacitance manometer; V = calibration gas mixing volumes; AV = rotary aliquot calibration valve; ● = vacuum valves.

SXP300 quadrupole mass spectrometer (MS, Fig. 2), forcing molecules to pass through the ionizing region, and providing the maximum possible sensitivity. The mass spectrometer itself has a volume of > 5 l and is continuously ion pumped and heated to maintain a low background. The ion pump is assisted by a liquid nitrogen trapped diffusion pump during analyses.

Ion detection and amplification by electron multiplier provides high sensitivity, and computer-controlled ion monitoring and data collection allow rapid recording of signals from the ion beams of interest.

The aliquot valve calibration system (Fig. 2) consists of a Rheodyne rotary injection valve originally intended for high-pressure liquid chromatography (HPLC) studies. Only stainless steel and fluoro-polymer contact the gases during use. The design described utilizes a six-port valve (AV, Fig. 2) with a 5- μ l external sample loop which can be alternately filled and discharged to the mass spectrometer assembly. One port is connected to the spectrometer valve block with a short length of wide-bore $\frac{1}{8}$ -in-o.d. (~ 3.2 mm) stainless-steel tubing, while another is similarly connected to the calibration gas reservoir (Fig. 2). Superfluous ports have been plugged and

act only as dead volumes which are pumped out between aliquots. Although fluoro-polymer sealing surfaces are used in this valve, vacuum-tight operation was possible at the moderate temperatures (50–80°C) used.

The calibration gas assembly includes two calibrated volumes of 50 cm³ (V, Fig. 2) and the various high-vacuum valves necessary for making controlled mixtures of volatiles. Gases are measured using an MKS 222 Baratron capacitance manometer (CM, Fig. 2) capable of reliable, linear pressure measurements over the range 0.1–30 Torr. This working pressure range was determined by the need to handle and mix dry gases and water vapor at pressures (< 10 Torr) below liquid H₂O saturation. The sample loop size (5 μ l, Fig. 2) was optimized to provide calibration gas ion signals similar in magnitude (Fig. 3a) to those from actual fluid inclusion gas discharges (Fig. 1).

3. Results and discussion

The 5- μ l volume aliquot valve provides 0.3 nmol/Torr which can be repetitively extracted from the gas reservoir, measured and rapidly released to the spectrometer for calibration. Release to the 5-ml volume upstream of the leak valve produces a rapid pressure drop of 10^{-3} Torr and leakage through the valve maintains ion source pressures at $\leq 10^{-5}$ Torr. A single aliquot calibration discharge of 4.1 nmol of air has been plotted in Fig. 3a, to illustrate the gross similarity in peak shape to that of gas “bursts” provided by fluid inclusion fracturing (Fig. 1).

Due to the small aliquot volume and the large (50–100 cm³) reservoir, an unlimited number of essentially identical calibration gas discharges (Fig. 3b) can be repetitively performed and averaged. Integrations under ion beam amplitude curves, for reasonably large peaks (N₂, O₂ and Ar, Fig. 3b) in calibration discharges of dry gases, reproduce within ± 1 –2% of the mean measured value. Repeatability of aliquot calibrations for minor constituents (CO₂, Fig. 3a and b) is often worse ($\pm 10\%$) due to background and digitization noise. Calibration statistics for polar phases such as water vapor (Fig. 4) are also poor (± 10 –15%), due to adsorption and the conse-

quently long integration time. It should be noted that even this poor precision is smaller than, or on the same order as natural variations between analyzed compositions of volatiles discharged by discrete inclusion ruptures from the same sample (Sloan, 1992; Williams and Taylor, 1996; this study). With care, single gas or simple mixture dynamic calibrations of fragmentation and sensitivity nearly as precise as those from steady-state calibrations can be made. Dynamic calibrations mimic most aspects of gas release, transfer and quantification of the abrupt "burst" of volatiles produced by inclusion rupture, whereas steady-state calibrations involve only mass spectrometer effects at relatively high, and unrealistically constant ion source pressures.

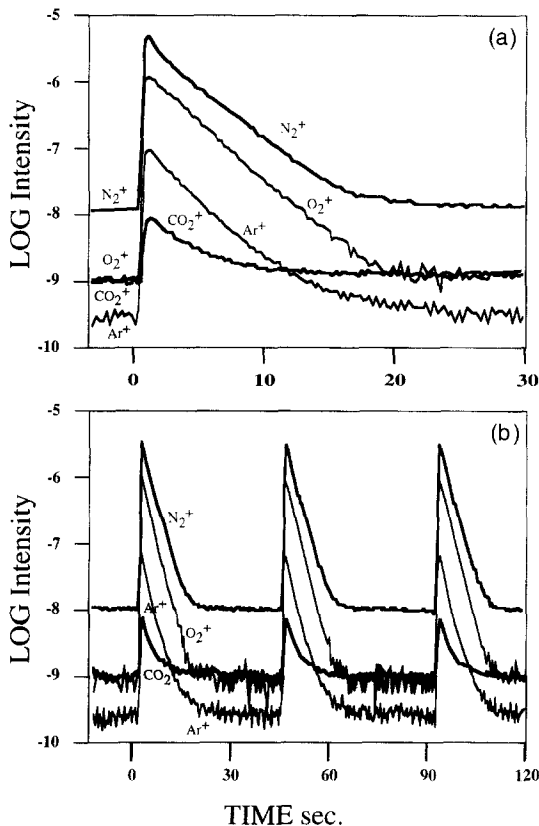


Fig. 3. a. *LOG Intens.* vs. *TIME* plot of mass spectrometer system response to a 5- μ l aliquot of air at 13.7 Torr. Traces represent dominant ion signals for N₂⁺ (28 amu), O₂⁺ (32 amu), Ar⁺ (40 amu) and CO₂⁺ (44 amu).

b. *LOG Intens.* vs. *TIME* plot of mass spectrometer response to a series of aliquots of air at 10.5 Torr. Traces shown are similar to (a).

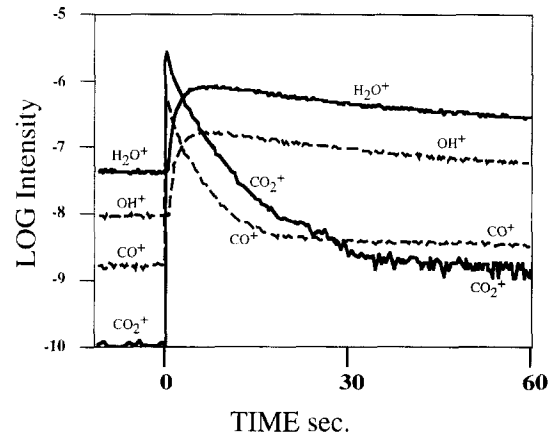


Fig. 4. *LOG Intens.* vs. *TIME* plot of mass spectrometer response to a 5- μ l aliquot of a mixture of 9 Torr H₂O (H₂O⁺ and OH⁺ fragment) and 1.5 Torr CO₂ (CO₂⁺ and CO⁺ fragment). Response curves differ due to adsorptive retention of water.

3.1. Ion fragmentation

Ion fragmentation data are necessary in deconvolution of complex gas mixtures where superimposed isobars (different ions with similar masses) must be separated. Ions of 28 atomic mass units (amu) serve as an example of such isobars in natural volatile mixtures, as this mass can be produced by any combination of ionized nitrogen (N₂⁺), carbon monoxide (CO⁺) or common ion fragments of carbon dioxide (CO₂⁺), organic compounds (C₂H₄⁺) or silicon-bearing gases such as SiF₄ (Si⁺).

Pure gases and known gas mixtures have been analyzed using the aliquot valve system to provide direct calibrations of ion fragmentation under conditions similar to inclusion rupture. Data illustrating the dependence of fragmentation on mass spectrometer source pressure are monitored as gas aliquots are discharged and gradually pumped away (Figs. 3a, b and 4). Such data can easily provide calibration of relative fragment abundance and linearity over a several order of magnitude range in source pressure (Fig. 5) as indicated by overall ion signal intensity. Calibration data for H₂O (Fig. 5) have been shown as an example.

In this graph, intensities of ion fragments due to single step ionizations (HO⁺, O⁺, H₂¹⁸O⁺; Fig. 5) show nearly linear relationships to the parent ion (H₂O⁺) intensity, (roughly proportional to ion source

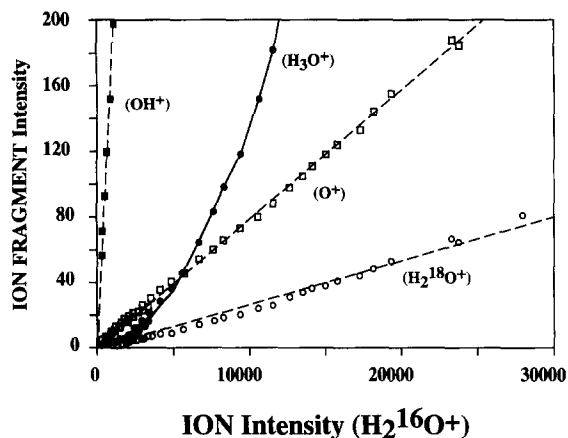


Fig. 5. Ion beam intensities of H_2O fragments (OH^+ , O^+ , H_3O^+ and $\text{H}_2^{18}\text{O}^+$) plotted against intensity of dominant $\text{H}_2^{16}\text{O}^+$ ion (roughly proportional to ion source H_2O pressure).

pressure), while those involving collisions of ions are strongly pressure-dependent (H_3O^+ , Fig. 5). Situations involving non-linear, pressure-dependent fragmentation must be carefully evaluated in deconvolving mixed gas analyses. An extreme example would be the quantification of fluorine (F^+ , 19 amu) ions in aqueous inclusion fluids which would need to be corrected for the non-linear, pressure-dependent 19-amu water fragment, H_3O^+ ion (Fig. 5).

Even in calibration gas mixtures where rates of release and transfer through the mass spectrometer differ due to adsorption (Fig. 4), the area beneath each ion intensity curve can be integrated to compute relative fragment ratios averaged over the whole gas "burst". To clearly illustrate differing adsorption dynamics of two gases, Fig. 4 accents only the initial stages of aliquot release. Integrations of the ion signals, however, would typically be performed to represent the entire analysis until all signals returned to baseline. The integrated area (ion yield, Σ_i) under each ions' (i) intensity curve (Figs. 1, 3 and 4) provides quantification of the total amount of each ion fragment produced by a calibration gas discharge to the mass spectrometer. If the overall shape of calibration curves (Fig. 3a and b) are similar to those of inclusion rupture (Fig. 1), integrated ion yield should provide a fragment ratio calibration that is a reasonable mimic of even non-linear fragmentation during inclusion gas "bursts". In the example shown in Fig. 4, both fragment production ratios and ioniza-

tion sensitivity of carbon dioxide (CO_2^+ , CO^+) and water (H_2O^+ , OH^+) can be evaluated by integrating curves produced from aliquots of known composition mixtures.

3.2. Absolute sensitivity and analytical system non-linearity

Integrations of ion yield (Σ_i) for discharges of known quantities of gas or known gas mixtures (Fig. 3 and Fig. 4) provide a direct measure of the absolute ionization sensitivity of the mass spectrometric system, observed (Σ_i) per mole (m) of any gas (Fig. 6). In addition to providing calibration factors with which to compute analyses of unknown gas mixtures, the wide partial pressure range and known discharge volume of the aliquot valve calibration system permits for the first time, direct evaluation of the pressure linearity of the entire analytical system.

The absolute sensitivity of our mass spectrometer system (Σ_i/m) to any gas under specific analytical conditions can be directly measured by integrating ion signals produced by known quantities of that calibration gas. Sensitivity of the system to nitrogen increases radically from 0.992 to 2.82 $\mu\Sigma_N/\text{nmol}$ as calibration aliquot size is reduced from 7.94 to 0.141 nmol N_2 (Fig. 6). Oxygen, argon and carbon dioxide absolute sensitivities measured over even wider pressure ranges in pure gases, artificial mixtures and in

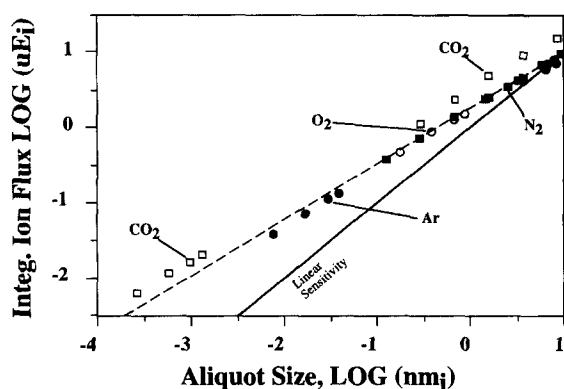


Fig. 6. Plot of integrated signal intensity ($\text{LOG}(\mu\Sigma_i)$) vs. aliquot quantity [$\text{log}(\text{nanomoles}) = \text{LOG}(nm_i)$] for air (Fig. 3a and b) and pure gas calibration aliquots. Filled squares = N_2 ; open circles = O_2 ; filled circles = Ar; open squares = CO_2 . Solid diagonal line indicates analytical linearity; dashed diagonal line is regression of nitrogen sensitivity relationship.

air also vary similarly. Data acquired for an array of separate calibration aliquots of air, and pure nitrogen, oxygen, argon and carbon dioxide (Fig. 3a and b) illustrate analytical system response to gases over a wide range of total and partial pressures (Fig. 6). In the example shown, none of the gas data show a direct, linear relationship (solid line, Fig. 6) between quantity of calibration gas released (nmol) and the observed ion yield (Σ_i).

The analytical non-linearity observed (Fig. 6) had not been noticed in any previous measurements of fragmentation of single gases (Fig. 5), or in steady-state, near-equimolar calibrations, but it becomes quite significant when gas mixtures having a several order of magnitude range in absolute and relative abundance are to be measured.

Pressure-related changes in sensitivity of the mass spectrometer system to different standard gases (Fig. 6) are apparently log-linear and nearly parallel, indicating that such variations may be computationally corrected in a straightforward manner. Sensitivity non-linearities under present analytical conditions appear to follow equations of the form:

$$\log(\text{nanomoles}) = 0.75 \log(\Sigma_i) + X_i$$

where the non-linearity is indicated by the $\log(\Sigma_i)/\log(\text{nanomoles})$ slope (Fig. 6) and relative sensitivities of different gases (i) are indicated by differing intercepts (X_i). Since actual fluid inclusion volumes and gas concentrations are often variable over 4–5 orders of magnitude, the large analytical non-linearity observed can, if not recognized, produce composition errors of several orders of magnitude when quantifying natural inclusion fluid compositions.

Because the aliquot calibration system described here remains on-line, non-linearity corrections and absolute sensitivities can be checked routinely by analysis of known gases between unknown fluid inclusion sample discharges. This convenience is important since analytical non-linearities may vary, not only between different systems, but also with varying operational settings of the mass spectrometer source, ion filter and detector/amplifier.

3.3. Relative sensitivity

Dynamic and steady-state calibrations with individual gases and known mixtures permit determination of the relative sensitivity of the mass spectro-

metric system to various volatile species. Such values are convenient for computing relative gas abundances from mass spectrometric data. On our log-log graph of absolute sensitivity (Fig. 6), differences between gases are indicated by intercept offsets between respective regression lines. For the atmospheric gases shown, nitrogen-relative sensitivities average 1.355 (CO_2), 0.921 (O_2) and 0.81 (Ar), quite similar to steady-state calibrations of the same mass spectrometer (1.375, 0.65 and 0.6, respectively) by Sloan (1992). Present analytical conditions produce nitrogen-relative sensitivities of 1.06 (H_2O), 1.23 (H_2S), 1.53 (SO_2), 0.65 (CH_4) and 11.5 (He), for other gases common in hydrothermal and magmatic environments.

3.4. Application to inclusion samples

In order to validate microsample calibration factors determined using the aliquot valve and dynamic conditions, volatiles in inclusion fluids were analyzed for minerals representing three distinctly different hydrothermal environments (Table 1; Fig. 7), where actual fluid compositions are known from field measurements and/or bulk fluid inclusion analyses. These samples include geothermal epidote crystals for which previous microsample inclusion analy-

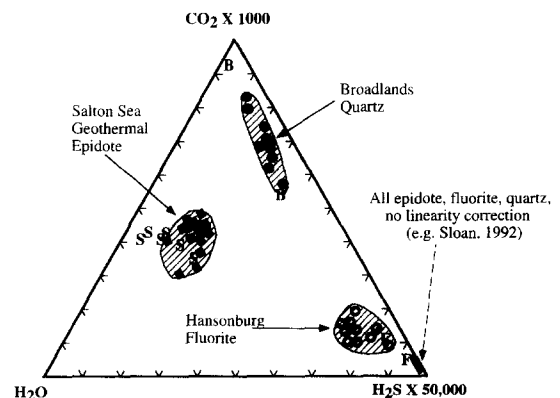


Fig. 7. Ternary plot of $\text{H}_2\text{O}:\text{CO}_2:\text{H}_2\text{S}$ molar compositions (Table 1) of known hydrothermal fluids (B = Broadlands geothermal system; S = Salton Sea geothermal system; F = Hansonburg ore deposit) and microsample fluid inclusion analyses (symbols and shaded fields). Inclusion analyses using steady-state calibrations only (Sloan, 1992) show anomalous H_2S - and CO_2 -rich compositions. Analyses with non-linearity corrections indicate compositions similar to known fluids.

ses (Sloan, 1992; Williams et al., 1992) indicated several order of magnitude composition errors when only steady-state calibrations were applied. Two other mineral samples which have been distributed as fluid inclusion standards were also utilized for validation.

Vein epidote samples ejected during testing of the 1866-m-depth flow zone (Caruso et al., 1988; Charles et al., 1988; Williams and McKibben, 1989) of the State 2-14 well in the Salton Sea geothermal system (SSGS), off California, were collected by the author. Presumed growth fluid compositions (S, Fig. 7) for these SSGS epidotes are constrained by measurements of thermal fluids produced directly from this and nearby veined fracture zones (SS, Table 1; Michels, 1986; McKibben et al., 1987; Charles et al., 1988; Williams and McKibben, 1989).

Fluorite samples from the Hansonburg Mississippi valley type (MVT) ore deposit in Nevada were distributed to fluid inclusion researchers by D. Norman. Volatile components in fluid inclusions of the Hansonburg fluorite sample (F, Fig. 7) are constrained by bulk inclusion mass spectrometric analysis (FL, Table 1; Norman and Sawkins, 1987).

Quartz fragments ejected during steam production from geothermal well BR-45 in the Broadlands geothermal system, New Zealand, were similarly provided by J. Hedenquist. The volatile composition of Broadlands quartz (B, Fig. 7) is constrained both by bulk gas chromatographic fluid inclusion analysis and by direct measurements of thermal fluids produced from well BR-45 (BR, Table 1; J. Hedenquist, pers. commun.; Hedenquist, 1990, respectively).

Inclusion volatile composition measurements of epidote samples, using steady-state calibrations (Sloan, 1992; Williams et al., 1992) and all recent analyses computed without the non-linearity correction (Fig. 6), plot near the H_2S -rich corner of the ternary molar plot (Fig. 7), far from the known compositions of SSGS and Broadlands geothermal fluids or bulk measurements of Hansonburg inclusions (Fig. 7). Fully corrected recent analyses of all three minerals, using the apparatus described in this investigation, are significantly modified by the non-linearity calibration, to compositions (filled circles, Broadlands; filled diamonds, SSGS; and open circles, Hansonburg) which correspond quite closely with those of presumed growth fluids (Table 1; Fig. 7).

4. Conclusions

HPLC valves and associated hardware are capable of leak-free operation at high-vacuum conditions. These relatively inexpensive and easily acquired components can be utilized to construct an on-line calibration system which mimics the dynamic gas release from decrepitating fluid inclusions. Although there appears to be recognizable adsorption of volatiles (particularly water vapor) on the valve and tubing surfaces, this can be minimized to acceptable levels by operating at low pressures and at elevated temperatures.

Calibrations for ion fragmentation and relative ionization sensitivity of various gases of interest can be determined under dynamic conditions nearly as easily and precisely as with previous steady-state calibrations. Additionally, known aliquot discharges permit direct measurement of absolute sensitivity, a parameter difficult to assess with steady-state methods. Aliquot discharges using single gases or gas mixtures provide all calibration parameters necessary for matrix deconvolution of mass spectrometric analyses of complex gas mixtures observed in actual fluid inclusions.

On-line dynamic calibrations of analytical linearity indicate that the mass spectrometric system utilized increases dramatically in its sensitivity as the quantity of gas decreases. Such non-linear effects, quite important over the wide range of partial pressures seen in actual analyses, have been nearly impossible to assess using only steady-state calibrations of single gases and nearly equimolar gas mixtures. Non-linearities, if present in other laboratories, may be responsible for some reported low water contents of inclusions and high trace gas abundances previously thought produced by adsorption effects or the presence of gas-rich inclusion populations.

Calibrations of mass spectrometric ion fragmentation, sensitivity and analytical system pressure-linearity can all be measured using discharges of single gases or of well-known gas mixtures, similar to "bursts" produced by actual fluid inclusion rupture. Calibrations which mimic dynamics of fluid release and pumpdown, have been shown to allow accurate computation of molar compositions from raw mass spectrometer data on fluid inclusions formed in environments of known composition. Such calibration

factors will presumably permit more accurate estimates of inclusion volatile compositions in minerals formed under otherwise unknown circumstances.

Aliquot valve calibrations involve simple hardware that remains on-line. Calibrations can therefore be made a routine part of fluid inclusion gas mass spectrometric analysis to control for variations in ion fragmentation, ionization sensitivity, transmission efficiency or detector sensitivity caused by aging of filaments or electron multiplier detectors, or when operating parameters change.

Acknowledgements

Development of the RATFI_nC mass spectrometry system at University of California, Riverside, was funded through DOE grant DE-FG03-89ER14088 to M.A. McKibben and A.E. Williams. Use of trade names is descriptive and does not constitute endorsement of specific products. The author gratefully acknowledges the helpful comments of C. Barker, editor S. Brantley and an anonymous reviewer. This is report No. 94/10 of the Geothermal Resources research group of IGPP/UCR.

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