In situ measurement of dissolved H₂ and H₂S in high-temperature hydrothermal vent fluids at the Main Endeavour Field, Juan de Fuca Ridge

Kang Ding [a],*, William E. Seyfried Jr. [a], M.K. Tivey [b], A.M. Bradley [b]

[a] *Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455, USA*
[b] *Woods Hole Oceanographic Institution, Woods Hole, MA 02543, USA*

Abstract

The first in situ measurements of dissolved H_2 and H_2S in high-temperature vent fluids were made at the Main Endeavour Field (Juan de Fuca Ridge) using the submersible *Alvin* and a newly developed electrochemical sensor. The measurements were successfully conducted in chimneys at sites of venting fluid and in pools of more quiescent hydrothermal fluid that underlie flanges on chimney structures at a depth of 2200 m below the sea surface. Fluid temperatures measured simultaneously with dissolved gas concentrations were up to 370°C. At the highest temperatures, dissolved H_2 and H_2S concentrations were 0.72 and 17.3 mmol/kg, respectively, which are consistent with data obtained at the same sites through conventional sampling methods. The relatively high concentration of dissolved gases measured by both techniques, however, may be linked to recent tectonic and volcanic activity. The ability to measure in situ dissolved gas concentrations simultaneously with fluid temperature in real time represents a major advance in the approaches available to study the origin and temporal evolution of seafloor hydrothermal systems at mid-ocean ridges. Although the present investigation is primarily based on sensor deployment for relatively short-term measurement of vent fluids, long-term monitoring of vent fluid holds great promise for further applications. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: hydrothermal vents; fluid phase; geochemical indicators; mid-ocean ridges; geochemistry

1. Introduction

Over the past decade, great progress has been made in our understanding of the chemistry of ridge crest hydrothermal systems. This has been largely driven by results of field and laboratory studies taking full advantage of recent advances in analytical and theoretical geochemistry [1–4]. Unfortunately, direct determination of vent fluid chemistry at elevated temperatures and pressures has not been realized owing to the lack of chemical sensors that can operate at the unusually challenging conditions characterizing seafloor hydrothermal systems. Moreover, the absence of these chemical sensors effectively precludes development of a continuous monitoring capability. This is an especially serious need for H_2, H_2S,

* Corresponding author. Tel.: +1-612-626-1860;
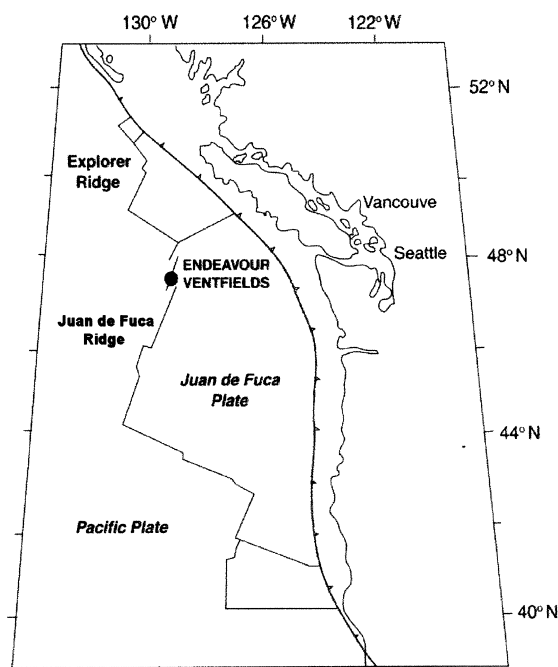Fax: +1-612-625-3819; E-mail: mlcd@tc.umn.edu

Fig. 1. Location map of the Juan de Fuca Ridge and the Main Endeavour Hydrothermal Field, at which in situ H_2 and H_2S measurements were made. Map was adapted from [12].

and pH, since these species are known to be highly sensitive to temperature and seawater mixing effects, and also play an important, although still uncertain, role in a wide range of geochemical and biologic processes, both at and beneath the seafloor.

Recent advances in material science and sensor technology have resulted in significant progress in the development of YSZ (yittria-stabilized zirconia) ceramic-based pH and H_2 sensors. These sensors have been used effectively in the laboratory at temperatures and pressures up to 400°C and 400 bars, and in fluids with dissolved Cl analogous to venting submarine hot springs ([5–9], and references therein). Here we extend these developments with the construction and testing of an array of sensors, which can be effectively operated in conjunction with the submersible *Alvin*, to conduct in situ measurements of H_2, H_2S and pH [10]. Following preliminary field tests in 1998 [11], we again deployed the sensor array on a series of *Alvin* dives to vents in the Main Endeavour Field (MEF) on the Endeavour segment (47°57′N, 129°06′W) of the Juan de Fuca Ridge (Fig. 1). Measurements were made on fluids venting from black smoker chimneys (Fig. 2), and on fluids ponded beneath flanges on the same vent structures (Fig. 3) at a depth of ~ 2200 m. These are the first real time, in situ chemical data reported for high-temperature vent fluids at mid-ocean ridges.

$\rightarrow$

Fig. 2. The in situ sensor being deployed at Sully vent (MEF). By gradually moving the sensor from cold seawater towards the hot fluid, temperature and concentration gradients can be recorded on a very fine scale. These data will enhance greatly our understanding of reaction processes in vent fluid–seawater mixing environments.

Fig. 3. In situ measurements of dissolved gases at Cantilever flange pool (MEF). (A) Letters designate sensor components, as follows: a: electronics package that processes mv signal from the sensor and allows communication with *Alvin* using an ICL; b: sensor head containing the array of electrochemical elements and thermocouples; c: sensor body, which is a pressure-sealed conduit linking sensor elements with the electronics package. The body is also the region of the sensor best suited for gripping by the *Alvin* mechanical arm (d). (B) The inset shows a close-up view of the sensor being used to measure the composition of flange pool fluids at Cantilever. It should be noted that the sensor head is tilted by about 30° to allow more easy access to vent fluids and flange pools.

Fig. 4. A close-up illustration of the configuration of the solid state sensor(s) used for H_2 and H_2S determination of vent fluids in the MEF. The YSZ pH sensor with titanium sheath is indicated by 'a', while 'b', 'c' and 'd' refer to the titanium J-thermocouple; H_2S electrode (Ag/Ag$_2$S), and H_2 electrode (gold), respectively. The protective titanium cap is depicted in the figure by 'e'. The distance between sensing electrodes is less than 0.5 cm.

Fig. 5. Examples of temperature and sensor signals $E(V)$ recorded in a real time mode during *Alvin* dive 3474 at flange pool at Cantilever. Temperature data are plotted in the time sequence shown (I), while data for dissolved H_2 and H_2S are simultaneously shown in (II) with the same time sequence. Data are labeled with letters from (A) to (E) for easy comparison and discussion (see text).
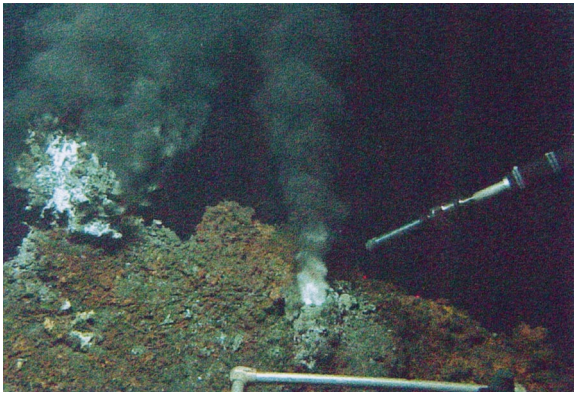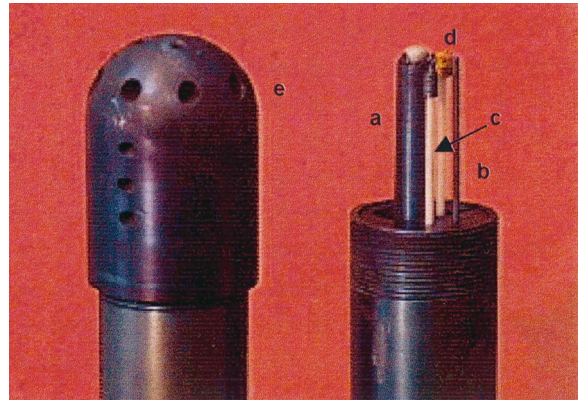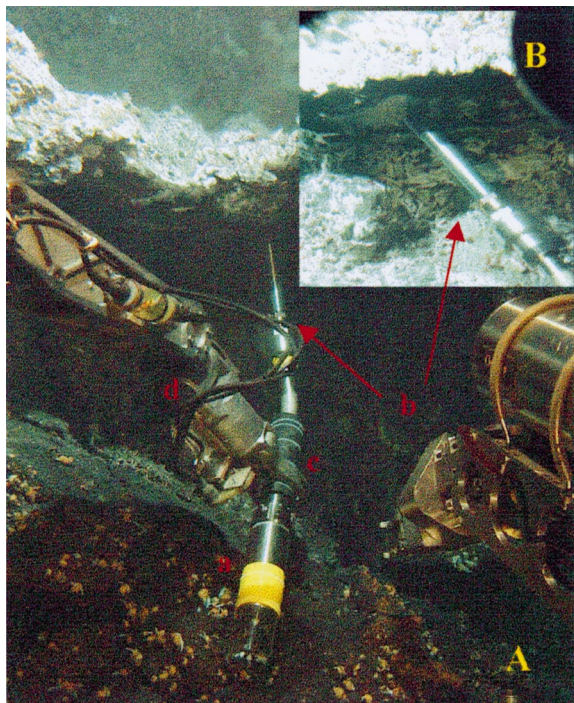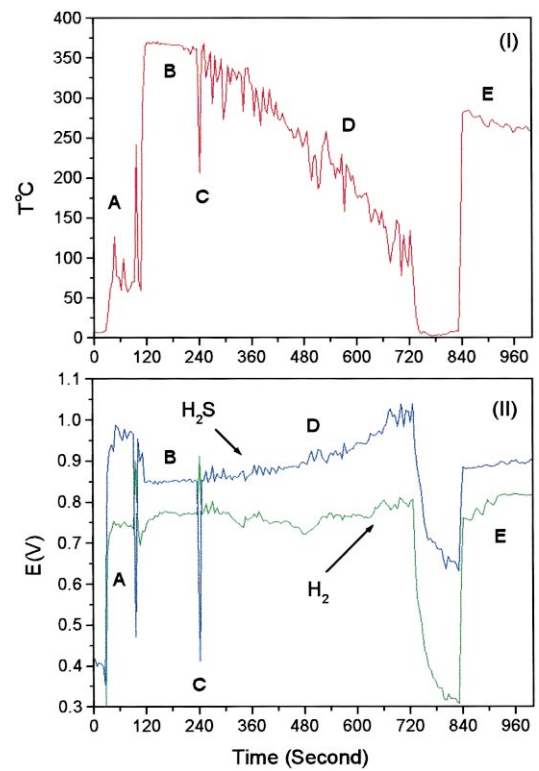
Fig. 2

Fig. 4

Fig. 3

Fig. 5

2. Sensor design and construction

To allow deployment in hot spring vent fluids (high temperatures/varying salinity), sensor design must take explicit account of material properties.

Thus, the external housing of the sensor was constructed entirely of titanium to achieve maximum stability and corrosion resistance in high-temperature, Cl^--bearing aqueous fluids. All titanium parts, however, were thermally pretreated to en-

hance formation of an oxidized surface layer thereby limiting further corrosion and precluding hydrogen generation during measurement of hydrothermal fluids. Moreover, at the sensor tip, the titanium case (2.5 cm o.d.) was specially designed to ensure fluid flow past the electrodes, while at the same time providing protection to the sensor if accidental impact with chimney walls were to occur. The total length and weight of the instrument are 1 m and 5 kg in air, respectively. To facilitate insertion of the sensor into vent fluids and flange pools using the *Alvin* mechanical arm, the head of the sensor was tilted at an angle of 30° (Fig. 3).

Signal processing involves two major sub-systems: solid state electrodes, which were constructed of highly corrosion resistant materials and situated at the head of the sensor assembly, and an electronics board capable of processing high impedance DC voltage from the sensors, and allowing data transfer to the submersible by an inductively coupled link (ICL).

The dissolved H_2 sensor was developed earlier and successfully tested in the lab at temperatures and pressures as high as 400°C and 400 bars [7,8]. It is characterized by a sensing element constructed of gold (Au) that is used in conjunction with an YSZ ($ZrO_2(9\%\ Y_2O_3)$)) membrane (YSZ), which serves as a reference electrode, as follows:

$$Au|H_2,\ H^+,\ H_2O|ZrO_2(Y_2O_3)|HgO|Hg \qquad (1)$$
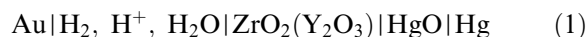
Gold is well suited for the sensing element for H_2 owing to its stability in Cl and H_2S-bearing aqueous fluids at elevated temperatures and pressures. Thus, H_2 fugacity (fH_2) can be determined directly from measured cell voltage $\Delta E(V)_{H_2;T,P}$, as follows:

$$\Delta E(V)_{H_2;T,P} = \Delta E_{H_2}^\circ - \frac{2.303 \cdot R \cdot T}{2 \cdot F} \log\left(\frac{fH_2}{a_{H_2O}}\right) \qquad (2)$$

where ΔE° is the standard state cell potential, aH_2O is the activity of H_2O, and R and F are the gas and the Faraday constants, respectively. Taking explicit account of the Henry's law constant $K_{H(H_2)}$ and activity coefficient (γ) for H_2 in NaCl dominated fluid [13–16], dissolved H_2 con-

centration (mH_2) can be obtained:

$$mH_2 = \frac{fH_2}{K_{H(H_2)} \cdot \gamma H_2}. \qquad (3)$$

In the case of dissolved H_2S, the conventional Ag/Ag_2S electrode was used in association with the YSZ pH electrode. Thus, the electrode configuration for determination of H_2S can be described as follows:

$$Ag|Ag_2S|H_2S,\ H^+,\ H_2O|ZrO_2(Y_2O_3)|HgO|Hg \qquad (4)$$
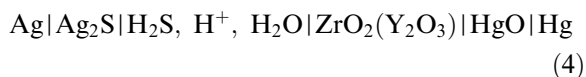
where measured emf potential ($\Delta E(V)_{H_2S;T,P}$) for Eq. 4 can be expressed as a function of H_2S fugacity (fH_2S) in a manner similar to that for H_2 (see Eq. 2):

$$\Delta E(V)_{H_2S};\ T,P = \Delta E_{H_2S}^\circ - \frac{2.303 \cdot R \cdot T}{2 \cdot F} \log\left(\frac{fH_2S}{a_{H_2O}}\right) \qquad (5)$$

Thus, the integrated system of sensors used to measure dissolved gases at Endeavour consisted of gold, Ag/Ag_2S, and YSZ electrodes. Moreover, a titanium shielded J-type thermocouple was included with the sensor array to constrain fluid temperature at the precise point of electrochemical response (Fig. 4). Indeed, all sensor elements, including thermocouple, were configured in such a way so as to restrict measurements to less than 0.6 cm from the tip of the sensor body. In order to limit the effect of temperature and concentration gradients on sensor response, the distance among the sensing electrodes and thermocouple tip was adjusted to be no more than 0.5 cm apart. To prevent damage to the YSZ ceramic by thermal shock, which occurs as a consequence of exposure to alternating hot and cold temperatures in the chimney/vent environment, a sheath of titanium was secured to the top 10 cm region of the YSZ electrode to help disseminate heat and enhance mechanical stability. As indicated by the aforementioned equations, sensor response is a function only of the activity/fugacity of H_2, H_2S and temperature. Thus, no additional data processing or corrections are necessary. In this way, more or

less continuous measurements can be made at a range of conditions in vent fluids providing valuable information on the effect of temperature (mixing) on the spatial variability of H_2/H_2S in and near the vent fluid environment.

Measurement of the chemistry and temperature of fluids was performed by voltage-monitoring electronics that in turn were powered by AA cells. Data communication was achieved by an ICL from the sensor electronics to a computer inside *Alvin*. The ICL interface allows non-contact serial communication via the pulsed ac magnetic field of a simple coil of wire, and can support half-duplex bi-directional communication at 9600 baud [17]. An RS-232 interface allows communication through the serial port of the computer within the submarine. WinWedge™ software was used to facilitate data acquisition, which was capable of recording data on a 5-s interval.

3. Results and discussion

Measurements were successfully carried out at four vent structures in the MEF (Hulk, Bastille, Dante, Cantilever), where temperatures were up to 370°C. Sensor response for H_2, H_2S, and temperature was both rapid and reversible. Indeed, measurements conducted in a flange pool at Cantilever vent over a period of 20 min revealed systematic co-variability of H_2, H_2S and fluid temperature, entirely in keeping with theoretical constraints (see below). As demonstrated by traces 'B' and 'E' (Fig. 5), for example, in situ measurements of H_2S and H_2 reveal steady state values that correspond well with steady state temperatures. This is confirmed further by trace 'C' (Fig. 5), which records a rapid reversal in temperature (370–210–370°C) and corresponding change in emf response for the H_2 and H_2S sensors changes that were triggered by a slight re-positioning of the sensor tip at the vent/seawater interface, where thermal and chemical gradients are unusually large. Fig. 5 also shows that at temperatures less than 125°C, chemical and temperature measurements are not in phase, providing evidence of the lower temperature limit for sensor response, which is in keeping with previous exper-

imental results [7,18]. Following attainment of steady state readings of temperature (± 2°C) and electrode potential (± 0.005 V), gas fugacity and aqueous activity/concentration of H_2 and H_2S were determined. Results indicate that at 330–370°C, H_2 and H_2S fugacity are 0.078–0.059 and 0.235–0.395, respectively. These values yield dissolved concentrations of H_2 and H_2S of 0.54–0.72 mmol/kg, and 5.43–17.3 mmol/kg, respectively.
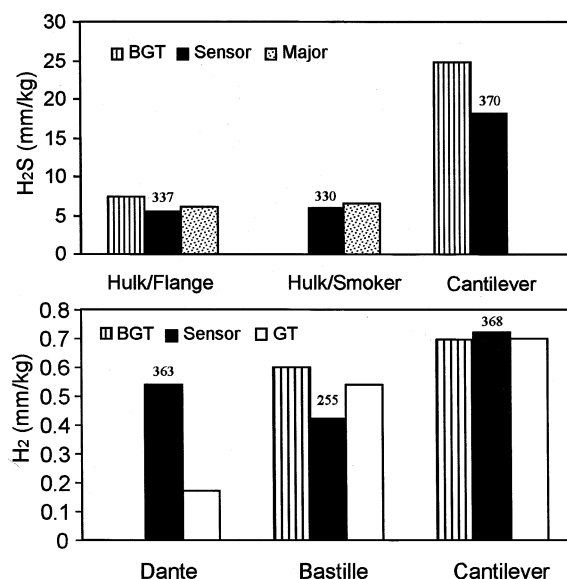

Fig. 6. Steady state concentrations of dissolved H_2 and H_2S measured for selected hot spring vent fluids and flange pools in the MEF. Fluid temperatures ranged from approximately 255 to 370°C, as labeled. In general, H_2 and H_2S concentrations are dominated by temperature and reaction zone characteristics unique to the different vent systems. The figure also provides a comparison of dissolved H_2 and H_2S concentrations obtained from the in situ sensor and for fluid samples at different vent sites using more conventional approaches. Major, GT, and BGT refer to major-element sampler, gas-tight sampler, and big gas-tight sampler, respectively. In all of these cases dissolved gases were determined by GC and the values presented are endmember concentrations (extrapolated to Mg = 0). Vent sites are indicated on the *x*-axis. Results show relatively good agreement between the different approaches. The apparent discrepancy for 'Dante' may be caused by the relatively low temperature (348°C) of fluid sampled and measured by the GT sampler in comparison with that measured by the in situ sensor, where the temperature was known to be significantly higher (see text).

Although H_2 and H_2S concentrations in fluids from specific vent structures tend to track together, large-scale intervent differences are apparent (Fig. 6). For example, the highest H_2 and H_2S concentrations are indicated for fluids issuing from chimney structures at Cantilever where the temperatures are highest and dissolved Cl concentrations lowest. Indeed, preliminary data for the Cantilever fluids reveal dissolved Cl concentrations as low as 18 mmolal (compared with approximately 550 mmolal for seawater). These results suggest phase separation processes very near the seafloor.

The reliability of the measured in situ concentrations of H_2 and H_2S can be constrained from data provided by analysis of fluid samples obtained from conventional gas-tight samplers and a newly developed internally pressurized gas-tight sampler [19]. The concentrations of dissolved H_2 and H_2S in these samples were determined by gas chromatography (GC) and conventional gravimetric methods on shipboard and onshore labs, and reported as endmember compositions [19,20]. As shown in Fig. 6, good agreement exists between these results and those obtained from the in situ sensors, although H_2 data from the Dante site differ in this regard. Unlike in situ sensor measurements, however, conventional fluid samples reported here did not permit simultaneous temperature measurement. Thus, the apparent discrepancy in the case of vent fluids at Dante may result from temperature variability. Dive records in fact reveal a fluid temperature of approximately 348°C just prior to acquisition of the conventional gas sample at Dante, which is nearly 15°C lower than the temperature recorded by the in situ sensor when deployed. At a seafloor pressure of 220 bars, even slight changes in temperature can cause relatively large changes in dissolved gas concentrations in fluid coexisting with an assemblage of iron oxides and sulfides [13–16]. This, together with the dynamic nature of the vent fluid/seawater environment, where changes in temperature and chemistry are likely, accounts best for the differences between results of the different measurement techniques. The capacity to measure continuously the dissolved concentration of inherently non-conservative species

in the mixing environment underscores the potential use of the sensor as a means of monitoring vent fluid chemistry for relatively long periods of time.

Interestingly, our measured in situ concentrations, as well as those measured using the conventional sampling devices, are substantially higher than previously reported concentrations at MEF, which, for high-temperature vent fluids, generally fall in the range of 0.16–0.42 mmol/kg H_2, and 2.9–4.9 mmol/kg H_2S [4,21]. Considering the general agreement of our results, different sampling and analytical approaches notwithstanding, the relatively high recently measured values can hardly be related to analytical uncertainties. Assuming a subseafloor pressure of 500 bars, results from the present study can be interpreted to indicate reaction with the relatively reducing assemblage, pyrite–pyrrhotite–magnetite (PPM) at temperatures up to 385°C [22]. Indeed, these investigators have argued that redox equilibria in subseafloor reaction zones evolve from an initially reducing state characterized by the PPM assemblage to a more oxidizing assemblage, which can be best represented by the assemblage, anhydrite–anorthite–clinozoisite–pyrite–magnetite. The shift in redox is hypothesized to be largely a function of changes in permeability that allow increasingly greater amounts of seawater-derived sulfate to penetrate into high-temperature reaction zones and react with calcic plagioclase, magnetite and pyrrhotite. Alternatively, the relatively reducing conditions at Endeavour discovered as a consequence of the present study may indicate the effect of an earthquake swarm which occurred about 3 months before the sensor measurements [23]. Indeed, preliminary data from Lilley et al. [20] reveal unusually high CO_2 concentrations in the same fluids having high H_2S and H_2, which based on comparison with other similar systems can best be linked to subseafloor tectonic events. Which of the two scenarios is correct is uncertain without the benefit of full analysis of the fluid chemistry, which has not yet been processed, together with additional time series measurements. Moreover, unpublished data from Butterfield [24] reveal conspicuously high H_2S concentrations in vent fluids at Endeavour in 1995, which may also

reflect subseafloor tectonic/volcanic activity. What is clear, however, is that the in situ sensor array deployed here represents a new tool with which the source of H_2 and H_2S variability can be better assessed, and ultimately, more accurately understood.
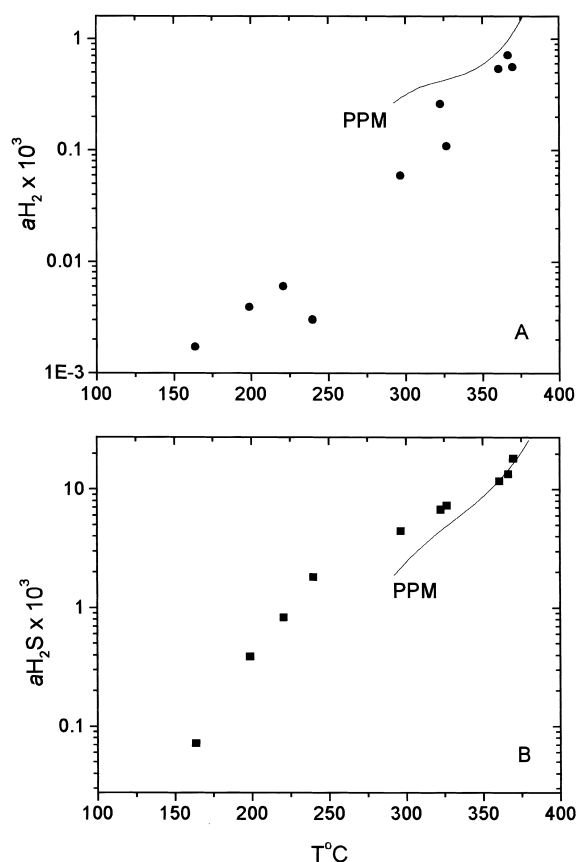

Fig. 7. Activities of dissolved H_2 and H_2S as a function of temperature at seafloor pressure. Results were determined from continuous measurement of fluid in a single flange pool at Cantilever (MEF) with the sensor gradually re-positioned to measure fluids at relatively higher and lower temperatures. For comparison, predicted aH_2 and aH_2S in fluid coexisting at equilibrium with PPM at 300–370°C are shown. By using activity terms, the effect of changes in salinity can be eliminated. Our results indicate that dissolved gases are at or near PPM levels at the highest temperatures measured, although both species decreased with decreasing temperature. The relative decreases for H_2 and H_2S, however, were not the same, suggesting species-specific kinetic effects. The temperature dependent changes cannot be accounted for by conservative mixing between seawater and endmember hydrothermal fluid.

In addition to making in situ measurements at steady state conditions to better understand phase equilibria controls, measurements were also carried out to constrain the role of seawater mixing and cooling on apparent rates of redox reactions as indicated by temperature dependent changes in H_2 and/or H_2S. For example, by gradually moving the position of the sensor in the flange pool, different temperature conditions could be studied. In effect, the hot-center (370°C), cool-outer (150°C) conditions reveal different degrees of mixing between hot hydrothermal fluid and cold seawater (trace 'D' in Fig. 5). Thus, this series of measurements allowed us to establish for the first time the spatial variability of dissolved gas concentrations and temperature in a hydrothermal vent. These data are plotted on Fig. 7, and reveal increases in H_2 and H_2S concentrations with increasing temperature. Indeed, the high-temperature data are in excellent agreement with a theoretical projection of H_2 and H_2S activity with temperature for the assemblage PPM, lending support to our previous interpretation on the nature of phase equilibria controls in subseafloor reaction zones at Endeavour. Perhaps more importantly, however, is that with cooling (seawater mixing), H_2 and H_2S concentrations decrease and increase, respectively, relative to values predicted for PPM. These data are very different than what would be predicted for simple conductive cooling, where it can be shown from experimental and theoretical data that H_2S should remain relatively unchanged with decreasing temperature, while H_2 should actually increase [22]. The difference, of course, is entirely related to thermodynamic and kinetic phenomena associated with seawater mixing reactions, which are largely non-conservative processes. That dissolved H_2S and H_2 concentrations are reduced at 300°C by approximately 75 and 90%, respectively, however, indicates the involvement of still other phenomena, which may require consideration of mineral precipitation kinetics. Even at temperatures as low as 200°C, however, the fluid still transports significant amounts of both dissolved H_2 and H_2S, which may be very significant in terms of energy sources for microbial ecosystems at mid-ocean ridges.

4. Implication

There can be no question that the results reported here reveal the development of an exciting new technology that can be used to study the composition of hot spring vent fluids at mid-ocean ridges. Thus, scientists in *Alvin* can now have access to real time chemical redox as well as temperature data. Although used here to measure vent fluid chemistry, the more important applications may involve monitoring to understand better a whole range of vent chemical, physical and biologic processes. There can be no question that present and future sensor applications will enhance greatly the range of observations and sampling strategies needed to unambiguously assess the origin and evolution of hot spring vent systems at mid-ocean ridges, and make progress in fulfilling the goal of using vent systems as natural laboratories for the study of complex hydrothermal phenomena.

References

[1] J.M. Edmond, C. Measures, R.E. McDuff, L. Chan, R. Collier, B. Grant, L.I. Gordon, J. Corliss, Ridge crest hydrothermal activity and the balances of the major and minor elements in the ocean: The Galapagos data, Earth Planet. Sci. Lett. 46 (1979) 19–30.

[2] K.L. Von Damm, Seafloor hydrothermal activity: Black smoker chemistry and chimneys, Ann. Rev. Earth Planet. Sci. 18 (1990) 173–205.

[3] K.L. Von Damm, Controls on the chemistry and temporal variability of seafloor hydrothermal fluids, in: S.E. Humphris, R.A. Zierenberg, L.S. Mullineaux, R.E. Thomson (Eds.), Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions, American Geophysical Union, Washington, DC, 1995, pp. 222–247.

[4] M.D. Lilley, D.A. Butterfield, E.J. Olson, J.E. Lupton, S.A. Macko, R.E. McDuff, Sediment involvement and phase separation in a volcanic-hosted mid-ocean ridge hydrothermal system, Nature 364 (1993) 45–47.

[5] L. Niedrach, A new membrane-type pH sensor for use in high temperature–high pressure water, J. Electrochem. Soc. 127 (1980) 2122–2130.

[6] S. Hettiarachchi, K. Makela, H. Song, D.D. Macdonald, The viability of pH measurements in supercritical aqueous systems, J. Electrochem. Soc. 139 (1992) L3.

[7] K. Ding, W.E. Seyfried Jr., In-situ measurement of dissolved H_2 in aqueous fluid at elevated temperatures and pressures, Geochim. Cosmochim. Acta 59 (1995) 4769–4773.

[8] K. Ding, W.E. Seyfried Jr., Gold as a hydrogen sensing electrode for in-situ measurement of dissolved H_2 in supercritical fluid, J. Sol. Chem. 25 (1996) 419–431.

[9] K. Ding, W.E. Seyfried Jr., Direct pH measurement of NaCl-bearing fluid with an in situ sensor at 400°C and 40 megapascals, Science 272 (1996) 1634–1636.

[10] K. Ding, W.E. Seyfried Jr., A.M. Bradley, M.K. Tivey (2001), in preparation.

[11] K. Ding, W.E. Seyfried, A.M. Bradley, M.K. Tivey, Real-time monitoring of chemistry in seafloor hydrothermal vents, EOS Trans. Am. Geophys. Union 79 (45) (1998) 67.

[12] D.J. Fornari, R.W. Embley, in: S.E. Humphris, R.A. Zierenberg, L.S. Mullineaux, R.E. Thomson (Eds.), Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions, American Geophysical Union, Washington, DC, 1995, 1–46.

[13] N. Kishima, H. Sakai, A simple gas analytical technique for the Dickson-type hydrothermal apparatus and its application to the calibration of MH, NNO and FMQ oxygen buffers, Geochem. J. 18 (1984) 19–29.

[14] N. Kishima, A thermodynamic study on the pyrite–pyrrhotite–magnetite–water system at 300–500°C with relevance to the fugacity/concentration quotient of aqueous H_2S, Geochim. Cosmochim. Acta 53 (1989) 2143–2156.

[15] K. Ding, W.E. Seyfried Jr., Activity coefficients of H_2 and H_2S in NaCl solutions at 300–425°C, 300–500 bars with application to ridge crest hydrothermal systems, EOS Trans. Am. Geophys. Union 71 (1990) 1680.

[16] W.E. Seyfried, K. Ding, Phase equilibria constraints on the chemistry of hot spring fluids at mid-ocean ridges, Geochim. Cosmochim. Acta 55 (1991) 3559–3580.

[17] A.M. Bradley, M.K. Tivey, S.P. Liberatore, A.R. Duester, Development and testing of thermocouple/thermistor

array packages for monitoring temperature at hydrothermal vent sites, EOS Trans. Am. Geophys. Union 71 (1995) 411.

[18] D.D. Macdonald, S. Hettiarachchi, S.J. Lenhart, The thermodynamic viability of yttria-stabilized zirconia pH sensors for high temperature aqueous solutions, J. Solut. Chem. 17 (1988) 719–732.

[19] J. Seewald, personal communication.

[20] M.D. Lilley, personal communication.

[21] D.A. Butterfield, R.E. McDuff, M.J. Mottl, M.D. Lilley, J.E. Lupton, G.J. Massoth, Gradients in the composition of hydrothermal fluids from Endeavour Ridge vent field:

Phase separation and brine loss, J. Geophys. Res. 99 (1994) 9561–9583.

[22] W.E. Seyfried, K. Ding, in: S.E. Humphris, R.A. Zierenberg, L.S. Mullineaux, R.E. Thomson (Eds.), Seafloor Hydrothermal Systems: Physical, Chemical, Biological, and Geological Interactions, American Geophysical Union, Washington, DC, 1995, 248–272.

[23] H.P. Johnson, M. Hutnak, R.P. Dziak, C.G. Fox, I. Urcuyo, J.P. Cowen, J. Nabelek, C. Fisher, Earthquake-induced changes in a hydrothermal system on the Juan de Fuca mid-ocean ridge, Nature 407 (2000) 174–177.

[24] D. Butterfield, personal communication.