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Direct pH Measurement of NaCl-Bearing Fluid with an in Situ Sensor at 400°C and 40 Megapascals

Kang Ding* and William E. Seyfried Jr.

The pH of concentrated NaCl-HCl fluids (0.57 mole of NaCl per kilogram of water) has been measured at supercritical conditions of water with a yttria-stabilized zirconia sensor in a titanium flow reactor. At 400°C and 40 megapascals, the in situ pH of the fluids, ranging from 3.3 to 6.2, differs greatly from its original value of 1.9 to 7.6 at ambient conditions. The measurements agree well with theoretical predictions, showing strong associations of HCl° and NaOH° complexes in high-temperature fluids. The pH sensor provides a powerful tool to investigate unambiguously the distribution of species in aqueous fluids at elevated temperatures and pressures.

The pH of hydrothermal fluids is a critical factor in assessing homogeneous and heterogeneous chemical reactions that occur in high-temperature aqueous solutions. Thus, direct pH measurement of chemically complex aqueous fluids at supercritical conditions (1) has long been a major challenge (2). At present, in situ pH is often indirectly estimated from pH measurement at ambient conditions (for example, $\mathrm{pH}_{25°\mathrm{C}}$) together with available thermodynamic data. Moreover, it is typically assumed that H^+- and OH^--bearing species in fluid at high temperatures (T) and pressures (P) behave conservatively with cooling. This often is not the case, however, especially for metal- and sulfide-bearing fluids, such as mid-ocean–ridge hydrothermal vent fluids (3). Considering the important role of pH in sea-floor and sub–sea-floor hydrothermal processes (4), direct determination of fluid pH at elevated T and P would lead to a significant advance in our understanding of these important hydrothermal systems.

Numerous efforts have been made to develop instruments suitable for pH measurement in hydrothermal fluids. For example, hydrogen concentration cells (5) and palladium hydride electrodes (6) have been used successfully to determine pH at subcritical T (<320°C) and relatively low P (<25 MPa). A yttria-stabilized zirconia (YSZ) (ZrO_2 with 9% Y_2O_3) membrane (7), however, provides an alternative method for measuring pH at relatively high T, and some preliminary measurements of low–ionic strength, high-pH fluids have been made at supercritical aqueous conditions (8–10).

Although these conditions may be appropriate for some applications, many natural geochemical systems (4, 11) and a wide range of industrial applications involving hydrothermal processes (12) are characterized by relatively high T, high P, high ionic strength, and low pH. For example, most axial hot-spring fluids are acidic, with dissolved Cl concentrations ranging from 40 to 200% of the seawater value (0.55 m), and have temperatures as high as ~400°C (13). Thus, to assess the viability of the YSZ membrane as a pH sensor in fluids with relatively high ionic strength (0.57 m NaCl) and low to moderate pH, we performed experiments at 400°C and 40 MPa and compared our results with theoretical predictions.

We performed experiments in a computer-controlled Ti flow reactor, which is especially resistant to corrosion by acidic NaCl-bearing fluids (9, 10, 14). An advantage of this facility is that the YSZ membrane and associated electrodes have direct access to the fluid phase at the experimental conditions, which ensures in situ measurements. Experiments commenced with the continuous flow (2 ml/min) of 0.57 m NaCl having $\mathrm{pH}_{25°\mathrm{C}}$ values between 1.9 and 7.6. We varied the pH of the source fluid by adding HCl. As the fluid flowed into the reactor, cell potential was measured with a Keithley (Cleveland, Ohio) 2001 electrometer with an input impedance of 10^{11} ohms. Uncertainties in the measurements were generally within ± 0.005 V at the 95% confidence level, which resulted in an uncertainty in $\mathrm{pH}_{T,P\ \mathrm{meas}}$ of <0.05.

The electrochemical cell for pH determination can be described as

$$\mathrm{Ag}|\mathrm{AgCl}|\mathrm{Cl}^-, \mathrm{H}^+, \mathrm{H_2O}|\mathrm{YSZ}|\mathrm{Hg}|\mathrm{HgO} \qquad (1)$$

As indicated, Ag/AgCl was used as a reference electrode (15), and because it was in direct contact with the test fluid, liquid junction potential was avoided. Other cell elements are described in (9, 10). Cell potential $\Delta E(V)_{T,P}$ as a function of $\mathrm{pH}_{T,P}$ can be described as

$$\Delta E(V)_{T,P} = \Delta E^\circ - \frac{2.303RT}{F}[\log a(\mathrm{Cl}^-) - \frac{1}{2}\log a(\mathrm{H_2O})] + \frac{2.303RT}{F}\mathrm{pH}_{T,P} \qquad (2)$$

where ΔE° is the cell potential at standard state, which can be calculated from the standard state potentials of $E^\circ_{\mathrm{Ag/AgCl}}$ and $E^\circ_{\mathrm{Hg/HgO}}$; R is the gas constant; F is the Faraday constant; and $a(\mathrm{Cl}^-)$ and $a(\mathrm{H_2O})$ are the activities of Cl^- and H_2O, respectively. Because the amount of HCl added to the test solution was negligible compared with the total amount of NaCl, the difference of the first two terms on the right side of Eq. 2 can be taken as a constant. In effect, changes in $\mathrm{pH}_{T,P}$ are reflected solely by changes in measured $\Delta E(V)_{T,P}$. Thus, at

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Department of Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455, USA.

*To whom correspondence should be addressed.

400°C, the Nernstian slope ($2.303RT/F$) depicted by Eq. 2 indicates that a unit change in pH is attended by a variation in potential of 0.134 V.

Fluid flowing from the reactor was routinely sampled (*16*). Fluid samples were analyzed for $pH_{25°C}$ and concentrations of Cl, Na, and trace elements (Zr, Y, Ca, Al, Si, Ag, and transition metals), which may originate from dissolution of sensor or reactor components. Other than $pH_{25°C}$, which was measured with an ORION Ross glass electrode, all analyses were performed by inductively coupled plasma mass spectroscopy or ion chromatography. The sensor and reactor components were extremely stable under experimental conditions: contaminant concentrations did not exceed a molality of 5×10^{-5} *m*, even for fluids with $pH_{25°C}$ as low as 1.9. Clearly, the YSZ sensor is highly suitable for use in natural or experimental systems, even under unfavorable conditions such as high temperatures, high NaCl concentrations, and low pH values.

In addition to its structural and chemical stability in corrosive fluids at elevated *T* and *P*, the sensor revealed rapid and reversible response to changes in acidity (Fig. 1). For example, when the source fluid was switched from an unacidified NaCl solution ($pH_{25°C} = 7.6$) to a distinctly acidic fluid ($pH_{25°C} = 2.6$), the sensor immediately recorded a decrease of 0.300 V. Subsequent increase of the source-fluid $pH_{25°C}$ to 3.5 resulted in a corresponding increase in cell voltage (Fig. 1).

The measured cell potential, which can be directly related to $pH_{T,P}$ (Eq. 2), can be compared with that theoretically predicted from the revised Helgeson-Kirkham-Flowers (HKF) equation of state for aqueous species together with other appropriate thermodynamic data (*17–20*). To carry out this independent assessment of cell potential, however, we had to calculate the distribution of aqueous species in the NaCl-HCl-H_2O system at 400°C and 40 MPa, explicitly taking into account mass action, mass balance, and charge balance constraints (*19*, *21*). The agreement between $\Delta E(V)_{T,P\ \mathrm{meas}}$ and the theoretically calculated cell potential $\Delta E(V)_{T,P\ \mathrm{calc}}$ is excellent (Fig. 2): The measured cell response is entirely consistent with available thermodynamic data for the system at the conditions investigated.

Perhaps the most definitive evidence of sensor response to $pH_{T,P}$ is the slope of the line depicting the change in $\Delta E(V)_{T,P\ \mathrm{meas}}$ relative to $pH_{T,P\ \mathrm{calc}}$, which can then be compared with the Nernstian slope. An excellent linear relation exists between $\Delta E(V)_{T,P\ \mathrm{meas}}$ and $pH_{T,P\ \mathrm{calc}}$ over the entire range of conditions investigated (Fig. 3). More importantly, however, the slope of the regression line (0.140 ± 0.004) agrees well with the Nernstian value of 0.134. Taken together, along with the data and relations depicted in Fig. 2, the Nernstian response between $\Delta E(V)_{T,P\ \mathrm{meas}}$ and $pH_{T,P\ \mathrm{calc}}$ provides strong support for the theoretical foundation and general validity of using the YSZ sensor to measure the pH of aqueous fluids at elevated *T* and *P*.

As a final analysis, we compared $pH_{T,P}$ determined from $\Delta E(V)_{T,P\ \mathrm{meas}}$ and theoretically predicted values (*17–21*) with $pH_{25°C}$ over the full range of pH values investigated. Such a comparison illustrates the effect of *T* and *P* on the relative stability of H^+- and OH^--bearing aqueous species. As predicted from theoretical considerations, $pH_{T,P}$ changed systematically with $pH_{25°C}$ (Fig. 4). For example, for all $pH_{25°C}$ values <5.0, there was a steep linear correspondence with $pH_{T,P}$ such that $pH_{T,P} > pH_{25°C}$, owing to the formation of $HCl°$ at high *T*. At $pH_{25°C} > 5.0$, however, the slope of the line relating $pH_{T,P}$ with $pH_{25°C}$ decreased dramatically. As a consequence, $pH_{T,P}$ remained virtually unchanged at $pH_{T,P}$ values greater than neutrality in spite of $pH_{25°C}$ increasing from approximately 5.0 to 7.6. This can best be accounted for by formation of NaOH° in high-*T* fluids. Thus, pH-dependent changes in the distribution of aqueous species have a dramatic effect on the response of $pH_{T,P}$ to changes in $pH_{25°C}$. In this particular chemical system, the relation between $pH_{T,P}$ and $pH_{25°C}$ represents a measure of the relative strength of the formation constants of HCl° and NaOH° complexes.

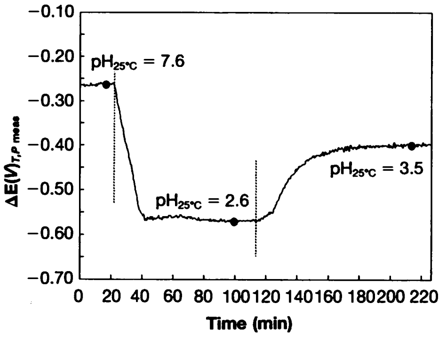

Fig. 1. Recording trace of cell potential $E(V)_{T,P\ \mathrm{meas}}$ versus recording time during a typical flow-through experiment with 0.57 *m* NaCl-HCl solution at 400°C and 40 MPa. Dashed lines indicate changes in the $pH_{25°C}$ (7.6 to 2.6 and 2.6 to 3.5) of source fluid. Solid symbols represent real-time measurements of $pH_{25°C}$ of fluid leaving the reactor. Taking into account reactor volume (50 ml) and flow rate (2 ml/min), which promotes continuous fluid mixing, cell potential responded rapidly to changes in the acidity of the pH-variable source fluid.

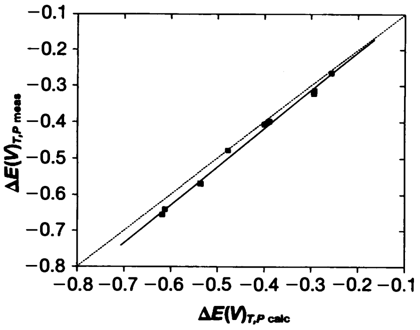

Fig. 2. Measured cell potential $\Delta E(V)_{T,P\ \mathrm{meas}}$ versus theoretically predicted cell potential $\Delta E(V)_{T,P\ \mathrm{calc}}$ in the system of 0.57 *m* NaCl-HCl at 400°C and 40 MPa. The plot demonstrates remarkable agreement between two independent approaches to assessing cell potential. In effect, the near unit slope and zero intercept of the regression line (solid line) [$y = (0.002 \pm 0.014) + (1.05 \pm 0.03)x$] indicates that the measured cell response agrees well with available thermodynamic data for the system at the conditions of the experiment. Dashed line shows ideal relation (1:1) between measured and predicted values.

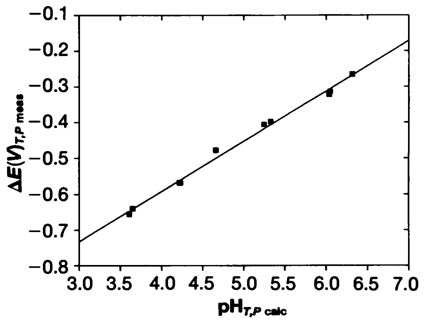

Fig. 3. Measured cell potential $\Delta E(V)_{T,P\ \mathrm{meas}}$ at 400°C and 40 MPa plotted against theoretically predicted $pH_{T,P\ \mathrm{calc}}$ to verify thermodynamic viability of our measurements. The excellent linear correlation and Nernstian slope (slope = 0.140 ± 0.004) suggests that the cell-sensor response is thermodynamically meaningful and a specific function of $pH_{T,P}$.

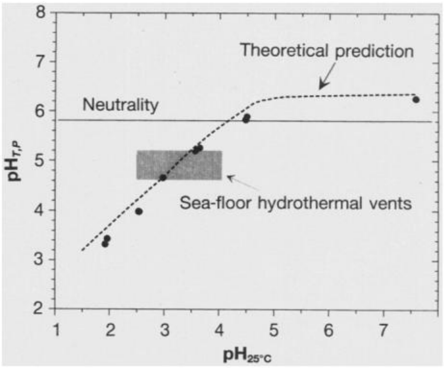

Fig. 4. $pH_{T,P}$ as a function of $pH_{25°C}$ in 0.57 *m* NaCl-HCl solution. Experimental measurements confirm the theoretically predicted relation between $pH_{25°C}$ and pH at 400°C and 40 MPa, especially in the $pH_{T,P}$ range similar to sea-floor hydrothermal vents fluids (*19*) (shaded region). Solid symbols stand for $pH_{T,P\ \mathrm{meas}}$, and the dashed line indicates theoretically predicted values. Neutrality at 400°C and 40 MPa is shown for reference.

Our measurements agree with theoretical data based on the revised HKF equation of state, with the possible exception of the lower pH range (Fig. 4). The slight offset may be caused either by improper assumptions in the calculation (*21*) or by an association constant for HCl° that is weaker than predicted (*18*). This needs to be confirmed, however, by additional experiments.

The YSZ membrane electrode provides a highly accurate means of measuring the pH of compositionally complex aqueous fluids at elevated temperatures and pressures. This is particularly relevant to the study of mid-ocean vent fluids (Fig. 4), where the sensor could be used to measure $pH_{T,P}$ directly, providing an unparalleled constraint on sub–sea-floor hydrothermal processes. Results of this study, however, are not limited to the field of geochemistry but are applicable to any study in which accurate pH values of aqueous fluids at supercritical conditions are needed.

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14. Temperature was maintained at 400° ± 0.5°C by time-proportioning solid-state controllers, and pressure was held at 40 ± 0.1 MPa by a transducer within a Shimatzu 7A HPLC pump, which served as the fluid delivery system.
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Climate Change During the Last Deglaciation in Antarctica

P. A. Mayewski,* M. S. Twickler, S. I. Whitlow, L. D. Meeker, Q. Yang, J. Thomas, K. Kreutz, P. M. Grootes,† D. L. Morse, E. J. Steig, E. D. Waddington, E. S. Saltzman, P.-Y. Whung, K. C. Taylor

Greenland ice core records provide clear evidence of rapid changes in climate in a variety of climate indicators. In this work, rapid climate change events in the Northern and Southern hemispheres are compared on the basis of an examination of changes in atmospheric circulation developed from two ice cores. High-resolution glaciochemical series, covering the period 10,000 to 16,000 years ago, from a central Greenland ice core and a new site in east Antarctica display similar variability. These findings suggest that rapid climate change events occur more frequently in Antarctica than previously demonstrated.

Among the rapid climate change events, the Younger Dryas (YD, a return to near glacial conditions during the last deglaciation) has received considerable attention because it is the most dramatic of the climate events that have occurred since the end of the last glacial period. It is well documented in the Northern Hemisphere by a variety of paleoclimate records (*1*). However, characterization of the YD in the Southern Hemisphere suggests that there may have been regional differences. In New Zealand, glacier advances occurred during this time (*2*), but along the Pacific rim of the Americas this period is characterized by glacier retreat (*3*). Stable isotope records developed from several Antarctic ice cores suggest that the most likely analog for the YD in Antarctica is a slight cooling [an Antarctic cold reversal (ACR)] that interrupts a two-step deglaciation comprising two warming trends (*4, 5*). To further investigate the ACR-YD association and additional complexities of interhemispheric climate change during the last deglaciation, we examined glaciochemical records for the period 10,000 to 16,000 years ago derived from a newly recovered east Antarctic record, the Taylor Dome ice core (Fig. 1).

Taylor Dome (77°47.7′S, 158°43.1′E, elevation of 2400 ± 20 m) is a local ice accumulation area that supplies ice to major valley glaciers in Southern Victoria Land, Antarctica. It has been dated through a combination of ice flow modeling, marker horizons (radioactive bomb layers and volcanic events), and the correlation of ^{10}Be, δ^{18}O of O_2, and stable isotopic measurements with other Antarctic ice cores, yielding a 2σ precision of dating of ~350 years for the period under study (*6, 7*). Comparison of the stable isotope records from Tay-

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P. A. Mayewski, M. S. Twickler, S. I. Whitlow, Q. Yang, J. Thomas, K. Kreutz, Climate Change Research Center, Institute for the Study of Earth, Oceans, and Space, and Department of Earth Sciences, University of New Hampshire, Durham, NH 03824, USA.
L. D. Meeker, Climate Change Research Center, Institute for the Study of Earth, Oceans, and Space, and Department of Mathematics, University of New Hampshire, Durham, NH 03824, USA.
P. M. Grootes and E. J. Steig, Quaternary Research Center AK-60, University of Washington, Seattle, WA 98195, USA.
D. L. Morse and E. D. Waddington, Geophysics Program, University of Washington, Seattle, WA 98195, USA.
E. S. Saltzman, Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, FL 33149, USA.
P.-Y. Whung, National Oceanic and Atmospheric Administration, Atlantic Oceanographic and Meteorological Laboratory, Ocean Chemistry Division, and Rosenstiel School of Marine and Atmospheric Sciences, University of Miami, Miami, FL 33149, USA.
K. C. Taylor, Water Resources Center, Desert Research Institute, University and Community College System of Nevada, Reno, NV 89506, USA.

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*To whom correspondence should be addressed.

†Present address: Leibniz Labor für Altersbestimmung und Isotopenforschung Christian-Albrechts-Universitat Kiel, 24118 Kiel, Germany.