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The in situ pH of hydrothermal fluids at mid-ocean ridges

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Abstract

Here we report the first in situ pH of hydrothermal vent fluids at mid-ocean ridges. Measurements were made during dives with DSV Alvin to the Main Endeavour Field (Juan de Fuca Ridge) and the East Pacific Rise at 21°N, and 9°–10°N using solid-state electrochemical sensors. Vent fluid temperature and pressure ranged from 180 to 384 °C and 220 to 250 bar, respectively. $\mathrm{pH}_{(\mathrm{in\ situ})}$ of the highest temperature vent fluid is only slightly acidic (5.1–5.4), although sharply lower values occur at the seawater/vent-fluid interface. Knowledge of $\mathrm{pH}_{(\mathrm{in\ situ})}$ is essential for unravelling the complex geochemical and biogeochemical processes controlling the evolution of seafloor hydrothermal systems.

Keywords: hydrothermal fluid; in situ pH; mid-ocean ridges

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1. Introduction and background

Since the discovery of deep-sea hydrothermal vents more than 25 yr ago, numerous efforts have been made to determine the pH of the hot venting fluid [1–8]. Owing to the extreme physical and chemical conditions at seafloor vents, however, direct pH measurement has not been possible, encouraging development of indirect approaches [3,5,6]. The challenge of determining pH of a chemically complex fluid at elevated temperatures and pressures ($\mathrm{pH}_{(\mathrm{in\ situ})}$) involves the need to explicitly account for temperature and pressure dependent changes in the distribution of aqueous species. Dissociation of H^+ and OH^--bearing aqueous complexes and ion pairs in response to cooling of a hydrothermal fluid to ambient seafloor conditions results in pH change, as follows:

$$m\mathrm{H}^{+}_{25\ ^{\circ}\mathrm{C}} = \sum m\mathrm{HX}^{\circ}_{T,P} + m\mathrm{H}^{+}_{T,P} - \sum m\mathrm{YOH}^{\circ}_{T,P} \tag{1}$$

where HX° and YOH° represent idealized acids and bases, respectively — the stability of which are

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explicit functions of temperature, pressure and fluid composition. Thus, the amount of free H^+ in the quenched fluid ($mH^+_{25\ °C}$) is clearly not the same as that at high temperature and pressure ($mH^+_{T,P}$). This is especially true for hydrothermal fluids near the critical point of seawater (408 °C) [9,10] where H^+-bearing aqueous complexes are particularly stable, but which can be rendered unstable with slight chemical and physical change. In addition to temperature and pressure dependent changes in homogeneous equilibria, cooling induced precipitation of metal sulphides and oxides from venting fluid, oxidation to metal oxyhydroxides and disproportionation of sulphur gases in plumes also affect pH. In spite of these difficulties, knowledge of vent fluid pH is sufficiently important to so many geochemical and biogeochemical processes at and below the seafloor that efforts to develop successful direct measurement strategies at elevated temperatures and pressures are well justified.

2. Methods and material

2.1. Sensor design and construction

Recent advances in material science, sensor technology, and experimental and theoretical geochemistry, have permitted development of pH sensors for use in seafloor hydrothermal systems. One such sensor makes use of YSZ (yittria-stabilized zirconia) ceramic, which has been used with success in laboratory studies to determine pH of aqueous fluids at high temperatures [11,12]. The solid-state design and its specific and response to a^+_H make the YSZ-based sensor well suited for seafloor applications. In its initial seafloor deployment, however, the YSZ-sensor was configured in such a way that pH was not explicitly determined, but rather pH response served as a reference permitting measurement of dissolved H_2 and H_2S [13]. In the present study, this configuration was changed in that the YSZ-sensor was combined with a Ag–AgCl reference electrode allowing $pH_{(in\ situ)}$ to be explicitly determined.

$$\mathrm{Ag|AgCl|Cl^-, H^+, H_2O|YSZ|Hg|HgO} \tag{2}$$

The cell potential ($\Delta E(V)_{TP}$) for Eq. (2) can be given as

$$\Delta E(V)_{TP} = \Delta E(V)^{\circ}_{TP} - \frac{2.303RT}{F} \times \left[\log a(\mathrm{Cl^-}) - \frac{1}{2}\log a(\mathrm{H_2O}) - \mathrm{pH}_{(\text{in situ})}\right] \tag{3}$$

Change in fluid pH will result a substantial change in sensor's emf signal. For instance, at 375 °C, one pH unit variation will result a change of 0.129 V for $\Delta E(V)_{TP}$, which is given by Nernstian slope in Eq. (3). Thus, $pH_{(in\ situ)}$ of a fluid at an elevated temperature and pressure, can be determined through the measurement ($\Delta E(V)_{TP}$) [12]:

$$\mathrm{pH}_{(\text{in situ})} = \frac{F}{2.303RT}\left[\Delta E(V)_{T,P} - \Delta E(V)^{\circ}_{TP}\right] + \left[\log a(\mathrm{Cl^-}) - \frac{1}{2}\log a(\mathrm{H_2O})\right] \tag{4}$$

where $\Delta E(V)^{\circ}_{TP}$ is the standard cell potential at appropriate temperatures and pressures as determined from standard state potentials of $E_{Ag/AgCl}(V)^{\circ}_{TP}$ and $E_{Hg/HgO}(V)^{\circ}_{TP}$; R is the gas constant; F is the Faraday constant; and, $a(Cl^-)$ and $a(H_2O)$ are the activities of dissolved chloride and H_2O, respectively. Activity of dissolved chloride is determined from the measured total chloride concentration taking explicit account of distribution of aqueous species calculations using appropriate thermodynamic data [14–24].

Titanium metal was selected for construction of the sensor housing. In general, the sensor can be defined in terms of three subunits: (1) electrode assembly; (2) transition unit; and, (3) electronics package. The electrode assembly is located at the tip of the sensor and housed in a titanium casing. The Ti-casing was designed to enhance the flow of fluid passing the electrodes, while at the same time protecting the electrodes from potential impact with rock or chimney structures. The outer diameter of the Ti-case holding the electrode assembly is 2.5 cm. A distance less than 0.5 cm separates all electrodes, including the Ti-sheathed J or E type thermocouple [see Fig. 4 in 13]. Moreover, the response region of the electrodes is limited to 0.6 cm from the tip, which allows unusually