# ISFET pH sensor pressure response: review of findings

MBARI Deep-Sea pH sensor ($Ta_2O_5$ ISFET, solid Ag/AgCl reference, Ti counter electrode) · Conversation summary, 4 Nov 2026 · Prepared with Claude for Gene, MBARI

**Bottom line.** The two different dV/dP slopes are a rate effect, not path-dependent hysteresis. Vrs is well described by an equilibrium term plus a transient that relaxes with a time constant of minutes. The equilibrium term, about 3.5 mV at 2067 dBar (≈1.7 µV/dBar), is close to the thermodynamic pressure dependence of the cell expected from the partial molar volume of HCl. It is nearly independent of temperature. The part specific to your sensor is the transient: its sign and size change with temperature, and it is largest near 2 °C, where floats spend most of the profile. Chamber adiabatic heating, the counter-electrode current, and the substrate current are all too small to explain the Vrs behavior. For floats, the die thermal lag in the thermocline is probably a larger dynamic error than the pressure transient.

## 1. Context and goals

Vrs (reference electrode to ISFET source) is calibrated against pressure and temperature in a pressure vessel filled with 0.01 M HCl. Pressure ramps to about 2067 dBar, holds, and ramps back. The ramp rate is set by the pump rate and the fluid bulk modulus, and cannot be programmed directly. The ISFET is sealed with a Viton o-ring. In service the sensor sits in a flow hood in the SBE41 CTD pumped flow path on Argo profiling floats. Your goals were:

- **Goal 1.** Understand the mechanisms at work in the sensor.
- **Goal 2.** Develop a model-based approach to calibration.
- **Goal 3.** Possibly use two kinds of P/T cycles: characterization (time constants) and mapping (data for the correction surface).
- **Goal 4.** Calibrate at more than three temperatures, with P and T varied so the least-squares fit is well conditioned.

### Data examined

| File | Contents | Notes |
|---|---|---|
| isfetCalDataAllCycles.mat | 19,886 samples over 166 h; 15 P cycles; T, P, Vrs, Ik, Ib | Temperature sequence 20 → 2 → 20 → 10 → 2 → 10 → 20 °C. Sample interval ~30 s. One NaN row (index 9430). |
| isfetCalData1Cycle.mat | Last 20 °C cycle (910 samples, 7.6 h) | Time is seconds from start of the full run. T = 19.73–19.76 °C. |

## 2. Findings from the data

### 2.1 Single-cycle model fit (19.7 °C)

Model: $V = V_0 + k_0 \cdot P + k_1 \cdot L_\tau[P]$, where $L_\tau$ is a first-order lag ($\tau \cdot dx/dt = P - x$) driven by the measured P(t).

| Quantity | Value |
|---|---|
| $k_0$ (instantaneous) | ≈ 0.40–0.45 µV/dBar (about 25–30% of total) |
| $k_1$ (lagged) | ≈ 1.26–1.31 µV/dBar (about 70–75%) |
| $\tau$ | ≈ 480–500 s for the whole-cycle fit; ≈ 320 s from the hold alone |

| Quantity | Value |
|---|---|
| Residual rms | 0.06 mV (noise floor ≈ 0.05 mV), after masking ~8–12 spikes of ~0.4 mV |
| Two- or three-τ fits | Collapse onto one τ with large, opposite-sign coefficients. At 30 s sampling the data constrain only one τ. |

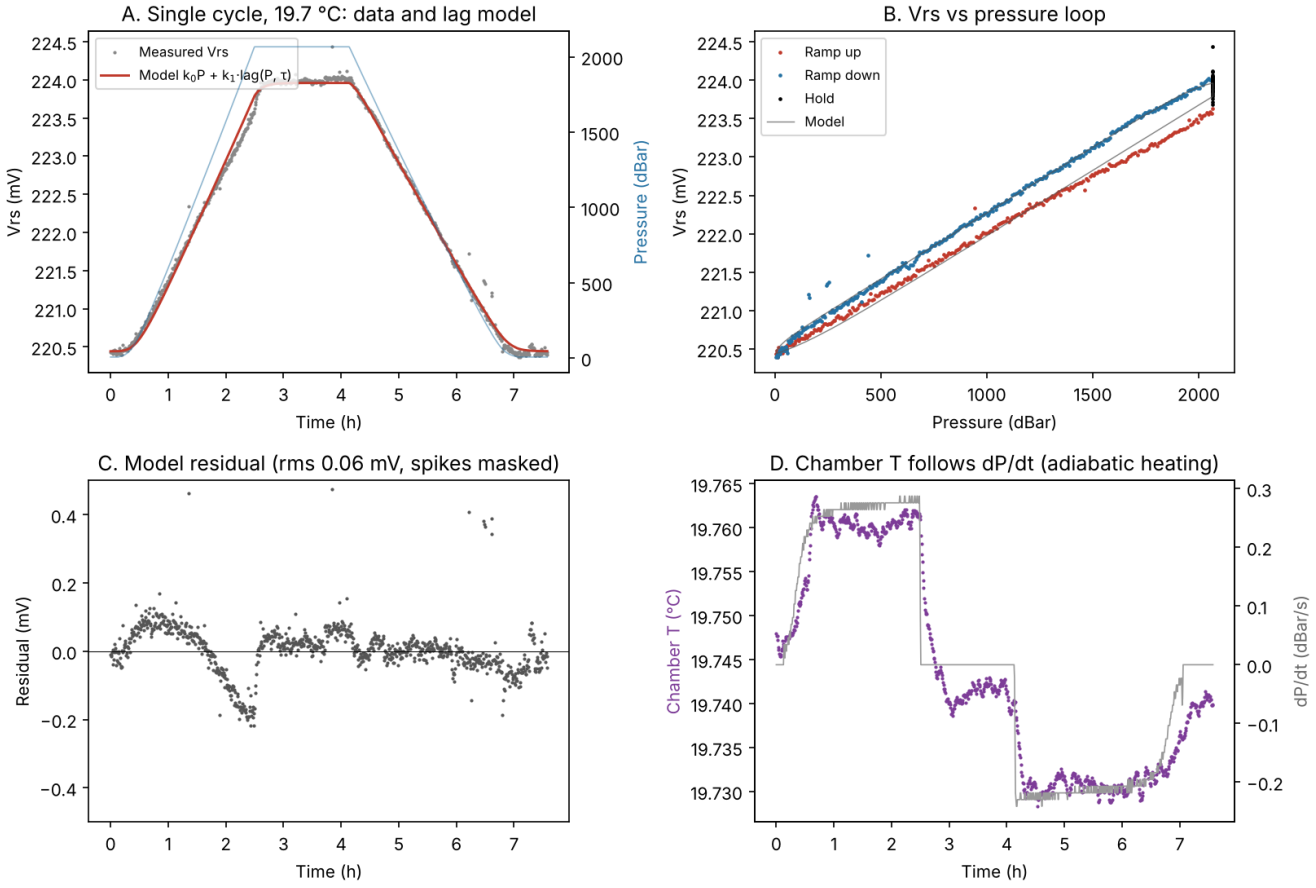



Figure 1. Single 20 °C cycle. (A) Vrs and the lag model. (B) The V–P loop: at 20 °C the down ramp lies above the up ramp. (C) Residuals. The structure near the end of the ramp up (±0.2 mV) suggests a distribution of relaxation times rather than a single τ. (D) Chamber temperature tracks dP/dt: adiabatic heating relaxing to the vessel wall.

## 2.2 The equilibrium term matches thermodynamics

With a bare Ag/AgCl pellet in the fluid, the cell is effectively ISFET | HCl(aq) | AgCl | Ag. Its potential should shift by about $-\nabla_{HCl}\cdot P/F$. For $\nabla_{HCl} \approx 17.8$ cm³/mol (dilute HCl, 25 °C), that is ≈ 3.8 mV at 2067 dBar (20.67 MPa). This is the same physics as the E*(P) term in the Deep-Sea DuraFET work (Johnson et al. 2016), which uses a seawater $\nabla_{HCl}(T)$. Measured end-of-hold responses on settled cycles (after ~30 h) agree to within about 10–20%, with no clear temperature trend:

| T | End of 95-min hold − rest before cycle (mV) | $k_{eq}$ from per-cycle fit (µV/dBar) |
|---|---|---|
| 20 °C | 3.25, 3.15, 3.80, 3.59 | 1.65, 1.59, 2.09, 1.75 |
| 10 °C | 2.86, 3.55, 3.48, 3.59 | 1.47, 1.63, 1.66, 1.72 |
| 2 °C | 3.08, 3.51 | 1.47, 1.59 |

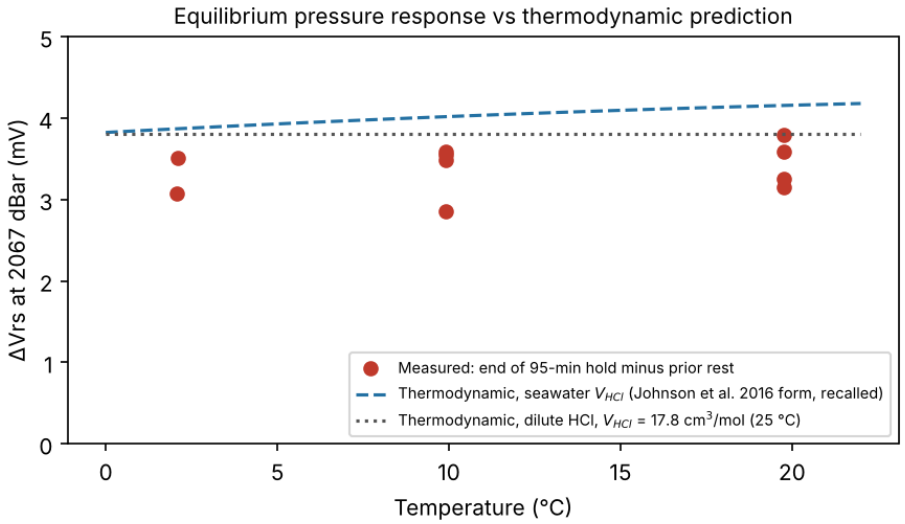



Figure 2. Equilibrium response vs temperature, compared with the thermodynamic prediction. The seawater curve uses the $\nabla_{HCl}(T)$ form as I recall it from Johnson et al. (2016). Please check it against the paper.

**Correction to an earlier statement.** In the first conversation, a table implied only ~2 mV of equilibrium response at 2 °C. That came from the first two 2 °C cycles (8–11 h into the run), which were still conditioning. Settled 2 °C cycles give 3.1–3.5 mV.

## 2.3 The sensor-specific part is the transient

The lag model is mathematically equivalent to $V = k_{eq}\cdot P + k_t\cdot(P - L_\tau[P])$, where $k_{eq} = k_0 + k_1$ and $k_t = -k_1$. The second term is a transient that decays to zero at constant pressure. Per-cycle fits, with a drift term, at ramp rates of about 0.25 dBar/s:

| T | Transient during ramps | τ | Fit rms | Comment |
|---|---|---|---|---|
| 20 °C | ≈ −0.3 to −0.5 mV (response lags) | ~20–30 min; poorly constrained | 0.06–0.1 mV | Down ramp above up ramp |
| 10 °C | ≈ −0.1 mV (almost none) | poorly constrained | 0.12–0.19 mV | Up ≈ down |
| 2 °C | ≈ **+0.9 mV** (overshoots, then decays during hold) | ~2–3 min | 0.33 mV | Single τ fits poorly; the largest and opposite-sign case |

A sign change with temperature implies at least two relaxing processes, with different temperature dependences and opposite signs.

## 2.4 Temperature effects in the lab

- **Adiabatic heating.** Chamber T correlates with dP/dt (r = 0.97). Fit: Γ ≈ 0.18 K per 1000 dBar (theory for water at 20 °C ≈ 0.15–0.17), vessel thermal τ ≈ 310 s, peak excursions +0.016 / −0.013 K. Its τ is close to the 320 s hold τ by coincidence.
- **Vrs temperature coefficient** (rest plateaus, with a drift term): ≈ 0.42 mV/K. Adiabatic heating therefore contributes ≈ 0.007 mV, which is negligible, so the transient is not thermal.
- **Drift.** Vrs rises ≈ 0.3 mV/day; the three 20 °C visits read 215.7, 218.7 and 220.4 mV. Residuals of the temperature-plus-drift fit are 0.4–0.7 mV. With only three temperatures, the temperature coefficient and the drift cannot be separated cleanly (Goal 4).

## 2.5 Counter-electrode current (Ik) and substrate current (Ib)

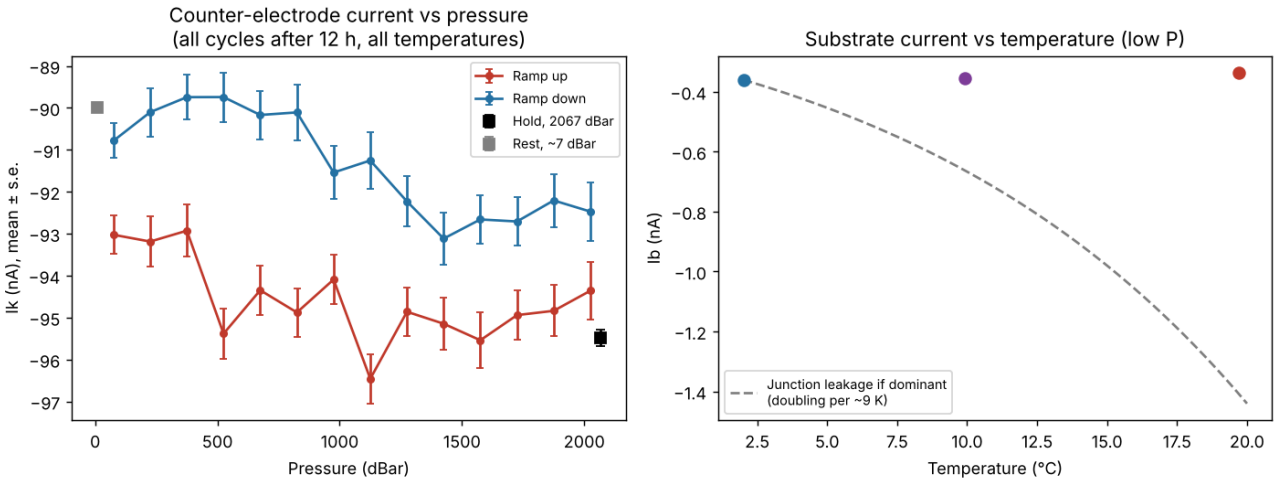



Figure 3. Left: Ik binned by pressure for up and down ramps, all cycles after 12 h. Right: Ib on the rest plateaus vs temperature, with what junction leakage would look like if it dominated.

- **Ik responds to pressure.** About −90 nA at rest and −95.5 nA at the hold (≈ −2.5 nA per 1000 dBar), at all temperatures. Ik has almost no T dependence (0.04 nA/K). At the same pressure it is 2–4 nA more negative going up than coming down; a dP/dt term is strongly favored (F ≈ 125). Ik settles within ~10 min of the hold, unlike Vrs. Per-sample noise is ~8 nA, so single-cycle fits are not possible.
- **Ik does not drive Vrs.** 0.01 M HCl has a conductivity of ≈ 4 mS/cm, so a 5 nA change across ~1 kΩ of solution is ~5 µV. Ik is best kept as a diagnostic. With Ib at only ~0.3 nA, most of the ~90 nA must return through some other conductor, possibly the vessel wall if it is metal and grounded. That is not yet confirmed.
- **Ib is not a die thermometer.** Junction leakage would roughly quadruple from 2 to 20 °C. Ib actually decreases in magnitude by ~7% (−0.360 → −0.336 nA). It shows no pressure dependence (0.6 ± 0.6 pA per 1000 dBar), which is reassuring for seal integrity. Ib is probably dominated by an electronics offset or a stable resistive path.

## 3. Mechanisms: current assessment

| Candidate | What it would explain | Status |
|---|---|---|
| Thermodynamic cell reaction ($\nabla_{HCl}$): Ag/AgCl + $H^+$/$Cl^-$ partial molar volumes | Equilibrium term ≈ 3.5–3.8 mV at 2067 dBar, weak T dependence | **Strongly supported.** Magnitude matches within ~10–20%. |
| Viton o-ring viscoelastic stress on the die (piezo-effects on threshold voltage and mobility; non-hydrostatic loading) | The transient. Deviatoric stress decays as the elastomer creeps, so the long-time response approaches hydrostatic. Strong T dependence of the elastomer. | **Leading candidate for the transient.** Untested. |
| $Ta_2O_5$ surface-site equilibria (ionization volume shifting surface $pK_a$ / $pH_{pzc}$) | A fast, mostly instantaneous offset with pressure | Possible contributor to the fast part. No literature on its pressure dependence that I know of. |
| Slow hydration or buried sites in the gate dielectric | Slow drift and hysteresis | Less likely. $Ta_2O_5$ is known for lower drift and hysteresis than $Si_3N_4$, which weakens this explanation. |
| Adiabatic heating of fluid | Rate-dependent thermal signal | **Ruled out** as a significant term (≈ 0.007 mV). |
| Counter-electrode or leakage currents | IR-drop artifacts | **Ruled out** (µV level). |
| Streaming current from compression-driven flow (o-ring crevice, porous pellet) | dP/dt term in Ik | Speculative. With no liquid junction this is weaker. Test by varying pump rate. |

## 4. Implications for Argo floats

- **Pressure transient on ascent.** If the cold transient scales with dP/dt, ascent at ~0.1 dBar/s gives roughly +0.35 mV (≈ 0.006 pH) in deep cold water. It shrinks and may change sign in warmer water near the surface. Because ascent rate is fairly constant, the deep part of this error is similar on every profile and is largely absorbed by the deep-reference adjustment (~1500 dBar). The part that varies with temperature is not. With τ of a few minutes when cold, any transient left from the descent from park depth decays before ascent.
- **Die thermal lag is likely the larger dynamic error.** In a sharp thermocline (e.g., 0.05 K/dBar at 0.1 dBar/s ≈ 5 mK/s), a die τ of 30–60 s puts the die 0.15–0.3 K behind the CTD temperature. At an order-of-magnitude 0.01 pH per K of temperature error, that is ≈ 0.002–0.003 pH, and more if $\tau_{die}$ is longer. Your E*(T) and slope coefficients set the exact value.
- **Lab vs field fluid.** The thermodynamic term differs between 0.01 M HCl and seawater. Applying it from theory with the right $\nabla_{HCl}$ for each medium removes the need for the lab fluid to mimic seawater.
- **SBE41 flow.** Pumped flow over the face couples the die to the water better than the stagnant vessel does, so a die thermal τ measured in the lab will overestimate the field value. The CTD-to-sensor transit delay (path volume / flow rate) is a fixed shift for aligning T with Vrs. Check for transients at pump start.

## 5. Proposed calibration approach (Goals 2–4)

Model structure:

$Vrs = V_T(T_{die}) - \nabla_{HCl}(T)\cdot P/F + \delta k_{eq}(T)\cdot P + k_t(T)\cdot(P - L_{\tau(T)}[P]) + drift(t)$, where $T_{die}$ = chamber T passed through a thermal lag $\tau_{die}$.

- Apply the thermodynamic term from theory. Fit each sensor only for the residual $\delta k_{eq}$ and the transient. If $\delta k_{eq}$ is small and consistent across sensors, the pressure part of production calibration simplifies considerably.
- Fit globally across all cycles, so ramps and transitions contribute and T enters continuously. Keep a polynomial fit as an independent check on the model residuals.
- **Characterization cycles** (a few sensors, rich dynamics, 1–5 s sampling): step-and-hold and several pump rates at fixed T; T steps at fixed P (near 0 and at 2000 dBar); repeat at several temperatures and check ln τ against 1/T.
- **Mapping cycles** (every sensor): 7–9 temperature levels, or a slow T sweep with P cycles at different phases. Three levels give no degrees of freedom to test the shape of T dependence; more levels matter more than more samples per level.
- Model the drift explicitly, or interleave revisits to a reference condition, so it is not confused with the temperature coefficient.

## 6. Proposed experiments

| Experiment | Question it answers |
|---|---|
| Same cycle at 2–3 pump rates | Does the transient scale with dP/dt (single τ vs distribution)? Does the Ik up/down gap scale with rate (streaming current)? |
| Step to pressure and long hold, 1–5 s sampling | Is $k_0$ truly instantaneous? Short-τ components hidden by 30 s sampling. |
| Different elastomer, durometer, or o-ring compression | Does the transient ($k_t$, τ) move? This is a direct test of the o-ring hypothesis. |
| Different fluid (buffer or seawater) | Does $k_{eq}$ track the medium's $\nabla_{HCl}$? Is the transient fluid-independent (mechanical)? |
| Second, independent reference electrode | How much of the pressure response sits in the reference. |
| Characterization sensor with die temperature | $\tau_{die}$ at SBE41 flow (can be done at 1 atm in a flowing bath with the real flow hood), and at pressure. |
| Second thermistor at the reference pellet | Separate thermal lag of the reference from that of the die. |
| More cold cycles (0–4 °C) | Pin down the large, poorly fit cold transient that matters most for floats. |

## 7. Open questions and information requested

- Does the current pressure correction already subtract the thermodynamic $\nabla_{HCl}$ term, or is it fully empirical?
- SBE41 flow rate, and the flow-path volume (or tubing length and inner diameter) from the CTD intake to the flow hood.
- Is the pressure vessel metal, and is it connected to circuit ground (where does the ~90 nA of Ik return)?
- Your sensor's E*(T) coefficient in seawater, to firm up the pH error per K of die-temperature lag.

- Whether the circuit allows the source–substrate junction to be forward-biased briefly on a characterization unit, as an alternative die thermometer. Ib as currently measured cannot serve this purpose.

## 8. Literature pointers (from memory; verify before citing)

- Johnson, K.S. et al. (2016). Deep-Sea DuraFET: a pressure tolerant pH sensor designed for global sensor networks. *Analytical Chemistry*. Thermodynamic E*(P) via $\nabla_{HCl}$.
- Millero, F.J. Partial molar volumes and the pressure dependence of ionic equilibria in seawater (e.g., 1995 *GCA* review).
- Distèche, A. (1959, *Rev. Sci. Instrum.*) and Distèche & Distèche (1967): pH and reference electrodes under pressure.
- Bousse, de Rooij & Bergveld (1983, *IEEE Trans. Electron Devices*): site-binding model. Bergveld (2003), “Thirty years of ISFETology.”
- Jamasb, Collins & Smith (late 1990s): ISFET drift models. J.C. Chou’s group: drift and hysteresis of $Ta_2O_5$ and other gate materials.
- Kanda (1982 and later): silicon piezoresistance; literature on stress-induced MOSFET threshold shifts.
- Search terms: “viscoelastic,” “stress-induced threshold voltage shift,” “encapsulant creep,” “Ag/AgCl high pressure,” “partial molar volume HCl,” “Ta2O5 ISFET hysteresis.”

Caveats: all fits are from one sensor at one ramp rate; the 2 °C transient is poorly described by a single time constant; the equilibrium-term agreement is an order-of-magnitude-plus check, not a proof; ocean error estimates are rough.