

## Physical properties of Crater Lake, Oregon: A method for the determination of a conductivity- and temperature-dependent expression for salinity

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### Abstract

Active inputs of thermally and chemically enriched fluids at the bottom of Crater Lake create small vertical and horizontal heterogeneities in the deep-lake temperature and salt distribution. Using an internally recording CTD and a precise definition for salinity as a function of in situ conductivity and temperature, we assess the significant effects of these inputs on the density structure and mixing processes in Crater Lake. To characterize the physical properties of the lake we have developed an experimental approach to derive a specific conductance and temperature-dependant expression for salinity in freshwater.

The use of an internally recording conductivity, temperature, and pressure sensor (CTD) with a narrow-range conductivity cell enables high-precision, in situ water-column measurements for limnological applications. These sensitive, high-precision measurements enable accurate characterization of the physical properties of lakes. Such precision is particularly important where small thermal and chemical anomalies may affect the overall physics of a lake. This work outlines a method for the careful calibration of the conductivity sensor, modified for low conductivity fluids, for a CTD (Seacat model SBE19, Sea-Bird Electronics, Inc.) and an approach for converting in situ conductivity and temperature into salinity or total dissolved solids (TDS). We apply the expression obtained for salinity in combination with the equation of state for waters in the limnological range (Chen and

Millero 1986) and determine the density and salinity structure for Crater Lake, Oregon, a well-mixed, ultra-oligotrophic lake which has active inputs of thermally and chemically enriched fluids.

In order to evaluate the distribution of TDS in a given system, it is usually necessary to convert in situ conductivity measurements to conductivity at a standard reference temperature or to a temperature-independent term. Snoeyink and Jenkins (1980) have defined an approximate relationship between TDS and conductivity at 25°C. Sorensen and Glass (1987) presented an equation which converts in situ specific conductance measurements to specific conductance at 25°C. Although the combined equations yield an approximate expression for TDS, we will show that this approach lacks the accuracy necessary for our applications.

An alternative to normalizing specific conductance to 25°C would be to experimentally determine the relationship between temperature, in situ conductivity, and salinity (or TCS relationship) in a given limnological system. We have determined the TCS relationship for Crater Lake water in a temperature-controlled environment with water collected directly from the lake. The

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accuracy of the resulting conductivity and temperature-dependent salinity measurement is limited by the analytical accuracy of the total salt determination for the lake water, while the precision of the relationship is limited by the precision of the conductivity measurement of the CTD.

Two basic assumptions to the approach of relating specific conductance to TDS or salinity are that the proportions of the major ions in the natural system are relatively constant, and that the "salinity" expression represents all the dissolved solids in the fluid. Because mixtures of different electrolytes will exhibit slightly different electrochemical responses, the major ions for an individual system must remain in constant proportion in time and space. Likewise, the importance of representing all the dissolved solids in a system has particular application to the current work where silicic acid is an important dissolved solid in the salinity measurement.

To evaluate TDS or salinity as a function of conductivity for a freshwater system requires that the major components of TDS be ionic and affect the conductivity of the water. Silicic acid, which is a common dissolved component in many freshwater systems, is a major contributor to the dissolved solids load and the density of Crater Lake water. The first dissociation constant of silicic acid is  $\sim 9.5$ , so silicic acid is completely protonated in lakes that are approximately neutral to acidic (Turner et al. 1981). Therefore silicic acid does not provide a strong conductometric response in solution. Thus, in using in situ CTD data to determine the salinity and density of a fluid, silicic acid must be measured directly or its concentration must be related to variations in the ionic material (conductance).

The assumption that the proportions of the individual ions in the natural system are relatively constant is usually met in lakes with long water and salt residence times relative to their characteristic mixing rate or in aquatic systems that have a single or dominant source for all the salts in the system. In addition, the approach and applications described here will be most useful for long-term studies of a single system. The value of a precise expression for salinity is

that it allows one to accurately characterize the vertical density structure, using an equation of state for lake water, and thus, the stability of a water column.

An equation of state for freshwater was presented by Chen and Millero (1977a,b, 1986). The equation of state describes the density of a fluid as a function of pressure, temperature, and salinity. Other physical and chemical properties of the fluid that are dependent on pressure, specific volume ( $\rho^{-1}$ ), and temperature (*PVT* properties), such as the temperature of maximum density ( $T_{md}$ ) and the specific heat capacity, are derived from this equation of state (Chen and Millero 1977a).

The vertical stability ( $E$ ) of a fluid parcel is generally assessed by considering the exchange of two adjacent water parcels. In practice, if the density of the water (calculated at some reference pressure) increases with increasing depth then the water column is stable. Mathematically this is defined by the relationship

$$E = -(\rho^{-1})(\partial \rho / \partial z^{-1}) \quad (1)$$

where  $\rho$  is the density the fluid would have at its in situ temperature, a reference pressure, and its salinity, and  $z$  is depth. For the case where we compare the density of a fluid with respect to the surface, we use the potential temperature, 1-atm pressure, and the in situ salinity, i.e.  $\rho = \rho(\theta, 0, S)$ .

Chen and Millero (1977a) pointed out that the density of a fluid is partly dependent on the total salt content and that systems near the  $T_{md}$  cannot necessarily be treated as pure water. When the in situ temperature is nearly at the  $T_{md}$ , the question of stability becomes particularly sensitive to the salinity of the medium because  $T_{md}$  is lowered by small increases in TDS. Additionally, it has been shown that pressure effects on the temperature of maximum density in limnological systems will affect the vertical stability of a displaced water parcel (Farmer and Carmack 1981; Carmack and Farmer 1982). It is apparent that when considering the vertical stability of a fluid parcel, the effects of both salinity and pressure on density must be included.

A common approach of characterizing fluid stability, which includes the gravita-

tional constant ( $g$ ), is the Brunt-Väisälä (buoyancy) frequency (Chen and Millero 1977a,b, 1986); the frequency  $N$  (radians  $s^{-1}$ ) is defined by the expression

$$N^2 = gE \quad (2)$$

where  $E$  is stability. When  $N^2$  is positive, a fluid parcel is stable, when it is negative, the parcel is unstable. Qualitatively, the buoyancy frequency is the oscillation frequency of a parcel of water after a small vertical displacement from its equilibrium level. Chen and Millero (1977a,b, 1986) provided an equation for the buoyancy frequency which is calculated from a combination of the polynomials presented in their work:

$$N^2 = (-g^2 V^{-2})[(\partial V \partial S^{-1})_p (dS dP^{-1}) + (\partial V \partial T^{-1})_p] \times [(dT dP^{-1}) - (\partial T \partial P^{-1})_{adia}] > 0 \quad (3)$$

where  $V$  is the specific volume ( $\rho^{-1}$ ),  $T$  the temperature,  $S$  the salinity,  $P$  the pressure, and  $(\partial T \partial P^{-1})_{adia}$  is the adiabatic temperature gradient. Because the salinity term appears in all of the expressions for the  $PVT$  properties of limnological interest, changes in the vertical salt distribution will affect the stability of a water column. The importance of salinity in determining the physical and chemical properties of a lake system is clearly demonstrated in Crater Lake which has a hyperadiabatic thermal gradient (Neal et al. 1971, 1972) which is stabilized by a salinity gradient.

Crater Lake rests inside the collapsed caldera of Mount Mazama in the Cascade Range of southern Oregon. At 590 m, it is the deepest lake in the United States. The lake is predominantly precipitation fed. About 80% of the precipitation falls directly on the lake surface with the remainder entering the lake system as runoff from the caldera slopes (Redmond 1990). Roughly half of the annual precipitation is lost due to evaporation with the remainder being lost due to seepage (Redmond 1990). The fetch is relatively short ( $\sim 10$  km), and the lake surface has some shielding from winds because of the steep caldera walls which extend to nearly 300 m above the surface. An extensive review of the geology, hydrology,

ecology, and chemistry of Crater Lake is given by Drake et al. (1990).

Evidence for the active input of hydrothermally enriched fluids into the bottom of Crater Lake has been reported (Williams and Von Herzen 1983; Dymond et al. 1989; Collier et al. 1990). Some investigators (Williams and Von Herzen 1983) have postulated that because the temperature gradient below 350 m is greater than the adiabatic gradient, the hypolimnion of the lake is unstable and undergoing convection. However, because high-precision data demonstrating increases in salinity with temperature were unavailable, their hypothesis was based solely on the thermal structure of the water. We will show that variations in the vertical and horizontal density structure of the water column are influenced both by saline and by thermal effects. As first pointed out by Collier et al. (1990) the hyperadiabatic temperature gradient in the lake is stabilized by a salinity gradient. In limnological systems like Crater Lake, where small variations in temperature and salinity may play an important role in the overall physics of the lake, high-precision temperature and salinity measurements are essential for understanding lake mixing processes.

### Methods

Cations were analyzed with a Perkin-Elmer 5000 flame atomic absorption spectrophotometer. Each sample was analyzed at least twice with multiple readings for each analysis and a standard was referenced between the two sample analyses. Chloride and sulfate analyses were performed with ion chromatography. Bicarbonate concentrations are the difference between the sum of the major cations and major anions on an equivalent ion basis. These results were consistent with the alkalinity and pH data obtained for the water in Crater Lake as determined by closed-system pH measurements and Gran titrations of alkalinity. Silicic acid was determined by a colorimetric molybdenum blue method using an Alpkem rapid flow analyzer.

Direct density measurements of water samples were made with a high-precision flow digital densimeter (model 02D, Sodev

Inc.) with a programmable circulating thermostat. The accuracy of the measurement is  $\pm 2$  ppm.

*Calibration of the conductivity sensor*—For this discussion we first consider the conductance theory relevant to our experiments. Then we outline the method used to calibrate the conductivity sensor. The fluid used for the conductivity cell calibration was a KCl solution ranging in concentration from 0 (distilled water) to 2.3 mM.

Specific conductance ( $\kappa$ ), in  $\text{S meter}^{-1}$ , is inversely proportional to the electrical resistance ( $R$ ) of 1 cm of fluid, such that  $\kappa = (1/R) \times (L/A)$ , where  $A$  is the area and  $L$  the length of the cell. The specific conductance of a strong electrolyte solution is the product of the equivalent conductance ( $\Lambda$ ) and the concentration of the salt ( $C$ ), in  $\text{equiv cm}^{-3}$ ,

$$\kappa = \Lambda C \quad (4)$$

where the equivalent conductance ( $\Lambda$ ) is the conductance of 1 g equivalent of the solute measured between two electrodes 1 cm apart for an aqueous electrolyte solution.  $\Lambda$ , which is itself a function of the concentration of the solute, is calculated from the Onsager equation (Conway 1952):

$$\Lambda = \Lambda_{\infty} - (F + \nu\Lambda_{\infty})C^{1/2} \quad (5)$$

where expressions for the relaxation effect ( $F$ ) and the effect of the viscosity of the fluid ( $\nu$ ) as a function of temperature for a specific salt (KCl) were generated from data presented by Conway (1952). A third-order relationship was derived from tabulated data presented by Robinson and Stokes (1955) for the equivalent conductance of KCl at infinite dilution ( $\Lambda_{\infty}$ ). Output from the CTD conductivity sensor is expressed as frequency and the calibrations are expressed in  $\text{S m}^{-1}$ , which we convert to the more conventional  $\mu\text{S cm}^{-1}$ .

We calibrated the conductivity sensor by placing the CTD into a plastic-lined, insulated bath which contained  $\sim 300$  liters of distilled water. A submersible pump was attached to the conductivity sensor to maintain a constant flow of the fluid through the conductivity cell, and a plastic sheet was used to cover the bath to minimize evaporation. We slowly increased the bath tem-

perature from  $2^{\circ}$  to  $20^{\circ}\text{C}$  while the CTD recorded data at 1-min intervals. We repeated this process with two separate additions of  $\sim 23$  g of KCl so that our calibration included the full range of specific conductance and temperature observed in the lake. Discrete water samples were taken from the large bath throughout the run for high-precision conductometric analysis in the laboratory. The KCl bath solutions are referred to as the standardizing fluid.

The specific conductances of subsamples of the standardizing fluid, taken from the bath during the calibration run, were determined against a separate set of high-precision KCl standards with a Radiometer CDM83 conductivity bridge. We derived a second-order relationship between observed specific conductance ( $\kappa$ ) and concentration of KCl. Small differences between the observed specific conductance, derived from the CTD and the calculated specific conductances based on Eq. 4 and 5, were well below the resolution of the CTD and for our application the Onsager model (Eq. 5) provided sufficient accuracy to calibrate the CTD conductivity sensor.

In Table 1, we present representative sample values used to calibrate the conductivity sensor. The three groups of  $\kappa_{25^{\circ}\text{C}}$  in Table 1 represent the distilled water bath, the first addition of KCl, and the second addition of KCl. The KCl concentrations represent approximations based on our KCl standards as described above. Despite cleaning the CTD, the insulated bath, etc., some contaminant salts remained because the distilled water bath gave conductivity readings. The CTD calculates conductivity from frequency and temperature with a relationship provided by Sea-Bird Electronics. There are no systematic errors in the instrument's interpretation of conductivity ( $\kappa_{\text{CTD}}$ ) when compared to the theoretical specific conductance ( $\kappa_t$ ) in Table 1. We define the error in the conductivity measurements as the difference between the theoretical specific conductance ( $\kappa_t$ ) and the specific conductance measured by the CTD ( $\kappa_{\text{CTD}}$ ) in Table 1. The SD of the errors is  $\pm 0.4 \mu\text{S cm}^{-1}$ , which is a measure of the absolute accuracy of the conductivity measurement. During the same calibration ex-

Table 1. Sample values for  $\kappa$  and KCl concentration (mM).  $T$  ( $^{\circ}\text{C}$ ) represents the temperature of the bath at the time a sample was taken.  $\kappa_{25^{\circ}\text{C}}$  is the specific conductance ( $\mu\text{S cm}^{-1}$ ) for the standardizing fluid samples measured at  $25^{\circ}\text{C}$  in the laboratory with a conductivity bridge.  $[\text{KCl}]$  is determined by the relationship relating the specific conductance to  $[\text{KCl}]$  for the laboratory standards.  $\kappa_t$  is the theoretical specific conductance for the samples at the collection temperatures during calibration and is calculated from Eq. 4 and 5.

$T$	$\kappa_{25^{\circ}\text{C}}$	$[\text{KCl}]$	$\kappa_t$	$\kappa_{\text{CTD}}$
5.608	26.1	0.177	16.7	16.5
10.538	26.1	0.177	19.1	19.2
19.414	26.1	0.177	23.4	24.3
15.652	185.0	1.263	152.1	151.6
2.784	186.0	1.270	109.5	109.1
2.940	334.0	2.305	198.2	199.5
21.123	334.0	2.305	310.1	310.0

periment, we also calibrated the CTD temperature sensor with a Mueller bridge, standard, triple-point cell according to the IPTS 68 temperature scale. On the basis of this calibration, the temperature sensor was accurate to within  $0.001^{\circ}\text{C}$  of the factory calibration.

The absolute accuracy of the conductivity measurement ( $\pm 0.4 \mu\text{S cm}^{-1}$ ) is only slightly greater than the resolution of the instrument ( $\pm 0.2\text{--}0.3 \mu\text{S cm}^{-1}$ ). Our experience indicates that conductivity and temperature recalibration may be necessary before each field season for optimum precision and accuracy when comparing data from year to year. In conjunction with the conducto-

metric calibration of the cell, it is also necessary to calibrate the response of the conductivity cell to the total salt content of the specific medium of interest, in this case Crater Lake water.

*Converting in situ specific conductance to salinity*—Having established a calibration method for the conductivity cell, we now describe a method that allows us to develop an equation which converts in situ specific conductance to the salinity of a natural body of water (i.e. Crater Lake). To accomplish this task, we placed  $\sim 150$  liters of Crater Lake water into our insulated bath and varied the temperature between  $2^{\circ}$  and  $20^{\circ}\text{C}$ . We measured temperature and conductivity at 1-min intervals throughout the experiment and collected water samples at each  $5^{\circ}\text{C}$  increase in temperature. We subsequently added  $\sim 150$  liters of distilled water to dilute the lake water and repeated the experiment. To ensure consistency between the lake-water samples used in the calibration and our water column samples, we cross-calibrated the “calibration water” samples with water samples of known composition. The ratio of the concentration of each solute measured in the diluted calibration water to the concentration of that solute in the undiluted calibration water permits a semiquantitative evaluation of the absolute accuracy of the data set (Table 2). The average ratio for each solute is 0.599, with a C.V. of 1.8%. Additionally, our data

Table 2. Results from the analysis of the undiluted lake water and diluted lake water used in the CTD calibration. Because  $\text{HCO}_3^-$  is calculated as the difference between cations and anions, an ion balance is not meaningful. The ratio of the concentration of each solute in the diluted lake water to that in the undiluted lake water will yield a measure of our analytical quality control. The C.V. for the various solute ratios is 1.8%.

Solute	Undiluted lake water			Diluted lake water			Solute ratio (Dlw : Ulw)
	Concn		C.V. (%)	Concn		C.V. (%)	
	(mM)	(mg liter <sup>-1</sup> )		(mM)	(mg liter <sup>-1</sup> )		
Na <sup>+</sup>	0.4475	10.29	0.170	0.2723	6.259	0.888	0.608
K <sup>+</sup>	0.04253	1.663	0.113	0.0259	1.011	0.190	0.608
Mg <sup>2+</sup>	0.1081	2.628	0.116	0.0649	1.577	0.416	0.600
Ca <sup>2+</sup>	0.1664	6.670	0.707	0.0986	3.951	0.573	0.592
Cl <sup>-</sup>	0.2577	9.137	0.995	0.1528	5.417	0.628	0.593
SO <sub>4</sub> <sup>2-</sup>	0.0996	9.572	0.495	0.0580	5.572	0.563	0.582
HCO <sub>3</sub> <sup>-</sup>	0.5821	35.52	N/A	0.3562	21.74	N/A	0.612
Σions	1.7039	75.5		1.0287	45.5		
H <sub>4</sub> SiO <sub>4</sub>	0.2964	28.50	0.233	0.1775	17.06	0.292	0.559
TDS (salinity)	2.0003	104.0		1.2062	62.6		

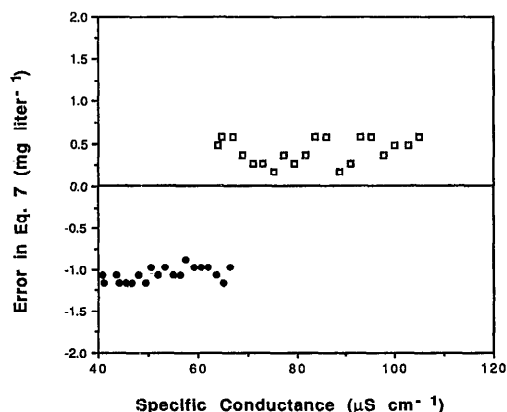


Fig. 1. Error in Eq. 7 vs. specific conductance. The error represents the difference between the measured concentration of ions (Table 2) and that predicted by Eq. 7 for subsamples of the lake-water calibrations. The sample specific conductances for TDS = 45.5 mg liter<sup>-1</sup> (□) and TDS = 75.5 mg liter<sup>-1</sup> (●) are taken from the CTD during calibration and vary with water temperature.

agrees with the USGS data set within the reported standard deviations of both data sets (Nathenson 1990).

Before detailing our development of an equation representing the salinity of a body of water, we will briefly review another approach to the problem of relating conductivity to the dissolved solids in a solution and demonstrate why this approach will not work for our applications.

In order to use published equations relating salinity (or TDS) to in situ conductance, we must first convert to conductivity at a fixed reference temperature. Sorenson and Glass (1987) presented an empirical relationship that relates the conductivity measurement of mixed electrolyte (environmental) samples at any temperature to conductivity at 25°C:

$$C_{25} = C_t(\eta_t/\eta_{25})^K \quad (6)$$

where  $C_t$  ( $\mu\text{S cm}^{-1}$ ) is the in situ conductivity,  $C_{25}$  ( $\mu\text{S cm}^{-1}$ ) the conductivity at 25°C,  $\eta$  the viscosity, and the exponent  $K$  was empirically derived as a function of the total hydrogen ion content. Approximations by Snoeyink and Jenkins (1980) relate the specific conductance ( $\mu\text{S cm}^{-1}$ ) to TDS:

$$\text{TDS} = 0.64 \times C_{25} \quad (7)$$

where TDS (mg liter<sup>-1</sup>) is now a direct function of the concentration of the electrolytes or salts.

Summation of the individual electrolytes ( $\Sigma$  electrolytes) for the calibration lake water (Table 2) yields a total ion concentration of 75.5 mg liter<sup>-1</sup> and for the diluted calibration lake water 45.5 mg liter<sup>-1</sup>. Because Eq. 7 only relates specific conductance to the dissolved ionic species, silicic acid is excluded from the total electrolytes reported in Table 2. Equation 7 overestimates the  $\Sigma$ , electrolytes by 1 mg liter<sup>-1</sup> for the total ion concentration = 75.5 mg liter<sup>-1</sup> and underestimates the  $\Sigma$  electrolytes by nearly 1.5 mg liter<sup>-1</sup> for the total ion concentration = 45.5 mg liter<sup>-1</sup> (Fig. 1). This offset in Eq. 7 suggests that there are systematic errors in the relationship which vary as a function of ion concentration. These errors are larger than the individual ion measurement errors that result from our analytical uncertainties. Such errors are too large to define the salt distribution of Crater Lake and demonstrate a need for an equation that converts in situ conductivity and temperature into salinity for the lake water.

To avoid errors in estimating salinity from conductivity (Fig. 1), we experimentally determined the TCS relationship for Crater Lake water. The salinity calibration covered ranges in temperature between 0° and 25°C and ranges in specific conductance between 40 and 120  $\mu\text{S cm}^{-1}$ . The applicable range for our Eq. 8 in the lake is ~60–120 mg liter<sup>-1</sup>, which is sufficient for our purposes. The primary reason for choosing natural lake water over artificial media was the very high concentration of silicic acid in Crater Lake which is difficult to reproduce in artificial media. For systems without high concentrations of silicic acid an artificial mixture of the appropriate salts would likely suffice.

Silicic acid accounts for a significant portion of the salinity in Crater Lake—more than 25% by weight (Table 2). Because salinity must represent all of the dissolved solids in solution for accurate calculation of the physical and chemical properties of lake water, we must include the concentration of silicic acid as part of our measurement of salinity. Although silicic acid is not an elec-

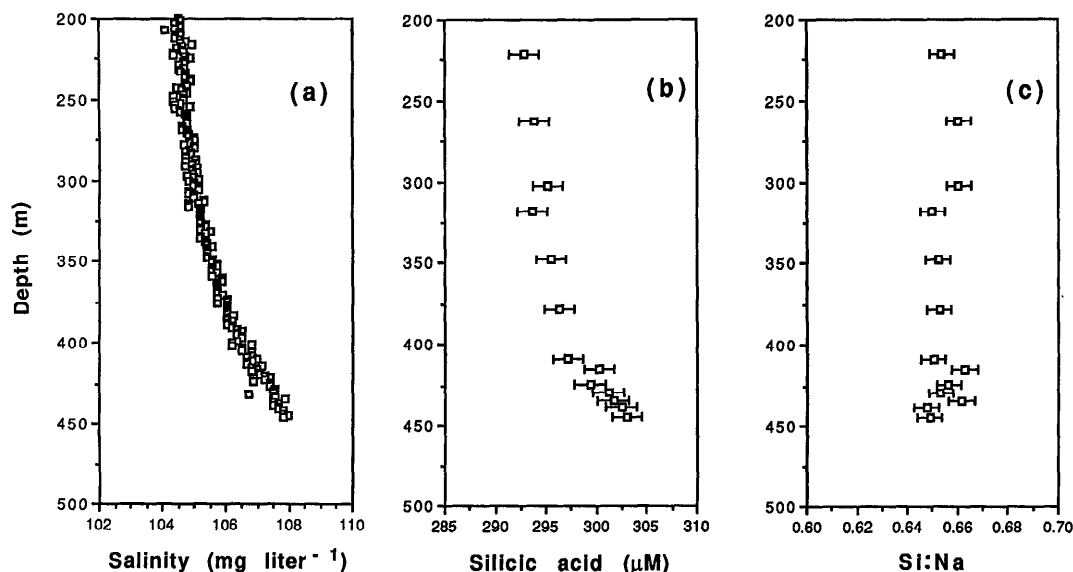


Fig. 2. CTD and chemistry data from August 1988. [a.] Salinity (including silicic acid) as calculated from Eq. 8, where  $a_0 = -50.5103$ ,  $a_1 = 1,836.3964$ ,  $a_2 = -1.3524 \times 10^4$ ,  $a_3 = 1.5624 \times 10^5$ ,  $a_4 = -3.00448 \times 10^5$ ,  $b_1 = 11,634.88$ ,  $b_2 = -1.1218 \times 10^4$ ,  $b_3 = 4,959.9155$ ,  $b_4 = -1,234.5981$ ,  $b_5 = 161.3464$ ,  $b_6 = -8.57375$ . [b.] Silicic acid. [c.] The ratio of silicic acid to sodium. The figure demonstrates the covariance of the dissolved constituents with depth in the deep lake and illustrates the constant ratio between silicic acid and the strong electrolytes (using Na as an example).

trolyte, the ratio of silicic acid to the major ions in the lake is constant as is suggested by Fig. 2. Because of this proportionality, silicic acid will vary directly with specific conductance. Therefore, salinity, which now includes silicic acid, is 104.0 and 62.6 mg liter<sup>-1</sup> for the lake water and diluted lake water respectively (Table 2).

Taking the conductivity and temperature data from the CTD in conjunction with the salinity data and using a least-squares regression, we obtain an expression for salinity as a function of conductivity and temperature that is similar in form to the expression used for seawater (Cox et al. 1967):

$$S = a_0 + a_1 C_i^{0.5} + a_2 C_i + a_3 C_i^{1.5} + a_4 C_i^2 + b_1 C_i T^{0.5} + b_2 C_i T + b_3 C_i T^{1.5} + b_4 C_i T^2 + b_5 C_i T^{2.5} + b_6 C_i T^3 \quad (8)$$

where  $a_i$  and  $b_i$  are constants which need to be determined for each individual system,  $S$  is salinity in mg liter<sup>-1</sup>,  $C_i$  the in situ conductivity, and  $T$  the temperature. Figure 3 demonstrates the precision of the equation

as a function of conductivity by illustrating differences between the laboratory-determined salinity of a sample and the salinity of the sample predicted by Eq. 8. There appear to be no systematic errors in the salinity expression with respect to conductivity (cf. Fig. 3 to Fig. 1) or temperature for either the low- (●) or the high-salinity water (□). The salinity calculated according to Eq. 8 has a SD of  $\pm 0.1$  mg liter<sup>-1</sup> for the bath samples; however, the resolution of the CTD conductivity measurement limits the precision of the salinity measurements to about  $\pm 0.2$  mg liter<sup>-1</sup>.

#### *The influence of silicic acid on the density of Crater Lake water*

In Crater Lake the change of salinity with depth parallels the change in silicic acid content (Fig. 2a, b). The covariation of salinity and silicic acid is also demonstrated by the uniform Si:Na values with depth (Fig. 2c). Therefore, although specific conductance is not a direct measure of silicic acid concentration, the concentration of silicic acid is

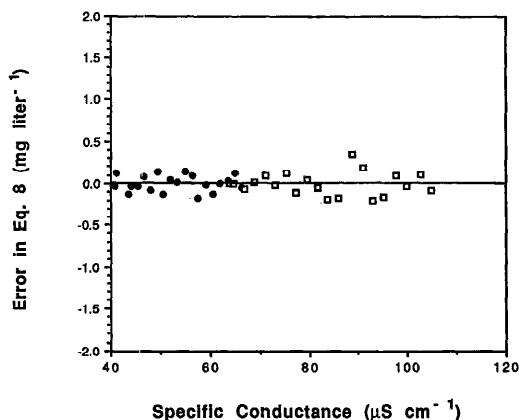


Fig. 3. The error in Eq. 8 vs. specific conductance. The error represents the difference between the salinity predicted from Eq. 8 and that of the calibration water (Table 2). The variation in specific conductance in the two data sets is due to the variation of temperature during the experiment.

directly proportional to conductance and dissolved ions in the lake. The dominant source of the strong electrolytes and the silicic acid to the lake is subsurface hydrothermal activity (Collier et al. 1990).

To evaluate the influence of silicic acid on the density of Crater Lake water, we measured the relative density ( $\Delta\rho$ ) of the water directly. Here the relative density of lake water is defined as the density of the fluid at 1-atm pressure and 25°C, minus the density of pure water at that temperature and pressure. We also used Eq. 8, with constants that include the silicic acid content of the lake as part of the total salinity, to calculate salinity from the CTD data collected at the same time as the water samples. We then applied the equation of state from Chen and Millero (1986) to this hydrographic data for a temperature of 25°C to match the laboratory density measurements. For comparison purposes, we applied an expression with the same form as Eq. 8, but which does not include the silicic acid content of the lake water, and the equation of state was again applied to the hydrographic data (Fig. 4). Within the accuracy of the equation of state ( $\pm 2$  ppm) and within the accuracy of the density measurement ( $\pm 2$  ppm), the agreement between the predicted  $\Delta\rho$ , derived from the hydrograph-

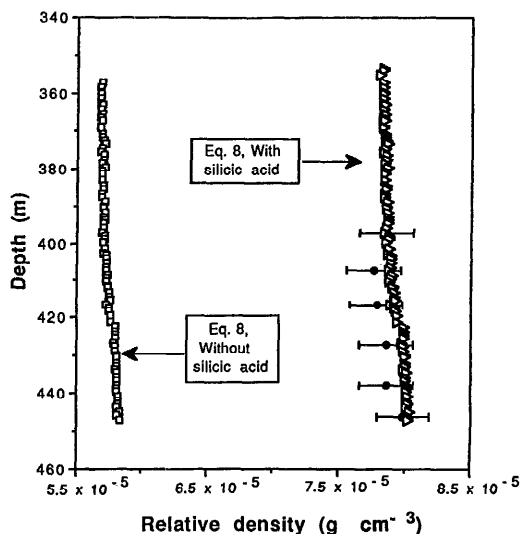


Fig. 4. The relative density ( $\Delta\rho$ ) of lake water as a function of depth.  $\Delta\rho$  is the density of the fluid at 1-atm pressure and 25°C minus the density of pure water at that temperature and pressure. The  $\Delta\rho$  of samples taken in the field ( $\bullet$ ) are compared to  $\Delta\rho$  based on the hydrographic data and the equation of state (Chen and Millero 1986) ( $\square$ ,  $\triangle$ ). Calculation of  $\Delta\rho$  with salinity that does and does not include silicic acid. Hydrographic data were taken at the same time as the field samples and the error bars represent  $\pm 2$  ppm, which is the accuracy of the equation of state (Chen and Millero 1986) and of the density measurement.

ic data which included the silicic acid content of the lake water, and the measured  $\Delta\rho$  from the samples collected in the field is striking. Likewise, when calculating density without including silicic acid, the relative density of lake water is underestimated by 27%.

Hydrothermal sources dominate the major ion and silicic acid content of Crater Lake waters (Collier et al. 1990; Nathenson 1990). In systems where silicic acid is not always proportional to the strong electrolytes in solution, silicic acid will need to be directly determined in addition to the strong electrolytes for accurate assessment of the density structure of the water. In biologically productive systems, silicate depletion by diatoms in surface waters and opal dissolution at depth could result in variations in the ratio of silicic acid to the major ions. Increases in silicic acid derived from the dissolution of diatom frustules could pro-



vide the necessary stabilization to balance the observed increases in deep lake temperature of Lake Michigan (Marmorino et al. 1980). Such processes which add or remove silicic acid from the water will change the ratio of silicic acid to the major ions and may also affect the stability of a water column if it is not otherwise strongly stabilized (i.e. by a thermal gradient in the summer thermocline).

To investigate the stability of a water column may require precise determination of the salinity and silicic acid content of the water. Our approach makes it possible to determine the precise density structure of a water column. This approach is particularly applicable to large, deep lakes where the proportions of major ions are relatively constant.

#### *Field results: The physical properties of Crater Lake*

Crater Lake has two semienclosed basins, one in the northeastern portion of the lake (north basin) has a maximum depth of  $\sim 590$  m and one in the southwestern section of the lake (south basin) with a maximum depth of  $\sim 485$  m. The basins are separated by a sill situated between 425- and 450-m depth.

The well-known clarity of the lake and intense surface mixing are factors that allow seasonal heat exchange to occur well below 200 m (Collier et al. 1990). This upper water is aerated twice annually and is generally isohaline and saturated with dissolved oxygen all year round. As the summer thermocline develops, evaporation at the surface results in small increases of salt content in the upper few meters of the lake. This process is observable under calm surface conditions coupled with sunny, cloudless skies which are common in the late summer-early fall.

To a first approximation the deep lake is isothermal (Fig. 5a) and isopycnal (Fig. 5b, d); however, inputs of heat and salt into the hypolimnion create measurable vertical and horizontal heterogeneities in the deep-lake temperature (Fig. 5c) and salinity structure (Fig. 2a). These heterogeneities in heat and salt result in vertical and horizontal heterogeneities in the density structure of the deep lake. Although the average of the adiabatic

gradient for Crater Lake from 300 to 560 m is  $4.7 \times 10^{-6} \text{ }^{\circ}\text{C m}^{-1}$ , the observed thermal gradient (Fig. 5c) over this depth range in the north basin is  $\sim 2.6 \times 10^{-4} \text{ }^{\circ}\text{C m}^{-1}$ —nearly two orders of magnitude greater than the adiabatic gradient. This hyperadiabatic gradient is balanced by a salinity gradient of  $8.8 \times 10^{-1} \text{ g kg}^{-1} \text{ m}^{-1}$  yielding an increase in density with increasing depth (Fig. 5d). These thermal and saline gradients are ubiquitous in the deep lake; however, there are temporal and spatial variations in the magnitude of these gradients. For example, the increase in temperature and salinity in the bottom 50 m of the south basin is much greater than that observed in the north basin (Fig. 6a, b). The combined increase with depth in temperature and salinity results in a stable vertical density gradient (Fig. 6c). The higher bottom-water temperature and salinity gradients, relative to the north basin, suggest that the south basin is a dominant source for hydrothermal inputs as has been suggested by others (Williams and Von Herzen 1983; Dymond et al. 1989; Collier et al. 1990).

Using Eq. 1 to evaluate the stability of the hypolimnion of the lake shows that the temperature and salinity gradients combine to yield a statically stable water column. The stability is illustrated by the general increase with depth of  $\sigma_{\theta}$  in Fig. 5d and  $\sigma_{(0.45, T)}$  in Fig. 6c.

The relationship between temperature and salinity ( $T$ - $S$ ) in the hypolimnion of the lake provides a powerful method for the comparison of the sources and evolution of north and south basin deep waters.

The bulk  $T$ - $S$  properties of the hypolimnion of Crater Lake document the warmer, more saline nature of the south basin deep water as compared to the north basin deep water (Fig. 7). In north basin waters there is a small increase in salinity below the thermocline as the waters become cooler with depth. The decrease in temperature extends through the midwater and reflects an exponential decrease in the mix between surface-warmed water and deep water with increasing depth. The elbow feature at the temperature minimum defines a trend for those waters influenced by hydrothermally enriched fluids entering at the bottom of the

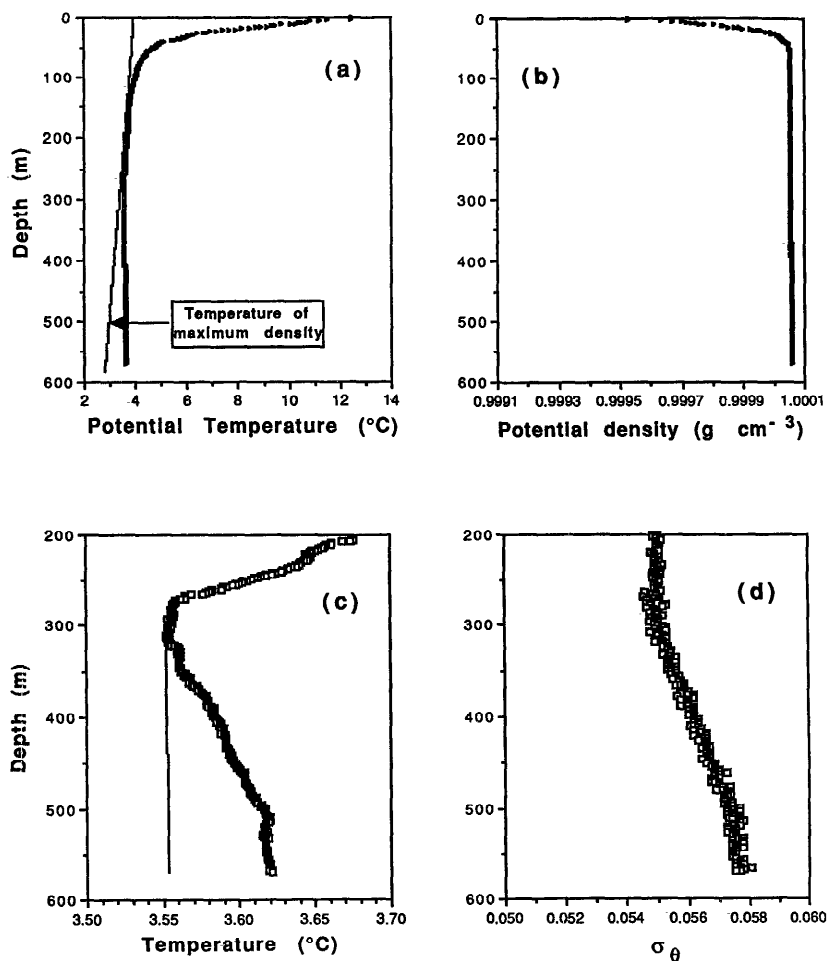


Fig. 5. Potential temperature, potential density, temperature, and  $\sigma_\theta$  as functions of depth in the north basin of Crater Lake on 17 July 1989. Note line demonstrating the adiabatic gradient in panel c and the restricted depth range in panels c and d.

lake. This influence is observed at a depth of  $\sim 350$  m. South Basin near-bottom water (1–5 m above bottom) extends from the north basin bottom-water end-member, to waters of high heat : salt ratio, and to waters of low heat : salt ratio. All near-bottom temperature and salinity data collected from the south basin during 1989 fall between the ③ and ⑥ arms of Fig. 7. In general, deep waters outside the south basin have similar  $T$ – $S$  characteristics to the north basin. These observations again support the hypothesis that the south basin is a dominant source of hydrothermally enriched fluids observed throughout the hypolimnion (Williams and

Von Herzen 1983; Dymond et al. 1989; Collier et al. 1990).

The lines in Fig. 7 represent isopycnals (curves of constant density) relative to 465 dbars (474 m) and are calculated from the equation of state presented by Chen and Millero (1977a,b, 1986). These isopycnals illustrate that the density of the near-bottom fluids increases along both  $T$ – $S$  arms and that the  $T$ – $S$  extrema are vertically stable with respect to background deep water (Fig. 7).

The range of  $T$ – $S$  combinations observed near the bottom of the south basin are incompatible with a simple two end-member

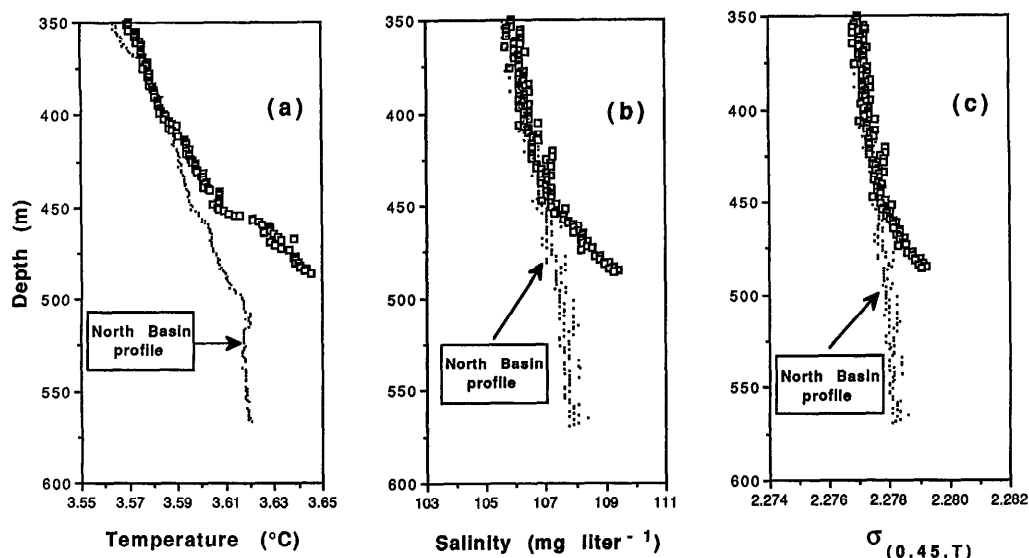


Fig. 6. Temperature, salinity, and  $\sigma_{(0.45, T)}$  all as functions of depth.  $\sigma_{(0.45, T)}$  is the density of the water column at a pressure of 450 dbars and the in situ temperature. Data taken from the south basin ( $\square$ ) and north basin ( $\bullet$ ) on 17 July 1989.

linear mixing of near-bottom waters. Points along the line extending from ③ to ① can be accounted for by mixtures of a warm, salty end-member with background water.

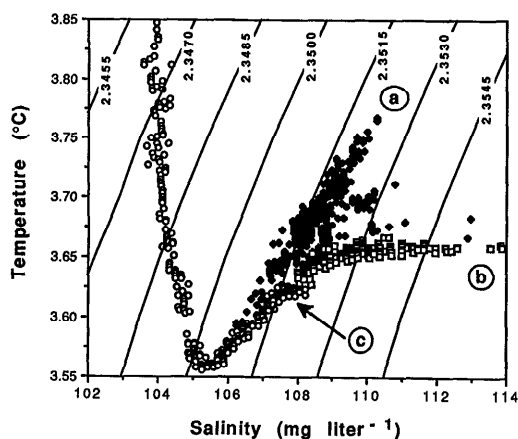


Fig. 7.  $T$ - $S$  diagram of the hypolimnion of Crater Lake.  $\circ$ —North basin deep water ③ with a bottom-depth of 589 m and extending to a depth of 150 m ( $\sim 3.75^\circ\text{C}$  and  $104 \text{ mg liter}^{-1}$ ). South basin deep water is represented by two  $T$ - $S$  end-member arms where ① represents water of high heat:salt ratio, and ② represents water of low heat:salt ratio. Isopycnals, relative to a 465-dbar surface, are calculated with the equation of state of Chen and Millero (1977a,b, 1986).

Points falling below this line, however, must be the result of an additional process or multiple end-member mixing. We suggest that small-scale double diffusion could lead to curvature in the  $T$ - $S$  distribution near the sediment-water interface. This curvature is apparent in the ③ to ② trend in Fig. 7. Curvature in the vertical  $T$ - $S$  distribution in the ocean has previously been attributed to double diffusion (Ingham 1966; Schmitt 1981) and the theoretical basis for the curvature has been described by McDougall (1983). This mechanism would lead to the differing heat:salt ratios near the sediment-water interface due to the preferential loss of heat relative to salt through molecular diffusion. Heat diffuses two orders of magnitude faster than salt, so the heat:salt ratio of a fluid will decrease with time if diffusive fluxes dominate the evolution of these near-bottom fluids (McDougall 1983). Such a process could be occurring within the sediments-debris that covers much of the bottom of the southeastern portion of the south basin (Barber and Nelson 1990). Alternatively, this process could be occurring in the water on small vertical and horizontal scales.

The mechanism for the  $T$ - $S$  distribution in the south basin appears to operate over

small spatial scales within the basin. If double diffusion were operating throughout the water column we would expect to observe steplike features in  $T$  and  $S$  as suggested by Newman (1976). Such features are not observed.

More elaborate models on the formation of these  $T$ - $S$  end-members will be presented elsewhere in relation to the physical limnology of Crater Lake. It is sufficient for our purposes here to demonstrate that the use of a precise definition for salinity permits recognition of distinct water sources in a limnological system that has otherwise been described as homogeneous.

In addition to spatial variations in the  $T$ - $S$  properties discussed above, there are also temporal variations in the deep-lake distributions of these properties which identify important mixing processes. These and other mixing phenomena will be examined in more detail elsewhere in a discussion of the overall physics of the lake.

Water-column stability is highly dependent on the total salt content when the temperature of the fluid is near the temperature of maximum density. Therefore, defining the temperature-conductivity-salinity relationship in deep lakes is critical to understanding the processes that control the redistribution of heat and salt through the water.

### Conclusions

In deep, well-mixed lakes, precise and accurate temperature and salinity measurements are essential for characterizing the physical properties of the water. If silicic acid represents a significant percentage of the TDS load in a system, it can be an important contributor to fluid density.

Without the high-precision measurements we used, the hypolimnion of Crater Lake would appear vertically and horizontally homogeneous. Our data have allowed us to identify active hydrothermal inputs which are responsible for an increase in temperature and salt with depth in the hypolimnion. The temperature and salinity gradients resulting from these inputs generally yield a stable water column. The horizontal heterogeneities in temperature and salinity and the increases in the temperature

and salinity gradients near the bottom of the south basin suggest that this portion of the lake has the largest hydrothermal inputs.

An understanding of the physical processes that control the redistribution of heat and salt in deep lakes is essential to modeling the biogeochemical cycling of ions in these lakes. The use of deep lakes such as the Great Lakes of North America or Lake Baikal as monitors of global change must include precise determination of the physical properties of their waters. We have outlined a method for accurately determining the physical properties of the water column in limnological systems and have demonstrated the utility of this method for Crater Lake.

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