O.E. MEINZER AWARD

Presented to
Donald C. Thorstenson

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U.S. Geological Survey-Denver

Citation by L. Niel Plummer

I am honored to introduce Donald C. Thorstenson as the recipient of the 2008 O.E. Meinzer Award of the Hydrogeology Division of the Geological Society of America. Don Thorstenson is a pioneering geochemist who has tackled some of the most difficult scientific problems in the hydrochemical sciences throughout his career. The impact that Don's science has had on the field of hydrogeochemistry is pervasive and multifaceted. He is a scientist who advanced the way we understand equilibria between impure solids and aqueous solutions, demonstrated the non-equilibrium nature of redox reactions in the environment, showed that individual molecules of isotopic gaseous species moved in accordance with thermodynamic theory in unsaturated zones, developed fundamental principles that govern modeling of geochemical reactions, and developed a means to calculate the distribution of individual isotopic species in aquatic systems.

Don's most significant publications include theoretical calculations and the application of theory to field experiments. One of the first papers Don published is from his doctoral research on the equilibrium distribution of small organic molecules in natural waters (Thorstenson, 1970, Geochim. Cosmochim. Acta, v. 34, p. 745-770). The paper explains how one can use equilibrium and irreversible mass transfer calculations to simulate reaction paths for species that are associated with the decomposition of organic matter. This paper set the stage for quantitative geochemical investigations involving redox reactions and has influenced the work of many who followed to study degradation of organic contaminants in ground-water systems.

At the USGS, Don began field investigations measuring the concentrations of multiple oxidation states of redox-active species in the Fox-Hills aquifer of North Dakota (**Thorstenson et al., 1979, Water Resources Research, v. 15, p. 1479-1498**). He then investigated the thermodynamic properties of the hydrated electron and the fundamental properties of the Standard Hydrogen Electrode (Thorstenson, 1984, U.S. Geological Survey Open-File Report 84-072, 45p). Through these studies, Don demonstrated, both in theory and in practice, that unique values of "the redox potential" could neither be defined nor measured in low-temperature natural environments. Don developed a convention for accounting for electron transfer that greatly facilitated modeling of geochemical reactions undergoing oxidation-reduction in ground-water systems.

In another area of research, Don and Niel Plummer investigated the thermodynamic behavior of impure solids in aqueous solutions. Don introduced the concept of "Stoichiometric Saturation", a thermodynamic state in which a mineral of variable composition reacts as if fixed in composition, a concept originally recognized by J. Willard Gibbs in the 1870s, but still on the back shelf of geochemistry. Don derived the fundamental thermodynamic relationships between solids that react to thermodynamic equilibrium and those in the kinetic state of stoichiometric saturation. He showed how to derive thermodynamic properties from stoichiometric saturation states. This research (**Thorstenson and Plummer, 1977, Amer. Jour. Science, v. 277, p. 1203-1223**) was the foundation on which numerous theoretical and experimental studies followed. The fundamental concepts developed by Don are now found in most geochemical textbooks, and are being employed in a variety of areas, such as nuclear waste disposal, cement stability and reaction behavior, and contaminant transport.

Don Thorstenson brought fundamental rigor to the study of unsaturated-zone gas transport processes. His work started with investigations of carbon isotopes in the unsaturated zone of the western Great Plains (Thorstenson et al., 1983, Radiocarbon, v. 25, 315-346). With Dave Pollock, Don brought the "dusty gas" model of porous media transport into the earth sciences and applied it to unsaturated-zone processes (**Thorstenson and Pollock, 1989, Water Resources Research, v. 25, p. 477-507**, and 1989a, Revs. Geophys., v.27, p. 61-78). Finally, Don applied his expertise to the assessment of nuclear waste disposal at Yucca Mountain (**Thorstenson et al., 1998, Water Resources Research, 34(6), 1507-1529**). Don recognized and demonstrated that isotopically different gaseous species of CO_2 ($^{14}CO_2$, $^{13}CO_2$, $^{12}CO_2$) had unique transport properties and therefore diffused independently and not simply with "total CO2" in natural porous media. Going further, he also reexamined the assumptions inherent in Fick's laws, and came to the conclusion that the application of Fick's laws could lead to significant errors in many real-world situations. His work advanced the understanding of unsaturated zone processes at Yucca Mountain. Working with Ed Weeks and others, Don showed that unsaturated-zone air residence times are only a few years in the shallow parts of the mountain.

Recently, Don Thorstenson developed a unified formulation that can be used to describe the transport and reaction of multiple isotopic species in gases, water and solids. Present approaches make such calculations using the average isotopic composition of the element, and do not explicitly allow consideration of individual molecular species interactions. In this latest research achievement (**Thorstenson and Parkhurst, 2004, Geochim. Cosmochim. Acta, v. 11, p 2449-2465**), Don went once again back to the basics, re-examining all the assumptions made in modern theories of isotopic fractionation, back through the classic works of Urey and others. In collaboration with David Parkhurst, this treatment has now been implemented in a version of the PHREEQC geochemical code. Don retired from the USGS National Research Program in 2003; however, he continues to expand the isotopic calculation capabilities of the PHREEQC code under the USGS Scientist Emeritus Program. It will likely be years before geochemists catch up with Don's research in this area.

For 20 years at the USGS, Don was one of the principal instructors for a training course on the geochemistry of ground-water systems. This course produced a generation of hydrologists and geochemists who

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* *Citation publications noted in bold.*

have gone on to apply their knowledge to many USGS programs at state and national levels. Don leaves a legacy of outstanding fundamental science that has profoundly influenced the application of thermodynamics and kinetics to hydrogeological systems. As recipient of the 2008 O.E. Meinzer Award, we thank Don Thorstenson for helping us get to where we are today and for the path he has put us on for the future.

Response by Donald C. Thorstenson

I would like to thank the Hydrogeology Division, the awards committee, all those involved in nominating me for this award, and Niel Plummer for his flattering citation. Many people are owed heartfelt thanks for the fact that I am here. First and foremost, the three most important people in my life, my wife Gail and sons Eric and Donald. Gail put me through school, raised the kids, helped support the family, and with Eric and Donald survived many summers in unexpected places. But most of all, she was always there with a sympathetic ear for uncounted hours when I would arrive home from work feeling the need to talk Had she been able to charge proffesional therapist rates, she would now be a wealthy woman.

In an amazing stroke of good luck for me, Bob Garrels, Hal Helgeson, and Fred Mackenzie all arrived at Northwestern University the year after I enrolled there as a graduate student in geology. In addition to his teaching, Bob spent many hours working with me on practice oral exams in the hope that I might survive the real thing, and Hal and his courses provided the theoretical and computational framework for my dissertation. Fred (who I worked with for another decade) showed me how to integrate it all in the field and laboratory, at times shared his home with me, and helped get my career off to a running start.

From Northwestern I moved to a faculty position at the Department of Geological Sciences at Southern Methodist University, where four graduate students deserve my thanks—Bob Leeper, Alfred Liaw, Jackie Pruitt, and Keith Talley. At SMU I developed an interest in groundwater studies, and through Blair Jones, was able to arrange a sabbatical year at the USGS Water Resources Division geochemical research group in Reston, Virginia. Two years later I moved to the USGS permanently.

Shortly after my sabbatical arrival, Don Fisher and I attended a USGS coal hydrology meeting in North Dakota, where we met Mack Croft, who introduced us to the Fox Hills Aquifer. Mack had the hydrologic expertise, Don the analytiical skills, I did the field work and modeling, and the result was the cited paper on Fox Hills geochemistry.

The second cited paper, with Niel Plummer, deals with magnesian calcites and solid solution theory.

Niel had a data set, I had some theoretical concepts, and the result was a paper outside the realm of conventional geochemical wisdom—the following year it received 33 journal pages of discussion, pro and con. The literature search for work supporting our concepts led me finally to the classic work of J. W. Gibbs (1878) where they were laid out clearly. Had he possesssed Niel's data set, and the aqueous speciation concepts available to us, he could have published our paper exactly 100 years earlier. It's hard to be truly original…

Niel mentioned in his citation the work on thermodynamics of hydrated electrons. This research was done with John Hostettler, a friend and physical chemist from San Jose State. John spent a sabbatical year at the USGS pursuing this topic and its implications for natural redox processes. The resulting publications could not have happened without him.

Early in my sabbatical year I also met Ed Weeks. Approximately a year later, Ed, myself, and Herb Haas were in the field to begin a 2-decade study of unsaturated-zone $^{14}CO_2$ distribution and gas transport. Herb was director of the radiocarbon laboratory at SMU, then DRI Las Vegas, and in addition to providing the ^{14}C analytics, worked in the field with us throughout these studies. Much of our early work was done at a lignite mine in North Dakota, where we noted small gradients in N_2 and argon at a site where advective transport processes other than barometric pumping appeared to be minimal. The quest to explain these gradients led to the literature of the "dusty gas" model.

The dusty gas mathematics are daunting, and I was near, or at, the limit of my abilities when another chance meeting occurred, this time with Dave Pollock. Dave's background is in chemical engineering, and he brought a new and much greater understanding to this work. We generated various applications of the dusty gas equations to the North Dakota field site, but the only contribution to the actual dusty gas model itself—showing that the equations kept the same form in terms of potentiometric head, as well as pressure—was produced entirely by Dave.

Ed Weeks eventually led our unsaturated-zone studies to Yucca Mountain. Here advective gas transport is dominant, exemplified by the "blowing boreholes" that Ed is noted for studying. The geochemical aspects of this study helped identify CO_2 sources and put a time frame on the transport processes in the mountain through the use of carbon isotopes and CFC's. Many thanks are due coauthors Ed Weeks, Herb Haas, Ed Busenberg, Niel Plummer, and Charlie Peters.

I also met Dave Parkhurst during my sabbatical—another personal and professional association to span three decades. Dave, Niel, and I worked on the geochemical modeling code PHREEQE, worked and published on forward and inverse geochemical modeling, and jointly taught a USGS-WRD geochemistry course for more than twenty years. Recently Dave and I published the last paper cited in this award. Once again I had some theoretical concepts, and in this case, Dave was able to implement them in PHREEQC, resulting in the ability to calculate individual isotope equilibrium constants from fractionation data. Originality was again hard to come by - in his classic 1947 paper, Harold Urey calculated fractionation properties for the individual species H_2O, HTO, and T_2O, to cite one example. Had today's aqueous speciation modeling capabilities been available then, it seems very likely that calculations of Urey and/or his colleagues would have taken the same direction that I did 60 years later.

I was very surprised to be invited out of near-retirement to receive this award, and extrordinarily pleased and honored to do so.