Geochemistry and the understanding of ground-water systems

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Abstract Geochemistry has contributed significantly to the understanding of ground-water systems over the last 50 years. Historic advances include development of the hydrochemical facies concept, application of equilibrium theory, investigation of redox processes, and radiocarbon dating. Other hydrochemical concepts, tools, and techniques have helped elucidate mechanisms of flow and transport in ground-water systems, and have helped unlock an archive of paleoenvironmental information. Hydrochemical and isotopic information can be used to interpret the origin and mode of ground-water recharge, refine estimates of time scales of recharge and ground-water flow, decipher reactive processes, provide paleohydrological information, and calibrate ground-water flow models. Progress needs to be made in obtaining representative samples. Improvements are needed in the interpretation of the information obtained, and in the construction and interpretation of numerical models utilizing hydrochemical data. The best approach will ensure an optimized iterative process between field data collection and analysis, interpretation, and the application of forward, inverse, and statistical modeling tools. Advances are anticipated from microbiological investigations, the characterization of natural organics, isotopic fingerprinting, applications of dissolved gas measurements, and the fields of reaction kinetics and coupled processes. A thermodynamic perspective is offered that could facilitate the comparison and understanding of the multiple physical, chemical, and biological processes affecting ground-water systems.

Résumé La géochimie a contribué de façon importante à la compréhension des systèmes d'eaux souterraines pendant les 50 dernières années. Les avancées ont portées sur le développement du concept des faciès hydrochimiques, sur l'application de la théorie des équilibres, l'étude des processus d'oxydoréduction, et sur la datation au radiocarbone. D'autres concepts, outils et techniques, ont aidé à l' élucidation des élucider les mécanismes d'écoulement et de transport dans les systèmes d'eaux souterraines, et à la compréhension des archives informations paléo-environnementales. Les informations hydrochimiques et isotopiques peuvent être utilisées pour interpréter l'origine et le mode de recharge des eaux souterraines, affiner l'estimation des temps de recharge et d' écoulements, déchiffrer les processus de réaction, apporter une meilleure information paléohydrogéologique et calibrer les modèles d'écoulement des eaux souterraines. Beaucoup de progrès ont besoin d'être réalisés pour obtenir des échantillons représentatifs. Des améliorations sont nécessaires dans l'interprétation des informations obtenues, et dans la construction et l'interprétation de modèles numériques utilisant des données hydrochimiques. La meilleure approches arsurément un processus itératif optimisé entre la collection de données de terrain et l'analyse, l'interprétation, et l'application d'outils de modélisation statistique, inverse et direct. Des avancées sont anticipées par les dans le demeine des études microbiologiques, dans la caractérisation des matières organiques naturelles, le marquage isotopique, les mesures de gaz dissous, les réactions cinétiques la compréhension des couplages. Une perspectives thermodynamique pourraient faciliter la comparaison et la compréhension des multiples processus physiques, chimiques et biologiques qui affectent les systèmes hydrogéologiques.

Resumen La geoquímica ha contribuido significativamente al entendimiento de los sistemas de aguas subterráneas durante los últimos 50 años. Entre los avances históricos puede incluirse el desarrollo del concento de facies hidroquímicas, la aplicación de la teoría de equilibrio, investigación de los procesos oxidación-reducción, y datación con radiocarbono. Otros conceptos, herramientas y técnicas hidroquímicas han ayudado a escla-

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recer los mecanismos de flujo y transporte en sistemas de agua subterránea, y han ayudado a descifrar un archivo de información paleoambiental. Información hidroquímica e isotópica puede utilizarse para interpretar el origen y modo de recarga de agua subterránea, descifrar procesos reactivos, aportar información paleohidrológica, y calibrar modelos de flujo de agua subterránea. Necesita avanzarse en la obtención de muestras representativas. Se necesitan mejoras en la interpretación de la información obtenida y en la construcción e interpretación de modelos numéricos que utilizan datos hidroquímicos. El mejor enfoque asegurará un proceso iterativo optimizado entre toma y análisis de datos de campo, interpretación, y la aplicación de herramientas de modelizado estadísticas, directas, e inversas. Se anticipan avances a partir de investigaciones microbiológicas, la caracterización de orgánicos naturales, caracterización isotópica, aplicaciones de mediciones de gas disuelto, y los campos de cinética de reacción y procesos acoplados. Se ofrece una perspectiva termodinámica que podría facilitar la comparación y entendimiento de los múltiples procesos físicos, químicos, y biológicos que afectan sistemas de aguas subterráneas.

Introduction

Over the past 50 years, advances in geochemical methods and approaches have aided our ability to interpret hydrochemical processes in ground-water systems, and improved understanding of how structural, geological, mineralogical, and hydrological features affect flow and chemistry in these systems. Significant advances have been made through laboratory experiments, and kinetic and thermodynamic data evaluation, providing essential reaction-process information. Improvements in analytical techniques for an increasing number of chemical/isotopic substances that can be measured in smaller samples and at lower concentrations have led to significant advances. Finally, increasing computational power has enhanced use of numerical modeling techniques and has provided increasingly sophisticated interpretations of ground-water flow/reaction systems.

There is considerable literature on the interpretation of geochemical processes in ground waters based on hydrochemical data and model simulations of hypothetical reactions. Geochemists have evaluated redox reactions and the partial equilibrium concept in aquifers in which chemical evolution is driven by one or more concurrent irreversible reactions. Carbonates, primary silicates, clays and sulfide minerals, ion exchange, and organic carbon reactions play important roles in driving chemical evolution in these systems. Ground-water geochemists have also addressed important environmental issues, such as arsenic contamination, nutrient and trace element transformations, the origins of acid-mine drainage water, and geomicrobiological reactions in the subsurface that affect

reaction rates, redox processes, and freshwater aquifer storage and recovery.

Back and Herman (1997) trace the origins of hydrogeology and hydrochemistry in the United States back to the early 1900s. Narasimhan (Hydrogeology Journal, this issue) also offers a historical perspective and refers to the pioneering works of Palissy (1580), Palmer (1911), Renick (1924), Piper (1944), and Hem (1959, 1992). This paper examines some major developments in hydrogeochemistry from the early 1950s until the present (2004). Significant historical advances include development of the hydrochemical facies concept, applications of thermodynamic equilibrium principles (and recognition of their limitations), increased understanding of redox reactions, and ground-water dating with cosmogenic ^{14}C. The paper also discusses progress and problems in more recent areas of research in hydrochemistry, such as (1) obtaining representative information from ground-water systems; (2) using ground-water tracers to understand ground-water flow and reactive processes; (3) obtaining ground-water system ages for various time scales; and (4) numerical modeling of geochemical processes and the application of geochemical transport codes. Philosophical considerations regarding geochemical investigations and numerical modeling also are discussed. The paper closes with some comments and opinions on the future of geochemistry as it relates to the further understanding of ground-water systems.

The field of ground-water geochemistry is too large to fully review here, and the authors apologize for the omissions that have been made. For example, some areas of active hydrogeochemical research that could not be addressed here include: contaminant hydrology, thermodynamic data evaluation, experimental and theoretical reaction kinetics, characterization of mineral-phases and their surfaces, sorption processes, natural organic geochemistry, and microbial processes. Further information on the geochemistry of ground waters can be found in Appelo and Postma (1993), Chapelle (1993), Drever (1997), Hem (1959, 1992), Hitchon et al. (1999), Langmuir (1997), Nordstrom and Munoz (1994), and Stumm and Morgan (1996).

The hydrochemical facies concept

Geochemical reactions along ground-water flow paths can lead to regional variations in water composition that evolve in the direction of flow. Isoconcentration contours of reacting dissolved constituents drawn on maps of water composition tend to align *normal* to the direction of ground-water flow. Recognition of geochemical patterns in aquifers can be traced to Cederstrom (1946), Foster (1950), Chebotarev (1955), Garmonov (1958), Kamensky (1958), White et al. (1963) and earlier papers, but it was Back (1960, 1966) who defined the hydrochemical facies concept, placing the geochemical observations in the context of ground-water flow in aquifers of relatively homogeneous hydrologic and mineralogic properties.

Sources of water entering ground-water systems also have been distinguished based on the presence of, or the concentration of, inert constituents or tracers. In cases where inert tracer concentrations vary spatially along the ground-water recharge area, the path followed by the tracer through the aquifer delineates the flow direction (e.g. Olmsted 1962; Robertson et al. 1974; Vogel and van Urk 1975; Siegel 1991). In this case, hydrochemical facies (sometimes referred to as "hydrochemical zones") will align *parallel* to the flow direction. In more complex cases, the concentration of reactive constituents may vary spatially and temporally along the recharge area, and may also evolve along the direction of flow. Extracting flow and hydrological information from geochemical observations requires understanding the aqueous reactivity of aquifer materials and the spatial and temporal distribution of recharge compositions. Many of the geochemical patterns observed in ground-water systems can also be related to heterogeneities in either reactive mineral abundances or in hydrologic properties, and may be difficult to resolve given the limited information typically available.

Flow patterns in regional aquifers, deduced from mapping hydrochemical facies and zones, can indicate flow directions that occurred over time scales considerably greater than the time scale over which present-day, or even predevelopment water levels were established. Differences between regional flow directions deduced from hydrochemical patterns and those indicated by a modern (predevelopment) potentiometric surface can indicate changes in hydraulic conditions (e.g. recharge rate) on a shorter, more recent time scale than those responsible for hydrochemical observations (Plummer et al. 2004a, 2004b, 2004c; Sanford et al. 2004a, 2004b).

Thermodynamic equilibrium and beyond

Thermodynamic equilibrium principles and models

In the early 1960s, geochemists applied to the speciation of natural waters the fundamental principles of thermodynamic equilibrium first established by Gibbs (1876, 1878). The primary question was: To what extent does mineral-water equilibrium control the chemical composition of natural waters? Following development of the first ion-association model applicable to natural waters (Garrels and Thompson 1962), efforts were made to extend those models to complex multicomponent systems, including ground-water systems. Several numerical models were developed (cf. review in Nordstrom et al. 1979)—including the PATHI speciation and reaction path model (Helgeson 1968; Helgeson et al. 1969, 1970) and the WATEQ speciation code (Truesdell and Jones 1974). Additionally, theoretical development and parameterization of the Specific Interaction Model for electrolyte solutions and their mixtures by K.S. Pitzer and colleagues, and the extensions made to natural waters by C.E. Harvie, N. Moller, J.H. Weare and others (e.g. Harvie et al. 1984), allowed the speciation of many highly saline natural waters (Pitzer 1991, 1994, and references therein). Numerical simulations of aqueous solutions and their reactions with other solid, gas, and fluid phases continues to be refined and extended through the measurement of additional thermodynamic data and improved theoretical descriptions of reactive processes (sorption, solid-solutions, kinetics of heterogeneous reactions, organic reactions, extensions to high temperature, pressure, and ionic strength).

Application of speciation models to low-temperature ground-water environments has led to several important principles/observations. Reactions among aqueous species that occur within the same oxidation state of the elements involved (e.g. $CO_2/HCO_3^-/CO_3^{2-}$; SO_4^{2-}/HSO_4^-) are rapid and equilibrium can be assumed; in contrast, equilibrium is usually not attained between aqueous species with differing oxidation states (e.g. SO_4^{2-}/HS^-; HCO_3^-/CH_4; Fe(II)/Fe(III)). A small number of minerals, usually of relatively high solubility, appear to behave reversibly in natural systems (e.g. calcite, gypsum, halite, fluorite); most other minerals do not react to equilibrium but can still have an important effect on natural-water chemistry (plagioclase, biotite, and other primary silicates). Metastable minerals tend to approach equilibrium more easily than their more stable polymorphs (Steefel and Van Cappellen 1990; amorphous ferric hydroxide instead of hematite). Some weathering products of primary silicates (e.g. kaolinite and gibbsite) tend to react to equilibrium, but kinetic processes are important in the formation of complex siliceous clay minerals such as smectites (Jones and Bowser 1978; Eberl et al. 1990; White and Brantley 1995; Drever 1997; Bowser and Jones 2002; Kim et al. 2004). Thermodynamic equilibrium can be defined as a reactive steady-state (microscopic reversibility) between an aqueous phase and a bulk solid phase. As the ability to observe mineral surfaces improved, it was recognized that on laboratory time scales, interfacial reactions that occurred only involved a few atomic layers of the bulk solid (Walton 1967; Buddemeier et al. 1972; Mozeto et al. 1984; Garnier 1985; Plummer et al. 1992).

Ground-water systems were recognized early on as partial equilibrium systems (Korzhinskii 1936; Helgeson 1968); that is, where some reactions respond reversibly while driven by one or more irreversible reactions (e.g. oxidation of organic carbon driving sulfate reduction, and/or carbonate mineral reactions; dissolution of anhydrite driving dedolomitization; dissolution of primary silicates driving the formation of clays and cementation with calcite and silica). These reactions are important in understanding geochemical evolution of ground-water systems, and can affect the hydrologic properties of aquifer systems. Some natural waters that appear to be at or near equilibrium with a given mineral phase, according to speciation calculations, may in fact be undergoing significant dissolution/precipitation of the mineral as a result of other irreversible reactions.

Reaction kinetics and reactive surface area

Much work remains in the area of mineral kinetics. Laboratory results have not translated well to natural environments, especially in the case of mineral-water reactions near equilibrium, where even trace concentrations of dissolved organic species, minor elements, or microbes can greatly alter reaction rates. The determination of rates of water–rock reactions from in-situ field observations offer the possibility of combining measurements of ground-water age/residence-time with estimates of mineral mass transfer determined from geochemical mass balances (Paces 1983; Aeschbach-Hertig et al. 1998; Burton et al. 2002; Burns et al. 2003). However, difficulties in determining reactive surface areas in aquifers limit the transfer value of the rates determined (White and Peterson 1990; Hochella and White 1990; White and Brantley 1995; Brantley and Chen 1995; White et al. 2001). Reaction rates also have been estimated in-situ by placing well-characterized mineral samples or aquifer materials in wells (Brown and Glynn 2003), in submerged limestone fracture zones (Plummer et al. 2000), or in streams (Herman and Lorah 1988; Dreybrodt et al. 1992; Liu et al. 1995), and measuring reactive gains/losses over time. This approach merits further investigation, although problems remain in relating in-situ experimental results to observed larger-scale field rates.

The determination of effective surface areas in undisturbed aquifers remains difficult. In fractured rock systems, geochemical techniques have provided reasonable estimates of the surface area of rock exposed per unit volume of slowly flowing water, a property important in assessing the potential for contaminant sorption and matrix diffusion. One promising technique involves the measurement of a short-lived, inert, radioisotope (e.g. ^{222}Rn) produced through decay of a longer-lived parent nuclide (e.g. ^{238}U) in the contacting rock (Andrews et al. 1986, 1989; Glynn and Voss 1999).

Solid solution and sorption processes

Although significant success was achieved in modeling reactions in which minerals were treated as pure phases of fixed composition, most minerals have variable compositions that can affect their solubility and behavior. Sometimes these "impure" phases (solid-solutions) react as if fixed in composition (as a metastable state). Alternatively, especially for more soluble phases, "impure" solids can quickly recrystallize and adjust their composition in relation to the changing composition of the contacting water. Thorstenson and Plummer (1977), Lippmann (1977, 1980), Busenberg and Plummer (1989), Glynn and Reardon (1990, 1992), Glynn et al. (1990, 1992), Glynn (1991, 2000), Gamsjäger et al. (2000), and Prieto et al. (2000) provide further information on this area of research. Solid-solution theory is currently applied to nuclear-waste disposal issues (relating mainly to the stability of metastable complex radionuclide phases and to the behavior of cement), and is sometimes important in understanding the chemistry of natural waters (e.g. fluo-

ride control in the Black Creek aquifer in South Carolina, Konikow and Glynn 2005, in press). As overall understanding of the controls and behavior of trace elements in natural waters improves, relatively complex theories of heterogeneous reactions (solid-solutions, ion exchange and surface complexation) will find greater application and require further development. Reviews of some of the most popular sorption and ion-exchange theories can be found in Davis and Kent (1990) and Appelo and Postma (1993).

Oxidation/reduction processes

The recognition that large irreversible nonequilibrium changes often accompanied changes in the oxidation states of elements in ground-water systems was an important development. Early aqueous-speciation models did not account for different redox states. Electrochemical theory and data originally developed by metallurgists (Pourbaix 1949) was applied to ground-water geochemistry. Krumbein and Garrels (1952), Baas-Becking et al. (1960), Garrels and Christ (1965), and Sillén (1967) recognized that pH and redox conditions could be used to characterize predominant aqueous speciation, mineral reactions and stabilities in a wide range of natural environments. Thorstenson (1984) and Hostettler (1984) provided a historical perspective on the concept of redox states and their application in geochemistry. A series of investigations of various redox couples in natural waters demonstrated that most redox reactions in natural systems are not at equilibrium, and indicated the difficulties involved in assessing the redox state(s) of natural waters (Morris and Stumm 1967; Thorstenson et al. 1979; Thorstenson 1984; Runnells and Lindberg 1990; Stumm and Morgan 1996). Others described the natural sequence in which various redox reactions occur in natural environments (Baedecker and Back 1979; Champ et al. 1979; Berner 1981; Stumm and Morgan 1996).

The PATHI code (Helgeson 1968; Helgeson et al. 1970) was the first code that attempted to model redox reactions (initially on the basis of the SO_4^{2-}/S^{2-} activity ratio). The method required tracking of extremely small numbers, such as the activity of S^{2-} in oxic environments, and led to inefficient methods and numerical dispersion. A simple electron conservation convention devised by D.C. Thorstenson (described in Parkhurst et al. 1980, 1982; Plummer et al. 1983) permitted extension of geochemical reaction modeling from relatively simple inorganic water–rock reactions to complex redox systems. This convention was adopted in PHREEQE (Parkhurst et al. 1980), BALANCE (Parkhurst et al. 1982) and NETPATH (Plummer et al. 1994). The convention is still used in NETPATH, but with increased computing capacity, was replaced by O and H mass-balance relations in EQ3/6 (Wolery 1979; Wolery et al. 1990) and PHREEQC, PHREEQCI (Parkhurst 1995; Parkhurst and Appelo 1999; Charlton et al. 1997; Charlton and Parkhurst 2002).

Thermodynamic equilibrium theory, applied to redox systems or to other reactions, provides reference states that are useful in assessing departures from equilibrium,

in calculating redox-reaction sequences, and in determining the potential for chemical and isotopic change in both biotic and abiotic systems.

Geochemical tracers of ground-water flow and reactive processes

Hydrochemical and isotopic data are useful in identifying sources of recharge to ground-water systems and in tracing ground-water flow. Differences in chemical and isotopic composition have been used to trace the infiltration of surface water, recognize leakage between aquifers, define areas of seawater intrusion, and investigate recharge rates through deep unsaturated zones. Cation-anion association (calculated according to relative salt solubility—SNORM) has been used to identify solute origin and trace movement through ground-water systems (Bodine and Jones 1986, 1990; Jones and Llamas 1989; Jones et al. 1994; Kauffman et al. 1998). Environmental tracers, such as temperature, ^2H, ^{18}O, ^{14}C, ^3H, $^3H/^3He$ and dissolved gases, have helped refine estimates of recharge and flow time scales, interpret the origin and mode of aquifer recharge, provide temporal and spatial information to aid in calibration of ground-water flow models, and recognize paleowater that is, for all practical purposes, a nonrenewable resource. Isotopic and trace-element information on representative solid phases and mineral forms also has aided in understanding paleohydrological conditions (e.g. Winograd et al. 1992, 1997; Coplen et al. 1994; Plummer et al. 1990; Wallin and Peterman 1999; Glynn and Voss 1999). Environmental tracers have enormous potential in assessing the sustainability and the vulnerability of ground-water resources.

A large number of tracer measurements can be made, yet it is not always obvious a priori which of the measurements will aid in interpreting flow and reaction processes that are or have occurred in the aquifer, and which will be redundant with others. Multiple measurements of multiple tracers are usually desired, but this is ultimately limited by available resources. "Intuition" and an understanding of the geologic, mineralogic, and hydrologic framework are key to making appropriate decisions.

Many of the innovative measurements that are in the vanguard today are not routinely available, except in limited numbers at a limited number of laboratories. Forty years ago, measurements of ^2H and ^{18}O or of ^3H and ^{14}C, now standard measurements, were also uncommon and available from a limited number of laboratories. Today, geochemists increasingly are including measurements of dissolved gases, trace elements, and the stable isotopes of elements such as Sr, Ca, S, B, N, C, Li, Cl, Fe, U, Th, and noble gases in ground-water. Isotope measurements on specific molecular species also are being conducted to provide information on reactive processes and on solute origins (Schmidt et al. 2004; Hunkeler et al. 1999).

Each added measurement adds complexity to the hydrogeochemical elucidation of water–rock interactions, mixed chemical and isotopic sources, and other physical or chemical processes. Inert tracers can provide direct information on ground-water origins, flow directions, and residence times (e.g. temperature, stable isotopes of water, noble gases, and initial ^3H [^3H + tritiogenic ^3He]). Reactive tracers (e.g. isotope compositions such as ^{13}C, ^{34}S, $^{87}Sr/^{86}Sr$, ^{15}N; dissolved constituents such as $N_{2,aq}$, CH_4 and other major/trace species) can provide information on geochemical processes, ground-water environments, recharge sources, and water ages. Kendall and McDonnell (1998), Clark and Fritz (1997), Cook and Herczeg (2000) and references therein provide excellent overviews of the use of isotope tracers in hydrology.

Process time scales in ground-water systems

The detection and measurement of an increasing number of chemical and isotopic tracers at ever-lower concentrations has led to an increase in estimates of ground-water ages over a wide range of time scales. Ground-water dating has proven useful in estimating recharge rates, calibrating flow models, and assessing the sustainability of ground-water extraction rates. Ground-water dating also has been used to extract information on rates of geochemical and microbiological processes in aquifers, to classify hydrogeologic environments on the basis of contamination potential (Nelms et al. 2003), to retrieve historical records of contaminant loading to aquifers (Böhlke and Denver 1995; Lindsey et al. 2003; Shapiro et al. 2004) and to estimate remediation times for contaminated ground-water systems.

"Ground-water age" refers to the travel time between the point of recharge and the point of sampling. Dating the water itself, through analysis of water isotopes, is an ideal way to obtain ground-water ages, but conservative tracers are commonly used instead. Typically, multiple tracers are used in estimating ground-water ages because of uncertainties in the available techniques, flow and transport complexities, and difficulties in obtaining representative data. A number of papers review the advantages and limitations of geochemical dating techniques in more detail than can be afforded here (Davis and Bentley 1982; Fontes 1983; Moser and Rauert 1983; Evans 1983; Florkowski and Rozanski 1986; Fröhlich 1990; Plummer et al. 1993; Lehmann et al. 1993; Małoszewski and Zuber 1996; Cook and Solomon 1997; Kipfer et al. 2002). The subject of dating of "young" ground water is covered in Cook and Herczeg (2000), Plummer (2005), and in the "IAEA Guidebook on the Use of Chlorofluorocarbons in Hydrology" (IAEA 2005).

Two conceptually different approaches are available to date ground water. The first approach involves the measurement of a "clock;" that is, the measurement of the concentration of an element or isotope having known (or assumed) initial concentration inputs, and a known rate of growth or decay in the ground-water environment. The second approach makes use of the known history of a time-dependent environmental "signal" in the water and/or in the solutes that recharge a ground-water system.

Clocks

Examples of dating with clocks include applications of cosmogenic isotopes such as ^{14}C, ^{32}Si, ^{39}Ar, ^{81}Kr, ^{36}Cl, and ^{35}S, or applications involving radionuclides of anthropogenic origin with a highly variable but relatively well-known recharge history, such as ^{3}H, $^{3}H/$ ^{3}He, and ^{85}Kr. In the cases of dating with cosmogenic isotopes, the initial concentration is known from atmospheric measurements (^{32}Si, ^{39}Ar, ^{81}Kr, and ^{35}S) or reconstructed from environmental records (^{14}C, ^{36}Cl). A range of time scales is possible with cosmogenic isotopes, depending on the half-life and analytical precision. The need to know the history of initial conditions can be eliminated if both the parent and daughter isotopes can be measured, such as in the $^{3}H/^{3}He$ dating technique, where age is calculated from measurement of ^{3}H and its decay product, tritiogenic helium-3, $^{3}He_{tri}$ (Schlosser et al. 1988, 1989, 1998; Bayer et al. 1989; Poreda et al. 1988; Solomon and Sudicky 1991; Solomon et al. 1993; Solomon and Cook 1999).

Dating techniques using other radionuclide pairs, or perhaps even chemical pairs (e.g. complex organic chemical/metabolite pairs such as those in pesticide degradation chains) may find some use in the future; development of such techniques will, however, require substantially more knowledge than is currently available on processes and conditions controlling growth/decay rates.

The most successful and extensively investigated "clock" in ground-water hydrology is that of carbon 14. The development of radiocarbon dating of dissolved inorganic carbon (DIC) in ground water provided an important link between ground-water chemistry and hydrology of large regional aquifers where flow can be on time scales of thousands to tens of thousands of years. Dating cosmogenic ^{14}C in ground water started in the late 1950s (Münnich 1957; Brinkmann et al. 1959, 1960). Studies in the 1960s and 1970s improved geochemical corrections in the technique, demonstrated ^{14}C-based estimates of travel times in aquifers, and showed the use of radiocarbon dating in estimating hydraulic conductivity (Ingerson and Pearson 1964; Hanshaw et al. 1965a, 1965b; Pearson and White 1967; Tamers 1967, 1975; Pearson and Hanshaw 1970; Mook 1972; Hanshaw and Back 1974; Fontes and Garnier 1979). With time, corrections/adjustments to the ^{14}C technique have become more sophisticated, accounting for a greater diversity of geochemical reactions and hydrologic effects such as matrix diffusion, isotopic exchange, carbonate–mineral recrystallization, and microbial degradation of multiple organic carbon sources (Wigley et al. 1978; Mook 1980; Sudicky and Frind 1981; Murphy et al. 1989; Fontes 1992; Wassenaar et al. 1991; Małoszewski and Zuber 1991; Plummer et al. 1994; Aravena et al. 1995; Sanford 1997; Kalin 2000; Plummer and Sprinkle 2001; Gonfiantini and Zuppi 2003). Radiocarbon dating can lead to adjusted ^{14}C ages of a few thousand to approximately 30,000 years. Ages younger than a few thousand years are affected by uncertainty in the initial ^{14}C activity; ages greater than 30,000 years have large uncertainties because of the extent of geochemical/hydrogeologic corrections required and because of the analytical uncertainty of low ^{14}C activities. Because multiple geochemical adjustment models can usually be constructed for a given water sample, multiple age estimates are possible. Pearson (1992) presented a calculation that determined the age distribution and uncertainty in adjusted ^{14}C ages based on reaction model uncertainty.

Following improvements in collection/processing/ procedures (Murphy et al. 1989; Wassenaar et al. 1991; Burr et al. 2001), it is now possible to determine the ^{14}C age of dissolved organic carbon (DOC) in some ground waters with less than 0.5 mg/l of DOC (Thomas et al. 2001; Morse 2002). Dating of DOC with ^{14}C can be useful in aquifers where geochemical corrections for water–rock interaction lead to large uncertainties in adjusted ^{14}C ages of DIC and can help eliminate some inorganic reaction models in nonunique situations.

Techniques continue to be developed to date waters younger than the several thousand year limit of radiocarbon dating, but older than the 0–50 years time scale for which anthropogenic signals and nuclear tracers/clocks are available (e.g. ^{3}H and $^{3}H/^{3}He$ dating). The cosmogenic radioisotopes ^{39}Ar (half-life 269 years) and ^{32}Si (half-life 140 years) have favorable half-lives for groundwater dating in the 50–1,000 years range, and continue to be investigated in ground-water systems (Loosli et al. 2000; Morgenstern 2000), but serious obstacles to their collection, measurement, and interpretation remain.

Research also progresses in efforts to date ground waters beyond the 30,000 years range of the ^{14}C technique. The need for dating old waters is often related to investigations into the potential suitability of groundwater environments for the isolation of nuclear waste. Chlorine-36 (^{36}Cl) (half-life: 301,000 years) has been considered a potential dating tool for old ground waters with some promising results (Bentley et al. 1986; Fabryka-Martin et al. 1987; Nolte et al. 1990; Torgersen et al. 1991; Phillips 1999; Lehmann et al. 2003), but multiple ^{36}Cl sources make dating attempts difficult in some environments (Balderer and Synal 1996; Fontes 1994). Application of the ^{36}Cl dating technique requires knowledge of the initial (pre-anthropogenic) ^{36}Cl concentration (Davis et al. 2000, 2003) and of processes controlling the transport and build-up of stable Cl in ground water (evapotranspiration, evaporite dissolution, fluid-inclusion sources, diffusion). ^{81}Kr offers another potential dating tool on the 100,000 years time scale (Lehmann et al. 1985, 2003; Collon et al. 2000). Measurements of ^{81}Kr recently showed a ground water in the Sahara to be at least one million years old (Sturchio et al. 2004).

^{4}He (a stable isotope) offers a potential dating technique for a wide range of fluid ages. ^{4}He accumulates in ground water through the decay of U and Th and all their alpha-emitting daughter products in the natural U and Th isotope series. The ^{4}He technique offers promise because (1) ^{4}He accumulates with time, (2) it does not depend on a variable cosmogenic source, and (3) ^{4}He sources are

widely distributed in aquifer materials. The ability to obtain accurate age estimates depends on two primary criteria (Torgersen 1992): (1) a known source function for the production and rock-to-water transfer of the ^{4}He isotope; and (2) a closed system evolution. In practice, ^{4}He offers at best a semiquantitative technique for waters that are more than tens of thousands of years old (e.g. Andrews and Lee 1979; Torgersen 1980, Andrews et al. 1982, 1985; Torgersen and Ivey 1985; Andrews 1991, 1992; Stute et al. 1992a, 1992b; Mazor and Bosch 1992; Marty et al. 1993; Castro et al. 1998a, 1998b, 2000). Dilute fresh water, apparently older than 280,000 years as determined by ^{4}He dating, was reported from the Aquia aquifer on the Atlantic Coastal Plain of the USA (Aeschbach-Hertig et al. 2002). For younger waters (10–10,000-year range), the ^{4}He technique has proven quite successful with adequate calibration of the ^{4}He release rate, either through laboratory experiments on the aquifer materials (Solomon et al. 1996), or through other age determinations, such as the chlorofluorocarbon (CFC) and SF$_6$ (Busenberg and Plummer 2000) dating techniques.

Another potentially promising ground-water dating technique involves calibrating the rate of geochemical weathering reactions, specifically for reactions that do not reach either equilibrium or partial-equilibrium states in an aquifer. The idea is to calibrate the rates of these irreversible reactions in parts of the aquifer where other dating methods apply. For example, Aeschbach-Hertig et al. (1998) showed that ^{3}H/^{3}He ages correlated with changes in solute concentration. Other studies have combined geochemical mass-balance models with ^{3}H/^{3}He and CFC dating to determine chemical weathering rates in crystalline-rock aquifers and watersheds (Rademacher et al. 2001; Burns et al. 2003). Burton et al. (2002) calibrated the release rate of Na and HCO$_3$ to ground water in siliciclastic rocks in the eastern USA using CFC dating on the 0–30 years time scale to estimate ages of more than 100 years for waters with elevated Na and HCO$_3$. For the same waters, ^{4}He accumulation indicated ages of 100–200 years. The geochemical method also has been used to extend dating beyond the ^{14}C time scale in the East Midlands aquifer in England (Edmunds and Smedley 2000).

Signals

In the "signal" approach, the ground-water system serves as an archive of prior, surficial, environmental conditions. Ideally, geochemical or isotopic processes do not contribute to the growth or decay of the signal constituents. Only hydrologic processes affect their distribution and concentrations and measurement/recognition of this information allows estimation of ground-water ages and flow velocities.

Examples of the signal approach in ground-water dating include using recognized variations in ^{2}H and ^{18}O (Małoszewski et al. 1983; Burgman et al. 1987; Vitvar and Balderer 1997; Rozanski et al. 1993), and in inert dissolved gas concentrations such as N$_2$, Ne, Ar, Kr and Xe (Mazor 1972; Andrews and Lee 1979; Bath et al.

1979; Stute et al. 1992a, 1992b; Stute and Schlosser 1999). Inert dissolved gases (e.g. Kipfer et al. 2002) can provide valuable information on recharge temperature, recharge altitude, and quantities of excess air trapped during recharge (Aeschbach-Hertig et al. 2000; Manning and Solomon 2003). Variations in ^{2}H, ^{18}O, and inert dissolved gases can be related to changes occurring on long time scales (e.g. the Little Ice Age, the 20,000 year glacial maximum) or on short ones (seasonal temperature changes or decadal changes in climate patterns). The investigation of discrete cyclic signals, such as seasonal variations in ^{18}O, ^{2}H, or dissolved inert gas concentrations, is an area for future development as improvements are achieved in sampling techniques and in analytical techniques. In the range of 2,000–35,000 years, Stute and Schlosser (1993) and Stute and Talma (1998) successfully identified synchronous variations in recharge temperatures in several aquifers around the world, through the measurement of a suite of noble gases and through ^{14}C dating.

For more recent ground waters, typically those recharged in the last 50 years, a number of datable anthropogenic signals are available: (1) chemical signals related to the history of use of surfactants (ABS or LAS), pesticides, and herbicides (Plummer et al. 1993); (2) radionuclide signals from atmospheric nuclear testing in the early 1960s (e.g. initial ^{3}H, ^{36}Cl; Rozanski et al. 1991; Phillips et al. 1988; Scanlon et al. 2002), from the reprocessing of fuel rods for nuclear power plants (^{85}Kr), or from the Chernobyl accident in the Ukraine (e.g. ^{106}Ru, ^{60}Co and ^{137}Cs; Ittner et al. 1991); (3) tracers released to the atmosphere by the advent of refrigeration (chlorofluorocarbons; Plummer and Busenberg 2000) or by the application of inert cover gases in electrical switches (e.g. SF$_6$, Maiss and Brenninkmeijer 1998; Busenberg and Plummer 2000).

In addition to an expanding list of anthropogenic compounds detected in ground waters (e.g. pharmaceuticals, personal care products), the future may also bring about the capability to measure signals in natural organic compounds, characterized chemically, isotopically, or genetically, and related to biological cycles (such as the 13-year and 17-year cycles of the various Cicada insect species). This possibility assumes that the biologically derived organic compounds have unique distinguishing characteristics, and are sufficiently resistant to degradation.

Different types of signal input functions, varying in time or spatial scale, as well as in form (cyclic, linearly/exponentially increasing/decreasing, step functions), are affected to different extents by dispersion and diffusion processes. Exponentially increasing signals, such as the increase in CFC-11, CFC-12 and CFC-113 until the early 1990s, or the increase in atmospheric ^{85}Kr, are minimally affected by dispersion when compared to peak input signals such as the 1964 ^{3}H bomb peak (Plummer et al. 1993). Different dating techniques and signals also can often only be applied to very specific and different time scales. The corollary to these statements is that the

measurement and use of multiple signals, or of decay/growth clocks, can help decipher the extent to which a flow system is affected by hydrodynamic dispersion (Plummer et al. 1993; Johnson and DePaolo 1996), or by transience in flow directions and velocities. Geochemical information also may provide a measure of the degree of heterogeneity in an aquifer (Winograd and Pearson 1976).

It is often assumed that the effects of dispersion and diffusion are small enough to allow recognition of the essential characteristics of a datable "signal." However, in systems of multi-layered aquifers and confining units, this assumption needs to be evaluated carefully in terms of the hydrogeologic properties of the system (Davidson and Airey 1982; Goode 1996; Sanford 1997; Weissmann et al. 2002) when interpreting tracer ages and signals. Furthermore, use of a signal to obtain a measure of ground-water velocities, in addition to ground-water ages, requires an implicit assumption that major flow directions have not significantly changed during the transmission of the signal through the ground-water system, or alternatively requires knowledge of the history of flow-field changes. Such knowledge is difficult to obtain, particularly over long time scales, but also for recent time scales, because of increasing use of ground-water resources (and consequent modification of piezometric surfaces from predevelopment times). The importance of this effect depends on the relative difference between the time scale of the hydrologic perturbation and the time scale of the predevelopment flow system.

Age models

Except in the case of pure piston flow (pipe flow), a ground-water age determination typically requires some type of model interpretation to relate the measured tracer concentration to an age-distribution in ground-water discharge and the mean age (residence time) of water in the aquifer. For example, if there were not a distribution of ages in discharge from some springs, it would be difficult to explain the arrival of a dye, days to weeks after release in the recharge area, in spring discharge that has an apparent age of years to tens of years determined from measurements of environmental tracers such as CFCs or ^{3}H/^{3}He. For many systems, not enough is known about the hydrogeology to be able to construct a ground-water flow model, and thus, for years, hydrologists have resorted to lumped-parameter models to interpret tracer data in ground-water discharge. Lumped-parameter "box" models (e.g. exponential, linear, linear-exponential) relate a tracer concentration measured in discharge from a well or spring to an average ground-water residence time, assuming different mixing or dispersion scenarios for the "box" or reservoir, different input functions, and various age-distribution models for the system. This approach, using lumped-parameter "box" models, is well documented in the literature (Eriksson 1958; Vogel 1967; Pearson and Truesdell 1978; Małoszewski and Zuber 1982, 1996; Grabczak et al. 1982; Małoszewski et al. 1983; Yurtsever 1983; Zuber 1986, 1994; Burgman et al. 1987; Cook and Böhlke 2000), and several software

packages are available (Małoszewski and Zuber 1996; Zoellmann et al. 2001b; Bayari 2002; IAEA 2005). In considering multiple lumped-parameter models, it is usually not possible to determine on the basis of a single tracer measurement which, if any, model describes the system under investigation. In cases of limited environmental tracer data, model selection is usually based on available geological and other technical information (Małoszewski and Zuber 1996), and a mean residence time is estimated on the basis of the selected model. When reporting estimates of ground-water age, it is necessary to qualify the age with the model on which it is based.

Recently, a number of investigations utilizing multiple environmental tracer data have demonstrated cases of piston flow and binary mixing of young and old water (Pearson and Truesdell 1978; Loosli et al. 2000; Talma et al. 2000; Katz et al. 2001; Plummer et al. 2001; Burton et al. 2002). Although mixtures of young and pretracer water are often recognized in water samples from fractured-rock environments, it is likely that many previously recognized mixtures were created in the process of extracting water from boreholes (Burton et al. 2002; Shapiro 2002). Yet, by using multiple tracers, it is sometimes possible to interpret age information on the young fractions in mixtures.

If sufficient hydrogeologic data are available, a preferable alternative to the use of box models is to develop a flow model for an entire ground-water system, calibrated through the use of geochemical tracer measurements and observed heads (e.g. Reilly et al. 1994; Sheets et al. 1998; Zoellmann et al. 2001a; Mattle et al. 2001; Sanford et al. 2004b). Ground-water age information (travel time) is then estimated from the flow model at specific points in the system (Szabo et al. 1996). The advantage of such a simulation is that it can take into account the effects of hydrodynamic dispersion on age, and in conjunction with measured environmental tracer data, the model and age simulation can be refined (Goode 1996; Engesgaard and Molson 1998; Varni and Carrera 1998; Bethke and Johnson 2002; Weissmann et al. 2002).

Obtaining representative information

Ground-water systems are difficult to observe, except in their surface expression (e.g. springs, sinkholes, marshes). Extracting ground-water samples is expensive, disruptive, and invariably affects the information obtained. Drilling generally introduces fluid and air into the aquifer, disturbs the natural spatial distribution of ground-water chemistry, and often mobilizes or re-suspends colloidal or fine particulate material. Hydraulic testing and tracer test measurements can further affect ground-water geochemistry. Consequently, geochemical sampling should generally precede hydrological testing.

Ground-water samples invariably are mixtures; the extent of mixing depends on well construction and on the hydrogeologic environment. Mixing may not be evident

in the major-element composition of samples taken from a generally homogeneous aquifer, but can have a major impact on environmental tracers with strong concentration gradients.

In the future, improvements in micro-sampling methods and instrumentation will aid in the characterization of ground-water geochemical environments, and in the deciphering of details of flow and transport processes. Diffusion sampling techniques and techniques that minimally disturb the flow environment (Sanford et al. 1996; Manning et al. 2003; Ronen et al. 1987; Magaritz et al. 1989) offer significant potential in measurement of fine-scale chemical variations in aquifers.

Colloids in ground-water environments affect the transport of radionuclides, microbes, organic compounds, and metals (Buffle and van Leeuwen 1993; McCarthy and Degueldre 1993, Harvey and Harms 2002). The presence and concentration of colloids can be affected by pumping rates, by geochemical changes caused by exposure to the atmosphere (or to light), or by mixing of different water compositions.

Detailed information on the spatial distribution and composition of reactive minerals is usually needed in interpreting geochemical processes in aquifers, but often difficult to obtain. Drilling is usually expensive, especially when part of the objective is to obtain representative core or aquifer material samples. The process also may involve a number of disturbances/problems, such as the introduction of drilling mud, changes in the redox environment caused by the introduction of oxygen, and loss of fine materials.

The problems that apply to describing reactive aquifer mineralogy and to obtaining representative colloid information also apply to the characterization of microbial communities in ground-water systems (Chapelle 1993). Typically, information is obtained either by bacterial cultures, by DNA, RNA, or species-specific lipid or protein extractions on water and/or aquifer materials, which have much greater bacterial concentrations. Bacterial cultures are easily contaminated and DNA or RNA extractions usually require large sample volumes.

Regional ground-water systems contain a wealth of historical and paleo-environmental information, but currently (2004), the ability to extract that information is limited. Part of the problem is caused by the dispersive or diffusive loss of environmental signals in aquifers; part is due to the difficulty in obtaining representative aqueous and solid samples from well-defined, narrow intervals in aquifers.

Numerical modeling of geochemical processes

Steady progress has been made over the past 35 years in the development of software for interpretation of geochemical processes. Concurrent with the development of ion association models, geochemists began quantitatively interpreting chemical evolution in ground-water systems. The development of numerical codes capable of quantitatively evaluating chemical evolution has proceeded in two directions, "inverse" and "forward" geochemical modeling.

The "inverse geochemical modeling" approach applies geochemical mass balances to the observed chemical and isotopic composition of evolutionary ground waters (as originally demonstrated by Garrels and Mackenzie 1967) to estimate masses of mineral and gas transfer in water–rock systems. Inverse geochemical modeling software includes BALANCE (Parkhurst et al. 1982), NETPATH (Plummer et al. 1994), PHREEQC (Parkhurst 1995; Parkhurst and Appelo 1999), PHREEQCI (Charlton et al. 1997; Charlton and Parkhurst 2002) and SPREADBAL (Bowser and Jones 2002). In contrast, in the "forward modeling approach," numerical models are used to simulate the outcome of hypothetical reactions (e.g. PATHI; EQ3/6; PHREEQE; PHREEQCI) based on a definition of initial conditions, on a postulated set of reactions, and on the use of a comprehensive thermodynamic database. Forward modeling calculates reaction extents, not only for homogeneous aqueous speciation reactions, but also for mass-transfer reactions between phases.

Inverse modeling

Inverse modeling is used to explain the observed chemical and isotopic evolution of natural (or contaminated) waters, rather than to predict future compositions (Plummer et al. 1983; Plummer 1985). Data required in inverse geochemical modeling include the compositions of an "initial" water and of a "final" water that are assumed chemically evolutionary, without the need to know the precise location of the flowpath the water followed through the aquifer. The water compositions chosen do not need to be on the same hydrologic flowpath provided they are representative of compositions attained through geochemical evolution of the initial water. The system considered does not need to be in chemical or hydrologic steady-state. An established hydrologic steady-state and the selection of initial and final waters from a specific flowpath are important though if the modeling is used to determine reaction rates or ground-water velocities (through combined geochemical dating, such as ^{14}C).

Inverse geochemical modeling can require appreciable knowledge and expertise. A complete list of the reactions that may be responsible for the observed evolution is needed. Therefore, mineralogical knowledge is needed to make reasonable guesses as to which minerals and gases might be dissolving, precipitating, or exsolving. Aqueous speciation results are used to eliminate mineral-water reactions that are thermodynamically impossible. Knowledge of the relative kinetics of reaction processes is needed to judge whether a process is likely to occur to the extent calculated given estimated travel and evolution times. Establishing a plausible hydrologic relation between the initial and the final waters, and estimating travel time between sampling points requires hydrological knowledge of the system and may involve application of a flow model. Conversely, inverse geochemical modeling may result in improved, or sometimes radically altered,

hydrologic understanding. For example, a situation where a final water is more dilute in an inert component than any of the initial waters it presumably evolved from is unreasonable and would require revising the conceptual model of flow (e.g. reversal of flow directions, non-steady-state input, nonevolutionary waters, additional source of dilution).

Inverse geochemical modeling can account for the possibility that multiple initial waters may have combined in the evolution to a final water composition. However, the actual processes that may be responsible for the "mixing" of the various initial waters are not simulated in detail. These include hydrodynamic dispersion, solute diffusion, mixing of various waters as a result of the sampling process (long screens, temporal variations in water chemistry), and other possibilities. The likelihood of these processes must be assessed.

Inverse geochemical modeling codes are already quite sophisticated, but offer the possibility of further refinements. The inverse-modeling capabilities of the PHREEQC and PHREEQCI codes consider the uncertainties associated with the definition of initial and final solution compositions (chemical and isotopic) and with the isotopic composition of reacting phases. The NETPATH code offers a complete suite of adjustment models for ^{14}C dating. These models (such as Fontes and Garnier 1979) are well known from the geochemical literature, and account for a few relatively simple geochemical reactions. NETPATH goes a step beyond these simple adjustment models; it uses inverse geochemical modeling to correct ^{14}C ground-water ages. For example, corrections considered relate to the oxidation of organic carbon, the precipitation/dissolution of carbonate minerals, and a full suite of other reactions that directly or indirectly affect ^{14}C activities in ground water. NETPATH also includes a mathematical description of isotopic evolution in systems with multiple reactants and multiple isotopically fractionating product phases (Wigley et al. 1978). NETPATH's solutions to the differential equations describing isotopic evolution permit reaction models to be tested for consistency with observed isotopic data, and allow the development of ^{14}C models that are specific for each water analysis and its modeled geochemical evolution (Plummer et al. 1991, 1994).

Inverse modeling can help the user determine what additional data may be needed to adequately understand ground-water evolution in a particular system. For example, sometimes no models are found. This can indicate that the selected waters are not evolutionary, that appropriate reactions have not been included, or that too many constraints have been imposed. In inverse geochemical modeling, inability to find an acceptable reaction model indicates inadequate data or an invalid conceptualization of the geochemical and hydrologic system.

Forward modeling

In recent years, the "forward modeling" approach has been extended to geochemical transport codes capable of simulating ground-water flow and the advection and dispersion of solutes, coupled with a complex array of geochemical processes. Most recently, completely specified isotopic reactions have been incorporated into geochemical mass-transfer and mass-transport codes (specifically into PHREEQCI and PHAST; Thorstenson and Parkhurst 2002, 2004), allowing a forward modeling description of the isotopic evolution of a ground-water system, along with its concurrent chemical evolution.

Increased sophistication in forward geochemical codes has outpaced improvements in the thermodynamic (and kinetic) databases needed to quantify and predict reaction extents. Further research is needed to better describe the thermodynamic properties and behavior of trace/minor elements (and even of major elements). Recent advances in development of thermodynamic databases are discussed by Nordstrom (2004). The ability of forward geochemical modeling to actually describe real systems depends in part on the quality of the input data and of the thermodynamic data used, and the extent to which the selected reversible and irreversible reactions are appropriate for the system.

Additional research remains in the development of forward geochemical modeling codes. Thermodynamic databases should be internally consistent, should consider all major aqueous species, and should be based on accurate measurements. Thermodynamic consistency (Nordstrom and Munoz 1994) means: (1) the data are consistent with basic thermodynamic relations; (2) common scales are used for temperature, energy, atomic mass, and fundamental physical constants; (3) appropriate choices of standard states were made and used for all similar substances; (4) the same mathematical and chemical models were used to fit different data sets; and (5) conflicts among measurements were resolved. Thermodynamic databases typically consider few organic species, even though these are important constituents in natural and in contaminated waters. Most codes and associated thermodynamic databases also are limited to modeling the speciation of relatively dilute waters with ionic strengths (or salinity) lower than seawater. The few codes that are available to model the speciation of saline waters and brines usually have little or no data available to model the speciation of minor elements, metals, radionuclides, or redox states. Finally, most speciation codes assume that the aqueous species present are at equilibrium with each other. Although most "homogeneous" aqueous-speciation reactions are fast, this is not always the case for reactions involving redox-active species and elements, and/or strong aqueous complexes and polymerized species. The kinetics of formation/dissociation of those species can be slow and the kinetics of redox reactions often depend on microbial catalysis.

In the past decade, significant efforts have been made to numerically simulate the coupling of ground-water flow, solute transport, and geochemical processes. Geochemical processes can affect the transport of solutes and the flow of ground water through their effect on aquifer porosity and permeability; in turn, ground-water flow can influence the rates of geochemical processes. Geochemi-

cal mass-transport codes (e.g. MST1D: Engesgaard and Kipp 1992; PHREEQC/PHREEQCI; PHAST: D.L. Parkhurst and K.L. Kipp, in preparation) incorporate all the limitations and uncertainties associated with the use of (1) geochemical reaction codes and (2) nonreactive solute-transport codes. Geochemical transport codes commonly have convergence and other numerical problems (e.g. numerical oscillations, numerical dispersion) associated with the solution of partial differential equations. In addition, physical transport processes are described at a much larger scale than the molecular scale of chemical reactions. This dichotomy of scale generates conceptual and numerical errors and uncertainties in the application and use of geochemical transport codes. Moreover, running geochemical transport codes can require large computer time and memory. Increases in computing power have been matched by the increasing sophistication and simulation capabilities of geochemical transport codes. Possible increases in the "realism" offered by more sophisticated and complex codes, however, are counterbalanced by increased data requirements and associated increases in the uncertainties relating both to the data entered and to the mathematical representation of the simulated processes (Oreskes 2000). Sensitivity analyses, where simulations are run multiple times to test the effects of the data and process uncertainties, are crucial to intelligent use of geochemical transport codes, but commonly are hampered by computer time requirements. Geochemical transport codes can be used to examine "best-case" and "worst-case" scenarios of contaminant transport, but in most cases are not exact predictive tools. Like other geochemical codes, geochemical transport codes are tools that can be used to improve conceptual understanding and to gain an appreciation of the relative importance of processes controlling the chemical evolution (and transport) of natural or contaminated waters.

Further information on the geochemical modeling of ground-water systems, its historical development, its purpose, and the current state of the art, can be found in Plummer et al. (1983), Plummer (1985), Plummer (1992), Parkhurst and Plummer (1993), Bethke (1996), Glynn and Brown (1996), Parkhurst (1997), Nordstrom (2004) and Konikow and Glynn (2005, in press).

Examples of the use of transport codes in geochemical modeling

Glynn and Brown (1996) review the use, assumptions, and limitations of geochemical modeling in the investigation of a dynamically evolving contaminated ground-water system in the Pinal Creek Basin in Arizona, USA. The authors used inverse modeling to determine a range of reaction model possibilities, which were then used together with other considerations, to construct a set of one-dimensional (1-D) reactive transport simulations. The simulations documented the sensitivity of movement of pH and redox fronts as a function of possible chemical reactions, mineral concentrations, and longitudinal dispersion. The sensitivity analysis was used to highlight, assess, and prioritize the uncertainties that needed to be resolved to obtain a better predictive model of contaminant transport at the site. Comparison between the transport sensitivity analysis, available field evidence, and laboratory-column experiments resulted in a range of predictive estimates for the movement of the low pH and high Fe(II) waters at the Pinal Creek site.

Solute-transport codes have been used to assess the performance of nuclear-waste disposal sites, and more generally to simulate contaminant transport in a variety of settings. Highly simplified single-species transport models have been used in most such efforts. These transport codes assume that the retardation of a reactive solute relative to a conservative tracer can be adequately described through a one-parameter linear sorption model (the constant K_d model), or through two-parameter models (e.g. Langmuir, Freundlich; cf. Drever 1997, for descriptions). These models ignore the effects of competitive sorption, aqueous complexation, pH and redox effects, precipitation and dissolution, and a multiplicity of other possible geochemical processes. Following an earlier critique by Reardon (1981), Glynn (2003) contrasts the use of highly simplified "reactive" transport codes with the PHREEQC geochemical transport code, a code limited to a 1-D description of flow and transport, but with a more complex, conceptually more accurate description of sorption mechanisms and multispecies geochemical processes. Effects of chemical heterogeneity on transport are also investigated.

Although a number of studies have shown the utility of 1-D geochemical transport modeling (including Appelo and Willemsen 1987; Appelo et al. 1990; Appelo and Postma 1993; Appelo 1994; Glynn and Brown 1996; Brown et al. 1998; Glynn 2003), there are relatively few studies that have used 3-D geochemical transport codes. In one example, geochemical modeling of the Central Oklahoma aquifer, Oklahoma, USA, succeeded in elucidating the factors controlling dissolved arsenic concentrations and the geochemical evolution of the ground waters (Parkhurst et al. 1992; Parkhurst, written communication 2002: described in Konikow and Glynn 2005, in press). Inverse and forward geochemical modeling were conducted, including a 3-D geochemical transport model using the U.S. Geological Survey (USGS) code PHAST. Parkhurst's geochemical transport model simulated the processes of ground-water flow and solute transport, with areal recharge in the eastern unconfined part of the aquifer and discharge to some bounding rivers. The model also considered ion-exchange reactions, the dissolution of calcite and dolomite, and pH-dependent surface-complexation reactions on hydrous iron oxides that affected the concentration of dissolved As in the water. Use of the PHAST code allowed an analysis of the magnitude and sensitivity of various factors affecting ground-water flow, solute transport, and geochemical evolution in the Central Oklahoma aquifer. The constructed model matched general hydrological and geochemical observations and explained the occurrence of high As concentrations in the western part of the aquifer. Parkhurst and Petkowich

(2002) and Parkhurst et al. (2003) document other applications of the PHAST code.

Other mathematical tools used in understanding ground-water geochemistry and flow systems

Though often misused, there is a place for the informed application of statistical principles in hydrochemistry—in particular for hypothesis testing. Factor analysis, cluster analysis, and principal component analysis have been advocated as tools that can provide understanding of the geochemistry of ground-water systems. In theory, these techniques can provide an unbiased description of a distribution of samples, the distribution of their compositions, and in the case of principal component analysis, can potentially describe the components that explain the variance in the distribution of compositions. In addition to the benefits of having "unbiased" descriptions of data, providing a statistical frame of reference for a given observation (or set of observations) and of its significance is also very useful. Maps of chemical (or other) variables can be created using statistical tools by combining observations with interpolation models that can sometimes incorporate simple process relations (Pebesma and Kwaadsteniet 1997; SPARROW code and application: Smith et al. 1997). In the experience of the authors (novices in the use and understanding of statistics), statistical tools used in ground-water geochemistry often confirm information obtained through simpler means. Alternatively, the extraction of nonintuitively obvious information may require highly advanced techniques, where the lack of bias of a particular technique and its proper use become highly debatable.

The authors have seen what they would consider questionable use of principal component analyses, where results of the analyses, carried out on a variety of both inert and reactive elements/isotopes in solution, were used to assess the degree of conservative mixing between "end-member" solution compositions, while ignoring the reactions that could cause the precipitation or dissolution of some the elements/isotopes used in the analysis. Statistical modeling tools have the potential to contribute to understanding ground-water geochemistry and flow, but their use can be complex, explanations of results can be highly abstruse, and there is significant potential for misuse, especially when use and results of these tools are not supported with basic geochemical and hydrogeologic knowledge.

Geochemical investigations and modeling philosophy

The primary value of model construction and of geochemical modeling is to force the user to put all available data within a conceptual framework. The user then confronts the available observations with his/her intuition/experience and a-priori understanding of the system. In geochemical modeling of ground-water systems, the observations may include hydrological, chemical, isotopic, and mineralogical data. Knowledge/assumptions concerning reaction thermodynamics and kinetics, mineral forms, geology, and hydrology are also essential. By itself, constructing a model should: (1) result in improved understanding of the chemical and isotopic reactions responsible for the observed evolution of the waters; (2) help refine/correct hydrological understanding of the system, and, most importantly; (3) help assess the nature of remaining uncertainties in the constructed conceptual framework.

The construction of an initially simple model is highly advisable. The number and complexity of processes considered should be increased gradually as the model is refined, to the extent needed to understand or explain available observations, or, stretching the use of the model further, to the extent needed to make simple testable predictions. The user must at some point decide when sufficient adjustments have been made to the representation of parameters and processes, and when the constructed model is adequate for its intended purpose. Alternatively, the user may reject the model as inadequate, and may need to construct an entirely different model and/or seek new data or information. In many respects, geochemical modeling is a process of elimination of hypothetical reaction models, within a given set of uncertainties relating to the input data, the thermodynamic data, and available system knowledge (Plummer et al. 1983). Forward geochemical modeling requires a valid initial conceptualization of the system that includes representative reaction possibilities and is consistent with geochemical intuition. A forward model that does not predict a geochemically reasonable result, or that does not agree with the limited observations that might be available, can be eliminated. In inverse geochemical modeling, multiple reactants and products are considered and reaction sets that are inconsistent with available observations are eliminated. In both types of modeling, the available observations are usually not sufficient to eliminate all the reaction possibilities.

As is true for practically any type of modeling effort, modeling designed primarily to explain the available data, such as inverse geochemical modeling, or inverse flow modeling, should be conducted preferably before predictive or "forward" modeling is conducted (such as geochemical transport modeling). Inverse geochemical modeling is best used early in the data-acquisition process because it forces the user to evaluate the nature and extent of knowledge gaps and uncertainties. Inverse geochemical modeling can be used to guide the field-data acquisition process, and can also be used to help construct "forward" geochemical models (Glynn and Brown 1996). Depending on the questions being addressed, inverse geochemical modeling may be all that is needed in a particular investigation.

Views on the application and use of "forward" numerical models differ amongst scientists and engineers. Some strive to construct numerical models that are as "realistic," and suitably complex as possible; they use the constructed models, after a "validation" exercise, to make predictions on the future state of a system. Other scientists

consider that a model is, by definition, a much simplified construct of assumptions that is meant to help understand some facet(s) of reality; they see models merely as tools that provide some understanding of possible system behavior, and they use sensitivity analyses (multiple model runs with varying parameters, boundary and/or initial conditions) to increase their quantitative understanding of process interactions and of the assumption construct. The validity of each approach depends to some extent on the type of modeling that is conducted, and on what predictions are sought. Nevertheless, the present authors tend to consider models as tools that should be used primarily to increase system understanding rather than to make predictions, and the discussion in this paper relates to their view. Konikow and Bredehoeft (1992), Nordstrom (1994, 2004), Oreskes et al. (1994), Oreskes (2000) and Konikow and Glynn (2005, in press) discuss some of the differing views relating to the philosophy of applying and testing ground-water flow and geochemical models.

Ground-water systems typically have less geochemical and hydrogeologic information known about them than may be desirable for predictive modeling of geochemical transport. Detailed hydrogeologic and geochemical studies often are too expensive to consider, particularly on large aquifer systems. The lack of chemical and hydrological data means that investigators should try to use, as efficiently as possible, all tools and knowledge available. A combination of inverse and forward modeling of ground-water flow and transport, and inverse and forward geochemical modeling, may often provide substantial knowledge gains, and at a minimum can be used to identify the most critical data needed to gain a better understanding of the ground-water system. In general, modeling (hydrological/geochemical; inverse or forward) should be conducted as part of a continuous iterative cycle, helping guide data acquisition, helping interpret the data obtained, and helping provide an integrated understanding of the ground-water system, to a desired (or financially feasible) level of detail.

Geochemical investigations

Geochemical studies have been conducted on numerous ground-water systems. Selected studies where geochemistry has improved understanding of ground-water systems are:

1. Major USA aquifers studied as a part of the U.S. Geological Survey (USGS) Regional Aquifer Systems Analysis program and summarized in the USGS Ground Water Atlas of the United States (Miller 1999).
2. The Floridan aquifer system, USA (Back and Hanshaw 1970; Sprinkle 1989; Plummer and Sprinkle 2001).
3. The Madison aquifer system, USA (Busby et al. 1983, 1991; Back et al. 1983; Plummer et al. 1990).
4. The Middle Rio Grande Basin, USA (Anderholm 1988; Bexfield and Anderholm 2002; Plummer et al. 2004a, 2004b, 2004c; Sanford et al. 2004a, 2004b).
5. The Carizzo Sandstone Aquifer of South Texas, USA (Pearson et al. 1983; Andrews and Pearson 1984; Stute et al. 1992a, 1992b).
6. The Central Oklahoma aquifer, USA (Parkhurst et al. 1992).
7. The High Plains aquifers, USA (Nativ and Smith 1987; Nativ and Gutierrez 1989; Dutton 1995; Mehta et al. 2000; Gosselin et al. 2001; Fryar et al. 2001; McMahon et al. 2004).
8. The Milk River aquifer, Canada (Hendry and Schwartz 1990; Nolte et al. 1990; Hendry et al. 1991; Ivanovich et al. 1992).
9. The East Midlands Triassic aquifer, UK (Bath et al. 1979; Andrews et al. 1984; Edmunds et al. 1982; Andrews et al. 1994; Edmunds and Smedley 2000).
10. The Paris Basin, France (Fu et al. 1990; Marty et al. 1993; Castro et al. 1998a, 1998b).
11. The Molasse Basin of Upper Austria (Andrews et al. 1985).
12. The Madrid Basin, Spain (Llamas and Martinez 1981; Jones and Llamas 1989).
13. The Great Hungarian Plain, Hungary (Déak et al. 1987; Stute et al. 1992a, 1992b).
14. The Great Artesian Basin, Australia (Torgersen and Clarke 1985; Herczeg et al. 1991; Torgersen et al. 1991; Andrews and Fontes 1993; Torgersen and Philips 1993).
15. The Murray Basin, Australia (Leaney and Allison 1986; Herczeg et al. 1993; Jones et al. 1994).
16. The Stripa and Äspö fractured rock sites in Sweden (Stripa: Andrews et al. 1988, 1989; Nordstrom et al. 1989; Äspö: Glynn and Voss 1999)
17. Underground laboratory studies in clay and clay rock (Boom clay at Mol in Belgium, Mont Terri in Switzerland, other sites in Canada, England, France and Italy; Bath et al. 2001; Pearson et al. 2003)
18. Crystalline Rock studies in Switzerland (Pearson et al. 1991)
19. Natural Analogue Studies (for radioactive waste disposal) around the world (Miller et al. 1994) and at the Poços de Caldas site in Brazil (Chapman et al. 1993)
20. Nuclear-waste disposal sites in the USA (Yucca mountain, Nevada: Paces et al. 2001; Thorstenson et al. 1998; WIPP site, New Mexico: Bodine and Jones 1990; Siegel and Anderholm 1994; Jones and Anderholm 1996)
21. The Great Basin aquifers of Nevada, USA (Winograd and Thordarson 1976; Winograd and Pearson 1976; Thomas et al. 1989a, 1989b; Winograd 2001). The 500,000 year climatic record determined for Nevada groundwaters (from the Devil's Hole limestone core) has been correlated with several other paleoclimate records and has even been used to refine the dating of the Vostok, Antarctica, ice-core paleoclimate record (Landwehr and Winograd 2001)!
22. Ground-water investigations in Africa, Asia and the Middle East (Nash and McCall 1994; Kurnub Group paleowaters in the Sinai-Negev province, Israel, Rosenthal et al. 1998)

Needs and future directions in the geochemical understanding of ground-water systems

This paper has reviewed a few key historical developments, and some current state-of-the-art techniques and approaches in the field of geochemistry, as specifically applied to the understanding of ground-water systems. There are many areas in which further research holds significant promise for improving understanding of ground-water systems. These include:

1. Advances in representative sampling (e.g. for waters, aquifer/aquitard materials, colloids, bacteria, unsaturated-zone gases) and uses of geophysical and minimally disturbing techniques to obtain hydrologic, geologic and geochemical information.
2. Advances in collection and measurement techniques for dissolved noble gas isotopes (e.g. ^{85}Kr, $t_{1/2}$ =10.76 years; ^{39}Ar $t_{1/2}$ =269 years; ^{81}Kr, $t_{1/2}$ =229,000 years). Current techniques generally require very large sample volumes, and complex, labor-intensive analytical methods that severely limit practical applications. Better techniques could significantly improve ground-water dating.
3. The study of homogeneous and heterogeneous reaction kinetics, inhibitory and/or catalytic processes, the measurement/estimation of effective surface areas, and the prediction of reaction rates in ground-water systems.
4. Investigations of bacterial activity and diversity, population distributions, and microbially mediated processes (Chapelle 1993), biofilms, microbe-mineral interactions, and microbial transport. Microbial evidence may include culturing as well as DNA, RNA, specific protein and/or lipid extractions, and characterization.
5. The processes affecting colloid transport, as well as the formation and decay of colloids. Understanding colloid processes, their generation, transport and decay is essential to many important water quality and supply issues, such as: the efficiency of bank filtration, the possibilities for aquifer storage and recovery, nuclear-waste disposal and other contaminant transport issues.
6. The characterization of organic molecules: their chemical composition and functional characteristics, reactivity, their stable and radioactive isotope contents (^{13}C, ^{14}C, ^{15}N, ...), and any other techniques that might allow dating and/or tracing of their origin (plant materials with different photosynthetic cycles and ^{13}C contents, fungi, molds, microbial growth, animal/insect waste products/debris).
7. The characterization of naturally occurring proteins, hormones, enzymes, and their degrades in ground-water systems. The ground-water recharge and discharge of these compounds (and anthropogenically introduced surrogates or inhibitor compounds) may play a key role in "environmental signaling". Environmental signaling through chemical means (e.g.

McLachlan 2001, and references therein) can strongly affect symbiotic relationships and the health, diversity and survival of species in ecological systems, and may provide key controls on the evolution and adaptation of these systems.

8. Isotopic fingerprinting of specific molecular species: this is a developing field that not only has significant promise in determining the sources of contaminants in ground-water systems, but may also help characterize natural tracers and solutes, and may provide information on water and solute origins, recharge modes, transport, and ages.
9. Studies of deep aquifer systems (e.g. sedimentary basins) and their interactions with shallow ground waters, heat convection, and geothermal reactions, salinity effects, diagenetic reactions, and detection and interpretation of magmatic emissions (such as N_2, CO_2, and He).
10. Unsaturated zone geochemistry: this area of research has not received as much attention as it should, except by soil scientists, perhaps because the physics of unsaturated zone flow and transport are by themselves a complex field of study. Nevertheless, coupling geochemical processes to unsaturated zone hydrology is critical to understanding processes that control and modify the recharge and source of environmental tracers in ground-water systems and may also offer information on paleo-recharge conditions (Scanlon and Cook 2002).
11. The study of geochemical processes occurring as a result of surface-water/ground-water interactions: research in this area may help understand and quantify the processes affecting the recharge of water and solutes to ground-water systems, as well as the processes affecting discharge into streams. Sediment transport may also be important to consider in these studies because of its impact on the geometry and nature of ground-water/surface-water interactions. Sediments often carry significant quantities of reactive constituents, such as organic matter and metals, and sediments may, through their chemical and physical characteristics, record past ground-water/surface-water interactions.

Ground-water environments with special needs

Some environments offer unique complexities and difficulties in conducting ground-water geochemistry research. Focused research on these systems can be expected to bring about significant advances not only in the understanding of system processes, but also in the development of new techniques and methods in ground-water geochemistry. Fractured rock and karst environments are perhaps best known for their complexity, but aquitards, geothermally affected ground waters, permafrost environments, glacially covered ground-water systems, coastal ground-water systems, and submarine ground-waters also are of significant relevance and complexity, or difficult to conduct studies on.

Fractured-rock environments are an important field of study because of their abundance, the difficulties in predicting their behavior with respect to flow and solute transport, their increasing importance for water supply, and their suggested use for nuclear-waste disposal. Karst environments are similarly complex, and highly relevant for study because of their importance for water supply around the world and their susceptibility to contamination.

Because of their slow response to hydrologic and chemical transients, aquitards and confining units are difficult to study, but may offer important controls on water supply and water quality in some ground-water systems (Neuzil 1986; Pucci 1999; Remenda 2001). Complex processes such as osmosis and ultrafiltration, compaction/subsidence and paleo-loading effects may affect some aquitards. Because of their sharp gradients in chemical and redox properties, aquitard/aquifer interfacial zones can support significant microbial activity (McMahon 2001) and can strongly affect water quality. Aquitards may also provide useful archives of paleo-environmental information.

Understanding the geochemistry and ground-water flow of geothermal systems is of significant societal interest because they offer a potential energy resource. In volcanically active areas, they also may offer potential clues to future eruptions (Evans et al. 2004); lastly, they test some of the limits of understanding of coupled processes. The hydrogeology and geochemistry of permafrost environments are also of interest because of their important role and expected modifications during climate change. Permafrost environments can act as significant sources of stored organic carbon, which may be oxidized and released as temperatures increase. Salting-out effects during freezing and the generation of dense salty waters affects the hydrogeology of permafrost systems and their very structure. The hydrogeology of permafrost environments is highly complex and geochemical investigations can be expected to provide key information. Glacially covered ground-water systems (e.g. under the Greenland and Antarctic ice sheets, under the Icelandic glaciers; cf. Glynn and Voss 1999; Glynn et al. 1999) are difficult environments to observe and sample. Their potential importance relates to performance assessments for the disposal of nuclear waste, and may also relate to the movement of glaciers and icesheets (through lubrication and through heat-flow impacts). Coastal ground-water systems have high relevance to societal needs due to the large and increasing coastal population, and due to the sensitivity of coastal ecosystems to salinity changes that are in part controlled by the ground-water flow regime and usage. In addition, ground-water inputs of nutrients may contribute significantly to hypoxia in coastal marine environments. Submarine hydrogeology, for example the investigation of "ground-waters" at mid-ocean ridges, is a field where research has hardly started. Investigations would likely be related to studies of manganese nodules and the formation of other mineral ores, or to the potential impacts of climate and sea-level changes on the forma-

tion, or abrupt disintegration of clathrates. Lastly, the last frontier in "ground-fluid geochemistry" may lie in the exploration of subsurface fluids on other planets and moons. Martian and extraterrestrial hydrology is already of interest (e.g. Baker et al., Hydrogeology Journal, this issue).

Some final thoughts

In addition to improved theoretical descriptions of natural processes, two major technological trends have led scientific advancements in the field of ground-water geochemistry over the last 40 years: (1) the development of analytical techniques capable of measuring an ever-increasing array of isotopes, elements, and molecular species at ever smaller concentrations; and (2) the development of computers and software capable of numerically simulating an ever-increasing number of hydrologic, geologic, and geochemical processes, at greater spatial and temporal scales, with ever-increasing refinement. These two trends are likely to continue to contribute to advancements in ground-water geochemistry for many years to come. Indeed, with every new measurement of the concentration of a new constituent in ground water, there is a new story to be told. New information is gained; a better understanding of the flow system may be achieved; a better assessment may be obtained of prior climates or of other surficial conditions preserved in the ground-water archive; an improved understanding of reaction processes/rates may be reached. Numerical simulations of flow and solute transport will improve as additional geochemical observations are taken into account. Use of environmental tracer data, such as ^{14}C observations, and locations of flow boundaries (boundaries between hydrochemical zones; Plummer et al. 2004b) in combination with particle tracking and inverse modeling procedures can provide a useful calibration procedure in which geochemical, hydrologic, and geologic data are combined (Sanford et al. 2004b). This process will develop further as new tracers become available, and as more sophisticated numerical models evolve that can incorporate diverse hydrochemical and hydrogeological data and that can account for a wide range of processes.

At the completion of a study, investigators often know better how the study should have been conducted. Hydrologic investigations would generally benefit from the development of numerical model(s) that utilized available data (geologic, hydrologic, and geochemical), as well as the investigators' initial concepts and intuition. Once an initial model is constructed, sensitivity analyses and hypothesis testing can be used to help identify additional data that should be collected to address specific questions. This should be part of an iterative cycle of model development and refinement, sensitivity analyses, and hypothesis testing and data gathering.

Integration and synthesis of information collected from a wide variety of fields of expertise across a diversity of spatial and temporal scales, using different conceptual approaches and perspectives, is one of the keys to future advances in ground-water geochemistry and in the un-

derstanding of ground-water systems. An approach expressing the various processes that affect a ground-water system in terms of mass and energy fluxes could provide a framework for the integration and synthesis of the information available, and would provide a better perspective of the relative importance of different processes and different pieces of information. The processes that affect ground-water systems are all dynamic in nature, even under steady-state conditions, and any information obtained from a ground-water system is usually interpreted in terms of its meaning for either a past or a future system condition. A great number of processes affect ground-water systems, and their importance in a particular study often depends on the time scale of interest. Potential processes to consider include sedimentation, compaction/subsidence, diagenesis, erosion, glacial (or ice sheet) advance/retreat, sea-level rise/decline, ocean tides, earth tides, regional or local tectonic stresses, fracturing or plastic deformation, heat flow, the growth/dormancy/decay of microbial populations, geochemical and/or biogeochemically mediated reactions, fluid advection, gas generation and transport, solute diffusion and advection, radioactive decay chains, and many others. Scientific understanding and investigation of all these processes is typically predicated on the laws of conservation of mass and of conservation of energy. And yet the processes are rarely described or compared to one another on the basis of mass and/or energy fluxes. Considering ground-water systems in the mass/energy-based framework of thermodynamics would provide significant insights into various processes and their relative importance. At a minimum, it would provide a framework that could be used to integrate and synthesize available information (current ground-water and geochemical-simulation codes offer only a limited step in this direction). Even more interestingly, because ground-water systems can be considered open thermodynamic systems with "dissipative" organization structures (e.g. Nicolis and Prigogine 1989; Kondepudi and Prigogine 1998), processes with high flux densities (i.e. with spatially concentrated high mass/energy throughput) may potentially reveal complex behavior. The formation of convective circulation cells due to high heat throughput or high mass density differences (Simmons et al. 2001; Prasad and Simmons 2003) is a relatively wellknown common occurrence of such "complex" behavior typical of an open thermodynamic system. Microbial growth is another example, on a much smaller spatial scale; so is the formation of Liesegang rings, or of other reactive patterns (Ortoleva 1994). Actually, there are a significant number of mass/energy transport processes that occur in ground-water systems that create ordering or patterns, i.e. that result in the formation of information (negative entropy). Providing a proper "open system" thermodynamic framework could help elucidate some of the commonalities that control, result from, or provide evidence on the transport of fluids and solutes in ground-water systems. Gibbs' (1876, 1878) theoretical work on closed-system thermodynamics led to significant advances and applications in geochemistry

about 75 years later. In similar fashion, the work of I. Prigogine (winner of the 1977 Nobel Prize in chemistry) and his co-workers on open-system thermodynamics may lead to significant advances in the understanding of ground-water systems and other natural systems.

References

Aeschbach-Hertig W, Schlosser P, Stute M, Simpson HJ, Ludin A, Clark JF (1998) A ^{3}H/ ^{3}He study of ground water flow in a fractured bedrock aquifer. Ground Water 36:661–670

Aeschbach-Hertig W, Peeters F, Beyerle U, Kipfer R (2000) Paleotemperature reconstruction from noble gases in ground water taking into account equilibrium with entrapped air. Nature 405:1040–1044

Aeschbach-Hertig W, Stute M, Clack JF, Reuter RF, Schlosser P (2002) A paleotemperature record derived from dissolved noble gases in groundwater of the Aquia Aquifer (Maryland, USA). Geochim Cosmochim Acta 66:797–817

Anderholm SK (1988) Ground-water geochemistry of the Albuquerque-Belen Basin, Central New Mexico. US Geol Surv Water Resour Invest Rep 86-4094, 110 pp

Andrews JN, Lee DJ (1979) Inert gases in groundwater from the Bunter Sandstone of England as indicators of age and paleoclimatic trends. J Hydrol 41:233–252

Andrews JN, Giles IS, Kay LF, Lee DJ, Osmond JK, Cowart JB, Fritz P, Barker JF, Gale J (1982) Radioelements, radiogenic helium and age relationships for groundwaters from the granites at Stripa, Sweden. Geochim Cosmochim Acta 46:1533–1543

Andrews JN, Balderer W, Bath AH, Clausen HB, Evans GV, Florkowski T, Goldbrunner JE, Ivanovich M, Loosli H, Zojer H (1984) Environmental isotope studies in two aquifer systems: a comparison of groundwater dating methods. In: Proceedings of Isotope Hydrology Conference 1983. International Atomic Energy Agency, Vienna, IAEA-SM-270/93, pp 535–576

Andrews JN, Goldbrunner JE, Darling WG, Hooker PJ, Wilson GB, Youngman MJ, Eichinger L, Rauert W, Stichler W (1985) A radiochemical, hydrochemical and dissolved gas study of groundwaters in the Molasse basin of Upper Austria. Earth Planet Sci Lett 73:317–332

Andrews JN, Hussain N, Batchelor AS, Kwakwa KK (1986) ^{222}Rn solution by the circulating fluids in a hot dry rock geothermal reservoir. Appl Geochem 1:647–657

Andrews JN, Fontes JCh, Fritz P, Nordstrom K (1988) Hydrogeochemical assessment of crystalline rock for radioactive waste disposal: the Stripa experience. Swedish Nuclear Fuel and Waste Management Co, SKB Tech Rep 88-05, 26 pp

Andrews JN, Ford DJ, Hussain N, Trivedi D, Yougman MJ (1989) Natural radioelement solution by circulating groundwaters in the Stripa granite. Geochim Cosmochim Acta 53:1791–1802

Andrews JN (1991) Noble gases and radioelements in groundwaters. In: Downing RA, Wilkinson WB (eds) Applied groundwater hydrology. Clarendon Press, Oxford, pp 243–265

Andrews JN (1992) Mechanism for noble gas dissolution by groundwaters. In: Proceedings of Consultants Meeting on Iso-

topes of Noble Gases as Tracers in Environmental Studies. International Atomic Energy Agency, Vienna, pp 87–110

Andrews JN, Fontes JCh (1993) Comment on "Chlorine-36 dating of very old groundwater: III. Further studies in the Great Artesian Basin, Australia" by Torgersen et al. Water Resour Res 29:1871–1874

Andrews JN, Edmunds WM, Smedley PL, Fontes J-Ch, Fifield LK, Allan GL (1994) Chlorine-36 in groundwater as a paleoclimatic indicator: the East Midlands Triassic sandstone aquifer (UK). Earth Planet Sci Lett 122:159–171

Andrews RW, Pearson FJ Jr (1984) Transport of ^{14}C and uranium in the Carrizo aquifer of south Texas: a natural analog of radionuclide migration. Materials Research Society Symposium Proceedings, vol 26. Elsevier, pp 1085–1092

Appelo CAJ, Willemsen A (1987) Geochemical calculations and observations on salt water intrusions, 1: A combined geochemical/mixing cell model. J Hydrol 94:313–330

Appelo CAJ, Willemsen A, Beekman HE, Griffioen J (1990) Geochemical calculations and observations on salt water intrusions, 2: Validation of a geochemical model with column experiments. J Hydrol 120:225–250

Appelo CAJ, Postma D (1993) Geochemistry, groundwater and pollution. Balkema Press, Rotterdam, The Netherlands, 536 pp

Appelo CAJ (1994) Cation and proton exchange, pH variations, and carbonate reactions in a freshening aquifer. Water Resour Res 30:2793–2805

Aravena R, Wassenaar LI, Plummer LN (1995) Estimating C-14 groundwater ages in a methanogenic aquifer. Water Resour Res 31:2307–2317

Baas-Becking LGM, Kaplan IR, Moore D (1960) Limits of the natural environment in terms of pH and oxidation–reduction potentials. J Geol 68:243–284

Back W (1960) Origin of hydrochemical facies of ground water in the Atlantic Coastal Plain. In: Proceedings of 21st International Geological Congress, Copenhagen 1960, Pt 1, pp 87–95

Back W (1966) Hydrochemical facies and ground-water flow patterns in northern part of Atlantic Coastal Plain. US Geol Surv Prof Pap 498-A

Back W, Hanshaw BB (1970) Comparison of chemical hydrogeology of the carbonate peninsulas of Florida and Yucatan. J Hydrol 10:330–368

Back W, Hanshaw BB, Plummer LN, Rahn PH, Rightmire CT, Rubin M (1983) Process and rate of dedolomitization: mass transfer and ^{14}C dating in a regional carbonate aquifer. Geol Soc Am Bull 94:1415–1429

Back W, Herman JS (1997) American hydrogeology at the millennium: an annotated chronology of 100 most influential papers. Hydrogeol J 5:37–50

Baedecker MJ, Back W (1979) Modern marine sediments as a natural analog to the chemically stressed environment of a landfill. J Hydrol 43:393–414

Balderer W, Synal HA (1996) Application of the chlorine-36 method for the characterization of the groundwater circulation in tectonically active areas: examples from northwestern Anatolia/Turkey. Terra Nova 8:324–333

Bath AH, Edmunds WM, Andrews JN (1979) Paleoclimatic trends deduced from the hydrochemistry of a Triassic sandstone aquifer, United Kingdom. In: Proceedings of Isotope Hydrology Conference 1978. International Atomic Energy Agency, Vienna, pp 545–568

Bath AH, Pearson FJ, Gautschi A, Waber HN (2001) Water–rock interactions in mudrocks and similar low permeability material. In: Cidu R (ed) Proceedings of 10th International Symposium on Water–Rock Interaction in Villasimius, Italy. Balkema Press, The Netherlands, pp 3–12

Bayari S (2002) TRACER: an EXCEL workbook to calculate mean residence time in groundwater by use of tracers CFC-11, CFC-12 and tritium. Comput Geosci 28:621–630

Bayer R, Schlosser P, Bonisch G, Rupp H, Zaucker F, Zimmek G (1989) Performance and blank components of a mass spectrometric system for routine measurement of helium isotopes and tritium by the ^{3}He in-growth method. Sitzungsberichte der Heidelberger Akademie der Wissenschaften, Mathematisch-naturwissenschaftliche Klasse, Jahrgang 1989, 5. Abhandlung, Springer, Berlin Heidelberg New York, 42 pp

Bentley HW, Phillips FM, Davis SN, Habermehl MA, Airey PL, Calf GE, Elmore D, Gove HE, Torgersen T (1986) Chlorine-36 dating of very old groundwater, 1. The Great Artesian Basin, Australia. Water Resour Res 22:1991–2001

Berner RA (1981) A new geochemical classification of sedimentary environments. J Sediment Petrol 51:359–365

Bethke CM (1996) Geochemical reaction modeling. Oxford University Press, New York, 397 pp

Bethke CM, Johnson TM (2002) Ground water age. Ground Water 40:337–339

Bexfield LM, Anderholm SK (2002) Spatial patterns and temporal variability in water quality from City of Albuquerque drinking-water supply wells and piezometer nests, with implications for the ground-water flow system. US Geol Surv Water Resour Invest Rep 01-4244, 101 pp

Bodine MW Jr, Jones BF (1986) The salt norm: a quantitative chemical–mineralogical characterization of natural waters. US Geol Surv Water Resour Invest Rep 86-4086, 130 pp

Bodine MW Jr, Jones BF (1990) Normative analysis of ground-waters from the Rustler Formation associated with the Waste Isolation Pilot Plant (WIPP), southeastern New Mexico. In: Spencer RJ, Chou I-M (eds) Fluid–mineral interactions: a tribute to H.P. Eugster. Geochem Soc Spec Publ No. 2, pp 213–269

Böhlke JK, Denver JM (1995) Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic coastal plain, Maryland. Water Resour Res 31(9):2319–2339

Bowser CJ, Jones BF (2002) Mineralogic controls on the composition of natural waters dominated by silicate hydrolysis. Am J Sci 302:582–662

Brantley SL, Chen Y (1995) Chemical weathering rates of pyroxenes and amphiboles. In: White AF, Brantley SL (eds) Mineral Soc Am Rev Mineral 31:119–172

Brinkmann R, Münnich KO, Vogel JC (1959) ^{14}C-altersbestimmung von grundwasser [C^{14} age determination of groundwater]. Naturwissenschaften 46:10–12

Brinkmann R, Münnich KO, Vogel JC (1960) Anwendung der C ^{14}-methode auf bodenbildung und grundwasserkreislauf [Application of the C ^{14} method to soil structure and the ground water cycle]. Geol Rundschau 49:244–253

Brown JG, Bassett RL, Glynn PD (1998) Analysis and simulation of reactive transport of metal contaminants in ground water in Pinal Creek Basin, Arizona. J Hydrol 209:225–250

Brown JG, Glynn PD (2003) Kinetic dissolution of carbonates and Mn oxides in acidic water: measurement of in situ field rates and reactive transport modeling. Appl Geochem 18:1225–1239

Buddemeier RW, Okamoto HS, Hurd DO, Hufen RR (1972) Effects of solution and exchange on the radiocarbon dating of sediments and natural waters. In: Proceedings of 8th International Conference on Radiocarbon Dating, R Soc N Z, Wellington, Vol 1, pp 297–310

Buffle J, van Leeuwen HP (eds) (1993) Environmental particles, vol 2, Lewis Publishers, Boca Raton, 426 pp

Burgman JO, Calles B, Westman F (1987) Conclusions from a ten-year study of oxygen-18 in precipitation and runoff in Sweden. In: Isotope techniques in water resources development. International Atomic Energy Agency, Vienna, pp 579–590

Burns DA, Plummer LN, McDonnell JJ, Busenberg E, Casile G, Kendall C, Hooper RP, Freer JE, Peters NE, Beven K, Schlosser P (2003) Geochemical evolution of riparian ground water in a forested Piedmont catchment. Ground Water 41:913–925

Burr CS, Thomas JM, Reines D, Jeffrey D, Courtney D, Jull AJT, Lange T (2001) Sample preparation of dissolved organic carbon in groundwater for AMS ^{14}C analysis. Radiocarbon 43:183–190

Burton WC, Plummer LN, Busenberg E, Lindsey BD, Gburek WR (2002) Influence of fracture anisotropy on ground-water ages

and chemistry, Valley and Ridge Province, Pennsylvania. Ground Water 40:242–257

Busby JF, Lee RW, Hanshaw BB (1983) Major geochemical processes related to the hydrology of the Madison aquifer system and associated rocks in parts of Montana, South Dakota, and Wyoming. US Geol Surv Water Resour Invest Rep 83-4093, 180 pp

Busby JF, Plummer LN, Lee RW, Hanshaw BB (1991) Geochemical evolution of water in the Madison aquifer in parts of Montana, South Dakota, and Wyoming. US Geol Surv Prof Pap 1273-F, 89 pp

Busenberg E, Plummer LN (1989) Thermodynamics of magnesian calcite solid-solutions at 25°C and 1 atm total pressure. Geochim Cosmochim Acta 53:1189–1208

Busenberg E, Plummer LN (2000) Dating young ground water with sulfur hexafluoride: natural and anthropogenic sources of sulfur hexafluoride. Water Resour Res 36:3011–3030

Castro MC, Jambon A, De Marsily G, Schlosser P (1998a) Noble gases as natural tracers of water circulation in the Paris Basin, 1. Measurements and discussion of their origin and mechanisms of vertical transport in the basin. Water Resour Res 34:2443–2466

Castro MC, Goblet P, Ledoux E, Violette S, De Marsily G (1998b) Noble gases as natural tracers of water circulation in the Paris Basin. 2. Calibration of a groundwater flow model using noble gas isotope data. Water Resour Res 34:2467–2483

Castro MC, Stute M, Schlosser P (2000) Comparison of ^{4}He ages and ^{14}C ages in simple aquifer systems: implications for groundwater flow and chronologies. Appl Geochem 15:1137–1167

Cederstrom DJ (1946) Genesis of ground waters in the Coastal Plain of Virginia. Econ Geol 41:218–245

Champ DR, Gulens J, Jackson RE (1979) Oxidation–reduction sequences in ground water systems. Can J Earth Sci 16:12–23

Chapelle F (1993) Ground-water microbiology and geochemistry. Wiley, New York, 424 pp

Chapman NA, McKinley IG, Shea ME, Smellie JAT (1993) The Poços de Caldas project: natural analogues of processes in a radioactive waste repository. Elsevier, Amsterdam

Charlton SR, Macklin CL, Parkhurst DL (1997) PHREEQCI—a graphical user interface for the geochemical computer program PHREEQC. US Geol Surv Water Resour Invest Rep 97–4222, 9 pp

Charlton SR, Parkhurst DL (2002) PHREEQCI–a graphical user interface to the geochemical model PHREEQC. US Geol Surv Fact Sheet FS-031-02

Chebotarev II (1955) Metamorphism of natural waters in the crust of weathering. Parts 1–3. Geochim Cosmochim Acta 8:22–48, 137–170, 198–212

Clark ID, Fritz P (1997) Environmental isotopes in hydrogeology. Lewis Publisher, Boca Raton, 328 pp

Collon P, Kutschera W, Loosli HH, Lehmann BE, Purtschert R, Love A, Sampson L, Anthony D, Cole D, Davids B, Morrissey DJ, Sherrill BM, Steiner M, Pardo RC, Paul M (2000) ^{81}Kr in the Great Artesian basin, Australia: a new method for dating very old groundwater. Earth Planet Sci Lett 182:103–113

Cook PG, Solomon DK (1997) Recent advances in dating young groundwater: chlorofluorocarbons, ^{3}H/^{3}He, and ^{85}Kr. J Hydrol 191:245–265

Cook PG, Böhlke JK (2000) Determining timescales for groundwater flow and solute transport. In: Environmental tracers in subsurface hydrology. Kluwer Academic Press, Boston, pp 1–30

Cook PG, Herczeg AL (2000) Environmental tracers in subsurface hydrology. Kluwer Academic Publishers, Boston, 529 pp

Coplen TB, Winograd IJ, Landwehr JM, Riggs AC (1994) 500,000-year stable carbon isotopic record from Devils Hole, Nevada. Science 263:361–365

Davidson MR, Airey PL (1982) The effect of dispersion on the establishment of a paleoclimatic record from groundwater. J Hydrol 58:131–147

Davis JA, Kent DB (1990) Surface complexation modeling in aqueous geochemistry. In: Hochella MF, White AF (eds) Mineral-water interface geochemistry. Mineral Soc Am Rev Mineral 23:177–248

Davis SN, Bentley HW (1982) Dating groundwater, a short review. In: Cutrie LA (ed) Nuclear and chemical dating techniques; interpreting the environmental record. Am Chem Soc Symp Ser 176, Washington, DC, pp 187–222

Davis SB, Fabryka-Martin J, Wolfsberg L, Moysey S, Shaver R, Alexander EC Jr, Krothe N (2000) Chlorine-36 in ground water containing low chloride concentrations. Ground Water 38:912–921

Davis SN, Moysey S, Cecil LD, Zreda M (2003) Chlorine-36 in groundwater of the United States: empirical data. Hydrogeol J 11:217–227

Deák J, Stute M, Rudolph J, Sonntag C (1987) Determination of the flow regime of Quaternary and Pliocene layers in the Great Hungarian Plain (Hungary) by D, ^{18}O, ^{14}C and noble gas measurements. In: Isotope techniques in water resources development. International Atomic Energy Agency, Vienna. IAEA-SM-299/39, pp 335–350

Drever JI (1997) The geochemistry of natural waters-surface and groundwater environments, 3rd edn. Prentice Hall, Upper Saddle River, NJ, 436 pp

Dreybrodt W, Buhmann D, Michaelis J, Usdowski E (1992) Geochemically controlled calcite precipitation by CO_2 outgassing: field measurements of precipitation rates in comparison to theoretical predictions. Chem Geol 97:285–294

Dutton AR (1995) Ground water isotopic evidence for paleorecharge in US High Plains aquifers. Quat Res 43:221–231

Eberl DD, Srodon J, Kralik M, Taylor BE, Peterman ZE (1990) Ostwald ripening of clays and metamorphic minerals. Science 248:474–477

Edmunds WM, Bath AH, Miles DL (1982) Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. Geochim Cosmochim Acta 46(11):2069–2081

Edmunds WM, Smedley PL (2000) Residence time indicators in groundwater: the East Midlands Triassic sandstone aquifer. Appl Geochem 15:737–752

Engesgaard P, Kipp KL (1992) A geochemical transport model for redox-controlled movement of mineral fronts in groundwater flow systems: a case of nitrate removal by oxidation of pyrite. Water Resour Res 28:2829–2843

Engesgaard P, Molson J (1998) Direct simulation of ground water age in the Rabis Creek aquifer, Denmark. Ground Water 36:77–582

Eriksson E (1958) The possible use of tritium for estimating groundwater storage. Tellus 10:472–478

Evans GV (1983) Tracer techniques in hydrology. Int J Appl Radiat Isot 34:451–475

Evans WC, van Soest MC, Mariner RH, Hurwitz S, Ingebritsen SE, Wicks CW Jr, Schmidt ME (2004) Magmatic intrusion west of Three Sisters, central Oregon, USA: the perspective from spring chemistry. Geology 32:69–72

Fabryka-Martin J, Davis SN, Elmore D (1987) Applications of ^{129}I and ^{36}Cl in hydrology. Nuclear Instrum Methods Phys Res B29:361–371

Florkowski T, Rozanski K (1986) Radioactive noble gases in the terrestrial environment. In: Fritz P, Fontes JCh (eds) Handbook of environmental isotope geochemistry: the terrestrial environment B, vol 2. Elsevier, New York, pp 481–506

Fontes J-Ch (1983) Dating of groundwater. In: Guidebook on nuclear techniques in hydrology, 1983 edn., International Atomic Energy Agency, Vienna, Tech Rep Ser 91:285–317

Fontes J-Ch (1994) Isotope paleohydrology and the prediction of long-term repository behaviour. Terra Nova 6:20–34

Fontes J-Ch (1992) Chemical and isotopic constraints on ^{14}C dating of groundwater. In: Taylor RE, Long A, Kra R (eds) Radiocarbon after four decades. Springer, Berlin Heidelberg New York, pp 242–261

Fontes J-Ch, Garnier J-M (1979) Determination of the initial ^{14}C activity of the total dissolved carbon: a review of the existing models and a new approach. Water Resour Res 15:399–413

Foster MD (1950) The origin of high sodium bicarbonate waters in the Atlantic and Gulf Coastal Plains. Geochim Cosmochim Acta 1:33–48

Fröhlich K (1990) On dating of old groundwater. Isotopenpraxis 26:557–560

Fryar AE, Mullican WF, Macko SA (2001) Groundwater recharge and chemical evolution in the southern High Plains of Texas, USA. Hydrogeol J 9:522–542

Fu Wei Huai, Ledoux E, de Marsily G (1990) Regional modeling of groundwater flow and salt and environmental tracer transport in deep aquifers in the Paris Basin. J Hydrol 120:341–358

Gamsjäger H, Königsberger E, Preis W (2000) Lippmann diagrams: theory and application to carbonate systems. Aquat Geochem 6:119–132

Garmonov IV (1958) Fundemental principles of hydrochemical zoning of underground waters in the European part of the Soviet Union. In: Proceedings of Symposium on Ground Water 1955, Central Board of Geophysics. Temple Press, Calcutta. Publ No. 4, pp 293–302

Garnier J-M (1985) Retardation of dissolved radiocarbon through a carbonated matrix. Geochim Cosmochim Acta 49:683–693

Garrels RM, Thompson ME (1962) A chemical model for sea water at 25°C and one atmosphere total pressure. Am J Sci 260:57–66

Garrels RM, Christ CL (1965) Solutions, minerals, and equilibria. Harper and Row, New York, 450 pp

Garrels RM, Mackenzie FT (1967) Origin of the chemical compositions of some springs and lakes. In: Equilibrium concepts in natural water systems. Am Chem Soc Adv Chem Ser 67:222–242

Gibbs JW (1876, 1878) On the equilibrium of heterogeneous substances. Connecticut Academy Transactions III:108–248, 343–524. In: The scientific papers of J. Willard Gibbs. Dover Publ, New York, 1961

Glynn PD, Reardon EJ (1990) Solid-solution aqueous-solution equilibria: thermodynamic theory and representation. Am J Sci 290:164–201

Glynn PD, Reardon EJ, Plummer LN, Busenberg E (1990) Reaction paths and equilibrium end-points in solid-solution aqueous-solution systems. Geochim Cosmochim Acta 54:267–282

Glynn PD (1991) MBSSAS: a code for the computation of Margules parameters and equilibrium relations in binary solid-solution aqueous-solution systems. Comput Geosci 17:907–966

Glynn PD, Reardon EJ (1992) Reply to Comment by Königsberger and Gamsjäger on "Solid-solution aqueous-solution equilibria: thermodynamic theory and representation". Am J Sci 292:215–225

Glynn PD, Plummer LN, Busenberg E, Reardon EJ (1992) Reply to a Comment by Dr. Stoessell on "Reaction paths and equilibrium end-points in solid-solution aqueous-solution systems". Geochim Cosmochim Acta 56:2559–2572

Glynn PD, Brown JG (1996) Reactive transport modeling of acidic metal-contaminated ground water at a site with sparse spatial information. In: Steefel CI, Lichtner P, Oelkers E (eds) Reactive transport in porous media: general principles and application to geochemical processes. Mineral Soc Am Rev Mineral 34:377–438

Glynn PD, Voss CI, Provost AM (1999) Deep penetration of oxygenated meltwaters from warm based sheets into the Fennoscandian Shield. In: Use of hydrological information in testing groundwater flow models: Technical Summary and Proceedings of a Workshop, Nuclear Energy Agency, ISBN 92-64-16153-8, pp 201–241

Glynn PD, Voss CI (1999) Geochemical characterization of Simpevarp ground waters near the Äspö Hard Rock Laboratory. Swedish Nuclear Power Inspectorate (SKI), SKI Rep 96:29, 210 pp

Glynn PD (2000) Solid-solution solubilities and thermodynamics: sulfates, carbonates and halides. In: Alpers CN, Jambor JL, Nordstrom DK (eds) Sulfate minerals—crystallography, geo-

chemistry and environmental significance. Rev Mineral Geochem 40:481–511

Glynn PD (2003) Modeling Np and Pu transport with a surface complexation model and spatially variant sorption capacities: implications for reactive transport modeling and performance assessments of nuclear waste disposal sites. Comput Geosci 29:331–349

Gonfiantini R, Zuppi GM (2003) Carbon isotope exchange rate of DIC in karst groundwater. Chem Geol 197:319–336

Goode DJ (1996) Direct simulation of groundwater age. Water Resour Res 32(2):289–296

Gosselin DC, Harvey FE, Frost CD (2001) Geochemical evolution of ground water in the Great Plains (Dakota) aquifer of Nebraska: Implications for the management of a regional aquifer system. Ground Water 39:98–108

Grabczak J, Zuber A, Maloszewski P, Rozanski K, Weiss W, Sliwka I (1982) New mathematical models for the interpretation of environmental tracers in groundwaters and the combined use of tritium, C-14, Kr-85, He-3, and Freon-11 for groundwater studies. Beitr Geol Schweiz, Hydrol 28:395–406

Hanshaw BB, Back W, Rubin M (1965a) Radiocarbon determinations for estimating groundwater flow velocities in Central Florida. Science 148:494–495

Hanshaw BB, Back W, Rubin M (1965b) Carbonate equilibria and radiocarbon distribution related to groundwater flow in the Floridan Limestone aquifer, USA. In: Proceedings of International Association on Science of Hydrology, Dubrovnik, 1965, pp 601–614

Hanshaw BB, Back W (1974) Determination of regional hydraulic conductivity through use of ^{14}C dating of groundwater. Mémoires de l'Association Internationale des Hydrogéologues, Congres de Montpellier, X-1, pp 195–196

Harvey RW, Harms H (2002) Use of microorganisms as tracers in groundwater. In: Britton G (ed) Encylopedia of environmental microbiology. Wiley, New York, pp 3194–3202

Harvie CE, Moller N, Weare JH (1984) The prediction of mineral solubilities in natural waters: The Na-K-Mg-Ca-H-Cl-SO$_4$-OH-HCO$_3$-CO$_3$-CO$_2$-H$_2$O system to high ionic strengths at 25°C. Geochim Cosmochim Acta 48:723–752

Helgeson HC (1968) Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions. I. Thermodynamic relations. Geochim Cosmochim Acta 32:853–877

Helgeson HC, Brown TH, Nigrini A, Jones TA (1970) Calculation of mass transfer in geochemical processes involving aqueous solutions. Geochim Cosmochim Acta 34:569–592

Helgeson HC, Garrels RM, Mackenzie FT (1969) Evaluation of irreversible reactions in geochemical processes involving minerals and aqueous solutions. II. Applications. Geochim Cosmochim Acta 33:455–481

Hem JD (1959, 1992) Study and interpretation of the chemical characteristics of natural water. US Geol Surv Water Supply Paper 1473, 269 pp, Revised and last reprinted in 1992

Hendry MJ, Schwartz FW (1990) Chemical evolution of ground water in the Milk River aquifer. Can J Ground Water 28(2):253–261

Hendry MJ, Schwartz FW, Robertson CR (1991) Hydrogeology and hydrogeochemistry of the Milk River Aquifer system—a review. J Appl Geochem 6:369–380

Herczeg AL, Simpson HJ, Mazor E (1993) Transport of soluble salts within a large semi-arid basin: River Murray, Australia. J Hydrol 144:59–84

Herczeg AL, Torgersen T, Chivas AR, Habermehl MA (1991) Geochemistry of ground waters from the Great Artesian Basin, Australia. J Hydrol 126:225–245

Herman J, Lorah M (1988) Calcite precipitation rates in the field: measurement and prediction for a travertine-depositing stream. Geochim Cosmochim Acta 52:2347–2355

Hitchon B, Perkins EH, Gunter WD (1999) Introduction to ground water geochemistry. Geoscience Publishing, Sherwood Park, Alberta, 310 pp

Hochella MF, White AF (1990) Mineral-water interface geochemistry. In: Hochella MF, White AF (eds) Mineral Soc Am Rev Mineral 23:603 pp

Hostettler JD (1984) Electrode electrons, aqueous electrons, and redox potentials in natural waters. Am J Sci 284:734–759

Hunkeler D, Aravena R, Butler B (1999) Monitoring microbial dechlorination of tetrachloroethene (PCE) in groundwater using compound-specific stable carbon isotope ratios: microcosm and field studies. Environ Sci Technol 33:2733–2738

Ingerson E, Pearson FJ Jr (1964) Estimation of age and rate of motion of groundwater by the ^{14}C-method. In: Recent researches in the fields of atmosphere, hydrosphere, and nuclear geochemistry, Sugawara Festival Volume. Maruzen Co., Tokyo, pp 263–283

International Atomic Energy Agency (2005) IAEA Guidebook on the use of chlorofluorocarbons in hydrology (in press)

Ittner T, Gustafsson E, Nordqvist R (1991) Radionuclide content in surface and groundwater transformed into breakthrough curves: a Chernobyl fallout study in a forested area in northern Sweden. Swedish Nuclear Fuel and Waste Management Co. (SKB), SKB Tech Rep 91-28, 16 pp

Ivanovich M, Frölich K, Hendry MJ, Andrews JN, Davis SN, Drimmie RJ, Fabryka-Martin J, Florkowski T, Fritz P, Lehmann BE, Loosli HH, Nolte E (1992) Evaluation of isotopic methods for the dating of very old groundwaters: a case study of the Milk River aquifer. In: Isotope techniques in water resources development 1991, Proceedings of symposium, Vienna, March 11–15, 1991. International Atomic Energy Agency, Vienna, pp 229–244

Johnson TM, DePaolo DJ (1996) Reaction-transport models for radiocarbon in groundwater: the effects of longitudinal dispersion and the use of Sr isotope ratios to correct for water–rock interaction. Water Resour Res 32(7):2203–2212

Jones BF, Anderholm SK (1996) Some geochemical considerations of brines associated with bedded salt repositories. In: Bottrel SH (ed) Fourth International Symposium Geochemistry of the Earth's Surface. International Association of Geochemistry & Cosmochemistry, pp 343–353

Jones BF, Bowser CJ (1978) The mineralogy and related chemistry of lake sediments. In: Lerman A (ed) Lakes: chemistry, geology, physics, chap 7. Springer, Berlin Heidelberg New York, pp 179–235

Jones BF, Hanor JS, Evans WR (1994) Sources of dissolved salts in the central Murray Basin, Australia. Chem Geol 111:135–154

Jones BF, Llamas MR (1989) Normative analysis of groundwaters from the Madrid Basin, Spain. In: Miles DL (ed) Proceedings of 6th International Symposium on Water–Rock Interaction, Malvern, 3–8 August 1989, Balkema, Rotterdam, pp 341–347

Kalin RM (2000) Radiocarbon dating of groundwater systems. In: Cook P, Herczeg AL (eds) Environmental tracers in subsurface hydrology, chap 4. Kluwer Academic Publishers, Boston, pp 111–144

Kamensky GN (1958) Hydrochemical zoning in the distribution of underground waters. In: Proceedings of the Symposium on Ground Water 1955. Central Board of Geophysics. Temple Press, Calcutta, Pub. No. 4, pp 281–292

Katz BG, Böhlke JK, Hornsby HD (2001) Timescales for nitrate contamination of spring waters, northern Florida, USA. Chem Geol 179:167–186

Kauffman SJ, Herman JS, Jones BF (1998) Lithological and hydrological influences on groundwater composition in a heterogenous carbonate-clay aquifer system. Geol Soc Am Bull 110(9):1163–1173

Kendall C, McDonnell JJ (1998) Isotope tracers in catchment hydrology. Elsevier Science Publishers, Amsterdam, 839 pp

Kim J, Dong H, Seabaugh J, Newell SW, Eberl DD (2004) Role of microbes in the smectite-to-illite reaction. Science 203:830–832

Kipfer R, Aeschback-Hertig W, Peters F, Stute M (2002) Noble gases in lakes and ground waters. In: Porcelli D, Ballentine CJ, Wieler R (eds) Noble gases in geochemistry and cosmochemistry. Rev Mineral Geochem 27:615–700

Kondepudi D, Prigogine I (1998) Modern thermodynamics: from heat engines to dissipative structures. Wiley, Chichester, 508 pp

Konikow LF, Bredehoeft JD (1992) Ground-water models cannot be validated. Adv Water Resour 15:75–83

Konikow LF, Glynn PD (2005) Modeling ground-water flow and quality. In: Selinus O (ed) Medical geology. Academic Press (in press)

Korzhinskii DS (1936) Mobility and inertia of components in metasomatism (in Russian). Izvestiya AN USSR Ser Geol 1: 35–60

Krumbein WC, Garrels RM (1952) Origin and classification of chemical sediments in terms of pH and oxidation–reduction potentials. J Geol 60:1–30

Landwehr JM, Winograd IJ (2001) Dating the Vostok ice core record by importing the Devils Hole chronology. J Geophys Res 106(D23):31, 853–31, 862

Langmuir D (1997) Aqueous environmental geochemistry. Prentice-Hall, Upper Saddle River, NJ, 600 pp

Leaney FJ, Allison GB (1986) Carbon-14 and stable isotope data for an area in the Murray Basin: its use in estimating recharge. J Hydrol 88:129–145

Lehmann BE, Oeschger H, Loosli HH, Hurst GS, Allman SL, Chin CH, Kramer SD, Payne MG, Phillips RC, Willis RD, Thonnard N (1985) Counting ^{81}Kr atoms for analysis of groundwater. J Geophys Res 90(B13):11547–11551

Lehmann BE, Davis SN, Fabryka-Martin JT (1993) Atmospheric and subsurface sources of stable and radioactive nuclides used for groundwater dating. Water Resour Res 29:2027–2040

Lehmann BE, Love A, Purtschert R, Collon P, Loosli HH, Kutschera W, Beyerle U, Aeschbach-Hertig W, Kipfer R, Frape SK, Herczeg A, Moran J, Tolstikhin IN, Groning M (2003) A comparison of groundwater dating with Kr-81, Cl-36 and He-4 in four wells of the Great Artesian Basin, Australia. Earth Planet Sci Lett 211:237–250

Lindsey BD, Phillips SW, Donnelly CA, Speiran GK, Plummer LN, Bohlke JK, Focazio MJ, Burton WC, Busenberg E (2003) Residence times and nitrate transport in ground water discharging to streams in the Chesapeake Bay watershed. US Geol Surv Water Resour Invest Rep 03-4035, 201 pp

Lippmann F (1977) The solubility product of complex minerals, mixed crystals and three-layer clay minerals. Neues Jahrb Min Abh 130:243–263

Lippmann F (1980) Phase diagrams depicting the aqueous solubility of binary mineral systems. Neues Jahrb Min Abh 139:1–25

Liu Z, Svensson U, Dreybrodt W, Daoxian Y, Buhmann D (1995) Hydrodynamic control of inorganic calcite precipitation in Huanglong Ravine, China: field measurements and theoretical prediction of deposition rates. Geochim Cosmochim Acta 59: 3087–3097

Llamas MR, Martinez A (1981) Application of different computer models to the study of solute transport in a vertical profile of the Madrid aquifer. Sci Total Environ 21:347–352

Loosli HH, Lehmann BE, Smethie WM Jr (2000) Noble gas radioisotopes: ^{37}Ar, ^{85}Kr, ^{39}Ar, ^{81}Kr. In: Cook P, Herczeg A (eds) Environmental tracers in subsurface hydrology. Kluwer Academic Press, Boston, pp 379–396

Magaritz M, Wells M, Amiel AJ, Ronen D (1989) Application of a multi-layer sampler based on the dialysis cell technique for the study of trace metals in groundwater. Appl Geochem 4:617–624

Maiss M, Brenninkmeijer CAM (1998) Atmospheric SF_6: trends, sources and prospects. Environ Sci Technol 32:3077–3086

Małoszewski P, Zuber A (1982) Determining the turnover time of groundwater systems with the aid of environmental tracers. 1. Models and their applicability. J Hydrol 57:207–231

Małoszewski P, Rauert W, Stichler W, Herrmann A (1983) Application of flow models to an Alpine catchment area using tritium and deuterium data. J Hydrol 66:319–330

Małoszewski P, Zuber A (1991) Influence of matrix diffusion and exchange reactions on radiocarbon ages in fissured carbonate aquifers. Water Resour Res 27:1937–1945

Małoszewski P, Zuber A (1996) Lumped parameter models for the interpretation of environmental tracer data, Manual on the mathematical models in isotope hydrogeology, IAEA-TEC-DOC-910, pp 9–58

Manning AH, Solomon DK (2003) Using noble gases to investigate mountain-front recharge. J Hydrol 275:194–207

Manning AH, Solomon DK, Sheldon AL (2003) Applications of a total dissolved gas pressure probe in ground water studies. Ground Water 41(4):440–448

Marty B, Torgersen T, Meynier V, O'Nions RK, De Marsily G (1993) Helium isotope fluxes and groundwater ages in the Dogger Aquifer, Paris Basin. Water Resour Res 29:1025–1035

Mattle N, Kinzelbach W, Beyerle U, Huggenberger P, Loosli HH (2001) Exploring an aquifer system by integrating hydraulic, hydrogeologic and environmental tracer data in a three-dimensional hydrodynamic transport model. J Hydrol 242:183–196

Mazor E (1972) Paleotemperatures and other hydrological parameters deduced from noble gases dissolved in groundwaters; Jordan Rift Valley, Israel. Geochim Cosmochim Acta 36:1321–1336

Mazor E, Bosch A (1992) Helium as a semi-quantitative tool for groundwater dating in the range of 10^4–10^8 years. In: Proceedings of Consultants Meeting on Isotopes of Noble Gases as Tracers in Environmental Studies. International Atomic Energy Agency, Vienna, pp 163–178

McCarthy JF, Degueldre C (1993) Sampling and characterization of colloids and particles in groundwater for studying their role in contaminant transport. In: Buffle J, van Leeuwen HP (eds) Environmental particles, vol 2. Lewis Publishers, Chelsea, MI, USA, pp 247–315

McLachlan JA (2001) Environmental signaling: what embryos and evolution teach us about endocrine disrupting chemicals. Endocr Rev 22(3):319–341

McMahon PB (2001) Aquifer/aquitard interfaces: mixing zones that enhance biogeochemical reactions. In: Remenda V (ed) Theme issue on confining units. Hydrogeol J 9:34–43 DOI 10.1007/s100400000109

McMahon PB, Bohlke JK, Christenson SC (2004) Geochemistry, radiocarbon ages, and paleorecharge conditions along a transect in the central High Plains aquifer, Southwestern Kansas, USA. Appl Geochem 19:1655–1686

Mehta S, Fryar AE, Banner JL (2000) Controls on the regional-scale salinization of the Ogallala aquifer, Southern High Plains, Texas, USA. Appl Geochem 15:849–864

Miller JA (1999) Ground water atlas of the United States, introduction and national summary. US Geol Surv, HA-730 (and volumes within the HA-730 series). http://capp.water.usgs.gov/gwa/index.html

Miller W, Alexander R, Chapman N, McKinley I, Smellie J (1994) Natural analogue studies in the geological disposal of radioactive wastes. Elsevier, Netherlands. Stud Environ Sci 57:412

Mook WG (1972) On the reconstruction of the initial ^{14}C content of groundwater from the chemical and isotopic composition. In: Proceedings of Eighth International Conference on Radiocarbon Dating, R Soc N Z, Wellington, New Zealand, Vol 1, pp 342–352

Mook WG (1980) Carbon-14 in hydrogeological studies. In: Fritz P, Fontes JC (eds) Handbook of environmental isotope geochemistry, Vol 1. Elsevier, Amsterdam, pp 49–74

Morgenstern U (2000) Silicon-32, Environmental tracers in subsurface hydrology. In: Cook P, Herczeg A (eds) Environmental tracers in subsurface hydrology. Kluwer Academic Press, Boston, pp 498–502

Morris JC, Stumm W (1967) Redox equilibria and measurements of potentials in the aquatic environment. In: Stumm W (ed) Equilibrium concepts in natural water systems, chap 13. Am Chem Soc Adv Chem Ser 67, Washington, DC, pp 270–285

Morse BS (2002) Radiocarbon dating of groundwater using paleoclimatic constraints and dissolved organic carbon in the southern Great Basin, Nevada and California. Unpubl. MS thesis, University of Nevada, Reno, NV, 63 pp

Moser H, Rauert W (1983) Determination of groundwater movement by means of environmental isotopes—state of the art. In: IAHS Symposium on Relation of Groundwater Quantity and Quality, XVIII IUGG Assembly, Hamburg, pp 1–30

Mozeto AA, Fritz P, Reardon EJ (1984) Experimental observations of carbon isotope exchange in carbonate-water systems. Geochim Cosmochim Acta 48:495–504

Münnich KO (1957) Messung des ^{14}C-Gehalts von hartem Grundwasser [Measurement of ^{14}C contents in hard ground water]. Naturwissenschaften 44:32–39

Murphy EM, Davis SN, Long A, Donahue D, Jull AJT (1989) ^{14}C in fractions of dissolved organic carbon in groundwater. Nature 337:153–155

Nash H, McCall JGH (1994) Groundwater quality. Chapman & Hall, London, 224 pp

Nativ R, Gutierrez GN(1989) Hydrogeology and hydrochemistry of Cretaceous aquifers, southern High Plains, USA. J Hydrol 108:79–109

Nativ R, Smith DA(1987) Hydrogeology and geochemistry of the Ogallala aquifer, southern High Plains. J Hydrol 91:217–253

Nelms DL, Harlow GE Jr, Plummer LN, Busenberg E (2003) Aquifer susceptibility in Virginia, 1998–2000. US Geol Surv Water Resour Invest Rep 03-4278, http://water.usgs.gov/pubs/wri/wri034278/

Neuzil CE (1986) Groundwater flow in low-permeability environments. Water Resour Res 22:1163–1195

Nicolis G, Prigogine I (1989) Exploring complexity: an introduction. WH Freeman, New York, 328 pp

Nolte E, Krauthan P, Heim U, Korschinek G (1990) ^{36}Cl measurements and dating of groundwater samples from the Milk River aquifer. Nucl Instrum Methods Phys Res B52:477–482

Nordstrom DK, Plummer LN, Wigley TML, Wolery TJ, Ball JW, Jenne EA, Bassett RL, Crear DA, Florence TM, Fritz B, Hoffman M, Holdren Jr GR, Lafon GM, Mattigod SV, McDuff RE, Morel F, Reddy MM, Sposito G, Thrailkill J (1979) A comparison of computerized aqueous models. In: Jenne EA (ed) Chemical modeling in aqueous systems. Am Chem Soc Symp Ser 93:857–892

Nordstrom DK, Ball JW, Donahoe RJ, Whittemore D (1989) Groundwater chemistry and water–rock interactions at Stripa. Geochim Cosmochim Acta 53:1727–1740

Nordstrom DK (1994) On the evaluation and application of geochemical models, Appendix II. In: Proceedings of 5th CEC Natural Analogue Working Group and Alligator Rivers Analogue Project: Toledo, Spain, October 5–19, pp 375–385

Nordstrom DK, Munoz JL (1994) Geochemical thermodynamics, 2nd edn. Blackwell Scientific Publications, Boston

Nordstrom DK (2004) Modeling low-temperature geochemical processes. In: Holland HD, Turekian KK (eds) Treatise on geochemistry, Vol 5, Drever JI (ed) Surface and ground water, weathering, erosion and soils, chap 5.02, 36 pp

Olmsted FH (1962) Chemical and physical character of ground water in the National Reactor Testing Station, Idaho. US Geol Surv IDO-22043-USGS

Oreskes N, Shrader-Frechette K, Belitz K (1994) Verification, validation, and confirmation of numerical models in the earth sciences. Science 263:641–646

Oreskes N (2000) Why believe a computer? Models, measures, and meaning in the natural world. In: Schneiderman J (ed) The earth around us. WH Freeman, New York, pp 70–82

Ortoleva PJ (1994) Geochemical self-organization. Oxford University Press, New York, 411 pp

Paces T (1983) Rate constants of dissolution derived from the measurements of mass balance in hydrological catchments. Geochim Cosmochim Acta 47:1855–1863

Paces JB, Neymark LA, Marshall BD, Whelan JF, Peterman ZE (2001) Ages and origins of calcite and opal in the Exploratory Studies Facility Tunnel, Yucca Mountain, Nevada. US Geol Surv Water Resour Invest Rep 01-4049

Palissy B (1580) Discours admirable de la nature des eaux et fontaines tant naturelles qu'artificielles, des metaux, des sels & salines, des pierres, des terres, du feu & des emaux [Discourse

on the nature of waters and fountains, both natural and artificial, and on metals, salts and brines, rocks, soils, fire and enamels]. M Le Jeune, Paris, 361 pp

Palmer C (1911) The geochemical interpretation of water analyses. US Geol Surv Bull 479:31

Parkhurst DL, Thorstenson DC, Plummer LN (1980) PHREEQE—a computer program for geochemical calculations. US Geol Surv Water Resour Invest Rep 80-96

Parkhurst DL, Plummer LN, Thorstenson DC (1982) BALANCE—a computer program for calculating mass transfer for geochemical reactions in ground water. US Geol Surv Water Resour Invest Rep 82-14

Parkhurst DL, Christenson S, Breit GN (1992) Ground-water-quality assessment of the Central Oklahoma Aquifer, Oklahoma: geochemical and geohydrologic investigations. US Geol Surv Open-File Rep 92-642, 113 pp

Parkhurst DL, Plummer LN (1993) Geochemical models. In: Alley WM (ed) Regional ground-water quality, Vol 9, pp 199–225

Parkhurst DL (1995) User's guide to PHREEQC–a computer program for speciation, reaction-path, advective-transport, and inverse geochemical calculations. US Geol Surv Water Resources Invest Rep 95-4227, 143 pp

Parkhurst DL (1997) Geochemical mole-balance modeling with uncertain data. Water Resour Res 33:1957–1970

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC—a computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. US Geol Surv Water Resour Invest Rep 99-4259

Parkhurst DL, Stollenwerk KG, Colman JA (2003) Reactive-transport simulation of phosphorus in the sewage plume at the Massachusetts Military Reservation, Cape Cod, Massachusetts. US Geol Surv Water Resour Invest Rep 03-4017, 33 pp

Parkhurst DL, Petkewich MD (2002) Geochemical modeling of an aquifer storage recovery experiment. Charleston, South Carolina. In: Aiken GR, Kuniansky EL (eds) US Geol Surv Artificial Recharge Workshop Proceedings, Sacramento, California: US Geol Surv Open-File Rep 02-89, pp 37–40

Pearson FJ, Arcos D, Bath A, Boisson J-Y, Fernández AMa, Gäbler H-E, Gaucher E, Gautschi A, Griffault L, Hernán P, Waber HN (2003) Mont Terri Project—Geochemistry of Water in the Opalinus Clay Formation at the Mont Terri Rock Laboratory. Bern, Switzerland, Federal Office for Water and Geology (FOWG), Geology Series 5, 319 pp

Pearson FJ Jr, Hanshaw BB (1970) Sources of dissolved carbonate species in groundwater and their effects on carbon-14 dating. In: Proceedings of Isotope Hydrology Conference 1970. International Atomic Energy Agency, Vienna. IAEA-SM-129/18, pp 271–286

Pearson FJ Jr, White DE (1967) Carbon-14 ages and flow rates of water in Carrizo sand, Atascosa County, Texas. Water Resour Res 3:251–261

Pearson FJ Jr, Balderer W, Loosli HH, Lehmann BE, Matter A, Peters TJ, Schmassmann H, Gautschi A (1991) Applied isotope hydrogeology: a case study in northern Switzerland. Stud Environ Sci 43:439

Pearson FJ Jr, Noronha CJ, Andrews RW (1983) Mathematical modeling of the distribution of natural ^{14}C, ^{234}U, and ^{238}U in a regional ground-water system. In: Stuiver M, Kra R (eds) Proceedings of 11th International Radiocarbon Conference, Seattle, WA. Radiocarbon 25:291–300

Pearson FJ Jr, Truesdell AH (1978) Tritium in the waters of Yellowstone National Park. In: Zartman RE (ed) Short Papers of the Fourth International Conference Geochronology Cosmochronology Isotope Geology 1978, Snowmass-at-Aspen, CO, Washington, DC. US Geol Surv Open-File Rep 78-701, pp 327–329

Pearson FJ Jr (1992) Effects of parameter uncertainty in modeling ^{14}C in groundwater. In: Taylor R, Long A, Kra R (eds) Radiocarbon after four decades. Springer, Berlin Heidelberg New York, pp 262–275

Pebesma EJ, de Kwaadsteniet JW (1997) Mapping groundwater quality in the Netherlands. J Hydrol 200:364–386

Phillips FM, Mattick JL, Duval TA, Elmore D, Kubik PW(1988) Chlorine 36 and tritium from nuclear weapons fallout as tracers for long-term liquid and vapor movement in desert soils. Water Resour Res 24:1877–1891

Phillips FM (1999) Chlorine-36. In: Cook PG, Herczeg AL (eds) Environmental tracers in subsurface hydrology. Kluwer Academic Publishers, Boston, pp 299–348

Piper AM (1944) A graphic procedure in the geochemical interpretation of water-analyses. Trans Am Geophys Union 25:914–923

Pitzer KS (1991) Ion interaction approach: theory and data correlation. In: Pitzer KS (ed) Activity coefficients in electrolyte solutions, chap 3, 2nd edn. CRC Press, Boca Raton, FL, pp 75–153

Pitzer KS (1994) Thermodynamics, 3rd edn. McGraw-Hill, New York, 626 pp

Plummer LN, Parkhurst DL, Thorstenson DC (1983) Development of reaction models for ground-water systems. Geochim Cosmochim Acta 47:665–686

Plummer LN (1985) Geochemical modeling: a comparison of forward and inverse methods. In: Hitchon B, Wallick EI (eds) Proceedings of First Canadian/American Conference on Hydrogeology, Banff, Alberta, June 1984. National Water Well Assoc Pub, pp 149–177

Plummer LN, Busby JF, Lee RW, Hanshaw BB (1990) Geochemical modeling of the Madison aquifer in parts of Montana, Wyoming, and South Dakota. Water Resour Res 26(9):1981–2014

Plummer LN Prestemon EC, Parkhurst DL (1991) An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH: US Geol Surv Water Resour Invest Rep 91-4078, 227 pp

Plummer LN (1992) Geochemical modeling—past, present, future. In: Kharaka Y, Maest AS (eds) Proceedings of 7th International Symposium on Water–Rock Interaction, Park City, UT, July 9–23, 1992, pp 23–33

Plummer LN, Busenberg E, Glynn PD, Blum AE (1992) Dissolution of aragonite-strontianite solid solutions in non-stoichiometric $Sr(HCO_3)_2$-$Ca(HCO_3)_2$-CO_2-H_2O solutions. Geochim Cosmochim Acta 56:3045–3072

Plummer LN, Michel RL, Thurman EM, Glynn PD (1993) Environmental tracers for age-dating young ground water. In: Alley WM (ed) Regional ground-water quality, Vol 11. Van Nostrand Reinhold, New York, pp 255–294

Plummer LN, Prestemon EC, Parkhurst DL (1994) An interactive code (NETPATH) for modeling NET geochemical reactions along a flow PATH—Version 2.0. US Geol Surv Water Resour Invest Rep 94-4169, 130 pp

Plummer LN, Busenberg E, Riggs AC (2000) In-situ growth of calcite at Devils Hole, Nevada: comparison of field and laboratory rates to a 500,000 year record of near-equilibrium calcite growth. Aquatic Geochem 6:257–274

Plummer LN, Busenberg E (2000) Chlorofluorocarbons. In: Cook P, Herczeg AL (eds) Environmental tracers in subsurface hydrology chap 15. Kluwer Academic Publishers, Boston, pp 441–478

Plummer LN, Busenberg E, Böhlke JK, Nelms DL, Michel RL, Schlosser P (2001) Ground-water residence times in Shenandoah National Park, Blue Ridge Mountains, Virginia, USA: a multi-tracer approach. Chem Geol 179:93–111

Plummer LN, Sprinkle CL (2001) Radiocarbon dating of dissolved inorganic carbon in groundwater from confined parts of the Upper Floridan aquifer, Florida, USA. Hydrogeol J 9:127–150

Plummer LN, Bexfield LM, Anderholm SK, Sanford WE, Busenberg E (2004a) Geochemical characterization of ground-water flow in the Santa Fe Group aquifer system, Middle Rio Grande Basin, New Mexico. US Geol Surv Water Resour Invest Rep 03-4131, 395 pp

Plummer LN, Bexfield LM, Anderholm SK, Sanford WE, Busenberg E (2004b) Hydrochemical tracers in the Middle Rio Grande Basin, USA: 1. Conceptualization of groundwater flow. Hydrogeol J 12(4):359–388

Plummer LN, Sanford WE, Bexfield LM, Anderholm SK, Busenberg E (2004c) Using geochemical data and aquifer simulation to characterize recharge and groundwater flow in the Middle Rio Grande Basin, USA. In: Hogan JF, Phillips FM, Scanlon BR (eds) Ground-water recharge in a desert environment: the southwestern United States. Am Geophys Union Monogr, Water Science and Application Series, Washington, DC, 9: 185–216

Plummer LN (2005) Dating of young groundwater. In: Proceedings of International Symposium on Isotope Hydrology Integrated Water Resources Management, May 19–23, 2003. International Atomic Energy Agency, Vienna, Austria (in press)

Poreda RJ, Cerling TE, Solomon DK (1988) Tritium and helium isotopes as hydrologic tracers in a shallow unconfined aquifer. J Hydrol 103:1–9

Pourbaix MJN (1949) Thermodynamics of dilute aqueous solutions. Edward Arnold and Co., London, 136 pp

Prasad A, Simmons CT (2003) Unstable density-driven flow in heterogeneous porous media: a stochastic study of the Elder (1967b) "short heater" problem. Water Resour Res 39(1), 21p(1007) doi:10.1029/2002WR001290

Prieto M, Fernandez-Gonzalez A, Becker U, Putnis A (2000) Computing Lippmann diagrams from direct calculation of mixing properties of solid-solutions: application to the barite–celestite system. Aquat Geochem 6:133–146

Pucci AA (1999) Sulfate transport in a coastal plain confining unit, New Jersey, USA. Hydrogeol J 7(2):251-263

Rademacher LK, Clark JF, Hudson GB, Erman DC, Erman NA (2001) Chemical evolution of shallow groundwater as recorded by springs, Sagehen basin; Nevada County, California. Chem Geol 179:37–51

Reardon EJ (1981) Kd's—can they be used to describe reversible ion sorption reaction in contaminant migration? Ground Water 19:279–286

Reilly TE, Plummer LN, Phillips PJ, Busenberg E (1994) Estimation and corroboration of shallow ground-water flow paths and travel times by environmental tracer and hydraulic analyses—A case study near Locust Grove, Maryland. Water Resour Res 30:421–433

Remenda V (2001) Theme issue on confining units. Hydrogeol J 9:123

Renick BC (1924) Base exchange in ground water by silicates as illustrated in Montana. US Geol Surv Water Supply Paper 520-D

Robertson JB, Schoen R, Barraclough JT (1974) The influence of liquid waste disposal on the geochemistry of water at the National Reactor Testing Station, Idaho: 1952–1970. US Geol Surv Open-File Rep IDO-22053, 231 pp

Ronen D, Magaritz M, Levy I (1987) An in situ multilevel sampler for preventive monitoring and study of hydrochemical profiles in aquifers. Ground Water Monit Rev 7:69–74

Rosenthal E, Jones BF, Weinberger G (1998) The chemical evolution of Kurnub Group paleowater in the Sinai-Negev province - a mass balance approach. Appl Geochem 13(5):553–569

Rozanski K, Gonfiantini R, Araguas-Araguas L (1991) Tritium in the global atmosphere: distribution patterns and recent trends. J Physics G, Nucl Particle Phys 17:S523–S536

Rozanski K, Araguás-Araguás L, Gonfiantini R (1993) Isotopic patterns in modern global precipitation. In: Swart PK, Lohmann KC, McKenzie J, Savin S (eds) Climate change in continental isotopic records. Am Geophys Union, Geophys Monogr 78: 1–36

Runnells DD, Lindberg RD (1990) Selenium in aqueous solutions: the impossibility of obtaining a meaningful Eh using a platinum electrode, with implications for modeling of natural waters. Geology 18:212–215

Sanford WE, Shropshire RG, Solomon DK (1996) Dissolved gas tracers in groundwater: simplified injection, sampling, and analysis. Water Resour Res 36(6):1635–1642

Sanford WE (1997) Correcting for diffusion in carbon-14 dating of groundwater. Ground Water 35:357–361

Sanford WE, Plummer LN, McAda DP, Bexfield LM, Anderholm SK (2004a) Use of environmental tracers to estimate parameters for a predevelopment-ground-water-flow model of the Middle Rio Grande Basin, New Mexico. US Geol Surv Water Resour Invest Rep 03-4286, 102 pp

Sanford WE, Plummer LN, McAda DP, Bexfield LM, Anderholm SK (2004b) Hydrochemical tracers in the Middle Rio Grande Basin, USA: 2. Calibration of a groundwater model. Hydrogeol J 12(4):389–407

Scanlon BR, Cook PG (2002) Theme issue on groundwater recharge. Hydrogeol J 10:237p

Scanlon BR, Healy RW, Cook PG (2002) Choosing appropriate techniques for quantifying groundwater recharge. Hydrogeol J 10:18–39

Schlosser P, Stute M, Dorr H, Sonntag C, Munnich KO (1988) Tritium/^{3}He dating of shallow groundwater. Earth Planet Sci Lett 89:353–362

Schlosser P, Stute M, Sonntag C, Munnich KO (1989) Tritiogenic ^{3}He in shallow groundwater. Earth Planet Sci Lett 94: 245–256

Schlosser P, Dunkle-Shapiro S, Stute M, Aeschbach-Hertig W, Plummer LN, Busenberg E (1998) Tritium/He dating of young groundwater: chronologies for environmental records. In: Isotope techniques in the study of environmental change. International Atomic Energy Agency, Vienna, pp 165–189

Schmidt TC, Zwank L, Elsner M, Berg M, Meckenstock RU, Haderlein SB (2004) Compound-specific stable isotope analysis of organic contaminants in natural environments: a critical review of the state of the art, prospects and future challenges. Anal Bioanal Chem 378:283–300

Shapiro AM (2002) Cautions and suggestions for geochemical sampling in fractured rock. Groundwater Monit Remed 22:151–164

Shapiro SD, Busenberg E, Focazio MJ, Plummer LN (2004) Historical trends in occurrence and atmospheric inputs of halogenated volatile organic compounds in untreated ground water used as a source of drinking water. Sci Total Environ 321:201–217

Sheets RA, Bair ES, Rowe GL (1998) Use of ^{3}H/^{3}He ages to evaluate and improve groundwater flow models in a complex buried-valley aquifer. Water Resour Res 34:1077–1089

Siegel DI (1991) Evidence for dilution of deep, confined ground water by vertical recharge of isotopically heavy Pleistocene water. Geology 19:433–436

Siegel MD, Anderholm S (1994) Geochemical evolution of groundwater in the Culebra Dolomite near the Waste Isolation Pilot Plant, southeastern New Mexico, USA. Geochim Cosmochim Acta 58:2299–2323

Sillén LG (1967) Master variables and activity scales. In: Gould RF (ed) Equilibrium concepts in natural water systems. Am Chem Soc Adv Chem Ser 67, Washington, DC, pp 45–56

Simmons CT, Fenstemaker TR, Sharp JM Jr (2001) Variable-density groundwater flow and solute transport in heterogeneous porous media: approaches, resolutions and future challenges. J Contam Hydrol 52:245–275

Smith RA, Schwarz GE, Alexander RB (1997) Regional interpretation of water-quality monitoring data. Water Resour Res 33:2781–2798

Solomon DK, Sudicky EA (1991) Tritium and helium 3 isotope ratios for direct estimation of spatial variations in groundwater recharge. Water Resour Res 27:2309–2319

Solomon DK, Schiff SL, Poreda RJ, Clark WB (1993) A validation of the ^{3}H/^{3}He method for determining groundwater recharge. Water Resour Res 29:2951–2962

Solomon DK, Hunt A, Poreda RJ (1996) Source of radiogenic helium 4 in shallow aquifers: implications for dating young groundwater. Water Resour Res 32:1805–1813

Solomon DK, Cook PG (1999) ^{3}H and ^{3}He. In: Cook P, Herczeg A (eds) Environmental tracers in subsurface hydrology. Kluwer Academic Press, Amsterdam, pp 397–424

Sprinkle CL (1989) Geochemistry of the Floridan aquifer system in Florida and in parts of Georgia, South Carolina, and Alabama. US Geol Surv Prof Pap 1403-I, 105 pp

Steefel CI, Van Capellen PV (1990) A new kinetic approach to modeling water–rock interaction: the role of nucleation, precursors, and Ostwald ripening. Geochim Cosmochim Acta 54:2657–2677

Stumm W, Morgan JJ (1996) Aquatic chemistry, 3rd edn. Wiley-Interscience, New York, 1024 pp

Sturchio NC et al (2004) One million year old groundwater in the Sahara revealed by krypton-81 and chlorine-36. Geophys Res Lett 31:L05503, doi:10.1029/2003GL019234

Stute M, Schlosser P (1993) Principles and applications of the noble gas paleothermometer. In: Swart PK, Lohmann KC, McKenzie J, Savin S (eds) Climate change in continental isotopic records. Am Geophys Union Monogr 78:89–100

Stute M, Schlosser P (1999) Atmospheric noble gases. In: Cook P, Herczeg A (eds) Environmental tracers in subsurface hydrology chap 11. Kluwer Academic Publishers, Boston, pp 349–377

Stute M, Sonntag C, Deak J, Schlosser P (1992a) Helium in deep circulating groundwater in the Great Hungarian Plain: flow dynamics and crustal and mantle helium fluxes. Geochim Cosmochim Acta 56:2051–2067

Stute M, Schlosser P, Clark JF, Broecker WS (1992b) Paleotemperatures in the southwestern United States derived from noble gases in ground water. Science 256:1000–1003

Stute M, Talma AS (1998) Glacial temperatures and moisture transport regimes reconstructed from noble gases and δ^{18}O, Stampriet aquifer, Namibia. In: Proceedings of Isotope Techniques in the Study of Environmental Change. International Atomic Energy Agency, Vienna, Austria, (1998) IAEA-SM-349/53, pp 307–318

Sudicky EA, Frind EO (1981) Carbon-14 dating of groundwater in confined aquifers: implications of aquitard diffusion. Water Resour Res 17:1060–1064

Szabo Z, Rice DE, Plummer LN, Busenberg E, Drenkard S, Schlosser P (1996) Age-dating of shallow groundwater with chlorofluorocarbons, tritium/helium 3, and flow path analysis, southern New Jersey coastal plain. Water Resour Res 32:1023–1038

Talma AS, Weaver JMC, Plummer LN, Busenberg E (2000) CFC tracing of groundwater in fractured rock aided with ^{14}C and ^{3}H to identify water mixing. In: Sililo O, Rotterdam O (eds) Groundwater: past achievements and future challenges, pp 635–640

Tamers MA (1967) Radiocarbon ages of groundwater in an arid zone unconfined aquifer. In: Stout GE (ed) Isotope techniques in the hydrologic cycle. Am Geophys Union Monogr 11:143–152

Tamers MA (1975) Validity of radiocarbon dates on groundwater. Geophys Surv 2:217–239

Thomas JM, Welch AH, Preissler AM (1989a) Geochemical evolution of ground water in Smith Creek Valley—a hydrologically closed basin in central Nevada, USA. Appl Geochem 4:493–510

Thomas JM, Carlton SM, Hines LB (1989b) Ground-water hydrology and simulated effects of development in Smith Creek Valley, a hydrologically closed basin in Lander County, Nevada. US Geol Surv Prof Pap 1409-E, 57 pp

Thomas JM, Morse BS, Burr GS, Reines DL (2001) Age dating groundwater using dissolved organic carbon - an example from southern Nevada, USA. In: Cidu R (ed) Proceedings of Tenth International Water–Rock Interactions Symposium, Villasimius, Italy, 10–15 June 2001. Balkema Press, pp 1581–1584

Thorstenson DC, Plummer LN (1977) Equilibrium criteria for two-component solids reacting with fixed composition in an aqueous phase- example: the magnesian calcites. Am J Sci 277:1203–1223

Thorstenson DC, Fisher DW, Croft MG (1979) The geochemistry of the Fox Hills-Basal Hell Creek aquifer in southwestern North Dakota and northwestern South Dakota. Water Resour Res 15:1479–1498

Thorstenson DC (1984) The concept of electron activity and its relation to redox potentials in aqueous geochemical systems. US Geol Surv Open File Rep 84-072

Thorstenson DC, Weeks EP, Haas H, Woodward JC, Peters CA (1998) The chemistry of unsaturated zone gases sampled in open boreholes at the crest of Yucca Mountain, Nevada-Data and basic concepts of chemical and physical processes in the mountain. Water Resour Res 34:1507–1529

Thorstenson DC, Parkhurst DL (2002) Calculation of individual isotope equilibrium constants for implementation in geochemical models. US Geol Surv Water Resour Invest Rep 02-4172, 129 pp

Thorstenson DC, Parkhurst DL (2004) Calculation of individual isotope equilibrium constants for geochemical reactions. Geochim Cosmochim Acta 68(11):2449–2465

Torgersen T (1980) Controls on pore-fluid concentration of ^{4}He and ^{222}Rn and the calculation of ^{4}He/Rn ages. J Geochem Explor 13:57–75

Torgersen T, Clarke WB (1985) Helium accumulation in groundwater, I: An evaluation of sources and the continental flux of crustal ^{4}He in the Great Artesian Basin, Australia. Geochim Cosmochim Acta 49:1211–1218

Torgersen T, Ivey GN (1985) Helium accumulation in groundwater, 2: A model for the accumulation of the crustal ^{4}He degassing flux. Geochim Cosmochim Acta 49:2445–2452

Torgersen T, Habermehl MA, Philips FM, Elmore D, Kubik P, Jones BG, Hemmick T, Gove HE (1991) Chlorine-36 dating of very old groundwater: III. Further studies in the Great Artesian Basin, Australia. Water Resour Res 27:3201–3214

Torgersen T (1992) Helium-4 model ages for pore fluids from fractured lithologies: discussion and application. In: Isotopes of noble gases as tracers in environmental studies, Vienna, Proceedings of a Consultants Meeting, May 29–June 2 (1989). International Atomic Energy Agency, Vienna, pp 179–201

Torgersen T, Philips FM (1993) Reply to comment on "Chlorine-36 dating of very old groundwater: III. Further studies in the Great Artesian Basin, Australia" by Andrews JN and Fontes JCh. Water Resour Res 29:1875–1877

Truesdell AH, Jones BF (1974) WATEQ: a computer program for calculating chemical equilibria of natural waters. US Geol Surv J Res 2:233–248

Varni M, Carrera J (1998) Simulation of groundwater age distributions. Water Resour Res 34(12):3271–3281

Vitvar T, Balderer W (1997) Estimation of mean water residence time and runoff generation by ^{18}O measurements in a Pre-Alpine catchment (Rietholzbach, Eastern Switzerland). Appl Geochem 12:787–796

Vogel JC (1967) Investigation of groundwater flow with radiocarbon. In: Isotopes in hydrology, Proceedings of Symposium on Isotopes in Hydrology, 14–18 November 1966. International Atomic Energy Agency, Vienna, pp 355–369

Vogel JC, Van Urk H (1975) Isotopic composition of groundwater in semi-arid regions of southern Africa. J Hydrol 25:23–36

Wallin B, Peterman Z (1999) Calcite fracture fillings as indicators of paleohydrology at Laxemar at the Äspö Hard Rock Laboratory, southern Sweden. Appl Geochem 14:953–962

Walton AG (1967) Formation and properties of precipitates. Wiley, New York, 232 pp

Wassenaar LI, Aravena R, Hendry MJ, Fritz P (1991) Controls on the transport and carbon isotopic composition of dissolved organic carbon in a shallow groundwater system, central Ontario. Water Resour Res 27:1975–1986

Weissmann GS, Zhang Y, LaBolle EM, Fogg GE (2002) Dispersion of groundwater age in an alluvial aquifer system. Water Resour Res 38(10):1198, doi:10.1029/2001WR000907

White AF, Peterson ML (1990) Role of reactive-surface-area characterization in geochemical kinetic models. In: Melchior DC, Bassett RL (eds) Chemical modeling of aqueous systems II. Am Chem Soc Symp Ser 416:461–475

White AF, Brantley SL (1995) Chemical weathering rates of silicate minerals. In: White AF, Brantley SL (eds) Mineral Soc Am Rev Mineral 31:583

White AF, Bullen TD, Schulz MS, Blum AE, Huntington TG, Peters NE (2001) Differential rates of feldspar weathering in granitic regoliths. Geochim Cosmochim Acta 65:847–869

White DE, Hem JD, Waring GA (1963) Chemical composition of subsurface waters. In: Data of geochemistry, 6th edn. US Geol Surv Prof Pap 440-F: F1–F67

Wigley TML, Plummer LN, Pearson FJ Jr (1978) Mass transfer and carbon isotope evolution in natural water systems. Geochim Cosmochim Acta 42:1117–1139

Winograd IJ, Thordarson W (1976) Hydrogeologic and hydrochemical framework, southcentral Great Basin, Nevada-California, with special reference to the Nevada Test Site. US Geol Surv Prof Paper 712-C, 126 pp

Winograd IJ, Pearson FJ Jr (1976) Major carbon-14 anomaly in a region carbonate aquifer: Possible evidence for mega scale channeling, south-central Great Basin. Water Resour Res 12:1125–1143

Winograd IJ, Coplen TB, Landwehr JM, Riggs AC, Ludwig KR, Szabo BJ, Kolesar PT, Revesz KM (1992) Continuous 500,000-year climate record from vein calcite in Devils Hole, Nevada. Science 258:255–260

Winograd IJ, Landwehr JM, Ludwig KR, Coplen TB, Riggs AC (1997) Duration and structure of the last four interglaciations. Quat Res 48(2):141–154

Winograd IJ (2001) Interbasin groundwater flow in South Central Nevada: A further comment on the discussion between Davisson et al. (1999a, 1999b) and Thomas (1999). Water Resour Res 37(2):431–433

Wolery TJ (1979) Calculation of chemical equilibrium between aqueous solution and minerals: The EQ3/6 software package. Lawrence Livermore National Laboratory, Livermore, CA. Rep UCRL-52658

Wolery TJ, Jackson KJ, Bourcier WL, Bruton CJ, Viani BE, Knauss KG, Delany JM (1990) Current status of the EQ3/6 software package for geochemical modeling. In: Melchior DC, Bassett RK (eds) Chemical modeling of aqueous systems II. Am Chem Soc Symp Ser 416:104–116

Yurtsever Y (1983) Models for tracer data analysis. In: Guidebook on nuclear techniques in hydrology, 1983 edn. International Atomic Energy Agency, Vienna. Tech Rep Ser 91, pp 381–402

Zoellmann K, Kinzelbach W, Fulda C (2001a) Environmental tracer transport (^{3}H and SF_6) in the saturated and unsaturated zones and its use in nitrate pollution management. J Hydrol 240:187–205

Zoellmann K, Kinzelbach W, Aeschbach-Hertig W (2001b) BOXmodel: evaluating environmental tracer data by the box-model approach, accessible at: http://www.baum.ethz.ch/ihw/boxmodel_en.html

Zuber A (1986) Mathematical models for the interpretation of environmental radioisotopes in groundwater systems. In: Fritz P, Fontes JCh (eds) Handbook of environmental isotope geochemistry, Vol 2: the terrestrial environment, B. Elsevier, New York, NY, pp 1–59

Zuber A (1994) On calibration and validation of mathematical models for the interpretation of environmental tracer data in aquifers. In: Mathematical models and their applications to isotope studies in groundwater hydrology. International Atomic Energy Agency, Vienna. IAEA-TECDOC-777, pp 11–41