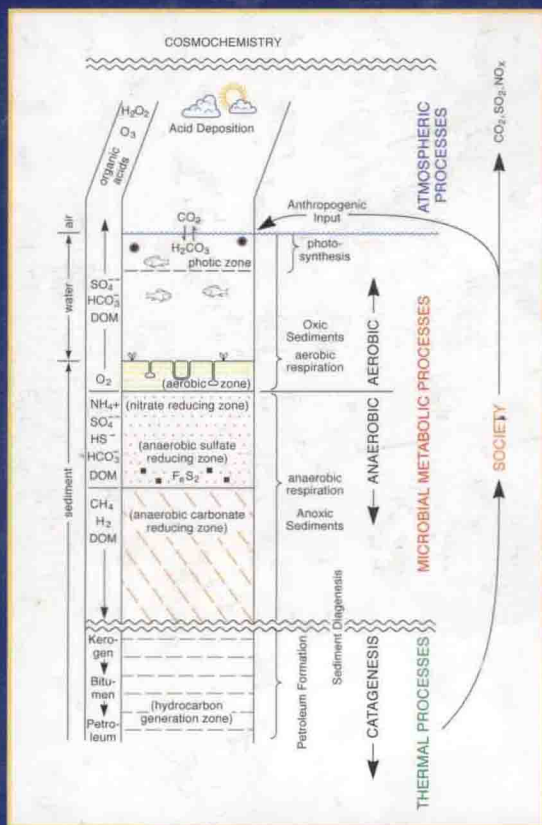


GEOCHEMICAL INVESTIGATIONS IN EARTH AND SPACE SCIENCE: A TRIBUTE TO ISAAC R. KAPLAN

EDITED BY

R.J. HILL, J. LEVENTHAL, Z. AIZENSHTAT, M.J. BAEDCKER,
G. CLAYPOOL, R. EGANHOUSE, M. GOLDHABER AND K. PETERS



Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan

Edited by:

Ronald J. Hill

U.S. Geological Survey, Denver, Colorado, USA

Joel Leventhal

U.S. Geological Survey, Denver, Colorado, USA

Zeev Aizenshtat

Department of Organic Chemistry and Casali Institute

The Hebrew University, Jerusalem, Israel

Mary Jo Baedeker

U.S. Geological Survey, Reston, Virginia, USA

George Claypool

Consultant, Lakewood, Colorado, USA

Robert Eganhouse

U.S. Geological Survey, Reston, Virginia, USA

Martin Goldhaber

U.S. Geological Survey, Denver, Colorado, USA

Kenneth Peters

U.S. Geological Survey, Menlo Park, California, USA

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USA

ELSEVIER Ltd
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Kidlington, Oxford OX5 1GB
UK

ELSEVIER Ltd
84 Theobalds Road
London WC1X 8RR
UK

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PREFACE

Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan is the written product of a technical session organized for the 2002 Geological Society of America in recognition of Isaac (Ian) Kaplan's many contributions to various fields of geochemistry. This volume is a collection of 29 papers written by former students, post-doctoral researchers, friends and colleagues from countries all over the world (including Sweden, Japan, Taiwan, New Zealand, Australia, Israel and the United States).

To say that Ian's career is defined by diverse, multidisciplinary, integrated studies is an understatement. Since 1953, Ian's scientific curiosity has led him to investigate the stable isotope geochemistry and biogeochemistry of carbon, nitrogen, sulfur, oxygen and hydrogen. Ian and his students, post-docs and colleagues have applied isotope geochemistry to a wide variety of problems including: 1) the isotopic and carbon chemistry of extraterrestrial materials, 2) the inorganic and organic geochemistry of interstitial water and the microbiology marine sediments, 3) the biogeochemistry of sapropels, humic materials, kerogens and petroleum, 4) paleo-dietary reconstruction of humans and other mammals, and 5) environmental and atmospheric chemistry. Ground-breaking research conducted in Ian's laboratory resulted in the widespread use of stable isotopes to investigate the biology of iron and sulfate-reducing bacteria, methanogenic archaeobacteria, cyanobacteria, fungi and marsupials. In addition, a series of experiments into the natural and laboratory simulated diagenesis and thermal alteration of organic matter led to advances in our understanding of the formation of petroleum and natural gas. An abiding interest in the application of organic geochemistry to environmental problems culminated in a variety of studies on the origin and fate of anthropogenic pollutants in natural environments. Thus, long before the term 'forensic geochemistry' was coined, Ian was developing and applying the principles that define the science today. As Ian enters his sixth decade of scientific investigation, it is fair to say that his work has touched or influenced innumerable scientists either directly or indirectly. It is certainly the case for the editors of this volume.

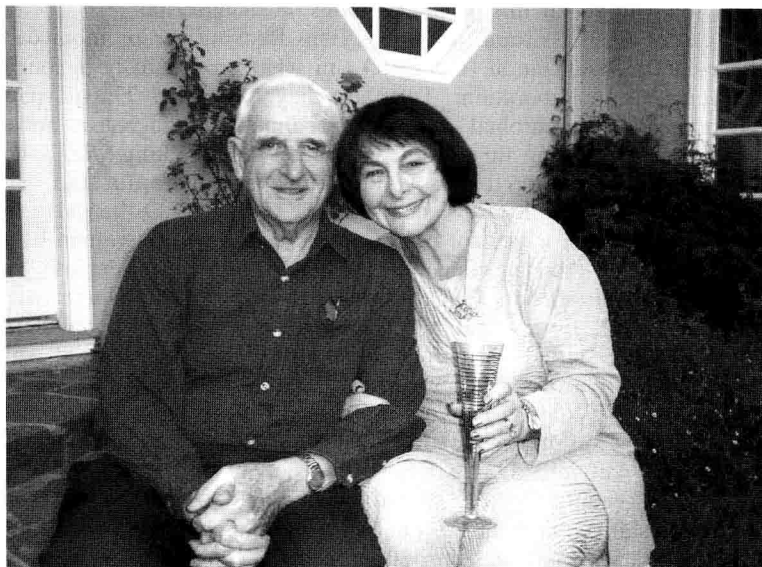
The first section of the volume is dedicated to stable isotopic studies of all kinds. Included in this section are investigations of carbon, sulfur, oxygen and boron from terrestrial and extraterrestrial systems. The second section of the volume focuses on geochemical investigations of environmental and atmospheric chemistry problems. The third section of the volume is concerned with various aspects of petroleum geochemistry, and the final section includes investigations of recent and ancient sediments.

We thank the Geochemical Society for providing the publication series necessary to make this volume possible. The Department of Earth and Space Sciences and the Institute of Geophysics and Planetary Physics at the University of California, Los Angeles and Shell International gave valuable financial support. The editors thank all of the referees who carried out reviews of the individual chapters in this volume. Finally, we wish to thank Lynne Newton for the tireless effort she put forth in compiling the history of the Kaplan group, Rosario De Leon for all of her help in compiling the list of invitees for the symposium and celebration and to symposium participant themselves, who traveled from Canada, Sweden, Japan, Taiwan, New Zealand, Australia, Israel and the United States to make the celebration a success.

RONALD HILL
JOEL LEVENTHAL
ZEEV AIZENSHTAT
MARY JO BAEDECKER
GEORGE CLAYPOOL
ROBERT EGANHOUSE
MARTIN GOLDHABER
KENNETH PETERS
October, 2003

A Tribute to ISAAC R. KAPLAN:

Scientist, Mentor and Friend



Ian and Helen Kaplan, 2003.

Isaac R. (Ian) Kaplan was born July 10, 1929, in Baranowicze, Poland, now a part of Belarus. He and his family moved to Christchurch, New Zealand in 1937. Ian attended Canterbury University in New Zealand where he earned a Bachelor's degree in Chemistry in 1952 and a Master's degree in Chemistry in 1953. He subsequently served as research officer in the Commonwealth Scientific and Industrial Research Organization (CSIRO), Division of Fisheries and Oceanography, Cronulla, N.S.W., Australia, from 1953–1957 before attending the University of Southern California (USC) to pursue a Ph.D., which he received in Biogeochemistry in 1961. While a graduate student at USC, Ian was a lecturer in geochemistry at the Geology Department (1959–1961). Following graduation, Ian completed a Postdoctoral Research Fellowship in Geochemistry with Sam Epstein at the California Institute of Technology (1961–1962). In October 1962, he accepted a position as Jacob Ziskind Visiting Scholar and Guest Lecturer, Department of Microbiological Chemistry, Hebrew University, Jerusalem, Israel, where he remained until 1965. Ian then returned to the United States where he took a position as Associate Professor of Geology and Geochemistry at UCLA, retiring in 1993 as Emeritus Professor.

During his career Ian and his colleagues published over 300 papers on environmental, sedimentary and petroleum geochemistry. He has served as associate editor and editor for several professional journals and is a Fellow of several professional societies including the American Association of Petroleum Geologists, American Chemical Society, American Institute of Chemists, American Association for the Advancement of Science, Geological Society of America, Geochemical Society and the European Association for Geochemistry, the Russian Academy of Natural Science. He has served on numerous advisory committees for the State of California and Federal agencies and has received numerous awards, including the 1993 Treibs Medal bestowed by the Geochemical Society for pioneering research in Organic Geochemistry. In 1998, he was elected a Foreign Member of the Russian Academy of Natural Science, and in 2002 he received the American Association of Petroleum

Geologists Division of Environmental Geology President's Award for career achievement in the field of environmental geology. In 1975 Ian founded Global Geochemistry Corporation (GGC), serving as its president until 1999 when GGC was acquired by ZymaX Envirotechnology, Inc., and emerged as ZymaX Forensics, Inc./Global Geochemistry Corporation, San Luis Obispo, California. Since then he has been consulting in the field of environmental forensic geochemistry and working on manuscripts.

Ian started his career as an assistant to Laurens Baas Becking at Commonwealth Scientific and Industrial Research Organization (C.S.I.R.O.) in what proved to be a long and fruitful friendship and scientific collaboration. Together they published classic papers on the sulfuretum, the influence of microbial process in sedimentary diagenesis and Eh and pH relationships in sediments. During this period Ian began collaborating with John Hulston, a high school friend and contributor to this volume, investigating sulfur and carbon isotope systematics in geothermal and volcanic systems. While at C.S.I.R.O., Ian also met someone who turned out to be the most important person in his life, a young woman by the name of Helen Fagot. A year after their marriage in 1957, Ian and Helen departed for southern California, so that Ian could pursue a Ph.D. in biogeochemistry at the University of Southern California with Drs. K. O. Emery and S. C. Rittenberg, pioneers in the field of marine diagenesis. At USC Ian started his groundbreaking work on bacterial sulfur isotope fractionation and the distribution of sulfur phases in recent sediments. This work prompted research into the sulfur cycle by groups around the world and laid the foundation for our understanding of bacterial sulfur isotope fractionation and the contemporary distribution of sulfur phases. In 1961, Ian joined Sam Epstein's group as a post doctoral fellow at the California Institute of Technology and started what would become a life long scientific relationship and friendship with Sam. At CalTech, Ian studied the fractionation of carbon isotopes during photosynthesis and was introduced to the geochemistry of meteorites. He also collaborated with William Holser (then at Chevron Oil Co.) on the measurement of large numbers of globally distributed anhydrites, whose depositional ages ranged from pre-Cambrian to Holocene. This resulted in the early publication (1966) of data providing evidence for changes in the chemical composition of the ocean over time, with implications for concomitant changes in the atmospheric oxygen content during the Phanerozoic epochs. Upon completion of his post doctoral fellowship with Sam Epstein, Ian was offered the Jacob Ziskind Visiting Scholar and Guest Lecturership in the Department of Microbiological Chemistry at Hebrew University in Jerusalem, Israel, where he conducted research on microbial processes in the supersaline Dead Sea. During this period, Ian came in contact with an outstanding group of students and asked many of them to join him when he accepted a faculty position at UCLA. Thus, Ian's first students included Yeshe Kolodny, Arie Nissenbaum, Sam Ben-Yaakov and Bobby Joe Presley. They were joined by visiting scholars, Robert Brooks, on sabbatical leave from Massey University, New Zealand and Ted Belsky, a Postdoctoral Fellow from University of California, Berkeley. Together, the first incarnation of the 'Kaplan group' vigorously addressed processes that influence the composition of interstitial waters in recent marine sediments. They studied bacterial processes and their effects on isotope fractionation and developed analytical methods for trace element distribution in interstitial waters. Sam Ben-Yaakov, an electronic engineer, developed the first instruments for in situ measurement of Eh, pH and carbonate saturation in the deep ocean. Yeshe Kolodny conducted research on the geochemistry of phosphorite nodules and developed a method for age dating their formation based on uranium disequilibrium. Ted Belsky measured the distribution and concentration of organic gases in meteorites.

By 1968, the research group began to expand. The second wave of students, lab technicians and visiting scholars arrived between 1967 and 1969. This group included Mary Jo Baedecker, George Claypool, Joel Cline, Martin Goldhaber, Emil Kalil, Ronald McCready, Robert Sweeney and Chari Petrowski. Joel Leventhal worked as a research assistant for one summer, designing a system to collect and quantify shipboard measurements of organic gases from Deep Sea Drilling Program. Paul Doose made his first appearance in the lab as an undergraduate lab technician. 1967 also saw the arrival of Lynne Newton as administrative

assistant and Ed Ruth as staff research associate and eventual lab manager. The investigation of processes occurring in recent sediments continued. Mary Jo Baedecker was involved in the characterization of organic matter in sediments of Saanich Inlet; her research also provided the earliest evidence of archaeobacterial products in Dead Sea sediments. Marty Goldhaber continued Ian's early work on microbial controls on sulfur geochemistry. Joel Cline investigated the microbial processes controlling the distribution of nitrogen compounds in seawater and recent sediments, while George Claypool was exploring methanogenesis in recent sediments and the formation of clathrates (gas hydrates). George and Ian were among the first to study naturally occurring gas hydrates, an area of significant research today. Emil Kalil addressed uranium distribution in recent sediments, following the work of Bobby Joe Presley and Yeshe Kolodny. Chari Petrowski examined the light element geochemistry of meteorites and lunar samples.

The decade of the 1970's was an extremely productive time in the Kaplan lab. The group continued to investigate microbial processes in recent sediments and became more involved in the transformations of organic matter. The investigation of lunar samples and meteorites reached its apex at this time, and the group began to investigate anthropogenic contaminants in recent sediments and the processes controlling petroleum generation. Some of the first laboratory simulations of hydrocarbon generation were performed during this time. Ian also co-founded Global Geochemistry Corporation (GGC) in 1975 and served as president of the company from 1977 through 1999. Ian credits much of what he learned regarding petroleum geochemistry and particularly environmental geochemistry to his investigation of many hundreds of case studies at GGC on the geochemistry of petroleum and its refined products. The application of geochemical principles to molecular characterization, age dating, and kinetics of diagenetic transformations, gelled into the field of study he refers to as "forensic environmental geochemistry."

Graduate students who joined the group in the 1970's include Paul Doose, Brian Rohrback, Mark Sandstrom, Kon-Kee Liu, Ken Peters, Bob Eganhouse, Shan-tan Lu, Henry Halpern, Peter Jenden and Erdem Idiz. Dave Winter worked in the lab for the first time in 1970 as an undergraduate lab assistant and became an integral part of the group upon graduation in 1973. He assumed responsibility for running the stable isotope ratio mass spectrometers and providing laboratory technique and methods expertise for students and faculty. Paul Doose made his second appearance in the lab, working on methanogenesis in recent sediments. Brian Rohrback, Mark Sandstrom and Kon-Kee Liu arrived in 1974 and were followed closely by Ken Peters in 1975. Brian and Ken conducted some of the first pyrolysis experiments simulating hydrocarbon generation. The Kaplan group was among the first to recognize bitumen as an intermediate product in petroleum generation. K.K. Liu continued work on the oceanic nitrogen cycle, measuring concentrations and $^{15}\text{N}/^{14}\text{N}$ changes in inorganic nitrogen compounds in the Santa Barbara Basin and off the coast of Peru. In 1976, Mark Sandstrom and Indira Venkatesen performed some of the first environmental organic geochemistry studies on eastern Bering Sea and Gulf of Alaska sediments. Bob Eganhouse joined the group 1976. As a doctoral student and post-doctoral research associate he carried out studies of the organic matter in urban runoff and municipal wastes and their impact on the coastal ecosystem off southern California. Shan-tan Lu, Henry Halpern, Peter Jenden and Erdem Idiz entered in 1978 and 1979 and brought the investigation of petroleum geochemistry and petroleum generation processes to the forefront of lab activities as the 1980's approached. Shan-tan explored the generation of petroleum from coals using pyrolysis techniques and quantitatively described the hydrocarbons generated by heating coal. Henry Halpern evaluated the role of minerals in hydrocarbon generation, initiating what would become a significant research effort in the lab during the 1980's. Peter Jenden documented changes in shale diagenesis and sandstone cementation and later, as an employee at GGC and Chevron, carried out studies on the origin of natural gas. Erdem examined interactions between organic matter, trace metals and sulfur in recent and ancient sediments, documenting the importance of sulfur in petroleum generation. Robert Haddad, who went on to earn a Ph.D. with Chris Martens at University of North Carolina, was an undergraduate researcher in

the lab in 1978 and 1979, and later became an employee at GGC where he worked on the Colorado uranium deposits.

The Kaplan lab also hosted numerous visiting scientists and postdoctoral researchers in the late 1960's and 1970's. It was at this time that Ian began collaborating with five other scientists who would become life-long friends, John Smith, Bill Schopf, Zeev Aizenshtat, Raphael Ikan and Keith Kvenvolden. John Smith joined the group as a visiting scholar in 1968 from C.S.I.R.O. in Australia and worked for two years on the geochemistry of meteorites and lunar samples. Raphael (Rafi) Ikan, who entered the scene in 1972 as a visiting professor from The Hebrew University, worked on humic acids in sediments, analyzed the lipid fraction of Dead Sea sediments and described the diagenetic pathway leading to pristane and phytane. Zeev Aizenshtat made his first journey to UCLA in 1970 as a postdoctoral researcher and for two years worked on naturally occurring lipids and perylene in marine sediments. Zeev and Rafi would make many other visits to the lab over the years. Ian and Bill collaborated on the organic geochemistry of Precambrian sediments and Ian also was part of Bill's Precambrian Paleobiology Research Group (PPRG) that examined the origin and evolution of life on earth. Ian and Keith shared an interest in the geochemistry of petroleum seeps, lunar samples and environmental geochemistry that resulted in many collaborative projects over the years.

Other visiting scholars in the 1970's included Hitoshi Sakai who traveled to UCLA in 1971 as a visiting professor from Okayama University in Japan. Hitoshi analyzed lunar samples and investigated anhydrite sulfur and oxygen isotope fractionation with Israel Zak, who arrived at about the same time as a visiting professor from the Hebrew University. Charles Curtis, from Sheffield, U.K., was a visiting lecturer in the Earth and Space Sciences department in 1970–1971 who studied trace metals in sedimentary rocks. Bob Sweeney, whose work on pyrite formation and habit had a major impact in this field and is one of the most highly cited of all of Kaplan's papers, graduated in 1972 and continued work on carbon and sulfur in recent sediments as a post doctoral fellow until 1975 when he joined GGC. Bohdan Bubela was a visiting scientist from the Baas-Becking Geobiology Institute in Canberra, Australia in 1974 and explored the use of chemostats for growing anaerobic bacteria. Ryoshi Ishiwatari was a visiting professor from Tokyo Metropolitan University, Japan from 1974–1975 and studied humic substances in recent marine sediments. Ryoshi also was involved in some of the first artificial maturation experiments with Brian Rohrbach and Mariko Ishiwatari (Ryoshi's wife) designed to simulate hydrocarbon generation. Dan Stuermer joined as a postdoctoral researcher in 1975 and began exploring the diagenesis of organic matter, particularly the conversion of humic acids to kerogen as a intermediate step in the formation of petroleum. John Kerridge started at UCLA in 1973 and remained part of Ian's lab until 1994. John became the primary cosmochemistry researcher in the lab and continued work on organic matter in meteorites and temporal solar compositional changes. David Ward (1975–1977) and Steve Zinder (1977–1979), postdoctoral fellows in microbiology, performed studies on the symbiotic relationships involved in methanogenesis during acetate fermentation in collaboration with Bob Mah of the Public Health School. Berndt Simoneit considered the diagenesis and transformation of organic matter in recent sediments and also characterized organic matter in natural petroleum seeps as a research associate between 1976 and 1979. Jaime Bonilla-Ruiz visited from Venezuela from 1976–1978 and worked on oceanographic studies of organic-rich sediments. Shmuel Brenner came from Hebrew University at the same time and studied the organic geochemistry of recent sediments in Alaska, the Guaymas Basin and the Atlantic. David Toth was also a postdoctoral researcher at this time working on kinetics of organic diagenesis. Indira Venkatesan, a member of the group since 1976, remains a fixture in the Kaplan lab today, studying the flux of carbon compounds in recent marine sediments. Phillip Crisp was a visiting scientist from Australia from 1977–1978 and performed some of the initial work on the analysis of petroleum hydrocarbons in marine sediments. Amati Katz landed in 1979 from Hebrew University as a visiting professor and studied the distribution of heavy metals in marine sediments along the California coast. Min-Sung Lee, a professor of Economic Geology, visited Ian's lab from Korea in 1979–1980 and worked on meteorite mineral geochemistry. Greg Rau, a postdoctoral fellow from 1979–1981,

worked on biogeochemistry and the ecology of coastal, pelagic and hydrothermal vent communities. He also was involved in marine pollution studies and measurements of stable isotope composition of human bones. The studies performed in the lab in the decade of the 1970's, spawned the field of Forensic Environmental Geochemistry.

The 1980's in the Kaplan lab were equally productive. Research centered on petroleum genesis and environmental topics with a new emphasis on atmospheric chemistry. Petroleum geochemistry research was focused on factors affecting petroleum generation and oil composition including the influence of minerals, brines, nuclear radiation and pressure. Environmental geochemistry studies into atmospheric chemistry and specifically the study of organic acid deposition were initiated. Bruce Barraclough, Jose Sarto, Jeremy Dahl, Brad Huizinga, Thomas Dorsey, Henry Ajie, Julie Bartley and Ronald Hill were graduate students in Ian's lab in the 1980's. Jose Sarto continued researching the factors affecting petroleum generation by performing some of the first experiments designed to address the role of brines in hydrocarbon generation. In collaboration with Eli Tannenbaum, Brad Huizinga further explored the role of minerals in hydrocarbon generation. Jeremy Dahl addressed the effect of nuclear radiation from uranium-enriched shale on petroleum composition in his study of the Alum Shale, Sweden. Thomas Dorsey studied controls on atmospheric carbon dioxide and factors influencing carbon transport to the deep sea. Henry Ajie compared carbon and nitrogen isotopes of bone collagen and osteocalcin protein for reconstruction of mammalian paleodiets and for assessing the reliability of ^{14}C age measurements. Julie Bartley worked with Ian and Bill Schopf on variations in the carbon isotopes of Precambrian environments. Ron Hill was the last graduate student to pass through Ian's lab. He evaluated the role of pressure in hydrocarbon generation and oil cracking and performed some of the early experiments in this area, quantifying chemical changes resulting from elevated pressures, emulating maturation resulting from burial.

In the 1980's, the Kaplan lab had many postdoctoral fellows conducting research on various topics. Kimitaka Kawamura was in the lab from 1981–1984 and worked on methods for the analysis of polar organic substances in acid rain. He showed that a significant amount of the acidity in Los Angeles originated from organic acids either directly released from automobile exhaust or from atmospheric oxidation processes. During this same time period, Masao Minagawa, a postdoctoral fellow from Japan, examined the behavior of carbon, hydrogen and nitrogen in biochemical systems and nitrogen isotopes in sedimentary organic matter. Likewise, Spencer Steinberg was in the lab at this time working on high performance liquid chromatography applications in atmospheric chemistry and lignin geochemistry. Eli Tannenbaum researched the role of minerals in petroleum formation; this resulted in a series of classic papers on the subject. In the mid to late 1980's, Hiroshi Sakugawa continued research on atmospheric oxidation processes resulting in organic and inorganic acid deposition in Los Angeles. Hiroshi also used radioactive and stable carbon isotope measurements of atmospheric carbon monoxide to determine its mode of formation. Paul Mankiewicz worked at GGC after receiving a Ph.D. in Civil Engineering from UCLA and later joined Exxon Production Research as a petroleum geochemist. In 1984, Rosario De Leon, an undergraduate student, joined the group as secretary and administrative assistant. She continued to work at UCLA until she graduated with a Master's degree in Public Health (1994) at which time she then joined GGC as a lab technician and later as office manager at ZymaX Forensics. In 2002 she accepted a job in the Contract Audit office at UCLA.

By 1994, Ian had retired to emeritus status at UCLA, Ian's last student had completed his degree, John Kerridge had moved to the University of California, San Diego, Ed Ruth had moved to Civil and Environmental Engineering Department at UCLA and Dave Winter was soon headed to the Department of Geology at the University of California, Davis. In all, 22 Ph.D. students and four Master's student completed degrees under Ian's tutelage. Indira Venkatesan remains at UCLA as the last group member and now has the pleasure of interacting with Ian in his emeritus role. In 1999, Global Geochemistry Corporation merged with ZymaX Envirotechnology to become ZymaX Forensics Inc./Global Geochemistry Corporation. Ian completed a three-year commitment to the new company in 2002 and transitioned to

semi-retirement. We organized the symposium held at the *Geologic Society of America* meeting in 2002 to commemorate Ian's move to the next stage of his career – grandfather, scientist, mentor and friend. Some things never change. Ian remains active at UCLA, still works on projects for ZymaX, and continues to publish results of his work. Friends, colleagues, former students and postdoctoral fellows have carried on the Kaplan legacy in the greater scientific community. We dedicate this volume to you, Ian, with utmost sincerity and love. You are a great scientist, mentor and most of all a great friend.

RONALD HILL
JOEL LEVENTHAL
ZEEV AIZENSHTAT
MARY JO BAEDECKER
GEORGE CLAYPOOL
ROBERT EGANHOUSE
MARTIN GOLDBABER
KENNETH PETERS
October, 2003

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Boron isotopes in DSDP cherts: fractionation and diagenesis

YEHOSHUA KOLODNY¹ and MARC CHAUSSIDON²

¹Institute of Earth Sciences, Edmond Safra Campus, Givat Ram, The Hebrew University,
Jerusalem 91904, Israel

²CRPG-CNRS, Vandoeuvre-les-Nancy, France

Abstract—Twenty samples of cherts from the Central Pacific (18 of them from DSDP, Leg 17, Hole 167) were analyzed for B content and $\delta^{11}\text{B}$ by ion-probe. In all samples $\delta^{18}\text{O}$, $^{87}\text{Sr}/^{86}\text{Sr}$ and Ge have been previously measured. $\delta^{11}\text{B}$ of DSDP cherts varies between -9.3 and $+8\text{‰}$, indicating a “bulk” fractionation of $32\text{--}45\text{‰}$ with respect to present day seawater B (39.5‰), the highest fractionation of any marine phase. This fractionation is similar to the previously observed values in opal-A radiolarians (having $\delta^{11}\text{B}$ of $+2$ to $+4.5\text{‰}$, *Earth Planet. Sci. Lett.* **117**, 1993, 567–580). Siliceous sediments are a significant sink of boron in the ocean, an even more significant sink of ^{10}B . Assuming no secular variation in $\delta^{11}\text{B}_{\text{sw}}$ our results can be the reflection of a three-stage precipitation–dissolution process of DSDP cherts: the first leading to opal-A and involving a large fractionation of B isotopes between tetrahedral boron in solution and opal-A, the second and third resulting in quartz via opal-CT. The dissolution–reprecipitation occurred at variable temperatures and water/rock ratios. The deepest cherts underwent diagenesis at higher temperature (low $\delta^{18}\text{O}$ values) and in closed system (low $\delta^{11}\text{B}$ values). Boron isotopic composition of marine cherts cannot be a clue to the paleochemistry (specifically paleo-pH) of seawater but indicates that some mineral phases might fractionate B isotopes differently than carbonates and thus be used in conjunction with carbonates to reconstruct paleo-pH and $\delta^{11}\text{B}$ values of seawater.

INTRODUCTION

THE FIRST MEASUREMENT of boron in siliceous sediments can be traced back to the founding fathers of geochemistry (GOLDSCHMIDT and PETERS, 1932). RANKAMA and SAHAMA (1950) in their classic text noted that (p. 488) in some structures $[\text{BO}_4]$ tetrahedra replace silica tetrahedra. “Accordingly, boron replaces silicon in oxygen tetrahedra”. Most of the research on the geochemistry of boron in the past 70 years focused on investigating one aspect of the tetrahedral substitution of boron for silicon—in clays. The basic assumption here was that since clayey sediments are strongly enriched in B, they are also the best monitors of changes both in the concentration and in the isotopic composition of boron in the hydrosphere.

GOLDSCHMIDT and PETERS (1932) were also the first to note the high concentration of boron in seawater (4.5 ppm) as opposed to its low content in fresh waters (10 ppb in average river, LEMARCHAND *et al.*, 2002). This contrast served as a basis for the numerous attempts to use boron content as a paleosalinity proxy (see LERMAN, 1966; WALKER, 1968), again primarily utilizing clays as the indicator phase.

Several reports on boron concentration in cherts appeared in the literature (HARDER, 1974; KOLODNY *et al.*, 1980; TRUSCOTT and SHAW, 1984). Retreating to the classics again, the boron–silica substitution should not be surprising in view of GOLDSCHMIDT (1958, p. 280) mentioning that both BPO_4 and BAsO_4 are closely structurally related to cristobalite. A close association between boron and high SiO_2 in deep-sea (DSDP) cherts from the Central Pacific ocean was noted by HEIN *et al.* (1981) who also observed a positive correlation between boron content and $\delta^{18}\text{O}$ in those cherts. KOLODNY *et al.* (1980) combined oxygen isotopic analysis with α -track mapping of boron in cherts of the Campanian Mishash Formation in southern Israel, to demonstrate the schizohaline origin of these rocks.

With the realization that the isotopic geochemistry of boron may yield interesting information on such parameters as paleo-pH (SCHWARTZ *et al.*, 1969; SPIVACK *et al.*, 1987, 1993; PALMER *et al.*, 1998; PEARSON and PALMER, 2000; LÉCUYER *et al.*, 2002) and the interaction between the

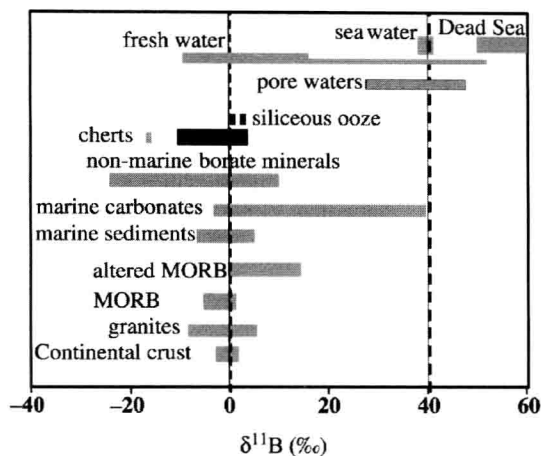


FIG. 1. Ranges of $\delta^{11}\text{B}$ values in different reservoirs on Earth (after schemes of VENGOSH *et al.* (1992), PALMER and SWIHART (1996) and LEEMAN and SISSON (1996)). The data on siliceous oozes and two Triassic cherts are from ISHIKAWA and NAKAMURA (1993). All other chert data (marked in black) were added in this study.

oceanic crust and seawater (SPIVACK and EDMOND, 1987) the range of subjects for B-isotope geochemical studies has been extended to carbonates (VENGOSH *et al.*, 1991; HEMMING and HANSON, 1992) as well as to fluid phases such as interstitial waters (BRUMSACK and ZULEGER, 1992; SPIVACK and YOU, 1997; KOPF *et al.*, 2000).

Isotopic analyses of boron in cherts are still very few. The most quoted values are the three measurements of two siliceous oozes and one Triassic chert by ISHIKAWA and NAKAMURA (1993) (see later) as part of their survey of the boron isotopic composition of marine sediments and sedimentary rocks.

The purpose of the present study is to measure and understand the isotopic composition of boron in purely marine cherts, thus expanding the database of $\delta^{11}\text{B}$ in sediments and sedimentary rocks (see Fig. 1). For this we use a sequence of cherts from the Deep Sea Drilling Project (DSDP). This suite of samples offers the possibility to determine the post-deposition changes in $\delta^{11}\text{B}$ that accompany silica transformations during diagenesis. These transformations pose strong limits on the use of B isotopes in marine cherts as a potential paleo-tracer.

METHODS

Deep sea chert samples

Twenty samples of cherts from the Central Pacific were selected for analysis. Of those, 18 are in stratigraphic sequence from DSDP Hole 167 (Leg 17). Hole 167 was drilled atop the Magellan Rise in the Central Pacific. It penetrated about 1200 m of nanofossil chalk, limestones and cherts, Tithonian to Pleistocene in age. Starting with core 33, at a depth of 605 m below sea floor (mbsf), cherts were recovered in the sequence. The cherts occur either as part of the carbonate sequence or, very often as broken fragments in the core catcher (marked "cc" in Table 1).

Between the Tithonian and the Late Cenomanian (1185–850 m, cores 61–94) sedimentation was continuous. The sedimentation rate was about 3–5 m/m.y. (SCHLANGER *et al.*, 1973). Above the Late Cenomanian, a sequence of hiatuses or stratigraphic gaps appear, associated with angular unconformities, representing probably the upper Cenomanian, Santonian and the longest one in all of the Paleocene to the middle Eocene (DOUGLAS *et al.*, 1973). Starting in the Middle Eocene and throughout the Tertiary, sedimentation at Site 167 was continuous and sedimentation rates high, varying between 9 and 18 m/m.y.

Table 1. Sample location, depth, age, boron concentration (by ion-probe and ICP-AES), $\delta^{11}\text{B}$, standard deviation from the mean of $\delta^{11}\text{B}$ and $\delta^{18}\text{O}$ for DSDP samples

Sample	Depth (mbsf)	Age (Myr)	B conc. (ppm) (ICP-AES)	B conc. (ppm) (I-probe)	I/B (ICP-AES)	$\delta^{11}\text{B}$ (‰)	$1\sigma(\delta^{11}\text{B})$ (‰)	$\delta^{18}\text{O}$ (‰)
167-33R-1W (127–129)*	605	42.5	67.8		0.0147	1.1	0.73	36.7
167-33R-1W (147–149)	605	43	75.8	74.5	0.0132	–0.1	0.05	34.6
167-34-cc*	620	43.5	69.5	95.9	0.0144	0.6	0.04	34.8
167-36-cc*	640	55	48.9		0.0205	4.4	1.3	34.4
167-38-cc	660	59.3	73.5	60.3	0.0136	0.8	1.26	34.8
167-40-cc	675	64	60.8	50.0	0.0165	–0.1	1.19	34.7
167-42-1 (130–131)	690	68.8	86.1	80.7	0.0116	2.7	0.27	35.7
167-44-1 (113–114)	710	71.1	85.0	83.5	0.0118	4.0	0.11	35.8
167-50-cc	770	74.3	97.3	104.3	0.0103	7.7	1.19	35.3
167-60-2 (81–82)	850	94.3	69.6	70.3	0.0144	1.4	0.55	35.1
167-61-2 (0–3)	860	97	85.9		0.0116	–5.2	1.99	34.1
167-65-1 (64–66)	890	101	70.9	68.2	0.0141	3.0	1.22	33.3
167-68-2 (100–101)	920	111.5	74.3	56.0	0.0135	–0.7	2.26	34.6
167-70-3	940	111.5	56.3	71.0	0.0178	–9.3	1.63	34.0
167-71-2 (37–38)	950	119	66.0	68.8	0.0152	–5.4	0.33	33.3
167-71-2 (42–44)	950	119	54.5		0.0183	–6.9	1.86	33.3
167-73-2 (90–92)	960	125.7	64.5		0.0155	–4.2	0.68	32.4
167-92-1 (64–67)	1160	141	53.3		0.0188	4.1	1.76	31.2
169-10-cc (0–1)	220	105	53.7	43.7	0.0186	1.0	0.99	31.9
195-B-3-1 (87–88)	390	130	52.8	75.5	0.0189	–0.6	0.07	32.9

*Samples containing a small (undetermined) amount of opal-CT.

(WINTERER, 1973; SCHLANGER *et al.*, 1973), but no chert younger than the Middle Eocene was recorded at this site. Two samples (one from each) are from Holes 169 and 195. All the samples reported on here were previously analyzed for $\delta^{18}\text{O}$ (KOLODNY and EPSTEIN, 1976), $^{87}\text{Sr}/^{86}\text{Sr}$ in the adjacent carbonate (KOEPNICK *et al.*, 1985), and Ge content (KOLODNY and HALICZ, 1988). All the relevant results are tabulated in KOLODNY and HALICZ (1988). The thermal history of these cherts was analyzed by PISCOTTO (1981). In most cases the original samples have been exhausted prior to our study; we hence resampled the cores at the designated or closest depths. Obviously, extrapolating results from one sampling site to the world ocean is risky. On the other hand there is something to be said in favor of analyzing a sequence that has been studied by several other tools.

We made a maximum effort to ascertain that the boron in our analyses is indeed related to a siliceous phase. All samples were analyzed by X-ray diffraction, specifically searching for opal-CT peaks. All, but three samples are practically pure microcrystalline quartz. In three samples (marked by “*” in Table 1), small opal-CT peaks were observed. The results for these samples should be viewed as possibly representing an admixture of opal-CT to quartz. All samples were examined under a scanning electron microscope both on a scale of 200 μ (field width) and 100 μ . On both scales, and at spot-counts, only Si and O peaks were observed (in some samples an Al peak slightly above background appeared). No cathodoluminescence is seen on all examined cherts in the visible wavelength region.

The solutions that were prepared by reaction of the cherts with HF, HNO_3 for boron analysis (see later) were also analyzed for other elements (Table 2). Aluminium (as reflecting clay) concentration averaged 0.5% and did not exceed 1%; the total of non-Si and Al cations did not exceed 0.5% in all but one case (1%), and averaged 0.4%. Most importantly B content is not correlative with the concentration of any of the measured elements.

Organic matter content was estimated by combustion of the samples on an elemental analyzer (EA-IRMS) coupled to a DeltaPlus-XL Finnigan mass-spectrometer. None of the samples contained more than 0.2% organic carbon.

To sum up our special tests, there is good evidence that all the analyzed samples consist practically of pure silica. In all but three, quartz is by far the predominant phase.

Table 2. Chemical composition of 18 DSDP cherts

Sample	B (ppm)	Na (ppm)	K (ppm)	Mg (ppm)	Ca (ppm)	Sr (ppm)	SO ₄ (ppm)	Li (ppm)	Ba (ppm)	Al (ppm)	C (org) (%)
167-33R-1W (127–129)	67.8	927	19	206	3870	22.3	609	2.6	99.5	1190	
167-33R-1W (147–149)	75.8	605	30	81.5	1920	9.5	428	1.4	28.3	6480	
167-34-cc	69.5	1110	357	685	4040	18.8	772	1.6	111	1200	0.18
167-36-cc	48.9	1190	509	227	1690	10.6	813	4.3	17.7	4630	
167-38-cc	73.5	1180	61	160	715	8.9	225	6.7	2.0	8390	
167-40-cc	60.8	1220	631	139	1380	11.7	243	8.1	4.4	3740	0.04
167-42-1 (130–131)	86.1	1070	611	163	767	6.2	151	3.8	3.0	7850	
167-44-1 (113–114)	85.0	1330	729	169	412	5.9	88.0	3.5	3.2	5290	
167-50-cc	97.3	1090	576	172	368	4.8	135	3.3	2.7	8290	
167-61-2 (0–3)	85.9	931	810	197	708	10.9	135	5.6	28.4	7120	
167-65-1 (64–66)	70.9	1170	938	319	1690	4.4	165	7.9	3.1	4050	
167-68-2 (100–101)	74.3	2100	1110	268	1280	22.9	284	19.9	8.9	6860	0.05
167-70-3	56.3	1840	869	265	845	12.2	213	24.5	4.1	6410	
167-71-2 (37–38)	66.0	1460	680	184	1720	10.5	284	15.0	3.5	7280	0.08
167-71-2 (42–44)	54.5	1150	494	158	1580	3.8	270	13.6	2.8	6690	
167-73-2 (90–92)	64.5	1750	522	154	1330	14.5	339	12.6	11.5	3880	
167-92-1 (64–67)	53.3	44	186	168	1060	2.6	765	25.8	6.5	4050	0.1
169-10-cc (0–1)	53.7	1510	1708	502	2890	7.4	344	61.6	6.7	3090	
Blank	1.8	0.0	0.6	5.0	106	1.2	152	0.0	0.2	50	

Specifically, there is no indication of the presence of a significant amount of either clay minerals or organic matter. Thus all our conclusions obtained on bulk samples apparently apply to chert as a pure, monomineralic quartz rock.

Determination of boron concentration and isotopic compositions by ion microprobe

The B contents and isotopic composition were determined by ion microprobe using a Cameca ims 3f instrument at CRPG-CNRS (Nancy). The analytical technique used was previously described for silicates and glasses (CHAUSSIDON and JAMBON, 1994; CHAUSSIDON *et al.*, 1997) and details can be found there. Because of their generally high B concentrations (50–100 ppm range), the problems of surface contamination and reduced precision due to low counting rates are not encountered for the analysis of B in cherts. The instrumental mass fractionation was determined using the GB4 glass standard (CHAUSSIDON *et al.*, 1997). It was reproducible on the GB4 glass to better than $\pm 0.8\%$ (2 sigmas) during the analytical sessions. The B isotopic composition is given in $\delta^{11}\text{B}$ notation relative to NBS 951, which has a $^{11}\text{B}/^{10}\text{B}$ ratio of 4.04558. Because of their heterogeneous appearance, *i.e.* color variations, several analytical points (between 3 and 6) were systematically measured at different locations on each polished sample of DSDP chert. The $\delta^{11}\text{B}$ values given in Table 1 correspond to the average of 3–6 measurements made on each chert sample. A general feature in these analyses is that a significant range of $\delta^{11}\text{B}$ values, of up to 4‰ for a few samples, is present in nearly all samples. This range is indicated in Table 1 by the 1 sigma on the mean of the different analyses made on a given sample.

The B concentrations were also measured by ion microprobe on a few chert samples, using a set of glass standards having B concentrations between 0.2 and 1000 ppm as previously described (CHAUSSIDON *et al.*, 1997).

Determination of boron concentration measurements by ICP-AES

As a double-check, the concentration of boron in all DSDP samples was redetermined by ICP atomic emission spectroscopy (ICP-AES). The chert samples were ground in a corundum mortar (Diamonite®) to pass a 200 mesh sieve, and were brought into solution following a modified version of the procedure of NAKAMURA *et al.* (1992). About 200 mg of sample powder was reacted with HF, HNO₃ and mannitol in sealed PFA Teflon®

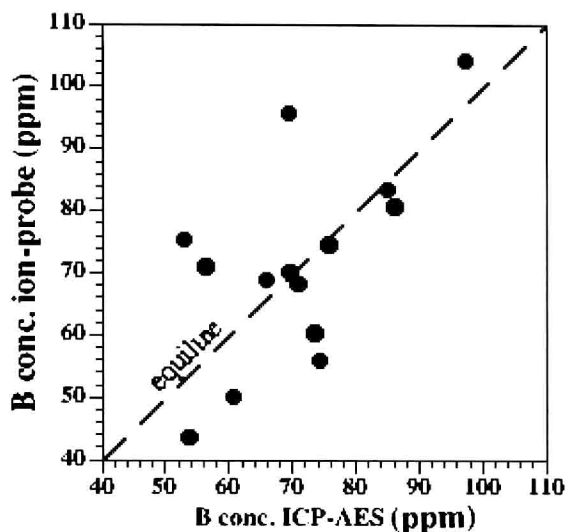


FIG. 2. Comparison of boron concentrations in DSDP cherts as determined by ion-probe (counting on discrete points of the polished rock) with an ICP-AES determination of bulk rock specimens. A line of perfect agreement (unity slope) is marked.

Advanced Composite Vessels (ACVs) and heated in a CEM microwave sample preparation system (Model MDS-2000). The peak pressure reached in the vessel was about 80 psi; temperature was not recorded, but apparently did not exceed about 70°C; total reaction time was 40 min. The vessels were left to cool overnight, and the fluoride was evaporated to dryness at 40°C. The dry residue was then dissolved in water and analyzed on a Perkin-Elmer Optima-3000 system. The 249.773 nm boron line was used. Samples were run in triplicate with a precision of 1–2% (RSD). The results of the comparison between wet chemical and ion probe analyses are shown in Fig. 2. Considering the fact that chert samples are certainly not perfectly homogeneous on the sampled scale (200 mg in wet vs. about 500 μm^3) the observed agreement seems excellent. Such agreement between boron concentrations determined by the two methods, suggests that the average boron isotopic compositions, as determined by ion probe, might also represent well the bulk isotopic composition of a sample.

RESULTS

B concentrations and isotopic compositions in DSDP cherts

Boron concentration in the analyzed DSDP cherts varies between 44 and 104 ppm and $\delta^{11}\text{B}$ value between $-9.3 \pm 1.6\text{‰}$ and $+7.7 \pm 1.2\text{‰}$ (Table 1, Fig. 3). The range of $\delta^{11}\text{B}$ values reported here overlaps and includes those observed in opal-A radiolarians and diatoms ($+2.2$ to $+4.5\text{‰}$, ISHIKAWA and NAKAMURA, 1993). Some of the DSDP cherts analyzed by us have very low $\delta^{11}\text{B}$ values lending further support to the general claim of LEMARCHAND *et al.* (2002) that boron sinks from the ocean are ^{10}B enriched. The two chert samples from Holes 169 and 195 have $\delta^{11}\text{B}$ values within the range defined by cherts from Hole 167 but tend to have low B concentrations and low $\delta^{18}\text{O}$ values.

Three of the four DSDP chert samples located at the top of core 167 contain traces of opal-CT (Table 1), implying that they have not been totally transformed into quartzose chert. These three samples have high $\delta^{18}\text{O}$ values compatible with isotopic equilibrium with seawater (KOLODNY and EPSTEIN, 1976) and have $\delta^{11}\text{B}$ values between -0.1 and $+4.4\text{‰}$ similar to those observed for opal-A radiolarians deposited on the seafloor (ISHIKAWA and NAKAMURA, 1993).