General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.

- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.

- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.

- This document is paginated as submitted by the original source.

- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

Produced by the NASA Center for Aerospace Information (CASI)

DRA

Papers Presented to the

CONFERENCE ON PLANETARY VOLATILES

(NASA-CR-170063) CONFERENCE ON PLANETARY VOLATILES (Lunar and Planetary Inst.) 137 p HC A07/MF A01 CSCL 03B

N83-20881

Unclas

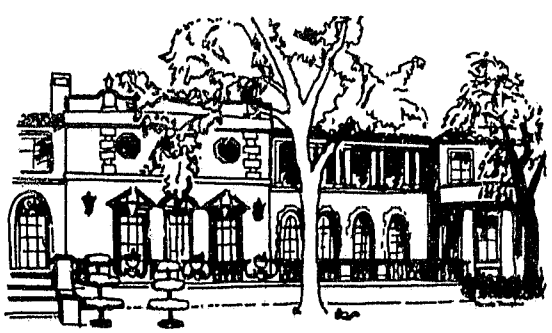
G3/91 15306

OCTOBER 9-12, 1982

JAN 1983
RECEIVED
NASA STI FACILITY
ACCESS DEPT.

Sponsored by

Lunar and Planetary Institute
National Aeronautics and Space Administration
National Science Foundation



UNIVERSITIES SPACE RESEARCH ASSOCIATION
LUNAR AND PLANETARY INSTITUTE
3303 NASA ROAD 1
HOUSTON, TEXAS 77058

PAPERS PRESENTED TO THE

CONFERENCE ON PLANETARY VOLATILES

SPONSORED BY:

LUNAR AND PLANETARY INSTITUTE
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
NATIONAL SCIENCE FOUNDATION

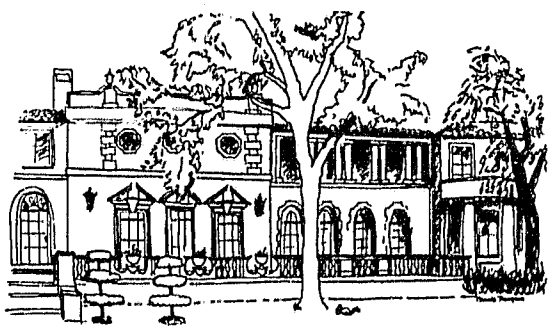
OCTOBER 9-12, 1982

Compiled by the
Lunar and Planetary Institute
3303 NASA Road 1
Houston, Texas 77058

LPI CONTRIBUTION 488

Material in this volume may be copied without restraint for library, abstract service, educational or personal research purposes; however, republication of any paper or portion thereof requires the written permission of the authors as well as appropriate acknowledgment of this publication.

ORIGINAL PAGE IS
OF POOR QUALITY



ORIGINAL PAGE IS
OF POOR QUALITY

PREFACE

The volume contains papers which have been accepted for publication by the Program Committee of the Conference on Planetary Volatiles. Papers were solicited which address one of the following major topics:

1. Initial and present volatile inventories and distributions in the earth, other planets, meteorites, and comets

2. Observational evidence on the time history of volatile transfer among reservoirs

3. Volatiles in planetary bodies, their mechanisms of transport, and their relation to thermal, chemical, geological and biological evolution

The Program Committee consists of A. L. Boettcher (*University of California, Los Angeles*), S. Chang (*NASA, Ames Research Center*), J. Kasting (*NASA, Ames Research Center*), R. O'Connell, Co-Convener (*Harvard University*), R. O. Pepin, Co-Convener, (*University of Minnesota*), J. B. Pollack (*NASA, Ames Research Center*), N. H. Sleep (*Stanford University*), and W. R. Van Schmus (*University of Kansas*).

Logistic and administrative support for this conference has been provided by Pamela Jones and LeBecca Turner (*Projects Office, Lunar and Planetary Institute*). This abstract volume has been prepared by Karen Hrametz and Linda Kofler (*Publications Office, Lunar and Planetary Institute*).

Papers are arranged alphabetically by the name of the first author. Indices by subject and author are provided.

The Lunar and Planetary Institute is operated by the Universities Space Research Association under contract No. NASW-3389 with the National Aeronautics and Space Administration.

ORIGINAL PAGE IS
OF POOR QUALITY

CONTENTS

The mantle atmosphere-hydrosphere system and the geochemical cycle for volatile elements
C. J. Allègre 1

Oxidation states of the upper mantle and controls on evolved volatiles
R. J. Arculus, D. A. Gust, and R. D. Holmes 2

Fluid inclusions in meteorites: Direct samples of extraterrestrial volatiles
L. D. Ashwal, M. T. Colucci, P. Lambert, D. J. Henry, and E. K. Gibson, Jr. 4

Model studies of O_2-biota coupling in the Precambrian
M. E. Baur 6

Implications of stable isotope variation in a banded iron formation for Precambrian volatile reservoirs
M. E. Baur, J. M. Hayes, and M. R. Walter 7

Volatiles and solar-nebula models
D. C. Black 8

Progress in the experimental investigation of volatile components in vapors and silicate liquids at high pressures
A. Boettcher 9

Microbial metabolism of organic material produced by chemical synthesis in a reducing atmosphere: Implications for the origin of life
P. J. Boston and C. Stoker 11

Brines at low temperatures
G. W. Brass and V. L. Thurmond 12

Was the Earth's atmosphere anoxic between 3.8 and 2.0 Ga ago?
K. Burke 14

Compositional clues to the history of the terrestrial planet atmospheres
A. G. W. Cameron 16

Models of the solar nebula: What determined the thermal structure?
P. M. Cassen 18

Prebiotic carbon cycle: Photochemical reduction of CO in Earth's primitive atmosphere
S. Chang and A. Bar-Nun 19

PRECEDING PAGE BLANK NOT FILMED

ORIGINAL PAGE IS
OF POOR QUALITY

Accretion of volatiles
S. Chang and J. F. Kerridge 21

Mechanisms for the vertical transport of H_2O within the martian regolith
S. M. Clifford 23

Comparison of He, Sr and Pb isotopic variations in the Icelandic 'hotspot'
M. Condomines, K. Gronvold, P. J. Hooker, R. K. O'Nions, and E. R. Oxburgh 25

Volatiles within the Earth's moon
J. W. Delano 27

Stable carbon isotopes in midoceanic basaltic glasses
D. J. DesMarais, H. Sakai, and J. G. Moore 29

High electrical conductivity in carbon-bearing rocks and meteorites: Implications for planetary interiors and asteroids
A. G. Duba and T. J. Shankland 31

Geochemistry of fluids in the terrestrial upper mantle
D. H. Eggler and M. E. Schneider 33

Ice-poor regolith development and destruction on small icy-dusty or icy-rocky objects
F. P. Fanale and J. R. Salvail 35

A condensation-accretion model for volatile element retention
B. Fegley 37

Homogeneity of argon and the $^{40}Ar/^{36}Ar$ ratio within the solid earth
D. E. Fisher 39

A review of distributions of sulfur in solar system objects
E. K. Gibson 41

Sputtering of volatile reservoirs
P. K. Haff 43

Metal-silicate redox reactions: Implications for core-mantle equilibrium and the oxidation state of the upper mantle
R. D. Holmes and R. J. Arculus 45

Boundary conditions on the paleoenvironment: The chemical compositions of pre-solar nebulae
W. M. Irvine 47

ORIGINAL PAGE IS
OF POOR QUALITY

Sources of volatiles in subduction zone magmas: Possible geologic cycling of chlorine and water
E. Ito and A. T. Anderson, Jr. 49

Exchange of water between the regolith, atmosphere, and polar caps of Mars
B. M. Jakosky 51

Terrestrial helium isotopic systematics
W. J. Jenkins 53

Trapping of gases and low temperature volatiles in lunar samples
S. Jovanovic and G. W. Reed, Jr. 54

Loss of a massive early ocean from Venus
J. F. Kasting and J. B. Pollack 56

Nonthermal escape of hydrogen and deuterium from Venus and implications for loss of water
S. Kumar, D. M. Hunten, and J. B. Pollack 58

Constraints on the evolution of the mantle from noble gas isotope ratios
M. D. Kurz and C. J. Allègre 60

Early volatiles accretion in inner planets
D. Lal and M. N. Rao 61

Processes of shock dehydration on accreting planets
P. Lambert and M. A. Lange 63

Accretion of water by the terrestrial planets
M. A. Lange and T. J. Ahrens 65

Volatile/mobile trace element fractionations in meteorite parent bodies
M. E. Lipschutz, T. Huston, and T. M. Walsh 67

Carbon in rocks from the Earth's mantle
E. A. Mathez, V. J. Dietrich, and A. J. Irving 69

The structure of the primordial atmosphere and the amount of grains
H. Mizuno 71

Chlorine concentrations in chondrites
C. B. Moore, K. L. Evans, and J. G. Tarter 73

Planetary abundances of volatile elements: A datum from the Earth's upper mantle
J. W. Morgan 74

ORIGINAL PAGE IS
OF POOR QUALITY

Equilibrium composition of the Mt. St. Helens magmatic volatile phase from the pyrrhotite-magnetite assemblage
B. E. Nordlie, S. E. Thieben, and D. R. Burggraf 76

Heat and volatile transport in planetary interiors
R. J. O'Connell, G. A. Houseman, and B. H. Hager 77

Relationships between heat and rare gas transport in the Earth
R. K. O'Nions and E. R. Oxburgh 78

Current compositions of planetary atmospheres
T. Owen 79

The sedimentary inventory of atmospheric xenon
F. A. Podosek, T. J. Bernatowicz, M. Honda, and F. E. Kramer 80

Noble gases in planetary atmospheres: Implications for the origin and evolution of atmospheres
J. B. Pollack and D. C. Black 82

Helium: Further evidence of a similar origin for Earth and Venus
M. J. Prather 83

Incorporation of noble gases in meteorites
S. Ramadurai 84

Volatiles as invaluable clues to planetogenesis
A. S. P. Rao 85

Numerical experiments with the geochemical cycle for carbon
S. M. Richardson and A. S. Grossman 87

Atmospheric evolution during accretion: A numerical model
S. M. Richardson, R. T. Reynolds, A. S. Grossman, and J. B. Pollack 88

Volatile element transport from the mantle: Experimental solubility data for S- system
M. J. Rutherford and M. Carroll 90

The noble gas record of the primitive nebula and the Earth
D. D. Sabu and O. K. Manuel 92

Comparative Ar-Xe systematics in the Earth's mantle
Ph. Sarda, Th. Staudacher, and C. J. Allègre 93

ORIGINAL PAGE IS
OF POOR QUALITY

Redox state and stable distribution of volatiles in planetary interiors
M. Sato 94

Early atmospheric oxygen levels: Constraints from Archaean photoautotrophy
M. Schidlowski 96

Impact basins and the storage/release of volatiles on Mars
P. H. Schultz and J. L. Rogers 97

Meander relicts: Direct evidence of extensive flooding in northern plains of Mars
D. H. Scott 99

Volatile exchange with the mantle at mid-oceanic ridges and the thermal history of the Earth's interior
N. H. Sleep 101

Origin and circulation of hydrothermal fluids at Larderello: Clues from noble gases
S. P. Smith 102

Importance of non-terrestrial volatiles to future space operations
R. L. Staehle 104

Bubble diffusion and composition of inert gases on Venus
A. S. Tamhane and G. W. Wetherill 106

Thermal and degassing histories of the Earth and Venus
G. Visconti 108

Cometary impacts on the terrestrial planets
P. R. Weissman 109

The use of tephra studies to determine volatile release during large explosive volcanic eruptions
J. A. Wolff and M. Storey 110

Evolution of solar ultraviolet luminosity
K. J. Zahnle and J. C. G. Walker 111

Mantle differentiation and crustal growth: An isotopic viewpoint
A. Zindler, S. Goldstein, and E. Jagoutz 113

Subject index *xi*

Author index *xiv*

THE MANTLE ATMOSPHERE-HYDROSPHERE SYSTEM AND THE GEOCHEMICAL CYCLE FOR VOLATILE ELEMENTS.

C.J. Allègre, Laboratoire de Géochimie, Institut de Physique du Globe, 4 Place Jussieu-75230 Paris cedex 05-France.

Atmosphere and hydrosphere systems have been formed (at least partially) by outgassing mantle processes. On the other hand, subduction processes inject into the mantle some material coming from the surface of the Earth. The (mantle) + (atmosphere + hydrosphere) can therefore be modelled as a two-reservoir complementary-coupled system. On the other hand, atmosphere, hydrosphere and sediments are linked by a set of equilibrium conditions, and the mantle can be divided into upper and lower mantle. The overall cycle also has a leak, which is the transformation of sediments into continental crust. Such complex systems can be described by coupled differential equations, and the time evolution can be examined using phase plane techniques in both linear and non linear cases. We have treated successively the three important cases :

a) evolution of concentration of volatile elements
b) evolution of mantle isotope ratios
c) evolution of radiogenic isotopic ratios

The models have been applied to different types of volatiles including rare gases, carbon, nitrogen, water, and chlorine. We can then model quantitatively the evolution of the mantle and the earth's surface through geological time under various conditions. The different elements are described by their transfer functions and their residence time in both reservoirs; the modelling results lead to major distinctions between the geochemical cycles of the various elements.

ORIGINAL PAGE IS
OF POOR QUALITY

OXIDATION STATES OF THE UPPER MANTLE AND CONTROLS ON EVOLVED VOLATILES. R.J. Arculus, D.A. Gust* and R.D. Holmes, Research School of Earth Sciences, Australian National University P.O. Box 4, Canberra, A.C.T. 2600, Australia. *Current address: N.A.S.A., L.B.J. Space Center, Houston TX 77058.

New measurements of the intrinsic oxygen fugacities (fO_2's) of (1) peridotites, (2) megacryst spinels, (3) kimberlite-hosted megacryst-ilmenite, and (4) alkali basalt-hosted magnetite-bearing cumulates have revealed dramatic variations in the redox state of these mantle-derived materials. These variations in fO_2 may exceed six orders of magnitude, and have significant implications for the characteristics of mantle-derived volatile species (volcanic gases) in the system C-H-O-S.

Type 1 (chrome diopside type) spinel peridotites from widely dispersed localities in Australia, U.S.A., West Germany and Japan have intrinsic fO_2's close to the iron-wüstite (IW) buffer curve in T-fO_2 space. Other intrinsic fO_2 data consistent with a reduced upper mantle have been published for marine-erupted Hawaiian basalt[1], the Bushveld[2] and Skaergaard[3] intrusions..

It has previously been argued[4] that a primitive terrestrial atmosphere buffered by an upper mantle close to IW in oxidation state, would include a large component of reduced gas species (e.g. H_2, CO, H_2S) in addition to predominant CO_2-H_2O-SO_2. However, subsequent measurements on rarer upper mantle-derived rock types and mineral species have revealed that oxidation states considerably higher than IW may exist in the upper mantle.

For example, megacryst ilmenites associated with several southern African kimberlite pipes have intrinsic fO_2's close to the Ni-NiO (NNO) and Fe_2SiO_4-SiO_2-Fe_3O_4 (FMQ) buffers, and display a coherent variation of intrinsic fO_2 as a function of Fe_2O_3/FeO ratios. Similar values have been obtained for megacryst ilmenite from the alnöitic breccia pipes in the Solomon Islands. Type 2 (aluminous augite type) peridotites from San Carlos and magnetite in cumulates from alkaline rock types in eastern New South Wales (Australia) are also close to, or more oxidized than the NNO buffer ($\log_{10} fO_2 \approx -9.0$ at 1000°C). We note that in none of our experiments conducted with CO_2-CO furnace gases has any autoreduction, attributed by others to the presence of carbon in the samples, been observed.

Type 1 peridotites are regarded by most petrologists as representative of the major portion of the shallower upper mantle. However the volumetrically minor sample represented by type 2 peridotites and by other deep-seated volcanic rock types point to the existence of strongly oxidized source areas in the upper mantle. Because these oxidized sources are associated with volatile-rich magmatism, their influence on the composition of erupted volcanic gases may be considerable in spite of their limited volume.

These observations prompt several important questions: (1) What are the relative proportions and significance of these various oxidation states within the upper mantle and what are the implications for volatile species associated with these zones? (2) What are the origins of these variable oxidation states? (3) How long has the dispersion in oxidation states in the upper

MANTLE OXIDATION STATES

Arculus, R.J. et al.

mantle persisted?

Possible explanations for the development of contrasted oxidation states in the upper mantle include: (1) long term (1 Gyr) recycling of ancient subducted lithosphere[5] and associated crustal layers previously exposed to hydrosphere-biosphere activity which may result in the localised oxidation of the mantle[6]; (2) Alternatively, oxidation may result from the upward fluxing of volatiles derived from zones in the lower mantle where segregation of Fe^{3+}-bearing silicate-oxide assemblages from core-forming Fe metal (produced during Fe^{2+} disproportionation reactions) has taken place. Consequences of both these processes are that active tectonic recycling of lithosphere and the large mass of the Earth (which allows Fe^{2+} disproportionation) may be the most important factors determining the relatively oxidized nature of the terrestrial upper mantle compared with small terrestrial planets (Mars, Moon, Mercury).

References

1. Sato, M. (1972) Geol. Soc. Am. Mem., 135, 289-307.
2. Flynn, R.T., Ulmer, G.C. and Sutphen, C.F. (1978) J. Petrol., 19, 136-152.
3. Sato, M. and Valenza, M. (1980) Am. J. Sci., 280A, 134-158.
4. Arculus, R.J. and Delano, J.W. (1980) Nature, 288, 72-74.
5. White, W.M. and Hofmann, A.W. (1982) Nature, 296, 821-825.
6. Arculus, R.J. and Delano, J.W. (1981) Geochim. Cosmochim. Acta, 45, 1331-1343.

ORIGINAL PAGE IS
OF POOR QUALITY

ORIGINAL PAGE IS
OF POOR QUALITY

FLUID INCLUSIONS IN METEORITES: DIRECT SAMPLES OF EXTRATERRESTRIAL VOLATILES. L.D. Ashwal [1], M.T. Colucci [1,2], P. Lambert [3], D.J. Henry[3], and E.K. Gibson, Jr.[3] (1) Lunar and Planetary Institute, Houston, TX (2) Rutgers Univ., New Brunswick, NJ (3) NASA Johnson Space Ctr., Houston, TX

Fluid inclusions have been found in 9 meteorites (both falls and finds) representing a wide variety of petrologic classes and types: diogenite ALHA 77256 and chondrites ALHA 77230 (L4), ALHA 77299 (H3), Bjürbole (L4), Faith (H3), Holbrook (L6), Jilin (H5), Peetz (L6), and St. Severin (LL6). Ample petrographic and other evidence exists to conclude that the inclusions are not artifacts introduced from terrestrial sources or during sample preparation (1).

Petrographic examination reveals that all these meteorites have experienced a complex sequence of events. For diogenite ALHA 77256 these include, from oldest to youngest: (A) crystallization and accumulation of orthopyroxene, (B) slow cooling in a plutonic environment, (C) shock induced fracturing, brecciation, and planar deformation ($P > 20GPa$), (D) thermal metamorphism ($T \simeq 900^{o}C$)(2), (E) mild shock ($P < 20GPa$). All chondrites examined show evidence of at least some shock and/or thermal effects possibly analogous to (C-E) of ALHA 77256. Fluid inclusions are generally restricted to large (1-2 mm), primary (?) orthopyroxene crystals in the diogenite, and to clear, transparent olivine in chondrules or chondrule fragments in the chondrites. Inclusions appear to be absent from mechanically deformed (i.e. highly fractured or brecciated) areas in all samples.

Two types of inclusions have been identified. Type 1 inclusions are most abundant and occur (in all 9 meteorites) either isolated or in small clusters. These inclusions have the following common properties: (a) variable shape and size (generally 5-10 μm or less; up to 100 μm), (b) presence of 2 phases (liquid + vapor) at T_{room}, (c) broad range of homogenization temperature (T_h) of L+V to L within individual meteorites ($T_h = 30^{o} - 300^{o}C$ with no preferred value), (d) apparent difficulty in observing freezing phenomena, i.e. recognition of an observable crystalline phase at low ($-180^{o}C$) temperatures, (e) continuous decrease in vapor bubble volume on heating from $-180^{o}C$ to T_h, and (f) strong fluorescence levels during laser Raman spectroscopic (LRS) analysis. Properties (a-c), along with an observed Raman vibration band at 3200-3600 cm^{-1} in ALHA 77256 (1) are consistent with an aqueous fluid, but the fluid cannot be pure H_2O because of (d-f). Warner et al. (1) inferred a large solute content, possibly salts, based on observations of change in vapor bubble morphology from deformed to spherical at -20° to $-25^{o}C$. Recent work indicates that

complex hydrocarbons may be an important constituent of these fluids (3). Evidence includes: (i) fluorescence of the inclusions under UV excitation, (ii) precipitation of graphitic material within the inclusions during some LRS experiments, (iii) detection of a broad Raman band at about 2900 cm^{-1}, characteristic of C-H stretching. The broadness of this LRS signal suggests a higher aliphatic hydrocarbon than simple methane. Type 2 fluid inclusions, identified thus far in diogenite ALHA 77256 and L4 chondrite Bjürbole occur exclusively along healed fractures. In the diogenite, these are parallel to major shock-induced fractures produced during event (C) above. Preliminary microthermometry on type 2 inclusions suggests that their compositions may be different than type 1 inclusions.

IMPLICATIONS: (a) The similarity of fluid inclusions in the chondrites and the diogenite may have implications which bear on current theories as to where meteorites come from. Plausible sources of fluids available for interaction with meteoritic material include hydrous or carbonated minerals, such as are present in carbonaceous chondrite matrices, and ices. These fluids may have been released from either source by heating due to impact processes (4) or to radionuclide decay (possibly of short-lived radionuclides such as ^{26}Al (5,6)). The origins of these fluid inclusions must await further characterization of their chemical compositions and distributions. (b) Different generations of fluid inclusions can be identified in these meteorites despite their complex histories. It appears likely that such inclusions are able to survive (but perhaps not intact) moderate shock and thermal events. This is in agreement with fluid inclusion studies of terrestrial impactites (7), and with our observations of surviving fluid inclusions in microcline which had been experimentally shocked at about 20 GPa. (c) A better understanding of the relationship between the observed fluid inclusions and the shock and thermal events must await experiments which address the behavior of such inclusions during varying shock conditions.

REFERENCES: (1) Warner, J.L. et al. (1982) Proc. Lunar Planet. Sci. Conf. 13th, in J. Geophys. Res., in press. (2) Hewins, R.H. (1981) Lunar & Planet. Sci. XII, p. 445-446. (3) Adar, F. et al. (1982) Meteoritics, in press. (4) Lambert, P. and Lange, M.A. (1982), this volume. (5) Lee, T. et al. (1976) Geophys. Res. Lett. 3, 109-112. (6) Irvine, W.M. et al (1980) Nature 283, 748-749. (7) Pagel, M. et al. (1975) Fortschr. Mineral. 52, 479-489.

ORIGINAL PAGE IS
OF POOR QUALITY

MODEL STUDIES OF O_2-BIOTA COUPLING IN THE PRECAMBRIAN

M. E. Baur, Department of Chemistry, University of California, Los Angeles, CA 90024

Microorganisms capable of O_2 respiration play an important role in setting the boundary between oxic and anoxic zones in present terrestrial soil and water environments. The division of environments into such zones indeed may reflect the markedly nonlinear behavior predicted by coupled kinetic equations for microbial growth and oxygen utilization in the presence of an initial mild O_2 gradient. If this type of kinetic model is applied to presumed Precambrian conditions, we reach the somewhat paradoxical conclusion that the development of fully anoxic zones could not occur until an O_2-dependent biota had evolved, that is, until atmospheric O_2 levels had reached some critical value in late Archaean or early Proterozoic time. Sequestering of reduced carbon in such anoxic zones may have acted in turn to accelerate atmospheric O_2 buildup, yielding a pronounced positive feedback effect between the rise in O_2 and the proliferation of O_2 respirers. If such a mechanism were indeed operative in late Archaean or Proterozoic time, then a quite rapid, even cataclysmic, rise in ambient O_2 levels may have occurred.

ORIGINAL PAGE IS
OF POOR QUALITY

IMPLICATIONS OF STABLE ISOTOPE VARIATION IN A BANDED IRON FORMATION FOR PRECAMBRIAN VOLATILE RESEROVOIRS M. E. Baur, Department of Chemistry, University of California, Los Angeles, CA 90024; J. M. Hayes, Department of Chemistry, University of Indiana, Bloomington, IN 47405; and M. R. Walter, P.O. Box 378, Bureau of Mineral Resources, Canberra A.C.T., Australia 2601

Powder samples milled from individual microband components in samples of banded iron formation (BIF) from the Precambrian (2.5 Ga) Hamersley Group of Western Australia have been analyzed for evidence of variation of $\delta^{13}C$ and $\delta^{18}O$ in the carbonate component present. The formations sampled included the Marra Mamba, Mt. Sylvia and Brockman, as well as the non-BIF Wittenoom dolemite. All the BIF show unequivocal evidence for a sharp and reasonably regular alternation of $\delta^{13}C$, with magnetite-rich zones being isotopically lighter. We infer from this that two distinct mobile carbon reservoirs were present in Hamersley time, contributing in varying proportion to the carbonate mineral deposited in sediment. One of these, presumably, was the atmosphere-hydrosphere CO_2 reservoir, yielding carbonate mineral with $\delta^{13}C$ near zero as on the present earth. The other seems likely to have been biologically coupled and to have contained isotopically very light carbon; a possible model is that it consisted of methane produced biogenically in bottom sediments and oxidized to isotopically light CO_2 in the water column. In view of the widespread occurrence of BIF in late Archaean and early Proterozoic time, such a model suggests that the biosphere was by then already playing an important role in controlling inventories and transfer of at least some volatiles.

ORIGINAL PAGE IS
OF POOR QUALITY

VOLATILES AND SOLAR-NEBULA MODELS. D.C. Black, NASA Ames Research Center, Moffett Field, CA

The study of planetary volatiles is a multi-faceted problem which can be divided into three general subproblems; the formation and evolution of the solar nebula, the interaction between planets and their environment, and the physical/chemical evolution of planets. These three are not mutually exclusive, but given the embryonic state of knowledge concerning planetary volatiles and the potential significance of enhanced knowledge in constraining our understanding of a variety of planetary and nebular phenomena, these subproblems are of heuristic value. The focus of this paper will be on the subproblem of the formation and early evolution of the solar nebula, emphasizing possible relationships between events/processes in that formation and evolution with the general problem of planetary volatiles.

Years of analysis of lunar, meteoritic, and terrestrial samples, and nearly two decades of spacecraft exploration of the solar system does not yet permit specification of even the more fundamental characteristics of the putative solar nebula. For example, there is no unequivocal evidence as to the mass of the nebula; was it massive ($\sim 1M_{\odot}$) or was it a so-called "minimum-mass" nebula (~ 0.01-$0.02M_{\odot}$)? There is also no clear evidence as to the thermodynamic evolution of the nebula, although the past decade of meteoritic studies have shown rather clearly that an earlier paradigm in which a reasonable portion of the nebula was hot (i.e., $\gtrsim$ 1500-2000K) is <u>not</u> consistent with available data.

One can identify at least four aspects of solar nebula formation and evolution which relate to the study of planetary volatiles. It would be useful to know how the elemental and isotopic composition of volatiles, in both the gas and solid (i.e., dust grains) phases varied in time and space as the nebula evolved. One would also like to know the evolution of physical conditions in the nebula in terms of the way(s) in which those conditions influence or control the process of planet formation. Finally, one would like to know the nature of planet-nebula interactions, specifically those which affect volatile inventories in planetary bodies.

The purpose of this paper is to present a brief review of competing models of the solar nebula, as well as to outline some rather general theoretical considerations which delineate generic nebular formation and evolution behavior. Possible consequences of those theoretical constructs for studies of planetary volatiles in general, and of the noble gases in particular, will also be discussed.

ORIGINAL PAGE IS
OF POOR QUALITY

PROGRESS IN THE EXPERIMENTAL INVESTIGATION OF VOLATILE COMPONENTS IN VAPORS AND SILICATE LIQUIDS AT HIGH PRESSURES: Art Boettcher, Institute of Geophysics and Planetary Physics and Department of Earth and Space Sciences, University of California, Los Angeles, California 90024

In the mid-60's, we achieved the capability of routinely experimentally examining the role of H_2O and other volatile components in melting and other phase transformations at pressures > 10 Kbar, i.e., pressures equivalent to those in the mantle of the Earth. At these pressures, aluminosilicate magmas (e.g., basaltic) can dissolve > 15 wt% H_2O -- i.e., > 70 mole% (1). At pressures < ∿ 10 Kbar, H_2O-saturated fusion curves of silicate and aluminosilicate minerals have negative dP/dT slopes; at higher pressures, they become positive as a result of the increasing density of H_2O and also of minerals as the result of phase transformations (2). In 1970, we (3) demonstrated that CO_2 is quite soluble in basaltic liquids at > ∿ 15 Kbar, and this has been substantiated in many synthetic silicate and aluminosilicate systems (e.g., 4, 5). Thus, at Earth-mantle pressures, anhydrous, as well as hydrous and/or carbonated, silicate systems have fusion curves with positive dP/dT slopes, but the latter are displaced to lower temperatures as the result of the solubility and negative free energy of mixing of the H_2O and/or CO_2 in the silicate liquids. Thus, when the proportion of H_2O and/or CO_2 is sufficient to saturate the system and form a vapor phase, the temperature of the beginning of melting and the composition of the first-formed liquids are functions of the ratio of H_2O/CO_2 (i.e., of the fugacities of these components) (6). However, when the proportions of CO_2 and H_2O are insufficient to make all of the potential hydrous and carbonate crystalline phases (e.g., amphiboles and dolomite), the values of μ_{H_2O} and μ_{CO_2} are isobarically invariant, and the temperatures of the beginning of melting and the compositions of the first-formed liquids are independent of total H_2O/CO_2 (7).

The discovery that CO_2 reacts with olivines and pyroxenes to form carbonates at depths < 100 km (8) is significant because primary (Mg-rich) carbonate is extremely rare in mantle-derived samples, suggesting to me that the mantle may be more chemically reduced (9) than accepted by many petrologists, and reduced C-bearing species may be more important. Reactions similar to the carbonation of olivines and pyroxenes may also occur in silicate liquids at about 20 Kbars, explaining the remarkable increase in the solubility of CO_2 in these liquids above this pressure (3, 10, 11). That is, the abrupt increase in the solubility and freezing-point depression may result from an increase in the ratio of CO_3^{2-}/CO_2 in the liquid (1, 4, 11). However, the presence of CO_3^{2-} in liquids requires non-bridging oxygen ions (e.g., 4) as well as cations such as Ca or Na for charge balance, and no CO_3^{2-} is expected in melts of SiO_2 composition. Nevertheless, recent experiments in the system SiO_2-H_2O-CO_2 (12) reveal that CO_2 is very soluable in the liquid above ∿20 Kbar, suggesting that molecular CO_2 is the major, if not the only, carbon-bearing species in the liquid.

Our recent studies of the melting of silicate and aluminosilicate minerals in the absence of vapors (13) and in the presence of H_2O-CO_2 vapors (11, 14) provide thermodynamic data for liquids and vapors at high pressures that previously were unobtainable. Nevertheless, problems occur with this approach because of a lack of knowledge of the absolute solubilities of carbon-bearing species in the liquids and of the effects of such solubilities on the values of γ_{H_2O}. For example, activity coefficients for H_2O determined experimentally in the systems albite-H_2O-CO_2 (11) and SiO_2-H_2O-CO_2 (12) yield values of γ_{H_2O} in the vapor that are strongly dependent on the ratio of H_2O/CO_2 in the vapor, whereas those determined in the system sanidine-SiO_2-H_2O-CO_2 are much more

ORIGINAL PAGE IS
OF POOR QUALITY

nearly those of ideal solutions (14). Despite these and other uncertainties, the experimental approach has enabled us to gain insight into the structures of silicate liquids and to derive thermodynamic parameters for them. This approach provides us with much more reliable fusion curves than those calculated from thermochemical data calorimetrically determined at atmospheric pressure and using metastable glasses rather than stable silicate liquids. For example, our experimentally determined, vapor-saturated solidi in the presence of CO_2-rich vapors in the system albite-H_2O-CO_2 are hundreds of Kelvins lower than those previously calculated. Similarly, phase transformations in aluminosilicate liquids at high pressures (particularly the $Al^{IV} \rightleftarrows Al^{VI}$ transformation) result in fusion curves that depart markedly from those calculated from volumetric and thermodynamic data obtained at atmospheric pressure (13, 15).

Continued experimentation at high pressures, coupled with calorimetric and spectrographic investigations of liquids, will enable us to more nearly quantify our understanding of the processes in the interiors of planets that involve volatile components, including melting and the origins of atmospheres and hydrospheres.

REFERENCES

(1) Burnham, C. W. (1979) in H. S. Yoder, Jr., ed., The Evolution of the Igneous Rocks: Fiftieth Ann. Appraisal, Princeton Univ. Press, Princeton, N.J., p. 439-482.
(2) Boettcher, A. L. and Wyllie, P. J. (1969) Amer. J. Sci., v. 267, p. 875-909.
(3) Hill, R. E. T. and Boettcher, A. L. (1970) Trans. Amer. Geophys. Union, v. 51, p. 438.
(4) Mysen, B. O. (1976) Amer. J. Sci., v. 276, p. 969-996.
(5) Eggler, D. H. and Rosenhauer, M. (1978) Amer. J. Sci., v. 278, p. 69-94.
(6) Mysen, B. O. and Boettcher, A. L. (1975) J. Petrol., v. 16, p. 520-548.
(7) Eggler, D. H. and Holloway, J. R. (1977) in Magma Genesis, State of Oregon, Dept. Geology and Min. Ind. Bull. 96, p. 15-36.
(8) Newton, R. C. and Sharp, W. E. (1975) Earth Planet. Sci. Lett., v. 26, p. 239-244.
(9) Arculus, R. J. and Delano, J. W. (1981) Geochim. Cosmochim. Acta, v. 45, p. 899-913.
(10) Wyllie, P. J. (1979) Amer. Mineralogist, v. 64, p. 469-500.
(11) Bohlen, S. R., Boettcher, A. L. and Wall, V. J. (1982) Amer. Mineralogist, v. 67, p. 451-462.
(12) Boettcher, A. L., in preparation.
(13) Boettcher, A. L., Burnham, C. Wayne, Windom, K. E. and Bohlen, S. R. (1982) J. Geology, v. 90, p. 127-138.
(14) Bohlen, S. R., Boettcher, A. L. and Wall, V. (1982) Abs., Geol. Soc. Amer. Ann. Mtg., in press.
(15) Burnham, C. Wayne (1982) in Rickard, D. and Wickman, F. E., eds., Chemistry and Geochemistry of Solutions at High Temperatures and Pressures, Pergamon Press, Ltd., p. 197-229.

MICROBIAL METABOLISM OF ORGANIC MATERIAL PRODUCED BY CHEMICAL SYNTHESIS IN A REDUCING ATMOSPHERE: IMPLICATIONS FOR THE ORIGIN OF LIFE

Penelope J. Boston, Dept. of Environmental, Population, and Organismic Biology, University of Colorado, Boulder, CO 80309
Carol Stoker, Dept. of AstroGeophysics, University of Colorado, Boulder, CO 80309

Tholins, a class of complex organic solids, have been produced under laboratory conditions using a reducing mixture of gases including methane and ammonia. (1). Tholin hydrolysis yields amino acids. Its pyrolysis products contain many other compounds of biological significance. We have isolated a variety of microorganisms which are capable of metabolizing tholins. The tar-like tholin (produced by sparking an equimolar mixture of NH_3 and CH_4 with 2.6% H_2O vapor) is probably used as a carbon on energy source for these organisms. Tholin-metabolizers have been obtained from Utah tarsands, several types of dry Colorado soils, and anaerobic mud samples. A basal salts-silica gel medium with tholin was used to establish its use as sole carbon source. No growth was observed in basal salts-silica gel controls without tholin. Light was excluded to inhibit phototrophs. Several of the bacterial isolates are sporeformers and some are facultative anaerobes. The majority of the organisms are microaerophilic, preferring to grow in reduced oxygen tensions. There is evidence that at least one of the isolates is a representative of the primitive archaebacterial group.

Production of organic precursor compounds by inorganic chemical means is a salient feature of virtually every scenario for the origin of life. In some of these scenarios, a highly reducing atmosphere including the constituents methane, ammonia and water prevailed on the primitive Earth. Tholin compounds, which could have provided a source for either the molecular building blocks of life or potential precursors to them, are easily synthesized in such a reducing atmosphere.

Recently a case has been made based on the atmospheric photochemistry of ammonia (2) and geochemical evidence that the primordial atmosphere consisted primarily of H_2, CO_2 and N_2(3). In such an atmospheric mix, however, it is difficult to produce the rich variety of organic compounds observed in tholins.

The demonstration of microbial growth on tholin has implications for the chemical environment that lead to the origin of life and early cellular evolution on Earth. The results suggest that terrestrial organisms originated in a chemical environment in which tholins were present as a source of energy and materials, either produced from in situ reservoirs of CH_4 and NH_3 or introduced by extraterrestrial menas such as meteoritic infall.

Information on the growth rates of organisms on tholins may provide a guide to the required concentrations of tholin in the prebiotic and biotic environment. This in turn will help to set limits on the production rate or required flux of tholin material into the early biosphere required to sustain the first organisms, assuming that tholins were the major food source before the development of primary production mechanisms such as chemotrophy and phototrophy.

Khare, B.N. and Sagan, C. (1979) Nature, Vol, 277, pp. 102-107
Ferris, J.P. and Nicodem, D.E. (1972) Nature, Vol. 238, p. 268-269.
Hart, M.H. (1978) Icarus 33, 23-39.

ORIGINAL PAGE IS
OF POOR QUALITY

BRINES AT LOW TEMPERATURES G. W. Brass and V. L. Thurmond, Rosentiel School of Marine and Atmospheric Science, University of Miami, 4600 Rickenbacker Causeway, Miami, FL

The freezing point of pure water is relatively high compared to temperatures prevailing on planetary bodies farther from the sun than Earth. Aqueous fluids are, however, stable at temperatures as low as 210°K if they are sufficiently salty. In fact, the presence of modest amounts of those salts with the greatest freezing point depression effects requires that aqueous brines form by reaction of salt crystals with ice.

The general rules of freezing point depression are: 1. Sulfates are less effective depressors than chlorides. 2. Alkaline Earth chlorides are more effective than alakli chlorides. 3. Sodium is more effective than potassium and calcium more effective than magnesium.

The four component system $CaCl_2$ - $MgCl_2$ - NaCl - H_2O begins to melt at 215°K (-58°C) (Linde, 1958). The effect of ferrous and ferric iron chlorides in combination with other salts is being investigated now with the differential scanning calorimeter and the results will be presented at the meeting along with a suggestion for the production of the red coloration of the martian regolith.

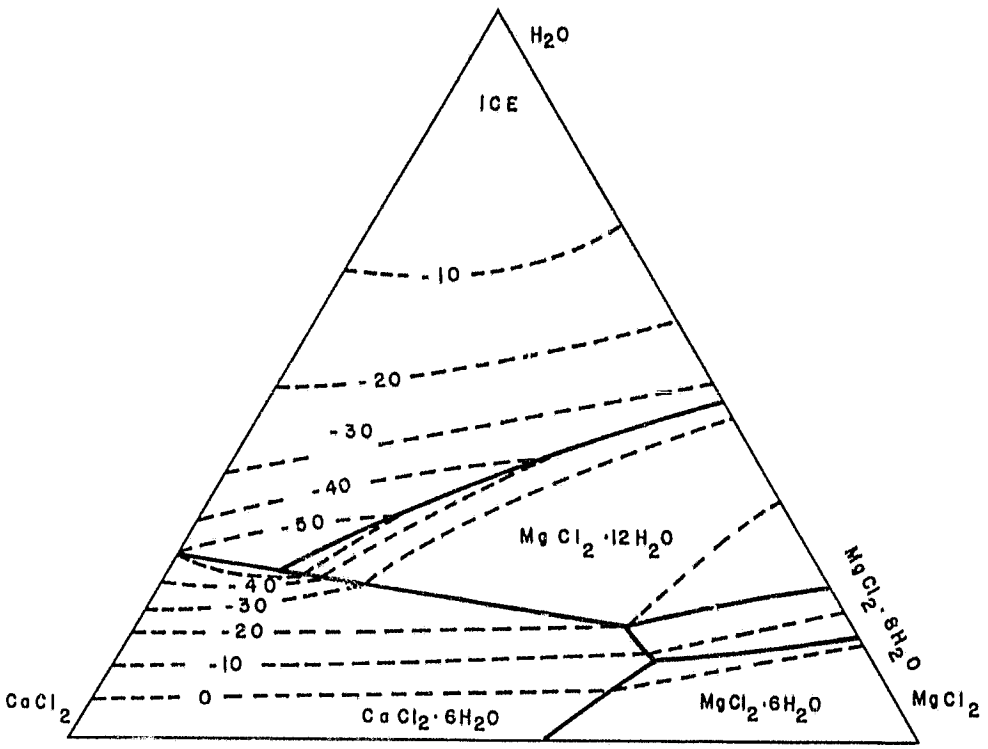
The ternary phase diagram for the system H_2O - $CaCl_2$ - $MgCl_2$ shows both a strong freezing point depression at the eutectic, and the stability of several highly hydrated salts at higher temperatures.

Evaporation of brine leads to the formation of these hydrated salts which may buffer the water content of planetary surfaces even in the absence of brine or ice.

Chlorine and sulfur are abundant components of the terrestrial excess volatiles. Their presence on other planetary bodies is now well established. Their effect on the behavior of water and ice at

ORIGINAL PAGE IS
OF POOR QUALITY

low temperatures is profound and must be taken into consideration in models of planetary volatiles.



(Figure reproduced courtesy of Academic Press, Inc.)

Stability fields in the system H_2O - $CaCl_2$ - $MgCl_2$, from Brass, 1980.

REFERENCES

Brass, G.B. (1980) Icarus 42, p.20-28.

Linke, W.F. (1958) Solubilities of Inorganic and Metal-Organic Compounds (2 volumes) Van Nostrand, New York.

ORIGINAL PAGE IS
OF POOR QUALITY

WAS THE EARTH'S ATMOSPHERE ANOXIC BETWEEN 3.8 and 2.0 GA AGO?

Kevin Burke, Department of Geological Sciences, State University of New York at Albany, New York, 12222 and Lunar and Planetary Institute, 3303 NASA Road 1, Houston, Texas 77058.

Attempting to assess the character of the ancient atmosphere from preserved Archean rocks is exceedingly difficult. Although a substantial proportion of the continental volume had fractionated from the mantle by 2.5 Ga ago, only about 2% of continental area exposes Archean rocks that have not been subsequently highly metamorphosed. More than half of this relatively unaltered terrane consists of plutonic rocks and volcanic rocks (mainly erupted under water) make up most of the rest. Archean sediments which constitute a relatively small volume of all Archean rocks were mostly deposited under water although some are fluviatile in origin. Diagenesis, usually under reducing conditions and low-grade metamorphism, have modified all ancient sediments. Curtis (1977) wrote "one thing is clear: it is difficult to link the mineralogy of ancient sediments with the composition of the atmosphere - only with the combined atmosphere/hydrosphere system".

Because of the prevalence of diagenetic modification some of the strongest evidence of the composition of the ancient ocean comes, somewhat paradoxically, from the occurrence of pseudomorphs. Gypsum pseudomorphs occur in the Barberton (>3.4 Ga) and Pilbara (>3.4 Ga) terranes. The implied occurrence of sulfate ions in ancient seawater seems indicative of at least slightly oxidizing conditions (but see Clemmey and Badham, 1982 and Lambert et al. 1978 for discussion of the significance of these occurrences). By the Early Proterozoic, evidence, [usually pseudomorphous], of gypsiferous evaporites is relatively common (e.g. Badham and Stanworth, 1977).

The close resemblance between the structures of Archean stromatolites and those of today which are built by photosynthesizing, oxygen-producing cyanophytes suggests that the ancient structures were produced in the same way indicating that free molecular oxygen was being released to the atmosphere-hydrosphere system by 3.5 Ga ago. Archean stromatolites are quite abundant, in spite of forming in environments in which preservation is relatively unlikely, indicating that molecular oxygen release associated with stromatolites was probably early a widespread phenomenon.

The occurrence of sediments and residual deposits which are red because of the presence of ferric iron is a strong indication of oxidizing conditions. Archean red beds, for example, in the Lake Shebandowan area of the Superior Province (Shegelski, 1980), have been interpreted as including both primary red beds (those involving the deposition of detrital hematite) and secondary red beds (involving diagenesis by oxidizing interstitial fluids). Gay and Grandstaff (1980) have described, from beneath Huronian sediments at Elliot Lake, an approximately 2.3 Ga old soil profile on granite which shows both iron-enrichment and oxidation. Subaerial residual soil profiles are likely to be among the most direct indicators of ancient atmospheric chemistry. Beneath an oxidizing atmosphere whether profiles are oxidized or reduced depends primarily on the position of the water-table; beneath a reducing atmosphere only reduced profiles form.

ORIGINAL PAGE IS
OF POOR QUALITY

WAS THE EARTH'S ATMOSPHERE ANOXIC

BURKE, K.

Ancient detrital uraninite has long been cited as evidence of a reducing atmosphere, but Simpson and Bowles (1977) showed that all the detrital grains from the Witwatersrand basin which they studied contained more than 1% Th O_2 and were similar to the thorian uraninites that survive today in the sediments of the Indus River under the modern oxidizing atmosphere.

Precambrian iron-ores have sometimes been considered related to a reducing atmosphere. Here again Curtis' (1977) comments are relevant:

> "At the present time (and through the Phanerozoic) almost all the oxidized iron entering the sedimentary column is reduced by organic matter"..... "Rather rare circumstances allow for oxidized sediment preservation: either a lack of deposition of organic matter within rapidly deposited terrestrial detritus from arid environments or its complete destruction within the uppermost oxidizing layer of extremely slowly deposited sediments. The predominance of reduced sedimentary iron minerals within the fragmentary Pre-Cambrian record therefore is not, of itself, very convincing evidence of a reducing atmosphere."

At one time there was a suggestion that most Precambrian iron-ores had formed at about the same time ~2.0 Ga ago possibly marking a transition in the oxidation state of the atmosphere. More dating has shown that some iron formations are older and many are younger than this age. There is no great concentration of iron formation of one age and even if there was it would be more likely to relate to selective preservation rather than selective formation. If there is a peculiarity of Precambrian iron ores it lies in their large numbers and the great size of individual deposits (Gole and Klein, 1981). Whether these properties indicate geochemically different conditions from today is not clear. What is clear is that we do not understand very well how Phanerozoic iron-ores were formed and that Precambrian iron-ores are themselves quite varied (Kimberley, 1978).

In conclusion it appears that evidence of an early anoxic atmosphere is less strong than was once thought and that numerous processes, but especially diagenesis, render making inferences about the oxidation state of the ancient atmosphere/hydrosphere system very difficult. Specifically isotopic compositions of such elements as sulfur and oxygen are more likely to reflect conditions at diagenesis than to reflect the composition of contemporary seawater.

REFERENCES

Badham, J.P.N. and Stanworth, C.W., 1977. Evaporites from the Lower Proterozoic of the East Arm, Great Slave Lake: Nature, v.268, p. 516-518.
Clemmy, H. and Badham, N, 1982. Oxygen in the Precambrian atmosphere: An evaluation of the geological evidence. Geology, v.10, p. 141-146.
Curtis, C., 1978. Sedimentary geochemistry; environments and processes dominated by the involvement of an aqueous phase. Roy. Soc. Lond. Phil. Trans. Ser. A, v.186, p. 353-372.
Gay, A.L. and Grandstaff, D.E., 1980. Chemistry and mineralogy of Precambrian paleosols at Elliot Lake, Ontario, Canada. Precamb. Res., v.12, p. 349-373.
Gole, M.J. and Klein, C., 1981. Banded iron-formations through much of Precambrian time. Jour. Geol. 89, p. 169-183.
Kimberley, M.M., 1978. Paleoenvironmental classification of iron formations, Econ. Geol., v.73, p.215-229.
Lambert, I.B., Donnelly, T. H., Dunlop, J.S.R., and Groves, D.I., 1980. Stable isotopic compositions of early Archean sulphate deposits of probably evaporitic and volcanogenic origins, Nature, v.276, p.808-811.
Shegelski, R.J., 1980. Archean cratonization emergence and red bed development, Lake Shebandowan area, Canada. Precamb. Res., v.12, p. 331-347.
Simpson, P.R. and Bowles, J.F.W., 1977. Uranium mineralization in the Witwatersrand and Dominion Reef Systems. Roy. Soc. Lond. Phil. Trans. Ser. A, v.186, p. 527-548.

ORIGINAL PAGE IS
OF POOR QUALITY

COMPOSITIONAL CLUES TO THE HISTORY OF THE TERRESTRIAL PLANET ATMOSPHERES, A.G.W. Cameron, Harvard College Observatory, Cambridge, MA 02138.

Much has been made of the so-called 'gradient' in the abundance of ^{36}Ar in going from Venus to Earth to Mars. Attempts to interpret this have led to some strange views of processes in the primitive solar nebula. However, my work on other aspects of the history of the Earth-Moon system has led me to suspect that the history of the Earth's atmosphere should have been quite unlike that of any of the other terrestrial planets. Viewed in this light, the abundances of the noble gases in the three terrestrial planet atmospheres would no longer form a 'gradient'.

The anthopomorphic tendency is to assume that the Earth represents the normal condition, and that departures from it are anomalies which need investigation. However, in this case it appears to me more likely that Venus represents the normal condition for the abundances of the noble gases, and the Earth represents the anomaly. The reason for this has to do with the presence of the Moon, which is itself a very anomalous body, and the likelihood that the formation of the Moon involved the Earth in an energetically violent episode.

The pattern of the noble gases in the terrestrial planet atmospheres resembles typical patterns of these trapped gas abundances in meteoritic materials. For a long time this has been very reasonably interpreted as implying that the bulk of the atmospheres were derived from solids impacting onto the planets during the accumulation process, rather than implying that the the gases were some sort of remnant of a concentration of the primitive solar nebula toward these gravitating bodies. I accept this interpretation. The simplest a priori expectation is that Venus and the Earth, being of about the same mass and mostly outgassed, would have about the same initial atmospheric content of the noble gases. This is consistent with the fact that the planetary CO_2 contents of these two objects seem to be about the same. Mars has a much smaller atmospheric mass per unit mass. Unless one is prepared to assume that outgassing has been grossly inefficient, it follows that Mars has suffered the bulk loss of a major part of its atmosphere, probably from collisions of incoming planetessimals.

If one accepts the above point of view, then it follows that the Earth must also have suffered a bulk loss of a major part of its atmosphere, in order to reduce the xenon to an intermediate level between that of Venus and Mars. In the case of the Earth, one cannot suggest that this has resulted from planetessimal impacts, for similar impacts would have produced similar effects on Venus. However, there may have been a much more violent event affecting the Earth.

Bill Ward and I have suggested (1,2) that a major collision with the protoearth was responsible for the formation of the Moon. The reasoning that led to this conclusion started with a calculation of the mass of an object hitting the protoearth tangentially that would be required to give the Earth-Moon system its present angular momentum. The mass is about that of Mars, an order of magnitude larger than the Moon. We then investigated the effects of such a collision.

If planetary accumulation takes place initially rather rapidly, as I think likely, then the initially rapid rate of heating will lead to prompt planetary differentiation, so that the two colliding objects are likely to have formed cores and their mantles may have been molten. At a collision velocity which must have been 11 km/sec or higher, solid rock is vaporized and molten rock is even more easily vaporized. Hence at the site of the major collision a large mass of vapor from rock decomposition products would be formed. After a small amount of expansion, these products will recondense. However, in the meantime, nongravitational forces in the form of pressure gradients will place a small part of the vaporized mass in orbit around the Earth. Most of the impacting object will be absorbed by the protoearth after less than one complete orbit away from the site of the collision.

The collision produces an extremely hot environment for the protoearth. I have estimated that the internal release of energy will expand the protoearth by about ten percent in radius. The disk of condensed vapors tends to clump and then shear (2), producing a strong tidal interaction with the protoearth, leading to a rapid spreading out and general recession from the protoearth toward the Roche limit, where accumulation of the Moon can begin. Dissipative friction keeps this material heated near the melting point. As a result of these processes, the Moon is formed strongly depleted in siderophile elements and the more volatile elements.

The protoearth is likely to lose practically all of its early atmosphere in this event, possibly in part because of the collision, but also because of the high temperature. There is evidence for

ORIGINAL PAGE IS
OF POOR QUALITY

this in the isotopic composition of atmospheric xenon. The fractionation pattern exhibited by the xenon isotopes is unique in nature but is consistent with the xenon being a remnant of a much larger reservoir that has been subject to distillation. Thus, if xenon has mostly thermally evaporated, then there would be no traces of lighter gases from the earlier protoearth atmosphere. The present atmosphere of the Earth would have been generated either from gases trapped in solid materials that accumulated onto the Earth after the major collision had taken place, or from materials that had not been outgassed from the interior before the collision. The persistence of the fractionation pattern in xenon suggests that the precollision component continues to dominate the abundance of that element.

The comparison of Earth to Venus as far as atmospheric content is concerned is subject to a compounding of possible errors of the order of factors of two or three, but nevertheless the differences are so great that a quantitative comparison is useful. In the Venus atmosphere the amount of ^{36}Ar is two orders of magnitude greater than in the terrestrial atmosphere, but there is only one-third as much ^{40}Ar (3,4). Since potassium is usually regarded as one of the more volatile elements, the reduced amount of it implied for Venus suggests that the initial and present atmosphere there is less than the initial Earth atmosphere by a similar small factor. Hence I would tentatively conclude that the ^{36}Ar presently in the Earth's atmosphere is reduced relative to that initially present by a factor of about 300, but the factor could be larger. The present ^{36}Ar is new argon, introduced since the collision. It follows that the present xenon, which is still mostly original fractionated xenon, has been depleted by a somewhat smaller factor. This seems just consistent with a gravitational escape fractionation process for the original xenon (5).

If it is assumed that the terrestrial planets formed entirely by accumulation of planetessimals, then the time scale for the process is of the order of 10^8 years (6). If, as I believe likely (7), the bulk of the terrestrial planets were formed as refractory precipitates in giant gaseous protoplanets which were then thermally evaporated, the subsequent accumulation of solids bearing volatile materials will still take roughly 10^8 years. It is clear that the giant collision discussed here must have taken place toward the end of this accumulation process, since so little gas was brought in afterwards. The time scale for the dissipation of the primitive solar nebula should not exceed about 10^6 years, so at the time under discussion the protoearth and the colliding object were isolated in space. Hence no additional gas can be added from the solar nebula. One possible origin for the colliding object is as a fragment of the unstable gaseous ring that led to the formation of the Earth giant gaseous protoplanet (8); smaller fragments are dynamically unstable against perturbation into eccentric orbits, and subsequently it is likely that a collision would occur with one of the terrestrial planets in a time of the order of 10^8 years. In principle, the colliding body could be a fragment of any of the unstable rings associated with the formation of protoplanets. However, the Moon will be formed almost entirely from material in the original protoearth, while the Earth will absorb most of the impacting material. Since the oxygen isotope ratios in the two bodies are the same, and since isotopic homogenization occurs rapidly around an orbit in the nebula, this is a mild argument for origin of the fragment in the same unstable ring as the protoearth.

REFERENCES

(1) Cameron, A.G.W. and Ward, W.R. (1976) Lunar Science VII.
(2) Ward, W.R. and Cameron, A.G.W. (1978) Lunar Science IX.
(3) Hoffman, J.H., Oyama, V.I., and von Zahn, U., (1980) J. Geophys. Res., **85**, 7871-7881.
(4) Hoffman, J.H., Hodges, R.R., Donahue, T.M., and McElroy, M.B. (1980) J. Geophys. Res., **85**, 7882-7890.
(5) Pepin, R.O., and Phinney, D. (1979) Preprint.
(6) Wetherill, G.W. (1980) Ann. Rev. Astron. Astrophys., **18**, 77-113.
(7) Cameron, A.G.W., DeCampli, W.M., and Bodenheimer, P. (1982) Icarus, in press.
(8) Cameron, A.G.W. (1978) Moon and Planets, **18**, 5-40.

MODELS OF THE SOLAR NEBULA: WHAT DETERMINED THE THERMAL STRUCTURE?

P.M. CASSEN, NASA Ames Research Center, Moffett Field, CA 94035

The time scale for the accumulation of kilometer-sized bodies (protoplanetary-sized, in some theories) in the solar nebula has been estimated to be 10^4 years or less. The time scale for the collapse of a protostellar cloud to form the protosun and its nebula is probably in the range 10^4-10^6 years. It therefore seems likely that the thermodynamic conditions under which volatiles become associated with the solid objects that eventually become the bodies of the solar system (planets, meteorites, comets, etc.) were those that prevailed during the formation of the nebula. The thermal structure during this stage was determined by the dissipative transport of mass and angular momentum. However, the processes by which this transport occurred would have been very different for a nebula with high angular momentum (as measured by an appropriate non-dimensional parameter) than for one with low angular momentum. In the former case, gravitational torques caused by shock-producing spiral density waves are expected; in the latter case, hydrodynamic turbulence may be the predominant mechanism of transport. We discuss quantitative formation models that illustrate these and other points that bear on the thermal structure of the nebula.

ORIGINAL PAGE IS
OF POOR QUALITY

ORIGINAL PAGE IS
OF POOR QUALITY

PREBIOTIC CARBON CYCLE: PHOTOCHEMICAL REDUCTION OF CO IN EARTH'S PRIMITIVE ATMOSPHERE. S. Chang, NASA Ames Research Center, Moffett Field, CA 94035, and A. Bar-Nun, Tel-Aviv University, Ramat Aviv, Israel.

Since the time of their earliest known occurrence, biological systems have been an integral part of the geochemical cycle of carbon (and other biogenic elements) involving, on the one hand, the transfer of carbon from atmosphere and hydrosphere into sediments and, on the other hand, the replenishment of the first two reservoirs as a result of the burial of sediments and the expulsion of volatiles from Earth's interior. Implicit in the view that biological systems arose by natural selection from chemical systems is the existence of an analogous prebiological carbon cycle driven by the natural fluxes of mass and energy at Earth's surface. Indeed, it may be hypothesized that a prebiotic cycle was a prequisite for the origin of life, and that the courses of planetary evolution responsible for the absence of such a cycle now on Venus and Mars are also responsible for the conditions inimical to life on these planets. In this context the origin of life on Earth and the origin of the geochemical cycle for carbon were inextricably intertwined. For these reasons, the development of models for the prebiotic carbon cycle would appear to be essential to gaining clearer understanding of the origin of life within the framework of geologic evolution. Among the data needed for development of such models are more quantitative assessments of geologically plausible pathways by which carbon in the prebiotic atmosphere may have been transferred into surface reservoirs through abiotic synthesis of organic matter.

The absence of a geological record makes a firm assessment of the atmospheric composition during Earth's first 0.8 billion years virtually impossible. Suppositions for the atmosphere range from H_2-rich, containing H_2-CH_4-NH_3-N_2-H_2O-H_2S, to H_2-depleted, containing CO-CO_2-N_2-SO_2. Although organic synthesis in hydrogen rich mixtures has been studied extensively, relatively little work has been reported on the CO-CO_2-N_2-H_2O system. Since solar radiation is the most abundant energy source in the atmosphere, photolytic investigations of the latter mixture are essential for an assessment of the full range of possibilities for the synthesis of organic matter on the primitive Earth. The photochemical experiments summarized below focused on the purely gas phase reactions of H_2O, CO, CO_2 and N_2; they were intended both to elucidate production mechanisms and to simulate reactions that could have occurred on the prebiotic Earth either above the cloud tops, at altitudes of about 10 km, where the abundance of water vapor is still considerable, or in an atmosphere containing few clouds.

Gas mixtures containing H_2O and CO with various proportions of H_2, CO_2, and N_2 were irradiated with 185 nm light or a simulated solar spectrum from which short wavelength uv was blocked by a filter cell containing O_2. The major products were H_2 and CO_2; alcohols, aldehydes, hydrocarbons, acetone and acetic acid were also formed; but no nitrogen-containing organic compounds were detectable. The initial step in the reactions involved photodissociation of H_2O molecules to yield hot H-atoms and hydroxyl radicals; the former reduced CO and recombined to H_2, while the latter oxidized CO to CO_2 and generated additional H-atoms. Changes in gas composition with irradiation time suggest that the organic products arose from a series of consecutive reactions in which CO was converted first to aldehydes and alcohols, which then were further hydrogenated to hydrocarbons. The overall apparent

ORIGINAL PAGE IS
OF POOR QUALITY

quantum yield for conversion of CO to organic carbon varied between 0.23 and 0.03 as a function of CO partial pressure between 0.39 and 0.004 atm. These results indicate that, even if the primordial atmosphere contained carbon only in the form of CO or a mixture of CO and CO_2, and no molecular hydrogen, a variety of organic compounds would have been produced by gas phase photochemical processes.

Upper and lower bounds can be crudely estimated for the "average" concentration of organic carbon in a hypothetical "global" ocean resulting from rain-out of compounds produced solely by photolysis of H_2O in the presence of CO. These calculations are made in the context of existing models for formation of the atmosphere and rely on estimates of primordial uv fluxes and terrestrial H and C inventories, coupled with the apparent quantum yields for synthesis of organic carbon. For the case in which the total carbon inventory was released as CO over 10^8 years, in 10^6 years, the concentration of organic carbon could have been as high as 0.02 M in a global ocean 30 m deep. For the case in which CO was released as a minor constituent and the inventory release time was 5×10^8 years, the concentration would have been 0.0004 M in 5×10^6 years.

Gas phase photochemistry was certainly only one of the many possible prebiotic production mechanisms for organic compounds. Other processes and reactants appear to have been required to produce nitrogen-bearing organic compounds (e.g., amino acids) in atmospheres containing N_2; and entire classes of heterogeneous reactions involving liquid-solid, gas-solid, and gas-liquid interfaces and other energy sources are virtually unexplored. It is uncertain whether the types and amounts of organic compounds discussed above were necessary or sufficient for the chemical evolution of organic matter to proceed beyond the monomer stage to attain higher levels of molecular organization. It is also unclear what the fate of these compounds would have been in the water column or how they may have been incorporated in sediments and at what rates. Resolution of these uncertainties awaits more detailed reconstructions of the prebiotic environment, more thorough accounting of the sources of simple organic compounds and the pathways for their conversion to more complex systems, and a better understanding of the interactions between organic and inorganic matter in that environment.

ORIGINAL PAGE IS
OF POOR QUALITY

ACCRETION OF VOLATILES. S. Chang, NASA Ames Research Center, Moffett Field, CA 94035, and J. F. Kerridge, University of California, Los Angeles, CA 90024

It seems likely that the terrestrial planets acquired their inventories of volatile elements as a late-accreting veneer of volatile-rich material [1, 2]. That hypothesis is reinforced by recent calculations which show that equilibration condensation could not have supplied the terrestrial planets with their initial endowments of C and N [3,4]. The hypothetical volatile-rich veneer is commonly identified with carbonaceous chondrite-like material [1,2]. Ages and elemental compositions of extant carbonaceous chondrites are broadly consistent with this view; we consider first the isotopic composition of C,H,N in such meteorites, as it bears upon this issue. Then, we consider the accretion of volatiles in the inner solar system within the context of nebular thermal history.

Reasonable estimates of $\delta^{13}C$, δD and $\delta^{15}N$ for the bulk earth may be made[2]; differences from these values, observed for some elements on Mars and Venus, are generally attributed to post-accretional fractionation [5,6]. Chondritic values may be found which are similar to terrestrial; for example, a mixture of CV3 chondritic material with a small proportion of CM2 material has been suggested as a suitable veneer [2].

Recent analyses of carbonaceous chondrites have revealed considerable inter- and intrameteorite variability in the isotopic composition of C,H,N [7,8,9]. For H and N this variability exceeds the fractionating capability of reasonable solar system processes. In addition, H and possibly N in meteorites and those terrestrial planets for which global estimates are available, are substantially enriched in the heavier isotope with respect to estimated protosolar values [10,11]. It seems likely that both nucleogenetic and mass-dependent processes have contributed to the observed variability. Ion-molecule reactions in interstellar clouds may account for the postulated mass-fractionation [10,12]. Apparently widespread survival of isotopic inhomogeneity in C,H,N has a number of implications for planetary accretion of these elements. It should be noted that this inhomogeneity could have been spatial, temporal or both.

First, the initial population of volatile-rich objects may have exhibited even greater isotopic variability than that currently observed in meteorites.

Second, different planets may have sampled different populations of volatile-rich objects. Assumptions of initially earth-like isotopic compositions of C,H,N for Mars and Venus may not be justified.

Third, temperatures in the inner solar system were apparently sufficiently low during the final stages of accretion to permit survival of C,H, N-bearing species. It is tempting to identify some of these with organic molecules synthesized in interstellar clouds.

Observations of interstellar clouds indicate that volatiles carried into the solar nebula would have included non-condensable gases; ices (H_2O, NH_3); organic compounds containing C,H,N,S,O; and carbonaceous grains. In accordance with the low temperature ($\sim$10 K) associated with the isothermal stage of protostellar collapse models, virtually all volatile elements, except H_2 and He, should have entered the nebula in the form of interstellar grains and interstellar atoms (including noble gases) and molecules (including CO, N_2, CH_4) accreted as mantles on grains. Apparently, on the sub-micron to micron scale of primitive dust and mantled dust grains, a variety of stellar and interstellar source regions could have been sampled, and heterogeneity in elemental, isotopic and molecular composition would have resulted. The degree

ORIGINAL PAGE IS
OF POOR QUALITY

to which heterogeneity would have been preserved must have been related to the thermal histories of these grains. Their thermal histories can be characterized by three stages: pre-accretion (gas-dust), accretion (planetesimal-parent body) and post-accretion (parent body); and volatiles could have been lost or gained (or both) at each of these stages.

In the past, most discussions of volatiles in primitive bodies focused on the origin of their carriers in the pre-accretion stage as a result of hypothetical nebular condensation processes. We emphasize the view that differential vaporization of pre-solar volatile carriers at both the pre-accretion and accretion stages may be a more relevant consideration for the distribution of volatile elements in the inner solar system. Throughout the adiabatic stage of protostellar collapse, the nebular thermal gradient within 5 AU would have caused evaporative and pyrolytic fractionation of the volatiles accreted into planetesimals. Moderately refractory carbonaceous grains (including presolar carriers of noble gases) could have survived and accreted closer to the protosun than ices, and ices closer than clathrates. After the nebula began to cool it would have become possible to condense, accrete and preserve the more volatile and thermally labile substances in regions where this was prevented earlier by higher temperatures. Thus, ices, clathrates and organic compounds in grains or planetesimals probably infiltrated the inner solar system late in nebular evolution by transport of material accreted at greater radial distances, by late infall of interstellar matter, or by accumulation of local material condensed and accreted from cooling residual gas (or combinations of these). We point out, however, that in carbonaceous meteorites the evidence for condensates formed by nebular gas-dust equilibration below 400 K is weak, at best [13].

The evidence of pervasive aqueous alteration on carbonaceous chondrite parent bodies [13] is consistent with a temporal separation between the accretion of anhydrous phases and their subsequent alteration by volatile-rich fluids. It is not clear, however, whether these hydrous fluids originated elsewhere within the parent bodies as a result of melting of solid phases (ices?) previously co-accreted with anhydrous phases or whether such fluids resulted from later addition of volatiles. In either case the accretion of parent bodies of aqueously-altered carbonaceous chondrites appears to be inconsistent with models of either homogeneous accretion or simple heterogeneous accretion of equilibrium condensates. Although these considerations suggest that similar models for planetary accretion may be inadequate, they are consistent with the hypothesis that the terrestrial planets acquired volatile inventories at a late stage in their accretion.

[1] Turekian K.K. & Clark S.P., EPSL 6, 346 (1969). [2] Anders E. & Owen T., Science 198, 453 (1977). [3] Lewis J.S. et al., Icarus 37, 190 (1979). [4] Fegley M.B., Meteoritics 16, 314 (1981). [5] McElroy M.B. et al., Science 194, 70 (1976). [6] Donahue T.M. et al., Science 216, 630 (1982). [7] Chang S. et al., Lunar Planet. Sci. IX, 157 (1978). [8] Kolodny Y. et al., EPSL 46, 149 (1980). [9] Robert F. & Epstein S., Geochim. Cosmochim. Acta 46, 81 (1982). [10] Geiss J. & Reeves H., Astron. Astrophys. 93, 189 (1981). [11] Kerridge J.F., Nature 283, 183 (1980). [12] Kerridge J.F., Lunar Planet. Sci. XI, 538 (1980). [13] Bunch T.E. & Chang S., Geochim. Cosmochim. Acta 44, 1543 (1980).

ORIGINAL PAGE IS
OF POOR QUALITY

MECHANISMS FOR THE VERTICAL TRANSPORT OF H_2O WITHIN THE MARTIAN REGOLITH. S. M. Clifford, Department of Physics and Astronomy, Univ. of Massachusetts, Amherst, MA. 01003.

Various lines of morphologic evidence suggest that substantial quantities of ground ice have existed in the equatorial regolith of Mars throughout its geologic history (1,2,3). However, recent calculations on the stability of ground ice in this region suggest that any ground ice, emplaced earlier than 3.5 billion years ago, may have long since been lost by evaporation to the atmosphere (4). It has been proposed that one possible explanation for the continued existence of ground ice in the equatorial regolith is that it may be replenished by subsurface sources of H_2O (5,6). For example, recent estimates of the planetary inventory of H_2O on Mars have ranged from a globally averaged layer some 10^2 - 10^3 meters deep (7,8). These estimates have led several investigators to suggest that Mars may possess subpermafrost groundwater systems of regional and possibly even global extent (1,5,6,9). The vertical transport of H_2O, from such groundwater systems, appears to be a viable mechanism for the replenishment of equatorial ground ice on Mars - even when the vertical distances separating the groundwater from the base of the ground ice layer are measured in kilometers.

In light of the photogeologic evidence for the widespread occurrence of volcanism on Mars (10), probably the most obvious mechanism for the vertical transport of H_2O is hydrothermal convection. This process has already been proposed as the possible cause of dark surface stains which appear just west of Olympus Mons (11) and has been suggested as a possible explaination for the origin of the numerous small channels which are frequently observed to eminate from the outside rims of craters in the heavily cratered terrain of Mars (5,12,13). Unfortunately, while hydrothermal convection may have been an important process for the vertical transport of H_2O on Mars - its magnitude and areal extent are, at present, impossible to quantify.

Similar difficulties arise when attempting to address the importance of shock-induced transport. Shock waves generated by earthquakes, impacts and explosive volcanic eruptions, can produce a transient compaction of water-bearing sediments which may force water up to the surface through regolith fractures and pores. During the great Alaskan earthquake of 1964, this process resulted in water and sediment ejection from the ground as far as 250 miles from the earthquake's epicenter (14). The energy released by this earthquake was approximately 2×10^{17} J (15) - or roughly equivalent to that of a 50 Megaton nuclear explosion. While the historical frequency of earthquakes of this magnitude on Mars may have been low, the martian cratering record provides abundant evidence that the planet has witnessed numerous events of a similar, and often much greater, magnitude. Indeed, the impacts that produced the larger basins such as Hellas and Argyre may alone have generated enough seismic energy to have replenished martian ground ice on a global scale. Even without these larger impacts, however, the density of craters found over much of the martian surface suggests that shock-induced transport resulting from smaller impacts may have been sufficient to replenish near surface ground ice over much of the planet.

Although far less dramatic and energetic than either of the two processes discussed above, perhaps the most important mechanism for the vertical transport of H_2O on Mars has been the process of thermal moisture movement (5). It has been known for almost 70 years that H_2O transport, in excess of that predicted by Fick's law, will occur in a porous medium under the influence of a temperature gradient - the direction of transfer being from warm to cold (16). The importance of this process on Mars is that the existence of a crustal geothermal gradient could provide the means necessary to thermally cycle H_2O between a deeply buried reservior of groundwater and the base of a near-surface layer of ground ice. Philip and deVries (17) and Taylor and Cary (18, 19) have formulated two different but widely accepted models for calculating the magnitude of this type of thermally driven moisture transfer. Despite the differences in approach, it has been shown that the final form of the flux equations for both models are identical (19,20). After Cary (21), we can describe the thermally driven vapor flux by the equation:

$$J_v = -\frac{\beta D_{AB} P_s H}{R^2 T^3} \frac{dT}{dz} \qquad (1)$$

where D_{AB} is the binary diffusion coefficient of H_2O in CO_2, P_s is the saturated vapor pressure of H_2O at a temperature T, H is latent heat of vaporization. R is the universal gas constant, and β is a dimensionless factor whose value (typically around 1.83 (20)) depends on regolith temperature, porosity, and water content. Making use of this equation we find that for a martian geothermal gradient of 45 K/km, the calculated flux of H_2O to the freezing front at the base of the ground ice layer is approximately 7×10^{-5} gm/cm^2 per martian year. At this rate, over the course of martian geologic history, the martian geothermal gradient could supply enough H_2O from a subpermafrost groundwater system to replenish a layer of ground ice nearly 1.7 km thick. Further, unlike the first two processes discussed in this abstract, this transport will occur on a continuous and global basis for as long as there exists a geothermal gradient and subsurface reservoir of H_2O.

Inspection of Equation 1 reveals that, for the higher temperatures expected at depth, the flux of H_2O leaving the groundwater surface greatly exceeds that which finally reaches the freezing front at the base of the ground ice layer. This difference is due to the decrease in saturated vapor pressure which occurs with decreasing temperature. As shown by Jackson et al. (22), once a closed system has been established (ie., the ground ice capacity of the near-surface regolith has been saturated under conditions where the ice exists in stable equilibrium with the atmosphere) a dynamic ballance of opposing fluxes is achieved. As water vapor rises from the warmer depths to the colder regolith above, it will condense - creating a circulation system of rising vapor and descending liquid condensate. In those instances where the system is not closed (eg., where ground ice is not in equilibrium with the atmosphere

H_2O TRANSPORT WITHIN THE MARTIAN REGOLITH

Clifford, S. M.

- such as near the martian equator) it is possible for H_2O transport to occur from the freezing front at the base of the ground ice to those areas undergoing depletion. Transport in this subfreezing region may occur via thin films of unfrozen water which are adsorbed on mineral surfaces (23,24). These films have been shown to exist down to very low temperatures - especially in the presence of potent freezing point depressors such as $CaCl_2$ (25). As before, this transport through the frozen regolith of Mars may be thermally driven (23,24).

A more detailed discussion of these processes and their potential importance to the distribution of equatorial ground ice on Mars is in preparation.

Acknowledgement: This research was supported under NASA Grant NSG 7405.

References: 1) Johansen, L. A. (1978) Proc. 2nd Colloq. Plan. Water and Polar Processes, 109. 2) Allen, C. C. (1979) Icarus 39, 111. 3) Rossbacher, L. A., and S. Judson (1981) Icarus 45, 39. 4) Clifford, S. M., and D. Hillel (1982) JGR (in press). 5) Clifford, S. M. (1980) Proc. 3rd Colloq. Planet. Water, 68. 6) Clifford, S. M. (1981) Proc. 3rd Int. Colloq. Mars, 44. 7) Pollack, J. B. and D. C. Black (1979) Science 205, 56. 8) Lewis, J. (1980) personal communication. 9) Carr, M. H. (1979) JGR 84, 2995. 10) Greeley, R. and P. D. Spudis (1981) Rev. Geophys. Space Phys. 19, 13. 11) Morris, E. C. (1980) NASA TM 81776, 162. 12) Pieri, D. (1979) Ph.D. Thesis, Cornell University. 13) Newsom, H. E. (1980) Icarus 44, 207. 14) Waller, R. M. (1968) The Great Alaskan Earthquake of 1964: Hydrology Part A., pp. 97-116, Pub. Nat. Acad. Sci.. 15) Stacey, F. D. (1977) Physics of the Earth, John Wiley & Sons. 16) Bouyoucos, G. J. (1915) J. Agr. Res. 5, 141. 17) Philip, J. R. and D. A. deVries (1957) Trans. A.G.U. 38, 222. 18) Cary, J. W. (1963) J. Phys. Chem. 67, 126. 19) Taylor, S. A. and J. W. Cary (1964) Soil Sci. Soc. Proc. 28, 167. 20) Jury, W. A., and J. Letey, Jr. (1979) Soil Sci. Soc. Amer. J. 43, 823. 21) Cary, J. W. (1966) Soil Sci. Soc. Amer. Proc. 30, 428. 22) Jackson, R. D., D. A. Rose and H. L. Penman (1965) Nature 205, 314. 23) Cary, J. W., R. I. Papendick, and G. S. Cambell (1979) Soil Sci. Soc. Amer. J. 43, 3. 24) Miller, R. D., J. P. G. Loch, and E. Bresler (1975) Soil Sci. Soc. Amer. Proc. 39, 1029. 25) Anderson, D. M., and A. R. Tice (1973) in: Ecological Studies. Analysis and Synthesis, Vol. 4., pp. 107-124, Springer-Verlag Berlin.

ORIGINAL PAGE IS
OF POOR QUALITY

ORIGINAL PAGE IS
OF POOR QUALITY

COMPARISON OF He, Sr AND Pb ISOTOPIC VARIATIONS IN THE ICELANDIC 'HOTSPOT', M. Condomines[1], K. Gronvold[2], P.J. Hooker[1], R.K. O'Nions[1] and E.R. Oxburgh[1], [1]Dept. Earth Sciences, University of Cambridge; [2]Nordic Volcanological Institute, Reykjavik, Iceland.

Basalts erupted in the neovolcanic zones of Iceland and Reykjanes Ridge exhibit a broad correlation between $^{87}Sr/^{86}Sr$ and $^{206}Pb/^{204}Pb$ ratios (1,2,3,4) indicating a coherence between Rb/Sr and U/Pb in the reservoirs that have contributed to the source of Icelandic magmas. These observations are commonly reconciled by models involving interactions between a depleted reservoir in the upper mantle and a relatively undepleted reservoir (generally the lower mantle). In the most simple models it would be anticipated that ^3He and other primordial rare gases should be principally stored in the less depleted reservoir and that $^3He/^4He$ should exhibit a coherent relationship with $^{87}Sr/^{86}Sr$ for example in erupted volcanics.

This possibility has been investigated in detail through the analysis of samples from the actively rifting neovolcanic zone of Iceland. Glassy samples appear to be the most appropriate for analysis of $^3He/^4He$ and the present suite includes basaltic pillow margins and hyaloclastites and glassy intermediate and acid lavas. He concentrations in these rocks are typically ca 10^{-8} cc g^{-}, some two orders of magnitude lower than most oceanic ridge glasses. He has been separated by total fusion with a typical blank of < 2×10^{-9} cc STP; which results in negligible blank corrections in most cases.

$^3He/^4He$ ratios are variable along the active rift zones and R/Ra $((^3He/^4He)_{rock}/(^3He/^4He)_{atmosphere}) \geqslant 5 \leqslant 24$ for basaltic rocks, and R/Ra ≈ 1 for intermediate and acid rocks. $^{87}Sr/^{86}Sr$ ratios measured on the same samples show no clear correlation with $^3He/^4He$, as might be expected from a simple 'hotspot' model. A crucial question however is whether the measured ratios in the erupted basalts are equal to the mantle values. There are two processes which may lead to their modification: isotope fractionation either during magma generation or in a shallow crustal reservoir, or during post-eruptive cooling of the lava. The comparatively low He concentrations in Icelandic basalts may be ascribed to the low pressure at magma eruption compared to ocean ridge basalts. As a consequence the trapped He is residual and may be isotopically fractionated relative to the He in the primitive parental magam. This may be the explanation for the difference between the ratios in gas samples (R/Ra ≈ 8.5) and lavas (R/Ra ≈ 5) in the presently active Krafla region of N. Iceland. Contamination of magmatic He by crustal He (with lower $^3He/^4He$ ratio) may occur either during transfer of magma through the crust or its residence in a magma chamber. In this respect it is noteworthy that the highest $^3He/^4He$ ratios are found in fissure basalts from the Reykjanes peninsula, and the lowest for central volcanoes in the centre of Iceland (Askja and Krafla) in parallel with the $\delta^{18}O$ and $(^{230}Th/^{232}Th)$ variations (5,6). The origin of low $^3He/^4He \approx 1$ in intermediate and acid rocks remains unclear. Post-eruptive equilibration with atmospheric He or formation of the magmas by melting or assimilation of hydrothermally altered crustal rocks with R/Ra ≈ 1 remain possible explanations at this stage.

Overall the results obtained from the classic Icelandic hotspot are not readily reconcilable with simple hotspot models. High-level processes operative within the crust leading to the modification of $^3He/^4He$ ratios must be better understood before all observed variations of $^3He/^4He$ can be ascribed to variability existing within mantle reservoirs.

ICELANDIC 'HOTSPOT'

ORIGINAL PAGE IS
OF POOR QUALITY

Condomines, M. et al.

REFERENCES

(1) Hart, S.R., Schilling, J.G., Powell, J.L. (1973) Nature Phys. Science, 246, 104. (2) Sun, S.-S., and Jahn, B.M. (1975) Nature 255, 527. (3) Sun, S.-S., Tatsumoto, M. and Schilling, J.G. (1975) Science, 190, 143. (4) Cohen, R.S. and O'Nions, R.K. (1982), J. Petrol. (in press). (5) Muehlenbachs, K., Anderson, A.T., Sigvaldason, G.E. (1974) Geochim. Cosmochim. Acta, 38, 577. (6) Condomines, M., Morand, P., Allegre, C.J. and Sigvaldason, G. (1981) Earth Planet. Sci. Lett. 55, 393-406.

ORIGINAL PAGE IS
OF POOR QUALITY

VOLATILES WITHIN THE EARTH'S MOON. J. W. Delano*, Dept. of Earth and Space Sci., State University of New York, Stony Brook, N. Y. 11794 (*Present address: Dept. of Geological Sci., State University of New York, Albany, N. Y. 12222)

INTRODUCTION

Most lunar samples are highly depleted in the volatile elements relative to the Earth and chondrites. Rb-Sr and U-Pb isotopic analyses indicate that this has been characteristic of the Moon's crust and upper mantle (i.e., $\lesssim$ 500 km depth) probably since its origin. Some investigators [e.g., 1] have extrapolated those results and concluded that the *whole* Moon must necessarily be poor in volatiles. The purpose of this abstract is to demonstrate that such generalizations appear to be incompatible with data derived from lunar volcanic glasses. Although significant portions ($\gtrsim$ 50%) of the lunar mass must indeed be highly depleted in volatiles, that feature may *not* persist through the entire Moon.

LUNAR VOLCANIC GLASSES

At least nineteen chemical varieties of volcanic glass are known to occur in the Apollo sample collection [2]. Those glasses are furnishing new constraints on the petrology and chemistry of differentiated regions within the Moon at depths of 400 to 500 km [e.g., 3]. Of importance to this symposium are the volatile elements associated with these glasses (Table). Those elements provide clear evidence for a gas phase having been present at the time of the volcanic eruptions [e.g., 4].

Isotopic analyses of the surface-correlated Pb [5] have shown that the reservoir within the Moon, from which these volatiles leaked, had two important characteristics. First, the source had a low (< 29) value for the $^{238}U/^{204}Pb$ ratio indicating that the reservoir was far richer in volatiles than other portions of the Moon. Second, the reservoir had a U-Pb model age of $\sim$ 4.6 AE, in contrast to the value of 4.3-4.4 AE observed in most lunar rocks [6].

These data suggest that an undifferentiated, volatile-rich reservoir occurs within the Moon at depths > 500 km. The implication is that the Moon accreted inhomogeneously. As discussed in the next section, more information about this component can be acquired through analysis of lunar volcanic glasses.

TRAPPED VOLCANIC GAS

The nature of the gas phase that accompanied some volcanic eruptions on the Moon has been deduced principally by analyses of condensates occurring on the surfaces of the volcanic glasses [e.g., 7]. Although *bona fide* samples of the actual gas have been sought, they have proven elusive and difficult to interpret [8,9]. However, carefully selected spheres of lunar volcanic glass should be capable of clarifying this situation.

Recently, the author identified a vesicle (i.e., gas bubble) sealed within a sphere of Apollo 15 green volcanic glass (Figure). This vesicle has a volume of 1.1×10^{-2} mm^3 and appears to be intact. Consequently, this sample may still contain gas expelled from the deep lunar interior at 3.35 AE [8]. Although vesicles are not common occurrences, they are nonetheless known to be present in other lunar volcanic glasses [10]. Chemical and isotopic analyses, particularly of the noble gases within such specimens, could furnish crucial data pertaining to the nature of the volatile component within the Moon. Furthermore, the data might also contain important new constraints bearing on the Moon's origin, since the noble gases trapped within the vesicular volcanic glasses would not suffer from the vagueness of provenance that has often afflicted studies of lunar rocks and breccias [e.g., 11] in the past.

Although vesicle-bearing, lunar volcanic glasses are not common, neither

ORIGINAL PAGE IS
OF POOR QUALITY

are they prohibitively rare [e.g., 10]. These samples could, therefore, provide answers to some of the most fundamental questions in lunar science.

REFERENCES

[1] Taylor S. R. (1982) Planetary Science: A Lunar Perspective (see page 300). [2] Delano J. W. and Livi K. (1981) Geochim. Cosmochim. Acta, 45, p. 2137-2149. [3] Chen H.-K. et al. (1982) Proc. Lunar Planet. Sci. Conf. 13th (in press). [4] Chou C.-L. et al. (1975) Proc. Lunar Sci. Conf. 6th, p. 1701-1727. [5] Meyer C., Jr., et al. (1975) Proc. Lunar Sci. Conf. 6th, p. 1673-1699; Silver L. T. (1974) EOS (Trans. Amer. Geophys. Union), 55, p. 681; Tatsumoto M. et al. (1973) EOS (Trans. Amer. Geophys. Union), 54, p. 614-615; Tera F. and Wasserburg G. J. (1976) Lunar Science-VII, p. 858-860. [6] Oberli F. et al. (1978) Lunar Planet. Sci.-IX, p. 832-834. [7] Wasson J. T. et al. (1976) Proc. Lunar Sci. Conf. 7th, p. 1583-1595. [8] Podosek F. and Huneke J. (1973) Earth Planet. Sci. Lett., 19, p. 413-421. [9] Eugster O. et al. (1980) Proc. Lunar Planet. Sci. Conf. 11th, p. 1565-1592. [10] Heiken G. H. et al. (1974) Geochim. Cosmochim. Acta, 38, p. 1703-1718; Heiken G. and McKay D. (1978) Proc. Lunar Planet. Sci. Conf. 9th, p. 1933-1943. [11] Niemeyer S. and Leich D. A. (1976) Proc. Lunar Sci. Conf. 7th, p. 587-597; Caffee M. et al. (1981) Proc. Lunar Planet. Sci. 12B, p. 99-115.

ELEMENTAL CONSTITUENTS OF LUNAR VOLCANIC GAS

B	Ar	Ag	Xe
C	Cu	Cd	Au
F	Zn	In	Hg
Na	Ga	Sb	Tl
S	Ge	Te	Pb
Cl	Br	I	Bi

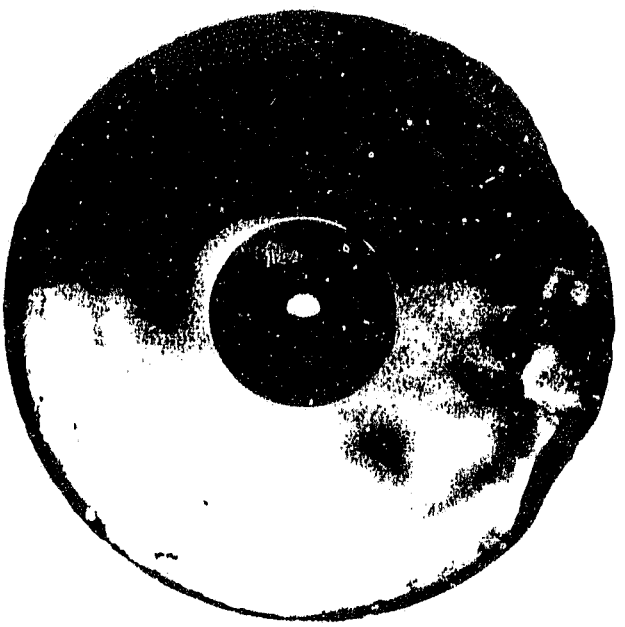


Figure caption:
Transmitted light photomicrograph of a sphere (455μm diameter) of Apollo 15 volcanic green glass containing a 138μm vesicle at its center. This glass belongs to chemical group B [2].

STABLE CARBON ISOTOPES IN MIDOCEANIC BASALTIC GLASSES.

David J. Des Marais, Ames Research Center, NASA, Moffett Field, CA 94035,
H. Sakai, Okayama University, Misasa, Tottori-ken, 682-02 Japan, and
J. G. Moore, U. S. Geological Survey, Menlo Park, CA 94025

Studies of the earth's carbon cycle and its history require that we know the average stable isotopic composition of carbon in the crust and upper mantle. Early estimates (1,2) of this value ($\delta^{13}C_{PDB}$ = -6 to -7) were obtained by mass balance estimates of the sedimentary carbon reservoir. This approach, though very useful, suffers both from inaccurate estimates of reduced sedimentary carbon inventories and from the possibility that the average carbon isotopic composition of the sedimentary reservoir has varied over geologic time, due to isotopically selective carbon losses to the lower crust. Igneous rocks offer another opportunity to measure the average crustal carbon isotopic composition, provided that any isotope effects associated with petrogenesis are understood. Midoceanic basaltic glasses were selected for this work because they constitute our best opportunity to analyze rocks which are free of sedimentary contamination. Previous work (3,4,5) has suggested that igneous rocks contain carbon whose isotopic composition is substantially depleted in ^{13}C, relative to the overall average composition reported for sediments. The present work indicates that, at least for midoceanic basaltic glasses, the carbon which is depleted in ^{13}C is not indigenous to the glasses.

Each of six midoceanic basaltic glasses was combusted sequentially at three temperatures (Table 1) using the method employed previously for lunar rocks (6). The lower combustion temperatures are intended to remove surficial carbon contamination while causing minimal losses of the indigenous carbon. That minimal indigenous carbon is lost is consistent with the very small losses at temperatures below 750°C of sulfur, which is presumed to be indigenous. Carbon released below 750°C is depleted in ^{13}C and probably represents surficial organic contamination.

The pattern of carbon abundances measured when the glasses melt support other observations (7,8) that carbon content is proportional to the depth of eruption. Note that the Hawaiian basalt #71-AP3 was erupted subaerially and apparently lost essentially all of its indigenous carbon. The ^{13}C-depleted trace of carbon that remains is likely either contamination or else a residuum which is highly fractionated isotopically. The carbon released from the glasses which erupted beneath the ocean has a remarkably constant carbon isotopic composition ($\delta^{13}C_{PDB}$ ranges from -5.8 to -6.4). Because carbon from such diverse localities is so similar, it appears that carbon isotopic fractionation associated with the petrogenesis of these glasses has been minimal. This isotopic composition resembles that of carbon dioxide which emanates from deep sea hydrothermal vents (9) and which is trapped in vesicles in midoceanic basaltic glasses (5). This isotopic composition is also remarkably similar to estimates obtained for the sedimentary carbon reservoir. If these new isotope values from the midoceanic basalts and hydrothermal vents indeed represent the isotopic composition of juvenile carbon, then the average carbon isotopic composition of crustal sediments has been remarkably constant over geologic time.

CARBON ISOTOPES IN MIDOCEAN BASALTS

ORIGINAL PAGE IS
OF POOR QUALITY

D. J. Des Marais et al.

Table 1. Carbon and sulfur data from the basaltic glasses.

Sample and Eruption Depth, m.	Temperature, °C	Carbon Abundance, μg/g	$\delta^{13}C_{PDB}$	Sulfur Abundance, μg/g
Cayman Trough	450	18	-24.8±0.2	2
(18°39'N,81°46'W)	710	20	- 9.3±0.2	1
6600m	1220	164	- 6.3±0.2	990
FAMOUS	488	34	-24.8±0.1	2
(~36°N,33°W)	730	17	- 6.7±0.2	2
#519-4; 2690m	1230	136	- 6.2±0.1	810
Galapagos Ridge	450	5.6	-21.6±0.2	0.1
(0°50'N,86°W)	750	0.5	-15.8±0.4	0.5
#717-3; ~2500m	1200	68	- 6.4±0.2	1310
Galapagos Ridge	450	3.6	-26.2±0.3	2
(as above), #714-1-A	1200	99	- 5.8±0.1	1360
Island of Hawaii	460	14	-22.1±0.1	0.5
#71 AP3; 0m (land)	740	4	-20.9±0.1	0.7
	1230	1.9	-23.7±0.3	38
Kilauea East Rift	440	19	-24.4±0.3	1
(19°40'N,154°30'W)	700	3	-20.2±0.2	2
#JM-1742; 1400m	1220	22	- 6.1±0.3	904

References

(1) Wickman F. E. (1956) Geochim. Cosmochim. Acta 9, 136-153.

(2) Craig H. (1953) Geochim. Cosmochim. Acta 3, 53-92.

(3) Hoefs J. (1973) Contr. Mineral. and Petrol. 41, 277-300.

(4) Fuex A. N. and Baker D. R. (1973) Geochim. Cosmochim. Acta 37, 2509-2521.

(5) Pineau F., Javoy M. and Bottinga Y. (1976) Earth and Planet Sci. Lett. 29, 413-421.

(6) Des Marais D. J. (1978) Proc. Lunar Planet. Sci. Conf. 9th, 2451-2467.

(7) Anderson A. T. (1975) Reviews Geophys. Space Sci. 13, 37-55.

(8) Moore J. G. (1979) Nature 282, 250-253.

(9) Welhan J. A. and Craig (1979) Geophys. Res. Lett. 6, 829; and Welhan J. A., personal communication.

ORIGINAL PAGE IS
OF POOR QUALITY

HIGH ELECTRICAL CONDUCTIVITY IN CARBON-BEARING ROCKS AND METEORITES: IMPLICATIONS FOR PLANETARY INTERIORS AND ASTEROIDS

A. G. Duba, University of California, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94550
T. J. Shankland, Los Alamos National Laboratory, University of California, Los Alamos, NM 87545

The electrical conductivity of the carbonaceous chondrite Allende has been measured to 950°C under controlled oxygen fugacity. The conductivity measured at a given temperature is a strong function of heating rate, similar to results reported for oil shale (Duba, 1982). Unlike oil shale with similar carbon content, the electrical conductivity of Allende remains high during dehydration (around 10^{-5} S/m) an indication that there is initial free carbon present at grain boundaries in this meteorite, as suggested by Duba and Shankland (1982) in their discussion of the high conductivity at 25°C observed by Brecher et al (1975) for carbonaceous chondrites. As the hydrocarbons which comprise Allende are pyrolyzed in flowing CO/CO_2 mixtures, the conductivity increases with time at constant temperature, again similar to behavior observed for oil shale. Such behavior is not observed for other rocks or for minerals at similar conditions. By 400°C, conductivity as high as 0.01 S/m is observed, depending on heating rate. The conductivity remains high and approaches 0.1 S/m until about 900°C, where it begins to decrease as a function of both time and temperature, apparently the result of volatilization of carbon in the unconfined sample.

Because graphite and amorphous carbon have conductivities of 10^4 to 10^5 S/m while dry rocks and minerals have values from 10^{-12} to 10^{-1}, it is not surprising that a small amount of carbon has such a large effect. These observations for oil shale and Allende allow us to speculate on the implications for planetary interiors if carbon is present as a grain boundary phase.

Examination of literature conductivity data for olivine and MgO indicates that small amounts of carbon at grain boundaries can strongly influence conductivity. Even at 1000°C where mantle minerals may have conductivities as high as $10^{-2.5}$ S/m, calculations indicate that about 100 ppm of carbon contamination at grain boundaries would cause conductivities as high as 1 S/m. Such concentrations of carbon are consistent with carbon petrology in mantle rocks. An interconnected amorphous or graphitic carbon phase on grain boundaries could provide sufficiently high conductivities to explain high conductivity layers in the mantle at subsolidus temperatures. Presumably a zone of carbon-enhanced conductivity is a less sensitive temperature probe than a partial melt zone would be.

If the early solar system experienced a T Tauri phase of the sun with high interplanetary electric and magnetic fields postulated by Sonett et al (1970), it is likely that a portion of the carbonaceous chondritic material present would have been subjected to considerable inductive heating because of its high electrical conductivity. With the reducing conditions implicit in the heating of a carbon-rich body in a vacuum, asteroid differentiation could have proceeded at a later time after condensation than that required by heating due to short-lived radionuclides.

ORIGINAL PAGE IS
OF POOR QUALITY

REFERENCES

Brecher, A., Briggs, P. L., and G. Simmons, The Low-Temperature Electrical Properties of Carbonaceous Meteorites, E.P.S.L. 28, 37-45, 1975.

Duba, A. G., The Electrical Conductivity of Oil Shale to 900°C, submitted to Fuel, 1982.

Duba, A. G. and Shankland, T. J., Free Carbon and Electrical Conductivity in the Earth's Mantle, Geophys. Res. Letts., in press, 1982.

Sonett, C. P., Colburn, D. S., Schwatz, K., and Keil, K., The Melting of Asteroidal Sized Bodies by Unipolar Dynamo Induction from a Primodial T Tauri Sun, Astrophys. Space Sci., 7, 446-488, 1970.

Work performed under the auspices of the Office of Basic Energy Sciences of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48 and by Los Alamos National Laboratory under contract number W-7405-ENG-36.

ORIGINAL PAGE IS
OF POOR QUALITY

GEOCHEMISTRY OF FLUIDS IN THE TERRESTRIAL UPPER MANTLE. David H. Eggler and Mark E. Schneider, Geosciences Department, The Pennsylvania State University, University Park, PA 16802

There are three important questions regarding fluid chemistry in the upper mantle: (1) Is there a free fluid and how much is there? (2) What are the gas species in the fluid? (3) What solids are dissolved in the fluid?

The first question cannot be answered by examination of nodular materials from the mantle or by experiment. The other two can. There are at least two lines of evidence that mantle fO_2 is sufficiently oxidizing that fluids are H_2O-CO_2, not CH_4-H_2O or CH_4. One is fO_2's calculated from mantle-derived nodules (Fig. 1), although those fO_2's are in conflict with "intrinsic" fO_2's from olivines and spinels (e.g., Arculus and Delano, 1981). The second is that the source region of kimberlites and carbonatitic magmas, presumed to be carbonated peridotite, must have fO_2 at EMOD (Fig. 1), essentially at the nodular values.

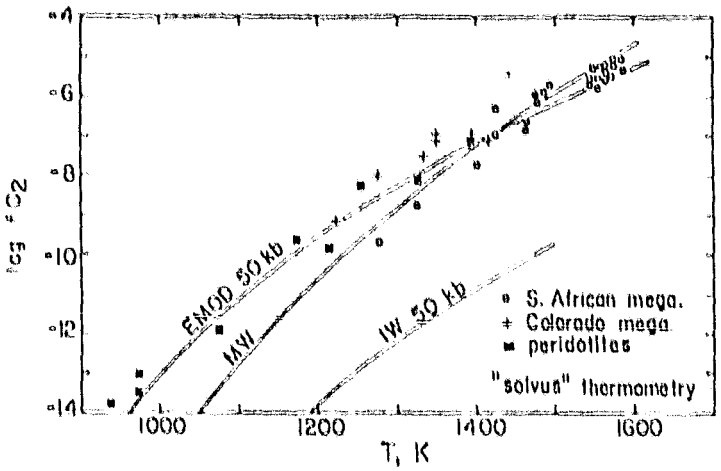


Fig. 1. Oxidation state of olivine-orthopyroxene-ilmenite-bearing nodules from kimberlites, calculated from the equilibrium $2Fe_2O_3 + 4FeSiO_3 = 8FeSi_{0.5}O_2 + O_2$, at a calculated paleopressure. Reference buffers: EMOD, enstatite-magnesite-olivine-diamond; MW, magnetite-wustite, TW, iron-wustite.

Fig. 2 shows that at fO_2 conditions of EMOD, or the equivalent EMOG in the graphite field, the mantle fluid (if there is a fluid) is dominantly H_2O at high pressures, with subordinate CO_2, and either H_2O-CO_2 or CO_2-H_2O at lower pressures, depending on temperature. At subsolidus conditions, compositions of H_2O-CO_2 fluids are buffered by amphibole peridotite assemblages or by carbonated peridotite assemblages, at least within their buffering capacity (Eggler, 1978a, 1978b; Wyllie, 1978, 1979). The effects of H_2O, CO_2, and buffered H_2O-CO_2 fluids are now well documented.

It can be seen in Fig. 2 that if upper-mantle fO_2 were substantially lower than EMOG-EMOD, fluids present would be dominated by CH_4. The effect of CH_4 upon melting of peridotite has been shown to be similar to that produced by H_2O (Eggler and Baker, 1982), but the total effects of CH_4 upon mantle mineralogy and upon solubilities of solids in fluids have yet to be evaluated.

Acting upon the conviction that fO_2's are not so reduced that CH_4 dominates, and mindful of the now numerous evidence from nodular mineralogy and from isotopic signatures that metasomatism has affected the source regions of alkaline magmas, solubilities of solids in H_2O-CO_2 fluids have been investigated. Fluids in equilibrium with individual peridotite minerals and with the assemblages enstatite-forsterite-phlogopite (+ kyanite) and enstatite-forsterite-diopside-spinel-amphibole have been directly analyzed in experiments at 15-20 kbar and 750-1100°C. Amphibole peridotite fluids

ORIGINAL PAGE IS
OF POOR QUALITY

Eggler, D. H. and Schneider, M. E.

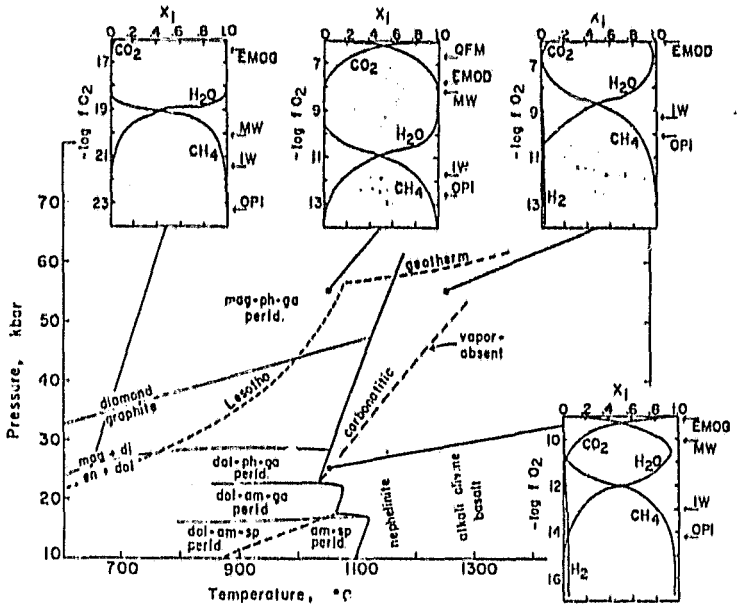


Fig. 2. Mineralogy of peridotite containing small amounts of H_2O and CO_2. Mag=magnesite, ph=phlogopite, ga=garnet, sp=spinel, dol=dolomite, am=amphibole. All assemblages contain olivine and two pyroxenes. The heavy line is the vapor-buffered solidus. Boxes show compositions of fluids at 4 P-T conditions as a function of fO_2, calculated with MRK thermodynamic functions.

more silica than metals. Alkali metasomatism would be accompanied by approx. equal molar alumina and considerable silica, which would alter peridotites to pyroxenites.

The region near 90 km, near the lower pressure limit of the carbonate stability and the upper limit of amphibole stability, is the most likely region of significant metasomatic alteration. This region probably yields highly alkaline magmas by partial melting, but highly alkaline kimberlite magmas appear to come from greater depths.

REFERENCES

Arculus R.J. and Delano J. W. (1981) GCA 45, 899-913.

Eggler D.H. and Baker D.R. (1982) Adv. High-P Res.

Eggler D. H. (1978) AJS 278,305-343

Wyllie P.J. (1978) J.Geol.86,687-713

Wyllie P.J. (1979) Am.Min.64,469-500

principally contain silica, alumina, and alkalies in total amounts less than 3 wt percent in H_2O fluids and less than 0.5 wt percent in H_2O-CO_2 fluids. Phlogopite peridotite fluids are broadly similar but contain a minimum of 16 wt percent solute. A typical fluid coexisting with en-fo-phlogopite at 15-20 kb, 1100°C contains 72 % SiO_2, 14 % Al_2O_3, 5.3 % MgO, and 8.4 % K_2O. Fluid with molar $H_2O/(H_2O+CO_2)$ = 0.8 at the same conditions contains 65 % SiO_2, 17 % Al_2O_3, 3.5 % MgO, and 15 % K_2O.

All fluids in equilibrium with peridotite assemblages are shown in Fig. 3. It is evident that only CO_2-bearing fluids dissolve alkalies in excess of alumina and that all fluids dissolve much

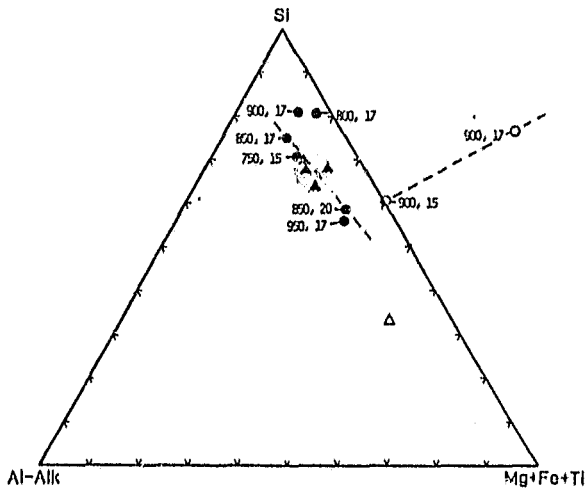


Fig. 3. Molar compositions of fluids in equilibrium with amphibole peridotite (circles) and phlogopite peridotite (triangles). Open symbols: H_2O-CO_2 fluid, closed symbols: H_2O fluid. Numbers indicate t, °C and P, kb, of amph. peridotite runs.

ORIGINAL PAGE IS
OF POOR QUALITY

ICE-POOR REGOLITH DEVELOPMENT AND DESTRUCTION ON SMALL ICY-DUSTY OR ICY-ROCKY OBJECTS, F.P. Fanale and J.R. Salvail, Planetary Geosciences Division, Hawaii Institute of Geophysics, University of Hawaii at Manoa.

Development of ice-poor/silicate-rich "mantles" on cometary objects has been described by several investigators and has been the subject of at least one detailed quantitative model (Brin & Mendis, 1979; Brin, 1980). Ice sublimation is the creator, the "boiler"/disrupter, and the launcher of ice-poor regoliths. In our model, the major physical processes which are quantitatively described are: 1) Modification of the periodic orbital thermal "wave" that reaches buried condensed volatiles, by the finite thermal conductivity of any overlying ice-poor regolith, 2) Modification of the vapor outflux by the finite and changing vapor diffusivity of the incipient regolith, 3) The effect of volatile flux and preferential launching of smaller grains on the thickness and grain size distribution of the regolith, 4) Continuous feedback of developing regolith properties into the thermal and vapor transport described in "1." and "2." 5) The compound effects of multiple passes.

The model includes latent heat effects, H_2O and CO_2 properties, obscuration by streaming dust, and possible transitions from one dominant volatile loss mechanism to another (see below). In its preliminary form, it does not currently include scattering effects of ice halos or global effects such as systematic launching of grains from one region on a comet accompanied by their systematic accretion on another. Also, because of the complexity of the mantle development model, we have not yet coupled it with sophisticated insolation histories for comets with appropriate rotation rates, orbits and obliquities. Rather we have so far considered only two latitudes on comets with archtypical orbits and an obliquity of 90 degrees. We hope to consider more interesting and realistic orbits, obliquities and rotation rates.

Despite the preliminary stage of the investigation, our results suggest some general inferences: An object in an "archtypical" short period cometary orbit can undergo at least three distinct phases of regolith development including 1) A molecular diffusion phase, when the gas:silicate ratio of the outflux is high but the gas flux is very low. This phase is most effective ~ 3-5 AU and a comet in near circular at this heliocentric distance would probably first develop a water ice and dust regolith poor in other volatiles and then, ultimately, a permanent silicate-rich regolith. In this phase, the regolith inhibits vapor flux and thermal flux via its porosity and absorptive properties which, in turn, are determined by grain size distribution and prior history. 2) A phase (onset ~3AU) in which the thermally controlled volatile flux can in turn control the regolith geometry by regolith-disrupting processes, commencing when gas pressure exceeds lithostatic pressure. The transition from molecular diffusion through a fixed regolith matrix to volatile flux control of the matrix geometry might be analogous in some ways to the transition from still evaporative processes to boiling. During the molecular diffusion phase launching of even small grains by H_2O sublimation alone (without participation of other ices) is extremely ineffective. However, during the disruption/boiling phase, H_2O sublimation rates approach free sublimation of dusty H_2O ice, and can generally launch a substantial dust flux, albeit still strongly weighted to finer grains. 3) At small heliocentric distances (~1AU) launching of grains can become indiscriminate and at very small distances (~.3AU) even H_2O sublimation can launch large boulders. However the dependence of launch ability on heliocentric distance and ice composition is greatly moderated by latent heat effects. Table I gives a rough idea of these dependencies. However it should be borne in mind that the values in this table are for idealized thermal histories - a fixed subsolar point or a fixed 60 degrees incidence angle - and may not be generally applicable to comets. During the indiscriminate launch phase, ejectae have the same H_2O: rock flux as the comet mass, and severe erosion occurs in steady state and is not accompanied by any ice poor-regolith retention.

An ice poor regolith is "self-protecting" and mantle growth is "self-aggravating" because a mantle modulates the thermal shock experienced at the buried ice interface near perihelion. Even with thermal transfer in radiative, conductive and convective modes, a static mantle of sufficient thickness and fineness can protect and enlarge itself because of its insulating properties and further suppress the volatile flux diffusing up through it for any given thermal history. Also, the thicker the existing regolith the less vulnerable it is to physical disruption by an excess of vapor pressure over its lithostatic pressure. Hence whether a particular comet undergoes the above transitions depends on whether incipient regolith growth achieved since the last perihelion is sufficient to protect the mantle against the next perihelion. If it is, then the mantle will

ORIGINAL PAGE IS
OF POOR QUALITY

irreversibly evolve to permanence. If not, the comet will cycle reversibly through the preceding stages until it is globally dissipated. It would appear that any virginal icy rocky object placed in an orbit with perihelion <1AU would have little chance of developing a permanent regolith (except for "global" effects mentioned above which are not considered here). Hence it would disappear after, say, hundreds of passes. On the other hand, any postulated existing initial mantle of ~4cm or more could protect itself even at a perihelion distance of ~1.7AU if only H_2O ice were present. A much greater initial thickness of ice poor mantle would be required if the comet expected to survive a typical Apollo perihelion passage at 0.7AU without beginning to cycle. If an ice-poor regolith did survive initial passage intact, it would stay in the molecular diffusion stage and would grow asymptotically with time to a thickness of perhaps several tens to hundreds of meters - depending on exact vapor diffusivity and heliocentric distances. Whether the "cometary" core of such an object would be detectable by remote sensing techniques in lieu of density measurements is a fascinating question, and the water flux itself is probably the most telling clue to such an object. The greater the sensitivity of gas flux measurements, and the greater the range of heliocentric distances at which these can be made on objects in eccentric orbits, the more chance of evaluating the actual nature of cometary regolith evolution by observing phenomena such as the sharp hypothesized transition between increasing molecular diffusion and the boiling/disruption phase or predicted strong variations in the H_2O: dust ratio.

In general, the main difference between our model results and those of others is that, where appropriate, we allow Knudsen flow (where mantle properties control the flux) and not continuum flow be the rate limiting mode of vapor transport. As a consequence, the inhibiting effect of any incipient regolith which develops toward aphelion is a very effective barrier to development of what would otherwise be a multicentimeter ice poor regolith.

Table I. Minimum* Requirements for Launching Silicates From a Comet With Albedo = 0.1, Radius = 2 km

Maximum Launchable (Radius, cm)	Required H_2O [CO_2] Flux, g/cm^{2}sec	Required T for Flux, °K	Required Insolation erg/cm^{2}sec	Required AU if Subsolar Point	Required AU 60° Latitude
1×10^{-4} (dust)	1.2×10^{-9} [2.3×10^{-9}]	151 [97]	2.6×10^{4} [4.5×10^{3}]	6.9 [16.8]	4.9 [11.9]
1×10^{-2} (sand)	1.1×10^{-7} [2.2×10^{-7}]	170 [113]	4.6×10^{4} [9.4×10^{3}]	5.2 [11.5]	3.7 [8.2]
1×10^{0} (pebbles)	1.1×10^{-5} [2.0×10^{-5}]	195 [135]	3.7×10^{5} [1.4×10^{5}]	1.8 [3.0]	1.3 [2.2]
1×10^{2} (boulders)	9.7×10^{-4} [1.7×10^{-3}]	229 [168]	2.8×10^{7} [1.1×10^{7}]	0.21 [0.34]	0.47 [0.76]
1×10^{3} (large boulders)	9.3×10^{-3} [1.7×10^{-2}]	250 [191]	2.6×10^{8} [1.0×10^{6}]	0.07 [0.11]	0.05 [0.08]

* assume launch accomplished with diurnal maximum flux

References: Brin, G.D. and Mendis D.A., Dust Release and Mantle Development in Comets, The Astrophysical Journal, 229, 402-408, 1979. Brin, G.D., Three Models of Dust Layers on Comet Nuclei, The Astrophysical Journal, 237, 265-279, 1980.

ORIGINAL PAGE IS
OF POOR QUALITY

A CONDENSATION-ACCRETION MODEL FOR VOLATILE ELEMENT RETENTION.

B. Fegley, MIT, Cambridge, MA 02139.

Chemical equilibrium calculations are widely used to discuss elemental fractionations among chondrites and planets. These calculations are now being applied to models of volatile element retention by the terrestrial planets. Recent work (1-4) suggests that equilibrium mechanisms can supply the planetary inventories of halogens, alkalis, and phosphorus. This same body of work also strongly suggests that, at least at high temperatures, equilibrium mechanisms cannot supply the planetary inventories of C, H, and N. These results, plus the earlier work of Anders and Owen (5) and Sill and Wilkening (6), indicate that accretion of meteoritic material and low temperature volatile-rich phases may supply the planetary inventories of C, H, N, and the noble gases. The present work attempts to quantify a condensation-accretion model for retention of these elements. This work deals with elemental abundances and does not address the question of isotopic fractionations.

Figure 1 illustrates the composition of low temperature equilibrium condensate as a function of T, P, and distance for an adiabatic model of the solar nebula (1-4). The calculations for this figure were done assuming incomplete conversion of CO to CH_4 and N_2 to NH_3 (4). The condensation temperatures for pure phases are: $H_2O(s)$ 160 K, $NH_4HCO_3(s)$ 155 K, $CO_2(s)$ 71 K, $Xe \cdot 6H_2O(s)$ 59 K, $CO \cdot 7H_2O(s)$ 50 K, $CH_4 \cdot 7H_2O(s)$ 48 K, $N_2 \cdot 7H_2O(s)$ 46 K, $Kr \cdot 6H_2O(s)$ 42 K, $Ar \cdot 6H_2O(s)$ 38 K. If $NH_4HCO_3(s)$ does not form, then $NH_4CO_2NH_2(s)$ condenses at 142 K. If $CO_2(s)$ does not form, then $CO_2 \cdot 6H_2O(s)$ condenses at 68 K. Unclathrated CO and N_2 condense in the vicinity of 20 K.

Previous workers (6) pointed out that the clathrate which forms is actually a solid solution whose composition is temperature dependent. This effect has been considered in this work and the composition of the clathrate in Fig. 1 has been calculated as a function of temperature. In this case the initial clathrate is practically pure $Xe \cdot 6H_2O(s)$. Once the temperature is below the condensation point of pure CO clathrate, however, the clathrate composition is dominated by CO and N_2. Further decreases in temperature lead to a progressively N_2-rich clathrate. The amounts of different noble gases in the clathrate are also temperature dependent. Xe is quantitatively retained in the clathrate below 59 K. Kr is completely condensed below 50 K and Ar is completely retained below 40 K.

Sill and Wilkening (6) also considered clathrate condensation in the solar nebula. Several important differences exist between this work and their results. They considered formation of CH_4 clathrate which is only a very minor component in this work. This is due to kinetic inhibition of the CO to CH_4 conversion (4). Second, they did not consider clathrates of any other carbon and any nitrogen compounds. Third, they concluded that clathration discriminates against the lighter noble gases at progressively lower temperatures. The present work shows that as the temperature decreases the amounts of Kr and Ar included in the clathrate increase.

Can accretion of low temperature equilibrium condensate supply the volatile inventories of the terrestrial planets? Table 1 displays H/C, H/N, and C/N ratios (gram/gram) for terrestrial surface reservoirs (atmosphere, crust, and oceans) from Barsukov et al (7), for three bulk earth models from Smith (8), for low temperature equilibrium condensate at 3 T points, for a special case called no clathrate, and for carbonaceous chondrites (5).

Table 1 and Figure 1 illustrate several important points. First, accretion of low temperature equilibrium condensate cannot match the terrestrial H/C, H/N, and C/N ratios for surface reservoirs or for bulk earth models. Linear combinations of any mixture of low temperature equilibrium condensate fail to match all three ratios, although the surface H/C ratio can be matched. Slow diffusion of gaseous molecules into H_2O ice may prevent clathrate formation. In this case (no clathrate) the condensate composition is frozen in at 70 K until $\sim$ 20 K where CO and N_2 condense. (These low temperatures were probably not reached in the solar nebula. In any case the match between terrestrial volatile ratios and low temperature equilibrium condensate then becomes worse). The no clathrate case is also unable to match the terrestrial volatile ratios.

Anders and Owen (5) suggested that accretion of small amounts of C3V-like material could supply terrestrial volatiles. However, the data in Table 1 show large differences between the terrestrial and meteoritic volatile ratios for all potential meteoritic volatile carriers. What about mixtures of low temperature equilibrium condensate and known meteorite classes? Again, linear combinations of these materials cannot match the terrestrial volatile ratios.

Volatile Accretion Model

Fegley, B.

ORIGINAL PAGE IS
OF POOR QUALITY

The concept that accretion of low temperature condensate and meteoritic material provided the volatile inventories of the terrestrial planets is very attractive. These preliminary results illustrate that the concept is difficult to quantify using known meteorite classes and condensate compositions from equilibrium calculations. Two approaches to this problem are now being pursued. First, using either the low temperature equilibrium condensate or different carbonaceous chondrites as one component, what are the compositions of additional components? Second, can the additional components be identified with materials such as comets, Brownlee particles, volatile-rich carriers in meteorites? Results illustrating compositions required to match the volatile inventories of the terrestrial planets will be given and discussed in terms of a condensation-accretion model.

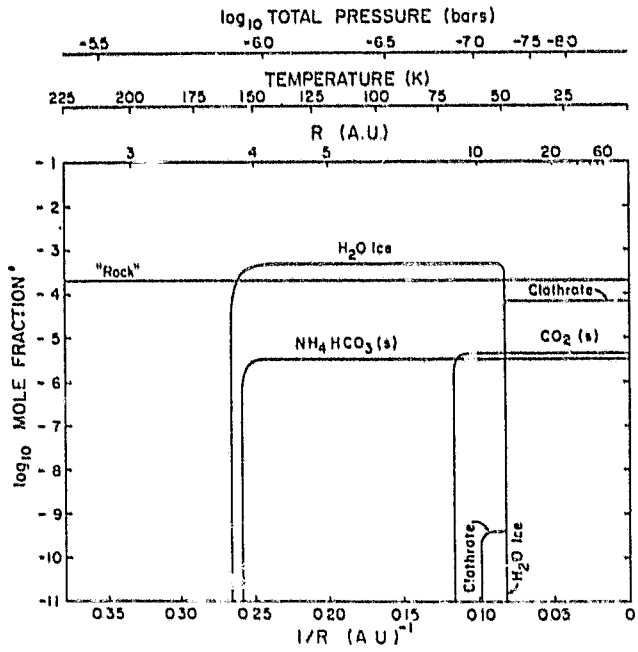
References: (1) Barshay, S.S. (1981) Ph.D. thesis, MIT; (2) Fegley, B. (1982) Proc. 13th LPSC, in press, (1981) Meteoritics **16**, 314, Fegley, B. and Lewis, J.S. (1980) Icarus **41**, 439–455; (3) Lewis, J.S. et al (1979) Icarus **37**, 190–206; (4) Lewis, J.S. and Prinn, R.G. (1980) Astrophys. J. **238**, 357–364; (5) Anders, E. and Owen, T. (1977) Science **198**, 453–465; (6) Sill, G.T. and Wilkening, L.L. (1978) Icarus **33**, 13–22; (7) Barsukov et al. (1980) Proc. 11th LPSC, 765–773; (8) Smith, J.V. Proc. 8th LPSC, 333–369.

Acknowledgments: I thank A.G.W. Cameron and J.S. Lewis for supporting this research under NASA Grant NGR-22-007-269 and NGL-22-009-521, respectively.

Table 1
Elemental Ratios (g/g)

Material	H/C	H/N	C/N
Earth:			
Barsukov	2.5	67	29
Smith SI	0.06	3	50
SII	0.41	3.7	8.9
SIII	1.0	3.1	3.1
Condensate:			
150 K	22	19	0.9
70 K	9.5	19	2.0
30 K	0.9	2.6	2.8
No clathrate	9.5	19	2.0
Chondrites:			
CI	0.24	2.8	13
CM2	0.39	5.9	15
CSV	0.07	8.2	110
CSO	0.21	17	78

CONDENSATION-ACCRETION MODEL
VOLATILE RICH PHASES



ORIGINAL PAGE IS
OF POOR QUALITY

HOMOGENEITY OF ARGON AND THE $^{40}Ar/^{36}Ar$ RATIO WITHIN THE SOLID EARTH, David E. Fisher, Rosenstiel School Of Marine And Atmospheric Science, University of Miami, Miami, Fl 33149

Argon fills a unique niche in the spectrum of volatile tracer elements, being: (1) a pure volatile, i.e., forming no solid compounds; (2) composed of two isotopes which have always been gases and one (^{40}Ar) which has spent most of its terrestrial life as a solid-state element, so that the ratio $^{40}Ar/^{36}Ar$ in the various terrestrial reservoirs will reflect the degassing history of those reservoirs; and (3) being heavy enough to have been quantitatively retained in the earth's atmosphere throughout geologic time. All three of these factors are shared by only one other element, xenon, in which the radiogenic component is so small as to be difficult or impossible to measure in many samples of geologic interest.

Ozima (1) first recognized that since today's atmospheric $^{40}Ar/^{36}Ar$ value is fixed at 295.5, determination of the value of this ratio within the solid earth would define the degassing history of the earth. The fact that oceanic basalts quantitatively trap magmatic argon has been coupled with Ozima's suggestion to suggest and investigate several models of earth degassing (2-6). But recent measurements both on basalts from various tectonic regimes and on ultramafic nodules which have been shown to trap interior-earth rare gases have raised the question of whether there exists in fact a unique $^{40}Ar/^{36}Ar$ ratio which can be described as characterizing the interior of the earth (7-14). Most tectonic earth models would predict a heterogeneous argon isotopic distribution: an upper depleted mantle will have lost nearly all its primordial Ar, and therefore will be low in total ^{36}Ar yet high in $^{40}Ar/^{36}Ar$ due to 40K-decay into the depleted system; an undepleted lower mantle will have more radiogenic ^{40}Ar but lower $^{40}Ar/^{36}Ar$ due to retention of much of its primordial ^{36}Ar.

In order to investigate these possibilities one must first disentangle the components of measured Ar values. In this paper I address the question of how to identify pristine trapped deep-earth gases, and to what extent the measured data reflect such values rather than values modified by exchange with atmospheric gases.

Oceanic basaltic glasses in general show high ($\sim 10^4$) but not identical $^{40}Ar/^{36}Ar$ values. I present new data here on many glass, interior rock, and altered rock samples to show clearly the effect of sea water alteration: lower ratios and higher total ^{36}Ar contents. Plots of $^{40}Ar/^{36}Ar$ vs. $(^{36}Ar)^{-1}$ for several samples from specific locations demonstrate that the glasses have quantitatively trapped and retained magmatic Ar. The values obtained from all samples for which sufficient data are available are remarkably similar, considering that they embrace the Atlantic, Pacific, and Caribbean; they show $^{40}Ar = 60\text{-}175 \times 10^{-8}$ cc/gm, $^{40}Ar/^{36}Ar \geq 7500$, and $^{36}Ar \leq 1.5 \times 10^{-10}$ cc/gm. Lower values of the ratio and higher values of ^{36}Ar are in all cases due to sea water alteration and/or atmospheric contamination. Data are also presented for an African non-tholeiitic basalt which has trapped magmatic argon and retained it quantitatively: $^{40}Ar = 400 \times 10^{-8}$ cc/gm, $^{40}Ar/^{36}Ar \geq 8000$, $^{36}Ar \leq 2 \times 10^{-10}$ cc/gm. This indicates a somewhat less depleted magmatic source.

Previous data in ultramafic nodules from Africa and Hawaii have shown $^{40}Ar/^{36}Ar$ similar to the atmospheric ratio, and models of mantle degassing and earth accumulation have been built on the postulate that these ratios represent the deep, undepleted mantle (5, 15). I present here data on two Hawaiian nodules that show clearly the presence of atmospheric (non-mantle)

ORIGINAL PAGE IS
OF POOR QUALITY

Ar; when this is accounted for the Ar isotopic ratios and absolute values are similar but not identical to the basaltic data quoted above.

In summary, for all samples in which it has been possible to clearly identify the trapped magmatic component there is a measureable difference in total Ar content and isotopic ratio in the samples from different tectonic regimes, but the difference is surprisingly small. Near-atmospheric ratios seem to disappear when atmospheric contamination is properly monitored.

References

1. Ozima, M., 1937. Geochim. Cosmochim. Acta, 39: 1127-1134.
2. Schwartzman, D.W., 1973b. Geochim. Cosmochim. Acta, 37: 2479-2495.
3. Hamano, Y. and Ozima, M., 1978. In: E.C. Alexander, Jr. and M. Ozima (Eitors), Terrestrial Rare Gases. Center for Academic Publications, Tokyo, pp. 155-172.
4. Fisher, D.E., 1978. In: E.C. Alexander, Jr. and M. Ozima (Editors), Terrestrial Rare Gases. Center for Academic Publications, (Tokyo), pp. 173-183.
5. Hart, R., Dymond, J. and Hogan, L., 1979. Nature (London), 278: 156-159.
6. Tolstikhin, I.N., Drubetskoy, Ye.R. and Sharas'kin, A.Ya., 1978. Geokhimiya, 4: 514-520.
7. Dymond, J. and Hogan, L., 1973. Earth Planet. Sco. Lett., 20: 131.
8. Dymond, J. and Hogan, L., 1978. Earth Planet. Sci. Lett., 38: 117-128.
9. Fisher, D.E., 1971. Earth and Planet. Sci. Lett., 12: 321-324.
10. Fisher, D.E., 1981a. Nature (London), 290: 42-44.
11. Kaneoka, I. and Takaoka, N., 1978. Earth Planet. Sci. Lett., 39: 382.
12. Kaneoka, I., Takaoka, N. and K., Aoki, 1978. In: E.C. Alexander, Jr. and M. Ozima (Editors), Terrestrial Rare Gases. Center for Academic Publications, pp. 71-83, Tokyo.
13. Saito, K., Basu, A.R., and Alexander, E.C., Jr., 1978. Earth Planet. Sci. Lett., 39: 274-280.
14. Takaoka, N. and Nago, 1978. Nature (London), 276: 491-492.
15. Manuel, O.K., 1979. In: E.C. Alexander Jr. and M. Ozima (Editors), Terrestrial Rare Gases. Center for Academic Publications, Tokyo, pp. 85-92.

ORIGINAL PAGE IS
OF POOR QUALITY

A REVIEW OF DISTRIBUTIONS OF SULFUR IN SOLAR SYSTEM OBJECTS

Everett K. Gibson, SN7, Geochemistry Branch, NASA-JSC, Houston, TX 77058

This contribution will review the abundances and distributions of sulfur as a volatile phase in planetary materials. Exploration of the solar system during the last decade has shown the element sulfur to be ubiquitous. It plays a very active role in the chemical processes operating beneath the surface, on the surface and in the atmosphere, and is essential to all life forms that we know. The geochemical versatility of sulfur may be attributed to its ability to exhibit a variety of valence states (-2, 0, +2, +4, +6) and to combine with both metals and non-metals via either covalent or ionic bonds. At the present time, sulfur abundances have been measured in situ on five planetary materials: earth, moon, meteorites, Mars and Venus. Remote measurements of sulfur abundances have been obtained for Jupiter, Io, the rings of Saturn, the sun, and at least one comet. Sulfur compounds have been observed in the interstellar dust clouds.

A summary of sulfur abundances for the five types of planetary objects sampled is shown in Fig. 1. As a group, meteorites contain the greatest sulfur abundances. Chondritic meteorites have sulfur contents up to 6% for CI carbonaceous chondrites. Within this class of meteorites sulfur is present in the reduced sulfide form, elemental sulfur, and oxidized sulfate. Distributions of these components reflect the past history of the primitive objects. Within the H, L, and LL chondrites the total sulfur abundances is very constant ($2.2 \pm 0.8\%$). Enstatite chondrites contain abundances approaching those of CI chondrites but all of the sulfur is present as sulfide. Achondrites typically have sulfur abundances ranging from 200 to 11,400 μgS/g (1). Eucrites typically range from 1000 to 1500 μgS/g whereas howardites have somewhat higher concentrations (1, 2, 3). It has been noted that sulfur abundances of shergottites are similar to terrestrial dolerites (2).

Average sulfur content of the earth crust has been given as 260 μgS/g (4). Despite the apparent low sulfur abundance for the earth's crust, sulfur has played a major role in the earth's history. The core of the earth is believed to be mostly iron with minor amounts of alloyed nickel with upwards of 10 to 20% sulfur, and Brett (5) has suggested that sulfur played an active role during core formation. The extraction of sulfur from the earth's crust and mantle during core formation has left the crust with abundances which are low when compared to other values shown in Fig. 1. Sulfur species observed in volcanic gases and emanations are H_2S, S_2, SO_2, and SO_3, with SO_2 dominating at magmatic temperatures (>1200°C) and with H_2S the major component at lower temperatures. Sulfur has recently been observed to be the major component outgassing from the active hydrothermal submarine vents. Presence of H_2S and CO_2 in the water surrounding the vents, along with sulfur-oxidizing bacteria, shows that sulfur plays an important role in the ecosystems and life related processes of primitive organisms. Basalts from the terrestrial ocean floors (MORB) range between 60 and 800 μgS/g (6), whereas subaerially extruded basalts contain 50 to 2000 μgS/g. It has been shown that sulfur contents decrease with degassing. Naldrett et al. (7) noted that Archean basalts had a wide range of sulfur abundances (0 to 8000 μgS/g) but an average of 1000 μgS/g was observed for most samples. High sulfur content of Archean basalts relative to recent basalts (mean of 200-400 μgS/g) suggest retention of sulfur as a result of the rapid accumulation of Archean volcanic rocks and their limited interaction with seawater.

Lunar basalts were found (8) to range from approximately 400 μgS/g for the Apollo 12 and 15 basalts to 2600 μgS/g for the Apollo 11 and 17 basalts. High sulfur contents are correlated with the high FeO and Ti contents of the basalts.

ORIGINAL PAGE IS
OF POOR QUALITY

Sulfur in Solar System Objects

Gibson, E. K.

Apollo 11 and 17 mare basalts were saturated with respect to sulfur, whereas those from Apollo 12 and 15 were undersaturated (8). Lunar anorthosites typically contain less than 60 μgS/g. The low sulfur contents of the crustal materials is probably a consequence of the fact that plagiclase cannot dissolve sulfur. The high sulfur contents of lunar basalts implies that the lunar mantle is enriched in sulfur. Sulfur abundances of lunar soils can be accounted for by mixing of various components present in the regolith.

The surface of Mars has been analyzed in two sites by the Viking landers. Data returned from the XRF instruments showed a regolith enriched in sulfur (2.0 to 3.5% S) (9). Samples of the upper crust (duricrust) were found to contain the greatest sulfur concentrations. Since the sampling sites appear to be areas where evaporation or sublimation processes have operated, the analysis may represent analysis of salts deposited within the regolith and are not representative of the planet as a whole. Similar sulfur enrichments have been noted from cold desert regions on earth (10).

Clark (11) has examined the Venera 13 and 14 XRF data of Surkov et al.(12) and found that the V-14 site contained about 0.1 to 0.5% sulfur. Data from Venera 13 could not be deconvoluted in a satisfactory manner. Data for the basalt-like sample at V-14 is similar in sulfur abundances to those found for lunar basalts, achondrites and terrestrial basalts. The atmosphere of Venus has been shown to contain sulfur species--especially sulfuric acid--within selected cloud regions. Formation of sulfuric acid appears to be the result of a series of photochemical reactions culminating in the formation of SO_2 and SO_3.

It can be seen from the data given in Fig. 1 that sulfur's abundances range from a major element in selected meteorites to a trace element in some basalts. Distribution of sulfur reflects the oxidation-reduction conditions and processes which operate on the particular solar system object. Sulfur is indeed an important planetary volatile whose abundances and distributions reflect major solar system processes and formational conditions.

References: 1. Moore C.B. (1981) per. comm.; 2. Gibson E.K. (1982) unpublished data; 3. Moore C.B. (1971) Handbook of Elemental Abundances in Meteorites (B. Mason, ed.); 4. Fairbridge R.W. (1972) Encyclopedia of Geochemistry and Environmental Sciences; 5. Brett P.R. (1973) Geochim. Cosmo. Acta 37, 165-170; 6. Moore J.G. and Fabbi B.P. (1971) Contrib. Min. Petrol. 33, 118-127; 7. Naldrett A.J. et al. (1978) Can. J. Earth Sci. 15, 715-728; 8. Gibson E.K. et al. (1977) Proc. Lunar Sci. Conf. 8th, 1417-1428; 9. Clark B. et al. (1982) J. Geophys. Res. (in press); 10. Gibson E.K. et al. (1982) J. Geophys. Res. (in press); 11. Clark B. (1982) per. comm.; 12. Surkov Y.A. et al. (1982) Anal. Chem. 54, 957A-966A.

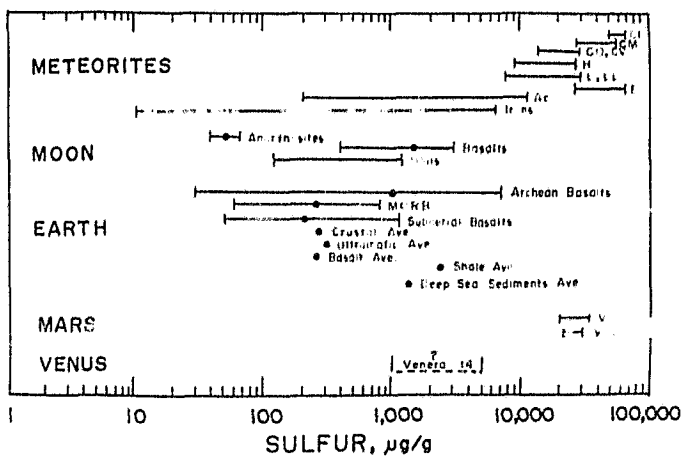


Figure 1. Sulfur abundances for five types of solar system objects which have had sulfur measurements carried out in situ.

ORIGINAL PAGE IS
OF POOR QUALITY

SPUTTERING OF VOLATILE RESERVOIRS

P. K. Haff, W.K. Kellogg Radiation Laboratory, Caltech, Pasadena, California 91125.

The term "sputtering" refers to the ejection from a "target" of atoms or molecules following the impact of an energetic atom or ion. Values of the sputtering yield can range from much less than unity to upwards of 1000. At low energies, below a few keV/amu, billiard ball-like collisions lead to ejection of surface molecules. At higher energies, energy deposited in electron excitation along the path of the incident particle is ultimately converted to kinetic energy of atomic motion, again with the subsequent ejection of target particles. High energy sputtering yields are often orders of magnitude greater than low energy yields. By combining theoretical models with laboratory experiments, we can gain some idea of the role which sputtering plays in the transport of volatile materials on planetary bodies.

There are two principal sources of energetic ions occuring naturally in the solar system: the solar wind and planetary magnetospheres. The solar wind may interact directly with planets and satellites not protected by a magnetic field, such as Venus, Mars, and the Moon. Planetary magnetospheres contain energetic particles which can impinge upon satellites and upon the planet itself. Thus, the Galilean satellites, the icy satellites of Saturn, and the Earth itself are all subjected to magnetospheric particle impact. Sputtering of airless bodies can lead to loss of matter to space, to redistribution of matter across a planetary body, and to generation of a thin sputter induced coronal atmosphere. Sputtering of a body already having an atmosphere can lead to depletion of this atmosphere, and to preferential loss of the lighter constituent molecules.

Examples of volatile transport mediated by sputtering are

(1)Direct solar wind impact into the upper atmospheres of Venus and Mars is retarded by shock-wave formation, but to the extent that the impinging particles can interact directly, otherwise gravitationally bound gases can be lost to space. Thus, on Venus He is lost by collision with solar protons at a rate which may be as large as 10^5 cm-2 s-1. This is about 10% of the assumed He outgassing rate.

(2)Likewise, to the extent that solar particles impinge the Martian atmosphere, CO_2 may be lost. While photochemical loss mechnisms predominate for O, sputtering is an efficient way in which C and N can be removed from Mars. Sputtering of the Martian atmosphere over geological times is calculated to have been capable of removing nearly 97% of the mass of the initial Martian N component and about 33% of the initial CO_2. Thus, N is removed preferentially with respect to CO_2, and lighter isotopes of C, N, and O are removed preferentially with respect to their heavier isotopes. Thus the present N poor atmosphere and the observed fractionation of the C and N isotopes can be attributed at least partly to sputtering.

(3)The atmosphere of the Earth itself is subjected to sputtering by precipitated magnetospheric particle fluxes. Using a hard-sphere model of low energy O-O collisions, Torr et al. [1974] calculated that earth satellite data on O precipitation meant that O escape fluxes as large as ~10^9 cm-2 s-1 could be attained locally. Averaging over the area of the earth and over time implies an escape flux of $3X10^7$ cm-2 s-1.This is comparable to the escape flux of H. Unpublished calculations by Haff which account for the O-O interaction in a more realistic way suggest that the loss of O by atmospheric sputtering is perhaps only 10^6 cm-2 s-1. This smaller result is only about 1% of the H escape flux, but nevertheless represents an interesting and possibly important escape route for O atoms.

SPUTTERING OF VOLATILE RESERVOIRS

ORIGINAL PAGE IS
OF POOR QUALITY

Haff P. K.

(4)Arnold [1979] and Lanzerotti et al [1981] have considered the question of whether solar wind impact could erode patches of ice on the Moon which might otherwise build up in permanently shadowed coldtraps in the lunar polar regions. The enhanced sputtering yields associated with energetic ion impact on H_2O ice [Brown et al, 1978; Cooper, 1982] have led to the conclusion [Lanzerotti et al, 1981] that ion erosion could be an effective mechanism for limiting the occurence of such ice pockets.

(5)In the Jovian system, possible SO_2 frost on Io, an Io SO_2 atmosphere, and the frozen H_2O surfaces of Europa, Ganymede and Callisto are all candidates for magnetospheric sputter erosion. As originally pointed out by Matson et al [1974], charged particle sputtering offers one mechanism which is energetic enough to inject heavy atoms like S, O, Na, and K into the Jovian magnetosphere. Haff et al [1981] calculated that sputtering of an unprotected Ionian surface by corotating S ions might be able to sustain the observed Na and K clouds, but would be unable to provide a sufficiently high escape flux to maintain the S torus. Sputtering of an SO_2 atmosphere would be able to supply the S torus only if the atmosphere were hot enough that the exobase lay at an altitude of ~2 R_{Io}.

(6)Sieveka and Johnson [1982] have studied the global transport of H_2O molecules on the icy Galilean satellites due to both low energy and high energy sputtering. Depending on the local surface temperature, sputtering can compete with sublimation as the most effective mechanism for volatile transport. Thus, especially in the polar regions, sputtering is the primary determinant of water mobility.

(7)Lanzerotti et al [1978] suggested that sputtering could lead to the formation of a thin atmosphere on otherwise airless satellites. Watson [1981] developed this idea in some detail, predicting an exospheric corona with a column density on the order of $5X10^{12}$ cm-2 on Europa.

(8)In the Saturnian system, sputtering plays a similar role. Morfill et al [1982], Cheng et al [1982], and Haff et al [1982] have discussed the role of ice sputtering near Saturn. They find that sputtering is unable to account for the H ring atmosphere, but that the lifetime of E-ring ice motes (~135y) is influenced strongly by low energy sputtering by co-rotating O ions. Atmospheric coronae are ill-developed,because the icy satellites are small compared to the Galilean satellites, but sputtering is a prime candidate for the source of heavy ions, presumably O, which have been detected inward from Tethys.

REFERENCES:Arnold, J. Geophys. Res. 84 ,5659, 1979; Brown et al, PRL 40, 1027, 1978; Cheng et al, JGR 87, 4567, 1982 Cooper, PhD Thesis, Caltech, 1982; Haff et al, sub. to Icarus, 1982; Haff et al, J. Geophys. Res. 86, 6933, 1981; Lanzerotti et al, Geophys. Res. Letters 5, 155, 1978; Lanzerotti et al, J. Geophys. Res. 86, 3949, 1981; Matson et al, Ap.J. 192, L43, 1974; Morfill et al, J. Geophys. Res., in press, 1982; Sieveka and Johnson, Icarus, in press, 1982; Torr et al, J. Geophys. Res. 79 ,5267 ,1974; Watson et al, Proc. Lun. Plan. Sci. Conf. 11, 2479,1980; Watson, Proc. Lun. Planet. Sci Conf. 12, 1569, 1981.

Work supported in part by NASA [NAGW-202 and -148] and by NSF [PHY79-23638].

ORIGINAL PAGE IS
OF POOR QUALITY

METAL-SILICATE REDOX REACTIONS: IMPLICATIONS FOR CORE-MANTLE EQUILIBRIUM AND THE OXIDATION STATE OF THE UPPER MANTLE.

R.D. Holmes and R.J. Arculus, Research School of Earth Sciences, Australian National University, P.O. Box 4, Canberra, A.C.T. 2600 Australia.

It is generally accepted that the core was formed early in the history of the Earth by the separation of a denser, Fe-rich metallic phase from a lighter silicate residue. However, the details of this process are still widely disputed, including such fundamental parameters[1] as the composition of the metallic phase, its original distribution within the proto-Earth, and its possible equilibrium or disequilibrium with the primitive mantle.

Recent measurements[2,3] of the intrinsic oxygen fugacity (fO_2) of mantle-derived peridotite nodules have suggested that the current redox state for the bulk of the upper mantle is close to or slightly below that defined by the iron-wustite (IW) buffer. One such investigation[4] concluded that these oxidation states were only about two $\log_{10} fO_2$ units more oxidized than that required for saturation with an Fe-Ni metal, and suggested that redox conditions during core separation would be controlled by the Fe-analogue of the Metal-Orthopyroxene-Olivine ("MOO") oxygen buffer: $2M + O_2 + M_2Si_2O_6 = 2M_2SiO_4$. Although iron is the most abundant aliovalent element in both the core and mantle systems, similar MOO-type reactions can be written for other transition metals and, if the present oxidation state of the mantle was established by metal(s.l.)-silicate equilibrium, thermodynamic analysis of the MOO reactions for different transition elements (e.g. Fe, Ni & Co) combined with the concentrations of these elements in peridotite samples should yield a single concordant estimate of fO_2.

Using oxygen-specific zirconia electrolyte cells, we have obtained new data on the standard free energies of the Fe, Ni and Co Quartz-Metal-Olivine ("QMO") buffers: $SiO_2 + 2M + O_2 = M_2SiO_4$. Using estimates of SiO_2 activity derived from the Quartz-Olivine-Orthopyroxene ("QOO") reactions ($SiO_2 + M_2SiO_4 = M_2Si_2O_6$) for Mg and Fe, the QMO data can be used to calculate equilibrium fO_2's exactly equivalent to those implied by the corresponding MOO reactions (MOO = QMO-QOO).

Application of these thermodynamic data to two spinel lherzolite nodules (#'s 270 & 271) previously studied in our laboratory[2] reveals large intrasample discrepancies (i.e. ~4 $\log_{10} fO_2$ units) between the Fe, Ni and Co QMO buffers. In spite of the low intrinsic fO_2's observed for these samples, this suggests that the redox state of these silicate assemblages is not compatible with the hypothesis of equilibrium with an Fe-Ni-Co(-O-S-C) metal of any geochemically reasonable composition. This implies either that core separation was a disequilibrium process or that, if core separation was an equilibrium event, the silicate phases involved in this process must have been of a fundamentally different nature to those of the present-day upper mantle. Significantly the intersample variations for the Fe, Ni, and Co QMO buffers are much smaller (<1 $\log_{10} fO_2$ unit) than the intrasample discordancies. This suggests that the redox conditions of the upper mantle, as represented by abundant spinel lherzolite nodules, is relatively uniform on a worldwide basis. This conclusion is

ORIGINAL PAGE IS
OF POOR QUALITY

supported by the results of intrinsic fO_2 measurements carried out on such peridotite nodules from a number of localities[3].

Similar calculations have been carried out for pallasitic meteorites, and the preliminary results show very good agreement between the Fe and Ni QMO buffers (∿0.4 $\log_{10} fO_2$ units). In contrast to the results for the upper mantle, this suggests that metal-silicate equilibrium was reached in the pallasites and that their redox state is controlled by oxygen buffers of the QMO or MOO type. The QMO equilibrium fO_2's calculated for the pallasites are only 1.5-2.0 $\log_{10} fO_2$ units more reduced than IW. This is in good agreement with the previously measured intrinsic fO_2 for the Salta Pallasite[5] (i.e. 1.9 $\log_{10} fO_2$ units below IW at 1000°C). These data suggest a comparatively simple redox history for the pallasite parent body.

References

(1) Ringwood (1979) Origin of the Earth and Moon, Springer-Verlag 295pp.
(2) Arculus, R.J. and Delano, J.W. (1981) Geochim. Cosmochim. Acta, 45, 899-913.
(3) Arculus, R.J., Gust, D.A. and Holmes, R.D. (1982) This volume
(4) Arculus, R.J. and Delano, J.W. (1980) Nature, 288, 72-74.
(5) Brett, R., and Sato, M. (1976) Meteorites, 11, 258-259.

ORIGINAL PAGE IS
OF POOR QUALITY

BOUNDARY CONDITIONS ON THE PALEOENVIRONMENT: THE CHEMICAL COMPOSITIONS OF PRE-SOLAR NEBULAE.

Dr. W. M. Irvine, Dept. of Physics and Astronomy, University of Massachusetts, Amherst, MA 01003

Accumulating evidence suggests that at least some interstellar volatile and particulate matter survived the formation of the solar system: anomalous noble gas isotope ratios in meteoritic carbonaceous host phases, the possible presence of carbynes in both interstellar clouds and carbonaceous chondrites, and models of cometary composition which best match the spectra of radicals and ions in the coma (e.g., (1), (2), (3)). The chemical composition of the condensing molecular cloud which formed the solar system (the "pre-solar nebula") thus provides basic initial conditions for the study of planetary volatiles, and is probably quite directly related to the present composition of cometary nuclei.

Direct analysis of this pre-solar nebula is unfortunately not possible, since it no longer exists. Solar-type stars are, however, being formed even today. If we could determine the type of region in which the sun formed, detailed studies might then specify the physical, chemical, and dynamical state of the protosolar system. Although it has been apparent for some years that star formation occurs in dense interstellar clouds of gas and "dust" (particulate matter), only recently is it becoming clear that such regions exhibit striking differences in chemical composition (4).

The so-called giant molecular clouds, of which that in Orion is the nearest example, are clearly the sites of on-going formation of stars considerably more massive than the sun. Whether the sun itself was formed in such a cloud is unclear, however, since low mass stars may also be born in the colder, more quiescent, lower mass regions known as "dark" clouds.

We have recently compiled the first systematic, continuous spectrum of the Orion molecular cloud in the region 72-91 GHz (5). Several molecular species and isotopic variants were identified which had not previously been detected in Orion, including methyl formate, isocyanic acid, acrylonitrile, ketene, and cyanobutadiyne. For heavier polyatomic species several rotational transitions were typically observed, making possible an accurate analysis of excitation and hence abundance.

The region called Taurus Molecular Cloud One (TMC 1) is an example of a dark cloud. It contains fragments with masses approximately equal to those postulated by Cameron (6) for the solar nebula and is cold (kinetic temperature ~ 10K) and quiescent. Such clouds had been believed to be chemically simpler than the giant clouds, but recently a number of molecular species have been found in TMC 1 which are not present in Orion or in the Galactic center cloud Sgr B2 (7, 8, 9). We have now succeeded in making the first detection of interstellar methylcyanoacetylene in this source (10).

PRE-SOLAR NEBULAE

ORIGINAL PAGE IS
OF POOR QUALITY

Irvine W. M.

Fractional abundances for known constituents of the Orion molecular cloud and for TMC 1 will be tabulated and compared. Particular attention will be given to the degree of saturation of simple nitriles in the two environments, and how this may relate to modes of molecular formation.

REFERENCES

(1) Hayatsu, R. and Anders, E. (1981). Topics Current Chemistry 99, 1.
(2) Huebner, W.F., Giguere, P.T., and Slattery, W.L. (1982). In Comets, ed. L. Wilkening (Tucson: U. Arizona Press), p. 496.
(3) Greenberg, J.M. (1982). In Comets, op. cit., p. 131.
(4) Irvine, W.M. and Hjalmarson, Å. (1982). In Cosmochemistry and the Origin of Life, ed. C. Ponnamperuma (Dordrecht: D. Reidel), in press.
(5) Johansson, L.E.B., Irvine, W.M., et al., in preparation.
(6) Cameron, A.G.W. (1978). In Protostars and Planets, ed. T. Gehrels (Tucson: U. Arizona Press), p. 453.
(7) Friberg, P., Hjalmarson, Å., Irvine, W.M., and Guelin, M. (1980). Ap. J. (Lett.) 241, L99.
(8) Irvine, W.M., Hoglund, B., Friberg, P., Askne, J., and Ellder, J. (1981). Ap. J. (Lett.) 248, L113.
(9) Avery, L.W. (1980). In Interstellar Molecules, ed. B.H. Andrew (Dordrecht: D. Reidel), p. 47.
(10) Avery, L.W., Irvine, W.M., et al., in preparation.

ORIGINAL PAGE IS
OF POOR QUALITY

SOURCES OF VOLATILES IN SUBDUCTION ZONE MAGMAS: POSSIBLE GEOLOGIC CYCLING OF CHLORINE AND WATER. E. Ito, Dept. Geology and Geophysics, University of Minnesota, Minneapolis, MN 55455; A.T. Anderson, Jr., Dept. Geophysical Sciences, University of Chicago, Chicago, IL 60637

Volatiles such as H_2O, HCl, CO_2, and He in subduction zone magmas may originate from surficial or deep sources. Surficial sources include aquifers and sedimentary rocks whose Cl/K_2O ratios are highly variable. Deep sources include lower crustal rocks, unmodified mantle, and subducted rocks. The Cl/K_2O ratio of deeper source material may be relatively uniform.

Assessment of production rate of volatiles by subduction zone magmatism requires the knowledge of magma production rate and average concentrations of volatiles in parental magmas. The magma production rate is between $3x10^{15}$ g/yr to $5x10^{15}$ g/yr (1,2). The compositional range of parental magmas may be identified from Cl/K_2O ratios of trapped melt in phenocrysts (3). High-alumina basaltic liquids (from diverse regions) are parental to new crust and have similar Cl/K_2O of about 0.08 which suggests a near uniform volatile source of subcrustal origin. Parental liquids from some volcanoes, however, show large and variable Cl/K_2O ratios. This may be due to crustal contamination: (1) at the Shasta region, the high Cl (and H_2O) probably comes from the nearby hydrous Trinity ultramafic body which are found as dehydrated xenoliths in Shasta rocks; and (2) at Asama, there is evidence of a separate body of silicic magma lying above the basaltic one. The average concentrations of Cl and H_2O found in parental magmas with $Cl/K_2O \sim 0.08$ are 0.09% and 2%, respectively.

Material subducted at trenches include igneous crust which has been subjected to some submarine alteration, and overlying sediment of variable composition and thickness. Average MORB (glass) contains about 0.005% Cl and 0.2% H_2O (e.g, 4,5). In crystalline MOR basalt and gabbros, some Cl resides in apatite, but Cl may also be present along intergranular surface. Water in crystalline rocks may be present in some amphibole, and also along intergranular surface. With alteration, main residence of Cl becomes hornblende, while that of H_2O becomes various hydrous minerals that are formed (6). The result of submarine alteration is 5x increase in H_2O concentration, and probably little change in Cl concentration.

How deeply the volatiles are subducted depends on the stability of host minerals in the P-T regime, the expulsion rate of sedimentary pore-waters, and the depth to which sediment is subducted. Some arc rocks show isotopic evidence of subducted sediment (e.g., 7,8), but other do not (e.g., 9). Chlorite and clays breakdown at less than 50 km depth, whereas hornblende (and epidote), which is the major reservoir of Cl, persists to about 80 km where it either melts or dehydrates (10). Released H_2O, probably rich in incompatible and volatile elements, or partial melt probably rises to overlying mantle where it takes part in generation of subduction zone magmas.

The Cl contained in subduction zone magmas is about equal to the amount in subducted amphibole. The H_2O in magmas is about twice the amount in amphibole but about one-fifth the amount in subducted crust. Taking a simple black-box approach, if the main source of subduction zone magmas were mantle, then some or most of the volatiles come from the subducted crust. This is further supported by the observation that Cl and H_2O concentrations in arc magmas are higher than those in MORB or hotspot magmas.

SOURCES OF VOLATILES

ORIGINAL PAGE IS
OF POOR QUALITY

Ito, E. and Anderson, A. T., Jr.

(1) Brown G.C. (1973) Nature Phys. Sci. 24, 26-27.
(2) Anderson A.T., Jr. (1975) Rev. Geophys. Space Phys. 13, 37-55.
(3) Anderson A.T., Jr. (in press) J. Geophys. Res.
(4) Schilling J.-G., Unni C.K. and Bender M.L. (1978) Nature 273, 631-636.
(5) Moore J.G. (1970) Contrib. Mineral. Petrol. 28, 272-279.
(6) Ito E. (1979) Ph.D. Thesis, University of Chicago.
(7) Magaritz M., Whitford D.J. and James D.E. (1978) Earth Planet. Sci. Lett. 40, 220-230.
(8) Hawkesworth C.J., O'Nions R.K. and Arculus R.J. (1979) Earth Planet. Sci. Lett. 45, 237-248.
(9) Ito E. and Stern R.J. (1981) Carnegie Inst. Wash. Yrbk. 80, 449-454.
(10) Wyllie P.J. (1982) Geol. Soc. Am. 93, 468-476.

ORIGINAL PAGE IS
OF POOR QUALITY

EXCHANGE OF WATER BETWEEN THE REGOLITH, ATMOSPHERE, AND POLAR CAPS OF MARS. Bruce M. Jakosky, Division of Geological and Planetary Sciences, Caltech, Pasadena, CA 91125.

Understanding the evolution of volatiles on Mars requires understanding the processes which are currently acting to cause exchange between the various reservoirs on annual and longer timescales. On the seasonal timescale, exchange of water can occur between the atmosphere and reservoirs of ice in the polar caps and of adsorbed water in the near-surface regolith covering the remainder of the planet. This exchange is driven by the seasonally-varying insolation and its consequent effects on the surface and subsurface temperatures and on the seasonal advance and retreat of the predominantly-CO_2 polar caps. On the longer timescale, exchange can occur between these same reservoirs, and is driven by the changing annual insolation patterns which result from the 10^5-year timescale variations in Mars' orbital elements (predominantly the orbital obliquity).

Observations of the seasonal water cycle and its variations from year to year from the Viking spacecraft and from Earth provide clues as to the importance of the various reservoirs on the seasonal cycle and provide boundary conditions against which models of the various processes can be compared. The results of the investigation of the seasonal behavior also have implications for the longer-timescale exchange of water between the reservoirs.

The water vapor content of the Mars atmosphere was measured from the Viking Orbiter Mars Atmospheric Water Detectors (MAWD) for a period of more than one Martian year, from June, 1976, through April, 1979. Column abundances vary between zero and about 100 precipitable microns (pr μm), depending on location and season, while the entire global abundance varies seasonally between an equivalent of about 1 and 2 km^3 of ice. The first appearance of vapor at non-polar latitudes as northern summer approaches, and the drop in abundance at mid-latitudes as summer ends, both strongly imply the existence of a seasonal reservoir for water within the regolith. There appear to be no net annual sources away from the poles that contribute significant amounts of water.

The strong annual gradient of vapor from north to south implies a net annual flow of vapor toward the south; this southward flow may be balanced in part by a northward flow during the global dust storms, by transport in the form of clouds or adsorbed onto dust grains, or during other years. The perennially-cold nature of the south-polar residual cap, along with the relatively large summertime vapor abundances over the cap, implies a net annual condensation of water onto the south cap. Estimates of the amount of water transported south each year are consistent with the movement of ice being important in the formation and evolution of the polar layered terrain, and with the formation of the individual layers at the rate of one per obliquity cycle (10^5 years).

Earth-based observations of the water vapor column abundance made over the last twenty years show that the seasonal cycle has a remarkable repeatability, except during 1969 when large vapor abundances were present during southern summer. This difference can be explained if all of the CO_2 had sublimed off of the south residual cap that year, exposing the underlying water cap. The ice would subsequently sublime and produce large amounts of atmospheric vapor at that season. The rate and amount of CO_2 sublimation may depend on the degree of dust storm activity each year and hence on the

ORIGINAL PAGE IS
OF POOR QUALITY

different thermal loads placed on the cap. The net effect of this different behavior is to remove the latitudinal gradient of water vapor and to mitigate the net southward transport of water that year.

The possible processes for producing seasonal changes in the atmospheric vapor abundances have been modeled in order to infer the relative importance of each process in the seasonal cycle. The equilibrium between water vapor and water adsorbed onto the regolith grains is sufficiently temperature-dependent that seasonal subsurface temperature variations are capable of driving a large exchange of water between the atmosphere and subsurface. For the likely range of regolith properties, this exchange can be from 10-150% of the observed seasonal change in atmospheric abundance; the differences between this exchange and the observed vapor abundances result from the effects of transport of vapor due to the atmospheric circulation. Due to the latitudinal gradient of atmospheric vapor, there will also be a gradient of subsurface adsorbed water, with the south regolith containing much less water than that in the north; this gradient in the regolith will result independent of the regolith vapor diffusivity, as the near-surface water will be able to equilibrate on some timescale.

Models have been constructed which include regolith exchange, polar cap formation, and atmospheric transport coupled together. Comparison of the model results with the vapor observations and with other data regarding the physical nature of the surface allows constraints to be placed on the relative importance of each process. The models are capable of satisfactorily explaining the gross features of the observed vapor behavior using plausible values for the regolith and atmospheric mixing terms. In the region between the polar caps, the regolith contributes as much water to the seasonal cycle of vapor as does transport in from the more-poleward regions, to within a factor of two. Globally, 10-50% of the seasonal cycle of vapor results from exchange of water with the regolith, about 40% results from the behavior of the residual caps, and the remainder is due to exchange of water with the seasonal caps. It is difficult to determine the relative importance of the processes more precisely because both regolith and polar cap exchange of water act in the same direction, producing the largest vapor abundances during the local summer.

The system is ultimately regulated on the seasonal timescale by the polar caps, as the time to reach equilibrium for exchange of water between the atmosphere and regolith or between the polar atmosphere and the global atmosphere is much longer than the time for the polar caps to equilibrate with water vapor in the local atmosphere. This same behavior will hold for longer timescales, with the polar caps being in thermal equilibrium with the insolation as it changes on the obliquity timescale (10^5 years), and the water vapor in the atmosphere and regolith following along. This long timescale exchange of water has implications for the Mars climate and for evolution of the polar layered terrain during the past billion years.

ORIGINAL PAGE IS
OF POOR QUALITY

TERRESTRIAL HELIUM ISOTOPIC SYSTEMATICS

Dr. W. J. Jenkins, Woods Hole Oceanographic Institution, Woods Hole, MA 02543

A study of terrestrial helium isotopic systematics is of interest for two reasons: (1) Because of their short atmospheric residence times, fluxes of these isotopes from the solid earth are "visible" and hence, in principle, measurable.

(2) Each of the two isotopes are dominated by different "source terms". ^{4}He is primarily radiogenic, being produced by U and Th decay. ^{3}He is primarily primoridal (inherited), although there is a small radiogenic contribution.

We see a bimodal distribution of isotopic (^{3}He/^{4}He) ratios in terrestrial systems. "Primitive" or deep, undepleted mantle is characterized by high ^{3}He/^{4}He ratios, typically in the range of 10^{-5} to 10^{-4}. Mid-ocean ridge basalts, the most prolific of mantle produced rocks, cluster near 10^{-5} whereas "plume basalts" are higher in ^{3}He/^{4}He. Continentally derived helium is characterized by a low ^{3}He/^{4}He, typically 10^{-8} to 10^{-7}, as would be expected from a U, Th rich, initially degassed source region.

Detailed studies of the distribution of He isotopes in rocks, gas wells and hydrothermal systems is revealing much about mantle structure, mantle-crust interaction and the large scale tectonic structure of the continental crust. What is also of value is the fact that we are able to measure the fluxes of these isotopes and thus place real constraints on not only the present day degassing rate of the earth but also, through isotopic ratio of the deep earth, the long term degassing history.

The study of the oceanic flux of ^{3}He by Craig and Clark (1) led to an estimate of the oceanic ^{3}He flux of 4 atoms $cm^{-2}s^{-1}$, a value which later, more detailed work has verified. Preliminary work at this laboratory on hot springs in the western U. S. show a ^{4}He/heat ratio of $(1.2\pm0.3)\times10^{-7}$cc(STP)/cal, or about 3.2×10^6 atoms ^{4}He/cm^2/s/H.F.U. This ratio is within the uncertainty of the calculated present day source ratio for the continents. Using the "shallow" (non-mantle) heat flow distribution to estimate a ^{4}He flux, we thus obtain a continental contribution of $\approx1.7\times10^{24}$ atoms ^{4}He s^{-1}, or a contribution roughly equivalent to the oceanic "mantle" contribution. The equivalent continental radiogenic ^{3}He contribution from Li $(n,\alpha)^3H \rightarrow {}^3He$ is entirely negligible compared to the mantle flux.

A simple bulk-earth coherent degassing model calculation using U, Th, K, He and Ar indicates that the terrestrial degassing rate was substantially greater in the past, and suggests that the earth had perhaps 1% of the ^{3}He abundance of chondritic material. This calculation also points to a deep earth ^{40}Ar/^{36}Ar of the order of 200-400.

(1) Craig, H., and Clarke, W. B. (1980) Earth Planet. Sci. Lett., 9, 45-48.

ORIGINAL PAGE IS
OF POOR QUALITY

TRAPPING OF GASES AND LOW TEMPERATURE VOLATILES IN LUNAR SAMPLES*

S. Jovanovic and G. W. Reed, Jr.
Chemistry Division, Argonne National Laboratory,
9700 South Cass Avenue, Argonne, Illinois 60439

The persistence of the gases, parentless ^{40}Ar and excess fissiogenic Xe, and of low temperature volatile non-gaseous Hg and Br in lunar surface material and, in the case of Ar, also in the atmosphere has posed a number of problems of fundamental importance in understanding the moon. These include the volatile or gaseous sources or reservoirs; how these elements are associated with substrate material, i.e. why they have not been totally depleted; their behavior in the regolith and in the lunar atmosphere; and as a result of their mobility, possible ponding in permanently shadowed cold traps.

Heymann and Yaniv (1970) and Manka and Michel (1970) first addressed the problem of parentless ^{40}Ar in lunar samples. Reed et al. (1971) discussed the presence of Hg and the fraction found to be volatile at subsolar temperature. Hodges and Hoffman (1975) reported on Ar in the lunar atmosphere. The Washington University team of Podosek, Hohenberg and others (Crozaz et al., 1972, Drozd et al., 1972 and Beratowicz et al., 1979 and included references) identified unsupported fissiogenic Xe in solar wind gas-rich breccias. Since any lunar atmospheric component will be electromagnetically accelerated and lost, all these (see also Hodges, 1982) attempted to explain why the various atmophile elements have persisted.

Activation energies for sorption or diffusion have been determined for Ar, Xe and Hg. Ar (Hodges, 1982) and Hg (Reed and Jovanovic, 1979) estimates were based on essentially in-situ lunar measurements; Xe was measured in the laboratory (Podosek et al., 1981; Bernatowicz et al, 1982). The Hg measurement was based on concentration gradients of Hg (and Br) in lunar soil in response to the subsolar heating; it is model dependent. The Ar measurement was based on mass spectrometric detection of pre-sunrise increases in Ar in the lunar atmosphere. Xe sorption measurements were made on pulverized terrestrial and on lunar soil samples after pumping and heating to generate clean surfaces.

Element	E^* (Kcal/mole)
Ar	6-7
Xe	5-7
Hg	8

Such low E^* should not permit surface adsorbed fractions to persist at the lunar surface. Hence, some other trapping mechanism appears to be required since returned samples contain these volatiles. Implantation by solar wind or acceleration back to the surface from the lunar atmosphere can be ruled out since Xe is found inside non-regolith rocks such as troctolite 76535 (Caffee et al., 1981). We have established that Hg is enriched on the underside of rocks relative to the interior or exposed surfaces, it is enriched in permanently shadowed areas under rock overhangs (see also Wegmüller et al., 1982) and at depth (5-8 cm) in drill cores. It should be noted that the excess Xe containing breccias range from extremely friable 14082 to tough 15455. The open (friable) rock has not lost Xe. In addition, during storage on earth mobile fractions of Hg and Br have not migrated to uniformly coat surfaces in cores.

Another observation relevant to the fixation of Hg on surfaces is from comparing vacuum sealed SRC (Apollo 16 and 17 sample return containers) with

ORIGINAL PAGE IS
OF POOR QUALITY

N_2-filled core tubes from Apollo 12 and 17. Surfaces were apparently not altered in the latter in a way that would cause desorption of Hg. A similar conclusion for Xe has been arrived at by Bernatowicz et al (1982). Storage time does not appear to be a factor either, since the Apollo 12 core was stored *ten* years. We have not measured 12027 dissected core samples but room temperature volatile Hg from whole core pumping is the same in the Apollo 12 core and the two SRC's (Jovanovic et al., 1981). Hg volatilized at room temperature from the 70002 core was lower than that from the Apollo 17 SRC.

Some other mechanism besides adsorption or implantation must account for gaseous and volatile element retention in the lunar regolith.

A caging effect may be the best explanation for immobilization of volatiles. In the rare gas cases, the cages have to be physical and are presumably opened at relatively high >500°C temperature; to our knowledge no lower temperature data are available. The cages for Hg and Br are probably chemical compounds that decompose at temperatures, 23°C < T < 130°C. If this is so, there is a "threshold" above room temperature where Hg and Br are released from their cages and migrate in a manner consistent with a low E*.

Probably the only way to resolve problems related to the storage of gases and low temperature volatiles in the lunar regolith is to conduct low temperature experiments. For Hg and Br this means extraction at or near room temperature, hence large samples (see Appendix 2). The mass spectroscopy experiment of Hodge and Hoffman (1975) can be considered a low temperature experiment for Ar. The Xe sorption study of Podosek et al. (1981) was carried out at low temperature and thus could match lunar conditions.

In the cases of both Ar and Xe, however, there apparently is no information on the *total* amount of gas present in the regolith. Oliver and Manuel (1981) have demonstrated that even at 150°C large fractions of Xe and Kr are released from shale samples, one of which is 3 b.y. old. Pristine lunar soil surfaces may have comparable adsorptive capacities as shale. Thus, could there be a significant fraction of low temperature Ar and Xe present in sealed sample containers such as core tubes 73001 and 73002?

*This work was supported by the National Aeronautics & Space Agency

References

Bernatowicz T. J., (1979) Proc. Lunar Planet. Sci. Conf. 10th, pp. 1587-1616.
Bernatowicz T., et al., (1982) Lunar Planet. Sci. XIII, pp. 39-40.
Caffee M., et al., (1981) Proc. Lunar Planet. Sci. Conf. 12th, pp. 99-115.
Crozaz G., et al., (1972) Proc. Lunar Sci. Conf. 3rd, pp. 1623-1636.
Drozd R. J., et al., (1972) Earth Planet Sci. Lett. 15, pp. 338-346.
Heymann D. and Yaniv A. (1970) Proc. Apollo 11 Lunar Sci. Conf., pp. 1261-1267.
Hodges, Jr. R. R., and Hoffman J. H., (1975) Proc. Lunar Sci. Conf. 6th, pp. 3039-3047
Hodges, Jr. R. R. (1982) Lunar Planet. Sci. XIII, pp. 329-330.
Jovanovic S. and Reed Jr. G. W. (1968) Geochim. Cosmochim Acta 32, pp. 341-346.
Jovanovic S. Reed Jr. G. W., et al, (1981) Lunar Planet. Sci. XII, pp. 522-524.
Manka R. H. and Michel F. C. (1970) Science 169, pp. 278-280.
Oliver L. L. and Manuel O. K. (1981) Lunar Planet. Sci. XII, pp. 788-780.
Podosek F. A., et al., (1981) Proc. Lunar Planet Sci. 12th, pp. 891-901.
Reed G. W., et al., (1971) Science 172, 258-261.
Reed Jr. G. W. and Jovanovic S. (1979) Proc. Lunar Planet. Sci. Conf. 10th, pp. 1637-1647.
Wegmüller F., et al., (1982) Lunar Planet. Sci. XIII, pp. 847-848.

ORIGINAL PAGE IS
OF POOR QUALITY

LOSS OF A MASSIVE EARLY OCEAN FROM VENUS, J.F. Kasting and J.B. Pollack, NASA Ames Research Center, Moffett Field, CA 94035

The recent discovery of a 100-fold enrichment in deuterium on Venus[1] strongly suggests that Venus was originally endowed with much more water than is now present in its atmosphere. If Venus and Earth had similar initial D/H ratios, the initial H_2O abundance on Venus must have been at least .14 percent that of Earth and may have been considerably higher if some deuterium has escaped or if juvenile water has continued to be degassed during the planet's history. The loss of water from the present Venus atmosphere occurs by nonthermal escape of hydrogen and oxygen to space[2,3]. The degree of deuterium fractionation depends upon which of several possible mechanisms is primarily responsible for hydrogen escape. In a primitive Venus atmosphere in which H_2O was much more abundant, these nonthermal escape mechanisms would have been superceded by rapid hydrodynamic outflow of hydrogen and loss of oxygen to the planet's crust[4,5]. Deuterium could have been lost effectively if the escape flux exceeded a certain critical value, so that a large D/H enrichment need not have occurred at this time[4]. The magnitude of the hydrodynamic escape flux depends upon the abundance of hydrogen in the Venus upper atmosphere, along with the rate of heating by absorption of solar EUV radiation. Watson et al.[4] estimated an upper bound of 1.1×10^{12} H_2 molecules $cm^{-2}s^{-1}$ for a pure molecular hydrogen thermosphere and an EUV heating efficiency of 30 percent, but did not show how closely the actual escape flux would have approached this limiting value.

We have repeated the hydrodynamic escape calculation using a coupled chemical-dynamical model of the Venus upper atmosphere. The escape flux is calculated as a function of the H_2O mass mixing ratio at the atmospheric cold trap, near 90 km for the present Venus atmosphere. The cold trap mixing ratio is then related in an approximate fashion to the H_2O concentration in the lower atmosphere, following the procedure formulated by Ingersoll[6]. Combination of these two calculations yields the variation of H escape flux versus H_2O mixing ratio in the lower atmosphere (Fig. 1). The solid portion of the curve was derived by solving the hydrodynamic equations from the cold trap out to infinity using $\lambda = 1/r$ as the vertical coordinate. The dashed portion of the curve represents classical Jeans escape of hydrogen. The transition from Jeans to hydrodynamic escape occurs at a lower atmosphere H_2O mass mixing ratio C_ℓ (H_2O) - 0.1, which corresponds to ~4 percent of a terrestrial ocean if the partial pressures of CO_2 and N_2 were the same as today. All water is presumed to have been in the vapor state due to an extremely high (> 750K) surface temperature. A full terrestrial ocean of water would yield C_ℓ (H_2O) = 0.74.

The escape fluxes calculated in our model depend upon several poorly known parameters, including the rate of heating by solar EUV radiation and the oxidation state of the lower atmosphere. The escape rates shown in Fig. 1 are for solar minimum EUV fluxes, a heating efficiency of 15 percent, and a neutral or mildly oxidizing lower atmosphere. The escaping gas is predominantly H, rather than H_2, and the maximum escape flux of 2.7×10^{11} H atoms $cm^{-2}s^{-1}$ is a factor of 5 smaller than the critical flux required to carry off significant amounts of deuterium. The escape flux rises roughly linearly with increasing EUV heating rate, so deuterium may have been lost if the heating efficiency or solar ultraviolet flux was higher than we have assumed. Accumulation of O_2 during the hydrodynamic escape phase would

have enhanced the hydrogen escape rate by increasing the absorption of ultraviolet radiation in the lower thermosphere. Escape rates would also have been higher if the lower atmosphere were reducing, as suggested by Watson et al[5], since escape of H_2 would supplement the loss of H.

Helium could have been swept away during the hydrodynamic escape process if the escape flux exceeded 7×10^{12} H atoms $cm^{-2}s^{-1}$. This mechanism might account for the low abundance of ^4He in Venus' present atmosphere compared to the amount expected from primordial and radiogenic sources[7].

References

1. Donahue, T.M., Hoffman, J.H., Hodges, R.R., and Watson, A.J. (1982), Science, 216, p. 630-633.

2. McElroy, M.B., Prather, M.J., and Rodriguez, J.M. (1982a), Science, 215, p. 1614-1615.

3. McElroy, M.B., Prather, M.J., and Rodriguez, J.M. (1982b), Geophys. Res. Lett., 9, p. 649-651.

4. Watson, A.J., Donahue, T.M., and Walker, J.C.G. (1981), Icarus, 48, p. 150-166.

5. Watson, A.J., Donahue, T.M., Kuhn, W.R., and Walker, J.C.G. (1982), Icarus, submitted.

6. Ingersoll, A.P. (1969), J. Atmos. Sci., 26, p. 1191-1198.

7. Pollack, J.B. and Black, D.C. (1982), Icarus, submitted.

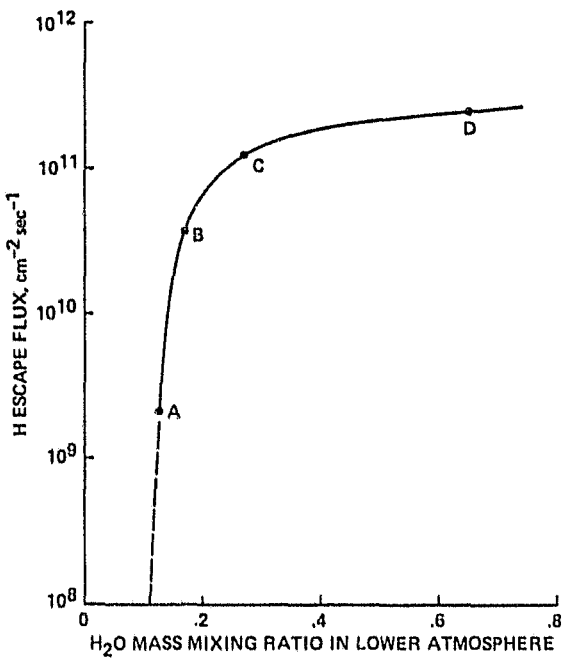


Figure 1

ORIGINAL PAGE IS
OF POOR QUALITY

NONTHERMAL ESCAPE OF HYDROGEN AND DEUTERIUM FROM VENUS AND IMPLICATIONS FOR LOSS OF WATER, S. Kumar, USC Center for Space Sciences, Tucson, AZ, 85713, D.M. Hunten, Lunar and Planetary Lab., University of Arizona, Tucson, AZ, 85721, J.B. Pollack, Space Science Division, NASA-Ames Research Center, Moffett Field, CA, 94305

Venus is known to be severely deficient in water compared to Earth. From Venera 11-12 entry probe data, Moroz et al. (1981) have derived an H_2O mixing ratio of 20 ppm at the surface which corresponds to 1.0×10^{-9} gm per gm of Venus mass; the corresponding water inventory on Earth is 1.6×10^{-4} gm per gm. The scenario that Venus has lost a substantial quantity of water is almost required by recent reports on D/H ratio of 1% deduced by McElroy et al. (1982) and a value of 1.6% obtained by Donahue et al. (1982). The one-hundredfold enhancement relative to the Earth value (1.6×10^{-4}) requires at a minimum the loss of 99% of the H, and much more if some of the D has been lost too.

If Venus did indeed start out with earth equivalent ocean of water in its atmosphere, H abundance in the exosphere would be so large that H could no longer be gravitationally bound and a controlled outflow would result (Watson et al. 1981). Such hydrodynamic escape of H would cease when H_2O mixing ratio at the cold trap drops to $\sim 10^{-3}$ which corresponds to a water mixing ratio of ~0.2 at the surface (Kasting and Pollack 1982). Jeans escape (or thermal evaporation) would also be utterly negligible; the estimated escape flux for present atmosphere is only 5×10^4 cm^{-2} s^{-1} for exospheric temperature of 300 K. We must therefore look to various nonthermal processes for further loss of H to account for the severe deficiency of H in the present atmosphere.

(1) Plasmaspheric Charge Exchange: Charge exchange between cold H and O atoms in the exosphere and high temperature H^+ ions in Venus' plasmasphere leads to production of nonthermal or hot H atoms a fraction of which escape to space. Since the nightside shows a remarkable bulge in H^+ in the predawn sector which corresponds to a 400:1 bulge in neutral H density in the exosphere (Brinton et al., 1980), the escape flux at present occurs from the night side. Using Pioneer Venus ion temperature data of Miller et al. (1980), we estimate a globally averaged escape rate of 2×10^7 cm^{-2} s^{-1}. In the past atmospheres when the H density would be higher, this source would be even more significant because the hot H production rate increases approximately as the square of the H density. If the source of ionization on the nightside is kept the same as what it is at present we estimate a maximum escape of flux of $\sim 2 \times 10^9$ cm^{-2} s^{-1} from this process in the past. The energy limited saturation would occur at an H abundance roughly 10 times the present value.

Although the escape of H from the charge exchange on the dayside is small at present, it would saturate at a flux much higher than nightside value for high H abundance since the ionization source is stronger on the dayside. We find that the dayside source would saturate at a maximum H escape flux of $\sim 10^{10}$ cm^{-2} s^{-1} which would occur at ~1000 times the present H abundance in the exosphere. Thus charge exchange can maintain the H escape flux close to the diffusion limit and provide the necessary escape mechanism once the hydrodynamic escape terminates.

(2) Hot O Impact Hot O atoms are produced by the recombination of O_2^+, and the subsequent impact of these hot O atoms on the exospheric hydrogen produces nonthermal H atoms some of which are energetic enough to escape giving a hydrogen escape rate of 8×10^6 cm^{-2} s^{-1} for the present atmosphere (McElroy, et al., 1982). This source works well at night and is significant for the

ORIGINAL PAGE IS
OF POOR QUALITY

escape of H at present because the O_2^+ ionosphere peak is observed at 145 km (Taylor et al., 1980) just below the exobase which is at ~152 km, making the hot O atoms available to the exospheric hydrogen. In the present atmosphere, the exobase level is determined by the atomic oxygen density, but in the past atmospheres when the H column density could be higher, it is the hydrogen gas that would determine the exobase level. Once the exobase level is above 260 km, approximately one scale height of H above the O^+ peak, this mechanism would operate very inefficiently as hot O and H atoms would collide with the cold H atoms and thermalize before they reach the exobase and contribute to H escape. We expect this source to saturate at an exospheric H abundance only a few times the present value giving a maximum escape flux of ~3 x 10^7 cm^{-2} s^{-1}. Hence this mechanism would be insignificant in the past compared to the charge exchange process described above.

(3) Ion-Molecule Reactions The important ion-molecule reaction for the production of nonthermal H atoms is the reaction of O^+ with H_2 and subsequent recombination of OH^+. The escape flux due to this mechanism clearly depends upon the H_2 mixing ratio, which is highly uncertain even for the present atmosphere. If the mass 2 ion observed by the PV-OIMS experiment is H_2^+, the implied H_2 abundance is about 10 ppm and the hydrogen escape rate on the day side is ~10^8 cm^{-2} s^{-1} (Kumar et al., 1981). This source has comparable strength on the nightside due to the presence of predawn density bulge in mass 2 ion. The mass 2 ion may, on the other hand, be D^+ (McElroy et al., 1982), in which case the H_2 mixing ratio could be quite low and the corresponding escape flux negligible. In past atmospheres, H_2 could have been more abundant due to higher outgassing rates or reactions of atmospheric H_2O with reduced minerals in the crust. But an H_2 abundance higher than 10 ppm would not lead to higher escape rate from the O^+-H_2 source because increasing H_2 density implies an increase in H density which in turn results in a drop in O^+ density. For past atmospheres the mechanism saturates at a flux of ~3 x 10^8 cm^{-2} s^{-1}. Even if this mechanism is important at present it is overtaken by charge exchange rapidly at higher H abundance.

Thus charge exchange is the major nonthermal escape mechanism for hydrogen. It is also the most important mechanism for escape of deuterium. At an ion temperature of 5000 K, the maximum measured at night, deuterium escapes with 44% the efficiency of hydrogen escape. At 2300 K, the ion temperature on the dayside, the relative efficiency drops to 11%. If the mixing ratios of H_2O in the lower atmosphere are 2 x 10^{-5} at present and 0.1 initially (onset of hydrodynamic flow), we calculate a D/H enrichment during nonthermal escape ranging from a factor of 3600 at T_i = 2300 K to 173 at T_i = 5000 K. The loss of a full terrestrial ocean of water is consistent with the observed D/H ratio if outgassing of juvenile H_2O has continued during the planet's history.

References

Brinton, H.C. et al. (1980) Geophys. Res. Lett., 7, 865.
Donahue, T.M. et al. (1982) Science, submitted.
Kasting, J.F. and Pollack J.B. (1982) Icarus, submitted.
Kumar, S. et al. (1981) Geophys. Res. Lett., 8, 237.
McElroy, M.B. et al. (1982) Science, 215, 1614.
Miller, K.L. et al. (1980) J. Geophys. Res., 85, 7759.
Moroz, I.V. et al. (1980) Nature, 284, 243.
Taylor, H.A., Jr. et al. (1980) J. Geophys. Res., 85, 7765.
Watson, A.J. et al. (1981) Icarus, 48, 150.

ORIGINAL PAGE IS
OF POOR QUALITY

CONSTRAINTS ON THE EVOLUTION OF THE MANTLE FROM NOBLE GAS ISOTOPE RATIOS.

M.D. Kurz and C.J. Allègre, Laboratoire de Géochimie, Institut de Physique du Globe, 4 Place Jussieu - 75230 Paris cedex 05-France

Numerous studies of Sr, Nd and Pb isotopic variations in basaltic rocks have shown that the terrestrial mantle is heterogeneous. Recent studies of the noble gases, particularly He, Ar, and Xe, provide important constraints on the origin and evolution of the heterogeneities. Measurements of the $^3He/^4He$ and $^{87}Sr/^{86}Sr$ ratios in oceanic basalts yield clear regional correlations (1),which shows that the two isotope systems (U-He, Rb-Sr) are not decoupled. The highest $^3He/^4He$ ratios allow identification of the source regions for Hawaii, Iceland, and Reunion as relatively undepleted, a result which is at odds with criteria for selecting "primitive" mantle based on the Sr-Nd correlation. The overall helium and strontium variations require the existence of at least three mantle reservoirs (1,2). A simple model to explain the variations includes undepleted, depleted and recycled mantle reservoirs. Although available measurements do not allow unambiguous identification of the corresponding argon and xenon isotopic composition for the reservoirs (partly because of contamination effects), recent measurements on MORB glass yield important information on the depleted mantle. The mean age of $>4x10^9$ years, calculated from Ar and Xe measurements (3, 4), not only suggests early outgassing, but also place limits on the extent of recycling. Consideration of the global ^3He flux, $^3He/^{36}Ar$ measurements, and atmospheric ^{36}Ar inventory shows that present day degassing rates are insufficient to generate atmospheric argon, which is consistent with early outgassing. ^3He concentrations for the different mantle reservoirs can be inferred from the measurements, and suggest that the present day ^3He flux, and the ^3He in MORB, is ultimately derived from the lower mantle.

1) Kurz M.D., W.J. Jenkins, J.G. Schilling and S.R. Hart, Earth Planet. Sci. Lett. 58, 1-14, (1982)
2) Kurz, M.D., W.J. Jenkins and S.R. Hart, Nature 297, 43-47, (1982)
3) Staudacher, Th., and C.J. Allègre, Earth Planet. Sci. Lett. (in press).
4) Sarda, Ph., Th. Staudacher, and C.J. Allègre, EOS 63, 458.

ORIGINAL PAGE IS
OF POOR QUALITY

EARLY VOLATILES ACCRETION IN INNER PLANETS

D.Lal and M.N. Rao
Physical Research Laboratory, Ahmedabad 380 009,India.

A few percent of the volatile-rich material covering the surfaces of Venus, Earth and Mars during the late stages of planetary accretion seems to be the major source for the generation of atmospheres by secondary processes on these inner planets. The similarity of noble gas abundance profiles as well as the N/C ($\sim$0.05) and Ne/Ar (0.3 to 0.5) ratios (Fig.1) in the atmospheres of Venus, Earth and Mars suggest that the source material controlling the composition of their atmospheres is not solar wind irradiated planetary matter. Instead it appears to be similar to the commonly observed carbonaceous chondrites.

Based on the results obtained in the case of thermal-release experiments of solar wind irradiated lunar soils, we infer that the source material for the planetary atmospheres is not solar wind-implanted planetary matter. To decrease the Ne-20/Ar-36 ratios from $\sim$40 to 50 in the solar wind irradiated material to the observed Ne-20/Ar-36 ratio of $\sim$0.4 in the atmospheres of Venus, Earth and Mars, the solar wind irradiated planetary matter has to be heated upto $\sim$1400°C. Thus the volatile-rich material has to be raised to this temperature before it is accreted on the surfaces of the inner planets. This conclusion presents a serious difficulty in explaining, how is it that the Earth (and also early Venus) retained so much water and other condensible volatiles in the same veneer-material, the degassing of which later generated oceans and atmosphere on our planet ? Further, this drastic heating of the solar wind irradiated material upto 1400°C is shown to be inconsistant with the observed Ne-20/Ne-22 ratios on Earth and Venus.

In the carbonaceous chondrites, the planetary noble gases are concentrated in minor host phases of fine-grained carbon ($\sim$0.1 %) of those meteorites. The elemental and isotopic abundances of the noble gases in the atmospheres of the inner planets are probably governed by the nature and content of the carbonaceous material, collected in the later stages of planetary formation. The nature of the carbonaceous material seems to depend on the location-distances of these planets from the sun and contents seems to be related to the size of the planet and the conditions of its formation.

The results of Ar-36/C ratios plotted for Venus, Earth, Mars and meteorites in Fig.1 show a smoothly decreasing trend from Venus to meteorites. The values for Ar-36/C ratio for Mars quoted in literature varies from 1.7×10^{-5} to 8×10^{-8}. As infered from Fig.1, it appears that a value of $\sim 10^{-7}$ seems to suit Mars best. This ratio alongwith the Ar-40/Ar-36 ratio of

VOLATILES ON VENUS, EARTH AND MARS.

ORIGINAL PAGE IS
OF POOR QUALITY

Lal D. and Rao M.N.

~3000 for Mars provides clues to our understanding of one-plate-tectonics in the early history of Mars.

In order to explain the large excess (~100 times) of argon and other noble gases in Venus compared to Earth, yet having similar CO_2 (considering total degassing) and H_2O (taking early Venus) contents on these two planets, we propose a model somewhat different from that of Wetherill (2) and McElroy and Prather (1).

1. McElroy M.B. and Prather M.J. (1981) Nature, 293, p.535-539.

2. Wetherill G.W. (1981) Icarus, 46, P.70-80.

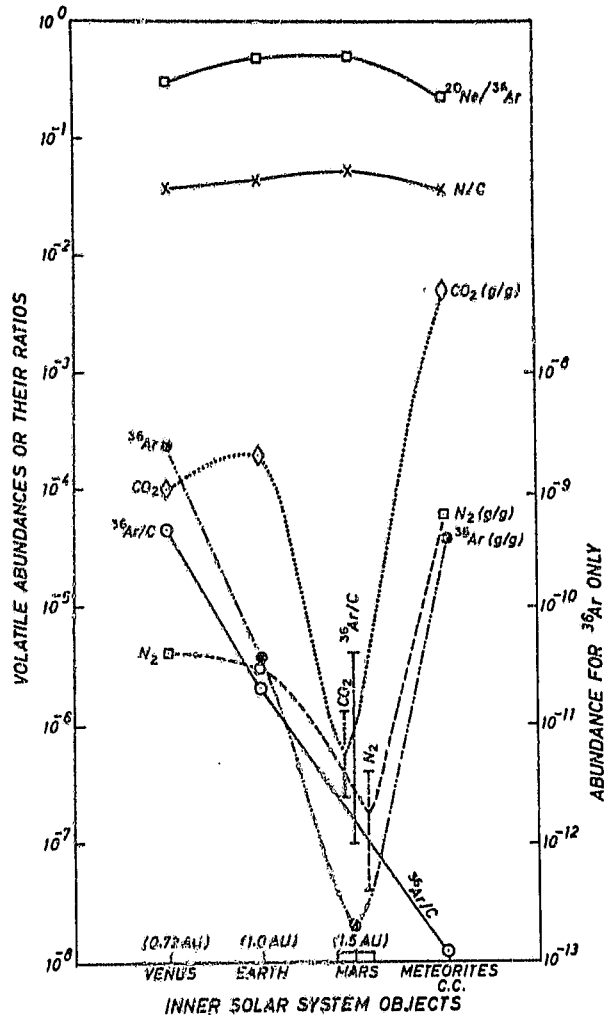


Fig.1. Comparison of abundances of N_2, CO_2 and Ar-36 as well as N/C and Ne/Ar ratios in Venus, Earth, Mars and meteorites.

ORIGINAL PAGE IS
OF POOR QUALITY

PROCESSES OF SHOCK DEHYDRATION ON ACCRETING PLANETS. P. Lambert, SN6/NASA JSC, Houston, TX 77058 and M. A. Lange, Seismological Laboratory, CALTECH 252-21, Pasadena, CA 91125

INTRODUCTION: Serpentine and serpentine-like layer silicates are the major water-bearing phases in carbonaceous chondrites (1,2). It appears that these minerals, and a poorly defined cometary contribution, were the most likely water-bearing phases in accreting planetesimals which led to the formation of the terrestrial planets (3,4). In several models (3,5,6) formation of a planetary atmosphere/hydrosphere is envisioned as a primary process, taking place during accretion. Water and other volatiles in minerals of the infalling planetesimals is released when these bodies hit the accreting planets, and is continually added to a growing proto-atmosphere. The aim of this study was to constrain the processes by which impact on accreting planet contributes to the evolution of the planetary volatiles. Two approaches were envisioned; (a) study of experimentally shocked minerals analog to the probable primordial water-bearing phases in accreting planet; (b) comparative study of carbonaceous chondrites.

MATERIALS/METHODS: Experimentally shocked material comprises brucite and antigorite (4,7), biotite and muscovite (8,9), talc and amphiboles (10). Experiments have been carried out with a 20 mm flat plate accelerator using impedance match technique and multiple shock reverberations. In brucite and serpentine experiments, vented and sealed target assemblies have been used to constrain vapor escape (4). Investigated pressure ranges from about 10 to 80 GPa (1 GPa $\simeq 10^4$ atm). The studied chondrites are C2 carbonaceous chondrites: Murchison, Murray, ALHA 77306 and ALHA 78261. The analytical techniques includes microprobe, SEM, IR spectroscopy, thermogravimetry and optical microscopy.

RESULTS: Shock induced dehydration of antigorite starts at P> 20 GPa and is complete at P> 60 GPa (Fig. 1). Shock dehydration of brucite and micas occur at lower pressures. Shock dehydration is more efficient in porous material (Fig. 1). Confinement favors readsorption of a portion of the shock released structural water by the shocked mineral. Dehydration intervals and activation energy for dehydration of shocked samples is less than that of the unshocked equivalent. Dehydration interval and activation energy for dehydration of a shocked mineral decreases with increasing shock pressure. Evidence of melting in experimentally shocked antigorite and micas is revealed by the highly vesicular and apparently homogeneous glasses. Shock induced melting in talc and amphiboles result in decomposition of the mineral and formation of an assemblage of vesicular glass and crystalline phases. Significant melting (affecting 10% or more of the initial phase) is detected at P> 30 GPa in micas and P> GPa in antigorite, talc and amphiboles. Compared to "dry" silicates, antigorite talc and amphibole shocked in the range 0- 50 GPa show remarkably very little deformation features.

Investigated C2 chondrites display a breccia texture characterized by an abundant matrix (50-80% of the meteorite). There is a hiatus in grain size between the matrix and the clast. The degree of "serpentinization" of clasts varies from one clast to another. Locally an oriented texture is observed in Murchison and in ALHA 77306. Preferred orientation is related to variations in the nature and/or texture of the matrix minerals and to deformation and elongation of the clasts. We have not observed vesicular phases similar to that described in the shocked serpentine (P>45 GPa) or shocked micas (P>30 GPa), in the matrix of studied C2 chondrites. There are fractures of local extension cutting through the matrix. These fractures are also filled by hydrated silicates. Shock in C2 is revealed by strong fracturing and by mosaicism in some of the clast minerals, preferentially in pyroxenes. Most remarkable is a strongly fractured enstatite fragment in Murchison which displays decorated planar elements resembling those commonly encountered in shocked tectosilicates from old and deeply eroded terrestrial impact structures (12-14). Terrestrial DPE are interpreted as result of post shock healing-dissolution processes in the mineral related to fluid interactions along shock produced planar discontinuities (15-16). Other type of healing features are also observed in olivine and pyroxenes of C2 in the form of planes of inclusions (see also (17)). Probable annealing features are observed in olivine and possibly in some pyroxenes.

IMPLICATIONS/CONCLUSION: Experimental shock does release H_2O in material analog to that considered to represent the primordial H_2O bearing phases of accreting planet. The major path for circulating H_2O vapor is represented by the presence of vesicles, their morphology and their location. Complete dehydration of serpentine is achieved by a single shock $\geqslant$ 60 GPa. This value can be considered as an upper limit. Successive shock and/or porosity will yield to a lower value of P for total water release by shock. Because of the lack of petrographic indicator for shock under 45-60 GPa in experimentally shocked antigorite, it cannot be decided from the present observations of C2 chondrites whether the matrix phases of C2 have been shocked or not. It can only be concluded (1) the minerals constituting the matrix have not experienced shock pressure in excess of 45-60 GPa because phyllosilicate glasses are not observed; (2) shock could be responsible for the localized fractures cutting through the matrix. Study of "veins" in C1 suggests superposed deformation events in the matrix (11). The difference of activation energy for dehydration of shocked and unshocked serpentine is considered as the most promising indicator for relatively weak shock in the matrix of C1-C2. Feasibility of the use of beam damaging under TEM to characterize this difference is currently being tested; (3) at least part of the clast population of C2 chondrites has been shocked. Healing features in clasts are significant of a thermal and possibly hydrothermal event(s). The same event(s) could be responsible for the alteration processes reported in the matrix of C chondrites (11, 17, 18). Some and possibly all

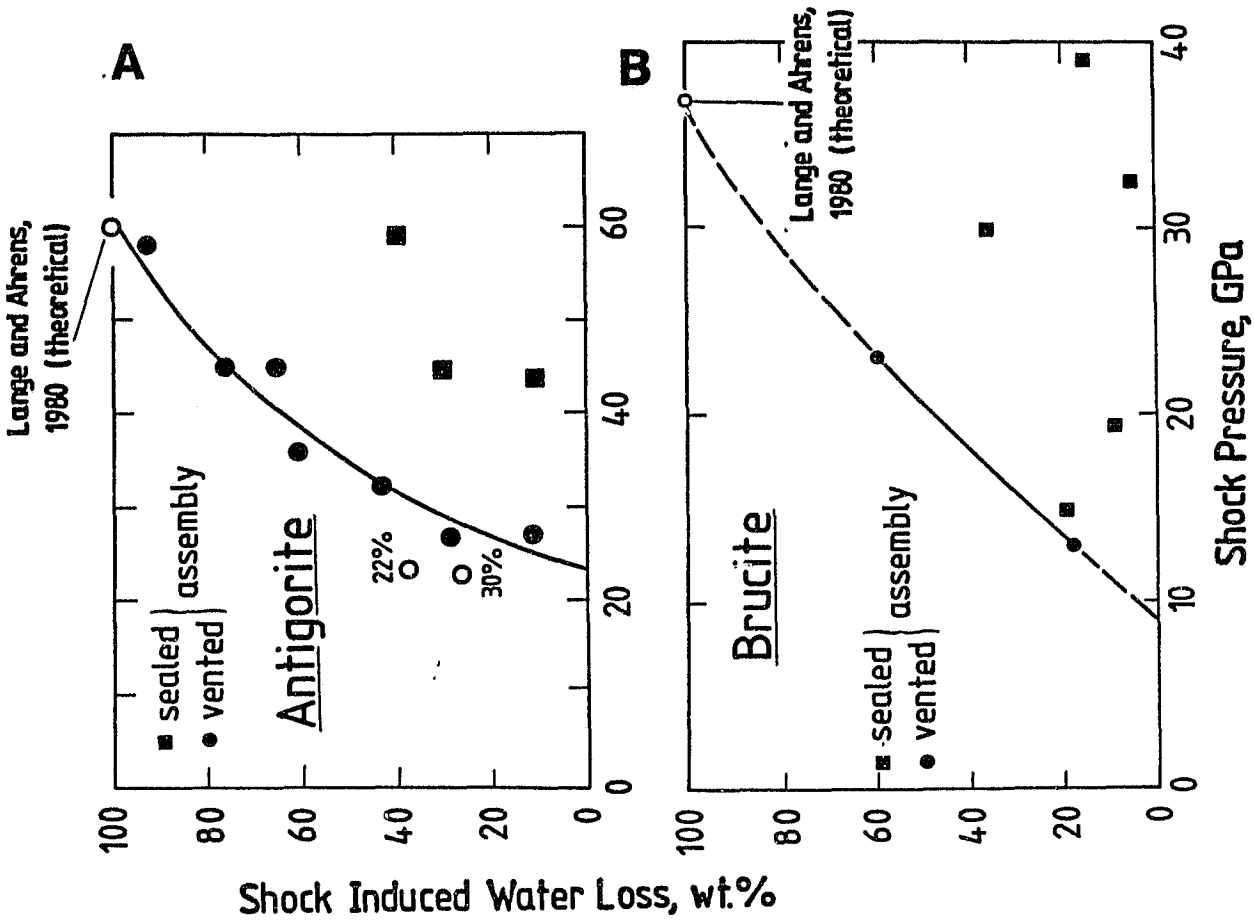
ORIGINAL PAGE IS
OF POOR QUALITY

the clasts of investigated C2 chondrites could have experienced a strong reheating event after shock deformation resulting in essentially complete annealing of all olivines and partial recovery of pyroxenes.

Highly vesicular glasses in the recovery experiments are significant of a congruent melting (with exception for H_2O) of serpentine and micas. Such glasses have not been reported in natural material nor in experimental petrology experiments. These glasses are supposedly metastable and are very likely to be strongly vulnerable to alteration and recrystallization processes. It is proposed as a working hypothesis that some (perhaps PCP and glass) if not most of the matrix of C1 and C2 is related to phyllosilicates melts and/or their alteration. The similarities between C2 chondrites and hydrothermally altered terrestrial impact melts are noteworthy: texture, matrix to clast ratio, hiatus of grain size between clast and matrix, variable degree of alteration of the clast (related to shock conditions in each clast), flow like and/or lamination texture, shock and annealing features in the clast. Finally, the constituents of C2 chondrites are probably not primordial material of an accreting planet but already represent material reprocessed since crystallization via shock, thermal and hydrothermal processes. These processes are possibly related to impact(s).

REFERENCES: (1) Wilkening, L. L., Die Naturwissenschaften 65, p. 73-79, 1978. (2) Barber, D. J., Geochim. Cosmochim. Acta 45, p. 945-970, 1981. (3) Arrhenius G., De B. R., Alven, H., in "The Sea," Goldberg E. D., Ed., Wiley, New York, p. 839-861, 1974. (4) Lange, M. A., Ahrens, T. J., in "Proc. Lunar Planet. Sci. 13," 1982, in press. (5) Benlow, A., Meadow, A. J., Astrophysics and Space Science 46, p. 293-300, 1977. (6) Lange, M. A., Ahrens, T. J., (Abs), Lunar and Planetary Sci. XI, p. 596-598, 1980. (7) Lange, M. A., Ahrens, T. J., Meteoritics, Abstract 45th Ann. Met. Society Meeting, 1982. (8) Lambert, P., Ph.D. Univ. Paris-Orsay, 515 pp, 1977. (9) Lambert, P., Meteoritics 14, p. 466-469, 1979. (10) Lambert, P., Meteoritics, Abstract 45th Ann Met. Society Meeting, 1982. (11) Richardson, S. M., Meteoritics 13, p. 141-159, 1978. (12) Robertson, P. B., Dence, M. R., Vos, M. A., in "Shock Metamorphism of Natural Materials" Ed. by French, B. M., Short, N., p. 433-452, 1968. (13) Engelhardt, W. V., Bertsch, W., Contrib. Mineral Petrol. 20, p. 203-234, 1969. (14) Stöffler, D., Fortschr, Miner. 49, p. 40-113, 1972. (15) Pagel, M., Poty, B., Fortschr, Miner. 52, p. 497-489, 1975. (16) Lambert, P., Contrib. Mineral Petrol. in press, 1982. (17) Bunch, T. E., Chang, S., Geochim. Cosmochim Acta 44, p. 1543-1577, 1980. (18) Mackinnon, I. D. R., Baker, M. B., King, T. V. V., Meteoritics 16, p. 352-353, 1981.

FIGURE 1: Shock-induced water loss in antigorite (A) and brucite (B) as a function of shock pressure in experiments. Numbers on open symbols indicate initial porosities of shocked samples.



ORIGINAL PAGE IS
OF POOR QUALITY

ACCRETION OF WATER BY THE TERRESTRIAL PLANETS

by M. A. Lange and T. J. Ahrens, Seismological Laboratory, 252-21, California Institute of Technology, Pasadena, CA 91125

Introduction

A primary atmosphere probably formed on the terrestrial planets due to the impact-induced release of volatiles in infalling planetesimals during accretion (1, 2, 3). We have previously (3, 4) examined constraints on the production of an impact-generated terrestrial atmosphere by examining the following processes: (i) the supply of volatiles by infalling planetesimals during accretion; (ii) the hydration of non-hydrous silicate minerals (forsterite and enstatite), which will take water from the existing proto-atmosphere; and (iii) the growth of a proto-atmosphere as a result of impact-induced devolatilization of hydrated surface layers of the growing planet. Model calculations led to a number of constraints on the conditions required to generate a primary impact-induced atmosphere. These conditions were met by the accretional environment of Earth and Venus. However, the models are limited by two assumptions. The release of volatiles as a result of shock loading was treated theoretically since data on this process were lacking and we did not model the interaction of metallic iron with water. Ringwood (5) has suggested that this interaction is a primary process by which atmospheric water is dissociated and subsequently lost.

We present new data on the shock-induced dehydration of two hydrous minerals, serpentine ($Mg_3 Si_2 O_5 (OH)_2$) and brucite ($Mg (OH)_2$), which define the amount of dehydration as a function of shock pressure and thus restrain more thoroughly the processes (i) and (iii) of our model calculations. In the present study we also consider reactions between iron and water, which bound the extent of the iron-water interactions during accretion of Earth and Venus.

Shock-Induced Dehydration of Serpentine and Brucite

We carried out shock-recovery experiments on antigorite-serpentine and brucite aimed to determine the amount of shock-induced water loss as a function of shock pressure (6). Thermo-gravimetric analysis of the shocked sample allows determination of its post-shock water content and, by comparison with the initially present water, yields the amount of shock-induced water loss. Figure 1 gives the results of these experiments, which define a single relation between water loss and shock pressure for each mineral. The experimental data agree well with the theoretical predictions for complete water loss (3) and justify the use of these predictions in previous models (3, 4). Shock pressures in serpentine, a likely water bearing phase in terrestrial planetesimals, can be related to impact velocities needed to reach these pressures. Assuming that infall velocities of planetesimals equal the increasing escape velocities of a growing planet, we can relate relative size r/R and relative mass m/M (R, M are final radius and mass of a planet, respectively)to shock pressures in antigorite-serpentine. Given the relations between shock-induced water loss and shock pressure (Fig. 1), we can determine the amount of impact-dehydration in the course of accretion of the terrestrial planets (Fig. 2). Complete water loss in serpentine occurs when Earth and Venus have grown to ~half their radius and have reached ~ 0.1 of their mass. On Mars, complete water loss in serpentine is never achieved during accretion. Thus, generation of an impact-induced atmosphere appears to be possible on Earth and Venus and less likely on Mars.

ACCRETION OF WATER

ORIGINAL PAGE IS
OF POOR QUALITY

Lange, M. A. and Ahrens, T. J.

Interaction of Iron and Water During Accretion

Ringwood (5) has proposed that the reaction of iron and enstatite with water upon accretion of chondritic planetesimals provides a dominant sink for atmospheric water. Assuming homogeneous accretion, a nearly chondritic composition may be approximated by the assemblage of 7.7 wt.% anorthite, 22.5 wt.% enstatite, 34.5 wt.% forsterite, 34.4 wt.% iron and ~3 wt.% water throughout accretion. Ringwood implies that reactions between iron and water on the surface of the growing Earth proceeds rapidly such that essentially all the water present is dissociated and the resulting H_2 subsequently escapes. This process would lead to a lack of a sizable terrestrial water reservoir and to the alteration of ~1/3 of the total iron due to the reactions with water. This would result in a post-accretional FeO content of the Earth of ~17 wt.%, if FeO is not a constituent of the Earth's core (7), i.e., well above current estimates for the iron content of the Earth's mantle of ~8 wt.% (8).

We have taken the present FeO content of the mantle as a constraint to the maximum amount of iron which could have participated in a reaction of the type which causes the mantle to become more olivine rich than chondrites:

$$MgSiO_3 + Fe + H_2O \rightarrow 1/2\ Fe_2SiO_4 + 1/2\ Mg_2SiO_4 + H_2\uparrow$$

In order for the Earth to retain its water complement, we conclude that either a sufficient amount of hydrous phases were accreted before the Earth had grown to ~10% of its final mass or that the Earth's water was accreted late in its formation as proposed by Smith (9).

References: (1) Arrhenius G., De B. R., and Alven H. (1974) In The Sea, 839-861, Wiley, N.Y. (2) Benlow A. and Meadows A. (1977) Astrophys. Space Science 46, 293-300. (3) Lange M. A. and Ahrens T. J. (1980) In Lunar and Planetary Science XI, 596-598, Lunar and Planetary Institute, Houston, TX. (4) Lange M. A. and Ahrens T. J. (1982a) Icarus, in press. (5) Ringwood A. E. (1979) Origin of the Earth and Moon, 295 pp., Springer, N.Y. (6) Lange M. A. and Ahrens T. J. (1982b) J. Geophys. Res., in press. (7) Watt J. P. and Ahrens T. J. (1982) J. Geophys. Res. 87, 5631-5644. (8) Wiley P. J. (1971) The Dynamic Earth: Textbook in Geosciences, 416 pp., Wiley, N. Y. (9) Smith J. V. (1977) Proc. Lunar Sci. Conf. 8th, 333-369.

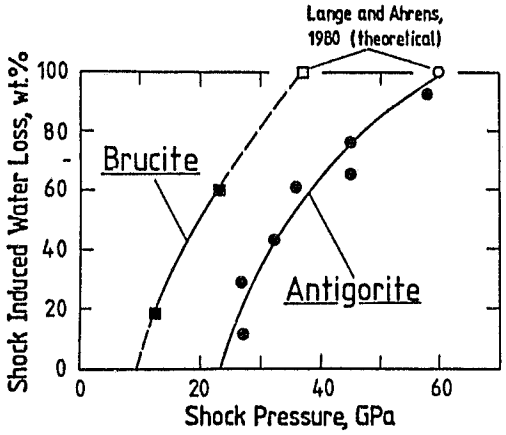


Figure 1: Shock-induced water loss in antigorite and brucite as a function of shock pressure in present experiments.

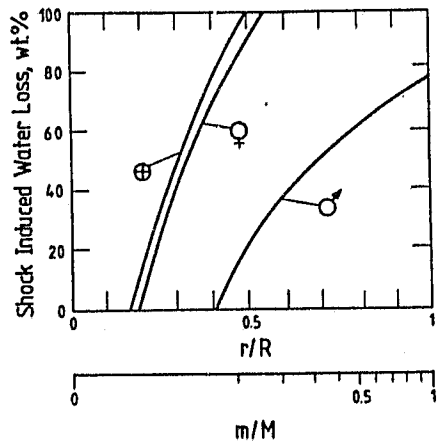


Fig. 2: Shock-induced water loss in antigorite (in wt. % of the total amount of structural water in antigorite) as a function of relative size (r/R) and relative mass (m/M) of the accreting terrestrial planets. Dehydration of antigorite in infalling planetesimals and proto-crusts of growing planets takes place when the threshold pressures as given in Figure 1 are exceeded. This takes place at different stages in the accretional sequence for each planet, the position of which depends on the mean density and the final size of the planetary body as given by the curves for Earth (⊕), Venus (♀), and Mars (♂). Further details, see text.

VOLATILE/MOBILE TRACE ELEMENT FRACTIONATIONS IN METEORITE PARENT BODIES,
M. E. Lipschutz, T. Huston, T. M. Walsh, Dept. of Chem., Purdue Univ., W. Lafayette, IN 47907

Meteorites probe, in space and time, the formation and evolution of solid bodies within the early solar system. Primary nebular processes (condensation and accretion) fractionated volatile/mobile elements: if subsequent processes left primary compositions unaltered, it should be possible to work backward and compute primary conditions from trace element contents. Until recently, it had been assumed that post-accretionary thermal episodes occurred under closed conditions leaving primary compositions unaffected. However, our studies demonstrate that this was not so. We use data from primitive chondrites, artificially heated for extended periods under conditions reasonable for specific thermal episodes, to study vaporization processes. We discuss, below, specific meteoritic groups whose compositions reflect secondary processes [solid state thermal metamorphism or fractionations involving a liquid phase in the parent body] or tertiary processes [shocked-induced vaporization and loss from debris generated during collisional break-up of the meteorites' parent].

Trace element contents of carbonaceous chondrites apparently reflect only primary processes. A model like that of Anders and co-workers (e.g. Ebihara et al., 1982) accounts for most trace element trends in these chondrites.

Enstatite meteorites (chondrites, achondrites and at least one stony-iron) compositionally reflect secondary processes within their parent body (Biswas et al., 1980). Contents of Ag, As, Bi, Cd, Co, Cs, Cu, Ga, In, Rb, Se, Te, Tl and Zn in artificially-heated Abee (E4) indicate that the achondrites (aubrites) and stony iron reflect fractional crystallization of a magma produced from enstatite chondrite-like parent material (probably E6) and late introduction of chalcophiles and mobile elements transported by FeS-Fe eutectic from an E4-6 region that underwent open-system metamorphism. The only primary process that affected E4-6 chondrites involved fractionation of nonvolatile lithophiles from sulfides and metal during nebular condensation and accretion of chondritic parent material.

Many meteorites, especially L4-6 chondrites, have been shocked in preterrestrial collisions to an extent sufficient to alter mineralogic/petrologic features and $^{40}Ar/^{39}Ar$ radiogenic ages. These alterations almost certainly do not reflect peak temperatures attained during the very short term passage of the shock wave but, rather, elevated residual temperatures which, after decompression, persist for days to years. Our studies demonstrate that many trace elements are more labile in heated chondrites than is radiogenic ^{40}Ar (cf. Bart et al. (1980) and Ngo and Lipschutz (1980) for earlier references). Hence, chondrites with disturbed Ar ages should contain lesser amounts of mobile elements than those with undisturbed long ages and such elements should potentially be thermometers for shock events. We analyzed trace elements Au, Co, Se, Ga, Rb, Cs, Te, Bi, In, Ag, Zn, Tl and Cd in two sample populations: Population I - 28 L4-6 chondrites of known shock exposure, for calibration purposes; Population II - 21 L4-6 and 12 H4-6 chondrites whose $^{40}Ar/^{39}Ar$ release characteristics were established previously by others.

The elements above are listed in order of increasing mobility, i. e. average loss from five different chondrites at 1000°C compared with the respective unheated materials (cf. Neal et al. (1981) for references). In chondrites of Population I, contents of the first 6 elements do not vary with degree of shock-loading: the next 7 do - mean contents in lightly shocked chondrites (<20 GPa) of facies a+b exceed those in moderately shocked samples (20-35 GPa) of facies c+d and these, in turn, exceed contents in heavily

ORIGINAL PAGE IS
OF POOR QUALITY

shocked specimens (>35 GPa) of facies e+f. For those 7, differences between mean contents in lightly and heavily shocked chondrites generally increase with elemental mobilities. We found significant differences between L chondrite sub-populations defined by S/Fe ratio (Neal et al., 1981), petrologic type and shock-loading: effects due to shock predominate over those associated with the first two.

Effective outgassing temperatures for $^{40}Ar/^{39}Ar$ ages may be even lower than calculated by Turner (1981). We treated L5 and L6 chondrites of Population II separately and compared trace element contents in meteorites having disturbed radiogenic ages with those having an undisturbed age or being of facies a, b or c. In each case, chondrites with disturbed ages had significantly lower contents of highly mobile elements indicating that shocks severe enough to alter $^{40}Ar/^{39}Ar$ ages were sufficient to cause trace element loss. Interestingly, contents of a few mobile trace elements are significantly lower in Population II chondrites having disturbed $^{40}Ar/^{39}Ar$ ages than in Population I samples of facies d-f.

In summary, trace element contents may be altered by secondary and/or tertiary processes. Potentially, it should be possible to "correct" for these and compute primary compositions. At the least, it should be possible to use mobile element contents as cosmothermometers for each fractionation process in suitable samples.

References

Bart G., Ikramuddin M. and Lipschutz M. E. (1980) Geochim. Cosmochim. Acta 44, 719-730

Biswas S., Walsh T., Bart G. and Lipschutz, M. E. (1980) Geochim. Cosmochim. Acta 44, 2097-2110.

Ebihara M., Wolf R. and Anders E. (1982) Geochim. Cosmochim. Acta, in press.

Neal C. W., Dodd R. T., Jarosewich E. and Lipschutz, M. E. (1981) Geochim. Cosmochim. Acta 45, 891-898.

Ngo H. T. and Lipschutz M. E. (1980) Geochim. Cosmochim. Acta 44, 731-739.

Turner G. (1981) Proc. Roy. Soc. Lond. A374, 281-298.

Walsh T. M. and Lipschutz M. E. (1982) Geochim. Cosmochim. Acta, submitted.

ORIGINAL PAGE IS
OF POOR QUALITY

CARBON IN ROCKS FROM THE EARTH'S MANTLE. E.A. Mathez[1], V.J. Dietrich[2], and A.J. Irving[1] ([1]Dept. of Geological Sciences, Univ. of Washington, Seattle, Wa., 98195; [2]Inst. Krist. und Petrog., ETH-Zürich, CH-8092 Zürich, Switzerland)

The absolute abundances of C and relative amounts of vapor phase C (mainly CO_2), condensed C, and carbonate have been determined in a representative suite of mantle-derived peridotite xenoliths from alkali basalts and kimberlites. Analyses were made of the interior portions of xenoliths least likely to have experienced chemical exchange with host lava. Samples were crushed to coarse (<1.4 mm) fragments, washed either in H_2O or in cold 1N HCl, and fused with a flux. Fusion in an oxygenated atmosphere liberated all C as CO_2, which was then determined by titration. Fusion in a reducing atmosphere (N_2) released only CO_2, while elemental C was largely retained in the charge.

A significant proportion of the C in nearly all samples is removed by acid-washing (fig. 1). This soluble fraction must consist almost entirely of carbonate present on grain boundaries. This material probably originated from a source external to the xenolith, judging from the fact that C abundances in the unwashed samples are highly variable compared to those in the acid-washed ones. In some samples, such as those from Kilbourne Hole (KH), contamination by meteoric carbonate is suspected. In samples from areas in which obvious meteoric sources are lacking, the xenolith carbonate probably originated by post-eruption redistribution of C derived originally from the host lava. Garnet lherzolite and eclogite xenoliths from kimberlites are typically carbonate-rich (90 to 1100 ppm carbonate C). In all of these rocks, truly "indigenous" carbonate is probably restricted to the dolomite and magnesite found in polymineralic inclusions in silicates (1,2) or as daughter products in CO_2-rich fluid inclusions (3). Carbonates in these occurrences are extremely rare, however.

Typical acid-washed Cr-diopside and spinel-bearing (Group I) lherzolites contain 10-40 ppm total C (fig. 2). Although Group I xenoliths are generally believed to be residues from which a partial melt was extracted (4), some of those from KH possess REE and isotopic characteristics that would permit mid-ocean ridge tholeiites (MORBS) to be generated from them (5,6). If the mantle below KH is indeed representative of that underlying the ocean basins, then source regions of MORBS contain approximately 20-25 ppm C.

The chemically more evolved Al-augite (Group II) pyroxenites have C abundances that are on average only slightly higher than those in the Group I rocks. This is in particular true for some composite KH xenoliths consisting of deformed lherzolites intruded by pyroxenite dikes (5,7). The close similarity of C abundances in the two rock types of the composite samples is not an expected consequence of the postulated formation of the pyroxenites as crystallization products of alkali basaltic magma. Possibly, the C signature of all KH rocks was imposed later than the initial fabric-forming deformation of the lherzolite and the subsequent igneous activity which produced the pyroxenites.

Within the spinel lherzolite suite, C abundances appear to be related to the degree of LREE enrichment (fig. 3). This is consistent with the generally accepted hypothesis that the incompatible trace element characteristics of these rocks are determined by metasomatic CO_2 or CO_2-H_2O-rich fluids (8). The behavior of C appears to be similar to that of the incompatible trace elements rather than being related to the overall degree of chemical evolution of mantle rocks (as expressed, for example, in their major elements or in absolute REE abundances).

CARBON IN THE EARTH'S MANTLE

ORIGINAL PAGE IS
OF POOR QUALITY

Mathez, E.A., et al.

Elemental C, possibly mixed with small amounts of organic matter, is observed on grain boundaries, on crack surfaces, and on the walls of fluid inclusions formed by annealing of microcracks (9). The condensed C is thought to have precipitated by disproportionation of CO according to the reaction $2CO \rightarrow C + CO_2$ at moderate to low pressures ($\lesssim$ 5 kb), possibly during post-eruptive cooling of the xenolith. Although considerable analytical uncertainty exists for individual measurements, the average mass ratio of $C:CO_2$ in the peridotites is $\sim$0.06. If all elemental C formed in the above manner, then the vapor from which C precipitated consisted of $\sim$30 mole % CO and 70 % CO_2 (on an anhydrous basis). This is similar to the estimated composition of vapor associated with MORB magmas (9).

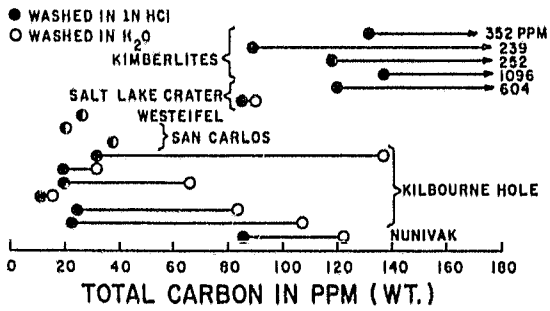


Fig. 1. Comparison of C abundances in water and acid-washed splits of some selected xenoliths.

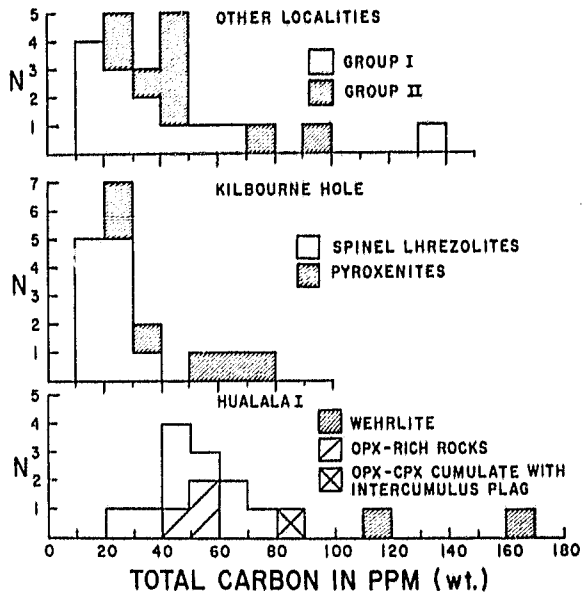


Fig. 2. C abundances for acid-washed xenoliths from alkali basalts. The Hualalai samples are believed to be mantle cumulates (10). Unlabelled Hualalai samples are dunites.

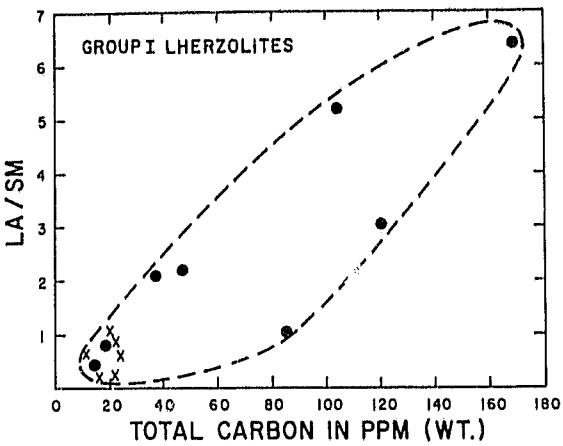


Fig. 3. Variation of C abundances in acid-washed Group I rocks with their degree of LREE enrichment. REE data from (5) and (11). (X) Kilbourne Hole; (●) other localities.

Refs: (1) McGetchin, T.R., and Besancon, J.R., 1973, Earth Planet. Sci. Lett., 18, 408-410. (2) Hervig, R.L., and Smith, J.V., 1981, Am. Mineral., 66, 346-349. (3) Rovetta, M.R., and Mathez, E.A., 1982, Abs, 3d Internat. Kimberlite Conf. (4) Frey, F.A., and Green, D.H., 1974, Geochim. Cosmochim. Acta, 38, 1023-1059. (5) Irving, A.J., 1980, Am. J. Sci, 280-A, 389-426. (6) Jagoutz, E., et al., 1980, Nature, 286, 708-710. (7) Bussod, G.Y., 1981, M.S. Thesis, Univ. Washington, Seattle. (8) Wendlandt, R.F., and Harrison, W.J., 1979, Contr. Mineral. Petrol., 69, 409-419. (9) Mathez, E.A., and Delaney, J.R., 1981, Earth Planet. Sci. Lett., 56, 217-232. (10) Jackson, E.D., et al., 1981, U.S.G.S. Open File Rept. 81-1031. (11) Basaltic Volcanism Study Project, 1981, Ch. 1.2.11.

ORIGINAL PAGE IS
OF POOR QUALITY

THE STRUCTURE OF THE PRIMORDIAL ATMOSPHERE AND THE AMOUNT OF GRAINS. H. Mizuno, Carnegie Institution of Washington, Department of Terrestrial Magnetism, 5241 Broad Branch Road, N.W., Washington, D.C. 20015

Two topics on the primordial atmosphere will be presented. First, the structure of the primordial atmosphere of the earth will be described in relation to the dissolution of rare gases. The second topic is an attempt to determine the grain opacity which is an important factor to govern the structure.

According to the theory of planet formation in the solar nebula, the primordial atmosphere forms around the earth and has significant effects on the initial state of the earth both thermally and chemically. One such effect is the dissolution of rare gases contained in the primordial atmosphere into the molten earth material. Numerical calculations show that the amount of dissolved rare gases depends on grain opacity in the atmosphere. The higher grain opacity gives the less amount of dissolved mass (1). The direct cause of this dependence is that the atmospheric pressure is lower in the higher grain opacity model. The computations indicate that the lower atmospheric pressure is a result of the fact that there exists less gaseous mass in the inner region of the atmosphere where the gravity is strong. This is explained in the following way: In general the high grain opacity lengthens the density scale height which gives a measure of density gradient. Moreover the density distribution of the primordial atmosphere is smoothly connected to the density of the solar nebula at the Hill sphere. Therefore, in the higher grain opacity model, we get a lower density or consequently lower gaseous mass in the inner region. Thus the high grain opacity yields the small mass of dissolved rare gases into the molten earth material.

The grain opacity is an important parameter, as seen above, when one considers the structure of the primordial atmosphere. How large is the grain opacity in the primordial atmosphere? What processes determine it? If there are not any sources of grains in the atmosphere, the grain opacity has the value of that for the solar nebula, that is, the order of 10^{-4} cm^2/g. This is because the primordial atmosphere is composed of the nebula gas. However one must not forget a possible source during the accretion phase of the earth. Let us consider a planetesimal which goes into the Hill sphere from near Lagrangian points. The motion of the planetesimal is approximately expressed as Keplerian motion around the earth. The gas drag force acting on the planetesimal gradually changes the orbital elements of the Keplerian motion. For example, the gas drag dissipates the energy and the semi-major axis becomes small. Finally it collides on the earth and contributes to the growth of the earth. While the planetesimal is moving in the primordial atmosphere in this way, it sprinkles its own material as grains into the atmosphere owing to the large relative velocity between the planetesimal and the atmospheric gas and owing to the high gaseous density. This process can be a source of grains during the accretion phase. On the other hand, the grains sprinkled by the planetesimal soon stop the motion relative to the atmospheric

PRIMORDIAL ATMOSPHERE AND GRAINS

Mizuno, H.

gas because of the strong gas drag, and begin to sink toward the earth owing to gravity. Hence the sedimentation can be a sink of grains in the atmosphere.

These two mechanisms are acting in opposite directions, that is, sprinkle and sedimentation of grains give the actual amount of grains in the primordial atmosphere. The essential parameters to determine the amount are the grain size and the fraction of the energy used to separate grains from the gravity field of planetesimals. Moreover, if a large convective region exists, the convective motion plays a role to retain the grains in the convective region for a longer time compared with the quiet atmosphere. It is found that, in order that the high opacity (~ 1 cm^2/g) is realized, the growth time scale during which the grains grow up to about 1 cm in the convective region is necessary to be longer than the time scale of sedimentation for the grains with the size of 1 cm ($\sim 10^{-2}$ yrs).

Reference:

(1) Mizuno, H., Nakazawa, K. and Hayashi, C. (1980) Earth Planet. Sci. Lett. 50, 202-210.

ORIGINAL PAGE IS
OF POOR QUALITY

ORIGINAL PAGE IS
OF POOR QUALITY

CHLORINE CONCENTRATIONS IN CHONDRITES: Carleton B. Moore, Keenan L. Evans and James G. Tarter, Center for Meteorite Studies, Arizona State University, Tempe, AZ 85287

The non-metallic and sometimes volatile elements chlorine, fluorine and sulfur have been determined in a suite of chondritic meteorites using a recently developed pyrohydrolytic-ion chromatographic method (Evans et al., 1981). Values for chlorine in falls of the different chondrite classes are given below:

Class	Average Cl (ppm)
C1	540
C2	340
C3	280
E4	670
E5	170
H	100
L	230
LL	90

A short experiment to determine water soluble constituents of carbonaceous and ordinary chondrites indicated nil solubility of fluoride, nitrate or phosphate ions. For the C2 chondrite Murchison 60% of the total chloride was leachable (200 μg/g). Twenty percent of the total sulfur was leachable (2.2%). This solubility and subsequent concentration on surface grains is presented as a possible model for the relatively high sulfur and chlorine concentrations of Martian soil. In the soil X-ray fluorescence analysis has indicated a 1:10 ratio of Cl:S. Liquid water with dissolved carbon dioxide has proven to be an effective solvent for chondritic material. If carbonaceous chondrites are as common in the Martian soil as in the lunar regolith and liquid water has been present during Martian history, the carbonaceous chondrites can selectively add soluble material to the Martian soil. In addition to the chlorine and sulfur noted above, this also includes hydrated ferric oxides.

ORIGINAL PAGE IS
OF POOR QUALITY

PLANETARY ABUNDANCES OF VOLATILE ELEMENTS: A DATUM FROM THE EARTH'S UPPER MANTLE

John W. Morgan, U.S. Geological Survey, Mail Stop 911, Reston, Virginia 22092

Planetary bulk composition and volatile complement can be examined from two ends of the evolutionary spectrum. The meteorites provide evidence of the material extant in the early history of the solar system and of the compositional range of the accretionary debris that formed the planets. The accessible parts of the planets reveal the end products of accretionary fractionation and of 4.5 b.y. of planetary evolution. Recent measurements of siderophile and volatile trace elements in terrestrial ultramafic xenoliths (1-3) provide a fixed point against which to test model compositions and conversely may be viewed in terms of the general framework of other planets.

Bulk Composition of Terrestrial Planets Estimates of the bulk compositions of the terrestrial planets can be made from the basic premise that planetary matter condensed from a cooling solar gas under equilibrium conditions (4). Three primary components formed sequentially; an early condensate, rich in Ca, Al, and refractories; metallic Ni-Fe; and Mg silicates. Below ~700K, metal and silicates take up volatile elements; metal reacts with H_2S to form a fourth component (FeS) and with H_2O to form FeO that enters the Mg silicates. Evidence from the chondritic meteorites suggests that the three primary components became mutually fractionated. Before or during accretion some material underwent a brief melting episode (analogous to chondrule formation) during which volatile elements were lost from the silicates and FeS was reduced to metal, thus providing two more components; remelted silicate and remelted metal. Finally, the highly volatile elements which were only partially condensed may be assigned to a seventh volatile-rich component. The elements may be divided into major groups on the basis of volatility, and, as members of the groups generally remain in approximately cosmic proportions, one well-chosen indicator element may represent the whole group. Index elements used to calculate bulk compositions of terrestrial planets are summarized in Table 1 (5-7). The index ratios are chosen because these incompatible elements are strongly correlated in crustal processes, but the choices are not unique. In the Earth, for example, Rb/Sr ratios derived from isotopic systematics could equally well be used. Indicator ratios differ significantly between planets. The K/U ratios on Earth and Venus are five or six times lower than they are in chondrites; they are even lower in smaller planets. Indicator ratios show that the more volatile elements are severely depleted on the Moon, Mars (and presumably Mercury). Where Tl abundances have not been measured directly, they may be approximated from data from planetary atmospheres; Ar^{36} on Mars (8), or C and N on Venus.

Table 1 Index elements and ratios for the calculation of terrestrial planet compositions

Component	T_{cond}(K)	Index	Mercury	Venus	Earth	Moon	Mars
Early condensate	>1400	U ppb	11	15	14.3	40	28
Metal	1400-1300	Core %	68	32	32.4	~2	19
Remelted silicate	1400-1300	difference					
Unremelted silicate	1300-600	K/U*	2000	10,000	9440	1900	2200
Volatile-rich material	<600	Tl/U*	0.004	0.27	0.27	0.0023	0.005
Wustite (FeO)	~900-500	$\frac{FeO}{(FeO+MgO)}$‡	0.03	0.07	0.12	0.20	0.23

Values underlined are poorly determined * Weight ratio ‡ Molar ratio

ORIGINAL PAGE IS
OF POOR QUALITY

VOLATILE ELEMENTS FROM EARTH'S UPPER MANTLE

Morgan, J.W.

Terrestrial Ultramafic Xenoliths In terrestrial ultramafic xenoliths (garnet lherzolites and spinel lherzolites) the most uniform and well-determined abundances are those of the moderately siderophile elements (2,3): On a C1 chondrite-normalized basis; Ni, 0.20±0.02; Co, 0.22±0.02; Ge, 0.027±0.004. The low Ge/Ni of 0.137 is apparently a reasonable reflection of the volatile depletion of the bulk Earth, and is essentially identical to the terrestrial model value of Ge/Ni = 0.138 (C1 chondrite-normalized) calculated from entirely independent assumptions (6). Absolute abundances of Ni, Co, and Ge in the Earth's mantle are significantly lower than calculated bulk estimates because significant amounts of these elements reside in the Earth's core. It could be argued, therefore, that the low Ge/Ni ratio results from metal-silicate fractionation during core formation. The argument can be countered by estimating the bulk Ni content of the Earth from observed mantle abundances by making the model-dependent, but cosmochemically reasonable assumption that Ge is about as abundant as the moderately volatile lithophile elements. [The assumption seems reasonable because the bulk (total Fe)/Si ratio of the Earth is essentially identical to the cosmic value, indicating little metal-silicate fractionation before or during accretion]. To derive a bulk Ni value from observed mantle xenolith abundances, Ge is scaled to Zn (a well-determined compatible element) to yield Ni = 1.8 percent; a result in excellent agreement with the bulk Earth value of 1.82 percent derived by model calculation (6). Many analysed xenoliths represent depleted mantle which may or may not have been metasomatized. Sheared garnet lherzolite PHN 1611 possibly represents a sample of mantle that is relatively undepleted and not seriously affected by metasomatism. Abundances of lithophile volatile elements in PHN 1611 tend to be higher than those in granular garnet lherzolites and spinel lherzolites, and more uniform when normalized to C1 chondrites. The homologous elements Zn (moderately volatile) and Cd (very volatile) behave as compatible elements in ultramafic xenoliths and observed abundances agree quite well with the model calculations when normalized to C1 chondrites and Si.

	Zn	Cd
Calculated	0.17	0.018
PHN 1611	0.14	0.032

The highly chalcophile elements Se and Te are strongly depleted in mantle xenoliths relative to elements of similar volatility and ~97 percent of the Earth's S, Se, and Te may reside in the outer core. Abundances of Te in the xenoliths are remarkably constant, and closely resemble the C1 chondrite-normalized abundances of such highly siderophile elements as the Pt group metals (PGM). The Te/PGM ratio is 0.8 in PHN 1611 and 0.5 in spinel lherzolites. The PGM's were apparently introduced by a late bombardment of the Earth after core formation (3,9), and if the observed Te/PGM ratio represents that in the bombarding population, then the average composition of the planetesimals may have been as high in volatiles as the C2 chondrites, which contain 8 percent H_2O. The late bombardment could then supply ~135 ppm H_2O, on 15 ppm H. This lower limit may be compared to a calculated value of 33 ppm H (6).

References: (1) Jagoutz, E., Palme, H., Baddenhausen, H., Blum, K., Cendales, M., Dreibus, G., Spettel, B., Lorenz, V., and Wanke, H. (1979) Proc. Lunar Planet. Sci. Conf. 10th, pp. 2031-2051. (2) Morgan, J.W., Wandless, G.A., Petrie, R.K., and Irving, A.J. (1980) Proc. Lunar Planet. Sci. Conf. 11th, pp. 213-233. (3) Morgan, J.W., Wandless, G.A., Petrie, R.K., and Irving, A.J. (1981) Tectonophysics, 75, pp. 47-67. (4) Ganapathy, R., and Anders, E. (1974) Proc. Lunar Planet. Sci. Conf. 5th, pp. 1181-1206. (5) Morgan, J.W., and Anders, E. (1979) Geochim. Cosmochim. Acta, 43, pp. 1601-1610. (6) Morgan, J.W., and Anders, E. (1980) Proc. Natl. Acad. Sci. USA, 77, pp. 6973-6977. (7) Morgan, J.W., Hertogen, J., and Anders, E. (1978) The Moon and Planets, 18, pp. 465-478. (8) Anders, E., and Owen, T. (1977) Science, 198, pp. 453-465. (9) Chou, C.-L. (1978) Proc. Lunar Planet. Sci. Conf. 9th, pp. 219-230.

ORIGINAL PAGE IS
OF POOR QUALITY

EQUILIBRIUM COMPOSITION OF THE MT. ST. HELENS MAGMATIC VOLATILE PHASE FROM THE PYRRHOTITE-MAGNETITE ASSEMBLAGE; B. E. Nordlie, S. E. Thieben, and D. R. Burggraf, Department of Earth Sciences, Iowa State University, Ames, Iowa 50011

On October 16, 1980, a pyroclastic eruption initiated the sixth major phase of activity at Mt. St. Helens since the preceding March. At Cougar, WA, 15 km southwest of the summit, the fall of dacitic pyroclastic material included a short period of pumice lapilli followed by a longer period of lithic- and pumice-rich crystal ash. Both the pumice lapilli and crystal ash include a glassy matrix and phenocrysts of plagioclase, pyroxene, hornblende, biotite, and magnetite; the crystal ash also includes a sulfide phase of pyrrhotite with minor intergrown chalcopyrite.

The association of magnetite and pyrrhotite was utilized to determine the Mt. St. Helens volatile phase equilibrium composition. Determination of d_{102} for the pyrrhotite by X-ray diffraction yields an Fe content of 61.65 weight percent. By microprobe analysis, the pyrrhotite composition is 58.57 wt. % Fe, 5.36% Cu, 36.84% S, and 0.09% Ni.

Molecular equilibrium calculations in the C-O-H-S gaseous system were carried out to determine the range of bulk gas compositions which can be in equilibrium with the pyrrhotite-magnetite assemblage. S_2 fugacity versus temperature in the volatile phase is specified by the measured pyrrhotite composition; the S_2/O_2 fugacity ratio is fixed by the coexistence of magnetite with pyrrhotite. Additional constraints were selected in order to bracket expected properties of the St. Helens volatile phase:

1) atomic bulk compositions which yielded equilibrium H_2O contents less than 75 vol. % were not considered, 2) atomic C/S was limited to the range 2.0 to 6.0, 3) O_2 fugacity and temperature limits were set between 10^{-9} to 10^{-10} and 950 to 1050°C, respectively, to widely bracket f_{O_2} and T determined by others from the magnetite-ilmenite f_{O_2} barometer. Total pressure was allowed to vary as dictated by the above conditions. Equilibrium compositions were determined from 650 to 1250°C in order to assess higher and lower temperature properties of the gaseous equilibrium.

Computed results show that f_{S_2} and f_{O_2} requirements can be satisfied only at temperatures above 1020°C. Bulk C-O-H-S compositions in equilibrium with the Po-Mt assemblage are severely restricted; the addition of H_2O to any specific "allowed" composition causes Po-Mt to become unstable. Minimum total pressures vary with temperature and atomic C/S and are in the range 13 bars (1020°C, C/S = 2.0) to 47 bars (1050°C, C/S = 6.0). Maximum total pressures calculated are from 27 to 130 bars. Higher total pressures are possible in very H_2O-rich systems but quickly exceed pressures expected in a sub-volcanic magma chamber.

Equilibrium molecular compositions show that the volatile phase is dominated by H_2O, CO_2, SO_2, and H_2S. H_2S/SO_2 varies from about 1 to 10. COS contents are lower but significant; CS_2 is present in trace amounts only.

Within the possible bulk composition range, those gases with low H_2O are most likely to coexist with Po-Mt assemblages since degassing during pressure decrease is expected to increase the H_2O content of the volatile phase.

ORIGINAL PAGE IS
OF POOR QUALITY

HEAT AND VOLATILE TRANSPORT IN PLANETARY INTERIORS

Richard J. O'Connell, G. A. Houseman, Department of Geological Sciences, Harvard University, Cambridge, Massachusetts.
B. H. Hager, Seismological Laboratory, California Institute of Technology, Pasadena, California

The transport of volatiles within the earth is closely related to heat transport. Thermal convection in the mantle determines large scale mass transport in the interior, and diffusing volatile species should mimic conductive heat losses near the surface. Most of the earth's present day heat loss is associated with magmatic transport of heat at mid-ocean ridges; this process should dominate volatile transport as well. Since the solid state diffusivities of most volatiles are lower than the thermal diffusivity, diffusive transport of volatiles should be slow, and volatile transport should be dominated by motions of volatile rich fluid phases, which may result in a relatively higher effective diffusivity.

Volatile losses at ridges can be modelled from simple numerical convection models that include lithospheric plates. The resulting transport depends on the pattern of thermally driven interior motions that bring material close enough to the surface beneath a ridge for partial melting, and volatile loss, to occur. At the present rates of plate motions, it would require nearly 5Gy to move the entire mantle through a zone 100 km beneath the mid-ocean ridges. This suggests that a substantial fraction of the original volatile inventory has not been lost. If the upper and lower mantle are separated and have non-mixing convection patterns, then volatiles, and heat, must traverse an internal conductive boundary layer to escape the lower mantle. Parameterized convection models can be used to estimate the relation between effective volatile diffusivities and transport across this boundary. Unless volatile diffusivities are comparable to or greater than thermal diffusivities, or direct transport of fluid phases occurs across the boundary, volatile loss from the lower mantle is small.

ORIGINAL PAGE IS
OF POOR QUALITY

RELATIONSHIPS BETWEEN HEAT AND RARE GAS TRANSPORT IN THE EARTH.

R.K. O'Nions and E.R. Oxburgh, Dept. of Earth Sciences, Cambridge University, Cambridge, England.

The isotopes ^{40}K, $^{235,238}U$ and ^{232}Th decay to produce heat and the rare gas isotopes ^{4}He and ^{40}Ar. The generation of heat and these radiogenic rare gases in the Earth are therefore coupled in space and time. The Earth's mantle loses about 60-70 mW m^{-2} of Earth's surface through the plates and the remaining portion of global heat flow arises from radioactivity within the continental crust. Heat lost from the upper mantle exceeds the estimates of the production rate within the upper mantle indicating derivation of stored heat (primordial and/or radiogenic) from deeper levels within the Earth. Primordial ^{3}He is probably also associated with this deeper reservoir, and its release must be associated with release of heat.

The observed relationships between heat flow and heat production in the continental crust are generally modelled by an exponential decrease of heat-producing elements with depth, with a characteristic depth of 8-12 km. If such models have general validity then the production rates of ^{4}He and ^{40}Ar in the continents will follow identical exponential distributions. The relationship between heat and rare gas transport in the continental crust is of fundamental importance, but poorly understood. The conductive thermal time constant for the continental crust is 10^{7} to 10^{8}a. Consideration of rare-gas abundances and production rates in high and low enthalpy geothermal systems developed in the upper part of the continental crust suggests that the crust acts as a variably semi-permeable membrane for rare gases and that the residence time for He may be of the order of 10^{7}a, and significantly shorter than ^{40}Ar. Diffusion of He from the mantle through the continental crust does not appear to be an important process. Transport of He by magmas to the surface or high levels in the crust and its subsequent ventilation through geothermal systems appears to be the principal mechanism of transport.

ORIGINAL PAGE IS
OF POOR QUALITY

CURRENT COMPOSITIONS OF PLANETARY ATMOSPHERES. Tobias Owen, Dept. of Earth and Space Sciences, State Univ. of New York, Stony Brook, New York 11794

The successes of Venera 13 and 14 at Venus and Voyagers 1 and 2 at Saturn have led to improved spacecraft data on the composition of the atmospheres of Venus, Saturn, and Titan. These new results can be compared with previous work on these objects and with other studies of Mars and Jupiter. We do not yet have observations from spacecraft of Uranus, Neptune, Pluto, and Triton, but ground-based and near-Earth observations give us a preliminary indication of atmospheric composition for these bodies. It is already clear, for example, that the atmospheres of Uranus and Neptune have different compositions from those of Jupiter and Saturn and from each other. We still need more information about Jupiter and Saturn to see how similar their atmospheres are and how closely their compositions reflect abundances that existed in the primordial solar nebula. Isotopic data will be helpful in this discrimination, but available values for D/H and $^{12}C/^{13}C$ are not completely consistent. Titan offers us an evolved, reducing atmosphere in which some of the chemistry may resemble reactions on the primitive Earth. The origin of that atmosphere seems tied to the formation of clathrate hydrates. This mechanism may also contribute to the incorporation of volatiles in comets, which may in turn provide a pathway for bringing material from the outer solar system to the inner planets.

In the inner solar system, we are seeking to determine just how similar are the volatile inventories of Mars, Venus, and Earth. Rough agreement between the atmospheric C and N on Venus with estimates of outgassed quantities of these elements on Earth has led in the past to the expectation of a common source of volatiles for all the inner planets. Viking studies of the atmosphere of Mars appeared consistent with this hypothesis although this smaller planet has evidently experienced much less outgassing than its larger neighbors. Isotopic information on Martian gases includes a high value of $^{15}N/^{14}N$ attributable to escape of nitrogen and high ^{129}Xe relative to terrestrial xenon. The recent discovery of a non-planetary pattern in the noble gases in the atmosphere of Venus requires a modification of the common reservoir hypothesis. Some local process has evidently enriched the neon and argon in that planet's atmosphere compared with the relative abundances found on Earth and Mars. However, the large amount of primeval water on Venus implied by the huge enrichment of deuterium in the present epoch suggests that distant sources did contribute volatiles to th. planet. These sources may again represent the common reservoir, or there may simply be no common reservoir.

A large step toward the resolution of these ambiguities could be made by a coordinated set of atmospheric probes and missions to comets. We may hope for considerable progress from planned investigations of Halley's Comet (Giotto, Vega) and the atmosphere of Jupiter (Galileo).

ORIGINAL PAGE IS
OF POOR QUALITY

THE SEDIMENTARY INVENTORY OF ATMOSPHERIC XENON

F. A. Podosek, T. J. Bernatowicz, M. Honda and F. E. Kramer, McDonnell Center for the Space Sciences, Washington University, St. Louis, MO 63130

Except for gases implanted during direct exposure to the solar wind, trapped primordial noble gases in meteorites occur in a characteristic and well-known elemental abundance pattern designated the "planetary" pattern. The planetary pattern appears in most meteorite classes and characterizes elemental composition across at least 3-4 orders of magnitude variation in total abundance. Several models for the trapping mechanism and the generation of the planetary pattern have been advanced, but none are compelling. Nevertheless, in the absence of contrary evidence it is reasonable to expect that noble gases in the major terrestrial planets, e.g. the earth, should have an origin similar to that for meteorites and should thus occur in planetary proportions.

The meteorite analogy thus suggests that if noble gases in the earth's atmosphere account for most of the total terrestrial inventory, or at least represent an unbiased sample, they too should occur in the relative abundances of the planetary pattern. The gases Ne, Ar, and Kr conform to this expectation quite well, and furthermore their total atmospheric abundances, per unit mass of the earth, fall within the range observed in meteorites. The atmospheric abundance of He is very much lower than extension of the analogy suggests, but this is understandable and does not weaken the analogy because He escapes from the atmosphere on a geologically short time scale. The abundance of Xe in air is also significantly lower, by a factor of about 23, than the analogy suggests, and in this case no straightforward excuse is evident.

A number of views concerning this apparent underabundance of Xe are possible. One is that the analogy with meteorites does not apply, and that the underabundance reflects basically different origins for Xe in the earth and meteorites; this position could also be argued on the basis of prominent isotopic differences between terrestrial and meteoritic Xe which have never been satisfactorily explained. A second is that the atmosphere is not an unbiased sample, and that Xe has been degassed from the solid earth into the atmosphere with a much lower efficiency than have the other gases. Both these views have interesting ramifications, the first for the origin of the earth and the second for its overall chemical evolution.

A third view is that the apparent underabundance is only apparent, i.e. that Xe in planetary proportions was indeed degassed into the atmosphere, but because of its interactions with sediments most of it has not remained in air. The possibility that most of the atmosphere's Xe was subducted in sediments warrants attention, but the usual variant of this "shale hypothesis" is that the apparently missing planetary Xe is still in the generalized atmosphere, but mostly in extant sediments, specifically shales, rather than in air (1,2). This view seems to have been widely adopted as the consensus explanation of the Xe underabundance problem.

The shale hypothesis has been challenged (3-5) on the grounds that neither the previously applied arguments (1,2), nor experimental results subsequently obtained, justify the conclusion that extant shales contain enough Xe to bring the atmospheric inventory up to planetary proportions. The reasoning is straightforward. The <u>average</u> Xe concentration needed for the estimated 10^{24} g of extant shale to account for this much Xe is higher than that found in <u>any</u> sedimentary rock so far. The distribution of available data in fact suggests that the inventory of Xe trapped in sediments is

ORIGINAL PAGE IS
OF POOR QUALITY

about an order of magnitude smaller than the air inventory. This assessment is not conclusive since not all potentially important reservoirs or rock types have been surveyed, but the hypothesis that sedimentary rocks account for the missing planetary Xe must be argued in spite of rather than because of available data.

All of the available data are normal trapped gas measurements, and all of them involve days to months of exposure to laboratory vacuum prior to analysis, usually with a day or more at temperatures around 100°C. It could be argued that such analysis grossly underestimates natural gas concentrations because most gas is very "loosely bound" - roughly speaking, merely adsorbed rather than trapped - and is lost during this vacuum exposure.

This possibility may be addressed by consideration of the extent of physical adsorption of Xe or shales. Available data suggest that Xe adsorbed on shales, in equilibrium with modern air, quite possibly makes a bigger contribution to the inventory than Xe trapped in the same shales, perhaps even makes a substantial contribution to the atmospheric inventory, but appears rather unlikely to make a big enough inventory contribution raise atmosphere Xe to the planetary level (5). Another qualification arises, however, in the suggestion (5) that Xe migration in shales might be so slow that laboratory measurements of physical adsorption also greatly underestimate the amount of Xe adsorbed on shales in nature.

These and other ambiquities about how much Xe is actually present in sedimentary rocks in nature can be greatly reduced by a modified experimental procedure now in use in this laboratory. The key step is sealing rock samples in air, with minimal alteration from their natural state, and not breaking the seal until all gas in the sample can be collected for analysis. In our procedure the samples are enclosed in close-fitting Al capsules sealed by pressure on an In gasket. Subsequent mass spectrometer analysis of capsule and contents yields the total gas content of the sample with no intervening loss in the vacuum system and without regard for the physical reasons for the presence of the gas. Preliminary results of such experiment and their relevance to the Xe inventory problem will be presented.

(1) Canalas R.A., Alexander E.C. and Manuel O.K. (1968) J. Geophys. Res. 73, 3331-3334.
(2) Fanale F. P. and Cannon W.A. (1971) Earth Planet.Sci.Lett.II, 362-368.
(3) Bernatowicz T.J. and Podosek F.A. (1978) in Terrestrial Rare Gases (eds. E.C. Alexander and M. Ozima), Tokyo, pp. 99-135.
(4) Podosek F.A., Honda, M. and Ozima M. (1980) Geochim. Cosmochim. Acta 44, 1875-1884.
(5) Podosek F.A., Bernatowicz T.J. and Kramer F.E. (1981) Geochim. Cosmochim. Acta 45, 2401-2415.

ORIGINAL PAGE IS
OF POOR QUALITY

NOBLE GASES IN PLANETARY ATMOSPHERES: IMPLICATIONS FOR THE ORIGIN AND EVOLUTION OF ATMOSPHERES. James B. Pollack and David C. Black, Space Science Division, NASA Ames Research Center, Moffett Field, CA 94035

The radiogenic and primordial noble gas content of the atmospheres of Venus, Earth, and Mars are compared with one another and with the noble gas content of other extraterrestrial samples, especially meteorites. The four-fold depletion of ^{40}Ar for Venus relative to the Earth is attributed to the outgassing rates and associated tectonics and volcanic styles for the two planets diverging significantly within the first billion or so years of their history, with the outgassing rate for Venus becoming much less than that for the earth at subsequent times. This early divergence in the tectonic style of the two planets may be due to a corresponding early onset of the runaway greenhouse on Venus. The sixteen-fold depletion of ^{40}Ar for Mars relative to the Earth may be due to a combination of a mild K depletion for Mars, a smaller fraction of its interior being outgassed, and to an early reduction in its outgassing rate. Based on the observed present day flux of ^{3}He from the Earth's interior and the ^{40}Ar content of the atmosphere, we estimate that the current outgassing rate of ^{40}Ar is about 7% of its time averaged value. Venus has lost virtually all of its primordial He and some of its radiogenic He. The escape flux of He may have been quite substantial in Venus' early history, but much diminished at later times, with this time variation being perhaps strongly influenced by massive losses of H_2 resulting from efficient H_2O loss processes.

Key trends in the primordial noble gas content of terrestrial planetary atmospheres include (1) a several orders of magnitude decrease in ^{20}Ne and ^{36}Ar from Venus to Earth to Mars; (2) a nearly constant $^{20}Ne/^{36}Ar$ ratio which is comparable to that found in the more primitive carbonaceous chondrites and which is two orders of magnitude smaller than the solar ratio; (3) a sizable fractionation of Ar, Kr, and Xe from their solar ratios, although the degree of fractionation, especially for $^{36}Ar/^{132}Xe$, seems to decrease systematically from carbonaceous chondrites to Mars to Earth to Venus; (4) and large differences in Ne and Xe isotopic ratios among Venus Earth, meteorites, and the Sun. Explaining trends 2; 2 and 4; and 1 pose the biggest problems for the solar-wind-implementation, primitive atmosphere, and late veneer hypotheses, respectively.

It is suggested that the grain-accretion hypothesis can explain all four trends, although the assumptions needed to achieve this agreement are far from proven. In particular trends 1, 2, 3, 4 are attributed to large pressure but small temperature differences in various regions of the inner solar system at the times of noble gas incorporations by host phases; similar proportions of the host phases that incorporated most of the He and Ne on the one hand (X) and Ar, Kr, and Xe on the other hand (Q); a decrease in the degree of fractionation with increasing noble-gas partial pressure; and the presence of interstellar carriers containing isotopically anomalous noble gases.

Our analysis also suggests that primordial noble gases were incorporated throughout the interior of the outer terrestrial planets, i.e., homogeneous accretion is favored over inhomogeneous accretion. In accord with meteorite data, we propose that carbonaceous materials were key hosts for the primordial noble gases incorporated into planets and that they provided a major source of the planets' CO_2 and N_2.

ORIGINAL PAGE IS
OF POOR QUALITY

HELIUM: FURTHER EVIDENCE OF A SIMILAR ORIGIN FOR EARTH AND VENUS

Michael J. Prather, Center for Earth and Planetary Physics, Harvard University, Cambridge, MA 02138

The abundance of noble gases provides clues to the origin and evolution of the terrestrial planets and, in addition, to the interaction of the solid body with the atmosphere through subsequent degassing of volatiles. We focus here on the radiogenic gases ^{40}Ar and ^{4}He. Argon is stored in the atmosphere; whereas escape is important in modifying the atmospheric abundance of helium. The rate for escape of ^{4}He, 10^{6} $cm^{-2}s^{-1}$, is similar for Earth and Venus, indicating like sources of helium from uranium and thorium in their respective crusts. Data on the abundance of crustal potassium and atmospheric ^{40}Ar also point to the basic similarity of the two planets.

ORIGINAL PAGE IS
OF POOR QUALITY

INCORPORATION OF NOBLE GASES IN METEORITES

S Ramadurai
Astrophysics Group, Tata Institute of Fundamental Research
Homi Bhabha Road, Bombay 400 005 INDIA

The incorporation of noble gases in meteorites poses a severe problem for the equilibrium solubility models. The recent Chicago experiments on the solubility in Carbon, Chromite and Magnetite have reavealed the inadequacy of this picture to yield the observed absolute abundances of noble gases in Allende. In this work, the experimental results of adsorption on micropores is used to determine the role of adsorption in the incorporation of noble gases in the primitive solar nebula. The physisorption energy increases as the size of the micropores decreases and hence the smaller , the pore size,the tighter is the binding. Further the microporosity leads to a volume filling effect as opposed to the normal surface effect. A full thermodynamic treatment of the adsorption on micropores yields important information on the characteristics of the meteoritic forming regions. Further the role of adsorption in the incorporation of planetary volatiles in the inner planets is examined and compared with the observations on the Earth, Mars and Venus.

ORIGINAL PAGE IS
OF POOR QUALITY

VOLATILES AS INVALUABLE CLUES TO PLANETOGENESIS

A.S.P.Rao, Dept. of Geology, Osmania University
Hyderabad - 500 007, (A.P.), INDIA.

According to successive accretion model proposed by the author (1,2) volatile rich materials accrete to the terrestrial planets only in the final stages of their formation. The sizes and masses of the planets are controlled by the abundance of materials available and condensed in order (6) from the primitive solar nebula, and also controlled by the volume of nickel iron cores (and its [illegible] state) that were available in the planets zone. The inferred core volumes of the terrestrial planets (Table-I) speaks against their derivation from accreted, melted and differentiated planets with chondritic like material into core, mantle and crust. The freshness of oldest craters on the terrestrial planets (except Earth) points to the fact that craters were unaffected by the processes of weathering and erosion due to absence of water. Any supply of water from the interior of planetary bodies, coupled with a melting process would have certainly left hydrated rocks on the surfaces (7).

The evolutionary history of the planet after its formation is primarily controlled by the interaction between the chemical phases that have gone into its formation and with its environs (2).

Hydrogen, deuterium and tritium carried in almost exclusivily in solar wind are extensively impregnating the outer surfaces of fragments in the lunar regolith. In addition, a large part of noble gases (^{3}He, ^{20}Ne, ^{22}Ne, ^{36}Ar, ^{38}Ar, and some isotopes of Kr and Xe) are also implanted by the solar wind (4).

The observed trend (reversal trend i.e. more ^{36}Ar in Venus than in Mars) of abundances of noble gases in the terrestrial planets (Table-II) is ascribed to the interaction between solar wind and the planetary environs (2).

The author concludes that the trend of planetary (primardial) abundances of noble gases must be read through an over print of subsequent impregnations of noble gases by solar wind.

Table-I:

% of core volumes (Ref.5)	
Mercury	~42
Venus	~12
Earth	~16
Mars	~9
Moon	~4

VOLATILES AS INVALUABLE CLUES OF PLANETOGENESIS

Rao, A.S.P.

ORIGINAL PAGE IS
OF POOR QUALITY

Table-II: Noble gases (Ref.3)

	Atoms ^{36}Ar (g per g)	Atoms ^{40}Ar (g per g)	Total ^{36}Ar (g per g)	$^{40}Ar/^{36}Ar$
Venus	2.4×10^{-9}	2.7×10^{-9}	2×10^{-8}	1.0
Earth	3.5×10^{-11}	1.2×10^{-8}	7×10^{-11}	296
Mars	2.0×10^{-13}	7.0×10^{-10}	8×10^{-12}	3000
Sun			3×10^{-5}	
Lunar fines			8×10^{-7}	

REFERENCES:

(1) Rao, A.S.P. (1967) Abst. 30th Ann. Met. Of Meteorit ical Society p.126, California.

(2) Rao, A.S.P. (1981) Abst. An. Intt. Conf. on the Venus Environment p.37, California.

(3) McElroy, M.B. and Prather, M.J. (1981) Nature 293, p.535-539.

(4) Short, M.N. (1975) Planetary Geology, Englewood Cliffs, New Jersey, Prentice Hall, p.1-361.

(5) Strom, R.G. (1979) Space Sci. Rev. 24, p.3-70.

(6) Larimer J.W. (1975) Geochim. Cosmochim Acta, 39, p.387-392.

(7) Gold, T. (1973) Personnel Communication.

...

ORIGINAL PAGE IS
OF POOR QUALITY

NUMERICAL EXPERIMENTS WITH THE GEOCHEMICAL CYCLE FOR CARBON. Steven M. Richardson, Dept. of Earth Sciences, Iowa State University, Ames, IA 50011 and Allen S. Grossman, Lawrence Livermore Laboratory, Livermore, CA 94550

The partitioning of carbon among major geochemical reservoirs is controlled at steady state by a variety of transfer processes, such as volcanism, chemical and mechanical weathering, and limestone deposition. The rates of these processes are, in turn, controlled by parameters such as atmospheric temperature, mean continental elevation, and mean oceanic depth. Over short periods of time, many transfer processes can be described adequately by linear first-order differential equations. Rate constants can often be measured or empirically derived by consideration of the control parameters. Over long periods of time, however, the rates of transfer processes are time-dependent. The carbon cycle attempts to maintain a dynamic steady state during episodic or continual changes in the geological environment. Equations to describe the long-term carbon cycle, therefore, are in general non-linear.

We have begun numerical experiments in which we extend the matrix method of Lasaga (1) to track the evolution of the steady state. For these initial experiments we consider only the simple cycle containing carbon, and do not consider the real world condition in which the carbon cycle is coupled to the cycles for oxygen, sulfur, and other elements, although the matrix method can be modified to treat such non-linear problems. The steady state for a short-term cycle can be described by examining the eigenvectors of a matrix composed of the first-order rate constants. If we treat the long-term cycle as a sum of suitably small short-term steps, between each of which a small change is made in selected rate constants, then the long-term evolution of the cycle can be effectively linearized and followed by this same eigenvector method. Changes of reservoir contents in response to two or more competing time-dependent transfer functions can be examined in this fashion.

1. A.C. Lasaga (1980) The kinetic treatment of geochemical cycles. Geochim. et Cosmochim. Acta: 44, 815-828.

ORIGINAL PAGE IS
OF POOR QUALITY

ATMOSPHERIC EVOLUTION DURING ACCRETION: A NUMERICAL MODEL. Steven M. Richardson, Dept. of Earth Sciences, Iowa State Univ.,Ames, IA 50011, Ray T. Reynolds, NASA Ames Research Center, Moffett Field, CA 94035, Allen S. Grossman, Lawrence Livermore Laboratory, Livermore, CA 94550, and James B. Pollack, NASA Ames Research Center, Moffett Field, CA 94035

Models of atmospheric evolution which favor an early "catastrophic" outgassing period are often difficult to reconcile with models of energy and mass deposition during accretion and with models for subsequent differentiation and thermal evolution. For accretionary times on the order of 10^7 to 10^8 years, the energy released by impacts alone is sufficient to cause appreciable planetary melting and may result in a global magma ocean. High planetary temperatures lead to maximum efficiency of outgassing, but may also lead to a dense atmosphere and runaway greenhouse temperatures.

We are investigating model conditions under which a runaway greenhouse can be either avoided or reversed during early outgassing. To do this, we consider a spherically symmetrical planet whose radius increases at a constant rate over a growth period of 5×10^7 years. In a fashion to Kaula (1), we assume that a fraction (μ = 0.1 to 0.5) of the energy of impacting particles is deposited below the surface of the planet, generating a melt zone which we take to be roughly 100 km deep. The melt zone is overlain by a thin, fragmented crustal layer analogous to the solid surface that develops on lava lakes. This crust is subject to puncturing by impacts and to tensional fracturing as the planetary radius increases. It serves as a cap of low thermal conductivity, restricting major heat losses from the melt zone to a small fraction of the total planetary surface. An approximate steady state balance between accretional energy gains and radiative heat losses across the surface is maintained by regulating the fraction of surface area covered by crust.

Heat transfer in the melt zone is convective and can be shown to be rapid relative to the rate of increase of the planetary radius. Hence, the thermal profile of the melt zone with depth is near to the melting curve for the magma. At the base of the melt zone, however, lithostatic pressure is high enough and accretional energy deposition is low enough that magma solidifies at a rate roughly comparable to the planetary growth rate.

Potential atmospheric components are concentrated in the melt zone as the planet grows and are continually expelled from the surface in regions of exposed magma. If the atmosphere is well-mixed and remains nearly in thermal equilibrium with the magma from which it came, then condensation of water vapor is precluded and runaway greenhouse conditions are implied, though they may be reversible once accretion stops and heat losses from the planetary surface become smaller. On the other hand, the atmosphere may attain thermal equilibrium with the larger fraction of the planetary surface, covered by thin crust. If so, condensation of water vapor may be possible, leading to the early formation of an ocean, the removal of carbon dioxide by precipitation of carbonate rocks, and the avoidance of runaway greenhouse conditions.

ORIGINAL PAGE IS
OF POOR QUALITY

1. W.M. Kaula (1979) The beginning of Earth's thermal evolution. Proc. Wilson Conf.:"The Continental Crust and Its Mineral Deposits", Toronto.

C-2

ORIGINAL PAGE IS
OF POOR QUALITY

VOLATILE ELEMENT TRANSPORT FROM THE MANTLE: EXPERIMENTAL SOLUBILITY DATA FOR S- SYSTEM. M.J. Rutherford and M. Carroll, Dept. of Geological Sciences, Brown University, Providence, RI 02912.

INTRODUCTION. The problem to be addressed in this paper is that of the relative degassing rates of C-O-H-S gas species from the mantle of a terrestrial-type planet such as the Earth, Mars or the Moon once the planet has formed a crust. Volatile elements could be brought from the mantle to the surface of such a planet in one of three states. The volatiles could be bound in crystalline phases of sufficiently low S.G. that they would be carried to the surface in magma derived from the mantle. Graphite (1,2) might be such a phase. Alternatively, volatiles could be dissolved in mantle - derived magma and carried to the surface with the magma. The third possibility is that a discreet vapor phase exists in the upper mantle, and this vapor comes up with or through the magma as a separate phase. In order to evaluate these possibilities for any one or a group of volatile elements, it is necessary to know the following: (1) The nature of the volatile-bearing crystalline phases and their stability as a function of depth (P,T,fo_2,etc.)in the mantle (2) The distribution of the volatile element of interest between the crystalline mantle phases and the coexisting magma (if present), and (3) Whether or not a separate vapor phase would coexist with a given mantle assemblage, and if it does, its composition. A considerable body of experimental and observational data has been gathered regarding H_2O and the C-O gases - the purpose of this paper is to present data for the behavior of sulfur.

UPPER MANTLE VOLATILE-BEARING CRYSTALLINE PHASES. On the basis of mantle xenolith studies, it is well established that in addition to the major silicates, the upper mantle of the earth does in places contain phlogopite (3) graphite, diamond (4) and possibly amphibole (3,5,6,7). Apatite is another volatile-bearing phase which may be present, although there is some question whether it is stable at basalt liquidus temperature in the mantle (8). Experimental studies (9,10) verify that these phases are stable under certain upper mantle conditions and also indicate that Ca-Mg carbonates may be present (11), particularly where geothermal gradients are low. Any or all of these phases could be mantle reservoirs of C-O-H gas species. The main reservoir for mantle S appears to be an FeS-rich sulfide based on its common occurrence as inclusions in silicates (12) and diamonds of mantle xenoliths (4).

SOLUBILITY OF C-O-H-S FLUIDS IN BASALTIC MAGMA. Experimental data indicates that the solubility of H_2O in basaltic magmas is large (∿10 wt% at 10kb and 1100°C, (13)). As a result there would be no difficulty in transporting H_2O to the surface of a terrestrial-type planet particularly if there were adiabatic mantle upwelling which would tend to carry hydrous phases out of their stability field. The solubility of C-O gas species in basaltic magmas is not likely to be as large as H_2O (14), but it is substantial. Thus there would be no problem bringing C, O or H up from hot mantle regions as species dissolved in basaltic magmas. However, the data on the solubility of S in basaltic magmas indicates that it would be very difficult to transport significant amounts of sulfur from mantle depths in the same way.

Figure 1 shows the data we have collected on S solubility in basaltic magmas under a variety of conditions along with some collected earlier (15) at 1 atm. The new data emphasize the findings of (15) indicating that X_{FeO} and X_{TiO_2} are important variables in determining S solubility. New data for the basalt-C-O-S system (2.7 wt% TiO_2) shows that there is essentially no pressure effect on this solubility up to 5 kb. Wendlandt (16) indicates there is probably a decrease in S-solubility with pressure in this system. Experiments on the same basalt (2.7 wt% TiO_2) in equilibrium with FeS and an

VOLATILES FROM MANTLE - S SOLUBILITY DATA

ORIGINAL PAGE IS
OF POOR QUALITY

Rutherford, M. J. and Carroll, M.

H-O-S fluid (Fig. 1) show a 30-50% increase in the S-solubility, but the amount of S present is still only 0.20 wt%. On the basis of these data it is concluded that dissolution of S in basaltic melt would not be an effective process for transporting sulfur from the mantle to the surface of terrestrial type planets, particularly in comparison to C,O and H.

DISCUSSION. If S cannot be effectively dissolved in basaltic melts, what is the explanation for the abundance of S gas species in volcanic gases and fluids (17)? Immiscible sulfide is not likely to be carried up in a basaltic melt. Two explanations seem likely. (1) There may actually be a vapor phase in the upper mantle which could come up with or through magmas. The high pressure CO_2-rich fluid inclusions found in many mantle xenoliths (18) often contain sulfide grains (19) indicating the possibility of C-O-S fluid. (2) Possibly S is only slowly removed from upper mantle regions and the sulfur evident in oceanic volcanic regions is largely recycled.

REFERENCES. (1) Sato, M. (1978) LPS, IX, 990-992. (2) Sato, M. (1979) Proc. Lunar Planet. Sci., 10, 311-325. (3) Boettcher, A.L. and O'Neil, J.R. (1980) Am. J. Sci. 280A, 594-621. (4) Gurney, J.J., Harris, J.W. and Rickard, R.S. (1979) Proc. Kimb. Conf., 2,1, 1-15. (5) Wass, S.V. (1979) Proc. Kimb. Conf., 2, 2, 366-374. (6) Irving, A.J. (1980) Am. J. Sci. 280A, 389-427. (7) Wilshire, H.G., Pike, J.E.N., Meyer, C.E. and Schwartzman, E.C. (1980) Am. J. Sci., 280A, 576-594. (8) Green, T.H. (1981) J. Volc. & Geoth. Res., 10, 405-422. (9) Modreski, P.J. and Boettcher, A.L. (1973) Am. J. Sci., 273, 385-414. (10) Eggler, D.H. (1978) Am. J. Sci., 278, 305-343. (11) Wyllie, P.J. (1979) Am. Min., 64, 469-500. (12) DeWaal, S.A. and Calk, L.C. (1975) J. Petrol., 16, 134-154. (13) Hamilton, D.L., Burnham, C.W. and Osborn, E.F. (1964) J. Petrol., 5, 21-39. (14) Eggler, D.H., Mysen, B.O., Hoering, T.C. and Holloway, J.R. (1979) E.P.S.L., 43, 321-330. (15) Haughton, D.R., Roedder, P.L. and Skinner, B.F. (1974) Ec. Geol., 69, 451-467. (16) Wendtlandt, R.F. (1981) GSA Abst. with Prog., 578. (17) Gerlach, T.M. (1980) J. of Volc. and Geoth. Res., 7, 295-317. (18) Roedder, E. (1965) Am. Min., 50, 1746-1782. (19) Moore, J.G., Batchelder, J.N. and Cunninghan, C.G. (1972) J. Volc. Geoth. Res., 2, 301-327.

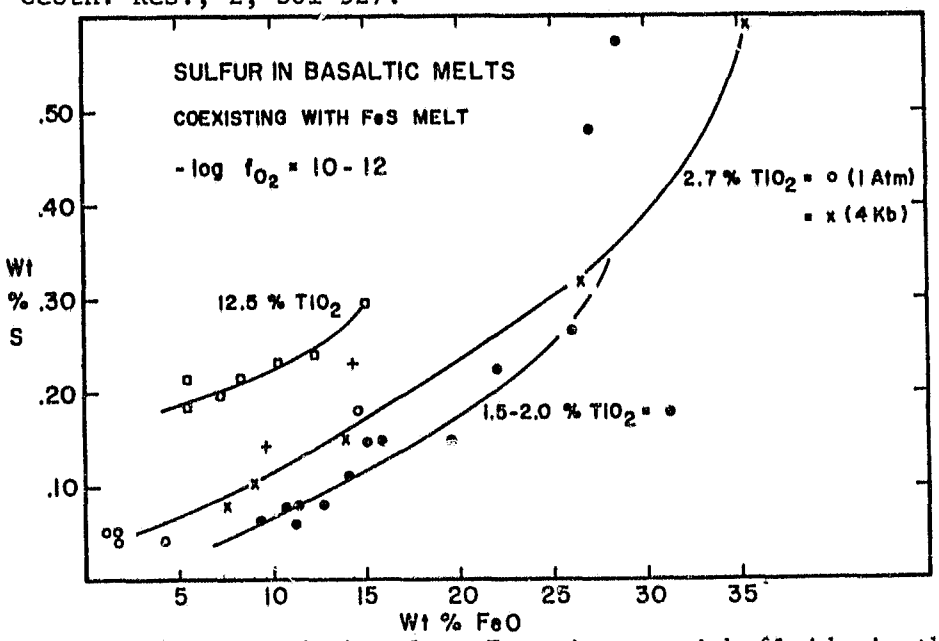


Fig. 1. Sulfur solubility in basalts. Experiments with fluids in the C-O-S system (o,x, ,) and the H-O-S system (+). The ( ) are from (15).

ORIGINAL PAGE IS
OF POOR QUALITY

THE NOBLE GAS RECORD OF THE PRIMITIVE NEBULA AND THE EARTH. D. D. Sabu, Box 552, Shreveport, LA 71162 and O. K. Manuel, Department of Chemistry, University of Missouri-Rolla, Rolla, MO 65401.

Elemental and isotopic ratios of the noble gases in terrestrial, lunar and meteoritic solids and in planetary atmosphere provide the following information on the initial distribution and evolution of these elements in the solar system:

(i) The primitive nebula contained basically two types of noble gases, type-X and type-Y. The central region contained type-Y noble gases, consisting of isotopically "normal" Ar, Kr and Xe but no He or Ne. The outer region contained type-X noble gases, a mixture of He, Ne and isotopically "strange" Ar, Kr and Xe.

(ii) Type-Y noble gases account for the bulk of the Ar, Kr and Xe in chondrites, ureilites, iron meteorites and in the four inner planets. Chondrites also contain type-X noble gases and this accounts for all of the "planetary" He and Ne in chondrites. Most of the He and Ne in the other types of meteorites and in the four inner planets were implanted on grain surfaces by an early solar wind.

(iii) The atmospheres of the terrestrial planets were produced by an early exhaustive degassing of specific regions. For Mars, Earth and Venus the degassed portions are about 1-2%, 17% and 100%, respectively. High values of $^{129}Xe/^{132}Xe$ and $^{40}Ar/^{36}Ar$ characterize the early degassed portion of the Earth.

(iv) Exhaustive degassing of the upper mantle-plus-crust system produced the Earth's atmosphere during the first 2×10^8 years. The lower mantle has retained most of its initial inventory of Ar, Kr and Xe, and leakage of ^3He from the lower mantle accounts for the frequent occurrence of $^3He/^4He$ ratios that are higher than that in air.

(v) Most of the ^{40}Ar in air was produced in the crust prior to solidification about 2×10^9 years ago. Subduction of sedimentary material into the upper mantle is responsible for observations of atmospheric-like values of $^{40}Ar/^{36}Ar$ and $^{129}Xe/^{132}Xe$ in some samples from the upper mantle.

ORIGINAL PAGE IS
OF POOR QUALITY

COMPARATIVE Ar-Xe SYSTEMATICS IN THE EARTH'S MANTLE

Ph. Sarda, Th. Staudacher, and C.J. Allègre,
Laboratoire de Géochimie, Institut de Physique du Globe,
4 Place Jussieu - 75230 Paris cedex 05 - France.

Argon and Xenon isotopic ratios and gas concentrations have been measured in glassy rims of dredged MORB samples, using a Reynold-type mass spectrometer, ARESIBO I. Total rock analyses and stepwise heating experiments have been performed.

We have obtained the first systematic ^{129}Xe anomalies even found in MORB with $^{129}Xe/^{130}Xe$ ratios up to 6.94. On the other hand, very high $^{40}Ar/^{36}Ar$ isotopic ratios, as high as 22 000, have been measured. Stepwise heating experiments allow the elimination of atmospheric contamination (by sea water dissolved gases) which drastically lowers the $^{40}Ar/^{36}Ar$ ratio. Our results also indicate large gas losses of the samples during their emplacement.

Such high $^{129}Xe/^{130}Xe$ and $^{40}Ar/^{36}Ar$ ratios are supposed to be close to the isotopic features of the source of MORB. We used them as constraints to study the kinetics of the atmosphere generation, by the way of ^{129}I-^{129}Xe and ^{40}K-^{40}Ar chronometric systems ($T_{1/2}$ = 17 10^6y and 1.25 10^9y respectively).

We describe the outgassing of the Earth's mantle in a two box-model, the only assumption being that the degassing did not grow with time (it is actually not a first order kinetics). The atmosphere is thus found to have a mean age > 4 10^9y using both argon and xenon results. However, a discrepancy does exist between argon and xenon derived mean ages, the latter being slightly older.

Such a difference leads us to consider a back flux of atmospheric gas into the mantle by sediment reinjection. Such reinjection should have a greater influence on the argon isotopic composition of the mantle due to the enormeous difference in the $^{40}Ar/^{36}Ar$ ratios of atmosphere and mantle (295.5 and>22 000 respectively), and thus decrease the argon derived mean age of the atmosphere.

ORIGINAL PAGE IS
OF POOR QUALITY

REDOX STATE AND STABLE DISTRIBUTION OF VOLATILES IN PLANETARY INTERIORS

Motoaki Sato, U. S. Geological Survey, Reston, VA 22092

It is a common concept that volatiles were lost in gaseous forms from terrestrial planets because these planets became hot at a certain stage of their evolution while the planets were not massive enough to accquire large enough gravitational fields to hold on to these gases. This may have been true for rare gases and for some elements such as nitrogen, but for many gas-forming elements, the redox state of the interior of a planet palys a a crucial role in determining whether an element exists mainly as gas. For example, carbon forms gases only under oxidizing conditions or H_2-rich reducing conditions; the elemental form is extremely refractory.

The presence of a metallic core is considered to be evidence that the interior of the planet is in a reduced state. One might entertain a notion that perhaps the larger the core is, the more reduced the interior is. Comparison of lunar rocks with terrestrial rocks, however, immediately brings up a seeming paradox. The Moon, which may not even have a core, has rocks ubiquitously containing metallic iron, whereas the Earth, which has a large core, has more oxidized mantle rocks. This paper aims at developing a thermochemical basis to assess the redox state of a planetary interior by extending my preliminary attempt(1) and gaining more insight into the behavior of gas-forming elements at various stages of planetary evolution.

An important factor overlooked by recent investigators of the chmistry of planetary interiors is the effect of gravity on chemical equilibria in the vertical direction. Brewer(2) suggested that the stable distribution of elements in the Earth is such that iron concentrates in the center and oxygen near the surface because of the gravitational contribution to the free energy term. Brewer did not go beyond a statement of the principle, however, because of "mathematical" difficulties for a non-isothermal body. The difficulty can be circumvented as shown below.

For a gas, the gravitational contribution appears as the barometric effect. For an ideal gas at constant temperature and gravitational acceleration, the difference in free energy per mole is given by:

$$G(h_2) - G(h_1) = M g (h_2 - h_1) = - R T \ln (p_2 - p_1) \qquad (1)$$

where g is the gravitational acceleration, M the molecular weight, h_1, h_2, and p_1, p_2 the heights and respective partial pressures, and R the gas constant. For a real gas, fugacities should be used instead of partial pressures. Where T and g vary, as in a planetary atmosphere or within a planetary interior, integration of these parameters as a function of height (=radial diatance) becomes necessary. So we have:

$$\log f_1 - \log f_2 = (M / 2.303 R) \int (g / T) dh \qquad (2)$$

The integration term decreases as a homogeneously accreted planet differentiates or its temperature rises; it increases as a planet cools.

The above relation should apply to rare gases as well as to any other gas. As the rare gases cover a wide range of molecular weight, it is evident that rare gases should not degass alike. To escape to the atmosphere, the fugacities of He3, He4, Ne20, Ar36, Kr84 and Xe132 in the present Earth's mantle (100 km, 1500 k) must be 1.25, 1.35, 4.51, 15.1, 562 and $10^{4.32}$ times higher, respectively, than those already in the atmosphere according to equation (2). These numbers suggest that if the material

ORIGINAL PAGE IS
OF POOR QUALITY

that formed the Earth had chondritic abundances, the atmosphere should be increasingly depleted of heavier rare gases. This conclusion is in agreement with the finding of (3).

In the initial stage of homogeneous accretion, the almost ubiquitous presence of metallic iron in chondritic matter presumably buffered the f_{O2} of the accreted matter at values lower than that of the Fe-FeO buffer throughout the interior. The f_{O2} of an oxygen buffer increases as either temperature or pressure increases. As the interior temperature increased due to radioactive decay, adiabatic compression, etc., and as the pressure increased by increased mass and gravity, the f_{O2} of such buffers increased. The fugacity of Fe increases likewise. The increases amounted to orders of magnitude for a planet of the size of the Earth. The increasing fugacities in the interior did not necessarily cause both oxygen and iron to move to the cooler, low-pressure areas, however. Equation (2) stipulates that f_{O2} and f_{Fe} should be orders of magnitude higher in the deep interior to maintain barometric equilibria. Only when corrections for the barometric effect are made, can one judge if the distribution of a volatile element is stable or not. A term called "equigravitational fugacity (symbol $f^{=}$)" to designate the fugacity of a gas which is corrected for the barometric effect has been introduced by (1). The reference datum was chosen at the surface of a planet.

Equigravitational fugacities of O_2, Fe, and gases of the C-S-O system buffered by various mineral assemblages have been computed for homogeneous protoplanets ranging in mass from that of the Moon to that of the Earth for Fe-FeS eutectic and peridotite melting temperature models. These fugacities have been computed also for the differentiated Earth with the known pressure gradient and an estimated temperature gradient.

The results obtained so far suggest the following. (i) In an accreting planetary body of the size of the Moon, very little redox differentiation would occur. Gaseous volatiles would be lost and sulfur would be retained. (ii) In a planetary body of the size of Mars, redox differentiation would be more significant. (iii) By the time a planetary body reaches the size of the Earth, a strong tendency would exist for Fe to concentrate in the core region and oxygen in the upper mantle. The tendency would decrease as the redox differentiation proceeds and the planet becomes stratified in density. (iv) The Earth has not yet reached the most stable state in terms of redox differentiation, because Fe still shows a tendency to move down to the core region from the lower mantle at the expense of FeO. Alternatively, if the Earth was very hot in the early Archean, the stable distribution of iron and oxygen may have once been closely approached and then subsequent cooling may have resulted in increased disequilibria, facilitating production of heat by increased redox differentiation to counter the cooling. (v) Neither sulfur, carbon, nor oxygen is stable in the outer core of the Earth. This suugests that the light element is likely to be silicon.

REFERENCES

(1) Sato M. (1980) In Lunar and Planetary Science XI, p. 974-976, Lunar and Planetary Institute, Houston. (2) Brewer L. (1951) J. Geol., v. 59, p. 490-497. (3) Kaneoka I., Takaoka N., and Aoki K. (1978) In Terrestrial Rare Gases (editors E. C. Alexander and M. Ozima), p. 71-83, Japan Scientific Societies Press, Tokyo.

ORIGINAL PAGE IS
OF POOR QUALITY

EARLY ATMOSPHERIC OXYGEN LEVELS: CONSTRAINTS FROM ARCHAEAN PHOTOAUTOTROPHY.

M. Schidlowski, Max-Planck-Institut f. Chemie, D-6500 Mainz, Germany-W.

Various independent lines of evidence suggest that photoautotrophic carbon fixation is a very ancient process that had attained control of the terrestrial carbon cycle as from at least 3.5×10^9 yr (if not 3.8×10^9 yr) ago. Since it is generally accepted that only biological processes were able to overwhelm the negligible oxygen pressures sustained on the early Earth by inorganic photochemistry (probably between 10^{-8} and 10^{-14}PAL), the advent of photoautotrophy would provide a limiting condition for the oxygenation of terrestrial near-surface environments. However, with the size of the free oxygen reservoir determined by the kinetics of the geochemically relevant oxygen-consuming reactions, we may wellnigh exclude that the start of photosynthetic oxygen production had resulted in an instantaneous buildup of modern P_{O_2}-levels. Low atmospheric oxygen pressures as mostly inferred for the Archaean and early Proterozoic Earth would, therefore, indicate extremely rapid processes of O_2-consumption in certain compartments of the ancient exogenic system (notably the hydrosphere) rather than the non-existence of photosynthetic oxygen production at this time.

ORIGINAL PAGE IS
OF POOR QUALITY

IMPACT BASINS AND THE STORAGE/RELEASE OF VOLATILES ON MARS.

Peter H. Schultz, Lunar and Planetary Institute, Houston, TX, John L. Rogers, American Petrofina, Houston, TX.

The Hellas and Argyre basins are the most obvious remnants of major impacts on Mars that must have had global effects. In addition, however, there are numerous other subtle impact basins whose deep-seated imprint in the crust not only has controlled volcanic/tectonic processes (in a manner analogous to basins on the Moon) but also influenced the distribution of volatiles. Impact-basin control of volatiles in the crust occurs by three primary mechanisms. First, central basin and concentric ringed depressions provide obvious topographic traps for aeolian or fluvial deposition. Second, the permeable ejecta facies represent significant reservoirs of volatiles whether trapped or precipitated during emplacement. Third, basin-controlled fractures become major release centers of volatile reservoirs during epochs of regional volcanic/tectonic rejuvenation. The expression of these three mechanisms for specific basins provides clues for the timing and style of volatile transfer.

Basin-controlled topographic lows and contained depressions represent one of the most obvious traps for martian volatiles. Recent studies (1) indicate that Mars may not be deficient in the number of major impact basins larger than 300km; rather they were nearly erased by active erosional and depositional processes early in geologic history. Such structures can be recognized on the basis of topography and the concentric arrangement of massifs, fractures, and scarps. Their subtle expression, however, underscores the potential volume of sediments that once were globally redistributed as: aeolian deposits; outwash deposits from fluvial activity indicated by convergent narrow valley networks and channels; widespread fall-out of suspended fine-size ejecta from major impacts accumulated over 4 billion years; and polar deposits trapped during previous locations of the geographic pole (2,3) The last process is active today on the periphery of the present poles where thick layered deposits occur on the floors of large craters.

Ancient martian impact basins typically have a pervasive network of narrow valleys along the outer rings and in the inferred ejecta facies. This selective occurrence, at the very least, indicates the ease with which impact ejecta can be eroded. More importantly the style of erosion suggests a sapping process (4) wherein the highly permeable ejecta facies provide an aquifer during periods of climate change and global heating. In several basins, certain narrow valleys emerge locally along a scarp in a manner consistent with an origin as spring-fed systems. Mapping of characteristic mass-wasting styles of terrains around Isidis, Chryse, Argyre, and Hellas indicates that inferred spring-fed processes are extensive around Isidis and exposed cratered terrains of Chryse but are highly localized around Argyre and Hellas. Although models can be envisioned where a vast aquifer localized volatiles within ejecta deposits well after emplacement, a more direct mechanism simply buries or mixes pre-existing volatile traps, e.g., polar deposits, with basin ejecta early in martian history. The formation of the basin and the passage of ejecta through the martian atmosphere could have had a direct effect on the early climate and the precipitation of certain volatile fractions, such as water. Considerations of more modest-size impacts on the Earth (5) suggest that the re-entry of high-speed ejecta heat the atmosphere and micron-size ablation/spallation products could form important nucleation centers.

Impact basins subsequently have played an important but largely unappreciated role in the release of volatile reservoirs. A recent study indicates that nearly all major outflow channels originate along a basin ring (1). Such occurrences are interpreted as basin-trapped ices that have been hydrothermally

ORIGINAL PAGE IS
OF POOR QUALITY

melted along ring fractures during a period of basin-controlled intrusive activity. On the Moon, analogous volcanism resulted in eruptions of basalt and the formation of sinuous rilles. On Mars, volatiles previously trapped in topographic lows were melted episodically and their release produced the major outflow channels. One of the largest systems is related to the Chryse Basin.

1. Schultz, P.H., Schultz, R.A., and Rogers, J.L. (1982) J. Geophys. Res. (in press).
2. Schultz, P.H. and Lutz-Garihan, A.B. (1981), in Papers Presented to the Third International Colloquium on Mars, pp. 229-231.
3. Schultz, P.H. and Lutz-Garihan, A.B. (1982) J. Geophys. Res. (in press).
4. Pieri, D.C. (1980) Science, 210, p. 895-897.
5. Schultz, P.H. and Gault, D.E. (1982) Proceedings of the Conference on Large-body Impacts on the Earth, GSA Special Paper (in press).

ORIGINAL PAGE IS
OF POOR QUALITY

MEANDER RELICTS: DIRECT EVIDENCE OF EXTENSIVE FLOODING IN NORTHERN PLAINS OF MARS; David H. Scott, U.S. Geological Survey, Flagstaff, Arizona 86001

Many morphologic features whose formation is commonly associated with running water also can be duplicated by other processes. On Mars this ambiguity has caused some controversy over the formation of channels (1). Although most planetary investigators now agree on the fluvial origin of the larger channels, there is less evidence and agreement on the extent of flood waters into the plains beyond the immediate vicinity of channel mouths. Previous studies (2) indicated that alluvial channels within the Chryse basin extended farther into the northern plains than had been mapped. However, this work was based primarily on the recognition of scour and depositional features associated with the rapid and turbulent flow of water. Their identification did not extend much beyond latitude 30° N.

One characteristic that is probably unique to formation by running water is the meander pattern developed along the courses of mature streams and rivers. As rivers swing from side to side in flowing across their floodplains, meanders gradually migrate down stream as bends in their channels are eroded. Cutoffs are formed where erosion develops shorter courses and eventually a pattern of abandoned meanders is marked by scars, scrolls, and oxbows on the floodplains.

Relict crescent-shaped depressions are very similar both in shape and size to meander patterns of terrestrial streams occur in Chryse Planitia (Fig. 1). These postulated meander scars are especially well developed along the lower course of Ares Vallis where they are confined within the sculptured banks of the main channel. However, the walls of the channel become more subdued in a downstream direction as the meander remnants become more prominent. This suggests that slope gradients had decreased sufficiently to allow a less turbulent type of discharge as floodwaters spread out over the plains. In places, the presumed meander loops terminate abruptly near channel walls where they may have been covered by slump material or debris flows. Elsewhere within the Chryse-Acidalia Planitia region, meander remnants have been buried more completely and do not show such well-developed forms. They generally can be recognized, however, by the narrow, near central ridge within the channel troughs, although they do not occur in similar appearing crescentic troughs in the Cebrinia quadrangle (45° N, 185°). The origin of these medial ridges is uncertain. They may represent point bars along the inside bends of meander channels that have coalesced to form continuous ridges. On terrestrial floodplains, scroll-like patterns of ridges are developed where shifting of meander flow channels has occurred. Whatever their origin, they appear to be diagnostic of meander channels in this region and afford a means of identifying fluvial channels from troughs produced by tectonic and other processes. Their recognition as far as 45° N. in Acidalia Planitia suggests that water flooding was pervasive in the northern plains.

References:

(1) Carr, M. H. and Clow, G. D. (1981) Icarus 48, 91-117.
(2) Tanaka, K. L. and Scott, D. H. (1980) Proc. Third Colloquium on Planetary Water, 76-79.

MEANDER RELICTS - MARS

ORIGINAL PAGE IS
OF POOR QUALITY

Scott, D. H.

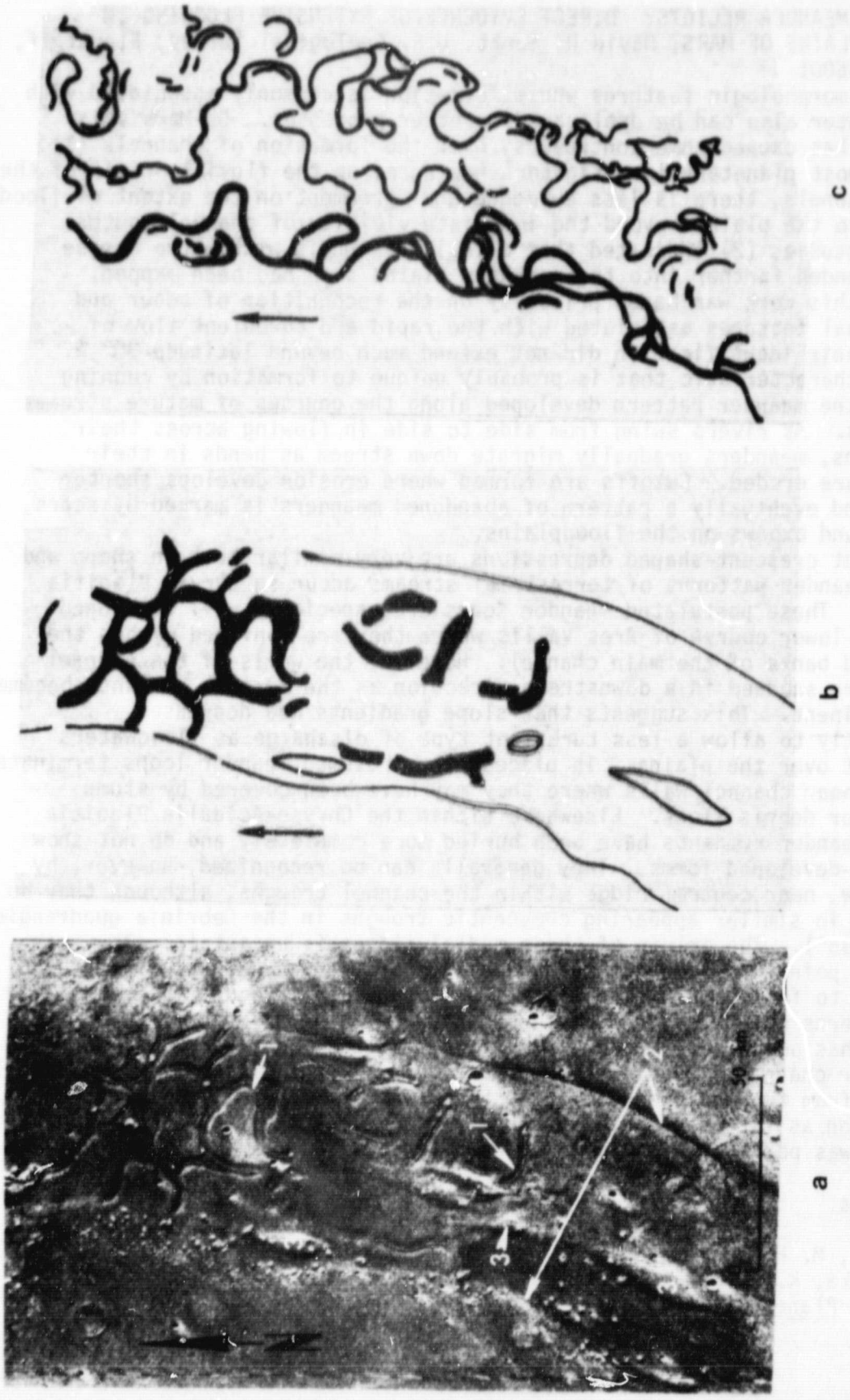


Fig.1 a - Ares Vallis (Viking frame 864A02). Meander scars (1), channels banks (2), streamlined erosional forms (3). Diagrams b and c show configurations of meanders in Ares Vallis and Missisippi river at same scale; arrows show direction of flow.

ORIGINAL PAGE IS
OF POOR QUALITY

VOLATILE EXCHANGE WITH THE MANTLE AT MID-OCEANIC RIDGES AND THE THERMAL HISTORY OF THE EARTH'S INTERIOR (Norman H. Sleep, Geophysics Department, Stanford University, Stanford, CA 94305)

Water, CO_2, Cl, and S are cycled into and out of the earth's mantle. About half of the earth's inventory of H_2O, CO_2, and Cl is in crustal reservoirs such as the ocean, limestones, and salt deposits. Sulfur is much less strongly concentrated in the crust. Mid-oceanic ridges are largely a sink of water hydrated into the crust and a sink for free Oxygen. Sulfur from the basaltic crust enters the ocean and sulfate in the ocean reacts to form sulfides in the oceanic crust. The potential for reaction is great as all seawater is cycled through hydrothermal vents once every 10 m.y. (or less). Hydrothermal vents at the ridge axis have been extensively sampled and indicate that the water has extensively reacted with the rock and is quantitatively depleted in some components. Thermal calculations constrained by the shape of the magma chamber (obtained from seismic reflection) indicate that about 1/10 of the circulation is through axial vents. Off-axis circulation probably reacts with the rock to a lesser extent. The correlation of S and C isotopes through the Phanerozoic is compatible with the relatively small chemical exchange with from the thermal models.

The amount of chemical exchange in the past is proportional to the global rate of seafloor spreading because all the reaction occurs within very young crust. Reaction is also favored by shallow water over the ridge axis such as near Iceland. A possible instability is that once the ocean is sufficiently shallow at the ridge axis, hydration would consume much of the remaining water. This never happen on the Earth but may have happen on Venus. The instability also precludes gradual build-up of the ocean through much of Earth history. Large losses of water at mid-oceanic ridges through geological time would change the ratio H_2O : NaCl and H_2O : CO_2. As there is no evidence for this change, the volitile data is most compatible with a gradually cooling interior of the earth and spreading rates comparable to the present through geological observable time.

ORIGINAL PAGE IS
OF POOR QUALITY

ORIGIN AND CIRCULATION OF HYDROTHERMAL FLUIDS AT LARDERELLO: CLUES FROM NOBLE GASES. Stephen P. Smith, Dept. of Physics, Univ. of California, Berkeley, CA 94720.

Spatial and temporal variations of the compositions of gases in steam from geothermal fields can be used to constrain models of the fluid circulation in the reservoir (1,2). Elemental and isotopic abundances were measured for noble gases in steam from five wells in the central and southern portions of the Larderello, Italy geothermal field. These data and literature data on the active gases (1,3) and noble gases (2,4) in other wells at Larderello suggest a complex picture of mixing among different components of volatiles from several atmospheric and juvenile sources.

RESULTS OF THIS STUDY. The elemental abundances of the non-nucleogenic gases appear to be dominated by two-component mixing between an air-like component (A) and a heavy-noble-gas-enriched component (HE). No compositions were measured that matched air-saturated water (ASW).

For helium, $^3He/^4He$ (=R) normalized to atmospheric $^3He/^4He$ (R_a=1.4 x 10^{-6}) gives R/R_a = 1.11 to 2.15, well outside of experimental uncertainty. This variation requires the presence of at least two components. High He/Ne ratios (275 to 2900 time atmospheric) rule out a significant atmospheric He component. The likely components present are crustal radiogenic He ($R/R_a \leq 0.1$) and a component enriched in ^3He, either primordial mantle He ($R/R_a \geq 30$) or ^3He from decay of bomb-produced tritium in young groundwater.

Neon yields atmospheric $^{20}Ne/^{22}Ne$ ratios, but 0 to 20 permil enrichments in $^{21}Ne/^{22}Ne$ compared to atmospheric Ne. The ratio of excess ^{21}Ne to ^4He is about 5 x 10^{-8}, consistent with crustal nucleogenic Ne from (α,n) reactions.

Enrichments in $^{40}Ar/^{36}Ar$ range from 0 to 15% over atmospheric reflecting an addition of radiogenic $^{40}Ar^*$ to Ar of atmospheric composition.

Isotopic compositions of Kr and Xe are atmospheric.

GAS COMPONENTS IN LARDERELLO STEAM. Model calculations show that both the compositions and concentrations of the non-nucleogenic noble gases are consistent with generation of the A and HE components from 10°C meteoric groundwater by separate Rayleigh distillation processes. The A component may represent gases from the initial stages of vapor separation at $\leq$100°C from an undepleted water body. The HE component appears to be derived at about 200°C from a substantially depleted reservoir (>90% Ar lost). The intersection of the mixing line defined by the sample data with calculated curves of compositions generated by Rayleigh distillation defines the endpoint compositions of the A and HE components ($^{132}Xe/^{36}Ar$ about 1 and 11 times atmospheric, respectively). This allows calculation of the concentration of both components in each sample. For this model, ^{36}Ar from A varies by a factor of about 10, and ^{36}Ar from HE by a factor of about 2.

Variations in the total ^3He concentration of the steam tend to parallel the variations in ^{36}Ar from HE, suggesting a possible genetic link or common mode of transport.

In the four wells containing detectable radiogenic $^{40}Ar^*$, the radiogenic and nucleogenic contributions to ^4He, ^{21}Ne, and ^{40}Ar form a coherent component (NUC). The ratio $^4He/^{40}Ar^*$ is constant (12.6 ± 0.2), as is $^{21}Ne^*/^4He$. Also, the absolute concentrations of ^4He and $^{40}Ar^*$ are constant within experimental uncertainty (0.58 ± 0.04 and 0.045 ± 0.003 ccSTP/kg steam, respectively). These constant concentrations appear to preclude any direct link between the bulk of the NUC gases and any other component showing variable concentrations. For example, The NUC component does not seem to correlate with the CO_2 content of these wells which varies from about 22 to 34 liters/kg steam.

ORIGINAL PAGE IS
OF POOR QUALITY

Thus the noble gases in the wells studied appear to comprise a minimum of three independent components; A (air-like non-nucleogenic), HE (heavy-enriched non-nucleogenic; possibly also including ^3He), and NUC (nucleogenic He, Ne, Ar).

PREVIOUS RESULTS; CIRCULATION MODEL. D'Amore and Truesdell (1) present a model for fluid circulation at Larderello in which geographic variations in CO_2, NH_4, H_3BO_3, Cl, and $\delta^{18}O$ are ascribed to outward lateral flow and progressive Rayleigh condensation of steam from central boiling zones. Insoluble gases are concentrated in the uncondensed fraction of the steam - e.g. CO_2 to steam ratios increase by a factor of 5 toward the periphery. Conversely, the soluble constituents are enriched in the liquid condensate.

According to this model, any noble gas components sharing an origin in the central boiling zones with the species listed above should show an enrichment toward the margin by at least a factor of 5. The data reported here serve to define primarily the concentrations in the central part of the field. Limited literature data for the heavier noble gases (2) suggest that a non-nucleogenic component may show a concentration increase parallelling CO_2. Elemental abundance ratios do not show a strong relative enrichment of either A or HE-type gases that might be expected if only one of the two components were radially concentrated. Clarification of this situation requires data from additional wells on the periphery of the field.

Literature data reveals little or no increase (less than x2) in radiogenic ^4He content across the field (2,4). As was suggested from the data on the central wells, CO_2 and ^4He are evidently not closely related. The principal source of steam produced by the wells is evaporation of the liquid condensate in the two-phase region (1). The constant He/steam ratios suggest that the bulk of the radiogenic ^4He in the steam from a given well was originally dissolved uniformly in the condensate and was leached locally from the aquifer.

He isotope data (4; this work) suggest that the $^3He/^4He$ ratio and hence ^3He concentration decrease toward the northern edge of the field. The ^3He and CO_2 appear not to share a common origin or transport mechanism. If the ^3He is of deep mantle origin, it is difficult to see how it could appear in the central Larderello wells without being subject to the same lateral flow that controls the CO_2 distribution. Perhaps this is telling us that the circulation model is incorrect. Alternatively, Torgersen (4) has suggested that the ^3He enrichments at Larderello could be the result of tritium decay in young groundwater such as is known to be recharging the southern part of the field (1). If this is the case, the lack of tritium (5) and very high He/Ne ratios in the wells showing elevated $^3He/^4He$ ratios require that old steam extracted most of the ^3He from the tritiated groundwater without significant hydrogen isotope exchange, and that the young groundwater was almost completely outgassed before the tritium decayed. Model calculations show that this scenario cannot be ruled out at present, although it seems uncomfortably ad hoc. The question of the origin of the ^3He in the Larderello fluids is clearly of great importance.

REFERENCES.

(1) D'Amore F. and Truesdell A.H. (1979) Proc. 5th Stanford Workshop and Geothermal Reservoir Engineering, p.283-297.
(2) Mazor E. (1979) Pageoph. 117, p.262-275.
(3) Truesdell A.H. and Nehring N.L. (1979) Pageoph. 117, p.276-289.
(4) Torgersen T. (1980) J. Geochem. Explor. 13, p.57-75.
(5) Nuti S. (1982) private communication.

ORIGINAL PAGE IS
OF POOR QUALITY

IMPORTANCE OF NON-TERRESTRIAL VOLATILES TO FUTURE SPACE OPERATIONS;

Robert L. Staehle, Advanced Projects Group, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

By 2000 the mass of equipment being placed into geostationary (Clarke) orbits annually may be 10^1-10^2 times the present level[1], making space transportation a multibillion dollar industry in terms of yearly revenues. Assuming advanced hydrogen/oxygen propellant upper stages, nearly 75% of the mass launched from Earth as payloads destined for geostationary orbit will be in the form of propellant[2], with perhaps 300 t/yr of oxygen. In terms of energy required for transport, the Moon is 10 times closer to low Earth orbit (LEO) than the Earth's surface, and several known asteroids are even closer at some times[3,4].

With the future space transportation industry becoming large enough to support its own supplier infrastructure, the possible availability of certain volatile elements on the Moon and some asteroids becomes attractive for reducing the costs of interorbit and other forms of space transportation. While the commercial breakeven point for extraterrestrial vs. terrestrial sources of commodities used in space operations cannot yet be predicted, current estimates of space transportation demand, particularly for civilian communications services, make such a breakeven conceivable within 20-30 years. Because of the lead times required in establishing even terrestrial resource operations, theoretical development and exploration over the next decade is likely to be decisive in choosing the first resource sites used to support space operations.

One important resource, oxygen, is abundant in many lunar minerals, and can be extracted via molten electrolysis[5] and possibly other techniques[6]. Other than oxygen, the key uncertainties for extraterrestrial resource operations involve the reducing agents hydrogen and carbon, the concentrations of which in known lunar materials are insufficient to be economically useful. Consequently, the most important issue for the investigation of planetary volatiles from the point of view of space resources is the possible presence of H and C in concentrations of 1-10 wt % or greater in unexplored regions of the Moon or on accessible asteroids.

The possibility of lunar permafrost in permanently-shaded polar crater floors has been advanced[7], and some meteoritic materials thought to be related to C-type asteroids have been found to have a component of water and carbon with non-terrestrial origin[8]. Limited exploration, combined with sound theoretical development, could result in the discovery of economically important reservoirs of volatile elements on the Moon, asteroids, and elsewhere.

The importance of potential extraterrestrial volatile resources is described, along with possible methods of locating valuable reservoirs. Some areas of scientific consideration are suggested which would be most helpful in determining and advancing the viability of extraterrestrial resources by reducing the costs of certain high-volume space operations.

References

1. Johnson Space Center (Author Unknown), Space Operations Center Presentation to JPL, "STS/SOC Traffic Model-Medium Options: Equivalent STS Flight -- Schedule 100 Baseline," Chart S-81-11734, 9/17/81.

ORIGINAL PAGE IS
OF POOR QUALITY

2. Staehle, Rob, "Propellant Estimate for Clarke Orbit Traffic in 2000," Jet Propulsion Laboratory IOM 312/82.3-1972, March 11, 1982.

3. French, J. R., and N. D. Hulkower, "Exploration of the Asteroids," Journal of the British Interplanetary Society, 35, pp. 167-171, 1982.

4. Hulkower, Neal D., "Opportunities for Rendezvous and Round Trip Missions to 1982 DB Based on Update Elements," JPL IOM 312/82.3-2046, June 7, 1982.

5. Kesterke, D. G., "Electrowinning of Oxygen from Silicate Rock," U.S. Bureau of Mines, RI 7587, 1971.

6. Criswell, David R., "Processing of Lunar and Asteroidal Materials," Extraterrestrial Materials Processing and Construction, Lunar and Planetary Institute, 30 September 1978.

7. Watson, K., B. C. Murray, and H. Brown, "The Behavior of Volatiles on the Lunar Surface," J. Geophys. Res., 66, 3033, 1961.

8. Kerridge, J. F., and T. E. Bunch, "Aqueous Activity on Asteroids: Evidence from Carbonaceous Meteorites," in Asteroids, T. Gehrels, ed., The University of Arizona Press, 1979.

ORIGINAL PAGE IS
OF POOR QUALITY

BUBBLE DIFFUSION AND COMPOSITION OF INERT GASES ON VENUS. A.S. Tamhane and G.W. Wetherill, Department of Terrestrial Magnetism, Carnegie Institution of Washington, Washington, D.C. 20015

The inert gases Ne and Ar have been observed to be more abundant on Venus by a factor of about 100 compared to Earth (1). One proposed hypothesis is that the inert gases were implanted, during the waning phase of a T Tauri stage, by an enhanced solar wind bombardment of the inner edge of a protoplanetary swarm. Material from the inner edge was then preferentially incorporated into Venus rather than the Earth (2). The present day solar wind ratio of $^{20}Ne/^{36}Ar$ is, however, $\sim$100 times higher than that observed in the atmosphere on Venus. This implies that a mechanism that would retain argon more efficiently than neon must be identified. Here we investigate the physical conditions under which one such mechanism, bubble diffusion (3), may give rise to fractionations similar to those observed.

Since ^{20}Ne is depleted by a factor of $\sim$100 with respect to ^{36}Ar, it is obvious that more than 99% of ^{20}Ne is lost from the grains. If this loss occurs in the form of bubbles, the bubble precipitation must take place at least up to the depth in the grains which corresponds almost to the end of the range of ^{20}Ne ions. It can occur only when the sputter erosion is low and the grains are saturated with implanted inert gases. This would require a solar wind bombardment of individual members of the <1 cm-diameter debris for a period of $\sim$100 years, assuming a flux enhanced by a factor of 500.

Bubble diffusion leads to fractionations in which heavier nuclides are enriched with respect to lighter ones. Assuming the energy of the primordial solar wind particles were equal to the present values, enrichment of ^{36}Ar by a factor of $\sim$100 with respect to ^{20}Ne would lead to a simultaneous enrichment of Kr with respect to ^{36}Ar by a factor of about 1.4. Analysis of Pioneer data suggests that the upper limit to Krypton mixing ratio most likely represents a measured concentration (4). The value of the most probable mixing ratio for Kr is 47 ppb which, if it is solely of solar wind origin, leads to an enrichment factor of 3.3, in disagreement with the prediction.

If the Pioneer measurement represents an actual detection of Kr, rather than an upper limit, one possible way of accounting for the higher enrichment factor would be to assume that the solar wind energy during the waning phase of the T Tauri stage was different than at present. If a higher energy is postulated, calculations indicate that the energy must have been in the range 20 Kev/n $< E \lesssim$ 100 Kev/n. Whether such an assumption can be justified is an open question. Some T Tauri stars exhibit rapid fluctuations in the ultraviolet, which are ascribed to the superposition of many simultaneous small flares (5). A

INERT GASES ON VENUS

ORIGINAL PAGE IS
OF POOR QUALITY

Tamhane, A.S. and Wetherill, G. W.

flare model based on this observation for the T Tauri stars could possibly provide a basis for the assumption (6).

Calculations are being made of the expected $^{36}Ar/Kr$ and $^{22}Ne/^{20}Ne$ fractionation at various energies in order to determine if there is an energy range for which the bubble diffusion mechanism is consistent with observation of inert gas abundances on Venus.

References:
(1) Pollack, J.B. and Black, D.C. (1979) Science 205, 55-99.
(2) Wetherill, G.W. (1981) Icarus 46, 70-80.
(3) Tamhane, A.S. and Agrawal, J.K. (1979) Earth Planet. Sci. Lett. 42, 243-250.
(4) Donahue, T.M., Hoffman, J.H. and Hodges, R.R., Jr. (1981) Geophys. Res. Lett. 8, 513-516.
(5) Kuan, P. (1976) Astrophys. J. 210, 129-136.
(6) Ulrich, R.K. (1978) in Protostars and Planets, T. Gehrels (ed.) 718-733.

ORIGINAL PAGE IS
OF POOR QUALITY

THERMAL AND DEGASSING HISTORIES OF THE EARTH AND VENUS

G. Visconti, Instituto di Fisica, Università dell'Aquila, 67100 L'Aquila, Italy

Recent work(1,2) suggests how the atmospheric temperature may influence the thermal history and tectonics of a terrestrial type planet. On the other hand the atmospheric temperature depends largely on the amount and chemical composition of the degassed material.

Calculations are presented on the thermal histories and evolution of the atmospheric temperature for the Earth and Venus for a number of degassing scenarios.

These calculations make use of a simplified radiative-convective model to evaluate the surface temperature and parameterized mantle convection to study the cooling of the interior and litospheric growth. Radiative calculations are based on the code given by Pollack (3) and opacities due to CO_2 and H_2O are evaluated on 13 wavelengths intervals. Cloudiness is included in the model and transfer of solar radiation through the atmosphere is evaluated using the δ -Eddington approximation. Parameterized convection in the mantle follows the scheme suggested in (2,4).

Results of the different degassing histories are discussed with particular emphasis on the influence of early water vapor degassing and possible feedback between mantle convection and atmospheric temperature.

REFERENCES

1) Phillips,R.J.,Kaula,W.M. McGill,G.E. and Malin,M.C.(1981), Science,212,879-887.

2) Phillips,R.J. and Malin,M.C.,to appear on "Venus". Proceeding of the Conference on the Venus Environment,Palo Alto,CA.

3) Pollack,J.B.(1969),Icarus,10,314-341.

4) Schubert,G.,Cassen,P. and Young,R.E.(1979),Icarus,38,192-211.

ORIGINAL PAGE IS
OF POOR QUALITY

COMETARY IMPACTS ON THE TERRESTRIAL PLANETS. Paul R. Weissman, Jet Propulsion Laboratory, Pasadena, CA 91109

Cometary impact rates for both long and short-period comets are calculated for each of the terrestrial planets. Impact probabilities are found using the standard Öpik (1976) formulae for encounters with planets in near-circular orbits. For the long-period (LP) comets a hypothetical distribution of near-parabolic orbits, uniformly distributed in perihelion distance and randomly oriented over the celestial sphere, is assumed. Everhart's (1967) flux of 16 LP comets/AU/yr brighter than absolute magnitude $H_{10} = 11.0$ is used. For the short-period (SP) comets the impact probabilities are based on the known sample of SP comets. Marsden (1979) has catalogued 113 SP comets of which 2, 9, 20, and 59 are Mercury, Venus, Earth, and Mars crossers, respectively. Results are shown in the table below.

	Long-period Comets		Short-period Comets				
	$\bar{p}$	$\bar{v}$ km s^{-1}	N_c	N_1	$\bar{p}$	$\bar{p}_y$ yr^{-1}	$\bar{v}$ km s^{-1}
Mercury	2.1×10^{-9}	81.2	1	1	2.4×10^{-9}	5.5×10^{-10}	41.5
Venus	3.7×10^{-9}	60.2	5	4	1.3×10^{-8}	2.0×10^{-9}	39.6
Earth	2.2×10^{-9}	51.7	13	7	6.6×10^{-9}	8.1×10^{-10}	37.4
Mars	6.8×10^{-11}	41.1	35	24	1.5×10^{-10}	2.2×10^{-11}	20.9

For the LP comets, $\bar{p}$ is the mean impact probability per comet per perihelion passage and $\bar{v}$ is the mean impact velocity. For the SP comets, N_c is the number of known planet-crossers of more than one apparition, N_1 is the number of one apparition planet-crossers, $\bar{p}$ is the mean impact probability per perihelion passage, $\bar{p}_y$ is the mean per year, and $\bar{v}$ is the mean impact velocity.

The dynamical evolution of comets in the Oort cloud and the flux of comets entering the planetary region has been modeled by Weissman (1982a, 1982b) using Monte Carlo simulation techniques. If comets originated in the Uranus-Neptune zone and were subsequently ejected to the Oort sphere, then they rapidly diffused back into the inner solar system with flux rates during the first 5×10^8 years of the solar system's history up to 200 times the current flux. However, if comets originated further from the sun on the fringes of the primordial solar nebula or even in satellite fragments of the nebula, then the enhanced early flux would be considerably less, possibly even less than the present observed flux. The integrated average flux over the history of the solar system could be as high as 30 times the current value for an origin in the Uranus-Neptune zone, or as little as 0.6 times the current flux for origin in nebula fragments at 10^4 AU from the sun. Estimates of the total cometary mass impacting on each of the terrestrial planets over the history of the solar system will also be made. This work was supported by the NASA Planetary Geophysics and Geochemistry Program.

References:

Everhart, E. 1967. Astron. J., 72, 1002.

Marsden, B. G. 1979. Catalogue of Cometary Orbits, Smithsonian Astrophysical Observatory, 88 p.

Öpik, E. J. 1976. Interplanetary Encounters, Elsevier, Amsterdam, 155 p.

Weissman, P. R. 1982a. in Comets, L. L. Wilkening, ed., Univ. Arizona Press, Tucson, pp. 637-658.

Weissman, P. R. 1982b. in GSA Special Paper No. 190, in press.

ORIGINAL PAGE IS
OF POOR QUALITY

THE USE OF TEPHRA STUDIES TO DETERMINE VOLATILE RELEASE DURING LARGE EXPLOSIVE VOLCANIC ERUPTIONS.

J.A. Wolff, Dept. of Geology, Imperial College, London SW7
and Geology Dept., King's College, London WC2
M. Storey, Geology Dept., Bedford College, Regent's Park, London NW1.

Outgassing at volcanoes occurs in two principal ways: via fumarolic activity and by direct release of magmatic volatiles during eruption. Juvenile and recycled components may contribute in each case. This contribution describes a geological/petrological approach to measuring the volatile flux due to large explosive eruptions from individual volcanoes. The method depends on accurate mapping of tephra blankets to obtain a value for the total erupted volume, and mineral chemistry studies to determine conditions of pre-eruptive phenocryst equilibration. Where air-fall tephra are present, the grain-size characteristics of individual eruptive units can be used to derive an independent estimate of magmatic volatile content. The principal value of this approach lies in the ability to measure the volatile release associated with prehistoric eruptions. The principal drawbacks are a lack of appropriate thermodynamic data for several gas species, and the related inherent inability to measure magmatic CO_2 contents. Species in the system H-O-S can however be determined for the majority of evolved magma types. Application of these methods to some Recent alkaline pumice deposits from Atlantic Ocean islands is discussed.

ORIGINAL PAGE IS
OF POOR QUALITY

EVOLUTION OF SOLAR ULTRAVIOLET LUMINOSITY, K. J. Zahnle and J. C. G. Walker, Department of Atmospheric and Oceanic Science, The University of Michigan, Ann Arbor, Michigan 48109.

A wealth of astronomical evidence indicates that the young sun was much more active than it is today; i.e., it was a much greater source of energetic particles and radiation. Here we restrict our attention to a tentative history of the solar UV derived from observations of solar analogs, as being both better constrained and obviously consequential to a conference on solar system volatiles.

Solar UV evolution naturally divides into an earlier "T Tauri" stage and a later "main-sequence" stage - the transition occurring some 10^7 years after the sun's formation.

For main-sequence stars, relationships have been established between 1) stellar activity and stellar rotation, 2) activity and age, and 3) rotation and age. Here we combine the observed relation between rotation and age with the various relations between activity and rotation to build our history.

Figure 1 presents our much simplified history of the various source regions that give rise to the solar UV. The relation between x-ray emission (i.e., the corona) and rotation velocity is valid for a wide range of stars, and takes the form $L_x \propto v_r^2$. The transition region is the source of line radiation by highly ionized species such as CIV λ1549. The relations between these lines and rotation take the form $L_t \propto v_r^s$, where $1.5 \lesssim s \lesssim 2.0$. The importance of the transition region should also roughly correlate with the helium lines and the Ly continuum - i.e., it should reflect the EUV ($\lambda \lesssim 1000$Å) flux (this radiation is astronomically unobservable owing to interstellar H). The chromospheric relationship ($L_c \propto v_r^{1.0}$), which is established both from UV and visible light observations, best describes UV from ~2000 >λ>~1500Å. Lyα (1216Å) is generated both by the chromosphere and the transition region, and hence its evolution should be somewhere in between curves 'c' and 't'. The photospheric evolution is indicative of solar flux for $\lambda \gtrsim 2000$Å.

Sunlike stars rotate more slowly as they age; empirically this has been described as $v_r \propto t^{-1/2}$, the angular momentum flowing away with the solar wind. This relation is implicit in the structure of fig. 1. It may be that only the outer layers of the star are effectively spun-down. Gough (1982) reviews evidence that the solar core rotates some six times faster than does the surface. If we assume that the sun once rotated rigidly at the core's angular velocity, an equatorial rotation velocity $v_r \approx 14$ km/sec is inferred and is indicated in fig. 1.

The extrapolation of solar activity back to its T Tauri stage (see fig. 1) is made simply by choosing representative observations of T Tauri stars made by the Einstein and IUE satellites. It is clear that the T Tauri sun would have had a profound impact on the evolving "solar" nebula and/or the evolving planetary atmospheres, if either existed at the time. In particular, EUV fluxes 10^4 times larger than those produced by the modern sun would have been very efficient at fueling the escape of massive hydrogen-rich atmospheres (e.g. Sekiya et.al) or at fueling the removal of the leftover material in the solar nebula, performing a function once ascribed to the T Tauri wind.

EVOLUTION OF SOLAR ULTRAVIOLET LUMINOSITY

ORIGINAL PAGE IS
OF POOR QUALITY

Zahnle, K. J. and Walker, J. C. G.

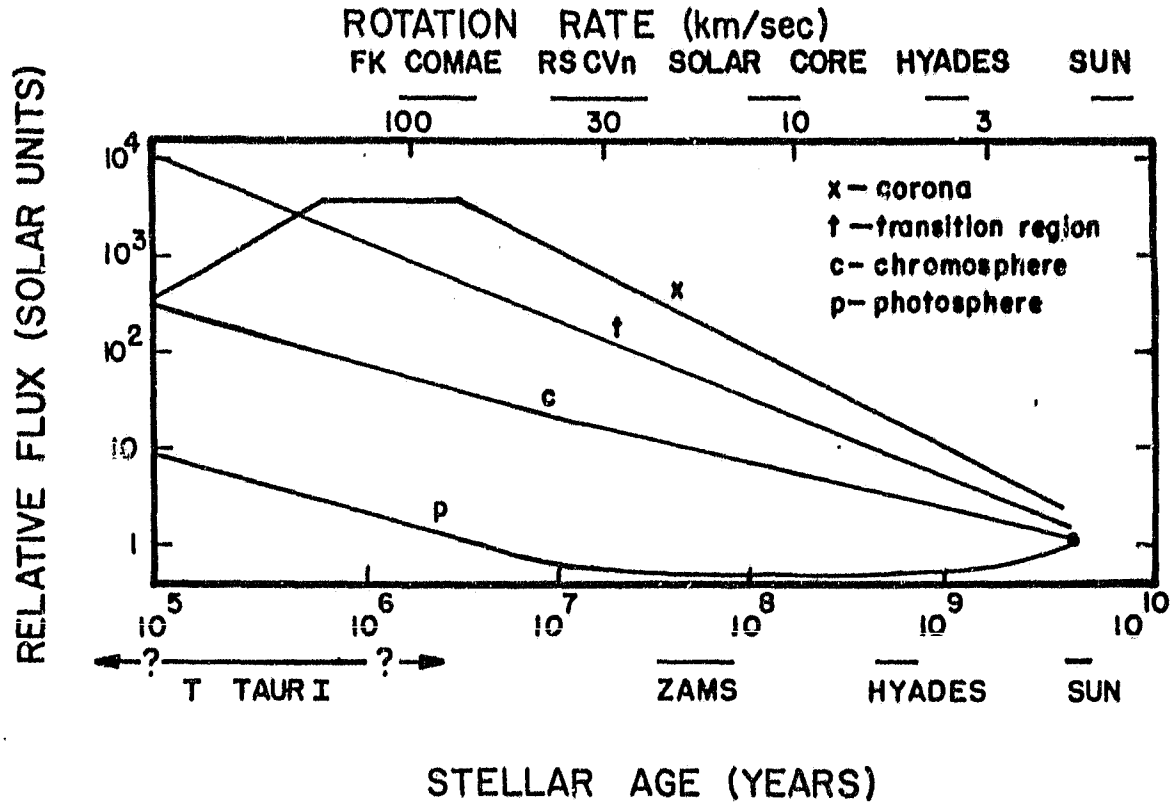


Figure 1. Simple picture history of solar ultraviolet. Labels on top axis refer to types of stars from which the rotation-activity relation has been derived, labels on bottom axis refer to types of stars for which the age-activity relation is found directly. ZAMS refers to the zero-age main-sequence sun.

References

Zahnle, K. J. and Walker, J. C. G. (1982) Rev. Geophys. and Space Phys., 20, p. 280-292.

Newkirk, G. (1980). The Ancient Sun, p. 293-320.

Gaustad, J. and Vogel, S. (1982). Origins of Life, in press.

Feigelson, E. (1982). Icarus, in press.

Gough, D. O. (1982). Nature, 298, p. 334-339.

Sekiya, M., Nakazawa, K., and Hayashi, C. (1982). Prog. Theor. Phys., 64, p. 1968-1985.

ORIGINAL PAGE IS
OF POOR QUALITY

MANTLE DIFFERENTIATION AND CRUSTAL GROWTH: AN ISOTOPIC VIEWPOINT.

Alan Zindler[1], Steve Goldstein[1], and Emil Jagoutz[2] (1-Lamont-Doherty Geological Observatory of Columbia University, Palisades, New York 10964; 2-Max Planck Institute fur Chemie, Saarstrasse 23, Mainz, West Germany.)

Recent geochemical modelling of mantle differentiation and crustal growth (1-5) has suggested that Nd and Sr isotopic variations in young mantle-derived rocks may be explained by mixing of two mantle components, "MORB-type" or depleted mantle material and undifferentiated or slightly enriched mantle material. In this context, apparently enigmatic variations in Pb isotope ratios have been interpreted as indicating that the U-Th-Pb system has undergone a more complex evolution in the earth than either Sm-Nd or Rb-Sr. As an alternative, we have suggested that variations in Nd, Sr, and Pb isotopic compositions of mantle-derived rocks indicate the existence of at least three chemically independent mantle components (see (6) for a detailed discussion of some of the ideas presented here).

The first order difference between the two and three component models is not simply the number of mantle components invoked, for any subdivision of the mantle into two, three, or n components is necessarily a simplification of the real situation. The basic difference lies in the nature of the mechanisms which must be called on to explain the differentiation of the mantle into its major observable components. Processes which involve the mobilization of silicate liquids or silica-rich fluids within the mantle are thought to fractionate parents from daughters in each of the isotope systems under consideration. Therefore, to propose that, in a gross sense, Nd and Sr isotopic variations may be explained by two mantle components while three or more components are required by Pb isotope variations is to imply that some geochemically active mantle process causes severe fractionations of U and Th from Pb without significantly affecting Rb/Sr and Sm/Nd ratios, and furthermore, that this process is not one governed solely by solid-liquid-fluid equilibria in a silicate system. Based on this kind of reasoning, several authors (1, 9-11) have proposed that Pb has been transferred from the mantle to the core in a sulfide phase throughout geologic time, causing a progressive increase in mantle U/Pb and Th/Pb ratios. Because the other elements under consideration are not chalcophile in nature, their relative abundances in the mantle will not have been affected by this process. In contrast, if Nd, Sr, and Pb isotopic variations support the existence of more than two mantle components, then fractionations of all three parent-daughter systems may conceivably be in response to magmatic or metasomatic processes operating within the mantle without calling on a special process to fractionate U and Th from Pb.

We have examined mantle Nd, Sr, and Pb isotopic variations in multi-dimensional space in order to investigate systematics which may be obscured in two-dimensional variation diagrams. In three, four, or five dimensions, average isotopic compositions for individual ocean islands or island groups and mid-ocean ridges define a planar array with a high degree of precision (Fig. 1) and indicate that mantle isotopic variations are best described by mixing between three chemically independent mantle components. These results suggest that: 1) processes which involve the mobilization of silicate liquids or silica-rich fluids within the mantle, such as metasomatism or magma generation, can account for differentiation of the three isotope systems without calling on a special process to produce apparently complex Pb isotope variations; and 2) mass-balance arguments which have been used to support convective isolation of the lower mantle (2-4) (and the resulting chemical stratification of the mantle) are not valid, due to the positive identifica-

ORIGINAL PAGE IS
OF POOR QUALITY

tion of an additional important mantle component.

Recognition of these systematics in the mantle places important constraints on the evolution of the crust-mantle system. A model has been developed which describes transport between a depleting MORB-type mantle component, the continental crust, and a high U/Pb mantle component, most clearly observed at St. Helena. An additional mantle component is assumed to be relatively undifferentiated. A Monte Carlo approach is used to investigate the effects of varying input parameters through geochemically reasonable ranges.

This modelling has shown that: 1) successful solutions may be generated with the total mass of interactive mantle ranging from 0.3 to 1.0 times the total mantle (Fig. 2; this is independent of the mass assigned to the high U/Pb component); 2) the high U/Pb component is chemically similar to basalt (Fig. 3) and must be generated primarily during the latter half of earth history (if this component is subducted ocean crust, the oldest portion must have been efficiently re-mixed into the mantle; and 3) "J-type" or future leads observed in oceanic basalts may be generated by mixing "B-type" depleted mantle with "J-type" (high U/Pb) mantle and with undifferentiated mantle which lies along the geochron.

References: 1. Allegre, C.J. (1982) Tectonophysics 81, 109; 2. O'Nions, R.K. et al. (1979) J. Geophys. Res. 84, 6091; 3. Jacobsen, S.B. and Wasserburg, G.J. (1979) J. Geophys. Res. 84, 7411; 4. DePaolo, D.J. (1980) GeochimCosmochim. Acta 44, 1185; 5. Anderson, D.L. (1982) Earth Planet. Sci. Lett. 57, 1; 6. Zindler, A. et al. (1982) Nature, in press; 7. L-DGO unpublished data; 8. White, W.M. and Hofmann, A.W. (1982) Nature 296, 821; 9. Vidal, P. and Dosso, L. (1978) Geophys. Res. Lett. 5, 169; 10. Dupre, B. and Allegre, C. J. (1980) Nature 286, 17; 11. Allegre, C.J. et al. (1980) Phil. Trans. R. Soc. Lond. A. 297, 447.

Fig. 1

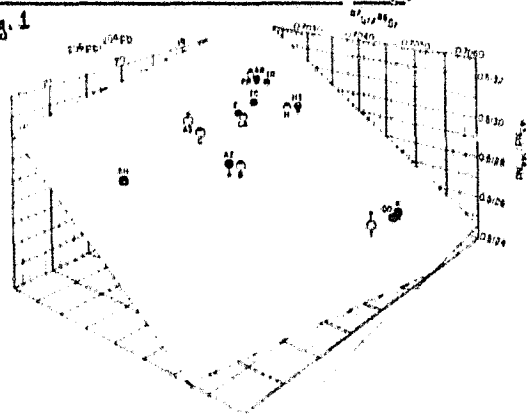


FIGURE 1. THREE-DIMENSIONAL PLOT OF AVERAGE Sr, Nd, AND Pb ISOTOPE RATIOS FOR BASALTS FROM OCEAN ISLANDS AND RIDGES. THE BEST-FIT PLANE IS SHOWN. CLOSED AND OPEN SYMBOLS LIE ABOVE AND BELOW THE "MANTLE PLANE", RESPECTIVELY. LINES CONNECTING THE POINTS TO THE PLANE ARE PARALLEL TO THE ND AXIS AND INDICATE THESE POINTS WHICH DO NOT INTERSECT THE PLANE. LOCALS ARE AS FOLLOWS: AR = MAR, PR = EPR; IR = INDIAN OCEAN RIDGES; IC = ICELAND; HI = HAWAIIAN ISLANDS; H = HAWAII; E = EASTER ISLAND; GA = GALAPAGOS; AS = ASCENSION; C = CANARIES; AZ = AZORES; B = BOUVET; SH = ST. HELENA; T = TRISTAN; GO = GOUGH; K = KERGUELEN. DATA ARE FROM THE LITERATURE.

FIGURE 2. VARIATION DIAGRAM OF ND VS. SR ISOTOPE RATIOS. FIELD OCCUPIED BY AVERAGE DATA POINTS IS SHADED AND SHOWN FOR REFERENCE. SUCCESSFUL SOLUTIONS FROM MONTE CARLO MODELLING ARE SHOWN TO BE COMPATIBLE WITH MANTLE ARRAY OF DATA, REGARDLESS OF THE PERCENTAGE OF INTERACTIVE MANTLE SPECIFIED.

FIGURE 3. CONCENTRATION RESULTS FROM MONTE CARLO MODELLING SHOWING FIELDS FOR THE CONTINENTAL CRUST AND MANTLE COMPONENTS. DATA ARE NORMALIZED TO CI CHONDRITE VALUES. A FIELD FOR AVERAGE MORB IS SHOWN TO COINCIDE WITH THE MODEL RESULTS FOR COMPONENT 3, THE HIGH U/Pb MANTLE COMPONENT, PROVIDING SUPPORT FOR THE SUBDUCTED OCEAN CRUST AS COMPONENT 3 HYPOTHESIS.

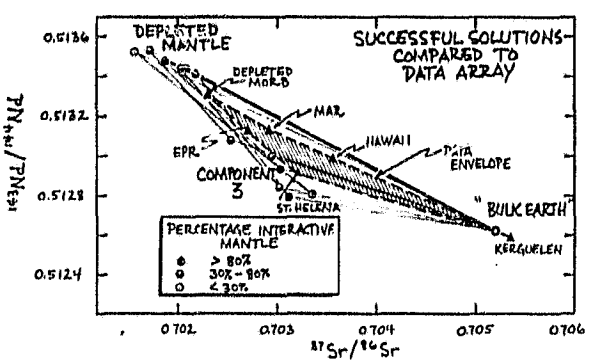


Fig. 2

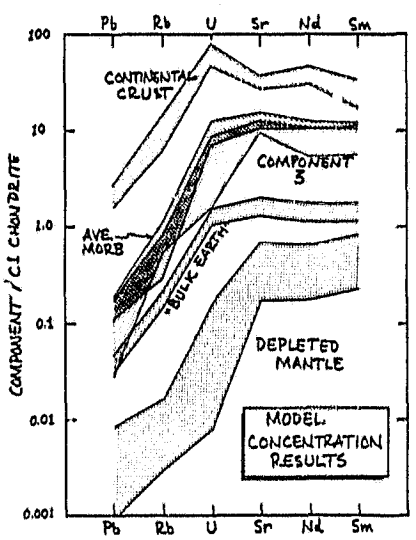


Fig. 3

SUBJECT INDEX

ORIGINAL PAGE IS
OF POOR QUALITY

Accretion 27, 63, 65, 85, 88
Adsorption 84
Alteration 63
Annealing 4
Argon 39
Asteroids 67, 104
Atmosphere 43, 79, 80, 88
  composition 16
  contamination 93
  evolution 79
  mean age 93
  outgassing 93

Basalt liquidus studies 90
Basalts 29, 41, 60
Brine 12

C-O-S-H gaseous system 76
Cadmium/zinc ratio 74
Carbon 69, 104
Carbon dioxide 4
Carbon isotopes 29
  abundances 69
  cycle 29, 87
Chemical evolution 11
Chemical synthesis 11
Chlorine 49, 73
Clathrates 37
Climate 51
Collisional impact 67
Comets 37, 47, 109
Core separation 45

Deuterium 56, 58
Dissolution of rare gases 71

Earth 61
Earth Trojans 104

Elemental abundances 79
Equilibrium condensation 37
Extraterrestrial resources 104

Flooding 99
Fluid chemistry 33
Fluid inclusions 4
Fluorine 73
Freezing point depression 12

Gas loss 93
Geothermal fluids 102
Germanium/nickel ratio 74
Greenhouse effect 88

Helium isotopes 53, 60
High pressures 9
Hotspots 29
Hualalai 69
Hydrodynamic escape 56
Hydrogen 104
Hydrogen escape 56, 58
Hydrothermal convection 23
Hydrothermal fluid circulation 102

Ice 12, 23, 43
Ilmenite 2
Impact 4
Impact degassing 63
Impact rates 109
Impact-generated atmosphere 65
Interaction 85
Interstellar molecules 47

ORIGINAL PAGE IS
OF POOR QUALITY

Inventory 80
Iron disproportionation 2
Iron-water interaction 65
Isotopic anomalies 92

Jupiter 79
Juvenile carbon 29

Kilbourne hole 69

Larderello 102
Lead isotopes 113
Lherzolite 69
Lithosphere recycling 2

MORB 29, 93
Mantle-crust 113
Mantle 2, 69, 93
  geochemistry 113
  heterogeneity 60
  outgassing 1
  oxidation state 33, 45
  reservoirs 1
  structure 113
Mars 12, 23, 51, 61, 79, 99
  atmosphere 51
  impact basins 97
  polar caps 51
  sulfur 41
Mass spectrometer 93
Meanders 99
Melting 63
Metal-silicate equilibrium 45
Metasomatic fluids 33
Meteorite sulfur abundances 41
Meteorites 4
  aubrites 67
Meteorites(CONTINUED)
  chondrites 37, 63, 67
Methane 33
Micropores 84
Midocean ridge 29
Molecular clouds 47
Moon 16, 27, 104
Mt. St. Helens 76

Narrow valleys 97
Neodynium 113
Noble gases 60, 61, 82, 92, 102
  impregnation 85
  in meteorites 84
Nonthermal escape 58
Nucleogenic gases 102

Oort cloud 109
Orbital dynamics 109
Organics 4
Origin of life 11
Outflow chemicals 97
Outgassing 88, 93
Oxygen fugacity 2

Pallasites 45
Peridotite 2, 69
Permafrost 23
Phyllosilicates 63
Planetary atmospheres 61, 79
Planetary formation 71
Planets 79
Platinum group metals 74
Pre-solar dust grains 8
Prebiotic chemosynthesis 11
Primitive biosphere 11
Primitive nebula 92
Primordial atmosphere 11, 16, 71
Propellant 104

ORIGINAL PAGE IS
OF POOR QUALITY

Protostellar disks 18
Pyrrhotite-magnetite assemblage 76

Radiogenic gases 102
Rayleigh condensation 102
Rayleigh distillation 102
Redox state 2, 94
Regolith 51

Salts 12
Satellites 79
Sediment reinjection 93
Sedimentary carbon 29
Sediments 80
Selenium 74
Shales 80
Shock 4
dehydration 63
experiments 63
heating 67
metamorphism 63
Siderophile elements 74
Solar activity 111
Solar evolution 111
Solar nebula 8, 16, 18, 47, 85
Solar radiation 111
Solar wind 43, 85
Solar x-rays 111
Space industry 104
Space transportation 104
Sputtering 43
Stepwise heating 93
Strontium 113
Subduction 49
Subduction zone magnetism 49
Submarine alteration 49
Sulfur 41, 73, 74, 90
Sun 111

T-Tauri phase 111

Tellurium 74
Terrestrial atmosphere 65
Terrestrial degassing 39, 53
Terrestrial hydrosphere 65
Terrestrial planets 37, 74
Terrestrial rare gases 39
Thermal diffusion of H20 23
Thermal metamorphism 63, 67
Thermodynamics 45
Titan 79
Trace elements 67

Ultramafic xenoliths 74
Ultraviolet radiation 111

Vapors 9
Venus 41, 56, 58, 61, 79
Vesicles 27
Volatile accretion 37
Volatile components 9
Volatile element abundances 74
Volatile exchange 51
Volatiles 8, 69, 104
Volatiles in magmas 90
Volcanic glass 27

Water 4, 9, 12, 23, 49, 51
cycling 49
loss 56

Xenon 16, 80

AUTHOR INDEX

ORIGINAL PAGE IS
OF POOR QUALITY

Ahrens T. J. 65
Allegre C. J. 1, 60, 93
Anderson A. T., Jr. 49
Arculus R. J. 2, 45
Ashwal L. D. 4

Bar-Nun A. 19
Baur M. E. 6, 7
Bernatowicz T. J. 80
Black D. C. 8, 82
Boettcher A. 9
Boston P. J. 11
Brass G. W. 12
Burggraf D. R. 76
Burke K. 14

Cameron A. G. W. 16
Carroll M. 90
Cassen P. 18
Chang S. 19, 21
Clifford S. M. 23
Colucci M. T. 4
Condomines M. 25

Delano J. W. 27
Des Marais D. J. 29
Dietrich V. J. 69
Duba A. G. 31

Eggler D. H. 33
Evans K. L. 73

Fanale F. P. 35
Fegley B. 37
Fisher D. E. 39

Gibson E. K., Jr. 4, 41
Goldstein S. 113
Grossman A. S. 87, 88
Grovold K. 25
Gust D. A. 2

Haff P. K. 43
Hager B. H. 77
Hayes J. M. 7
Henry D. J. 4
Holmes R. D. 2, 45
Honda M. 80
Hooker P. J. 25
Houseman G. A. 77
Hunten D. M. 58

Irvine W. M. 47
Irving A. J. 69
Ito E. 49

Jagoutz E. 113
Jakosky B. M. 51
Jenkins W. J. 53
Jovanovich S. 54

Kasting J. F. 56
Kerridge J. F. 21
Kramer F. E. 80
Kumar S. 58
Kurz M. D. 60

Lal D. 61
Lambert P. 4, 63
Lange M. A. 65
Lipschutz M. E. 67

ORIGINAL PAGE IS
OF POOR QUALITY

Manuel O. K. 92
Mathez E. A. 69
Mizuno H. 71
Moore C. B. 73
Moore J. G. 29
Morgan J. W. 74

Nordlie B. E. 76

O'Connell R. J. 77
O'Nions R. K. 25, 78
Owen T. 79
Oxburgh E. R. 25, 78

Podosek F. A. 80
Pollack J. B. 56, 58, 82, 88
Prather M. J. 83

Ramadurai S. 84
Rao A. S. P. 85
Rao M. N. 61
Reed G. W., Jr. 54
Reynolds R. T. 88
Richardson S. M. 87, 88
Rogers J. L. 97
Rutherford M. J. 90

Sabu D. D. 92
Sakai H. 29
Salvail J. R. 35
Sarda P. 93
Sato M. 94
Schidlowski M. 96
Schneider M. E. 33
Schultz P. H. 97
Scott D. H. 99
Shankland T. J. 31
Sleep N. H. 101
Smith S. P. 102
Staehle R. L. 104
Staudacher T. 93
Stoker C. 11
Storey M. 110

Tamhane A. S. 106
Tarter J. G. 73
Thieben S. E. 76
Thurmond V. L. 12

Visconti G. 108

Walker J. C. G. 111
Walter M. R. 7
Weissman P. R. 109
Wetherill G. W. 106
Wolff J. A. 110

Zahnle K. J. 111
Zindler A. 113

NASA-JSC