

PROCEEDINGS OF THE
27TH INTERNATIONAL
GEOLOGICAL CONGRESS

VOLUME 11
GEOCHEMISTRY AND
COSMOCHEMISTRY

56.5085
I 61-1
1984(27)-11

Proceedings of the
27th International Geological Congress
Moscow 4-14 August 1984

Volume 11

GEOCHEMISTRY AND COSMOCHEMISTRY

WVNU SCIENCE PRESS///

Utrecht, The Netherlands
1984

VNU Science Press BV
P.O. Box 2073
3500 GB Utrecht
The Netherlands

© 1984 VNU Science Press BV

First published 1984

ISBN 90-6764-020-4 Volume 11
ISBN 90-6764-009-3 set of 23 volumes

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise, without the prior permission of the copyright owner.

Printed in Great Britain by I. W. Arrowsmith Ltd, Bristol

PREFACE

The leading scientists in the many different fields of geology were invited by the Organizing Committee to present a paper on a specific problem in present-day geological science at the 27th International Geological Congress. The published proceedings of the Congress consist of twenty-three volumes. Each volume is dedicated to a particular aspect of geology. Together the volumes contain all of the contributions presented at the Congress.

The Organizing Committee is pleased to acknowledge the efforts of all of the participating scientists in helping to produce these proceedings.

Professor N. A. BOGDANOV
General-Secretary of the
Organizing Committee

CONTENTS

Preface	v
Accretion of the Earth and the inner planets	
G. Dreibus and H. Wänke	1
Long-lived radioactivities in cosmochemistry	
M. Honda	21
On nucleosynthesis of the solar system matter in the light of new data of isotopic anomalies	
A.K. Lavrukhina	39
Some short-lived radioactive nuclei in the early solar system	
G.J. Wasserburg	53
Venus' surface rock mineral composition: physicochemical simulation	
V.P. Volkov and I.L. Khodakovsky	73
Petrology of lunar materials: highland, mare, and regolith	
J.J. Papike and S.B. Simon	91
Mineralogy of some achondrites and the early evolution of their parent bodies	
H. Takeda and H. Mori	137

Geochemistry of chondrules: fractionation processes in the early solar system G. Kurat	155
Some problems of meteorite classification A.A. Yavnel	199
Primitive $^3\text{He}/^4\text{He}$ ratio in terrestrial diamonds and its implication on the origin of noble gases in terrestrial planets M. Ozima and S. Zashu	219
Xe isotopes and the origin of the volatile elements in the Earth Yu.A. Shukolyukov	233
Occurrence and chemical form of volatiles in the mantle S. Matsuo	253
$^{13}\text{C}/^{12}\text{C}$ of diamonds. Vertical zonality of diamond formation in the lithosphere E.M. Galimov	279
Evolution of the silicate shells of the Earth and the atmosphere in the light of recent isotopic data I. Azbel and I. Tolstikhin	309
Recycling on the evolving Earth: geochemical record in sediments J. Veizer	325
Sources of matter and the problem of the sedimentary shell and Earth crust evolution A.B. Ronov, A.A. Migdisov and A.A. Yaroshevsky	347

Recent advances in oxygen 18 geochemistry R. Letolle	367
Inhomogeneity of the Earth's upper mantle and alkaline magmatism L.N. Kogarko	389
The oxidation state of the upper mantle: thermochemical modelling and experimental evidence M. Sato	405
Problems of redox regime of the upper mantle and ways of its degassing in the process of melting A.A. Kadik and O.A. Lukanin	435
Mantle convection and geochemical cycles D. Turcotte	449
Quantitative principles of correlation between silicate melt properties and their water contents N.I. Khitarov and E.B. Lebedev	467
Pb, Sr, and Nd isotopes in ocean island basalts M. Tatsumoto, D.M. Unruh, P. Stille and H. Fujimaki	485
What can accessory minerals tell us about felsic magma evolution? A framework for experimental study E.B. Watson and T.M. Harrison	503
Hydrothermal solution self-mixing in the production of ore veins and wall-rock alterations aureoles V.L. Barsukov, M.V. Borisov and A.A. Pek	521

Endogenic fluid regime and its role in hydrothermal ore formation G.B. Naumov	537
Certain peculiarities of composition and structure of primary geochemical aureoles in main types of hydrothermal ore deposits in the People's Republic of Bulgaria A.I. Panayotov	559
Dispersed organic matter of sediments in the process of petroleum generation I.S. Kovacheva	573
Geologic/geothermal patterns in the oil and gas potential of the world oceans A.A. Geodekyan and V.Ya. Trotsyuk	595

ACCRETION OF THE EARTH AND THE INNER PLANETS

G. DREIBUS and H. WÄNKE

Max-Planck-Institut für Chemie, Saarstrasse 23, 65 Mainz,
F.R.Germany

ABSTRACT

The chemical composition of the Earth's primitive mantle (present mantle + crust) yields important information about the accretion history of the Earth. For the upper mantle reliable data on its composition have been obtained from the study of unaltered ultramafic xenoliths (Jagoutz et al. 1979).

Besides the high concentrations of moderately siderophile elements (Ni, Co, etc.) in the Earth's mantle the similarity of their C 1 normalized abundances with that of moderately volatile (F, Na, K, Rb, etc.) and partly even with some highly volatile elements (In!) is striking. To account for the observed abundances an inhomogeneous accretion from two components was proposed. According to this model accretion started with the highly reduced component A, with all Fe as metal and even Si and Cr, V and Mn partly in reduced state and almost devoid of moderately volatiles and volatiles, followed by the accretion of more and more oxidized matter (component B), containing all elements including moderately volatile and at least some volatile elements in C 1 abundances.

Recently, it became evident that the SNC meteorites with almost certainty represent Mars rocks. From the composition of the SNC meteorites we have estimated the bulk chemistry of their parent body (SPB = Mars). The data obtained in this way clearly show that the two component model is also valid for Mars. However, contrary to the Earth Mars seems to have accreted almost homogeneously. From the composition of its surface rocks as analysed by Venera 13 and 14 (Surkov et al. 1983) an inhomogeneous accretion is proposed for Venus.

CHEMISTRY OF THE EARTH

The mass of the Earth's mantle amounts to about two-thirds of the total mass of our planet. Except for the most incompatible elements for which the contribution of the crust (0.59 % of the mass of the mantle) becomes important, the mantle determines the chemistry of the Earth for all lithophile elements.

Violent volcanic eruptions of basaltic magmas carry more or less unaltered solid mantle material in form of ultramafic nodules to the surface. These nodules very frequently became severely contaminated by various processes, before, during, or after their eruption. Jagoutz et al. (1979) succeeded to select five nearly uncontaminated spinel-lherzolite nodules. Trace element as well as isotope studies (Jagoutz et al. 1980) proved the primitive, i.e. almost unfractionated character of one of these nodules. From the study of these lherzolite nodules the following abundance trends have been recognized (Fig.1, Table 1). The abundances have been obtained by normalizing the observed concentrations to Si and C 1 (carbonaceous chondrites type 1; data for C 1 compiled by Palme et al. 1981, are used throughout this paper).

1. Refractory oxyphile elements $x (1.3 \pm 0.15)$
(Al, Ca, Ti, Sc and most refractory trace elements)
and Mg enriched
2. V, Cr, Mn depleted $x (0.25 \text{ to } 0.7)$
3. Fe and moderately siderophiles $x (0.1 \text{ to } 0.2)$
(Ga, Cu, W, Co, Ni) depleted
4. Moderately volatiles (Na, K, Rb, F, $x (0.1 \text{ to } 0.2)$
Zn) and the highly volatile element In depleted
5. Highly siderophiles (Ir, Os, Re, Au) $x (0.002)$
strongly depleted
6. Highly volatiles (Cd, Ag, I, Br, $x (10^{-2} \text{ to } 10^{-4})$
Cl, Te, Se, C) strongly depleted

depletion of Mn on these planetary objects. For both, the EPB and SPB depletion of moderately volatile elements like Na or K comparable or higher to that of the Earth is beyond any doubt. The most likely explanation of the depletion of Mn and to a lesser extent of Cr and V in the Earth's mantle is their removal into the Earth's core, either in reduced form as metals or sulfides or as oxides. Segregation into the core in form of sulfides had been suggested by Hutchison (1974), to explain the low concentration of Cr. Removal as oxides could be expected if the Earth's core contains a large amount of dissolved FeO as proposed by Ringwood (1977).

The uniform enrichment of Mg and the refractory lithophile elements relative to Si could also be interpreted in terms of a Si deficiency (Ringwood 1958). It was suggested that the missing Si went into the core in metallic form, which would indicate gross chemical disequilibrium between mantle and core. Alternatively, the high Mg/Si ratio found for the upper mantle might be compensated by a smaller ratio in the lower mantle. The slightly higher abundances of Al, Ca and refractory trace elements (average 1.4) as compared to Mg (1.18) might be real but could also reflect inhomogeneous distribution (less Al, Ca, etc. than Mg in the lower mantle).

ACCRETION SEQUENCE OF THE EARTH

To explain the observed elemental abundance pattern of the Earth's mantle the following inhomogeneous two component accretion model has been set up (Wänke 1981).

Accretion started with highly reduced material free of moderately volatile and volatile elements but containing all other elements in C 1 abundance ratios. Fe and all siderophile elements as metals (W!), Si partly as metal, Cr, Mn and V as metals or sulfides. Component A.

After accretion of about 2/3 of the earth and after core formation more and more oxidized material (Fe, Co, Ni, W! as well as all other siderophile and lithophile elements as oxides) was added containing all elements including moderately volatile and at least some volatile elements (In, etc.) in C 1 abundances. Component B.

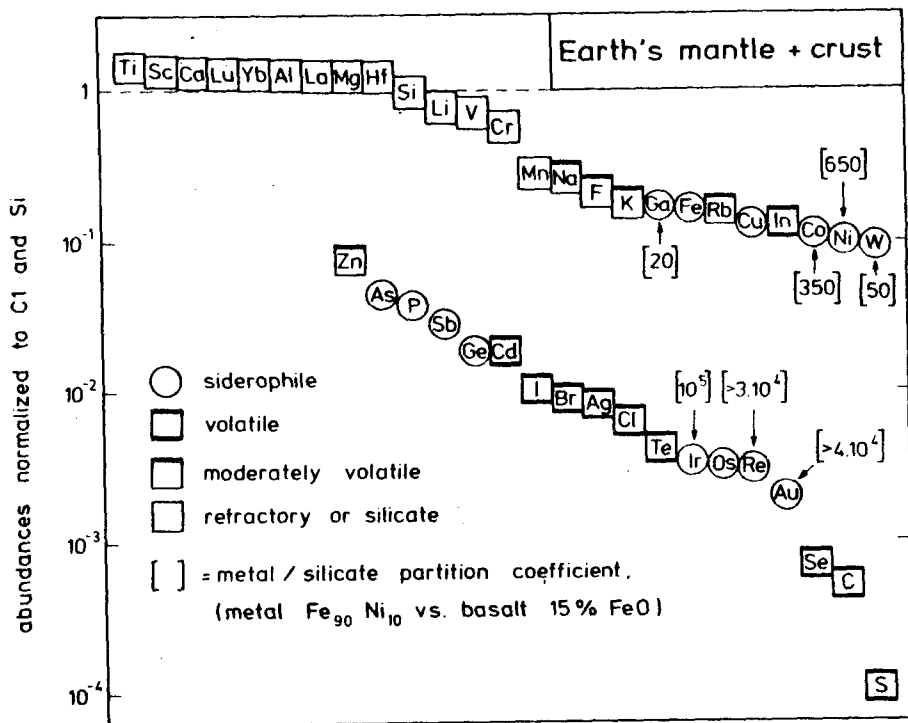


Fig. 1 Composition of the Earth's mantle (+ crust) normalized to C 1 and Si derived from the analyses of primitive spinel-lherzolites (Jagoutz et al. 1979; Wänke 1981, and unpublished data of the Mainz laboratory).

Relative to Si and C 1 all oxyphile refractory elements and Mg have abundances between 1.2 and 1.5. The depletion of V, Cr and Mn first noted by Ringwood (1966) is striking and as we shall see very informative. Ringwood and Kesson (1977) favored a depletion mechanism based on the higher volatility of Cr and Mn when compared with Si. Dreibus and Wänke (1979) presented evidence which makes the depletion of Cr, Mn and V by volatility highly improbable. Meteoritic basalts from the eucrite parent body (EPB), formed under lower oxygen fugacity than terrestrial basalts as well as those from shergotty parent body (SPB), formed under higher oxygen fugacity, indicate no

Table 1: Bulk composition of Earth and Mars

EARTH		M A R S			
	Wänke	this	Anderson	Morgan a. Anders	Ring- wood
	(1981)	work	(1972)	(1979)	(1981)
Mantle + crust:					
MgO %	38.0	30.2	27.4	29.8	29.9
Al ₂ O ₃	4.14	3.02	3.1	6.4	3.1
SiO ₂	45.1	44.4	40.0	41.6	36.8
CaO	3.54	2.45	2.5	5.2	2.4
TiO ₂	0.22	0.14	0.1	0.3	0.2
FeO	7.82	17.9	24.3	15.8	26.8
Na ₂ O	0.36	0.50	0.8	0.1	0.2
P ₂ O ₅	0.017	0.16	-	-	-
Cr ₂ O ₃	0.45	0.76	0.6	0.6	0.4
MnO	0.13	0.46	0.2	0.15	0.1
K ppm	185	315	573	59	218
Rb	0.77	1.12	-	-	-
Cs	-	0.07	-	-	-
F	24	32	-	-	-
Co	104	68	-	-	-
Ni	2080	480	-	-	-
Cu	28	2.6	-	-	-
Zn	50	74	-	-	-
Ga	3.2	6.6	-	-	-
W ppb	16	105	-	-	-
Th	-	56	77	113	60
U	21	16	17	33	17
Core					
Fe %	80.27	77.8	72	88.1	63.7
Ni	5.46	7.6	9.3	8.0	8.2
Co	0.27	0.36	-	-	-
S	-	14.24	18.6	3.5	9.3
O	-	-	-	-	18.7
Si,Mn,Cr	14.00	-	-	-	-
core mass %	33.5	21.7	11.9	19.0	18.2

Small amounts of metal from component A still present but in decreasing amounts as accretion proceeded are thought to be responsible for complete extraction of highly siderophile elements (Ir, Au, etc.) into the core. Component B also contained volatile elements such as halogens, H₂O and carbon. Presence of H₂O as well as of Fe³⁺ were responsible that metallic Fe finally became unstable and the highly siderophile elements contained in the last 0.2 % of the mass added to the Earth remained in the mantle in chondritic abundance ratios.

The moderately volatile elements and some volatile elements as well as the siderophile elements observed in the Earth's mantle are exclusively derived from component B. Thus the similarity of the C 1 normalized abundances of moderately volatile (F, Na, K, Rb, etc.) and moderately siderophile elements (Ni, Co, Cu, Ga, W, etc.) in the Earth's mantle is readily explained. Assuming a C 1 composition for component B, the Earth would consist of 80 % of component A and 20 % of component B.

Ringwood (1977 and 1979) has previously proposed a model to build the inner planets from a reduced volatile-free and an oxidized volatiles containing component. He assumed homogeneous accretion in which both components are added to the growing planet simultaneously and equilibrated with each other. As outlined above, the observed chemical composition of the Earth's mantle - though not really in contradiction with homogeneous accretion - seems to be explained in a more straightforward way by an accretion sequence in which the oxidized component is added only after the accretion of about 2/3 of the Earth's mass and after segregation of the metal phase (i.e., after core formation).

Anders (1965) extended a two component model originally formulated for meteorites (Anders 1964) to also explain the abundance patterns of planets but did not pursue this model in later publications (Ganapathy and Anders 1974).

CHEMISTRY OF MARS AS DERIVED FROM SNC-METEORITES

Besides Earth and Moon there are a number of planetary objects from which we have samples in form of meteorites for thorough laboratory investigations. Two of these objects gained exceptional interest because among the meteorites derived from them, there are rocks of igneous and basaltic composition.

The first of these objects, the eucrite parent body (EPB), has been studied since several years and estimates on its bulk composition and evolutionary history have been published by various authors (Hertogen et al. 1977; Consolmagno and Drake 1977; Morgan et al. 1978; Dreibus and Wänke 1980). It turned out that the eucrites have altogether crystallization ages close to 4.5 b.y. (Birk and Allègre 1978) and, hence, represent the oldest basalts known. The eucrites and other classes of meteorites which are chemically and according to their oxygen isotopes related to them come from a small object. The asteroid Vesta has been proposed as possible parent body as its reflectance spectra resemble those of eucrites (Chapman 1976), respectively howardites, which are mechanical mixtures of eucrites and diogenites.

Lately meteoritic basalts known as shergottites became famous. There are only four examples known, two of them were recently found in Antarctica. One of the Antarctic shergottites consists of two very different lithologies so that we have in fact five shergottites. It was found that shergottites have crystallization ages of not more than about 1.36 b.y. (references given in Wood and Ashwal 1981). Similar low ages were also found in two other types of rare meteorites, i.e. nakhlites (three meteorites), and in Chassigny. Geochemical studies (Dreibus et al. 1982; Burghelle et al. 1983) as well as oxygen isotope measurements (Clayton and Mayeda 1983) tell us that shergottites, nakhlites and chassignites (SNC-meteorites) come from one and the same parent body. Because of the low crystallization ages an object considerably larger than asteroids seems to be required and that it is why Mars was suggested as shergotty parent body (SPB), (see Wood and Ashwal 1981). Bogard and Johnson (1983) found in a shergottite a trapped rare gas component with element

and isotope ratios different to those observed in other meteorite classes but almost exactly matching the rare gases in the Mars' atmosphere. Finally, Becker and Pepin (unpublished presentation at the XIVth Lunar and Planetary Science Conference, Houston, 1983) found that the same shergottite (EETA 79001) contains trapped nitrogen with the very characteristic isotope ratio of the Mars' atmosphere. Summing up there seems to be no doubt that SNC-meteorites represent Mars rocks.

In the following we will show how rough but reliable estimates of the bulk composition of a differentiated object can be obtained by using the compositional data of basalts and other rocks from this object. We use the composition of the SNC-meteorites (Dreibus et al. 1982; Burghelle et al. 1983) to estimate the bulk composition of their parent body. We assume that Mg, Si and all oxyphile refractory elements are present in strictly C 1 abundance ratios in the mantle of the SPB. On Earth and Moon the deviations from the C 1 values are less than 30 %.

FeO and MnO: Under normal planetary conditions (ol + opx + cpx, being the major FeO and MnO bearing phases), the liquid-solid partition coefficients for FeO and MnO are only slightly above 1. The absolute concentrations of MnO in SNC-meteorites vary between 0.45 and 0.55%. As shown below, 0.45 % MnO correspond to a C 1 abundance in the SPB mantle. Hence like on the EPB, Mn is present in C 1 abundance in the SPB, too. The FeO/MnO ratio of all shergottites and Nakhla (nakhlites) is 39.1 ± 1.5 . Compared to the C 1 FeO/MnO ratio of 100.6, we find with a Mn abundance of 1.00 an abundance of 0.39 for FeO in the SPB mantle.

K, Rb and Cs: Like for the Moon, the EPB, and to a lesser extent also for the Earth (Wänke 1981), we find an excellent correlation of K vs. La in all SNC meteorites yielding a K/La ratio of 655 (Fig. 2), compared to the C 1 K/La ratio of 2110. Assuming a La abundance of 1.00, we find 0.31 to be the abundance of K. Shergottites have a K/Rb ratio of 282 ± 39 and a Rb/Cs ratio of 15.2 ± 0.8 compared with the C 1 values of this ratio (251, resp. 10.8) and the K abundance we find abundances for Rb = 0.28 and Cs = 0.20.

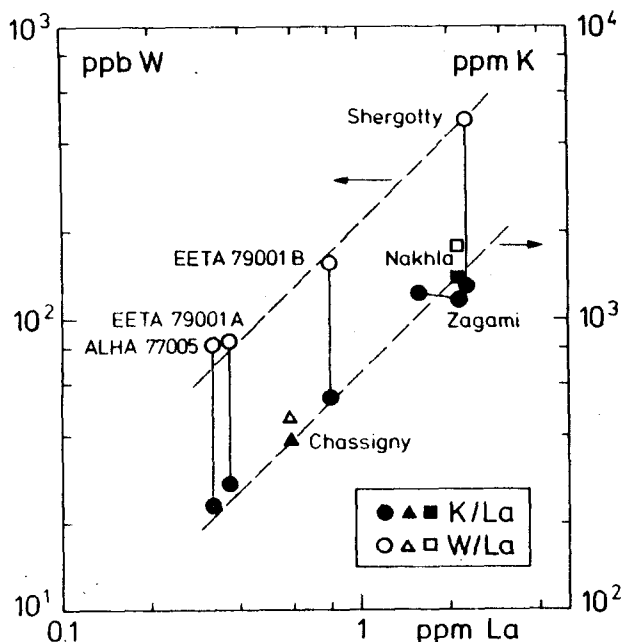


Fig. 2 Correlation of the moderately volatile element K and the moderately siderophile refractory element W with the refractory element La in all SNC meteorites.

W: An excellent correlation of La vs. W is observed in shergottites (Fig. 2). The W/La ratio yields a W abundance of 0.60, equal to 105 ppb.

P: For P the best correlation is found with the heavy rare earth elements yielding an abundance $P = 0.35$ (Weckwerth, 1983).

F: For F the best though weak correlation is found with Li, yielding a very rough estimate of the F abundance of 0.31, assuming a Li abundance of 1.00.

Na, Ga: The three elements Na, Ga, and Al correlate well with each other in all shergottites (Fig. 3). The mean ratio of the two moderately volatile elements Na/Ga of 525 comes very close to the C 1 ratio of 551. Again assum-