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**Introduction:** Estimates of $f_{O_2}$ for mare basalts and the lunar mantle have been made using a variety of approaches: intrinsic $f_{O_2}$, mineral assemblages, melt and mineral compositions and the oxidation state of multiple valence cations. Although each approach has its limitations, most indicate that mare basalts crystallized at $f_{O_2}$ between the iron-wüstite buffer (IW) and the ilmenite breakdown reaction [i.e. 1-4]. It has also been inferred from these estimates that the lunar mantle is also highly reduced lying at conditions below IW. Here, we illustrate some of the indicators of $f_{O_2}$ in lunar basalts and the implications for the lunar mantle.

**Mineral Assemblage:** To a first approximation, the presence of metallic iron or Ni,Fe alloys in mare basalts indicates that they crystallized at $f_{O_2}$ conditions below the iron-wüstite buffer. The metal-melt equilibrium and the Cr content of the olivine (+spinel) were interpreted as indicating a pre-eruptive $f_{O_2}$ of IW-1.3 for the lunar picritic glasses [4]. Some lunar basalts show textural and mineralogical evidence for further subsolidus reduction. Reported subsolidus reactions such as ulvöspinel $\rightarrow$ ilmenite + metallic iron and fayalite $\rightarrow$ cristobalite + metallic iron take place at a range of $f_{O_2}$ below both IW and FIQ buffers.

**Intrinsic $f_{O_2}$:** Intrinsic $f_{O_2}$ measurements and thermodynamic gas equilibria calculations show that the range of temperature and $f_{O_2}$ for mare basalt crystallization are relatively small, varying from $10^{-13}$ at 1200 C to $10^{-16}$ at 1000 C [1-4]. Relative to standard buffer curves, these values are approximately 0.2 to 1.0 log units below iron-wüstite (IW) and above the univariant curve that defines the stability of ilmenite.

**Mineral Compositions:** Mineralogical observations such as the total absence of ferric iron in both silicates and oxides and the presence of reduced valance states of Cr and Ti [5] are consistent with the above observations. The composition of spinels in basalts has been shown to partially reflect $f_{O_2}$ [5,6,7]. The spinel crystallization trajectories are consistent with conditions below IW. Differences in spinel compositions have not been related to differences in $f_{O_2}$ among lunar basalts.

**Basalt Compositions:** The FeO content of the lunar basalts has been interpreted [8] as indicating that the mare basalts were generated at $f_{O_2}$ of IW-1. The Cr content of liquids coexisting with spinel varies considerably with $f_{O_2}$, such that Cr is low (1000 ppm) at FMQ and high (>2700 ppm) at IW [9]. This is due to Cr$^{3+}$ being less soluble in spinel in the mantle at reducing conditions and therefore remaining in the melt. The Cr content of primitive lunar basalts (2700–6300 ppm) is significantly higher than similar terrestrial basalts (<1500 ppm). Therefore, if spinel was a residual phase in the lunar mantle and the Cr content was near chondritic, the high Cr content of the mare basalts suggests a reduced lunar mantle [9,10].

**Multiple Valence Cations:** Reduced valences of oxidized species pairs appear to be common in lunar basalts. For example, the existence of divalent Eu and Cr, trivalent V, and even trivalent Ti have been documented in mare basalts. The ratio of oxidized species to reduced species provides a potential quantitative tool for determining $f_{O_2}$. The ratio of $(\text{Eu}/\text{Gd})_{\text{plag}}/(\text{Eu}/\text{Gd})_{\text{px}}$ in mare basalts and highland plutonic rocks although somewhat different indicate $f_{O_2}$ at IW-1 or slightly more reducing. Vanadium valence for the lunar volcanic glasses ranges from 2.7 to 2.9. These values are substantially lower than measurements made on terrestrial basaltic glasses (3.7-4.2) [11]. Using the V valence in these basaltic glasses reflect a range of $f_{O_2}$ from IW-1 to IW-2.2 [11].

**Discussion:** Many oxybarometers have been used to estimate the $f_{O_2}$ of lunar basalts. Estimates for lunar basalts range from IW-0.4 to IW-2.2. Do these reducing conditions reflect reducing crust and mantle environments or reduction processes during magma transport and eruption? Proposed mechanisms for the eruption of the lunar picritic glasses require the reduction of the magma via the oxidation of graphite (i.e. $\text{Cr}_2\text{O}_3 + \text{C} \rightarrow 2\text{CrO} + \text{CO}$). Such a reaction is also suggested by metal droplets in some of the glasses. However, there does not appear to be a significant difference in reduced species/oxidized species in these glasses [11] nor do the proposed reactions result in a dramatic change in the $f_{O_2}$ of the basaltic melt. An interesting observation is the difference in mare basalts and parental basalts to the magnesian-suite that were emplaced in the lunar crust prior to mare magmatism. Preliminary results indicate that the magnesian-suite magmas had lower Cr, Ni, and Co and higher $(\text{Eu}/\text{Gd})_{\text{plag}}/(\text{Eu}/\text{Gd})_{\text{px}}$ than the mare basalts. Whether this is simply a product of different source regions or different $f_{O_2}$ needs to be investigated further.

**Introduction:** The study of evaporation and condensation processes of substance has attracted considerable interest for understanding of the problems relating to the chemical evolution of protoplanet substance in the process of successive condensation of incandescent gases at forming space objects as physicochemical systems. Recently we observed the linear dependence of logarithm of vapor total pressure over the CaO-MgO-Al2O3-SiO2 compounds vs. the molecular oxygen content in vapor (or the degree of its dissociation) [1]. It points to the fact that there is a relationship between the red-ox reactions in the gaseous substance and the condensation processes. In this connection it seems to be useful to consider the observed regularities on example of another oxide compounds.

**Calculations:** In the present study the composition and partial pressures of 305 vapor species along with the total pressures over 198 most investigated oxides and its compounds were calculated in terms of thermodynamic approach for the temperature range 1700-2200 K using the own experimental and reference data on the constants of gas-phase and heterogeneous equilibriums and the oxide activities in oxide compounds [2-7]. The choice of the study temperature range was caused by the condensation temperatures of most important compounds formed at cooling of substance in the solar nebula. The total vapor pressure over oxide compounds were calculated by summing over the proper partial pressures of the vapor species taken for the case of chemically neutral conditions.

**Results and Discussion:** Some obtained data are presented in Figures. As may be seen from Fig. one can subdivide oxides and its compounds into two main groups with respect to the dissociation degree of the molecular oxygen in vapor.

The first group (1-4) is characterized by the different content of molecular oxygen in vapor and the atomic-to-molecular oxygen ratio being the same as in the case of pure oxygen (6). A number oxide compounds (Al2O3, CaO, Fe2O3, MgO, SiO2, etc.) denoted (1) in Fig. possess the minimal total vapor pressure at maximal molecular oxygen content in vapor. The minimal molecular oxygen content in vapor have BeO, CeO2, HfO2, TbO2, ZrO2, etc. denoted (3) in Fig.

The significant dissociation of the molecular oxygen in vapor (x(O2) < 1 mole %) is typical for the second oxide group (B2O3, BaO, H2O, MoO3, NbO2, Nb2O5, P2O5, PbO2, Re2O6, RhO2, SO3, ThO2, Ti2O3, UO3, V2O5, WO3, etc.), which denoted (5) in the Fig.

The suggested oxide classification based on the molecular oxygen dissociation degree gives an opportunity to make some conclusions on the general features of the condensation processes and provides rather accurate estimations of the total vapor pressures over oxide compounds.


**Figures:** The total vapor pressure over oxide compounds vs. molecular oxygen content (a) and ratio of partial pressures of atomic and molecular oxygen (b) in vapor at 2000 K (see text for explanation).
**Oxygen Profile of a Thermo-haliophilic Community in the Badwater Salt Flat.**

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Badwater is the lowest, saltiest, and hottest, place in North America. This extreme environment is 86 meters (282 feet) below sea level surrounded by four mountain ranges. Due to the geographical location Badwater does not receive moisture from the prevailing winds, this intern results in a hot, arid, and salty environment. Despite these extreme living conditions, microbes manage to flourish within the salt flat. The salt acts as an insulator making life just beneath the surface more comfortable. In this paper, we compare the microbial population versus oxygen concentration; and the importance of and the role of oxygen in metabolic functions by these thermo-haliophiles. Furthermore a model of the oxygen profile will also provide an insight to the oxygen cycle in salty environments. This research has implications for the limits of life on Earth and Mars. Recent results from the MER rovers show that water on Mars was very salty. Measuring the oxygen profile in these salty environments on Earth provides a framework within which potential life on Mars can be evaluated. The use of an oxygen profile could also be used as a search criteria for life.
OXYGEN BAROMETRY USING SYNCHROTRON MICROXANES OF VANADIUM. S.R. Sutton1,2 (sutton@cars.uchicago.edu), J.M. Karner1, J.J. Papile2, J. S. Delaney3, C.K. Shearer1, M. Newville4, P. Eng3, M. Rivers5, and M. D. Dyar3 1Department of Geophysical Sciences and 2Consortium for Advanced Radiation Sources, University of Chicago, Chicago, IL 60637; 3Institute of Meteoritics, Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131-1126; 4Geology Department, Rutgers University, New Brunswick, NJ 08903; 5Department of Earth and Environment, Mount Holyoke College, South Hadley, MA.

A promising proxy for oxygen fugacity is the valence of vanadium because it has a large number of possible valence states in nature (2+, 3+, 4+ and 5+) and is ubiquitous in earth and planetary materials. A new, non-destructive method for valence determinations of vanadium and oxygen fugacity estimates with spatial resolution of a few micrometers is synchrotron x-ray absorption near edge structure (XANES) spectroscopy [1-3].

In XANES spectroscopy, the x-ray absorption edge of the element of interest is mapped with high energy resolution. Typically, the XANES spectrum is obtained by measuring the intensity of a characteristic fluorescence line (in this case, V Kα) as the incident x-ray energy is scanned over the appropriate absorption edge. The valence determination uses a pre-edge peak intensity versus oxygen fugacity for a few micrometers is synchrotron x-ray absorption near edge structure (XANES) spectroscopy [1-3].

Vanadium K XANES spectra were measured using the undulator-based microprobe at Sector 13 (GeoSoilEnviroCARS) at the Advanced Photon Source, Argonne National Laboratory [5].

Five suites of experimental glasses of basaltic or komatiitic composition with ~1% V2O3 dopant were studied for valence and oxygen fugacity standardization purposes: Schreiber suite (H. Schreiber, Virginia Military Inst): FAD and FAS composition [6] 1500 °C at log fO2 from 0 to ~-9. V valences (V5+ to V3+) were previously obtained independently by optical spectrometry. Hanson suite (B. Hanson, Corning Glass; J. Jones, NASA-JSC): FAD composition [7], 1310 or 1320 °C at fO2 from air to the Cr-CrO buffer. Canil suite (D. Canil, University of Victoria, Canada): Komatiitic composition [8]; 1225 to 1425 °C at log fO2 from ~-5.5 to ~-10.7. Beckett suite (J. Beckett, Cal. Inst. Tech.): CMAS composition; an isobaric experiment (logO2 = -8), 1274 to 1425 °C. Karner suite (J. Karner, U. New Mexico): Lunar green and orange glass composition; logO2 = 1W +1 to -2, 1430 °C.

A plot of vanadium pre-edge peak intensity versus known valence state for the Schreiber glasses shows a well-defined trend. Using this calibration curve, the effective valences of other glasses can be determined. The Beckett suite and several of the Hanson samples represent isobaric couples that were used to determine the magnitude of valence variations due to temperature differences. The fractional intensity change per degree was found to be -0.0027 ± 0.0002.

In this way, a calibration curve for peak intensity vs. oxygen fugacity can be produced for liquidus temperature of each unknown. Increased basicity of the melt leads to increased valence of a redox couple [6] and work is in progress to quantify this effect on vanadium valence. A “calibration curve” for low Ti standard glasses at 1400 °C is shown in Figure 1.

Because site geometry can also affect pre-edge peak intensity, we make the implicit assumption that changes in coordination in basaltic glasses occur in unknowns in an analogous way to those in the standards. MicroEXAFS data for both natural and synthetic glasses support this assumption and can be satisfactorily interpreted within a coordination sequence involving octahedral coordination of V for valences between V3+ and V4+ with smaller coordination numbers becoming dominant for oxidized samples between V5+ and V6+.

The vanadium redox system is a robust oxybarometer. Further work is in progress to improve our understanding of the effects of melt composition and temperature.


Figure 1: Pre-edge peak intensity versus oxygen fugacity for standard glasses after temperature correction to 1400 °C.
MASS-INDEPENDENT ISOTOPIC FRACTIONATION OF SULFUR FROM SULFIDES IN THE HURONIAN SUPergroup, CANADA. S. Tachibana1, T. Hirai1, K. Goto1, S. Yamamoto1, J. L. Kirschvink2, R. E. Kopp2, N. Ohkouchi3, Y. Isozaki4, R. Tada4, E. Tajika4, N. T. Kita5 and Y. Morishita6, 1Dept. of Earth and Planet. Sci. (Bldg. 1), Univ. of Tokyo, 7-3-1 Hongo, Tokyo, 113-0033, Japan (tachi@eps.s.u-tokyo.ac.jp), 2Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, CA 91125, USA, 3 Institute for Frontier Research on Earth Evolution, 2-15, Natsushima, Yokosuka 237-0061, Japan, 4Dept. of Earth Science and Astronomy, Univ. of Tokyo, 3-8-1 Komaba, Meguro, Tokyo 153-8902, Japan, 5 Geological Survey of Japan, AIST Tsukuba Central 7, Tsukuba 305-8567, Japan.

Mass-independent isotopic fractionation (MIF) in sulfur isotopes from sedimentary rocks older than 2.47 Gy has been attributed to the low oxygen content of the atmosphere [e.g., 1-3]. The recent finding of near-zero MIF of sulfur in pyrites from ~2.32 Ga shales of the Rooihoogte and Timeball Hill formations, South Africa, suggests that atmospheric oxygen may have reached ~10^3 PAL by 2.32 Ga [4].

The Huronian Supergroup of Canada was deposited between 2.45-2.22 Ga, possibly overlapping with deposition of the Rooihoogte and Timeball Hill Formations, and preserves a record of three glaciations. Small MIF of sulfur (43S < 0.5‰) has been reported for sulfides from the Huronian Supergroup (McKim, Ramsay Lake, and Pecors Formations) [5]. We have started in-situ analyses of the sulfur isotopic compositions of sulfides for formations overlying those reported by [5], including the second and third glacial diamictites (Bruce and Gowganda Formations), using the Cameca ims-1270 ion microprobe at the Geological Society of Japan. Some sulfides are rounded, and some are aligned parallel to lamination, which implies that they are of detrital origin.

Our preliminary analyses show that sulfides from Pecors, Missisagi, Bruce, Espanola, Gowganda, and Gordon Lake Formations appear to have Δ34S ≲0.3‰, consistent with [5]. Except in the youngest formation, the Gordon Lake Formation, Δ34S is less than +4‰. The low Δ34S (<0.3‰) implies that either oxygen levels had increased by Huronian time, or that the Huronian was characterized by enhanced, glacially-driven mixing of S reservoirs. The relatively low Δ34S of formations underlying Gordon Lake Formation may indicate a sulfate content of <200μM during deposition of those formations [6], while the increase in Δ34S in the Gordon Lake Formation is consistent with other indicators of increased sulfate, including pseudomorphs after gypsum.

**Introduction:**

With the discovery of the mass independent isotopic fractionation process by Thiemens and Heidenreich in 1983, a new technique to understand various natural processes became available. Since that time, a quantum mechanical basis for understanding this effect became available. This has strengthened the ability to understand how this unique fractionation process may occur in nature. It has now been demonstrated that for example, in the Earth’s atmosphere, every oxygen bearing molecule, with the exception of water, is mass independently fractionated. The molecules include: CO, CO₂, O₂, O₃, H₂O₂, N₂O and solid aerosol nitrate and sulfate.

From ice core studies, the evolution of the oxidative capacity of the Earth has now been tracked and quantified on a > 100,000 year time scale. The analysis of sulfate and nitrates has provided a unique way to understand and quantify the alterations in the oxidative capacity of the earth. In addition, the measurements have lead to a highly specific quantification of oxidative processes and their chemical reaction mechanisms, e.g. relative roles of homogenous and heterogenous oxidation.

From oxygen isotopic analysis of secondary minerals from SNC meteorites, the interaction between the atmosphere and regolith has been resolved at a much higher degree of specificity. This work has shown that the record of the planetary processes may be captured in the isotopic record and maintained on billion year time scales.

In sum, the use of mass independent isotopic measurements has provided new details regarding a wide range of natural processes in the atmosphere, hydrosphere, and geosphere. In the future, such measurements will amplify understanding of planetary bodies, their interactions and evolution. Future return sample missions will additionally benefit from these measurements.
ELECTRICAL CONDUCTIVITY, OXYGEN FUGACITY, AND MANTLE MATERIALS. James A. Tyburczy, Department of Geological Sciences, Arizona State University, Box 871404, Tempe, AZ 85287-1404, jim.tyburczy@asu.edu.

Introduction: Knowledge of electrical properties of Earth materials under conditions of the Earth’s interior can contribute to our understanding of the temperature profile of the interior, the phases present at depth, and, potentially, the chemical environment and oxygen fugacity of the interior. Electrical properties of rocks are generally strongly dependent on temperature, on oxygen fugacity, and on the presence (or absence) of highly conducting mineral phases, fluids or melts, or pathways [1-5]. Laboratory determinations of mineral conductivities have advanced sufficiently that it is now possible to compare conductivity models that include temperature and composition constraints with observed mantle conductivity profiles.

The point defect chemistry governing conductivity at low pressures in olivine is well constrained [6,7], with conductivity governed by ferric iron on a magnesium site (the ‘small polaron’). Lateral conductivity variations at 200 km depth between continental shields and oceanic regions are about 1.5 log units. If the sole cause of this variation is oxygen fugacity, this implies a difference of 4-8 log units in oxygen fugacity between these regions. At 400 km depth, the difference of about 0.5 log units would be caused by a difference in oxygen fugacity difference of 2-3 log units, assuming small polaron hopping in olivine is the dominant conduction mechanism.

High pressure measurements been made on olivine, wadsleyite, ringwoodite, perovskite, and magesiowustite under sufficiently controlled conditions to permit modeling of the transition zone and lower mantle [8-10]. Conductivity at depth is consistent with the sharp seismic boundaries corresponding to the olivine to wadsleyite to ringwoodite to perovskite transitions. Anhydrous wadsleyite and ringwoodite exhibit conductivities as much as two orders of magnitude greater than olivine of the same composition. With these results, it is possible to model mantle conductivities with models incorporating composition and temperature variations [9]. Detailed point defect models for these phases are not yet available; they are important for complete understanding of the process and extrapolation to conditions not easily studied in the lab, such as oxygen fugacity variations at very high pressures.

Hydrogen diffusion studies [11] suggest that olivine conductivity will be greatly enhanced by the presence of plausible mantle levels of hydrogen [12], and that the lattice preferred orientation dependence of hydrogen-enhanced conductivity will be much greater than that of dry olivine [13]. Preliminary data indicate an increase in conductivity of wadsleyite with the addition of water, but the increase is smaller than predicted for olivine [14]. Details of the point defect chemistry of hydrogen in nominally anhydrous transition zone minerals remain to be resolved. The inferred conductivities of hydrogen-bearing olivine lead to interpretation of oceanic conductivity profiles as indicating the presence of H-rich sublithospheric mantle [4] and the interpretation of continental conductivity profiles as indicating that sub cratonic mantle is unusually dry [15].

For perovskite, lab high P conductivity measurements are consistent with inferred lower mantle conductivities [16]. Conductivity appears to be dominated by ionic conduction (oxygen vacancies) [16]. Al$^{3+}$ in perovskite stabilizes Fe$^{3+}$ in the structure [17]. This may reduce the effect of oxygen fugacity on the conductivity in the lower mantle.

Conclusion: Significant progress has been made in determination of conductivities of mantle minerals at mantle pressure and temperature conditions with control of environmental conditions. Petrologic models of mantle conductivity can be made for comparison with observed conductivity profiles. Quantitative point defect models of high pressure phases and direct measurement of the influence of oxygen fugacity and hydrogen content on conductivity of nominally anhydrous minerals are needed for the proper interpretation of Earth electrical conductivity profiles in terms of the temperature and physical state of the mantle.

CRUSTAL EVOLUTION AND MATURATION ON EARTH: OXYGEN ISOTOPE EVIDENCE
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Zircon is a common accessory mineral in intermediate to felsic igneous rocks and also occurs in some mafic rocks. Zircons provide the most reliable record of magmatic oxygen isotope ratio as well as U-Pb age if significant radiation damage is avoided. No other mineral permits 18O(magma) to be confidently determined and coupled to age of crystallization (1). Zoned magmatic zircons serve as time capsules, preserving isotopic, trace element and mineral/melt inclusion evidence of evolving magmatic conditions.

Igneous zircons of known age (3.6 Ga to 0.2 Ma) from Earth have been analyzed for 18O by laser fluorination at the University of Wisconsin from over 1100 rocks worldwide. In addition to laser analyses of zircon concentrates (1-3 mg), single detrital zircons (4.4 to 3.0 Ga) from the Jack Hills, Western Australia were analyzed in situ (30 micron spot, ~2 ng) by ion microprobe (2).

The range and variability of 18O in all Archean samples is subdued (18O(Zrc)=5 to 7.5‰). Most samples have 18O= 5-6.5‰, consistent with high temperature equilibrium with mantle values (Zc=5.3±0.3‰) or mildly evolved composition. No magmatic zircons have been analyzed from the Archean with "S-type" values (18O above 8‰). This includes samples from Superior Province (3.0 - 2.7 Ga), Lewisian (2.7 Ga), Slave Province (2.7 Ga), and Barberton (3.5 to 2.7 Ga). Zircons analyzed by ion microprobe from the Jack Hills are indistinguishable in 18O from other Archean samples. The highest values (7.4‰) are interpreted to result from exchange of pre-magmatic protolith with surface water, even in the Early Archean zircons (4.4-4.0 Ga) (3).

Values of 18O(Zc) from the Proterozoic and Phanerozoic are significantly more variable. Many zircons are above 8‰ showing that magmas with 18O(WR) > 9-10‰ became common only after ~1.5 Ga. The increased variability of the oxygen isotope ratios of intermediate to felsic magmas occurs in the Middle Proterozoic. Since fractionation of oxygen isotopes to values higher than the mantle requires low temperatures where fractionation is large, the greater variability in 18O must reflect recycling of supracrustal lithologies and progressive maturation of the crust. The dominant sources of high- 18O are sediments, and rocks weathered or altered by surface waters at low temperatures. Clearly such protoliths have increasingly been involved in genesis of younger magmas on Earth.

The variability of 18O in terrestrial magmas should not be seen on planets lacking a liquid water hydrosphere or processes of magmatic recycling of surface rocks.


Figure 1. Compilation of 18O(Zrc) vs. age for zircons from over 1100 rocks with published age. Oxygen isotope ratios were analyzed by laser fluorination at the University of Wisconsin (most samples) or in situ by ion microprobe at the University of Edinburgh (Jack Hills zircons). Samples range in age from 4400 to 0.2 Ma and come from many terranes on seven continents. A remarkable uniformity is seen in the Archean, values cluster near the mantle (18O(Zc) = 5.3 ±0.3‰) with some values as high as 7.5 due to recycling of supracrustal material. High 18O, above 8‰ becomes common after 1.5 Ga, reflecting recycling of high 18O sediment and maturation of the crust. (Valley, Lackey, Basei, Bindeman, Clechenko, Ferreira, King, Peck, Sial, Sinha, and Spicuzza, unpd)
THE OXYGEN ISOTOPE COMPOSITION OF THE MOON: IMPLICATIONS FOR PLANET FORMATION. U. Wiechert1, 1Institute for Isotope Geology and Mineral Resources, ETH-Zentrum NO, 8092 Zürich, Switzerland. E-mail address: wiechert@erdw.ethz.ch

Introduction: The Moon is widely considered to have formed during a collision between the proto-Earth and a Mars-sized planet (named Theia). Assuming this model to be correct the Moon was formed from materials from the proto-Earth, Theia and any additional material added later. Oxygen isotope variations in differentiated planetary bodies like the Earth, Mars or the HED parent body are largely mass-dependent, i.e. the data define a characteristic line with a slope of ~0.52 in a graph of $^{17}$O vs. $^{18}$O. In general, different parent bodies define distinct parallel trends reflecting different bulk compositions for the parent bodies. The differences are usually expressed as $\delta^{17}$O, which is the deviation from the mass-dependent fractionation trend defined by terrestrial samples in per mil $^{17}$O. The first oxygen isotope data for lunar samples published by Clayton and Mayeda [1] fell along a linear array overlapping with the terrestrial samples. However, these early oxygen isotope data for the Moon have a large range of ~0.3‰ which may reflect some isotopic heterogeneity of the Moon. Therefore, lunar samples have been re-investigated with a high precision CO2 laser fluorination method [2].

Results: With this method the oxygen isotopic composition of 31 lunar samples averaged $^{17}$O=0±0.005‰ (3 sigma standard error of the mean). Even at this very high precision no resolvable difference between the Earth and Moon is detectable despite the fact that oxygen isotopes are very heterogeneous in the solar system. The simplest explanation for an identical oxygen isotope composition would be that the proportions of material from the impactor and the proto-Earth were identical in the Earth and Moon. Most giant impact simulations indicate that the majority of the material that formed the Moon originated from Theia rather than the proto-Earth. Given that the most of the Earth was already built by the time of the Giant Impact the proportions cannot be the same. The only explanation that is consistent with Giant Impact simulations is that Theia and the proto-Earth had identical or very similar oxygen isotope compositions.

Discussion: If Theia and the Earth formed from raw materials that were identical in oxygen isotopes, why then are they so different in terms of their chemical composition? For example the Moon and Earth have very different depletion in volatiles and the lunar mantle has a high FeO content. Some of this could result from the giant impact or differentiation of the proto-Earth, Theia, the Moon, or the present Earth. Comparing the Moon with other planetary bodies such as Mars or the HED parent body indicates that the Fe content of the lunar mantle is “normal” and the Fe content of the terrestrial mantle is unusually low. Therefore, the difference might be completely related to more protracted and extensive terrestrial core formation, but this is far from settled.

Another striking difference between the Earth and Moon is the strong depletion of the Moon in volatile elements compared with the Earth. Potassium isotopes have been used to argue that the depletion of alkalis and other volatiles in the inner solar system must have occurred during the condensation of precursor dust from a hot stage of the solar nebula [3]. This seems to favor an origin of Theia from material with a higher degree of depletion in volatiles. However, recently it has been argued that the Moon lost volatiles during its accretion [4]. The latter is supported by the timing of the moderate volatile element loss for the Moon >10 Myrs after cooling of the solar nebula [5]. This is inconsistent with models that assume a very early volatile loss. In fact, it supports the view that more moderately volatile elements have been lost during accretion. Therefore, the oxygen isotope composition of the Moon provide evidence that objects as different as the Moon and Earth have been made out of an identical mix of material. The mechanism of volatile element loss without corresponding mass-dependent fractionation is the subject of ongoing research.

OXYGEN ISOTOPE COMPOSITION OF EUCRITES AND IMPLICATIONS FOR THE FORMATION OF CRUST ON THE HED PARENT BODY. U. Wiechert\(^1\), A. N. Halliday\(^1\), H. Palme\(^2\) and D. Rumble\(^3\),
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**Introduction:** Oxygen isotopes are a powerful tool for assessing the provenance of early solar system material [1]. This approach can be used to assess the number of parent bodies of differentiated silicate meteorites, or achondrites. The largest group among these meteorites are howardites, eucrites and diogenites, often referred to as HED meteorites. To evaluate whether all HEDs formed on a single or several parent bodies we have determined precise abundances of \(^{16}\)O, \(^{17}\)O and \(^{18}\)O for 34 HED meteorites using a CO\(_2\) laser fluorination technique. This also allows us to evaluate whether eucrites formed by melting poorly mixed primitive material [2] or a homogeneous reservoir such as might be produced in a magma ocean [3].

**Results:** The \(^{17}\)O' values of 6 howardites, 24 eucrites, and 4 diogenites range from -0.245 to -0.057‰. HEDs, excluding Ibitira, fall along a mass-dependent fractionation line that lies at -0.219 ±0.002‰ (2 standard error mean) relative to the terrestrial fractionation line (TFL) whereas Ibitira falls 0.064‰ below the terrestrial fractionation line. Also individual analyses of Caldera, Pasamonte, and ALHA78132 are different, with 95% confidence, from the HED average.

**Discussion:** The oxygen isotope data provide evidence that most meteorites are derived from a common, well-mixed pool. The eucrites (without Ibitira, Pasamonte, Caldera, and ALHA78132) and diogenites average \(^{17}\)O' = -0.219 ±0.004‰ and \(^{17}\)O' = -0.224 ±0.006‰ (2 mean error) respectively and are indistinguishable from each other. Therefore, there is no evidence that eucrites and diogenites are from systematically distinct parent bodies or reservoirs. However, whether this “oxygen pool” that is sampled by most of the HED meteorites is representative of an entire parent body is now unclear because there are resolvable differences for the basaltic eucrites Ibitira, Pasamonte, ALHA78132, and Caldera. If one considers the \(^{17}\)O to be a parent body “fingerprint” [1] these meteorites could come from an asteroid that is distinct from the main group parent body. One would then expect differences in chemical compositions and these should be largest between the most distinct eucrite, Ibitira, and the main group eucrites, but this is not observed.

A second possibility is that the HED parent body is heterogeneous in oxygen isotopes. In this case oxygen isotopes allow us to draw some conclusions on the petrogenesis of eucrites.

Stolper [2] presented a model for eucrite petrogenesis in which basaltic eucrites represent primary partial melts of an undifferentiated parent body. In this model the parent body underwent minimal heating and only localized melting occurred. If the HED parent body was never homogenized completely then some primary oxygen isotope heterogeneity should be found among eucrites, which is inconsistent with the oxygen isotopes for most eucrites presented in this study. Others have proposed that the HED mantle underwent a global magma ocean stage [3]. Such a magma ocean would help explain why extremely early basaltic eucrites are derived from a parent body that appears to have been completely homogeneous in terms of oxygen isotopes within a few million years of the start of the solar system. However, such a model is in conflict with the oxygen isotope composition of Ibitira, Caldera, Pasamonte, and ALHA78132.

Gosh and McSween [5] suggested a model for the evolution of Vesta which assumes partial melting of the silicate mantle and low temperatures for near-surface layers. The thickness of an outer unaltered layer decreases with increasing degree of melting and, for 25% melting, the outer 10 km of the asteroid never reached melting temperatures. Such outer layers could have retained some isotopic heterogeneity. In contrast to the global magma ocean scenario [3] this model predicts mixing and perfect homogenisation of the interior but also allows for some oxygen isotope heterogeneity in an outer layer of the HED parent body. In this model crust formed by extrusion of basaltic melts at the surface. Therefore, it also explains why no anorthositic crust has been found on Vesta, which may be a much better model for the formation of early crust on Earth than the Moon.

THE ROLE OF WATER IN DETERMINING THE OXYGEN ISOTOPIC COMPOSITION OF PLANETS.
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Introduction: It is becoming increasingly likely that reactions between water and rock (and rock melts) were the primary by which planetesimals, and eventually terrestrial planets, obtained their oxygen isotopic signatures. Two processes were responsible. One is photochemistry in the early solar nebula [1, 2]. The other is reactions between liquid water ice melt and rocks within protoasteroid environments [3, 4].

Photochemistry: Self shielding of CO to produce oxygen depleted in 16O [5] is sure to have occurred at some level in the diffuse regions of the early solar nebula. Calculations show that attenuation of a stellar flux of UV photons illuminating the disk surface is small enough that many Earth masses of oxygen with large depletions in 16O relative to the starting materials would have been produced above and below the midplane of the early solar nebula over time scales > 10^3 yrs. The most likely sink for the 16O and 18O-rich oxygen liberated by photolysis of CO (Q*) would have been adsorption onto solid dust grains followed by surface reactions to produce water. Settling of these dust grains and radial transport toward the accreting star brings this source of 16O-depleted oxygen into the nascent inner solar system where it can react with gases, minerals, and liquids that form planet precursors.

Many observations are consistent with photodissociation of CO in the diffuse regions of the solar nebula as an explanation for the slope-1 line in oxygen isotope δ-δ space. It accounts for the fact that H2O was almost certainly depleted in 16O (enriched in H2Q*) relative to silicates and other metal oxides in the solar system. Reactions between H2Q* and CO in the inner solar nebula (at higher T) would not affect the slope-1 relationship in three isotope space because the mass-dependent fractionation between H2O and CO is small at all relevant temperatures. Production in the outer solar nebula also provides a natural explanation for the correlation between 16O and refractory nature of solids.

Asteroid hydrology: Much of the 16O-poor oxygen isotopic signal incurred by photochemistry may have been imparted to protoplanetary material and water that was 16O-poor relative to the bulk of solar system material. This history began photochemistry prior to the formation of rocky bodies and continued through the geological evolution of planetesimals.

Conclusions: The oxygen isotopic composition of solar system bodies records of a long history of reactions between protoplanetary material and water that was 16O-poor relative to the bulk of solar system material. This history began photochemistry prior to the formation of rocky bodies and continued through the geological evolution of planetesimals.