

**EARLY OUTGASSING OF THE EARTH AND MARS: INFERENCES FROM THE GEOCHEMICAL BEHAVIOR OF IODINE AND XENON;** Donald S. Musselwhite, Michael J. Drake and Timothy D. Swindle, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721

**Introduction**  $^{129}\text{Xe}$  is enriched in Mid-Ocean Ridge Basalts (MORBs) and, hence, the MORB mantle source compared with the atmosphere and Ocean Island Basalts (OIBs). Allegre *et al.* [1,2] proposed a catastrophic degassing scheme to explain this excess. In this scheme, the upper mantle, the proposed source for MORBs, degassed early in Earth history, thereby enhancing its I/Xe ratio. The lower mantle, the proposed source for OIBs, remained undegassed and therefore had a low I/Xe ratio when  $^{129}\text{I}$  was extant. Consequently, subsequent decay of  $^{129}\text{I}$  had little effect on the Xe isotope ratios. This lower-mantle reservoir is the source for OIBs with atmospheric Xe composition. This model is consistent with Sm/Nd and Rb/Sr isotopic studies of [3,4] which indicate that the source for MORBs is separate from the source for OIBs and that these sources have been largely separate for most of Earth history. Ozima *et al.* [5] proposed that heterogeneous accretion was responsible for the excess  $^{129}\text{I}$  in MORBs. In this scheme, the MORB source formed from material which was volatile poor but contained extant  $^{129}\text{I}$  and the atmosphere formed later from volatile rich material.

Experiments investigating the partitioning of noble gases in anorthite-melt, forsterite-melt, spinel-melt and diopside-melt systems [6,7] reveal that the noble gases do not have identical behavior during igneous melting. The lightest noble gases are incompatible in mantle minerals with mineral/melt partition coefficients increasing with increasing atomic number and Xe being relatively compatible. This observation raises questions concerning whether early catastrophic outgassing can enhance the I/Xe ratio of the upper mantle.

**Iodine Mineral/Melt Partitioning Experiments** One poorly constrained factor in previous discussions of this problem has been the partitioning behavior of I relative to Xe in mantle melting events. We have carried out I mineral/melt partitioning experiments at 1 atm in a muffle furnace [8] and 15 kbar in a piston cylinder in the system di-an-fo [9]. The 15 kbar data have not been previously published. Starting materials were mixtures of pure oxide powders with 2 wt. % I added as KI. Oxide mixtures were sealed in Pt capsules. In the 1 atm experiments the temperature was raised above the liquidus and held there for one half to one hour, then brought down to liquidus temperature (1300°C) and held for 3 to 5 days. The charges were then quenched in air. In the 15 kbar experiments, the assembly was brought up to pressure quickly, then up to run temperature (1475°C) in 2 hours, held there for 8 to 24 hours, quenched by cutting the power (< 10 sec) and brought down to atmospheric pressure. Charges were analyzed by electron probe and, in some cases, by PIXE. Partition coefficients were determined by direct peak height comparisons of mineral and glass.

**Mineral/Melt Partitioning Data for I and Xe** Values for mineral/melt partition coefficients for I,  $D(\text{I})$ , from these experiments are shown in Table 1 along with the lowest values of  $D(\text{Xe})$  from [6,7]. Errors indicated for values of  $D(\text{I})$  are two sigma based on the counting statistics. Upper limits are 3 sigma. Comparison of values of  $D(\text{I})$  with  $D(\text{Xe})$  for any given mineral/melt pair indicates that I will be less compatible than Xe in a mantle melting event. These data show that I will be essentially quantitatively removed from the solid phase into the liquid phase during a mantle melting event. It follows that the I/Xe ratio of the mantle cannot be significantly increased as a result of partial melting, thus presenting a problem for the catastrophic degassing hypothesis of [1,2].

**Outgassing of Earth and Mars** An alternative method of fractionating I from Xe is required. We note that I is highly soluble and Xe highly insoluble in water. We present a model for separating I and Xe during early degassing which makes use of this extreme difference in their solubilities in water (figure 1).

**Early Outgassing of the Earth** (1) Condensation and accretion commence at 4.55 Ga and proceed to 4.45 Ga. At the start of solar system formation,  $^{129}\text{I}/^{127}\text{I} = 10^{-4}$  [10]. During the process of accretion, we assume that the Earth has a steam atmosphere [11]. (2) No earlier than 4.45 Ga, conservatively, accretion ceases, the steam atmosphere condenses, and liquid water becomes stable at the Earth's surface.  $^{129}\text{I}/^{127}\text{I} = 10^{-6}$  at this time. (3) Outgassing of the MORB source occurs at this point. Since both I and Xe have low solubilities in silicate melts ( $\approx 10^{-4} - 10^{-5}$  ccSTP/g-atm), both will be substantially outgassed. (4) Iodine, being highly soluble in water ( $S_{\text{I,aq}} \geq 27$  g/l), goes into solution. Because of its short residence time ( $\approx 10^6$  years for present ocean), I is rapidly incorporated into sediments or hydrothermally altered crust. Xenon, with an extremely low water solubility ( $S_{\text{Xe,aq}} \leq 5 \times 10^{-10}$  g/l), is partitioned into the atmosphere. (5)  $^{129}\text{I}$  now residing in the crust decays to  $^{129}\text{Xe}$  and is subsequently reincorporated into the now volatile depleted MORB source by crustal recycling. This model explains the high  $^{129}\text{Xe}/^{132}\text{Xe}$  of 1.00 - 1.14 in MORBs, the low total noble gas concentrations in MORBs, and the similar  $^{129}\text{Xe}/^{132}\text{Xe}$  for the Earth's atmosphere (0.985) and OIBs (0.988).

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**Early Outgassing of Mars** Mars's atmosphere has an extremely high  $^{129}\text{Xe}/^{132}\text{Xe}$  of 2.5 [12]. Assuming the SNC meteorites are from Mars, there is a reservoir within Mars's mantle that has a  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio of 1.0 to 1.5 [13]. Thus, the situation on Mars is the reverse of that on the Earth in that Mars's atmosphere has the more radiogenic  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio. (1 - 4) The early evolution of Mars (figure 2) is the same as for the Earth with condensation and accretion occurring between 4.55 Ga and 4.45 Ga and liquid water becoming stable at the surface by the end of accretion. Iodine and Xe are outgassed at this time, with I going into solution and becoming incorporated into the crust while Xe is partitioned into the atmosphere. (5) At this point the evolution of Mars diverges from the Earth owing to the difference in size between the two planets. Calculations show that atmospheric blow off from heavy bombardment is significant for Mars but not for the Earth [14]. Impact erosion will diminish the martian atmosphere to nearly its present level by 4.0 Ga ago. Since the atmosphere is not heated by this process, water not directly involved in impacts will remain standing. (6) As with the Earth,  $^{129}\text{I}$  in the crust will decay to  $^{129}\text{Xe}$  but, unlike in the Earth, it is not recycled as evidenced by the lack of plate tectonics and vast expanses of ancient terrain on the martian surface. (7)  $^{129}\text{Xe}$  incorporated in the crust is then released over geologic time into the now diminished atmosphere, thereby enhancing the  $^{129}\text{Xe}/^{132}\text{Xe}$  of the atmosphere. Such outgassing is consistent with  $^{40}\text{Ar}$  enrichment in the martian atmosphere which results from release of  $^{40}\text{Ar}$  produced by slow decay of  $^{40}\text{K}$  over geologic time.

**Discussion** The timing of the events described above is crucial given the short half-life of  $^{129}\text{I}$ . For a given  $^{129}\text{Xe}/^{132}\text{Xe}$  (and hence  $^{129}\text{I}/^{132}\text{Xe}$ ) ratio, the elemental I/Xe ratio required is given by:  $[I/Xe]_{\text{required}} = \{^{129}\text{I}/^{132}\text{Xe}\} \times \{^{132}\text{Xe}/\text{Xe}_{\text{total}}\} + \{^{129}\text{I}/\text{I}_{\text{total}}\}$ . Thus, the I/Xe ratio at 4.45 Ga necessary to account for the observed  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio for the MORBs is  $6.2 \times 10^3$  (0.72 x CI). This ratio is approximately the same as the estimate of  $3.6 \times 10^3$  (0.42 x CI) for the I/Xe ratio for the Earth [12]. Thus the ratio of the the amount of I incorporated into the ocean crust to the amount of Xe remaining in the MORB source need only be approximately equal to the ratio for the bulk Earth, thereby leaving plenty of room for loss of I or  $^{129}\text{Xe}$  prior to and during reincorporation of the protocrust into the MORB source mantle. If early outgassing occurs much later than 4.40 Ga, however, the resulting lower  $^{129}\text{I}$  abundance requires an excessive I/Xe ratio. By 4.40 Ga, the  $^{129}\text{I}/\text{I}_{\text{total}}$  ratio is  $1.5 \times 10^{-7}$ , and requires an I/Xe ratio for the MORB source of  $5.3 \times 10^4$  or about ten times the estimate for the bulk Earth [11]. To account for the  $^{129}\text{Xe}/^{132}\text{Xe}$  ratio of the martian atmosphere with outgassing occurring by 4.45 Ga requires an I/Xe ratio of  $3.1 \times 10^5$  or assuming that 99% of the atmosphere was removed,  $8.9 \times 10^3$  (=CI).

**Table 1: Mineral/Melt Partition Coefficients**

	Iodine		Xenon <sup>[6,7]*</sup>
	1 Atm 1300°C	15 Kb 1475°C	1 Atm 1300°C
Forsterite	≤0.04	—	0.14
Enstatite	—	0.016 ± 0.009	—
Diopside	≤0.003	≤0.02	0.5
Anorthite	≤0.02	—	0.27

\* Lowest determined values

**References** [1] Allegre *et al.* (1983) *Nature*, 303, 762-766 [2] Allegre *et al.* (1988) *EPSL* 81,127-150 [3] DePaolo and Wasserburg (1979) *Proc NAS USA* 76, 3594-3598 [4] DePaolo (1980) *GCA* 44, 1185-1196 [5] Ozima *et al.* (1983) *Nature* 315, 471-474 [6] Broadhurst *et al.* (1988) *LPSC XIX*, 138-139 [7] Hiyagon and Ozima (1986) *GCA* 50, 2045-2057 [8] Musselwhite *et al.* (1989) *LPSC XX*, 748-749 [9] Presnall *et al.* (1978) *Cont. Min. Pet.* 60, 203-220 [10] Swindle *et al.* (1986) in *Origin of the Moon* 331-357 [11] Abe and Matsui (1986) *Nature* 322, 526-528 [12] Anders and Owen (1977) *Science* 198, 453-465 [13] Dreibus and Wänke (1987) *Icarus* 71, 225-240 [14] Melosh and Vickery (1989) *Nature* 338, 487-489

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**Figures 1 and 2**

