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17 September 1992; accepted 30 November 1992

Noble Gas Partitioning Between Metal and Silicate Under High Pressures

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Measurements of noble gas (helium, neon, argon, krypton, and xenon) partitioning between silicate melt and iron melt under pressures up to 100 kilobars indicate that the partition coefficients are much less than unity and that they decrease systematically with increasing pressure. The results suggest that the Earth's core contains only negligible amounts of noble gases if core separation took place under equilibrium conditions.

The Earth's mantle, at least the upper mantle, has undergone extensive degassing during the early history of the Earth. Mantle degassing models based on the comparison of $^{40}Ar/^{36}Ar$ isotopic ratios between the mantle and the atmosphere strongly suggest that the degassing of the upper mantle was very extensive; that is, more than 80% of the primordial volatiles have been degassed (*1*). In view of this extensive degassing, it is puzzling that primordial ^{3}He and ^{20}Ne are still degassing from the Earth's interior (*2*, *3*). In particular, helium has such a high diffusivity that one would assume that this element has almost completely degassed. Davies (*4*) therefore suggested that the primordial helium is retained in the core and has been escaping slowly. The crucial assumption in this suggestion is that helium was partitioned preferentially into the iron core rather than into silicates (the mantle) under high pressure. Stevenson (*5*) also suggested that the apparent depletion of xenon in the terrestrial atmosphere might have been caused by the preferential incorporation of this element into the metallic core. To evaluate these predictions, we measured the noble gas (He, Ne, Ar, Kr, and Xe) partitioning between iron and silicates under high pressures.

Our experiments were carried out on a mixture of basalt powder (48.7% SiO_2, 2.1% TiO_2, 16.3% Al_2O_3, 12.1% Fe_2O_3, 0.2% MnO, 5.9% MgO, 9.3% CaO, 4.0% Na_2O, 0.9% K_2O, and 0.5% P_2O_5) and Fe powder (commercial reagent with a purity of 95%, grain size <150 μm) in a ratio of about 1:3 by weight. Basalt powder, chosen because of its low melting temperature compared to that of peridotite, was ground in an agate mortar and was estimated to have a grain size of <100 μm. The basalt-iron mixture was put into a small capsule and subjected to high pressures. The porosities of the starting material were 30 to 40%. We used three types of high-pressure presses: a piston press at Kobe University (5 and 20 kbar), a cubic anvil press at Osaka University (60 kbar), and a uniaxial split-sphere press at Okayama University (100 kbar). For the 5- and 20-kbar experiments, the samples were directly loaded into a cylindrical graphite heater (0.14 cm^3) and were heated at 1600°C for 3 hours after high pressures had been attained. For the 60- and 100-kbar experiments, the samples were put into a boron nitride tube (about 0.03 cm^3), which was set in a graphite (60 kbar) or a rhenium (100 kbar) heater. For the 60-kbar measurements, the samples were held at 1600°C for 40 min after the highest pressure (60 kbar) had been attained. In the 100-kbar experiments, pressure and temperature were raised simultaneously (to a pressure above ~70 kbar), but the heater broke when the highest temperature and pressure were attained. In all cases, we were able to quench the samples from the highest temperature by turning off the heater, and then the pressure was slowly reduced to zero. All samples showed a clear segregation of a metallic phase from

Table 1. Noble gas concentrations in metal and silicate glass as measured in distribution experiments under high pressures. The noble gas concentration was analyzed with a static mass spectrometer. The reproducibility in the analysis was less than 10% in most cases. The procedural blank levels were as follows: ^{4}He = (3.0 to 6.3) × 10^{-11} cm^3 STP (standard temperature and pressure), ^{20}Ne = (0.83 to 5.0) × 10^{-12} cm^3 STP, ^{36}Ar = (0.76 to 2.4) × 10^{-12} cm^3 STP, ^{84}Kr = (1.2 to 7.9) × 10^{-13} cm^3 STP, and ^{132}Xe = (0.64 to 6.6) × 10^{-14} cm^3 STP. The blank correction was applied to the data. The data are in parentheses when the blank corrections were 20 to 90%, for which cases the concentrations have errors of up to a factor of 2 when we take blank variation into account. If blank corrections were more than 90%, upper limits are shown without blank correction. M, metal samples; G, silicate glass sample; ST, starting material.

Pressure and time	Sample	Sample weight (mg)	^{4}He	^{20}Ne	^{36}Ar	^{84}Kr	^{132}Xe
			($\times10^{-8}$ cm^3 STP/g)			($\times10^{-10}$ cm^3 STP/g)	
ST	Fe powder	1718.01	(0.0639)	0.0583	0.196	0.777	0.130
ST	ER-24	563.86	3.89	0.0467	0.245	1.51	0.355
5 kbar,	DIS8M	187.62	(0.260)	(0.162)	0.44	0.979	(0.0513)
180 min	DIS8G	5.80	(6.43)	(1.81)	3.04	10.5	(1.57)
20 kbar,	DIS5M	119.95	(0.149)	(0.0699)	0.249	0.956	(0.125)
180 min	DIS5G	3.04	(10.4)	(4.17)	8.69	48.2	15.1
60 kbar,	DIS11M	117.70	(0.567)	0.828	1.58	3.45	0.158
40 min	DIS11G	4.80	529	781	1250	2720	82.6
100 kbar,	DIS12M	13.74	<16.5	(0.214)	(0.411)	(0.606)	<0.219
<1 min	DIS12G	2.12	(160)	624	1050	2090	50.5

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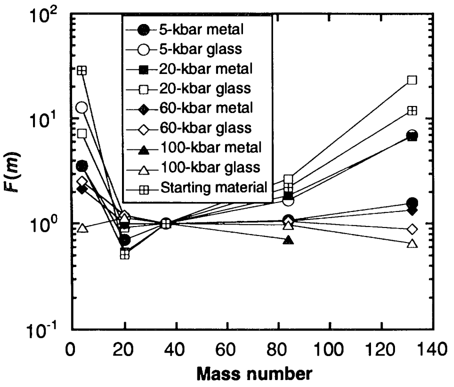

Fig. 1. The elemental abundance patterns are represented as a fractionation factor

$$F(m) = ({}^{m}X/{}^{36}Ar)_{sample}/({}^{m}X/{}^{36}Ar)_{air}$$

where ${}^{m}X$ denotes a noble gas isotope of mass m. All patterns show a depletion in heavy noble gases relative to that in the starting material except for ${}^{4}He$. The high ${}^{4}He$ is due to the in situ radiogenic component derived from basalt.

a silicate phase. We carefully separated the metallic phase from the silicate glass by hand-picking under a microscope and measured the noble gases with a mass spectrometer at Osaka University (Table 1). The experimental procedures for the purification and separation of the extracted gases were the same as those used in our previous work (6).

We assumed that noble gases in the pore space (intergrain pore space and the dead space where the sample was inserted) were partitioned under equilibrium conditions between iron melt and silicate melt at the highest temperature (and pressure). Noble gas compositions that equilibrated with iron melt and silicate melt at the highest temperature may not have been representative atmospheric values, because some fraction of the intergrain gas must have escaped from the capsule before it was compressed tightly enough to retain the intergrain gas. Because light gases would escape most easily, the remaining gas would be enriched in the heavier noble gases. The noble gases adsorbed on the starting material grains would also have been enriched in heavy noble gases, the amounts of which we estimated to be comparable to those in the pore space. This prepartition fractionation may account for the relative enrichment of heavier noble gases both in silicate melt and in iron melt (Fig. 1), which is contrary to what we expect from Henry's law. However, such fractionation should not affect the calculated partition coefficient because it is based not on the absolute amounts of noble gases but only on their ratios. If the diffusion coefficient of a noble gas is 10^{-7} cm^2/s (7), the distance this noble gas would diffuse during 40 min would be about 150 μm. Because of the small sample size and the length of time during which the samples were held at the highest temperatures, we assume that equilibrium was attained except in the 100-kbar experiment, where because of the failure of the electric heater the sample was held at the highest temperature for less than 1 min. However, because the result for the 100-kbar experiment is consistent with the general trend deduced from the lower pressure experiments (Fig. 2), the 100-kbar sample may also have attained equilibrium.

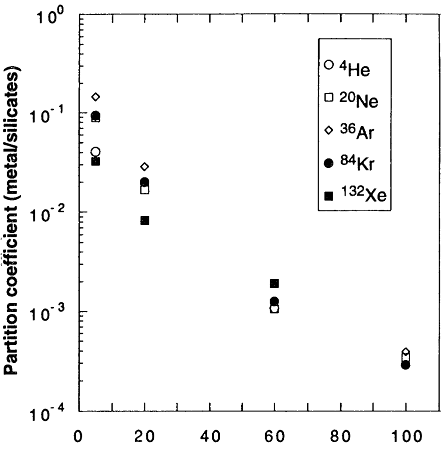

Fig. 2. Partition coefficients of noble gases between iron melt and silicate melt (the concentration of the noble gas in iron melt divided by that in silicate melt) are plotted against pressure. The partition coefficients are much less than unity and decrease with increasing pressure.

The measured noble gas partition coefficients (He, Ne, Ar, Kr, Xe) are much less than unity, and they decrease significantly with increasing pressure (Fig. 2). Possible disturbances in the experiment are (i) silicate contamination of the metal and (ii) diffusion loss of noble gases from the sample during quenching from equilibrium (the highest) temperature. Silicate contamination of the metal will give an apparently high partition coefficient, because noble gas concentrations are much higher in silicate than in metal (Table 1). The noble gas contents in silicate glass are high at high pressure. Therefore, the observed trend of decreasing partition coefficients could not be due to silicate contamination because the degree of silicate contamination was similar from one experiment to the next. Noble gas diffusion would also give a high apparent value. Because the thermal conductivity of silicate is lower than that of metal, the temperature would be higher and would be maintained longer in silicate than in metal during quenching, which would lead to higher noble gas diffusion in silicate than in metal. Even if these effects were significant, the experimental results still give the upper limit for the partition coefficients. Recently, Wolfer *et al.* (8) estimated the solubility of helium in nickel (both solid and melt) at high temperatures and obtained values much smaller than experimental values. It remains to be seen whether the discrepancy is due to nonequilibrium phenomena, as argued by Wolfer *et al.*, or to inadequacy of the theory.

The marked decrease of the partition coefficient with increasing pressure can be understood qualitatively as follows. Following the theoretical model (9), we assume that the solubility of a noble gas in a melt is proportional to $\exp(-a\gamma/RT)$, where a is a positive numerical constant proportional to the square of the radius of the noble gas atom, γ is the surface tension of the melt, R is the gas constant, and T is the absolute temperature. At atmospheric pressure, silicate melt (*10*) has a smaller surface tension than iron melt (*11*). This relation is consistent with the observation that noble gas was partitioned more in the silicate melt than in the iron melt. With increasing pressure, surface tension generally increases (*12*). The rate of increase is likely to be smaller for silicate melt than for iron melt, and at very high pressure the surface tension of silicate melt may decrease because of polymerization (*13*). An increase in the surface tension at high pressure in iron melt relative to that in silicate melt suggests either that more noble gas partitions in silicate melt than in iron melt or that the partition coefficient decreases with pressure.

It is not well known how over the history of the Earth the metal core was separated from the silicate mantle. However, our favored scenario (*14*) is that metal-silicate separation took place at a late stage in the Earth's accretion, that is, at shallow depth in the Earth comparable to the pressure range in the present experiments. According to this scenario, iron drops separating from silicate melt (most likely in magma ocean) would sink toward the center of the Earth. At shallow depths, the segregated metal drops would be small and hence would sink slowly; equilibrium partitioning of noble gases between the metal and the surrounding silicate melt would be maintained. With further sinking, these iron drops would grow larger and sink faster; exchange of noble gas between the sinking iron drops and the surrounding silicate might practically cease. Hence, if this scenario were correct, noble gas partitioning between metal and silicate would essentially be established at relatively shallow levels comparable to the pressures in the present experiments.

Using the experimental partition coefficients, we can estimate the noble gas contents in the core: for example, $^{20}\text{Ne} < 3.7 \times 10^{-12}$ cm^3 STP/g, which is much less than the estimated amount of neon (1.01×10^{-8} cm^3 STP/g) in the mantle (*15*). Hence, we conclude that, if core separation took place under equilibrium conditions, the core contains only negligible amounts of noble gases. However, if the core contains measurable amounts of noble gases, core separation must have proceeded either under conditions quite different from the above core formation scenario, such as nonequilibrium partitioning, or under an extremely dense primitive atmosphere.

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3 August 1992; accepted 20 November 1992

Evidence from Claw Geometry Indicating Arboreal Habits of *Archaeopteryx*

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The Late Jurassic *Archaeopteryx* has been thought to have been a feathered predator adapted to running that represented a terrestrial stage in the evolution of true birds from coelurosaurian dinosaurs. Examination of claw geometry, however, shows that (i) modern ground- and tree-dwelling birds can be distinguished on the basis of claw curvature, in that greater claw arcs characterize tree-dwellers and trunk-climbers, and (ii) the claws of the pes (hind foot) and manus (front hand) of *Archaeopteryx* exhibit degrees of curvature typical of perching and trunk-climbing birds, respectively. On this basis, *Archaeopteryx* appears to have been a perching bird, not a cursorial predator.

The fossil organism that has been the focus of most discussions of avian origins and the origin of flight (*1–3*) is the Late Jurassic (150 million years ago) *Archaeopteryx* found in the Solnhofen Limestone of Bavaria. There are now six well-preserved specimens that have been found (*4*). Two major theories for the evolution of avian flight—the cursorial theory, in which flight evolved from the ground up, and the arboreal theory, in which flight evolved from the trees down—are based on interpretations of the paleobiology and behavior of this primal bird. The genus *Archaeopteryx* has been envisioned in many ways: as an earthbound, cursorial predator that evolved feathers as insect traps (*5*), which would be a terrestrial stage in the evolution of avian flight (*6*); as a wader that used its wings, as do some modern herons and storks, to shade the water, which would aid in the capture of prey (*7*); and as a cliff clinger and climber (*8*). One hypothesis is that hot-blooded dinosaurs were clothed with feathers for insulation and were therefore preadapted for flight, an example of "exaptation" (*9*). Because claws may be an important indicator of avian habits, in this report I present data on claw geometry that are used to evaluate the habits of *Archaeopteryx*; and I discuss other morphological evidence to help define its behavior and paleobiological role in Late Jurassic ecosystems.

To determine if the geometry of the claws of the pes is a useful index for arboreal versus terrestrial habits in birds, I examined more than 500 species of birds, photographed approximately 400 claws (digit III), and traced and measured the claw arcs (*10*). These measurements were of the central angle formed by radii from the ends of the claw (Fig. 1) and represented the amount of a circle in a claw arc (*10*). Ten species each were chosen among ground-dwelling birds (five orders, seven families, ten genera), perching birds (four orders, eight families, ten genera), and trunk-climbing birds (three orders, five families, ten genera) (*11*). Birds with unusual adaptations—such as raptors, long-legged marsh birds, long-legged birds (for example, seriamas) that roost and nest low in bushes or trees, birds that resemble *Archaeopteryx*, and so forth—were avoided to eliminate as much as possible birds with claws adapted for strange habits or perceived to be generally convergent with those of *Archaeopteryx* for whatever reason.

The major separation of birds on the basis of claw arc measurements is between ground-dwellers and all others (Fig. 2). The mean for the ground-dwellers ($n = 98$) was 64.3°, and the means of individual species ranged from 52.2° to 77.6°; perching birds ($n = 94$), the closer of the other two groups, had a mean of 116.3°, and their individual means ranged from 101.8° to 125.3°. Of all ground-dwelling birds analyzed, only one individual, a *Neomorphus*, had a greater claw arc than that of a perching bird, a *Cyanocitta*.

Perching birds and trunk-climbers were for the most part separable; 100 trunk-climbers had a mean of 148.7° and means for species ranged from 129.5° to 161.6°. There was, however, some overlap of individual measurements. Some climbing species with lesser claw arc measurements, *Sitta*, *Phoeniculus*, *Certhia*, and *Trichodroma*, overlapped with some individual perchers; but only a few woodpeckers (Picidae) overlapped with the few individual perchers

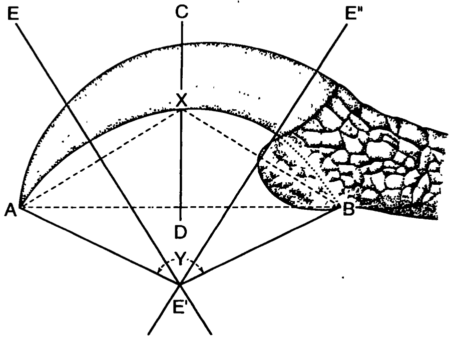

Fig. 1. Diagram of geometric measurements of claw curvature (*10*). A perpendicular (CD) is drawn to bisect the chord (AB) of the inner arc, which is itself bisected at the point X. Perpendiculars are drawn (EE′ and E′E″) to bisect the chords AX and XB. These perpendiculars, when extended, meet at the center (E′) of the circle of which the arc is a part. The radii are then drawn to each end of the arc (AE′ and BE′). The angle (Y) between these radii (read directly from a protractor) is a measure of the degrees of arc.

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