

Mantle degassing of noble gases – Implications of recent experiments

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Helium (He), argon (Ar), neon (Ne), krypton (Kr) and xenon (Xe) form the group of rare gases that are relatively inert and do not unite in nature among themselves or with other elements and hence also known as 'noble gases'. The source of these gases is believed to be from the accreting planetessimals, which were the building blocks of our planet. Melting of the planetessimals due to mounting compressional forces, augmented by heat from decaying radioactive elements in them as well as from freshly impacting bodies, are supposed to have generated a magma ocean. Chemical differentiation of this magma followed, an outcome of which was the 'out-gassing' or the release of gases that were present originally in the planetessimals. The purged gases that surfaced are believed to have formed the primeval atmosphere. Though this is the established view of the origin of earth and various gases including noble gases, over the past few decades, planetary evolutionists seem to be shifting to the earlier nebular-disc model or the chemical-condensation-sequence model of origin. According to this model, the extremely hot primordial nebular gas disc cooled, giving rise to a central plane of solid compounds, minerals, surrounded by nebular gas atmosphere. These solid compounds gradually clumped to form chunks or planetessimals or the planetary nucleus, which on attaining sufficient mass could hold a solar-composition proto-atmosphere. The latter, however, was steadily removed by the intense solar wind (blow-off) but not before incorporation of the noble gases and other volatile elements in the magma ocean that had formed¹. This view has gained much support from the geochemistry of volcanic samples examined from the earth's deep mantle considered to represent materials of most primitive composition. These samples have yielded noble gases having the same isotopic composition that characterize the sun²⁻⁶. The opinion, therefore, is divided about the incorporation of the various noble gases into early earth – whether directly from the H-He-rich proto-atmosphere

into magma ocean of the proto-earth as envisaged in the nebular-disc model or during the post-accretionary melting phase of the evolving earth, as visualized in the planetesimal hypothesis. However, their subsequent exit from the interior of earth by outgassing processes has been an accepted mode of their origin in the earth's early atmosphere.

Unlike gases like hydrogen, oxygen and nitrogen, which are highly reactive and could combine with other elements to form stable chemical compounds over geologic time, the noble gases being inert, are believed to have escaped from the earth's interior to the surface and atmosphere during the early degassing phase. A comparison of earthly abundance of these gases and other elements with those in the meteorites, the extra-terrestrial bodies which are also part of the solar system retaining the primordial composition, show certain disparities. While there is a general agreement with all elements, the noble gases show deficiencies, particularly the lighter ones among them, as they were supposed to have escaped from the gravitational pull of early earth. Especially in the case of Xe, the heaviest rare gas, deficiency was found to be maximum and this was attributed by some to absorption by shales and Antarctic ice caps, though this was later disproved⁷⁻⁹. Evolutionary models proposed to explain the observed isotopic diversity of noble gases in the earth's atmosphere have brought out the inadequacy of comparisons with meteoritic compositions. For example, the isotopes of Ne, and in particular considerable amounts of those of Xe, are decay products of extinct parents ¹²⁹I and ²⁴⁴Pu and are quite different from that of planetary meteorites^{2,6,10}. Hence, views have been expressed that much of the noble gases may, possibly, be retained within the earth itself, probably in the deep mantle or core^{5,10}.

Several aspects of the physics and chemistry of the noble gases have made them useful for tracing the structure and evolution of the earth's interior. The volatile nature of their isotopes, the different half-lives of their parents (⁴⁰K,

²³⁸U, ²³²Th, and the extinct ²⁴⁴Pu, ¹²⁹I) and the wide range of their atomic size and number have helped to gain a good insight about mantle magmatism, episodes of degassing, formation of oceanic and continental crusts, intra-crustal magmatic processes, recycling, or in short, the earth's evolution through time^{1,2,6,11,12}. During partial melting of the mantle, the noble gases are expelled and dissolved in the melt. Their solubility is explained in terms of a dissolution process in 'holes' or 'channels', the accommodating sites in the glass or silicate structure: The distribution of these 'holes', controls the 'ionic porosity' of the melt (i.e. the difference between bulk volume of material and calculated volume of constituent anions and cations) and this factor is thought to regulate the abundance of noble gas in the silicate structure (with a few exceptions)¹²⁻¹⁵. Since the potential of noble gases as geochemical tracers is much connected to their solubility in silicate melts, investigation of the parameters that influence this in melts of different compositions have increasingly engaged researchers, especially after the development of the diamond anvil cell for conducting high pressure experiments. In separate studies, Eva Chamorro-Pérez along with Philippe Gillet, James Badro and Paul McMillan (Institut Universitaire de France, Lyon) and Albert Jambon (Université de Paris, Paris) studied the solubility of argon in silicate melts at high pressures¹⁶, while Andrew Jephcoat (University of Oxford, England) carried out investigations on Kr and Xe, which exist as solids at high pressures prevailing deep in the earth¹⁷. Their results have now offered fresh explanations for the observed noble gas deficiency.

Several experimental studies on rare gas solubilities in silicate liquids and glasses, at pressures below 2.5 GPa, have been conducted earlier^{13,15,18} and now Chamorro-Pérez *et al.* have extended Ar solubility tests to pressures above 2.5 GPa, up to 5 GPa, which corresponds to pressures at 150 km depth in the mantle. Their initial experiments with pure SiO₂ melt showed increasing Ar

solubility till about 5 GPa and a decrease thereafter. In order to observe the trend, they chose natural olivine [(MgFe)₂SiO₄], a mineral close to mantle composition, and repeated the experiment. They used a polished single crystal of this mineral (in slices of size 100 × 100 × 20 μm³) and heated it up to 2300–2700°K, in a diamond anvil cell, by focussing a beam of CO₂ laser. The sample was kept compressed in solid Ar (as pressure transmitting medium) and the pressure was slowly increased from 2.5 GPa up to 11 GPa (equal to pressures at about 330 km mantle depth) and increments of pressure were monitored by measuring the shifts in Raman spectral lines of the mineral. The heating produced beads or droplets of melted olivine and Ar, which were quenched rapidly to glass by shutting-off the laser heating. After decompression, the sample was subjected to electron microprobe analyses for estimation of the incorporated Ar in the partial melt glass. This revealed a steady increase in Ar solubility with pressure up to 4–5 GPa, but above this value, the solubility showed a decline by an order of magnitude. The authors explained this change in Ar solubility as due to the reduction in ionic porosity (i.e. the availability and size of the 'holes' in the silicate melts) resulting from a decrease in volume of the melt with the pressures above 5 GPa to such an extent that the available hole or site sizes crossed the Ar radius, effectively decreasing Ar solubility¹⁶. However, at low pressures, up to 2.5 GPa, the available sites are relatively more but not completely filled by Ar and therefore the effect of pressure here is to increase solubility, as observed. They expect similar behaviour in the mantle melts for the other noble gases, particularly the heavier Kr and Xe.

Minoru Ozima¹⁹ (Dept of Earth and Planetary Sciences, University of Tokyo, Japan), however, raised a pertinent question as to where the noble gases could go if they do not dissolve in the melts at high pressures. Also, these findings, he points out, will mean that the mantle below 150 km (5 GPa) is left undegassed. Therefore, he argues, the general geochemical assumption that noble gases are preferentially fractionated into the melt will be true only to mantle melts up to 150 km depth and beyond this, they will be strongly incompatible. In the opinion of Ozima, these findings of Chamorro-

Pérez *et al.* would amount to rejecting the seismologically identified boundary at 670 km, separating the degassed upper mantle from the lower mantle, and raise this boundary to a shallower depth of 150 km thus suggesting existence of two types of layered mantle – a geochemically layered one with a boundary at a depth of 150 km and seismologically defined one down at 670 km. Though Ozima has a point with regard to the fate of undissolved Ar, it may be mentioned that the 670 km junction represents a distinct mineral phase change in the mantle which has been inferred from seismic wave velocity variation and not by the presence or absence of a few elements at a few parts per billion (ppb) levels. In fact, views are veering away from this concept of mantle layering ever since oceanic plates were found by seismic tomography to pierce the 670 km barrier. Further, recent seismic studies of the mantle have indicated velocity changes at much greater depths²⁰. The 150 km threshold emerging from studies by Chamorro-Pérez *et al.* should, perhaps, be considered as the depth limiting noble gas compatibility in partial mantle melt. Also, Ozima is hesitant to apply their data derived from experiments using high Ar concentrations (0.1 wt%) inasmuch as the natural concentration of Ar in the mantle is extremely low, < 1 ppb. At this extreme dilution, he feels, there should be enough holes or sites of matching size to accommodate Ar¹⁹.

The second investigation by Jephcoat¹⁷ relates to Xe behaviour in mantle and core conditions. At high pressures (up to 137 GPa), earlier work had shown that this gas acquires metallic close-packed structure²¹ and many believed that such a change may facilitate chemical combination with iron in the core and that this behaviour can explain the missing Xe problem. But high pressure experiments, combined with theoretical energy calculations for Xe-Fe reaction to form compounds (up to 500 GPa) revealed that such chemical combinations are not feasible thus discounting the views that Xe may have partitioned into the core as a metal inside the earth²². Now, Jephcoat¹⁷ explains the presence of Xe in the core from a different perspective. He suggests that Xe, Ar and Kr exist as solids of high density in the mantle, and possibly in the core, and remain there undegassed without forming compounds.

Close-packed solids of these gases, known to form under adequate pressure at room temperature, are observed to melt at very high temperatures with increasing pressure. Through diamond anvil cell experiments, Jephcoat derived pressure-temperature and pressure-density relationships for Ar, Kr and Xe. His data have indicated that the density of solid Ar at 2500 K (representing mantle temperature) is approximately equal to the density in the lower mantle, solid Kr has a density equal to the core and solid Xe is significantly denser than both the core and iron. He, therefore, argues that Xe, Kr and Ar would have formed high density inclusions and would have settled down in the deeper portions during the differentiation phases of early earth to form a separate lower mantle/core reservoir. Likewise, radiogenic ⁴⁰Ar produced from ⁴⁰K in both the lower mantle and probably the core throughout the earth's history (incorporation of K through chemical combination with Fe in the core is strongly suspected^{23,24}) would also accumulate in the lower mantle and the core in high density solid phase¹⁷ and similarly for Kr and Xe isotopes. This sinking of particles would also explain the observed deficiency of Xe in the earth relative to extraterrestrial materials (meteorites). But Ozima doubts if there could be a suitable mechanism to segregate the extremely low contents (1 part in 10¹²) to a suitable size to gravitate to depths. Verification of the geochemical implications emerging from these experiments by Chamorro-Pérez *et al.* and Jephcoat now would require samples representing these depths. We now know that their geochemistry must have considerably departed from primeval composition in the light of recent observations about intermixing of layered mantle zones, crustal recycling through plunging plates deep up to the core-mantle boundary apart from compositional heterogeneities inferred within the mantle itself²⁴⁻²⁷.

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SCIENTIFIC CORRESPONDENCE

Diffused palmoplantar keratoderma – A case study of dominant mutant type of congenital syndrome in Midnapore, India

Local thickening of palm and sole accompanied by fissuring in human beings is quite common in certain season. Such fissuring may arise due to environmental toxicants like arsenic^{1–5} but diffused palmoplantar keratoderma (PPK. Syn. Tylosis, Unna-Thost Syndrome) which is characterized by the thickening of horny layer of palm and sole is hereditary in nature. This syndrome, usually developed at an early stage of infancy⁶, shows considerable interfamily variations especially with regard to age, onset and severity. Early severe effect may be seen in infancy⁷. Two genetically distinct forms of palmoplantar keratoderma, which are clinically similar are – a common form with an autosomal dominant mode of inheritance^{8,9} and a severe form with an autosomal recessive inheritance^{8,10}. Tylosis with lethal effect after 60 years of age has been reported by Howel-Evans *et al.*¹¹. Lethal effect of PPK is caused by chromosomal translocation¹², lethal genetic combination^{13,14} or by EPPK gene-type-I keratin gene cluster¹⁵. PPK with hyperpigmentation¹⁶, mental retardation, early loss of teeth with atrichia¹², deaf mute¹⁷ acroosteoly-

sis and type-II hereditary motor sensory neuropathy, ansdspastic paraplasia may also sometime be associated with oesophageal carcinoma¹⁸, lymphoma¹⁹, squamous cell carcinoma, skin malignancy²⁰, and melanoma²¹. In the present investigation an interfamily pedigree with respect to PPK syndrome has been made and analysed along with the symptoms of this syndrome.

PPK syndrome appears to be quite common in Egra–Potashpur region of

Midnapore district in West Bengal where the present study was conducted. Thirty five individuals have been found affected with this syndrome. Other cases have been traced back to Jaleswar, Baleswar and Baripada of Orissa state where either they have migrated from this region or have established marital relation. All the individuals affected by this syndrome have been found to have a blood relation and therefore the syndrome appears to be hereditary in nature. A survey was con-

Table I. Phenotypic symptoms associated with tylosis through six generations

Associated phenotypic symptoms	Generations					
	F ₁	F ₂	F ₃	F ₄	F ₅	F ₆
Thickening of keratinized layer of palm and sole	+++	+++	+++	++	++	+
Painful fissuring	+++	+++	+++	++	++	+
Occasional bleeding from fissuring	++	++	+++	++	+	-
Hyperhydrosis	++	++	++	++	+	+
Thickened nails	++	+++	++	++	+	-
Displastic nails	++	++	++	+	-	-
Nail dystrophy	++	++	++	+	+	-
Clubbed fingers	++	++	++	+	+	-

+++ Severe, ++ Prominent, + Slight, - Absent.