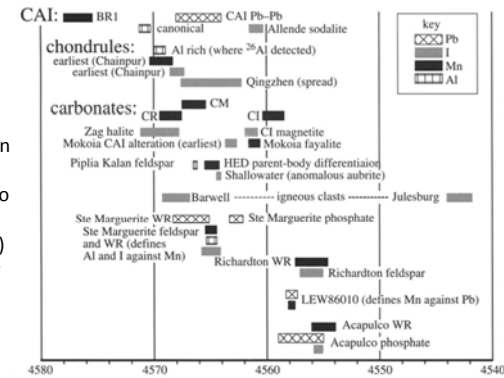


Lecture 9: Atmosphere-ocean formation

Isotopic evidence for early formation, volatile retention and loss, on-going terrestrial degassing

Chronometric triangulation...

Detailed timing (to Ma resolution) obtained from decay products of extinct radioactivities like ^{26}Al , ^{60}Fe , ^{53}Mn , ^{129}I in primitive meteorites and then anchored to the "absolute time scale" (w.r.t. present) by Pb-Pb chronology



Gilmour and Saxton, 2001, Proc. Roy. Soc. 359, p2037-2048

Figure 2. An altered chronology of the early Solar System based on assuming the identity of closure ages of Al-Mg and I-Xe in Ste Marguerite feldspar and Mn-Cr in Ste Marguerite whole rock (WR). The absolute age-scale is once again derived from the Pb-Pb-to-Mn-Cr calibration of LEW86010. See text for references to sources of data and discussion.

Lecture 9: Atmosphere-ocean formation

- **Done and dusted?**
- Volatile retention and loss
- Isotope evidence for early atmosphere/ocean formation
- Isotopic signatures of on-going terrestrial degassing

Done and dusted?

- Discovery of excess ^{60}Fe in ferromanganese crusts on ocean floor
 - No way it's cosmogenic!
 - Must be nucleosynthetic
- Happened 2.8 Ma ago
 - Peak "width" is ~ 0.8 Ma
 - But oceanic Fe residence time is ~ 100 -200 y
- Some controversy
 - other r-process nuclides, e.g., ^{244}Pu , not seen

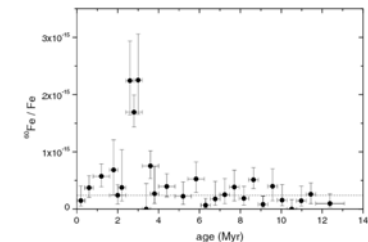


FIG. 1. $^{60}\text{Fe}/\text{Fe}$ ratios versus the age of the layer. The data are not corrected for radioactive decay, background, and uptake of Knie et al, 2004, Phys. Rev. Lett. **93**, (17), 171103

Lecture 9: Atmosphere-ocean formation

- Done and dusted?
- **Volatile retention and loss**
- Isotope evidence for early atmosphere/ocean formation
- Isotopic signatures of on-going terrestrial degassing

The formation of the Solar System

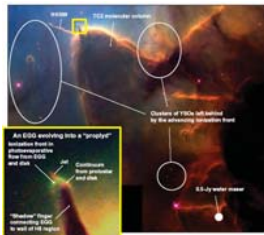
- There was a temperature gradient throughout the pre-solar disk (cooling more rapidly on outer edges)
 - gradation in planetary composition outward
 - the denser, more “refractory” planets sunward
 - lighter, more “hydrogenous” planets* outward
- *compositionally most like the sun!

	Mercury	Venus	Earth	Mars	Jupiter	Saturn	Uranus	Neptune	Pluto
Mass (Earth = 1)	0.05	0.81	1.00	0.11	318	95	14.5	17.3	0.03
Density (g/cc)	5.1	5.0	5.5	3.9	1.33	0.71	1.27	2.22	??

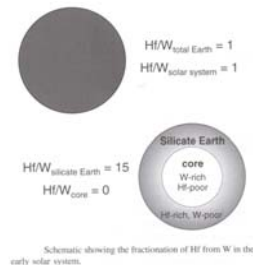
- Evidence of radiational stripping by young sun and neighbouring new stars

Origin and Age of the Atmosphere

- Early solar history:
 - Sun extremely luminous (Tau-Tauri phase)
 - Solar radiation strips volatiles from inner protoplanet in first 1 Ma
 - Earth formed by “dry accretion” of more refractory material
 - Gravitational collapse, impactors, and ^{26}Al , ^{36}Cl , ^{60}Fe , ^{244}Pu enough to melt earth
 - Giant impactor helps form moon & core

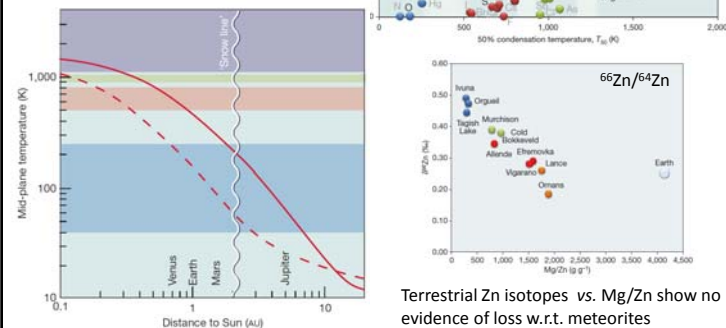


So if earth was “dry” and hot enough to melt, where did the volatiles come from?



Elements characterized by volatility as a function of temperature

Models of early protoplanet temperature distribution as a function of radius indicates inner planets could not have accumulated volatiles (especially water)



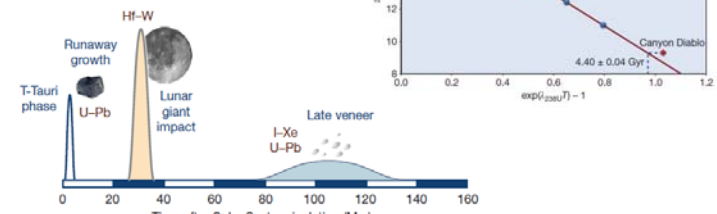
Lecture 9: Atmosphere-ocean formation

- Done and dusted?
- Volatile retention and loss
- **Isotope evidence for early atmosphere/ocean formation**
- Isotopic signatures of on-going terrestrial degassing

Proposed Scheme:

- Earth's volatiles “plastered on” as a late veneer from outer-solar system material (beyond the snow line)
- Note that Pb is a volatile and terrestrial $^{206}\text{Pb}/^{204}\text{Pb}$ trend “younger” than meteoritic

Albarede, F. (2009) Volatile accretion history of the terrestrial planets and dynamic implications. *Nature* **461**, 1227- 1233



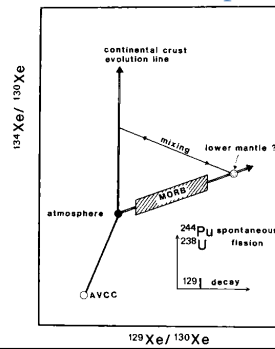
cf. Allegre et al (2008) The major differentiation of the Earth at ~4.45 Ga. *EPSL* 267 p386-398

Origin and Age of the Atmosphere

What is the timing of the Atmosphere's formation?

If atmosphere and mantle separated when there are significant amounts of ^{129}I around, then since $^{129}\text{I} \rightarrow ^{129}\text{Xe}$, then you will see Excess ^{129}Xe in the

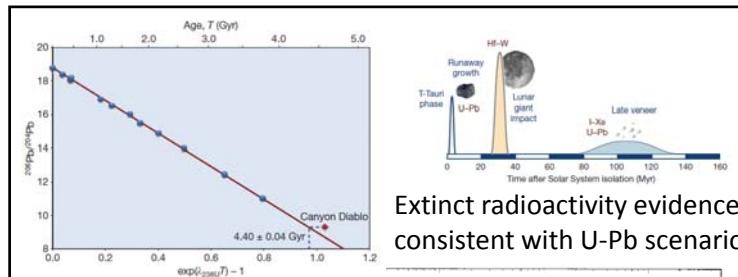
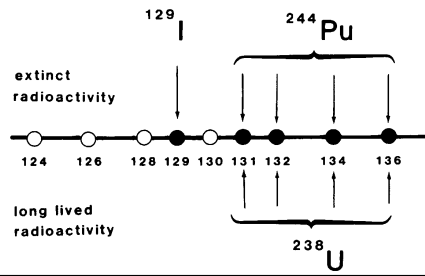
Xenon Isotopes



residual rocks vs the atmosphere

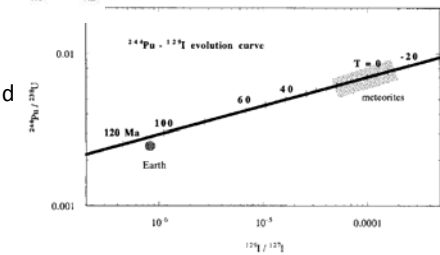
^{129}I $t_{1/2} = 15.7$ Ma

^{244}Pu $t_{1/2} = 82$ Ma



Extinct radioactivity evidence consistent with U-Pb scenario

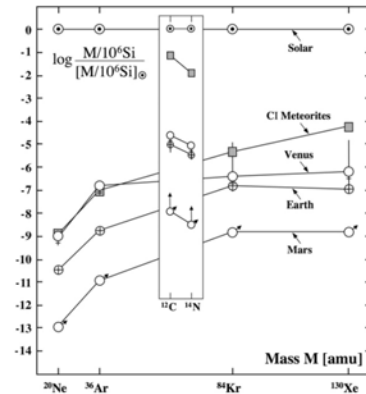
But this is still an area of debate*. Common ground is that the atmosphere formed within the first ~100-150 Ma.



e.g., Pepin, R. O., and D. Porcelli (2006), Xenon isotope systematics, giant impacts, and mantle degassing on the early earth, *Earth and Planetary Science Letters*, 250(3-4), 470-485.

Planetary patterns of non-radiogenic noble gas isotopes show strong depletion w.r.t. solar, and Ne & Xe deficits w.r.t. meteorites

1. Ne deficit indicative of significant loss over geologic time
2. Xe deficit still remains a mystery (hints in isotopic patterns); sorption and/or reactivity?

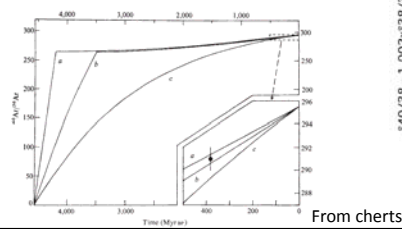


Lecture 9: Atmosphere-ocean formation

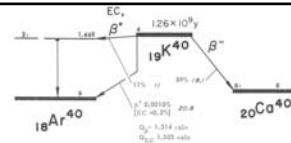
- Done and dusted?
- Volatile retention and loss
- Isotope evidence for early atmosphere/ocean formation
- **Isotopic signatures of on-going terrestrial degassing**

The argon story

- The primordial $^{40}\text{Ar}/^{36}\text{Ar}$ should be order 1 or less
- Atmospheric $^{40}\text{Ar}/^{36}\text{Ar} = 298.6$ due to decay of ^{40}K ($t_{1/2} \sim 1$ Ga) and release to atmosphere
- Even higher $^{40}\text{Ar}/^{36}\text{Ar}$ ratios in MORB and continental rocks



From cherts



From Ice Core bubbles

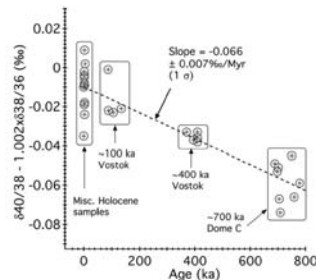


Fig. 1. Paleoatmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio plotted versus age.

The Helium Story

- Although it is the second most abundant element in the universe, it is only ~ 5 ppm in the atmosphere. Why?

Important News Bulletin!!!!

Headlines:

- Discovery of He and Kinetic Gas Theory Ignites Debate in Literature:

PHILOSOPHICAL TRANSACTIONS.

I. The Kinetic Theory of Planetary Atmospheres.

By G. H. BRYAN, Sc.D., F.R.S.

Received March 15,—Read April 5, 1900.

1. THE possibility of applying the Kinetic Theory to account for the presence or absence of different gases in the atmospheres surrounding the various members of our Solar System, and in particular to explain the absence of any visible atmosphere from the Moon, was first discussed by WATERSTON in 1846, in his memorable paper

Important News Bulletin!!!!

Headlines:

- Discovery of He and Kinetic Gas Theory Ignites Debate in Literature:

PHILOSOPHICAL TRANSACTIONS.

I. The Kinetic Theory of Planetary Atmospheres.

By G. H. BRYAN, Sc.D., F.R.S.

Received March 15,—Read April 5, 1900.

THE PERMANENCY OF PLANETARY ATMOSPHERES, ACCORDING TO THE KINETIC THEORY OF GASES.

By S. R. COOK, Case School of Applied Science, Cleveland, Ohio, dated September 3, 1902.

1. HISTORICAL.

Since the development of the kinetic theory by Clausius, Meyer, and Maxwell, and especially since it has been shown by Maxwell and Boltzmann that the molecules of any gas may have velocities ranging from zero to infinity, it has been a problem of intense interest to many scientists to determine the probability that the molecules of highest velocity may escape from the outer limits of an atmosphere, and hence deduce the condition of atmospheric permanence.

a account for the presence
using the various members of
us of any visible atmosphere
1846, in his memorable paper

Important News Bulletin!!!!

Headlines:

- Discovery of He and Kinetic Gas Theory Ignites Debate in Literature:

PHILOSOPHICAL TRANSACTIONS.

THE PERMANENCY OF PLANETARY ATMOSPHERES, ACCORDING TO THE KINETIC THEORY OF GASES.

By S. R. COOK, Case School of Applied Science, Cleveland, Ohio, dated September 3, 1902.

1. HISTORICAL.

ESCAPE OF GASES FROM THE ATMOSPHERE.

By Dr. G. JOHNSTONE STONEY, F. R. S.

[Reprinted from London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, June, 1904, 6th series, vol. 7, p. 620.]

A letter under the above heading by Mr. S. R. Cook, in Nature of the 24th of March, 1904,¹ puts forward views that ought not to remain on record without reply; and as between thirty and forty years ago I carried on the investigation into the rate at which gases can escape from atmospheres in the same way as Mr. Cook has done, and arrived, from the premises employed by him, at substantially the same conclusions, perhaps the best answer will be to state the considerations which led me to distrust that line of argument and finally to abandon it. To do this, however, requires more to be said

Important News Bulletin!!!!

Headlines:

- Discovery of He and Kinetic Gas Theory Ignites Debate in Literature:

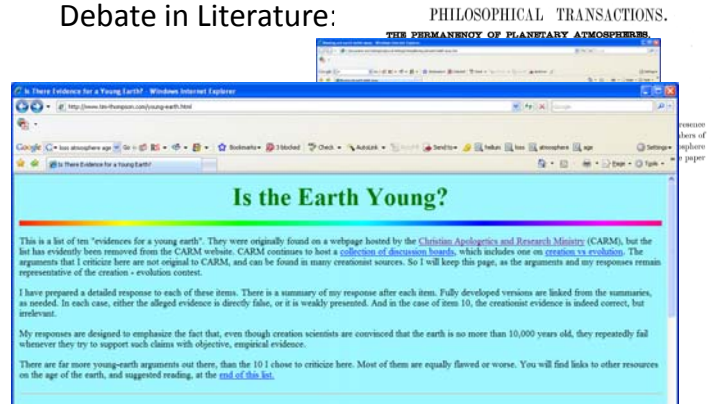
PHILOSOPHICAL TRANSACTIONS.

THE PERMANENCY OF PLANETARY ATMOSPHERES.

Important News Bulletin!!!!

Headlines:

- Discovery of He and Kinetic Gas Theory Ignites Debate in Literature:



The Helium Story

- Although it is the second most abundant element in the universe, it is only ~ 5 ppm in the atmosphere. Why?
- Helium is lost at a significant rate to outer space: residence time in the atmosphere is only ~ 1 Ma, yet the earth is ~4500 Ma old. Why is there so much He in the atmosphere?

Then $U, Th \rightarrow Pb + He$ was discovered:
there's a flux from the solid earth

- Crustal degassing rates $\rightarrow$ 1- 2 Ma residence time in atmosphere... He must be in steady state in the atmosphere against...

- Jeans (thermal) escape:
 - M-B distribution of velocities, some exceed V_{escape}
 - Far too slow to match crustal degassing rates
- Dominant (non-thermal) mechanisms:
 - Polar wind: plasma flux tubes connecting with solar wind
 - Exothermic charge-exchange collisions:

$$He^+ + N_2 \rightarrow He + N_2^+$$

Lie-Svendsen & Rees (1996) JGR 1010 p2435
Shizgal & Arkos (1996) Rev. Geophys. 34 p483

The Discovery of Oceanic Volcanic ^3He

The Big Question in the 1960s:

“What is the source of geothermal heat?”

or

“Is the Earth chondritic?”

Compositional models for U, Th-based alpha decay generated $\sim 10^5 - 10^6$ atoms $^4\text{He cm}^{-2} \text{ s}^{-1}$

Using the oceans as a flux integrator

- Residence time of oceans ~ 1000 years, He solubility $\sim 10^{-2}$ so...
 - If residence time of ^4He in the atmosphere $\sim 1 \text{ Ma}^*$ should see $\sim 10\%$ anomaly against atmospheric background
- Problem: air-sea exchange/bubble processes produce significant atmospheric excesses
 - Answer: measure $^3\text{He}/^4\text{He}$ because the radiogenic He will be $\sim$ pure ^4He and lower the ratio unambiguously

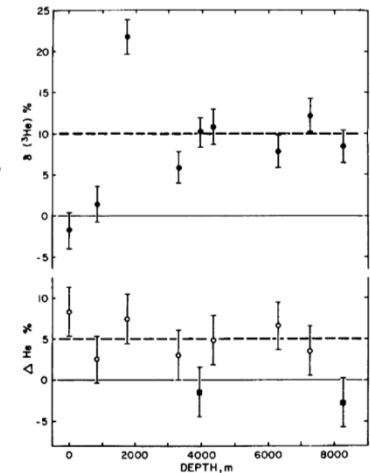
* He lost to outer space via "Polar Wind" and charge-exchange acceleration reactions

Oops! An Oceanic Flux of Volcanic ^3He

Clarke et al (1969) EPSL 6, p213-220

- First reported profile of $^3\text{He}/^4\text{He}$ in Pacific
- Mean excess $\delta^3\text{He}^* \sim 10\%$
 $\rightarrow 300 \text{ fmol/m}^3$
- Upwelling (from Munk, 1966) $\sim 5 \text{ m/y}$
 $\rightarrow 1.5 \text{ pmol/m}^2/\text{y}$
 $\rightarrow \sim 500 \text{ mol/y}$
- All based on one profile...

$$* \delta^3\text{He} \equiv \left(\frac{(^3\text{He}/^4\text{He})_x}{(^3\text{He}/^4\text{He})_{\text{Air}}} - 1 \right) \times 100\%$$



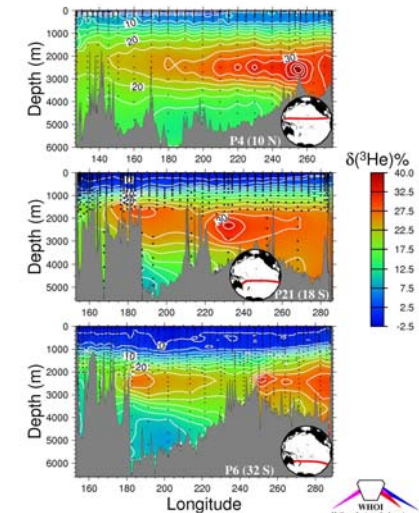
But wait a minute...

Atmospheric $^3\text{He}/^4\text{He} = 1.4 \times 10^{-6}$ (about 100 X lower than solar/primordial)

- It's low due to radiogenic alpha production/degassing
- ^3He time constant ($\sim 750 \text{ Ka}$) against loss to outer space is even smaller than for ^4He
 - Why is the ratio so HIGH?
- There is a flux of ^3He
 - But only production modes are:
 - Spallation by cosmic rays in stratosphere and
 - $^7\text{Li}(n,\alpha)^3\text{H} \rightarrow ^3\text{He}$ in rocks
 - Total production $\sim 10\text{X}$ too small...
 - It must be "primordial" and from a persistent reservoir

The Oceanic Flux of Volcanic ^3He

- A wide-spread signature in the deep waters of the Pacific, Indian, and South Atlantic Oceans
- Biggest signal in the Pacific (fastest crustal spreading rates)



The Oceanic Flux of Volcanic ^3He

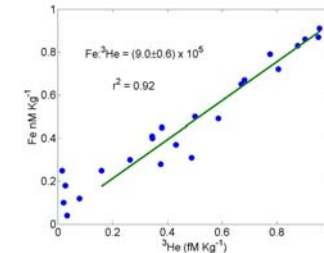
- Clarke, Beg, & Craig (1969) EPSL 6, p213-220
 - First reported profile of $^3\text{He}/^4\text{He}$ profile in Pacific
- Craig & Clarke (1970) EPSL 9, p45-48
 - Used Munk 1-D balance to estimate flux
 - Based on radiocarbon $\rightarrow$ 500-1000 mol/y
- Farley et al (1995) JGR 100 p3829-3839
 - Estimated global flux based on Hamburg Model & observed ^3He distributions $\rightarrow$ 1000 mol/y
- Bianchi et al (2010), EPSL 297, p379-386
 - Based on improved GCM & WOCE data $\rightarrow$ 500 mol/y

The Oceanic Flux of Volcanic ^3He

So who cares (other than me)?

1. It's the only documented/quantified current terrestrial degassing flux
 - Note that He is inert, so a conserved tracer
2. It is a valuable "flux gauge" if we use property ratios w.r.t. ^3He (e.g., $\text{Fe}:^3\text{He}$)

Correlation of Fe and ^3He in southwest Pacific ultimately from hydrothermal injection at EPR.



$$\frac{\text{Fe}}{^3\text{He}} \times 1000 \text{ mol y}^{-1} \approx 10^9 \text{ mol Fe y}^{-1}$$

The Oceanic Flux of Volcanic ^3He

So who cares (other than me)?

1. It's the only documented/quantified current terrestrial degassing flux
 - Note that He is inert, so a conserved tracer
2. It is a valuable "flux gauge" if we use property ratios w.r.t. ^3He (e.g., $\text{Fe}:^3\text{He}$)
3. There are huge variations in $^3\text{He}/^4\text{He}$ ratio from 10^{-8} (continental crust) to atmospheric (1.4×10^{-6}) to MORB (1.5×10^{-5}) to mantle plumes (7×10^{-5})
4. Implies the existence of persistent primordial reservoirs

Lecture 9: Atmosphere-ocean formation

- Done and dusted?
- Volatile retention and loss
- Isotope evidence for early atmosphere/ocean formation
- Isotopic signatures of on-going terrestrial degassing