Radiogenic Isotopes - Th-U-Pb, Re-Os, and Hf-W - insights into core formation

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(Dated: June 6, 2019)

Extant and extinct radiogenic isotope systems provide insights into the formation of the Earth core, the planet's greatest differentiation event. The Th-U-Pb systems provide constraints on the sequestration of lead (Pb), a chalcophile element, into the core relative to uranium (U) and thorium (Th), both lithophile elements. The measured and time integrated Th/U ratios of rocks from the silicate Earth constrains the relative fractionation of these elements during metal - silicate and crust - mantle fractionation processes. The absolute abundances of Re, Pt and Os, their elemental ratios, and their time integrated Os isotopic ratios in rocks from the silicate Earth collectively constrain metal - silicate partitioning and core formation models. The ^{182}Hf-^{182}W isotope system provides the strongest time constraint on core formation, indicating core formation between 10 and 100 Ma follow the solar system formation. Finally, the age of Moon formation sets an additional maximum limit on the age of core formation. The core likely formed between 30 $\pm$ 20 Ma after t_0.

I. SUMMARY

These three isotope systems are used in geochronology and as tracers of processes in Earth sciences and cosmochemistry:

Th-U-Pb and the U-series isotope systems: the most important system in the geochemist's toolbox, as it is the premier quantitative method for geochronology, including establishing the age of Earth and the geological time scale. It also is used to date core and crust formation and its short-lived systems provide critical age and process information for young (<400 ka) geological events. In addition, Fission track - apatite dating and U-^{4}He dating are other important chronometric tools relating to these isotopes.

^{187}Re - ^{187}Os, ^{190}Pt - ^{186}Os isotope system : this radiogenic clocks is used to date rocks, particularly some ore deposits, constrain core formation models, and applications in cosmochemistry.

^{182}Hf-^{182}W : this extinct isotope system ($t_{1/2}$ = 8.9 Ma) gives evidence to a supernova initiation of the solar system. Because the parent isotope ^{182}Hf is lithophile and the daughter isotope, ^{182}W, is siderophile, it provides a powerful time constraint on core - mantle fractionation. Recently, it has been combined with other isotopic observations to define the age of Jupiter formation.

A. *β and α decay schemes in these isotope systems*

(half-lives from Begemann et al (2001) Geochimica et Cosmochimica Acta, Vol. 65, pp. 111 - 121)

Long lived U-Pb and Th-Pb systems

1) ^{238}U $\rightarrow$ ^{206}Pb + 6β^- + 8α + Q (51.7 MeV) ($t_{1/2}$ = *4.4683 $\pm$ 0.0024 Ga*)

2) ^{235}U $\rightarrow$ ^{207}Pb + 4β^- + 7α + Q (46.4 MeV) ($t_{1/2}$ = *0.7038 Ga*)

3) ^{232}Th $\rightarrow$ ^{208}Pb + 4β^- + 6α + Q (42.6 MeV) ($t_{1/2}$ = *14.0 Ga*)

Short lived U-Series systems

4) ^{238}U $\rightarrow$ ^{234}Th + α + Q (4.270 MeV) ($t_{1/2}$ = *4.470 Ga*)

5) ^{234}Th $\rightarrow$ ^{234}U + 2β^- + Q (2.468 MeV) ($t_{1/2}$ = *24.1 days*)

6) ^{234}U $\rightarrow$ ^{230}Th + α + Q (4.860 MeV) ($t_{1/2}$ = *246 ka*)

7) ^{230}Th $\rightarrow$ ^{226}Ra + α + Q (4.770 MeV) ($t_{1/2}$ = *75.4 ka*)

Os and W isotope systems

8) ^{187}Re $\rightarrow$ ^{187}Os + e^- + $\bar{\nu}_e$ + Q (0.0025 MeV) ($t_{1/2}$ = *43.3 Ga*)

9) ^{190}Pt $\rightarrow$ ^{186}Os + α + Q (3.249 MeV) ($t_{1/2}$ = *651.1 Ga*)

10) ^{182}Hf $\rightarrow$ ^{182}W + 2e^- + 2$\bar{\nu}_e$ + Q (2.196 MeV) ($t_{1/2}$ = *8.9 Ma*)

– *Note*: α particles are abundantly produced by U and Th decays and mostly end up as ^{4}He atoms in the Earth's interior. Sramek et al (2017, GCA) estimated that a kg of average upper crustal rock produces about 533 α particles per second. Moreover, α from U and Th have on average between 5 and 6 MeV when produced and will travel through a mineral lattice up to ~30 microns. They leave an accompanying alpha recoil track, the recoil of the heavy daughter nuclide, of ~3 microns, which is comparatively small when compared to fission track (~15 microns).

Each α is emitted with specific kinetic energy and it progressively loses this energy via inelastic scattering on atomic electrons and elastic scattering on nuclei. Once an α particle loses its kinetic energy it gains electrons and becomes a ^{4}He atom. There is a finite proability that the α particle enter another nucleus and create a new atom, given sufficient kinetic energy to overcome the nucleus' Coulombic barrier, the electromagnetic repulsion between the target nucleus and the charged α particle. There are many potential (α, n) reactions that produce many free neutrons (~10,600/yr/kg upper crustal rock) and a wide range of short-lived and stable isotopic products (i.e., nucleogenic isotopes, e.g., ^{21}Ne, ^{39}Ar, see figure below).

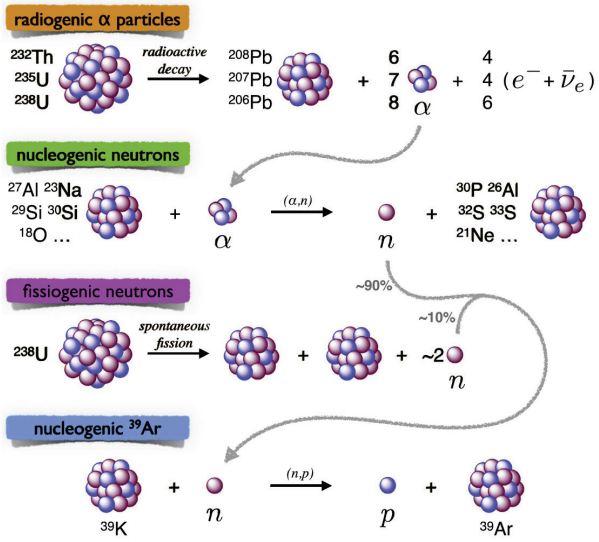

Figure 1: Overview of U and Th decay α and neutron production leading to nucleogenic isotopes

B. *The U-Pb and Th-Pb isotope systems: β and α decays*

Here is the basic *isochron equation*, which can be applied to the 3 long lived systems. Application of this equation assumes that all rocks or minerals used to form a line on and isochron have the same initial isotopic composition – they are co-genetic. I will not cover the short lived U-decay series in this course. Here are some useful concepts in Th-U-Pb.

$$\left(\frac{^{238}U}{^{204}Pb}\right) = \mu\,, \quad \left(\frac{^{235}U}{^{204}Pb}\right) = \beta\,, \quad \left(\frac{^{232}Th}{^{204}Pb}\right) = \omega\,, \quad \left(\frac{^{232}Th}{^{238}U}\right) = \kappa\,, \quad \left(\frac{^{208}Pb^*}{^{206}Pb^*}\right) = \kappa_{\mathrm{Pb}}$$

$$\left(\frac{^{238}U}{^{204}Pb}\right) = \left(\frac{U}{Pb}\right) * \left(\frac{Abs{-}abund.^{238}U * Atomic{-}weight{-}Pb}{Abs.{-}abund.^{204}Pb * Atomic{-}weight{-}U}\right) \approx \left(\frac{U}{Pb}\right) * 63$$

$$\left(\frac{^{206}Pb}{^{204}Pb}\right) = \left(\frac{^{206}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{238}U}{^{204}Pb}\right)\left(e^{\lambda_{238}t} - 1\right)$$

$$\left(\frac{^{207}Pb}{^{204}Pb}\right) = \left(\frac{^{207}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{235}U}{^{204}Pb}\right)(e^{\lambda_{235}t} - 1)$$

$$\left(\frac{^{208}Pb}{^{204}Pb}\right) = \left(\frac{^{208}Pb}{^{204}Pb}\right)_0 + \left(\frac{^{232}Th}{^{204}Pb}\right)(e^{\lambda_{232}t} - 1)$$

The subscript "*0*" indicates the initial ratio. By simultaneously treating the ^{207}Pb and ^{206}Pb systems

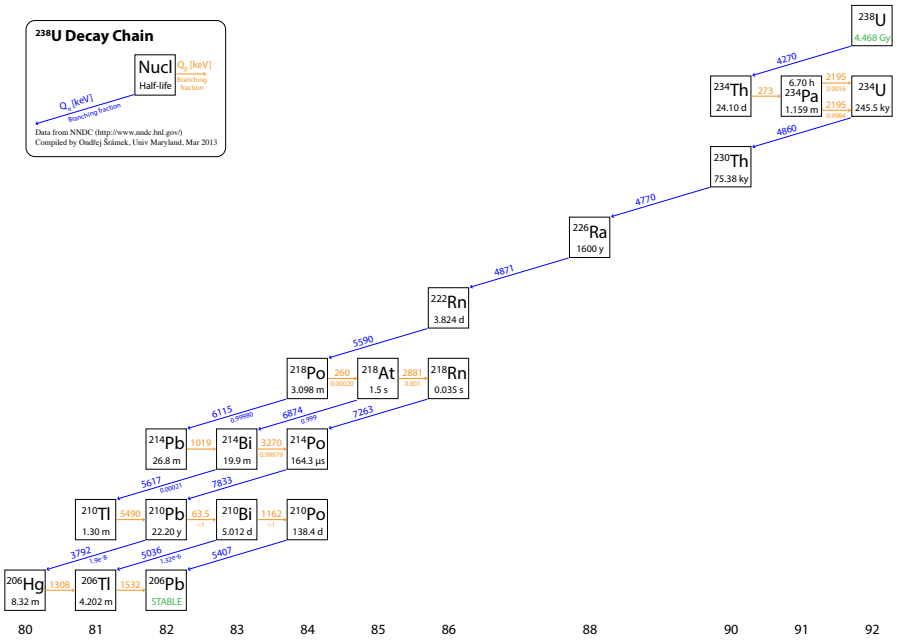

Figure 2: Decay chains for ^{238}U, with half lives, decay energies, and branching ratios

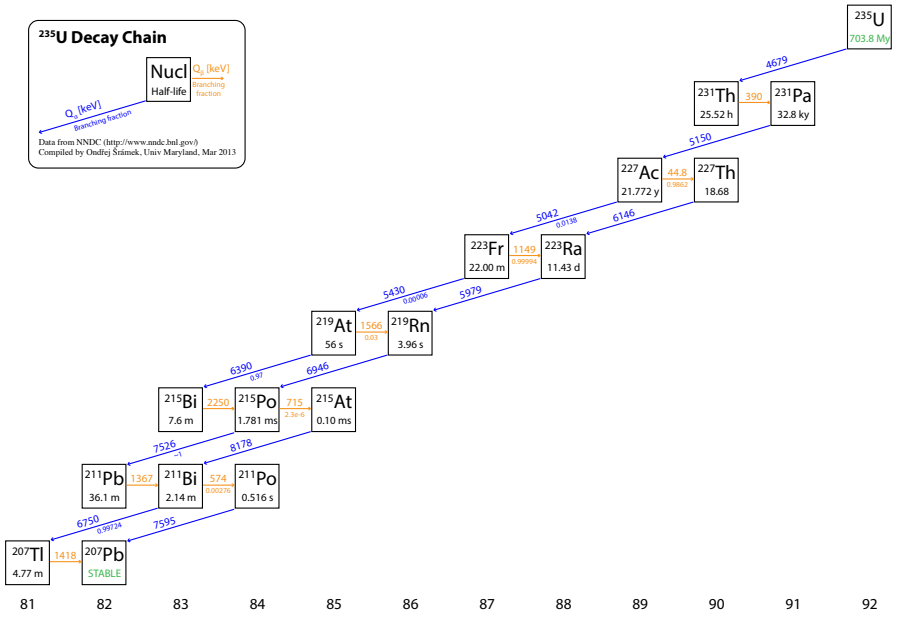

Figure 3: Decay chains for ^{235}U, with half lives, decay energies, and branching ratios

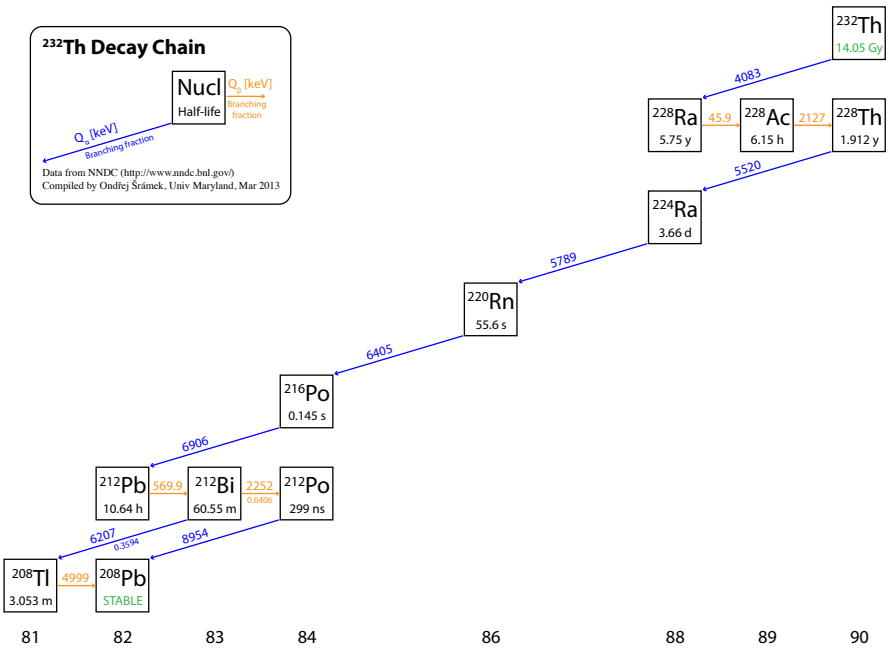

Figure 4: Decay chains for ^{232}Th, with half lives, decay energies, and branching ratios

C. *Pb-Pb geochronology*

For the U system you have these two simple decay equations that, when combined, lead to an equation that only has age dependence:

$$^{206}\text{Pb}^* = {}^{238}\text{U}\ (e^{\lambda_{238}t} - 1)\ ;\ {}^{207}\text{Pb}^* = {}^{235}\text{U}\ (e^{\lambda_{235}t} - 1)\ ; \rightarrow \left(\frac{^{207}Pb^*}{^{206}Pb^*}\right) = \left(\frac{^{235}U(e^{\lambda_{235}t}-1)}{^{238}U(e^{\lambda_{238}t}-1)}\right); \rightarrow$$

$$\left(\frac{^{207}Pb^*}{^{206}Pb^*}\right) = \left(\frac{(e^{\lambda_{235}t}-1)}{137.88(e^{\lambda_{238}t}-1)}\right), \text{where } 137.88^* = {}^{238}\text{U}/{}^{235}\text{U}$$

**Recently, the natural ratio has been shown to be closer to 137.84 [Hiess, J., Condon, D. J., McLean, N. and Noble, S. R. $^{238}U/^{235}U$ systematics in terrestrial uranium-bearing minerals. Science 335, 1610-1614 (2012)].*

By determining the ^{206}Pb/^{204}Pb and ^{207}Pb/^{204}Pb values of a series of genetically related rocks or minerals you can establish their age of formation.

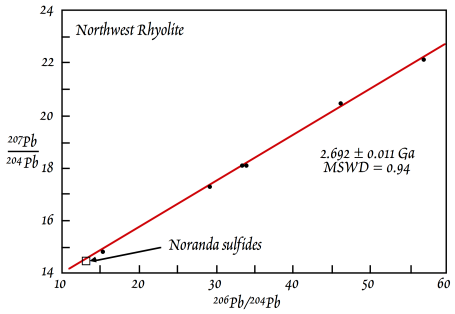

Figure 5: Pb-Pb isochron for volcanic rocks from Quebec, Canada, Noranda Cu-Zn sulfide deposit. Fig from W. White Isotope Geochemistry textbook

D. *Determining Th/U ratios two ways*

Although, often considered to be geochemically similar, Th and U can fractionate and so this ratio can vary in the Earth. The chondritic Th/U ratio is taken to be ∼3.9, whereas the modern mantle has a low Th/U ratio (∼2.5 to 3) and the continental crust has a complementary high ratio (≥4.2). However, these values can be tested by both the measured Th/U ratio and the time integrated ratio from their decay schemes.

Above κ was defined as the molar ratio of ^{232}Th/^{238}U. By subtracting the planetary initial Pb isotopic ratio ratio from the decays products of these two systems we can determine the time-integrated Th/U ratio.

$$\left(\frac{^{208}Pb^*}{^{206}Pb^*}\right) = \left[\left(\frac{^{208}Pb^*}{^{204}Pb^*}\right)_{measured} - \left(\frac{^{208}Pb^*}{^{204}Pb^*}\right)_{CanyonDiablo}\right] / \left[\left(\frac{^{206}Pb^*}{^{204}Pb^*}\right)_{measured} - \left(\frac{^{206}Pb^*}{^{204}Pb^*}\right)_{CanyonDiablo}\right]$$

$$\kappa_{Pb} = \left(\frac{(\frac{^{208}Pb^*}{^{206}Pb^*})(e^{\lambda_{238}t}-1)}{(e^{\lambda_{232}t}-1)}\right)$$

The initial Pb isotopic composition for the solar system has been determined from the analyses of troilites (Fe-sulfides) from iron meteorites. These minerals are known to have formed within the first few million years of solar system history and they have high concentrations of Pb and negligible U and Th contents. The solar system initial composition is taken to be (Blichert-Toft et al (2010) *Earth and Planetary Science Letters 300:152-163*):

$^{206}Pb/^{204}Pb$ = 9.3059 (15), $^{207}Pb/^{204}Pb$ = 10.3071 (10), $^{208}Pb/^{204}Pb$ = 29.5319 (29)

– <u>*Note*</u>: Along similar line of reasoning, Claire Patterson (1956, *GCA*) used this primordial lead isotopic compositions to determine the age of the Earth at 4.55 ± 0.07 Ga, an age that we still use today.

The abundance and distribution of thorium (Th) and uranium (U) and its Th/U value have been assess for the bulk silicate Earth (BSE), core, modern mantle and continental crust. These heat producing elements power the Earth's engine and are recorders of atmospheric oxidation and biologically mediated processes. Several thousand measured Th/U values (κ) and the time-integrated Pb isotopic values from the decay of Th and U ($\kappa_{\rm Pb}$) are evaluated for the BSE, continental crust (CC) and modern mantle (MM), with the latter represented by mid-ocean ridge basalts (MORB) and ocean island basalt (OIB). The $\kappa_{\rm Pb}$ values for these complementary enriched and depleted domains of the BSE (i.e., $^{CC}\kappa_{\rm Pb}$ = 4.1 ± 0.2 and $^{MM}\kappa_{\rm Pb}$ = 3.8 ± 0.1, respectively) narrowly bracket the solar system initial ($^{SS}\kappa_{\rm Pb}$ = 3.88 ± 0.02) with an uncertainty of $\leq \pm 5\%$) and demonstrate that negligible Th/U fractionation accompanied accretion, core formation, and crust - mantle differentiation. Experimental studies find marked differences in the partitioning of U and Th during core formation and thus, the $^{BSE}\kappa_{\rm Pb}$ of 3.9 ± 0.2 dictates that Th and U were excluded from the core. Small differences between the $^{CC}\kappa_{\rm Pb}$ and $^{MM}\kappa_{\rm Pb}$ reveals that U^{6+} recycling back into the mantle has either been a relatively recent process or that limited recycling followed atmospheric oxygenation at 2.4 Ga and evolved slowly with time.

E. *Re → Os and Pt → Os isotope systems*

The β decay of ^{187}Re → ^{187}Os ($t_{1/2}$ 43 Ga) and the α decay of ^{190}Pt → ^{186}Os ($t_{1/2}$ 650 Ga) are potential geochronmeters, with the former being most useful for Mo deposits. Both elemental ratios of Re/Os and Pt/Os and their isotopic ratios can be used to show that the Earth's mantle has chondritic proportions of these elements, with uncertainties on the order of only a few percent. This observation is highly significant

because it limits the potential processes that operated during core formation. These elements along with Ru, Rh, Pd and Au are classified as the highly siderophile elements (HSE), which means that their metal-silicate partition coefficients ($^{metal-silicate}D_{HSE}$) are order $>10^3$ to 10^6 during core formation.

Such high partition coefficients belie the fact that their abundances in the mantle are estimated at 10^{-3} times chondritic levels. Consequently, these observations lead to the hypothesis called the *Late Veneer*. This hypothesis holds that the Earth's mantle received it complement of HSE through the addition of meteoritic material after core formation (and cessation of mass exchange). The mass of this meteoritic addition is estimated to be on the order of $\leq 1\%$ the mass of the Earth, which is approximately a lunar mass. It is speculated that this meteoritic addition occurred perhaps during the episode that accompanied the *Late Heavy Bombardment* (some 4.2 to 2.8 Ga) that produced the enormous lava-filled craters on the Lunar surface.

Moreover, experimental studies have shown that over a range of pressure and temperature conditions envisaged for core formation, the ($^{metal-silicate}D_{HSE}$) should differ from one another by at least an order of magnitude. Consequently, chondritic Os isotopic ratios define the time-integrated conditions for Re/Os and Pt/Os values of the mantle and it too re-enforces the requirement for invoking the *Late Veneer* hypothesis.

F. *Tungsten (W) isotopes*

The double β decay of ^{182}Hf $\rightarrow$ ^{182}W ($t_{1/2}$ 8.9 Ma), has a short β decay step at ^{182}Ta ($t_{1/2}$ 61.5 minutes) before reaching ^{182}W. Given the half-life of this system, it reached its usefulness at $\approx$50 Ma (approximately 5 half-lives) after t_0, the time of solar system formation. Importantly, Hf is a lithophile element and W is a siderophile element; the Bulk Silicate Earth (BSE) hosts nearly 100% of the planet's budget of Hf, whereas the core is estimated to have about 90% of the planetary budget of W, with the remainder in the BSE. [Please keep in mind that all elements have a $^{metal-silicate}D$ value; thus a $^{metal-silicate}D_W \sim 10^3$ and $^{metal-silicate}D_{Hf} \sim 10^{-3}$ implies some, albeit negligible amounts, of Hf in the Earth's core.]

In 2002 it was demonstrated that the ^{182}W/^{184}W composition of the BSE is 0 $\epsilon_{^{182}W}$ is distinctly higher than that of chondritic meteorites (i.e., $\sim$-2 $\epsilon_{^{182}W}$ units), implying that much of the W in the Earth was isolated (extracted into the core) from the decaying ^{182}Hf atoms. This difference, given that both Hf and W are refractory elements and are therefore accreted on to the Earth in chondritic proportions, meant the core's ^{182}W/^{184}W composition (i.e., $\sim$2.2 $\epsilon_{^{182}W}$ units) is slightly lower than that of chondrites in order to balance the bulk Earth's ratio.

The consequence of this isotopic observation finally provided a paramount and unequivocal constraint on the timing of core formation. Prior to this observation, the U-Pb system provided a weak constraint that was consistent with core forming over the first 100 Ma of Earth's history (i.e., 4.45 Ga). Importantly, to explain this 2 $\epsilon_{^{182}W}$ unit difference between the BSE and chondrites, models required that the mean life time of core formation could be as little as $\sim$12 Ma or as long as $\sim$150 Ma after t_0. The former age was the minimum time over which the isotopic differences could have been established, while the latter age reflected the latest age of Moon formation. The importance of Moon formation comes from the fact that its bulk composition (and oxygen isotopic composition) matches that of the BSE; thus the Moon formed from a differentiated Earth that gave up a negligible core contribution.

The most recent constraint on the upper age limit for core formation comes from Barboni et al (2017, Sci. Advances). Using U-Pb concordant ages for lunar zircons and Hf isotopic composition for these same samples, they showed that the Moon had formed by at least 4.51 Ga and thus core formation is now known

to have occurred sometime between ∼10 and 50 Ma after t_0, most likely ∼30 ± 20 Ma after the start of the solar system.

Finally, Kruijier et al (2017, PNAS) showed that iron meteorites, the earliest forming differentiated bodies in the solar system, formed and separated cores and mantles under magmatic conditions within the first 1 to 3 Ma of solar system history. These bodies formed before the accretion of chondritic parent bodies. Their data provide clear evidence that two groups of meteoritic materials, which they called the non-carbonacous (NC) and carbonacous (CC) meteorites, necessarily formed in different locations in the early nebula because of their distinctive isotopic composition, which included markedly different Supernovae-derived, nucleuogenic contributions. From this they concluded that much of Jupiter (e.g., ≥50 Earth masses, note Jupiter is 320 times the mass of the Earth) must had already formed (accreted in <1Ma) in order to have a second massive body, beside the Sun, dispersing and sorting material into different regions in the nebular disk.

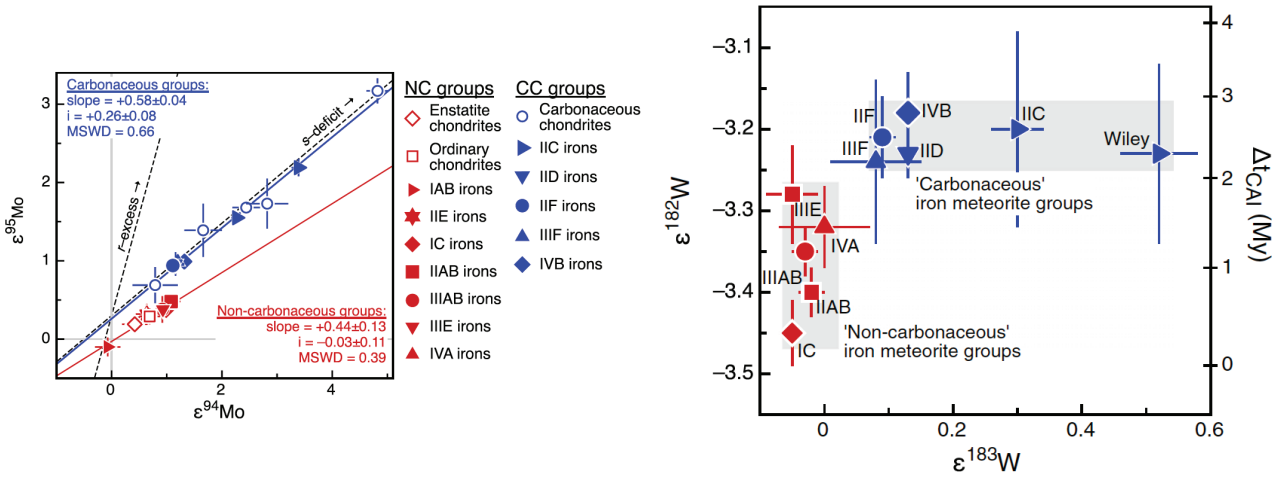

Figure 6: Mo and W isotopic dichotomy of iron meteorite groups