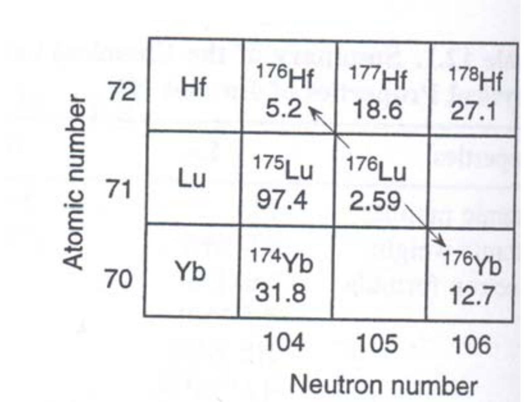
Lu-Hf method

^{176}Lu decays to ^{176}Hf by β-decay,

decay process: $^{176}Lu \rightarrow {}^{176}Hf + \beta^{-} + \nu$

^{176}Lu=2.6%
1 other isotope
Lu = HREE

^{176}Hf=5.2%
5 other isotopes



Hf resembles Zr in its crystal chemical behaviour

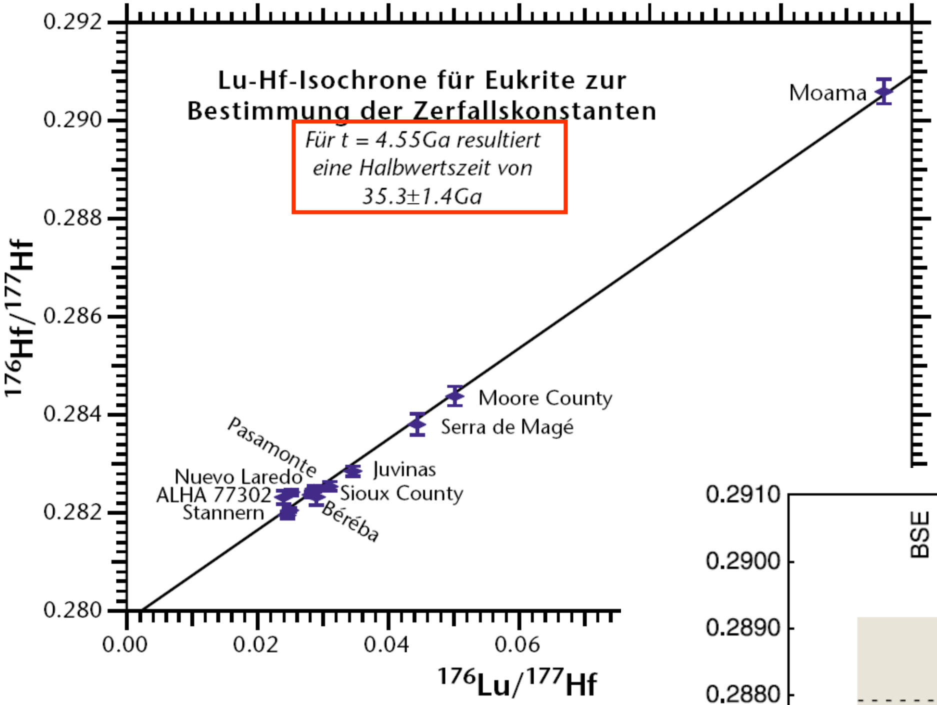
Lu-Hf concentrations

Lu- und Hf-Gehalte sowie Lu/Hf-Verhältnisse von Gesteinen und Mineralen

	ppm Lu	ppm Hf	$^{176}Lu/^{177}Hf$
Chondrite	0.033	0.14	0.033
Achondrite	0.25	1.25	0.028
MORB	0.5 (0.1–1)	2.5 (1–15)	0.005–0.05
kontinentale Basalte	0.25 (0.1–0.7)	4 (2–20)	0.002–0.02
granitische Gesteine	0.5	7	0.010
Sandsteine, Quarzite	0.05–0.5	0.5–20	0.001–0.04
Tonschiefer	0.15–0.8	1–7	0.01–0.03
rote Tiefseetone	0.8–3	3–5	0.03–0.1
Zirkon	10–100	10000	<0.002
Granat	0.5–5	<1	>0.1

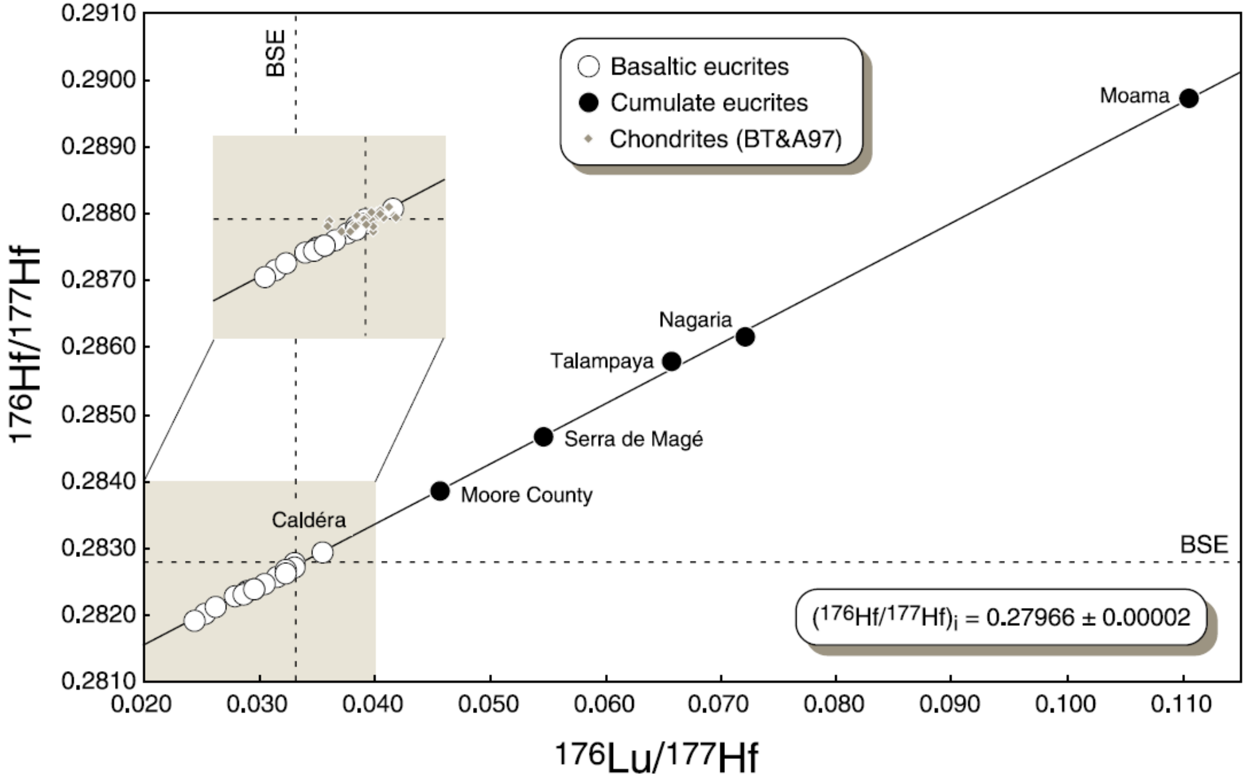
Stosch: Isotopengeochemie 2004

Lu-Hf method



Patchett & Tatsumoto (1981)

Blichert-Toft et al. (2002)



Lu-Hf calibrations

^{176}Lu decay constant

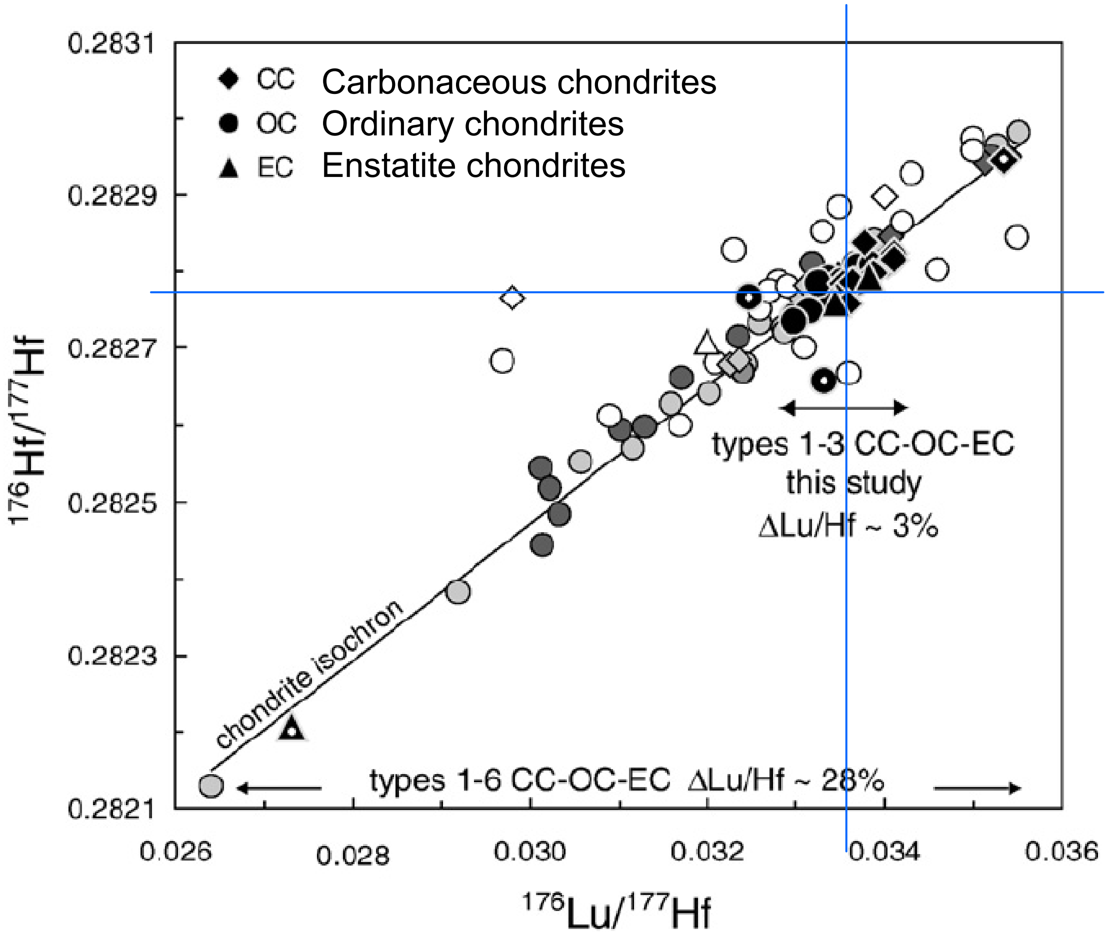
	λ	$T_{1/2}$
Tatsumoto et al. (1981):	$1.94 \times 10^{-11}\ yr^{-1}$,	35.7 Ga
Scherer et al. (2001):	$1.875 \times 10^{-11}\ yr^{-1}$,	37.2 Ga
Bizzarro et al. (2003):	$1.983 \times 10^{-11}\ yr^{-1}$,	35.0 Ga
Söderlund et al. (2004):	$1.867 \times 10^{-11}\ yr^{-1}$,	37.1 Ga

Lu-Hf CHUR values

Bouvier et al. (2008):

$^{176}Lu/^{177}Hf = 0.0336 \pm 1$

$^{176}Hf/^{177}Hf = 0.282785 \pm 11$



Lu-Hf method

TIMS analysis of Hf limited by poor ionisation efficiency

Better data obtained by plasma-source mass spectrometry

Hf isotope ratios can be expressed using the ε-notation developed for Nd (parts per 10 000 deviation from the chondritic evolution line). Unfortunately, changes in the Lu decay constant also have a major impact on the calculation of ε-Hf values because they change the slope of the chondritic growth line.

$$\varepsilon_{Hf} = \left[\frac{\left({}^{176}Hf / {}^{177}Hf \right)_{Probe}}{\left({}^{176}Hf / {}^{177}Hf \right)_{Chondrite}} - 1 \right] \times 10^4$$

Blocking temperature of the Lu–Hf system (in garnet) appears to be greater or equal to that of the Sm–Nd system

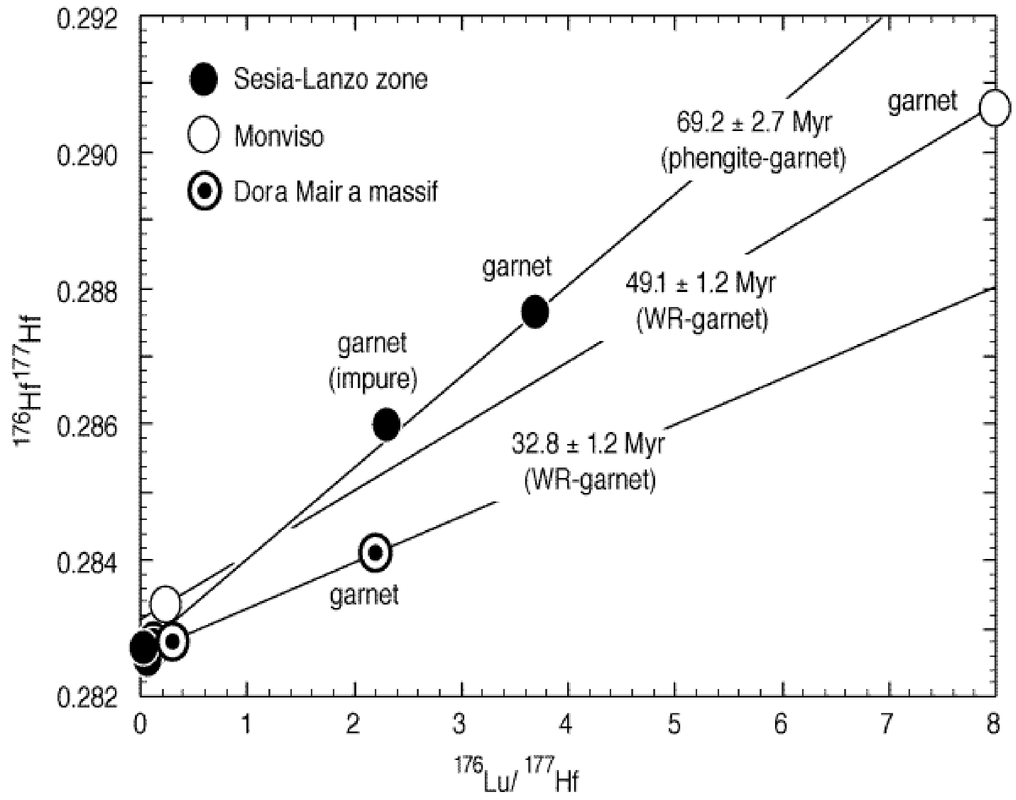
Lu-Hf method

The high Lu/Hf ratios found in garnets make these minerals useful for Lu–Hf dating of metamorphic events.

Eclogites from three units of the western Alps give diachronous Lu–Hf garnet ages.

→ Alpine high-pressure metamorphism did not occur as a single episode

Duchěne et al. 1997 Nature **387** p.586



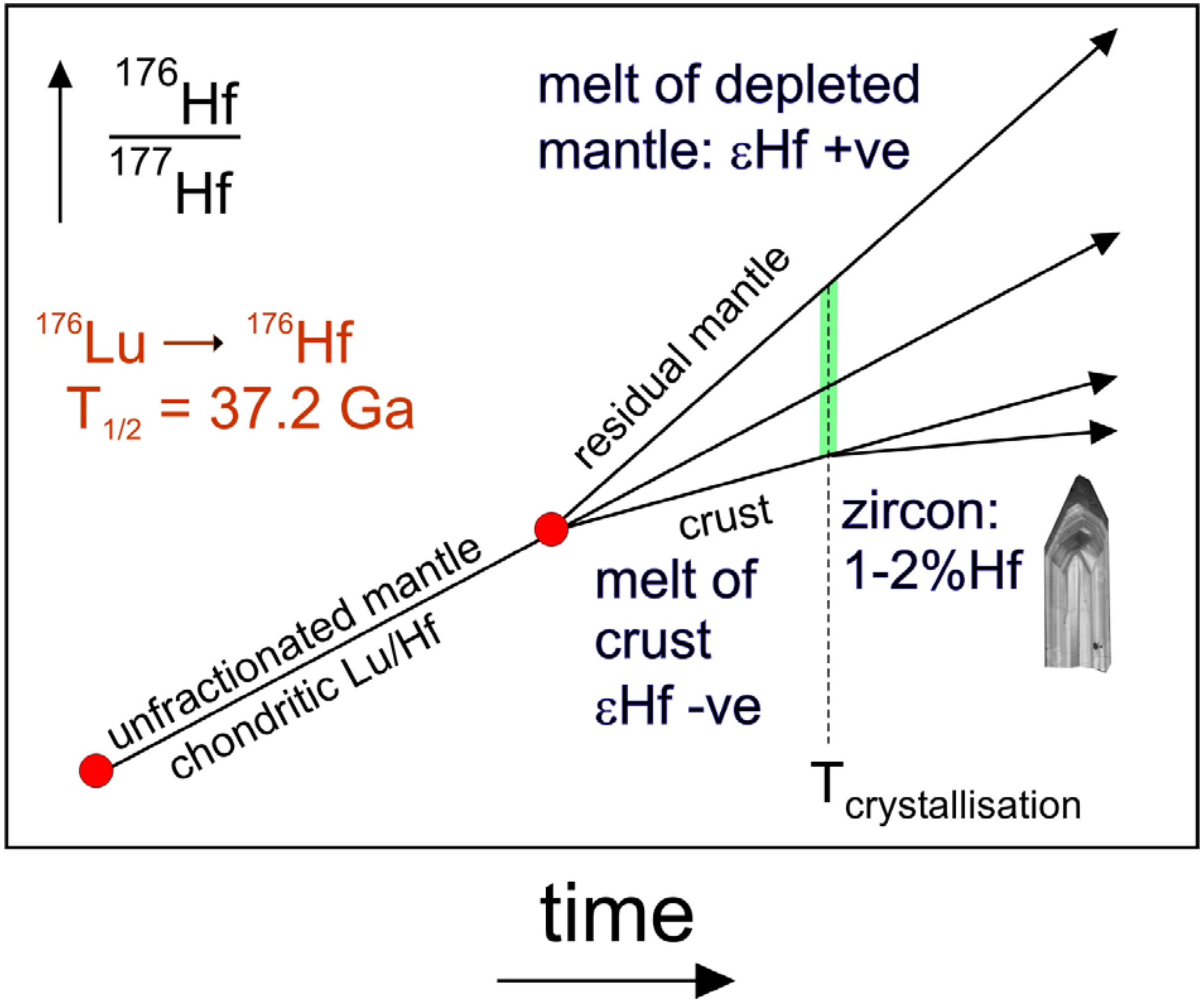
But: Discordance in metamorphic garnet, if the rock contains pre-metamorphic zircon grains which did not equilibrate with garnet under peak metamorphic conditions.

Hf isotope evolution

Zircon is an excellent mineral for Hf isotope analysis for several reasons:

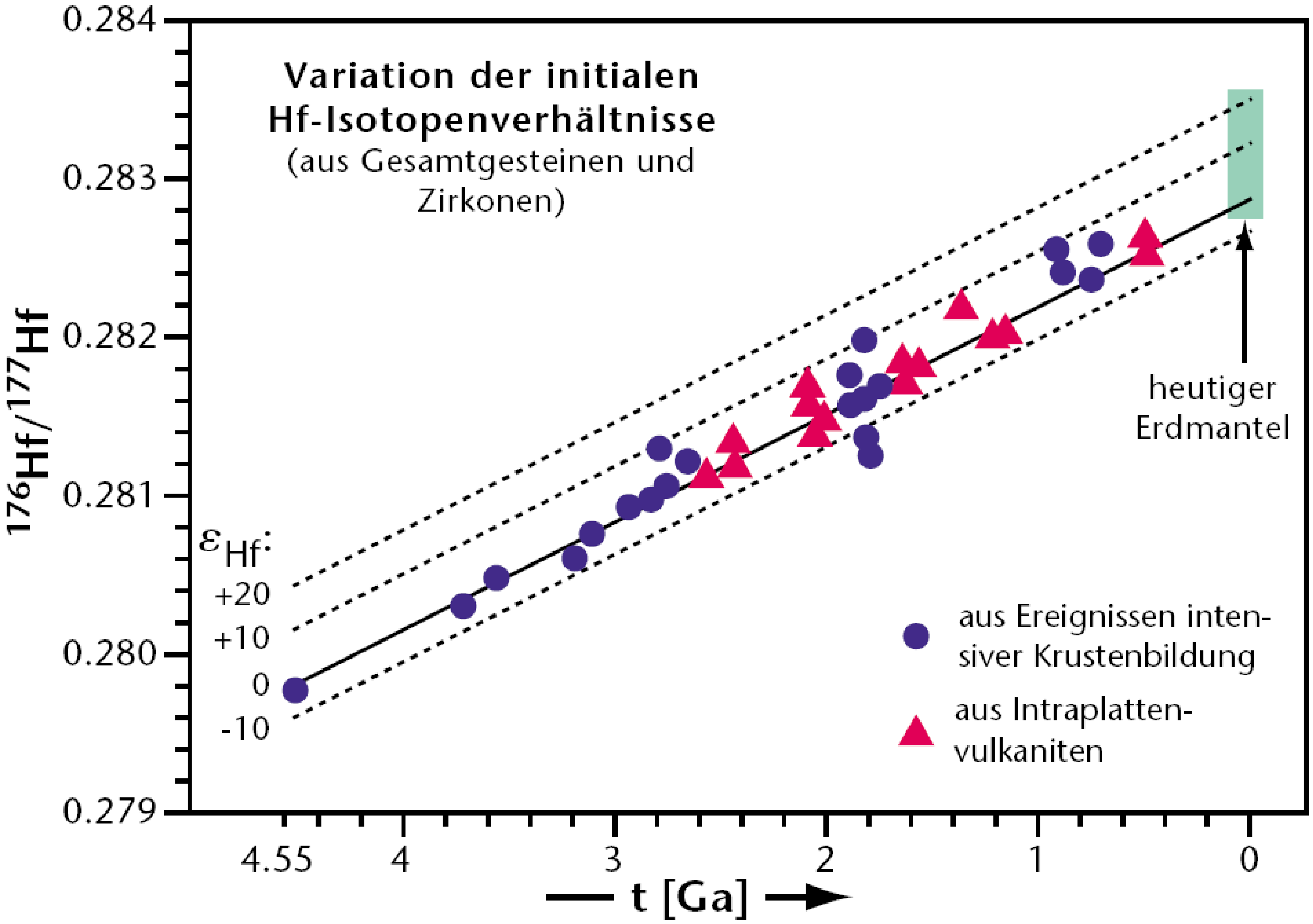
1. Hf forms an integral part of the zircon lattice, which is therefore very resistant to Hf mobility and contamination.
2. The very high Hf concentrations in zircon (ca. 10 000 ppm) yield very low Lu/Hf. Zircon essentially freezes the $^{176}Hf/^{177}Hf$ ratios of the source magmas.

Hf isotope evolution

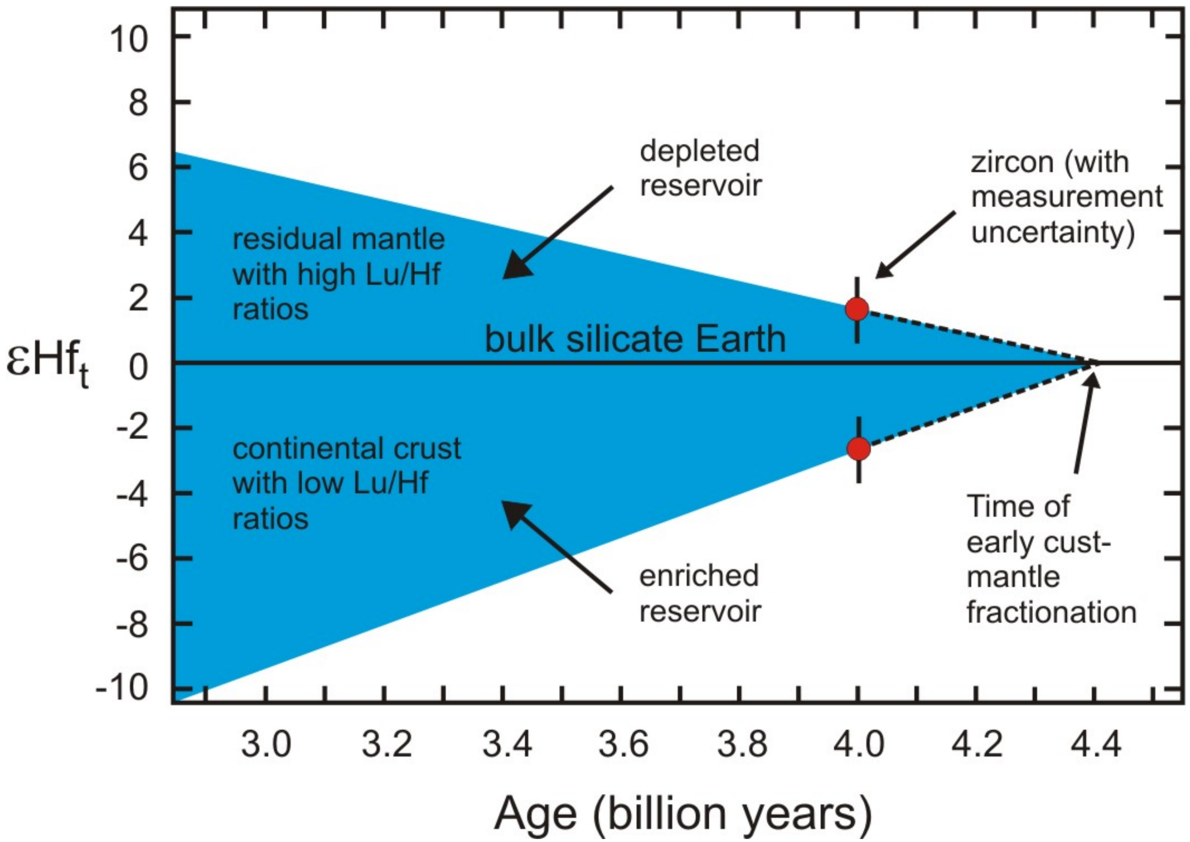


Hf isotope evolution

Stosch: Isotopengeochemie 2004



Hf isotope evolution



Plot of εHft versus age. The age refers to the U-Pb age derived from single zircon crystals. εHft represents the deviation of the $^{176}Hf/^{177}Hf$ ratio (in parts per 10 000 and back calculated to the time of zircon formation) from this ratio for the bulk silicate Earth, which is modeled on the composition of chondritic meteorites: $\varepsilon Hf = [(^{176}Hf/^{177}Hf)_{sample}/(^{176}Hf/^{177}Hf)_{CHUR} - 1] \times 10^4$.

Consider the case of two data points from 4.0 billion year old zircon crystals, one with a positive, one with a negative εHft deviation from bulk silicate Earth.

A positive εHft value indicates that the material which melted to form the magma from which the zircon crystallized was derived from a mantle which had experienced an earlier depletion event, i.e., period of melt removal. The zircon with the negative εHft value indicates that pre-existing continental crust was involved in magma genesis. Back projection of the Hf isotope growth lines with the bulk silicate Earth (dotted lines, based on Lu/Hf ratios) yields ages of ~4.4 billion years for the time of development of the two distinct reservoirs. **The Lu-Hf systematics of zircon provides progress in understanding the early development of crust/mantle differentiation.**

Siebel, W., Van den haute, P. (2007) RADIOMETRIC DATING AND TRACING

Lu-Hf and Sm-Nd isotope correlation

Vervoort et al. 1999 EPSL 168

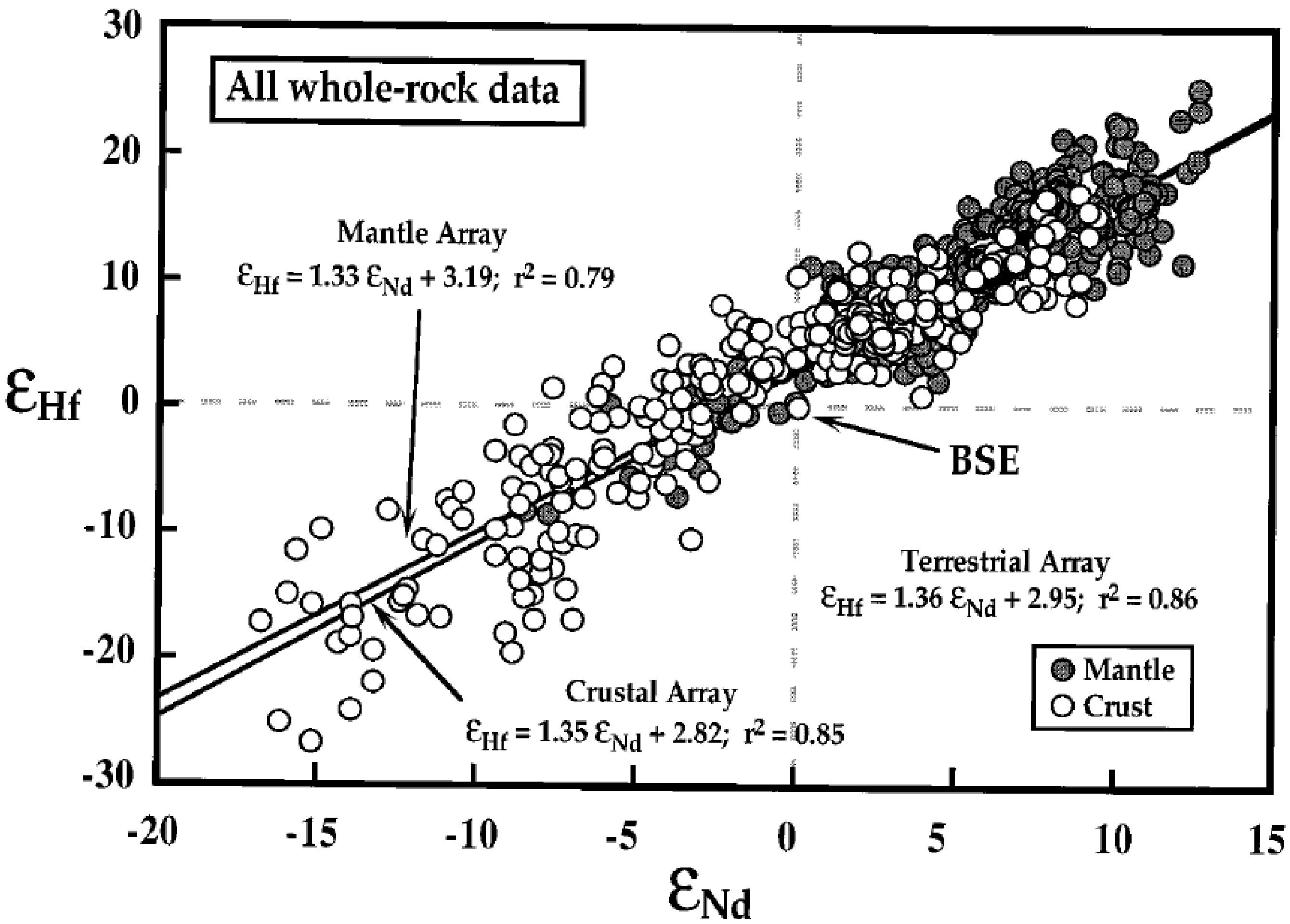
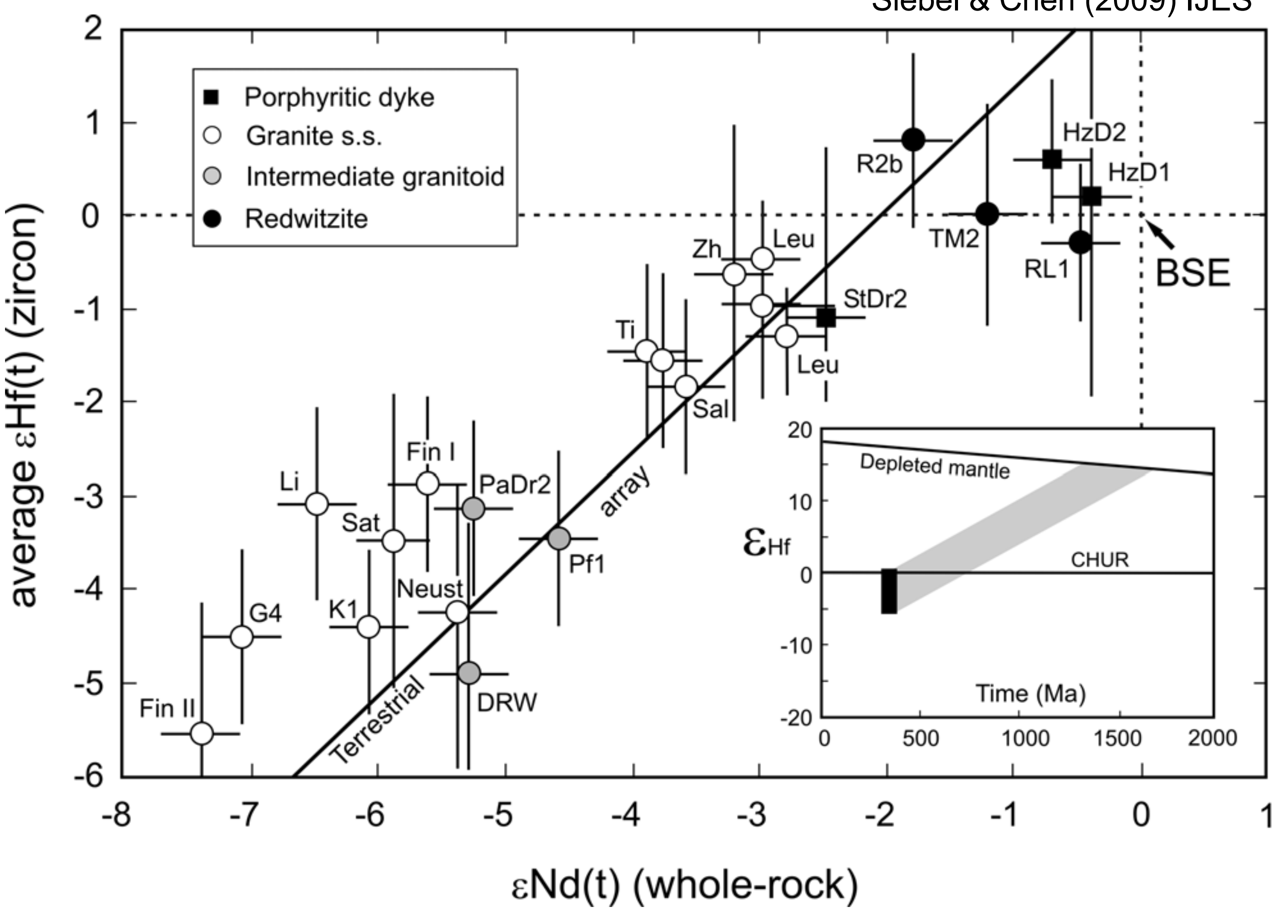


Fig. 5. Initial ε_{Nd} vs. ε_{Hf} for all terrestrial whole-rock samples in relation to bulk silicate Earth (BSE). All data fall along a single coherent array ($\varepsilon_{Hf} = 1.36\varepsilon_{Nd} + 2.95$) known as the 'terrestrial array', and is composed of two complementary arrays: the mantle array ($\varepsilon_{Hf} = 1.33\varepsilon_{Nd} + 3.19$) and the crustal array ($\varepsilon_{Hf} = 1.35 + 2.82$). All arrays pass above BSE as currently defined. See text for further explanation. Data sources as in Figs. 3 and 4.

Lu-Hf and Sm-Nd isotope correlation

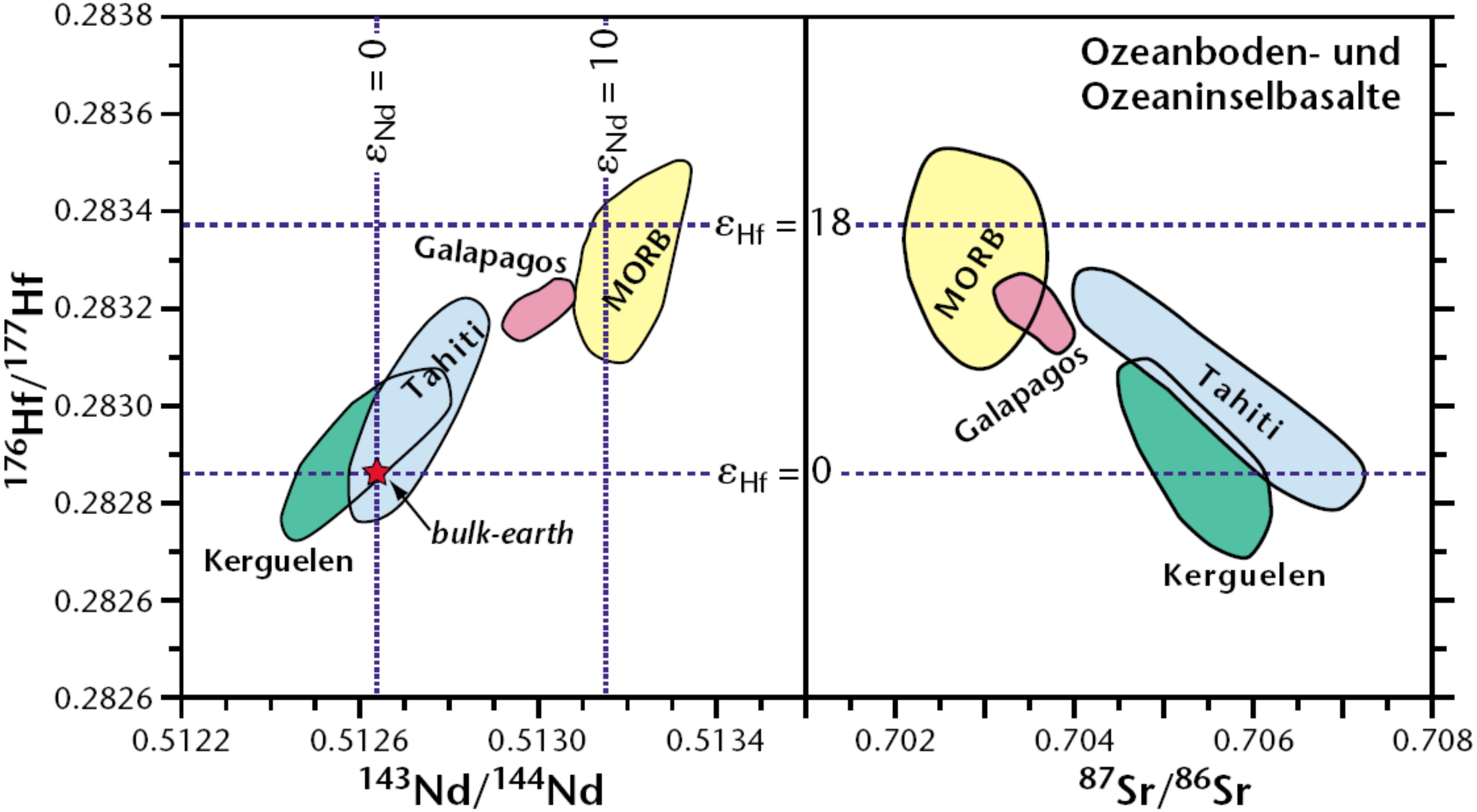
Siebel & Chen (2009) IJES



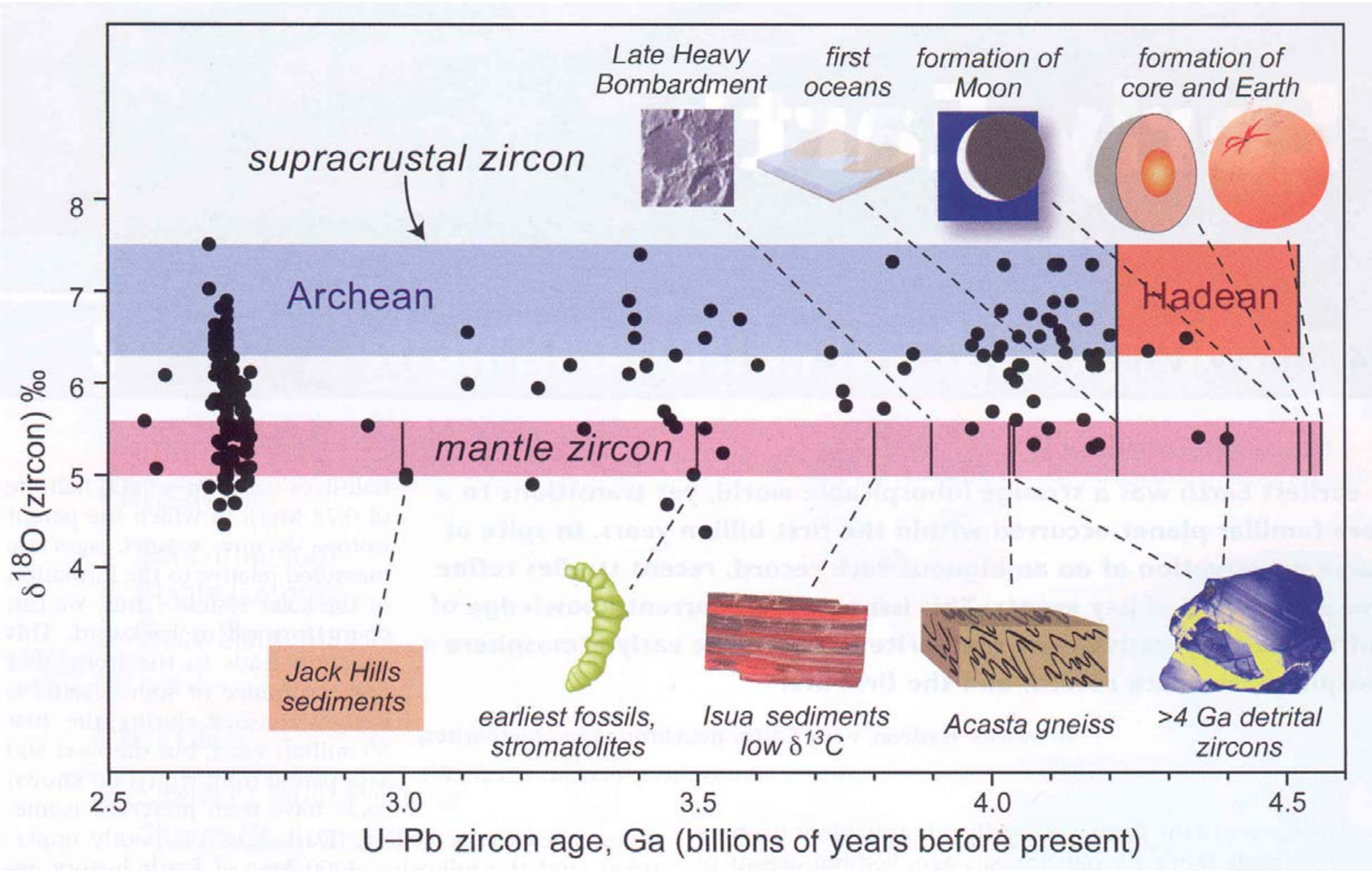
εHf values of melt-precipitated zircons versus εNd whole rock values in Bavarian granitoids at the time of crystallization. The slope of the trend defined by the granitoids overlaps the overall trend for terrestrial samples; terrestrial array (solid trend line) from Vervoort et al. (1999).

Hf—Nd—Sr isotope correlation

Stosch: Isotopengeochemie 2004

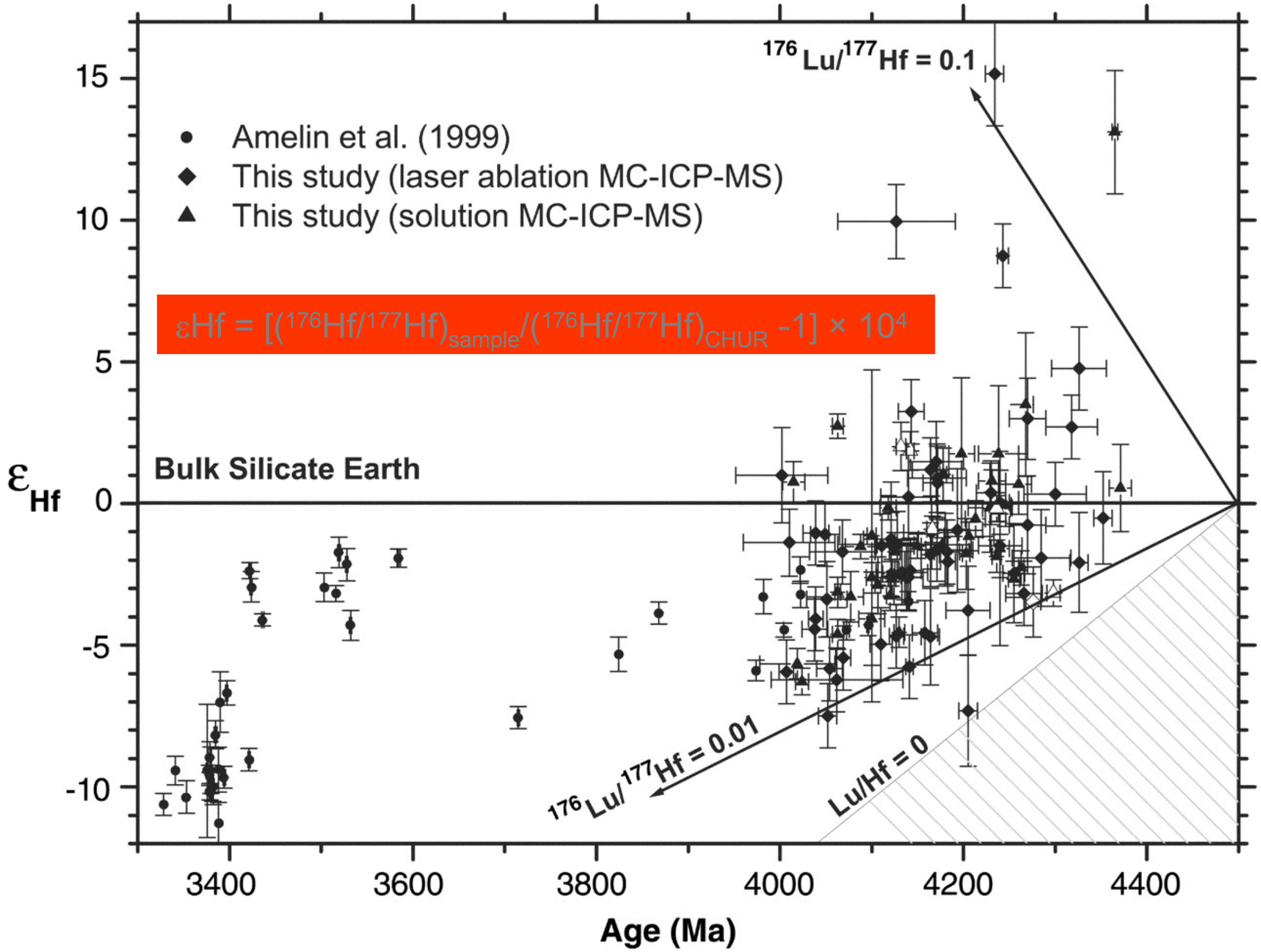


Key events in the first billion years of Earth history



Valley: Elements 2, 2006

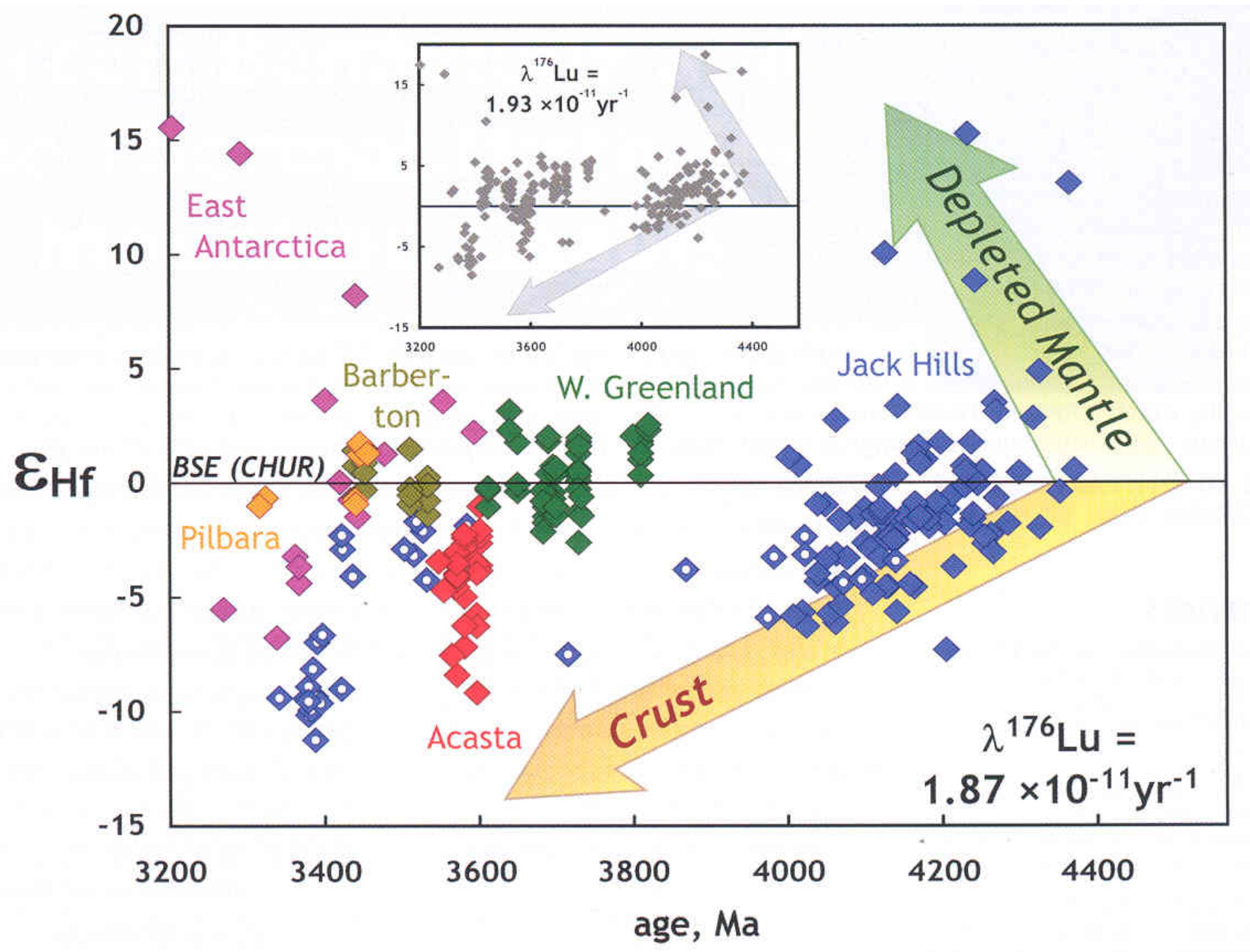
Plot of {epsilon}Hf(T) versus age for new MC-ICP-MS Hf isotope analyses recalculated using the "terrestrial" 176Lu decay constant



T. M. Harrison et al., Science 310, 1947 -1950 (2005)

Published by AAAS

The Earth's early differentiation history

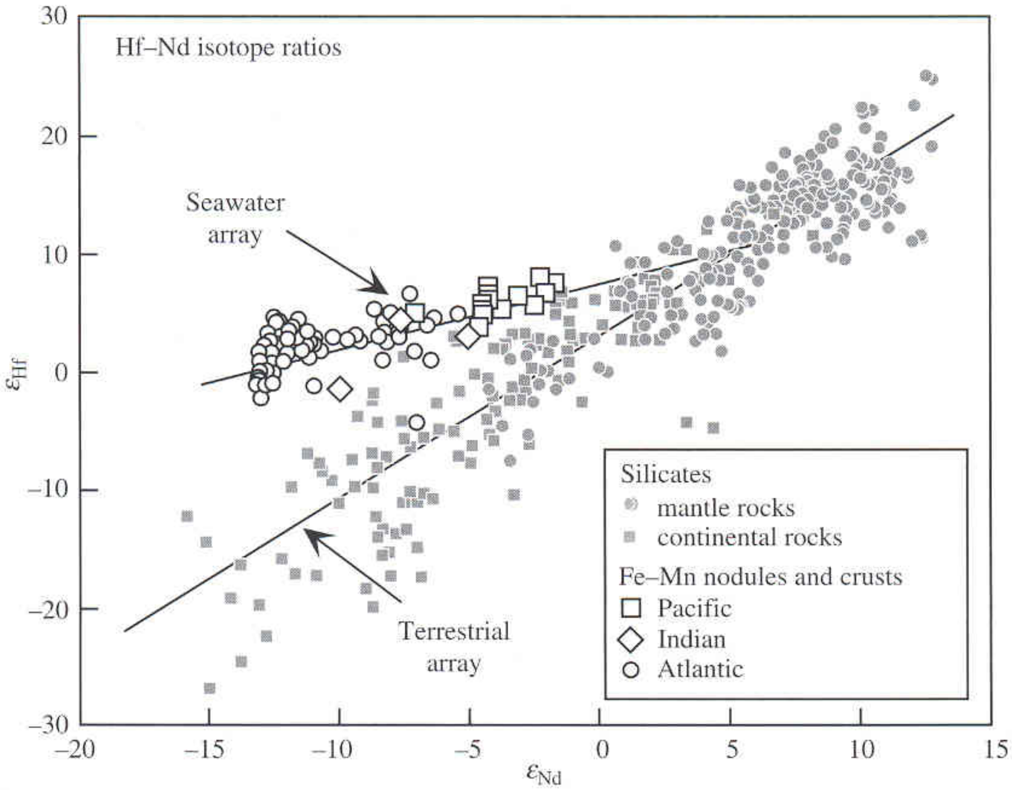


Scherer, Whitehouse, Münker: Elements 3, 2007

Nd-Hf in the oceans

Hf: shows relative homogeneous signature in seawater.
Mixing between crustal (negative) and mantle (basaltic crust, pos. Hf values) sources.
Crustal source reflects composition of **non-zircon-bearing sediments.**
Mantle-like end member with high εHf (~ +16).

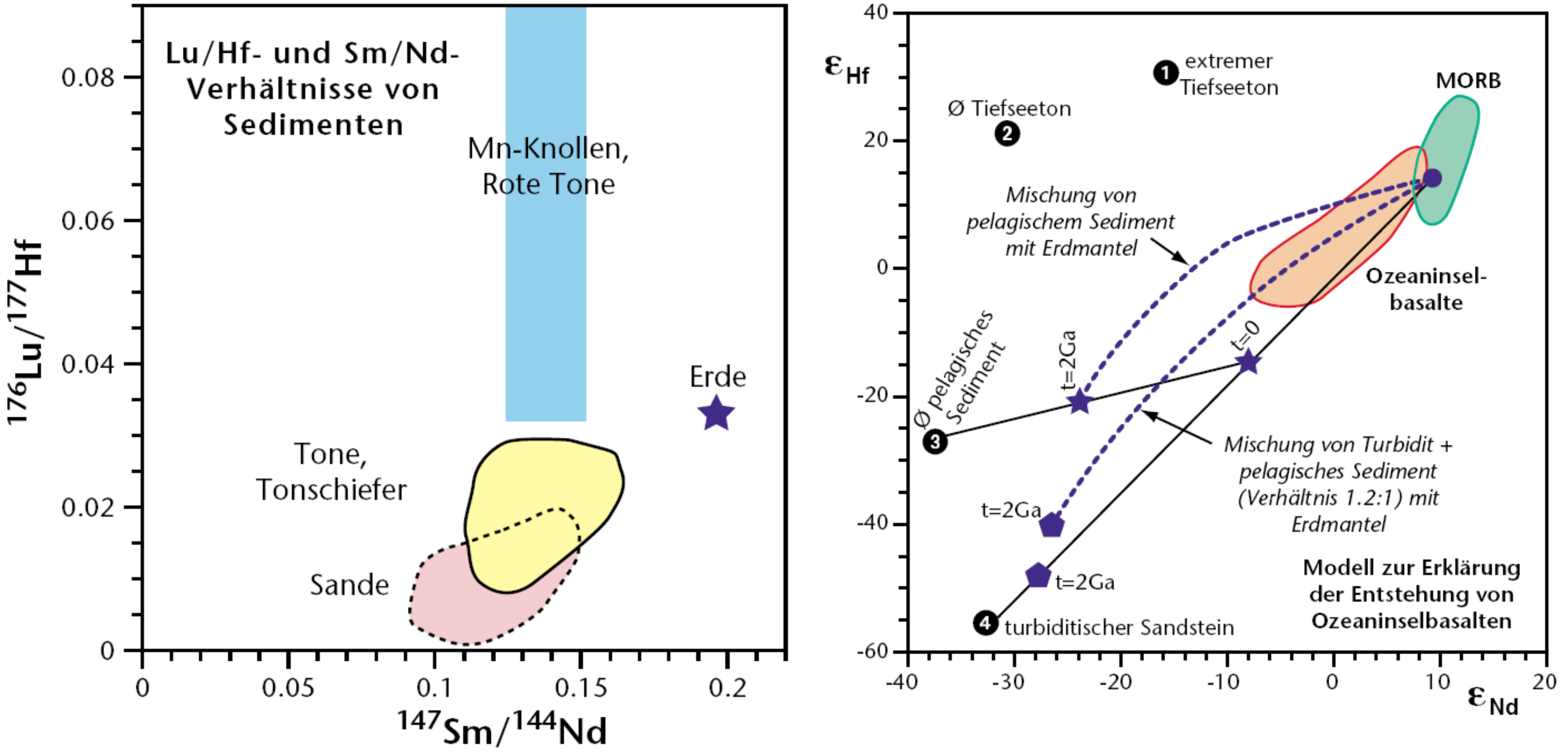
Deduced range of seawater Hf is much smaller than range between end-members → Hf must have a long residence time in seawater (longer than Nd, shorter than Sr), to allow such high degree of homogenisation.



from Goldstein & Hemming (2004): Treatise on Geochemistry, Vol.6

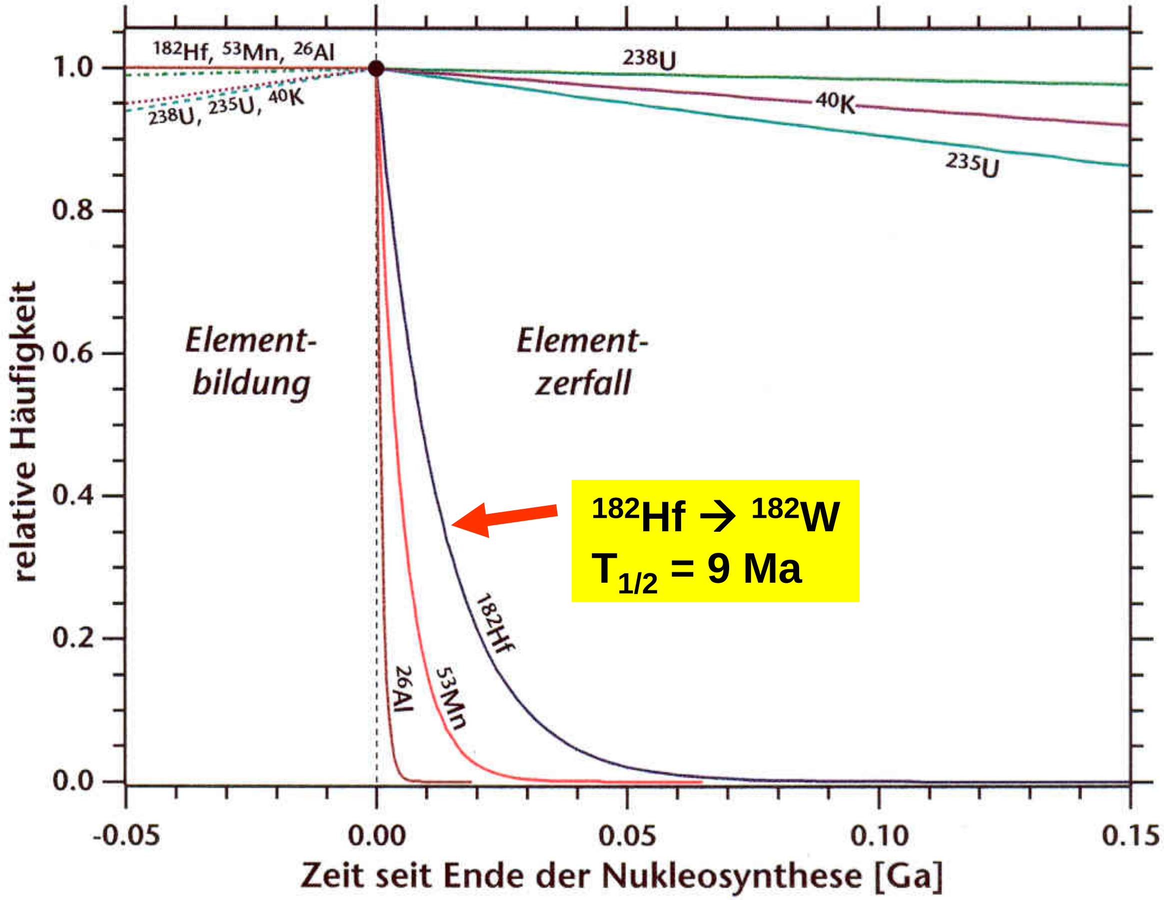
Nd-Hf in marine sediments

Stosch: Isotopengeochemie 2004



Core formation from Hf-W chronometry

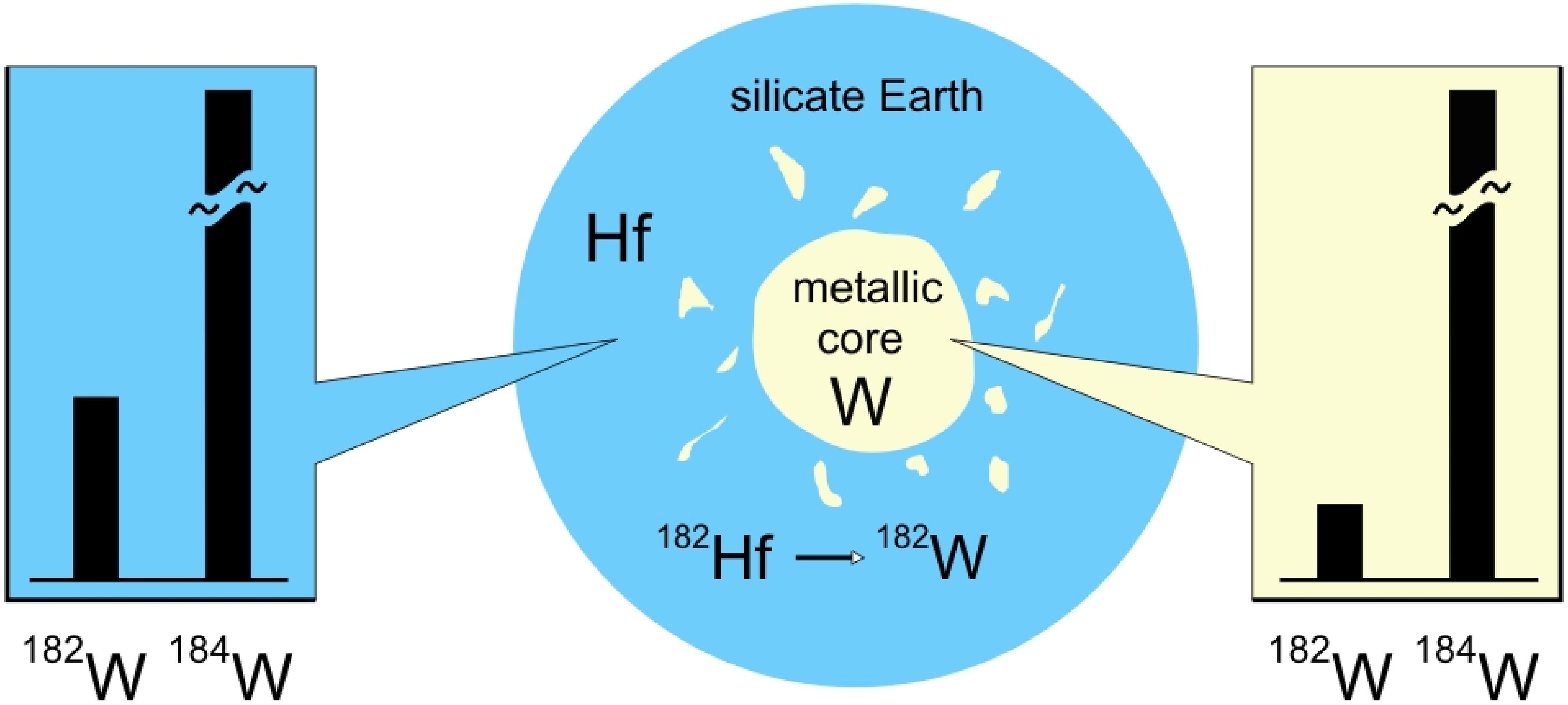
Stosch: Isotopengeochemie 2004



^{182}Hf → ^{182}W

$T_{1/2}$ = 9 Ma

Core formation from Hf-W chronometry



Core formation of the Earth based on Hf-W chronometry. Hafnium and tungsten are fractionated by core formation because tungsten tends to partition into metal whereas hafnium remains in the silicate portion of the Earth. If core formation took place during the lifetime of ^{182}Hf (half-life = 9 Ma), the silicate Earth must have a higher ^{182}W abundances (or higher $^{182}W/^{184}W$) compared to the core. High precision isotope analyses show that the silicate Earth indeed has a higher $^{182}W/^{184}W$ ratio compared to undifferentiated chondrites implying that the core formed largely during the lifetime of ^{182}Hf, i.e., within the first 30 million years.

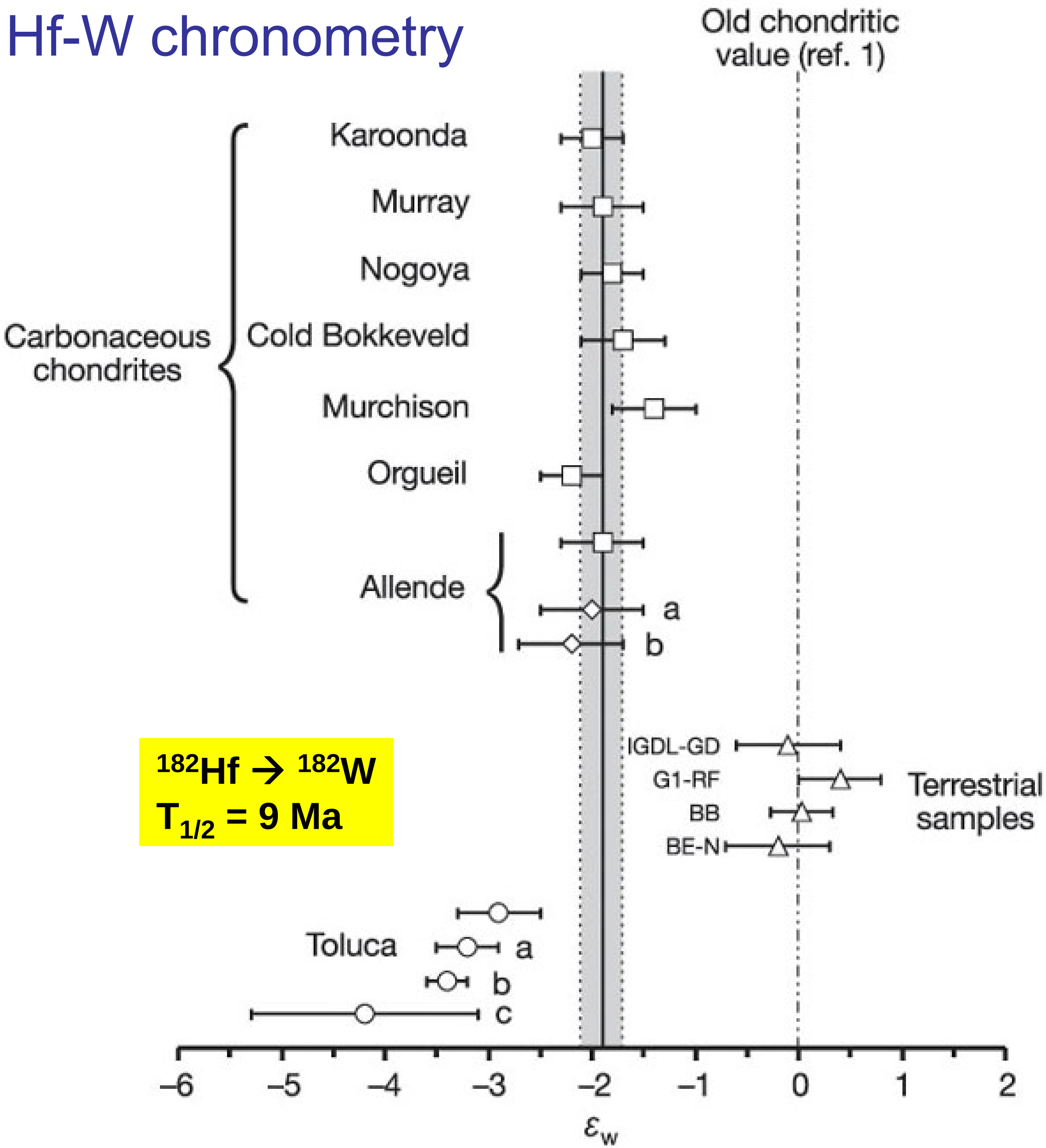
Siebel, W., Van den haute, P. (2007) RADIOMETRIC DATING AND TRACING

Core formation from Hf-W chronometry

The decay of now extinct ^{182}Hf to ^{182}W is an ideal chronometer for tracing the rate of terrestrial core formation because Hf is retained in the silicate mantle while W is largely partitioned into the core during core segregation.

Core formation took place when there was still ^{182}Hf on Earth. The W remaining in the silicate mantle developed an excess abundance of ^{182}W relative to that of chondrites.

Lee & Halliday 1995: Nature 378
Kleine et al. 2002: Nature 418
Yin et al. 2002: Nature 418



$^{182}Hf \rightarrow {}^{182}W$
$T_{1/2}$ = 9 Ma

$$\varepsilon_W = \{[(^{182}W/^{184}W)_{sample}/(^{182}W/^{184}W)_{standard}] - 1\} \times 10^4$$