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Appendix C. New geochemical considerations on the assumed abundances of U, Th, and K

C1. Geochemical Introduction

Geodynamic processes are intrinsically tied to geochemical realities. Therefore the adequateness of a numerical modeling of geodynamics heavily depends on the quality of the geochemical assumptions. A pivotal question is the *initial* chemical composition of the mantle. Apart from the primordial heat, *the distribution of the abundances of the three significant heat-producing elements, U, Th and K, is crucial for powering the mantle motor.*

Palme and O'Neill (2003) recapitulate the knowledge on the major element composition. They compare the mass ratios of Al/Si, Mg/Si, Fe/Si, Na/Si, Zn/Si, S/Si and O/Si between the Sun and the major group of chondritic meteorites, namely CI, CM, CO, CV, H, L, LL, EH, and EL. The best concordance between solar and meteoritic abundances is with CI-meteorites. There are, however, certain deviations. The Earth and carbonaceous chondrites have, e.g., a common depletion of manganese. Obviously, Earth and carbonaceous chondrites commonly keep records of a fractionation process in the inner solar system.

C2. Should we apply a non-chondritic Earth model?

On the other hand, Boyet and Carlson (2005, 2006) analyzed measurements of ^{142}Nd/^{144}Nd in kimberlites, carbonatites, komatiites, ocean island basalts and Pacific and Indian-Ocean basalts. The terrestrial Nd standard has a ^{142}Nd/^{144}Nd about 20 ppm or 18±5 ppm (Jackson and Carlson, 2012) higher than in chondrites. All terrestrial rocks younger than 3.5 Ga have virtually the same ^{142}Nd/^{144}Nd. Evidently, three cases are possible.

I. The Earth accreted from non-chondritic building blocks.

II. The Earth accreted from chondritic meteorites or from differentiated planetesimals that previously formed from chondritic meteorites. The low ^{182}W/^{184}W ratio in iron meteorites (Harper and Jacobsen, 1996; Kleine et al.,

2002; Schoenberg et al., 2002) shows that the already differentiated planetesimals contributed a larger percentage to the accretion of the Earth. A very early differentiation of the antecedent Earth is highly probable. A large early depleted reservoir (EDR) that explains the ^{142}Nd/^{144}Nd observations was formed and, complementary a smaller early enriched reservoir (EER).
Sub-case IIa: The EER was near the Earth's surface and was lost very early through collisions (O'Neill and Palme (2008)).
Sub-case IIb: There is a mechanism that keeps the EER somewhere in the deeper mantle and, furthermore, prevents sampling. Relating to the further thermal and chemical evolution of the Earth, the cases I and IIa result in much the same thing. Boyet and Carlson (2006) emphasize that the abundances of U, Th and K in the EDR are only 60% of that of a chondritic mantle. In this case, a high percentage of the laterally averaged surface heat flow, *qob*, would originate from the primordial heat. The present-day value of the laterally averaged heat flow, q_c, at the core-mantle boundary (CMB) would be much higher than previously thought. For a case of type IIa, O'Neill and Palme (2008) deduce that, satisfying the Sm-Nd and Lu-Hf constraints, the U and Th abundances in the Earth's mantle are 10 to 30% lower than in a chondritic mantle. White and Morgan (2011) show that, in compliance with the mentioned requirements, a steady-state geodynamics or a geodynamics with *small* variations of the spatially averaged kinetic energy of mantle creep is impossible. If I or IIa would be true then we would find, in case of *heavy* depletion, an indication that the present-day rate of slab subduction is not sustainable or, in case of *moderate* depletion, the present-day mantle is in a phase of faster than normal plate motion.

It is possible that, in the meantime, the EDR has been detected. The ϵ^{143}Nd of high ^{3}He/^{4}He Baffin Island lavas (Stuart et al., 2003; Starkey et al., 2009) coincides with the ϵ^{143}Nd value of EDR (Jackson et al., 2010; Jackson and Carlson, 2012). – It is feasible to run the program of our numerical model, i.e. Terra, with a chemical-differentiation extension, for *different* geochemical initial assumptions. The calcium-aluminum rich inclusions (CAIs) in the carbonaceous chondritic meteorites have only a small scatter of age determinations. Jacobsen et al. (2008), e.g., found an age of 4567.6±0.4 Ma for a CAI from the Allende chondrite. Following Carlson and Boyet (2009), we assume an age of 4567.6 Ma for the start of the radioactive decay of U, Th and K in our model. The ^{182}W/^{184}W ratio of the most iron meteorites scarcely differ from the CAI initial ^{182}W/^{184}W. Therefore Carlson and Boyet (2009) assume that the metal-silicate differentiation occurred within less than

1 Ma. According to Wood et al. (2006), the “depleted” ^{182}W isotopic composition in iron meteorites shows that the core formation in asteroidal parents took place in less than 5 Ma. However, the accretion of the Earth from planetesimals with metallic iron cores and the Earth's core segregation took 30 to 40 Ma. The latter exact numbers are not used in our dynamic model because we can start the run only for that instant of time when the mantle is nearly totally in the crystalline state. The reason for this is our determination of the viscosity profile from solid-state considerations and the fact that the mantle was essentially solid in the course of Earth's history. If too large volumes of the mantle are still fluid, the runs result in a numerical breakdown.

C3. Recent evidence of a chondritic mantle model

Similar to the mentioned manganese depletion, the terrestrial planets reveal also other departures from the rest of the solar system. Marty et al. (2010, 2011) show that the terrestrial values of $^{15}N/^{14}N = 3.676 \times 10^{-3}$ and $D/H = (1.5 \pm 0.3) \times 10^{-4}$ are similar to the $^{15}N/^{14}N$ and D/H values of Venus, the interior of Mars, CI and CM carbonaceous chondrites. We suppose that CI and CM are the most primitive carbonaceous chondrites. Also the $\Delta^{17}O$ of the Earth is close to the $\Delta^{17}O$ of CI carbonaceous chondrites. On the other hand, the $^{15}N/^{14}N$ ratio of the solar wind is $(2.178 \pm 0.024) \times 10^{-3}$ (Marty et al., 2011). This value is close to the $^{15}N/^{14}N$ ratio of Jupiter. So, the Earth and CI/CM chondrites are enriched in ^{15}N relative to the protosolar nebula (PSN) if the present-day Earth is considered largely consistent with this nebula. The D/H value of the PSN is $(2.5 \pm 1.5) \times 10^{-5}$. Therefore also deuterium is enriched in Earth and CI/CM chondrites in comparison to the PSN. Marty (2012) reveals that, for the bulk Earth, water, carbon, neon, argon and krypton are in *chondritic* relative proportions. Formerly, proposals have been made that the volatiles of the Earth origin from comets. According to Marty et al. (2010), however, comets show ratios of $^{15}N/^{14}N = 7.5 \times 10^{-3}$ and $D/H = 3.0 \times 10^{-4}$. Therefore it is probable that the Earth's material is essentially derived from carbonaceous chondrites or asteroidal parents that stem from chondritic matter, presumably mixed with a small solar component because the accretion took place earlier than previously expected.

The clustering of zircon age determinations and the present work show that the growth of continental crust (CC) was episodic, also during the Archean. Each episode of CC-growth starts with rocks having a *chondritic* ϵ_{Hf} (Moyen and Martin, 2012) that, after the beginning of the episode, gradually evolves towards negative ϵ_{Hf} values. The Archean grey gneisses in the trondhjemite, tonalite and granodiorite (TTG) domains exhibit a ^{176}Lu/^{177}Lu ratio that remained nearly constant throughout the Archaean and persisted close to the *chondritic* value of 0.0336 (Bouvier et al., 2008; Moyen and Martin, 2012). The TTGs obviously develop in several differentiation steps from an undepleted part of the mantle. One possible option is the extraction of thick mafic oceanic plateaus that survive a long time. After an age of 3.0 Ga, the oceanic plateaus will be subducted and suffer a further chemical differentiation. However, our model is not necessarily bound to this assumption. Guitreau et al. (2012) emphasize that the ^{176}Lu/^{177}Lu ratio varied only in an interval between 0.032 and 0.038 during the last 3800 Ma. These values fluctuate around the *chondritic* value of 0.0336. Therefore they suggest a derivation of CC from a primitive mantle by progressive stages, where this primitive mantle stems from a *chondritic* primordial Earth.

Here we want to indicate in what manner the conflict between the observations and interpretation of Boyet and Carlson (2005, 2006) on the one hand, and the *novel* arguments for a chondritic origin of the Earth on the other hand could be resolved. Graham (2002) uses the low ^{129}Xe/^{130}Xe ratios of ocean island basalts (OIBs) as evidence for the existence of an undegassed lower mantle reservoir. Mukhopadhyay (2012) shows beyond this statement that low ^{129}Xe/^{130}Xe in OIBs cannot be explained by mixing atmospheric Xe with Xe in mid-oceanic ridge basalts (MORBs). He demonstrates by new He, Ne, Ar and Xe measurements from Icelandic rocks that there are differences in the concentrations of chemical elements and ^{20}Ne/^{22}Ne ratios between MORBs and OIBs. Because ^{129}Xe is produced from the radioactive decay of ^{129}I, and ^{129}I became extinct at about 100 Ma after the start, that was at an age of 4567.6 Ma, the MORB and OIB mantle sources must have been separated by differentiation previous to about 4470 Ma. *Mixing must have been limited.* A similar figure of thoughts would be the idea that the primordial mantle *had* a chondritic Nb/U, the EDR has a superchondritic Nb/U and the obviously hidden EER has a subchondritic Nb/U (Graham, 2010), where the Baffin Island mantle possibly represents the EDR. If it is possible to unite these ideas then the mentioned sub-case IIb would be a possible solution. There are different proposals how to generate and to maintain an effective isolation of the deep EER or of similar reservoirs for all geologic time. E.g., Lee et al. (2010) proposed that in the magma ocean for pressures between 10 and 15 GPa, consequently in a layer around the later 410-km discontinuity, the liquids were denser than the correspondent PREM densities (cf. Dziewonski and Anderson, 1981). For smaller pressures, low-density melts rise to the surface and form a preliminary crust. The layer between 10 and 15 GPa, however, founders and forms a new layer immediately above the CMB. This layer is *enriched* in incompatible elements, e.g. in heat-producing elements, and enriched in noble gases (^{3}He, ^{22}Ne, ^{40}Ar) and CO_2. The $CO_2/^3$He ratio is approximately constant because the observed ratios in both MORBs and OIBs are not considerably different (Otting and Zähringer, 1967). But this would be only *one* possible explanation of an apparently *primordial part of the lower mantle*.

C4. Heat production: Which abundances of U, Th and K should we accept for our model?

According to the chondritic Earth models, the refractory lithophile elements have chondritic relative abundances in the bulk silicate Earth (BSE) (Jagoutz et al., 1979; McCulloch and Bennett, 1994; McDonough and Sun, 1995; Palme and O'Neill, 2003). Hofmann (2003) describes a typical schedule of chemical differentiation based on a chondritic mantle. The continental growth removes elements with larger ionic radii from BSE leaving behind a depleted mantle (DM), in this simplified scheme directly from BSE. Depending on the assumed abundances of the heat-producing elements, DM ranges from 30 to 80% of the mantle's mass according to Hofmann (2003), from 30 to 60 % according to Bennett (2003). As an example for the order of magnitude of the concentrations in the geochemical reservoirs, we compile Table 1 of the main text, comparing different proposals. Finally, we use the data by McCulloch and Bennett (1994) because of their internal consistency. The 250 ppm K in BSE, recorded in column McC & B of Table 1, has been introduced by Jochum et al. (1983), who proposed K/U=12000, whereas according to column McC & B of Table 1 a nominal value of K/U=12315 is obtained.

According to the EDR-proposal by Boyet and Carlson (2006), a potassium abundance of 160 ppm is possible whereby no or nearly no ^{40}Ar is necessary for the present-day mantle whereas for the 250 ppm K of the chondritic model about 50% of ^{40}Ar should be stored somewhere in the mantle, presumably in the deep mantle. Similarly, the abundance of U and Th in the EDR would be only 60% of the chondritic abundance. The bulk heat production due to radioactive decay of U, Th and K would be only 12 TW. However, measurement based estimates of the present-day total surface heat flow range from 44 to 47 TW (Pollack et al., 1993; Davies and Davies, 2010). This poses a major problem to the EDR hypotheses of the variants I and IIa. From these variants it follows that the primordial heat would be considerably larger than previously thought.

The following facts argue against I and IIa. With regard to our numerical model, we should assume an initial age of $\tau = 4567.6\,\text{Ma}$ (Jacobsen et al., 2008; Carlson and Boyet, 2009). Ryder (2002) shows a plot of the number of lunar craters with diameters greater than 1 km versus age in Ga. If the hypothesis would apply that Ryder's exponentially decreasing curve could be extrapolated backward for $\tau > 4100\,\text{Ma}$, we would indeed arrive at significantly higher values of the primordial heat of the Moon and, therefore, also of the Earth because the intense continuous meteoritic bombardment would also hit the nearby Earth. On the other hand, we find on the Moon an anorthositic crust with an age $\tau = 4456\,\text{Ma}$. From this it follows that the continuous meteoritic bombardment hypothesis is wrong. Therefore we have to assume a late heavy bombardment (LHB) from 3950 to 3870 Ma. On the one hand it is very probable that the Earth had a magma ocean 4567.6 Ma ago, on the other hand Harrison et al. (2005) observed $^{176}\text{Hf}/^{177}\text{Hf}$ initial ratios of 4010 to 4370 Ma detrital zircons. Harrison et al. (2008) continued these investigations using concurrent Lu-Hf and $^{207}\text{Pb}/^{206}\text{Pb}$ analyses and determined ages between 4560 and 4200 Ma for the extraction of the zircon's protoliths. Scarcely anybody anticipated such an early emergence of the Earth's crust. In our model we assume, somewhat conservative, a maximum crustal age of 4490 Ma. Harrison et al. (2008) even concluded that by 4350 Ma a silicious crust had begun to form. Iizuka et al. (2006) estimated U-Pb zircon ages of 4200 Ma in a 3900 Ma granitic rock in the Acasta Gneiss Complex in Canada. Blichert-Toft and Albarède (2008) investigated 63 zircons from the Jack Hills, Australia, that were formed 4100 ± 100 Ma ago, and that were derived from a 4300 to 4360 Ma old protolith. From these investigations, it becomes clear that there was a relatively cool early Earth *before* the LHB which strongly favors the earlier estimates of the initial heat of the Earth.

If, however, the primordial heat is considerably lower than assumed according to the EDR hypothesis (variants I or II a), then e.g. the initial K abundance should be higher than in EDR. In agreement with this direction, Marty (2012) concludes that the isotope signatures of H, N, Ne and Ar can be explained by mixing between two end-members of chondritic and solar compositions and that a significant portion of ^{40}Ar (that is generated by the decay of ^{40}K) must still be stored in the present-day silicate Earth. A recent estimation of the K/U ratios is given by Arevalo et al. (2009): K/U(DM) = 19 000 ± 2600; K/U(OIB) = 11 900 ± 2200; K/U(CC) = 13 000 ± 3000; K/U(BSE) = 13 800 ± 2600. They find 280±60 ppm K for BSE; this interval contains the estimated K abundances of BSE of Jochum et al. (1983) and of Table 1. From McCulloch and Bennett (1994) or column McC & B of Table 1 we get K/U(DM) = 16 700; K/U(CC) = 10 100; K/U(BSE) = 12 300; K/U(OIB) not specified. Also these numbers are within the error limits of Arevalo et al. (2009). In comparison to Walzer and Hendel (2008), we have also incorporated a number of other essential improvements to our mantle convection model. E.g., we use here, the dependence of melting temperature, T_m, on the variable water abundance. Therefore also the shear viscosity, η, depends on the water abundance. With this assumption,the start of chemical differentiation is earlier. For a better physical comprehension by comparison of the present solutions of our system of equations (cf. Appendix A) with the 2008 results, we abstain from the initially intended modernization of the assumed U, Th, K abundances because all values stay within the error limits, i.e. we use the three columns McC & B of Table 1 of the main part of this paper.

Furthermore, geoneutrino measurements by Gando et al. (2011) suggest high U and Th concentrations of the Earth's mantle. Therefore also a high K abundance is expected. These new results argue against the proposal that the K abundance of BSE is only half as high to obtain a virtually ^{40}Ar-free present-day mantle. The mentioned results are also contradictory to the variants I and IIa of the EDR hypothesis.

Stracke et al. (2011) present new Hf and Nd isotope analyses of clinopyroxene from peridotites from the Gakkel Ridge, the Southwest Indian Ridge and the southern Atlantic. They conclude that the average DM is *considerably more depleted* than conventionally derived from MORB investigations. The residual peridotite of DM often exhibits a multi-stage depletion history. DM is *not*, as earlier supposed , homogeneous but often contains large ultra-depleted domains similar to the Gakkel Ridge peridotites. In the conventional model of O'Nions et al. (1979), e.g., a mass fraction of DM of about 50% of the total mantle was estimated. Stracke et al. (2011), however, expect that the present-day mantle contains only about 20% DM. This result is, of course, in stark contrast to the low-K-abundance model and to the EDR proposal (variants I and IIa). For good geochemical, but also numerical reasons, we continue to use the conventional concentrations of incompatible elements according to McCulloch and Bennett (1994), in *this* paper, particularly because they are in the midst of the most recent geochemical proposals. All physical assumptions have been updated. Using *conventional* geochemical assumptions, e.g. McCulloch and Bennett (1994), McDonough and Sun (1995), etc., we do not have any numerical problems. Using the variants I and IIa, however, especially the large values of the assumed primordial heat gradients at CMB cause a numerical breakdown.

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