The mantle isotopic printer.

Basic mantle plume geochemistry for seismologists and geodynamicists

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"*Sunt aliquot quoque res quarum unam dicere causam non satis est, verum pluris, unde una tamen sit*"
(There are phenomena for which it is not sufficient to infer a single origin, but it is necessary to propose several, among which, however, only one is true).

Lucretius. De Rerum Natura (VI, 703-705)

17   Abstract

18   High-temperature geochemistry combined with igneous petrology is an essential tool to infer the

19   conditions of magma generation and evolution in the Earth's interior. During the last thirty years a

20   large number of geochemical models of the Earth, essentially inferred from the isotopic

21   composition of basaltic rocks, have been proposed. These geochemical models have paid little

22   attention to basic physics concepts, broad-band seismology, or geological evidence, with the effect

23   of producing results that are constrained more by assumptions than by data or first principles. This

24   may not be evident to seismologists and geodynamicists.

25   A common view in igneous petrology, seismology and mantle modelling is that isotope

26   geochemistry (e.g., the Rb-Sr, Sm-Nd, U-Th-Pb, U-Th-He, Re-Os, Lu-Hf, and other more complex

27   systems) has the power to identify physical regions in the mantle, their depths, their rheological

28   behaviour and the thermal conditions of magma generation. We demonstrate the fallacy of this

29   approach and the model-dependent conclusions that emerge from unconstrained or poorly

30   constrained geochemical models that do not consider physics, seismology (other than teleseismic

31   travel time tomography and particularly compelling colored mantle cross sections) and geology.

32   Our view may be compared with computer printers. These can reproduce the entire range of colors

33   using a limited number of basic colors (black, magenta, yellow, and cyan). Similarly, the isotopic

34   composition of oceanic basalts and nearly all their primitive continental counterparts can be

35   expressed in terms of a few mantle end-members. The four most important (actually "most

36   extreme", since some are extraordinarily rare) mantle end-members identified by isotope

37   geochemists are DMM or DUM [Depleted MORB (mid-ocean-ridge basalt) Mantle or Depleted

38   Upper Mantle], HiMu (High-Mu, where Mu = μ = $^{238}U/^{204}Pb$), EMI and EMII (Enriched Mantle

39   type I and type II). Other mantle end-members, or components, have been proposed in the

40   geochemical literature (e.g., PHeM, FoZo, LVC, PreMa, EMIII, CMR, LoMu, and C) but these can

41   be considered to be less extreme components or mixtures in the geochemical mantle zoo.

42   Assuming the existence of these extreme "colors" in the mantle isotopic printer, the only matter

43   for debate is their location in the Earth's interior. At least three need long-time insulation from

44   convection-driven homogenization or mixing processes. In other words, it needs to be defined

45   where these extreme isotopic end-members are located. In our view, no geochemical, geological,

46   geophysical and physical arguments require the derivation of any basalt or magma from the deep

47   mantle. Arguments to the contrary are assumption-based. The HiMu, EMI and EMII end-members

can be entirely located in the shallow non-convecting volume of the mantle, while the fourth, which is by far the more abundant volumetrically, (DMM or DUM) can reside in the Transition Zone.

This view is inverted compared with current canonical geochemical views of the Earth's mantle, where the shallowest portions are assumed to be DMM-like (ambient mantle) and the EMI-EMII-HiMu end-members are assumed to be isolated, located in the deep mantle, and associated with thermal anomalies. We argue that the ancient, depleted signatures of DMM imply long-term isolation from recycling and crustal contamination while the enriched components are not free of contamination by shallow materials and can therefore be shallow.

1. Introduction

Despite nearly half a century of detailed study, a consensus on the thermal state and chemical composition of the Earth's interior has not yet been reached. The current canonical models of geochemistry evolved essentially independently of classical physics, thermodynamics- and seismology-based models. Secondary issues are not well resolved, and the gross features of the Earth are the subject of debate. Among these, the geothermal gradient of the deep Earth and the chemical vs. thermal causes for absolute and relative changes in seismic wave speed with depth are debated (e.g., Anderson, 2007, 2011, 2013; Foulger et al., 2013). To constrain the basic features of the Earth's structure, it is essential to understand the dynamics of our planet in terms of petrogenetic processes.

The origin of igneous activity in intra-plate settings remains far from fully understood. At one time it was considered to be a solved problem. In one view cracks and fractures tapped existing melts in the low-velocity zone under the fast-moving plates (the 'jet-stream' of Wilson, 1963), but other views were that deep sources were required for the existence of island chains and melts in the shallow mantle away from plate boundaries required deep, hot upwellings (e.g., Morgan, 1971, 1972). Recent high-resolution global marine gravity models of the oceanic basins reveal a wealth of buried tectonic structures many of which may be of igneous origin (Sandwell et al., 2014). These features obscure the early defined oceanic chain trends allowing the hypothesis of more widespread igneous activity, possibly related to the close-to-solidus condition of the shallow mantle.

While a general consensus has been reached on the causes of partial melting of the shallow mantle beneath oceanic ridges and along subduction zones, the origin of intra-plate igneous activity is still the subject of two different models based on opposite philosophical views.

Plume-based model

The first model argues that in order to have melts in areas away from plate boundaries it is necessary to invoke thermal anomalies in the form of solid, deep mantle upwellings called mantle plumes. In this model, the buoyancy of mantle plumes is related to their derivation from the lowermost mantle (the seismic D" region) and its superadiabatic gradient. Adiabaticity is related to relaxation as pressure decreases. The assumed adiabatic gradient for solid mantle rocks is ~ 0.4-0.6 °C/km, while more compressible liquids are characterized by higher adiabatic gradients around 1 °C/km (McKenzie and Bickle, 1988; Anderson, 2007). A superadiabatic gradient refers to temperature decrease (with decreasing pressure) >0.6 °C/km. Superadiabatic gradients are necessary for convection.

The mantle plume model requires important assumptions: *1)* a chemically homogeneous upper mantle characterized by a restitic (refractory) composition (harzburgitic to low-clinopyroxene lherzolite) unable to produce large amounts of basaltic melts (e.g., Cadoux et al., 2007; Pfander et al., 2012; Hart, 2014); *2)* a maximum temperature at the base of the seismic LID (the outermost shell of Earth characterized by an increase of seismic waves with depth) of ~1300 °C (e.g., McKenzie and Bickle, 1988; Fullea et al., 2009); *3)* low-T and isothermal conditions for the entire sub-lithospheric mantle down to the TZ (assumed in some mantle plume numerical modelling), the mantle volume extending between the olivine/wadsleyite polymorph transition (~410 km) and the ringwoodite/bridgmanite transition (the first is an olivine polymorph, while the second is Mg-Fe silicate perovskite), occurring at ~660-670 km (e.g., Sobolev et al., 2011); *4)* the presence of a primitive (i.e., never before, or only poorly melted or degassed) lower mantle resembling CI-chondrites (i.e., the most primitive compositions in the solar system). An alternative model relates the gas-rich D" region to accumulation of noble-gas-rich recycled hybrid pyroxenites and subducted eclogites (e.g., Davies, 2011); *5)* an overall adiabatic geotherm for the bulk of the mantle (from ~250 to ~2800 km depth; e.g., Glisovic and Forte, 2014) and *6)* high "excess" potential temperatures (Tp) of plume mantle (hypothesized on the basis of geochemical arguments relating to magma compositions; Putirka 2005; Herzberg, 2011), where Tp is the temperature of a solid rock brought to the surface adiabatically, resulting in a decrease of ~0.6 °C/km; *7)* negative vp and vs seismic anomalies imply temperature excess (Montelli et al., 2004; White, 2010; Faccenna and Becker, 2010).

110   On these grounds, partial melting in the shallow intra-plate mantle is considered improbable (at

111   least to high degrees) given that this volume is assumed to be too cold and too refractory.

112   Consequentially, the source of intra-plate magma was considered to be related to solid mantle

113   upwellings from depths as great as 2800-2900 km (e.g., Morgan, 1971, 1972; White, 2010, Li et al.,

114   2014). The requirement of a single convection system, involving the entire sub-lithospheric mantle

115   is a conundrum in this model.

116   High Tp of mantle plumes cannot be directly measured and are assumed on the basis of the high

117   Fo (Forsterite) content [Fo = Mg/(Mg+Fe)] of olivines found in basaltic melts. Olivines are

118   common minerals in equilibrium with high-temperature melts, whose composition is essentially

119   represented by the Fo content. During peridotite partial melting, Fe in olivines (and all other

120   common silicate minerals present in the mantle, orthopyroxene, clinopyroxene and garnet) is

121   preferentially partitioned into the melt compared to Mg. At the same time, when olivine crystallizes

122   in a cooling basaltic magma, it preferentially hosts Mg compared to Fe. This means that the

123   maximum Fo content in an olivine crystallizing from a primitive basaltic melt (typically 0.75-0.85)

124   is always lower than the Fo content in the peridotite (typically 0.88-0.93).

125   In order to have a Fo-rich olivine in a basaltic magma, a lot of Mg must be available in the

126   crystallizing melt. According to the common view (e.g., Herzberg, 2011), in order to have a lot of

127   Mg in a basaltic melt very high temperatures are required (because, otherwise, MgO prefers

128   remaining into the solid residua). The typical rationale is, then, high-Fo olivine in a melt = high

129   MgO in the crystallizing magma = high T to generate such magma = high Tp of its mantle source to

130   extract as much MgO as possible from the peridotite. As we show below, high temperature regimes

131   are only one of the possible ways to explain a high MgO content in a melt.

132

133   Shallow Earth dynamics-based model

134   The second model considers the presence of chemical, rather than thermal, anomalies to explain

135   partial melting processes and seismic wave speed heterogeneities. Olivine-poor lithologies

136   characterized by low solidus temperature can melt under "normal" conditions, without requiring a

137   thermal anomaly. In other words, in order to have partial melt production in the mantle it is

138   necessary to have high homologous temperature (the ratio of the mantle absolute

139   temperature/solidus temperature) not high absolute temperature (e.g., Anderson, 2007; Foulger,

140   2010). In this view the upper mantle is completely different from that hypothesized in the previous

model. It is a chemically, mineralogically, thermally and rheologically heterogeneous *melange*, a sort of a sheared baklava, marble-cake or plum-pudding system. Here, volumetrically predominant olivine-rich lithologies (harzburgitic to lherzolitic matrix) are associated with olivine-poor to olivine-free, garnet±phlogopite±amphibole±pyroxene-rich lithologies, representing subducted lithologies, frozen basaltic melts, or the reaction products of melts derived from carbonated-hydrated subducted lithologies within the peridotitic matrix (e.g., Niu et al., 2011; Mallik and Dasgupta, 2014; Pilet, in press).

Melts characterized by high bulk MgO content are commonly associated with high MgO-olivines, with forsterite as high as 95%. A Fo content >95% means that 95 atoms out of 100, excluding Si and O and other minor bivalent constituents, are Mg, the remaining being Fe^{2+}. These high-MgO melts and minerals are found also in very low volume continental Ca-Na-Al-Ti-poor ultrapotassic subduction-related rocks, which are certainly unrelated to mantle plumes (e.g., Prelevic and Foley, 2007). High MgO content in magma and associated olivine, coupled with low content of "basaltic" components (i.e., elements that typically partition into the melt during mantle anatexis) indicate that the source material was depleted [i.e., was involved in former partial melt extraction event(s)]. This rules out any connection between the MgO content (in melt and olivine) and absolute temperature of formation (e.g., Keiding et al., 2011), but rather associates MgO-rich melts and Fo-rich olivines with depleted sources. Also the Fo-rich olivines and the high MgO content of picrites and other MgO-rich volcanic rocks (komatiites and meimechites, all rocks with >12 wt% MgO and >52 wt% SiO_2) could be due at least partially, if not entirely, to the presence of MgO-rich cumulitic olivine or to ultra-depleted compositions, as for example recorded in Gorgona Island komatiite melt inclusions (Arndt et al., 1997).

Recent geophysical and petrological considerations (e.g., Kawakastsu et al., 2009; Anderson, 2011, 2013) have modified the shallow mantle model for intra-plate volcanism, hypothesizing the presence of diffuse melt lamellae in the Low Velocity Zone, a volume known from seismology since the 1960s (Gutenberg, 1959; Fig. 1b). Vp and Vs wave speeds are consistent with a ~100-150 km-thick layer at depths of 200 km ± 50 km containing small melt pods. These melt lamellae, aligned in a peridotitic matrix, are not usually in physical contact with each other and, therefore, cannot easily escape to the surface.

The solidus temperature of a natural system is the temperature at which the first melt is produced. Natural systems can experience partial melting if temperature increases. This is the basis on which

172 the mantle plume theory rests. A temperature excess is expected to be associated with upwelling of

173 solid diapirs from the base of the lowermost mantle. Alternatively, melts can be produced under

174 "normal" conditions (i.e., without invoking absolute temperature excess) if H and/or C is available.

175 Hydrogen can break the bonding oxygens connecting the SiO_4^{4-} tetrahedrons of mantle minerals and

176 eventually lead to strong viscosity reduction and partial melting.

177 The maximum amounts of H_2O that can be stored in pyroxenes, olivine and garnet in the shallow

178 mantle (i.e. at depths <14 GPa, corresponding to 410 km depth) does not exceed 0.1-0.2 wt%.

179 Higher amounts of H_2O can be stored in the upper mantle in so-called "exotic" mantle silicates such

180 as mica and amphibole, minerals that can host up to ~3 wt%. Rarely up to 10-12 wt% can be stored

181 in other silicates such as antigorite, chlorite and lawsonite (Schmidt and Poli, 2014; Vitale

182 Brovarone and Beyssac, 2014). The presence of these minerals, however, is conditioned to the

183 presence of light elements such as K (for the phlogopite mica) and Ca (for pargasite amphibole and

184 lawsonite) and low temperature regimes in general. With increasing pressure, olivine polymorphs

185 (wadsleyite and ringwoodite) become more prone to host water, and up to 2.5 wt% H_2O can be

186 forced into their lattices (Pearson et al., 2014).

187 In contrast with hydrogen, carbon is a completely incompatible element in typical silicate mantle

188 minerals. This means that, even at small levels, it forms its own solid phases (e.g., graphite,

189 diamond, carbonates, iron carbides) or partitions into melts (e.g., Hirschmann and Dasgupta, 2009).

190 The water storage capacity of a mantle rock is the weighted sum of the maximum amount of H_2O

191 that can be stored in the minerals. This capacity is variable and generally low – no more than 0.4-

192 0.5 wt% at depths <3 GPa, reducing to <0.1 wt% in the pressure range 3-12 GPa (Green et al.,

193 2010). A water content below the maximum storage capacity means that no free water is available,

194 all the H_2O being stored in silicate minerals. Under these circumstances the effect of the water in

195 breaking the bonding oxygens is weak. Only if vapour-saturated conditions are reached (i.e., the

196 amount of water exceeds the maximum water storage capacity of the mantle rocks) is partial

197 melting encouraged, as the solidus temperature abruptly drops. The difference in solidus

198 temperature between volatile-free and vapour-saturated conditions can be as high as 500 °C at 4

199 GPa (e.g., Litasov et al., 2011).

200 The most common hydrous phase in the mantle (pargasitic amphibole) is stable at depths lower

201 than ~100 km. The other hydrous phases (the so-called alphabetic phases, synthesized in the

laboratory only, like Phase A, B, E, Super E, 10 Å, and so on) stable only at temperatures much lower than "normal" geotherms (e.g., Litasov and Ohtani, 2003; Schmidt and Poli, 2014).

The presence of stable carbonate minerals (essentially in the form of dolomite [$CaMg(CO_3)_2$] to magnesite [$MgCO_3$]) contributes to lowering the solidus temperature of the peridotitic assemblage, favouring melts with carbonatitic to carbonate-silicate compositions (e.g., Lee et al., 2000; Gudfinnsson and Presnall, 2005; Keshav and Gudfinnsson, 2014). This happens because the solidus temperature of carbonate minerals at mantle depths is several hundred degrees lower than for volatile-free silicate minerals (with a $\Delta T >500$ °C at 4 GPa).

The presence of melt may thus be related not to absolute temperature excesses but to small amounts of CO_2 (easily prone to react with mantle silicates to produce Mg-Ca-Fe carbonates, minerals characterized by low melting temperature), high water contents (above the water storage capacity) or the absence of hydrous minerals at "normal" geotherm values. In other words, melting can be present in conditions of high homologous temperature.

2. How to understand the Earth's interior

Earth's thermal profile.

As stated by White (2010), "*the plume hypothesis is essentially a physical one*". Also Hofmann (2014) underlines that "*most geochemical tracers carry no information about the specific mantle depth being sampled*" and that "*geochemistry cannot prove mantle plumes*", meaning that the mantle plume concept is based on a hypothetical structural model of the Earth's interior, and geochemistry is an ancillary discipline serving to strengthen the model. Foulger et al. (2013) highlighted the fundamental limitations of, and uncertainties in, seismic tomographic results. These uncertainties include the difficulty of defining background models and obtaining absolute seismic anomalies. These uncertainties derive from the variable chemical compositions and thermal states of the upper mantle. In order to translate into temperature a seismic wave speed anomaly, it is necessary to know the physical parameters of that volume (bulk and shear moduli, thermal expansion and compressibility parameters, anisotropy, presence of volatiles, melts and exotic phases, Fe-Mg ratios in the main minerals, grain-size, and so on). Only assuming *a priori* chemical, mineralogical and lithological compositions may the tomographic results be interpreted in terms of mantle temperature. Clearly, these parameters cannot be known everywhere for heterogeneous systems like the upper mantle. Smith (in press) underlines that when anisotropy is taken into

consideration, the wave speed reduction interpreted as temperature anomalies in classical tomographic images (assuming isotropic mantle structure) simply disappear.

Fluid dynamic simulations of the Earth's interior and geochemical arguments on basaltic volcanism typically assume core temperatures maintained constant by the release of latent heat of crystallization of the liquid core (e.g., Schuberth et al., 2009; Campbell and Griffiths, 2014; Nakagawa and Tackley, 2014).

The classical seismological scheme of Earth's mantle involves four main regions (Regions B, C, D' and D"; Fig. 1b), with the crust representing Region A. The uppermost ~200 km of the Earth (Regions A and B) is characterized by a superadiabatic gradient, with rapid temperature increase over a relatively small depth range, passing from temperatures near to zero to about 1300-1500 °C at its base (Fig. 1).

The lower part of Region B (known as B") is a thermal and shear boundary layer. The bulk of the mantle (all but Region B) is usually assumed to be adiabatic down to the core-mantle boundary layer at ~2700-2800 km. This cannot be the case for an internally heated or secularly cooling mantle. The base of the lowermost mantle, Region D" is characterized by another sharp increase of temperature (superadiabatic gradient) estimated between 800 and 1300 °C (Jeanloz and Morris, 1986; Boehler et al., 1995; Campbell and Griffiths, 2014; Fig. 1b).

According to this classical view, the two most important thermal boundary layers of the Earth's interior are the very shallow regions (which contain the lithosphere, LID, and plate – Regions A and B'; see Anderson, 2011 for a review of the different meanings and implications of these terms) and Region D", located at ~2800-2900 km depth. The canonical view assumes, to resume, an adiabatic geotherm for the bulk of the mantle, a superadiabatic D" (caused by the strong heating from below), a vigorous whole-mantle convection below Region B', a consequent chemical homogeneity, lack of layering, no internal heating and no slabs to cool its interior (Figs. 1a and 1b). According to this pot-on-the-stove view, the Earth's mantle is heated from below by a constant-temperature heat source.

A corollary of fluid dynamic simulations is a self-compressed Earth heated by a constant temperature core-mantle boundary triggering whole-mantle overturn, with limited obstruction, if any, by the TZ. Hot, solid, but narrow mantle blobs are assumed to depart from the D" layer, moving through the entire mantle, and eventually melting when they reach shallow mantle depths (Fig. 1b). Both early and recent modelling (e.g., Griffiths and Campbell, 1990; Farnetani and

264 Richards, 1994; Ballmer et al., 2013; Cloetingh et al., 2013; Bull et al., 2014; Li et al., 2014),

265 assume prescribed and constant temperatures, modes of convection, adiabaticity, and non-cooling

266 interfaces.

267 Alternatively, mantle convection could be caused by heat lost from the surface to space rather than

268 by heat released by the crystallizing liquid core. The differences are not subtle. In the former case,

269 surface cooling triggers convection, favouring delamination of cold portions of the shallow mantle

270 and passive upwelling in the mantle (e.g., Anderson and King, 2014; Anderson and Natland, 2014).

271 Moreover, the mantle cools the core, while in plume modelling and in canonical geodynamic and

272 geochemical models the core warms the mantle and convection is caused by heat excess at D".

273 The thick line indicated with (1) in Fig. 1b represents schematically the classically accepted

274 geotherm with two thermal boundary layers characterized by superadiabatic regimes, one close to

275 the surface (Regions A + B') and the other on top of the core (Region D"), with the bulk of the

276 mantle characterized by adiabatic geotherm (Regions B", C and D'). The thin line indicated with (2)

277 in the same figure is one of the possible geotherms (Schubert et al., 2009) characterized by

278 superadiabatic and subadiabatic trends and no adiabatic gradients. In the first scheme, with the

279 exclusion of D", maximum Tp is reached at the base of the lithosphere (~90-100 km in oceanic

280 basins), with Tp as high as ~1300 °C. Deeper mantle is hotter because it is self-compressed, but

281 when brought to a reference pressure (e.g., the Earth's surface) it is characterized by the same Tp

282 (~1300 °C) as the sub-lithospheric mantle. This temperature is considered the ambient mantle Tp, as

283 recorded by MORB (e.g., McKenzie and Bickle, 1988). The most important differences between the

284 two type of geotherms are: *a)* the maximum Tp of geotherm-1 is lower than that of geotherm-2; *b)*

285 the maximum Tp of geotherm-1 is reached at shallower depths than geotherm-2; *c)* after the thermal

286 bump at ~200 km the Tp in geotherm-2 decreases with depth while the Tp in geotherm-1 remains

287 constant for nearly the entire mantle; *d)* D" in geotherm-1 is characterized by higher Tp than the

288 entire mantle, while in geotherm-2 much of D" is characterized by lower Tp.

289 The dashed lines in Fig. 1b represent the adiabatic upwelling of two samples of the lowermost

290 mantle starting at temperatures compatible with geotherm-1 (star) and geotherm-2 (square). In the

291 first case (the classical mantle plume scheme) upwelling of solid mantle from D" is characterized by

292 higher Tp, recorded in high-Tp magma (inferred on the basis of high Mg/Fe ratios of melts and

293 associated olivines). In the second case (the fluid dynamically and internally heated compatible

294 model) upwelling of solid mantle from D" is characterized by lower Tp. The highest measurable Tp

295 in this case is associated with mantle corresponding to the LLAMA (*Laminated Lithology with*
296 *Aligned Melt Accumulations* or *Layer of Laterally Advecting Mass and Anysotropy*) region of
297 Anderson (2011), around 200-250 km depth, corresponding to the worldwide, well-defined Low
298 Velocity Zone (LVZ). What emerges is the (apparent) paradox that the deeper the source the colder
299 the Tp. The importance of this region (also corresponding to the old Perisphere of Anderson, 1995)
300 has been recently emphasized by Smith (in press).
301
302 Can geochemistry help?
303 The reason why plumes are still part of the canonical models of mantle geochemistry and
304 dynamics can be traced to insufficient interdisciplinary understanding, unquestioning acceptance of
305 the conclusions of others, and semantics. This is known in philosophy as incommensurability.
306 Seismologists are generally not fully aware of the assumptions underlying geochemical inferences
307 and simply accept the conclusions regarding primordial and undegassed mantles and the meaning of
308 concepts such as high ^{3}He/^{4}He or given Pb isotopic ratios. Likewise, geochemists are generally not
309 completely aware of the modelling assumptions in teleseismic travel time tomography and tend to
310 interpret color images of the mantle as thermometry. High-resolution seismic tomography has
311 confirmed that the mantle features used as evidence for active plumes are thousands of kilometres
312 in lateral extent and therefore probably neutral, passive and rising only slowly if at all. As a
313 consequence an alternative view (i.e., they are not thermal plumes nor active upwellings) has been
314 proposed (e.g., Anderson and Natland, 2014). It has also been confirmed that intra-plate volcanoes
315 such as Hawaii tap into a thick sheared shallow boundary layer that is sufficiently hot, fertile, large
316 and slowly moving to explain volcanic chains (Anderson, 2011; Smith, in press). Surprisingly, this
317 was originally proposed by Wilson (1963). This shallow layer is disrupted by 3D deep passive
318 upwellings that feed ridges and near-ridge hotspots.
319 The canonical paradigm of mantle dynamics and geochemistry includes whole-mantle convection
320 and whole-mantle plumes. It has been supported by three lines of evidence: radiogenic isotope
321 geochemistry, fluid dynamic simulations, and relative travel-time tomography. Each of these has
322 undergone paradigm shifts, even reversals, requiring reconsideration of the whole canonical model.
323 In the next sections we focus on those isotopic systematics most widely used in basalt petrogenesis.
324 We demonstrate how geochemical concepts do not require deep-mantle upwelling and,
325 consequentially, cannot be used as "smoking guns" for mantle plumes. Phrases such as "*the X value*

326 *of the Y isotopic systematic indicates the involvement of deep mantle plumes*" are simply incorrect.

327 Geochemistry does not have not the power to detect upwellings from the deep mantle and has only

328 limited power to infer the thermal state of the melt source.

329

3. Principles of geochemistry applied to igneous petrology

331 The upper thermal boundary layer, the upper 150-200 km of the Earth, is physically and

332 geochemically heterogeneous. This is confirmed by the mineralogy and geochemistry of mantle

333 xenoliths exhumed by alkali basaltic melts from the shallowest (typically 50-120 km depth; Nixon,

334 1987).

335 Despite this, the upper mantle is commonly assumed to be homogeneous, isotropic, chemically

336 depleted, olivine-rich and nearly H-C-free by geochemists and geophysical modellers (e.g., Cadoux

337 et al., 2007). In particular, the shallowest rigid portion of the mantle is considered to be stiff and

338 virtually incapable of producing basaltic melts unless at unrealistically high temperatures.

339 Sometimes the lithosphere is equated to the seismic LID or to the whole boundary layer. These

340 background hypotheses have important implications for interpreting isotopic "anomalies" in mantle-

341 derived materials and the travel-time anomalies of teleseismic waves. The LID and the lithosphere

342 are thin and this is one reason why geochemists look much deeper for magma sources.

343 In the standard geochemical model, the deep mantle is not involved in chemical differentiation. It

344 maintained a primordial chemical composition despite being continuously modified (enriched in

345 basaltic components) by arrival of subducted material that pierced the TZ. Several geochemical

346 models, based on unconstrained assumptions and forcing selected set of data to converge towards a

347 pre-fixed results, attempt to explain this paradox (e.g., Jackson et al., 2010, 2014; Davies, 2011).

348 Standard geochemical models require background lower mantle or liquid core thermal and

349 chemical inputs to explain the genesis of Ocean Island Basalts (OIB) and other supposed plume-

350 related volcanoes. In geochemistry, OIB is a generic term for intra-plate oceanic rocks characterised

351 by a large range of incompatible element content and a very large range of isotopic ratios. This

352 rock group comprises volumetrically predominant tholeiitic (i.e., Na-K-poor and with relatively

353 high Fe/Mg) and minor sodic alkaline basalts, along with very rare differentiated (i.e., silica-richer)

354 compositions such as trachytes and phonolites. In isotope geochemistry the term OIB is too vague

355 and several prefixes (e.g., HiMu, EMI, EMII and so on, which we explain later) are needed to

356 distinguish the various compositions.

357   In particular, isotope geochemistry is often considered by geochemists and geophysicists to be the

358   smoking gun for mantle plumes. We explain here why isotope geochemistry cannot be used as

359   evidence, much less definitive proof, for mantle plumes.

360

361   **The Rb-Sr isotope system.** This is the oldest and best studied isotopic system applied to igneous

362   petrogenesis (e.g., Faure and Powell, 1972). It is based on the natural decay (i.e., transformation) of

363   a radioactive isotope of Rubidium, ^{87}Rb (representing about 27.8% of the isotopes of Rb, the

364   remaining being the stable ^{85}Rb). Strontium has four stable isotopes, with atomic masses 84 (0.6%

365   of the Sr isotopes), 86 (9.9%), 87 (7%) and 88 (82.6%). The abundance ratios among the Sr isotopes

366   remain constant, with the exception of ^{87}Sr, which is continuously produced by ^{87}Rb decay.

367   The half-life of ^{87}Rb is $4.8*10^{10}$ yr (Table 1). Given that the age of the Earth is one tenth of this

368   half life, clearly the original ^{87}Rb at the time of the Earth's formation has been reduced only by a

369   small amount and the amount of ^{87}Sr has increased by only the same amount. The amount of ^{87}Sr

370   now measured in a rock (sedimentary, metamorphic or igneous) is the sum of the original ^{87}Sr plus

371   the amount produced after the decay of ^{87}Rb. Obviously, the higher the original content of Rb (and

372   hence ^{87}Rb) and the older a rock, the larger the amount of radiogenic ^{87}Sr produced.

373   During partial melting or fractional crystallization processes, the most important differentiation

374   processes in igneous geochemistry (except for the noble gases and stable isotopes), two isotopes of

375   the same element (e.g., ^{88}Rb and ^{87}Rb or ^{87}Sr and ^{86}Sr) are not fractionated and their ratios remain

376   unchanged. What may change is the elemental ratio of the parent and daughter isotope pairs. The

377   ionic radius of Rb (1.66 Å, where Å = Angstrom = $1*10^{-10}$ m = 0.1 nm) is not much different from

378   that of K (1.52 Å). Also the charge of Rb and K is the same (+1). These two characteristics render

379   Rb an element with a geochemical behaviour very similar to that of K. In other words, Rb can

380   substitute or replace K in minerals (e.g., K-feldspars or biotite). On the other hand, Sr (1.32 Å; +2

381   valence) shares much more geochemical affinity with Ca (1.14 Å; +2 valence). The Earth's mantle

382   has more Ca than K (Ca/K ratio of primitive mantle estimate being ~75; Lyubteskaya and

383   Korenaga, 2007).

384   During partial melting of a volatile-free peridotitic source, K behaves as a strongly incompatible

385   element (i.e., it has a strong tendency to prefer the melt phase), because there are no minerals in

386   which it can exist. Element incompatibility must always be expressed with respect to a given

387   mineral (or mineral assemblage) and a given melt composition. The compatibility of an element is

388   the ratio of its abundance in the mineral to its abundance in the liquid that is in equilibrium with it.

389   There is no element that is always "incompatible" (i.e., prefers the liquid phase) or "compatible"

390   (i.e., prefers the solid phase) under all conditions (e.g., Fedele et al., 2015).

391   Rubidium is incompatible in a peridotitic mantle. This means that, in the presence of melt, Rb is

392   preferentially partitioned there instead of remaining in the solid rock residuum. The same Rb is

393   compatible in a crystallizing rhyolitic melt (an alkali feldspar-rich volcanic rock). This means that

394   Rb will preferentially move into the crystallizing alkali feldspar as it precipitates.

395   Calcium behaves as a moderately incompatible element (because the only mineral in which it can

396   be stored, clinopyroxene, is among the first phases to melt). In a carbonated peridotite Ca continues

397   to behave as a moderately incompatible element, since carbonates are the first phases to melt, due to

398   their very low melting temperature compared with the other silicate minerals. The same holds in the

399   presence of garnet, a phase that can host large amounts of Ca at large depth in its Ca-majoritic form,

400   but that is among the first phases to melt. As a consequence, the K/Ca ratio (and also Rb/Sr) in a

401   partial melt of a peridotite (e.g., basalt) is higher than the K/Ca (or Rb/Sr) in the source. The higher

402   Rb/Sr, the higher $^{87}Rb/^{86}Sr$, where the numerator is a radioactive nuclide and the denominator is a

403   stable primordial isotope of Sr. With time, the higher $^{87}Rb/^{86}Sr$ evolves into higher $^{87}Sr/^{86}Sr$ because

404   ^{87}Rb slowly transforms to ^{87}Sr, while the ^{86}Sr content does not change.

405   The present-day $^{87}Sr/^{86}Sr$ isotopic ratio of the Bulk Silicate Earth (BSE, which represents the solid

406   Earth, excluding the core), is now known to be around 0.70445. This is the ratio the entire Earth

407   should have, assuming an original undifferentiated Earth $^{87}Rb/^{86}Sr$ ratio (~0.09, present-day value)

408   and an initial $^{87}Sr/^{86}Sr$ of 0.69897 (Fig. 2). The initial $^{87}Sr/^{86}Sr$ of the Earth, called BABI (Basaltic

409   Achondrite Best Initial) is the Sr isotopic ratio of a basaltic achondrite meteorite with no Rb (and

410   thus no ^{87}Rb). This means that all the ^{87}Sr in that meteorite represents the primordial ^{87}Sr content of

411   the solar system. In other words, during its 4.56 Gyr life, the $^{87}Sr/^{86}Sr$ ratio of the Earth has

412   increased from 0.69897 (BABI) to 0.70445 (BSE), i.e., by only 0.00548, as result of ^{87}Rb decay.

413   Modern thermal ionization mass spectrometers can easily measure these very small ratio

414   differences, with the typical precision of $^{87}Sr/^{86}Sr$ ratios being $\pm 5*10^{-6}$.

415   The present-day BSE value assumes an unchanged Rb/Sr isotopic ratio (Fig. 2). This is true if we

416   consider the entire Earth as a single system. But what happens if we consider the basalt-restite

417   mantle pair? (Restite is the residuum after extraction of partial melt.) Basalts are characterized by

418   Rb/Sr ratios higher than the original mantle and the restitic mantle. As a consequence, with ageing

419   we should expect in the basalt higher $^{87}Sr/^{86}Sr$, while the restitic mantle should be characterized by

420   lower $^{87}Sr/^{86}Sr$.

421   But how can the $^{87}Sr/^{86}Sr$ ratios in igneous rocks be used to constrain their origin? Let us assume

422   that at a given moment (e.g., 2 Gyr after its formation), the Earth experiences partial melting (Fig.

423   2; 1st partial melting event). This is a differentiation process, producing a partial melt which

424   eventually will solidify forming an igneous rock, leaving a restitic mantle. The first rock is

425   characterized by higher Rb/Sr, while the second shows lower Rb/Sr. After ~2.5 Gyr, the rock with

426   higher Rb/Sr (and thus higher $^{87}Rb/^{86}Sr$) will be characterized by a higher $^{87}Sr/^{86}Sr$ ratio compared

427   with the restitic source (Fig. 2). Both sources will have $^{87}Sr/^{86}Sr$ higher than at the moment of

428   partial melting, but the $^{87}Sr/^{86}Sr$ ratio of the igneous rock will be much higher than that of the

429   restite. The $^{87}Sr/^{86}Sr$ ratio of the restite (i.e., the mantle from which a given amount of partial melt

430   has been extracted in the past) is characterized by a $^{87}Sr/^{86}Sr$ ratio lower than the present-day BSE

431    $^{87}Sr/^{86}Sr$. The solidified partial melt can experience partial melting itself (2nd partial melting event

432   in Fig. 2). In this case, this process produces a new partial melt with higher Rb/Sr and a residual

433   source with lower Rb/Sr that will evolve towards different $^{87}Sr/^{86}Sr$ ratios (Fig. 2).

434   A second partial melting event of the first mantle residuum (3rd partial melting event in Fig. 2) will

435   produce a new melt and an even more depleted residuum. The final isotopic ratios of the different

436   partial melts and melt residua will depend on the initial $^{87}Sr/^{86}Sr$ ratios, the age of melt extraction,

437   the degree of Rb/Sr fractionation (essentially a function of source mineralogy and degree of

438   melting) and the ^{87}Rb half-life (Gast, 1960). In other words, a basalt (but also any other kind of

439   igneous rock) characterized by $^{87}Sr/^{86}Sr$ ratio lower than BSE is considered derived from a depleted

440   (i.e., non-primitive) mantle source. At very large degree melting, the liquid will have Rb/Sr ratios

441   converging to the original (primordial) values. Such large degrees of melting occurred only during

442   the accretion of the Earth.

443   What should the present day $^{87}Sr/^{86}Sr$ ratio of a basalt derived from a primitive mantle be (i.e., the

444   composition assumed for the lower mantle in some models)? Such a rock should have an $^{87}Sr/^{86}Sr$

445   ratio similar or very close to the BSE estimate. A conundrum for the classical mantle plume model

446   is that nearly all rocks whose origin is postulated to be related to plumes (e.g., HiMu-OIB) are

447   characterized by $^{87}Sr/^{86}Sr$ ratios <BSE, implying non-primitive mantle source compositions and

448   former partial melt extraction. Only a few OIB (EMI and EMII types) are characterized by $^{87}Sr/^{86}Sr$

449   ratios higher than BSE, but essentially none has the same isotopic composition as BSE (Stracke,
450   2012).

451   Igneous rocks are not all confined to $^{87}Sr/^{86}Sr$ ratios <BSE. An important part of the Earth
452   (essentially the upper crust) is characterized by sedimentary, metamorphic and igneous rocks with
453   $^{87}Sr/^{86}Sr$ ratios >BSE. This results from faster radiogenic growth of ^{87}Sr in rocks with $^{87}Rb/^{86}Sr$
454   ratios higher than the primordial Earth value. The average upper crust (as represented by the global
455   subducting sediment compilation of Plank, 2014) is old and characterized by high Rb (84 ppm;
456   compare this value with 0.46 ppm Rb of the primitive mantle), high Rb/Sr (0.27, compared with
457   0.03 of the primitive mantle), resulting in strongly radiogenic $^{87}Sr/^{86}Sr$ (0.7124; Plank, 2014).

458   Subduction is a process during which upper crust lithologies (or alteration products of them) are
459   recycled back to the mantle. During this process, rocks with high $^{87}Sr/^{86}Sr$ ratios are again mixed
460   with an upper mantle matrix characterized by $^{87}Sr/^{86}Sr$ ratios <BSE. If such a crust-contaminated
461   mantle experiences a new partial melting process, it is possible to obtain melts with a wide range of
462   isotopic compositions, with values lower to much higher than the BSE estimate.

463   In conclusion, the $^{87}Sr/^{86}Sr$ ratios of igneous rocks can be used to constrain the depleted (low
464   $^{87}Sr/^{86}Sr$, indicating long-time evolution of a low Rb/Sr system, indicating old melt extraction, with
465   Rb more incompatible than Sr) or the enriched (high $^{87}Sr/^{86}Sr$, indicating, high Rb/Sr) character of
466   their sources. This can be done quantitatively only if the age of the melt extraction events, their
467   number, the amount of the melt extracted (the Rb/Sr of the melt varying as function of the degree of
468   melting), the age of the recycling process during subduction, the isotopic and elemental
469   composition of the original crustal material entering the trench, the metamorphic reactions in the
470   subducting slab (able to fractionate Rb from Sr) and the style of interaction between fluids/melts
471   released from the slab with the supra-subduction mantle wedge are precisely known. This is never
472   the case. These factors can only be estimated, guessed or assumed and as a consequence the results
473   of a geochemical modelling are only qualitative or semi-quantitative at best.

474   Partial melting decreases the $^{87}Rb/^{86}Sr$ ratios of the mantle residuum, ultimately resulting in
475   $^{87}Sr/^{86}Sr$ ratios <BSE. Recycling of upper crustal lithologies increases $^{87}Rb/^{86}Sr$ and the $^{87}Sr/^{86}Sr$
476   ratio of the supra-subduction mantle wedge, forcing it to higher $^{87}Sr/^{86}Sr$ ratios and towards values
477   >BSE. What is clear is that the $^{87}Sr/^{86}Sr$ isotopic composition of an igneous rock <BSE clearly
478   indicates derivation from a mantle source that has experienced partial melt extraction in its past, and
479   $^{87}Sr/^{86}Sr$ ratios >BSE indicate derivation from a mantle that is not primitive.

480　　Despite these simple considerations, $^{87}Sr/^{86}Sr$ ratios in basalts as low as 0.7025 are considered to

481　　reflect derivation from enriched end-members classically identified with deep mantle upwelling in

482　　the form of mantle plumes (e.g., Merle et al., 2009). Ironically, such low $^{87}Sr/^{86}Sr$ values (coupled

483　　with high $^{143}Nd/^{144}Nd$ ratios, see below) were originally regarded as evidence of derivation from a

484　　depleted MORB-like source (e.g., Gast, 1968).

485

486　　**The Sm-Nd isotope system.** Samarium and Neodymium belong to the Rare Earth Element (REE)

487　　group, a suite of 14 incompatible elements all with the same charge with atomic number (Z)

488　　increasing from La (Z = 57) to Lu (Z = 71). The ionic radius of the REE decreases slightly from La

489　　(1.17 Å) to Lu (1.00 Å). The same +3 valence of Nd (Z = 60) and Sm (Z = 62), but the slightly

490　　lower ionic radius of the latter (1.12 Å vs. 1.10 Å for Nd and Sm, respectively), renders Nd slightly

491　　more incompatible than Sm during mantle partial melting and basaltic melt crystallization (Fig. 3).

492　　Samarium is present in seven different isotopes with masses 144 (3.1%), 147 (15%), 148 (11.2%),

493　　149 (13.8%), 150 (7.4%), 152 (26.7%) and 154 (22.7%), of which only ^{147}Sm and ^{148}Sm are

494　　radioactive.

495　　The half-life of ^{148}Sm is very long ($7*10^{15}$ yr) and consequentially it can be considered to be a

496　　stable element on the timescale of the Earth. On the other hand, the half-life of ^{147}Sm is shorter

497　　($1.06*10^{11}$ yr) and its decay chain is relevant to geology. ^{147}Sm is transformed by α-decay into

498　　^{143}Nd and the ^{147}Sm-^{143}Nd system works in the same way of the ^{87}Rb-^{87}Sr system discussed above

499　　(Table 1). Given the higher half-life of ^{147}Sm (106 Gyr) compared to that of ^{87}Rb (48 Gyr), less

500　　^{143}Nd than ^{87}Sr has been produced during Earth's lifetime. In absolute terms, however, the number

501　　of radiogenic ^{143}Nd atoms (15% of all the Nd isotopes) produced in 4.56 Gyr is higher than the

502　　number of radiogenic ^{87}Sr atoms because of the higher amount of ^{147}Sm compared with ^{87}Rb (7% of

503　　all the Rb isotopes). The only substantial difference with the Rb-Sr system is that the radioactive

504　　(parent) isotope (^{147}Sm) is less incompatible than the radiogenic (daughter) isotope ^{143}Nd. The

505　　definition "less incompatible" is here preferred to "more compatible" to highlight the general

506　　incompatible character of both Sm and Nd during peridotite partial melting.

507　　Also in this case the radiogenic ^{143}Nd isotope is measured against a stable Nd isotope (^{144}Nd)

508　　according to the classical relation $^{143}Nd/^{144}Nd$. The Earth's primordial $^{143}Nd/^{144}Nd$ isotopic ratio is

509　　assumed to be the same as chondritic meteorites and is constrained to 0.512638 (defined as ChUR =

Chondritic Uniform Reservoir), while the ^{143}Nd/^{144}Nd at the time of formation of the solar system was 0.50669. In other words, ^{143}Nd/^{144}Nd during the last 4.56 Gyr has increased by 0.00595.

Several attempts have been made to modify the accepted concept of chondritic Earth to solve the problem raised by another Nd isotope (^{142}Nd), suggesting for the whole Earth a ^{143}Nd/^{144}Nd isotopic ratio more radiogenic than ChUR (0.5130; Caro and Bourdon, 2010; Jackson and Jellinek, 2013). It is worth noting, however, that any modification of the accepted chondritic Earth assumption raises a large number of additional problems (e.g., for a super-chondritic ^{143}Nd/^{144}Nd value for the Earth, the depleted major- and trace-element content of MORB would be at odds with their "new" primitive Nd isotopic composition). As a consequence, we continue using the classically accepted chondritic (ChUR) value.

Nd is slightly more incompatible than Sm during partial melting, so a restitic mantle is characterized by lower Nd/Sm (and hence higher ^{147}Sm/^{144}Nd) than the pre-melting composition and the basaltic melt. A rock with high ^{147}Sm/^{144}Nd will evolve, with ageing, to high ^{143}Nd/^{144}Nd isotopic ratios (Fig. 3). Following the rationale described for the Rb/Sr isotopic system, an anciently depleted mantle source will be characterized by ^{143}Nd/^{144}Nd higher than ChUR and much higher than solidified partial melt (characterized by lower Sm/Nd, i.e., lower ^{147}Sm, and consequentially lower ^{143}Nd produced for a given amount of stable ^{144}Nd). Also in this case, igneous rocks interpreted as the products of mantle plumes, tapping primitive mantle sources should be characterized by ^{143}Nd/^{144}Nd ratios very close to ChUR. However, they are nearly constantly shifted towards isotopically depleted (i.e., ^{143}Nd/^{144}Nd >ChUR) compositions ruling out the existence of such primitive mantle compositions.

The Sr-Nd isotopic pair is at the base of isotope geochemistry applied to igneous petrology. All basaltic compositions, erupted in oceanic or continental intra-plate settings plot along a trend, defined originally as the mantle array (e.g., Sun, 1980; Figs. 4, 5a). This connects the isotopically depleted field (characterized by ^{87}Sr/^{86}Sr <BSE and ^{143}Nd/^{144}Nd >ChUR) with the isotopically enriched field (^{87}Sr/^{86}Sr >BSE and ^{143}Nd/^{144}Nd <ChUR), passing through BSE-ChUR values (Fig. 4). MORBs plot entirely in the depleted field, HiMu-OIB plot nearly entirely in the depleted isotopic field, while EMI- and EMII-OIB extend to the enriched field (Fig. 5a).

In Fig. 5a a recent compilation of oceanic basalt isotopic data (Stracke, 2012) is plotted together with the four basic colors of the mantle isotopic printer. The DMM-HiMu-EMI-EMII irregular quadrilateral envelops >99% of oceanic basalts. As a consequence, their Sr-Nd isotopic

composition can be simply explained in terms of the relative contribution of these four extreme values. This is the basis of isotope geochemistry applied to the petrogenesis of oceanic (and also continental, Fig. 5b) basalts. Up to this point there is no fundamental disagreement between the geochemical and petrological communities except for the precise position of the four end-members in Sr-Nd-Pb isotopic space. Problems emerge when trying to translate into geological terms these four end-members, assigning thermal, rheological, physical, depth and mineralogical meaning to these "colors".

The U-Th-Pb isotope system. The Uranium-Thorium-Lead system is more complex than the Rb/Sr and Sm/Nd systems. Here there are three radiogenic isotopes (^{235}U, ^{238}U and ^{232}Th) that decay into three different radiogenic Pb isotopes (^{206}Pb, ^{207}Pb, ^{208}Pb, respectively), with different half-lives and energy emissions. Uranium is present as two radioactive isotopes with masses 235 (0.72%) and 238 (99.28%). Thorium is present only as ^{232}Th, while Pb is present as four stable isotopes with masses 204 (1.4%), 206 (24.1%), 207 (22.1%) and 208 (52.4%).

As discussed previously, the ^{206}Pb, ^{207}Pb and ^{208}Pb abundances slowly but continuously increase due to the decay of ^{235}U (half-life = 0.7 Gyr), ^{238}U (4.5 Gyr) and ^{232}Th (14.0 Gyr). In this case the three radiogenic Pb isotopes are normalized to one of the stable Pb isotopes, ^{204}Pb. As a consequence, the U-Th-Pb isotopic system is conventionally reported as three separate isotopic ratios: $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$. The $^{238}U/^{204}Pb$ isotopic ratio is defined as μ (mu), while the $^{232}Th/^{238}U$ is defined as κ (kappa). Strictly speaking, the Greek letter μ should be spelled as "mi", not "mu". This means that the classical HiMu mantle end-member should be defined as "HiMi". The Earth's $^{238}U/^{235}U$ ratio is 137.88.

Given that the ^{235}U half-life is much shorter than that of ^{238}U, $^{207}Pb/^{204}Pb$ increases more rapidly than $^{206}Pb/^{204}Pb$. As a consequence, in a $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plot the Pb isotopic evolution (i.e., the Pb isotopic ratios of a rock with increasing age) follows a convex-upward curve (Fig. 6a).

Let us assume that the early Earth, with initial solar $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios X0 and Y0, respectively (Fig. 6a), evolved as a single system (i.e., without any differentiation process such as partial melting) for a period t_1 with a $^{238}U/^{204}Pb$ ratio = μ_1 (Fig. 6a). After a time t_1 the new Pb isotopic composition of the Earth would be X1,1 and Y1,1 (Fig. 6a). If the Earth, during this period had a different μ value (e.g., $\mu_2 > \mu_1$), but the same initial Pb isotopic composition, after the same time t_1 it would have had different (higher) Pb isotopic ratios (X1,2 and Y1,2; Fig. 6a). The dashed

572 line t_0-t_1, obtained by connecting the isotopic composition of different reservoirs with the same

573 initial Pb isotopic composition, but with different μ, represents the *isochron* after time t_1.

574 What happens if the same uniform reservoirs (assumed to evolve with $^{238}U/^{204}Pb$ ratios $μ_1$ or $μ_2$

575 but the same initial isotopic ratios) allow Pb isotopic ingrowth for an additional time t_2? After this

576 additional time, both the hypothetical reservoirs (with $μ_1$ or $μ_2$) will be characterized by higher

577 $^{206}Pb/^{204}Pb$ and $^{207}Pb/^{204}Pb$ ratios. Obviously, sources with $μ_2$ will be characterized by more ^{206}Pb

578 and ^{207}Pb, having higher U/Pb. At a time t_2 the Pb isotopic composition of a system with $μ_1$ will be

579 X2,1 and Y2,1, while a system with $μ_2$ will be X2,2 and Y2,2 (Fig. 6a). The dashed line connecting

580 t_0 and t_2 represents the *isochron* at t_2.

581 Present day Earth (t_3 = 4.56 Gyr), with hypothetical $μ_1$ or $μ_2$, should have $^{206}Pb/^{204}Pb$ at X3,1 and

582 X3,2, and $^{207}Pb/^{204}Pb$ ratios at Y3,1 and Y3,2, respectively (Fig. 6a). Whatever the μ of the Earth,

583 the *total* Pb isotopic composition of our planet *must* plot on the isochron t_3. The isochron at 4.56

584 Gyr is defined as the *meteoritic isochron* or *Geochron*. The entire solar system (as determined by

585 the composition of meteorites) plots on the 4.56 Gyr Geochron, with $^{206}Pb/^{204}Pb$ ratios ranging from

586 ~10 to ~50 and $^{207}Pb/^{204}Pb$ ratios ranging from ~9 to ~37. This does not mean that *all* the Earth's

587 rocks must plot on the Geochron.

588 In principle rocks can plot on the left or on the right of the Geochron. The various shells of the

589 Earth (crust, mantle, core) have a common origin (i.e., the same primordial solar Pb isotopic

590 composition; X0 and Y0 in Fig. 6a), but have accreted or consumed at different times and evolved

591 with different μ values. In particular, these reservoirs evolved with different $^{207}Pb/^{204}Pb$, $^{206}Pb/^{204}Pb$

592 and $^{208}Pb/^{204}Pb$ ratios.

593 Each partial melting stage (i.e., to produce new crustal material) produces at least two different

594 new sources characterized by different U/Pb (and μ) that will evolve with fast (high μ) or slow (low

595 μ) producing variable ^{207}Pb and ^{206}Pb isotopic growth. Let us assume that a uniform system evolved

596 with primordial solar system Pb isotopic ratios for a time t2 and a $^{238}U/^{204}Pb$ ratio = μ1. Its isotopic

597 composition is indicated by the white star in Fig. 6b. If a partial melting event occurs, this originally

598 uniform system is split into two reservoirs, one evolving with low $^{238}U/^{204}Pb$ (the restitic mantle)

599 and the other with high $^{238}U/^{204}Pb$ (the partial melt). The elemental fractionation between U and Pb

600 happens because the two elements have slightly different compatibility in mantle minerals and,

601 consequentially, they are fractionated by partial melting and fractional crystallization processes.

602   Assuming that $t_2 = 2$ Gyr, these two complementary reservoirs (the mantle residuum and the

603   solidified partial melt) will evolve up to the present day with different μ, but the same initial Pb

604   isotopic composition. After 2.56 Gyr, the two reservoirs will have different isotopic compositions,

605   represented by the star labelled R1 (Residuum) and M1 (Melt). The total Pb isotopic composition of

606   the two systems must plot on the intersection between the Geochron and the R1-M1 segment.

607   Similarly, if the original isotopic system evolved with higher $^{238}U/^{204}Pb$ (μ2), a partial melt

608   extraction at $t_2 = 2$ Gyr will produce, at $t_3 = 4.56$ Gyr, two systems R2 and M2 (Fig. 6b). Whatever

609   the original μ and the μ produced during partial melt formation, the total composition of the system

610   must plot somewhere along the Geochron.

611   It is important to understand that the whole Earth system, not the single solid reservoirs, must plot

612   along the Geochron. During the Earth's chemical stratification, the upper crust evolved with higher

613   U/Pb (given that U is slightly more incompatible than Pb during partial melting processes) and the

614   residual mantle evolved towards lower U/Pb. This, coupled with the different initial Pb isotopic

615   compositions of these two most extreme reservoirs, means that upper crustal rocks, having higher

616   U/Pb are also characterized by higher μ and, consequentially, should plot somewhere to the right of

617   the Geochron.

618   On the other hand, residual mantle rocks, characterized by lower μ, should have retarded ^{207}Pb and

619   ^{206}Pb isotopic growth, and consequentially they should plot to the left of the Geochron. What is

620   anomalous is that both upper crustal rocks (various estimates grouped in the small orange field in

621   Fig. 6a) and depleted mantle rocks (or partial melts, i.e., MORB; part of the yellow field in Fig. 6a)

622   all plot to the right of the Geochron. Also >99.9% of OIB plot on or to the right of the Geochron

623   (OIB and MORB grouped with the same yellow field in Fig. 6a). This is called the first Pb paradox

624   (Allègre, 1969).

625   If both partial melts and residual mantle compositions all plot to the right of the Geochron, some

626   hidden or poorly represented reservoir must exist somewhere. This reservoir must be placed well to

627   the left of the Geochron, so that the whole Earth Pb isotopic composition plots somewhere along

628   this line. The only terrestrial reservoir characterized by compositions plotting to the left of the

629   Geochron (and characterized by low to extremely low $^{206}Pb/^{204}Pb$, down to ~10 and μ ~0) is the

630   ancient lower continental crust.

631   In Fig. 6a both the fields of ancient lower crustal xenoliths (sky blue field) and the model old

632   continental crust (star; Lustrino, 2005; Bolhar et al., 2007) are shown. The metamorphic reactions

occurring during basalt to granulite/eclogite facies are indeed characterized by U/Pb fractionation, with U leaving the system more easily than Pb. The consequence is that a metamorphosed (eclogitic s.l.) lower crust is characterized by very low μ and consequentially its $^{206}Pb/^{204}Pb$ (but also $^{207}Pb/^{204}Pb$) remains virtually frozen and does not increase with time, as there is little if any ^{238}U (and ^{235}U). If such an eclogitization process is old, the Pb isotopic ratios are stopped at their infant stage, close to values more similar to primordial solar system values ($^{206}Pb/^{204}Pb = 10.29$; $^{207}Pb/^{204}Pb = 9.31$) than the typical igneous rock range ($^{206}Pb/^{204}Pb \sim 17$-$21$; $^{207}Pb/^{204}Pb = \sim15.2$-$15.8$; $\mu = 4$-16).

Foundering of this dense lithology (which is much denser than the shallow lithospheric mantle) in the form of a mafic keel in overthickened collision zones can explain the extreme rarity of these compositions on the Earth's surface. This dense eclogite may be now stored in the TZ, as originally proposed by Anderson (1989).

The lead isotope system is particularly important in basalt petrogenesis especially because it is considered to be one of the milestones of geochemical mantle plume modelling, suggesting lower mantle derivation for OIB. Ironically, it was Pb isotopes that led Tatsumoto (1978) to conclude that OIB were from the shallow mantle and MORB from the deeper mantle, thus agreeing with the classical physics-based models (e.g., Birch. 1952).

Two of the four "colors" of the Earth's mantle (i.e., the mantle end-members manifested in oceanic basalts away from subduction zones) are essentially identified on Pb isotopic grounds. One of these colors is represented by the EMI end-member (e.g., Lustrino and Dallai, 2003), whose type localities are identified in the Pitcairn islands and seamounts in French Polynesia (e.g., Woodhead et al., 1993), the east-central Atlantic Ocean (Walvis Ridge; Salters and Sachi-Kocher, 2010), some SW Indian ridge sectors, the Aphanasy-Nikitin seamount chain (Mahoney et al., 1996; Borisova et al., 2001) and the Ko'olau-stage lavas of Oahu island (Hawaii; Tanaka et al., 2002; Huang and Frey, 2005). This hypothetical mantle end-member is characterized by its peculiar low $^{206}Pb/^{204}Pb$ (down to ~16.7; Fig. 7), associated with non-unique mildly radiogenic $^{87}Sr/^{86}Sr$ and strongly unradiogenic $^{143}Nd/^{144}Nd$ (Fig. 5).

The other mantle color/end-member defined on the grounds of Pb isotopes is HiMu, represented by a very rare group of rocks cropping out in French Polynesia (Rurutu, Tubuai and Mangaia islands; Chauvel et al., 1995; Stracke et al., 2005; Hanyu et al., 2013) and, with less extreme compositions, on the island of St. Helena (Kawabata et al., 2011; Hanyu et al., 2014). The HiMu

end-member is characterized by the most radiogenic Pb isotopic compositions recorded in oceanic basalts (Fig. 7a). The other two colors of the mantle isotopic printer are EMII and DMM.

The EMII mantle end-member is characterized by $^{206}Pb/^{204}Pb$ intermediate between EMI and HiMu (~19) and relatively high $^{207}Pb/^{204}Pb$ for a given $^{206}Pb/^{204}Pb$ (Fig. 7a). The relative $^{207}Pb/^{204}Pb$ enrichment of EMII lavas can be mathematically shown as a positive Δ7/4Pb value, a parameter proposed by Hart (1984) to emphasize the vertical shift of southern hemisphere oceanic basalts compared with northern ones (defining the so-called NHRL, Northern Hemisphere Reference Line) in $^{207}Pb/^{204}Pb$ vs. $^{206}Pb/^{204}Pb$ plots (Fig. 7a). The vertical shift from the NHRL (that can be identified also for $^{208}Pb/^{204}Pb$; Δ8/4Pb) is also defined as the DupAl anomaly (after the two researchers who first described it; Dupré and Allegre, 1983).

The last color of the mantle isotopic printer is DMM (Fig. 7a). This "color" is by far the most common and nearly always present in portraits of oceanic and continental intra-plate basalts. It is also a constant feature of partial melts generated in supra-subduction mantle wedges. Despite the fact that DMM is necessary in almost every recipe to model oceanic basalts, the Pb isotopic composition of DMM is not well constrained. Indeed, there have been several attempts to estimate the $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ of this end-member, with estimates ranging from ~16.8 to ~18.4 ($^{206}Pb/^{204}Pb$), from ~15.3 to ~15.4 ($^{207}Pb/^{204}Pb$) and from ~36.5 to ~38 ($^{208}Pb/^{204}Pb$). The quadrilateral with the four mantle end-members at the apexes also envelopes continental rocks, as shown in Fig. 7b. Surprisingly, from a mantle plume point of view, DMM is not a focal point on isotope plots, i.e. trends do not converge toward DMM compositions. They converge toward FOZO (Focal Zone) or C (Common component; Stracke et al., 2005; Jackson et al., 2014).

The Sr-Nd isotopic resemblance between DMM and HiMu (plotting in the same depleted field) disappears when observing these two end-members from different perspectives (i.e., Pb isotopes). Fig. 7 clearly indicates their different origins. The position of the DMM reservoir is compatible with a U-depleted composition, while the extremely radiogenic $^{206}Pb/^{204}Pb$ (but also of the other Pb isotopic pairs) of the HiMu end-member requires high U/Pb and Th/Pb in their genesis. This is classically attributed to recycling of Pb-poor lithologies in the deep mantle, in regions not involved in strong convective systems (e.g., Chauvel et al., 1992, 1995). These Pb-poor lithologies probably are hydrothermally-altered oceanic crust where Pb was first concentrated in sulphides which were then removed when the slab entered the trench. The oceanic crust residuum would be, as a consequence, characterized by high U/Pb, not because of elevated U content, but rather because of

low Pb. Storage of such high U/Pb lithologies and insulation for long periods would allow radiogenic growth of ^{206}Pb and ^{207}Pb, which are the most striking characteristics of the HiMu end-member (Fig. 7). In other words, the Pb isotopic composition of the HiMu end-member (classically identified as the strongest geochemical evidence for a mantle plume) requires long periods of insulation of high U/Pb lithologies, not thermal anomalies or deep sources. With the present state of knowledge, it is not possible to say that a given Pb isotopic composition is proof for the existence of a mantle plume as often used as an *a priori* conjecture.

The U-Th-He isotope system. Helium is the lightest noble gas, present in two isotopes, ^{3}He and ^{4}He, whose ratios in igneous rocks are classically used to constrain mantle structure and infer its evolution (e.g., Ballentine, 2012). ^{3}He is the primordial isotope trapped inside the Earth during its accretion, and is continuously escaping from the Earth's surface when mantle melts degas at shallow depths. During the decay into stable Pb isotopes, ^{235}U, ^{238}U and ^{232}Th produce ^{4}He isotopes as α-particles. Helium isotopes are classically reported as ^{3}He/^{4}He ratios (R) over atmospheric ^{3}He/^{4}He (Ra = $1.38*10^{-6}$cm^{3}/g). This reverses the usual geochemical convention of the unstable isotope (e.g., ^{87}Sr or ^{143}Nd) normalized to the stable isotope (e.g., ^{86}Sr or ^{144}Nd). In the case of Helium the stable isotope (^{3}He) is normalized to the unstable one (^{4}He). This convention is carried over into the interpretation of ^{3}He/^{4}He ratios where variation in ^{4}He is usually not considered and high ^{3}He/^{4}He is typically attributed to high ^{3}He derived from a deep-sourced, undegassed mantle region (e.g., Davies, 2011). Despite increasing criticism in using He isotope sistematic to infer the existence of primordial deep-mantle reservoirs for "plume magmas" (White, 2010), high ^{3}He/^{4}He ratios in basaltic melts continue to be considered the strongest isotopic signal of a deep mantle provenance of their sources (Jackson et al., 2014).

MORB are characterized by ^{3}He/^{4}He ratios (R/Ra) ranging from ~1 to ~22, but with nearly all the samples concentrated in the narrow interval 8 ± 1 R/Ra (e.g., Meibom et al., 2003; Graham et al., 2014). In contrast to MORB, magmas emplaced in oceanic and continental intra-plate settings are characterized by variable ^{3}He/^{4}He ratios, with R/Ra ranging from ~5 to ~50 and a poor correlation with other isotope systematics (e.g., Rb-Sr, Sm-Nd, U-Th-Pb) and incompatible trace element ratios (e.g., Peters and Day, 2014). This can be understood in part from the central limit theorem (high degree melts and large volume samples average over large volumes and have smaller variances) and

from the fact that helium isotope ratios are partly controlled by degassing as well as by melting (Meibom et al., 2003).

Earth materials are characterized by ^{3}He/^{4}He ratios much lower (<50 R/Ra) than the cosmic solar wind (~310 R/Ra) because of the continued ^{3}He loss and the continued ^{4}He production by radioactive decay. Plate tectonics moves primordial ^{3}He from the Earth's interior to the surface via partial melting and degassing, while subduction recycles back to the mantle ^{4}He in the form of U-Th-rich crustal lithologies. The result is that the ^{3}He/^{4}He ratio of the Earth has been continuously decreasing since the Earth's accretion (Fig. 8a). The two exceptions are in sediments that are rich in cosmic spherules (solar ^{3}He-rich) and in lithium-rich rocks (e.g., Smith, in press).

Despite the common view (e.g., Gonnermann and Mukhopadhyay, 2009; Davies, 2011; Ballentine, 2012), high ^{3}He/^{4}He ratios indicate high time-integrated ^{3}He/(Th+U) ratios, not automatically high absolute ^{3}He content. Similarly, low ^{3}He/^{4}He ratios are not proof of absolute low ^{3}He content. Relatively low ^{3}He/^{4}He ratios in MORB have been related to relatively U+Th-rich concentrations associated with variable He loss through magma degassing in the upper mantle (i.e., ^{4}He-rich rather than ^{3}He-poor; Meibom et al., 2003) and the presence of He-rich bubbles trapped in cavities and nucleating on the surface of early-forming olivine crystals (Natland, 2003). Similarly, high ^{3}He/^{4}He ratios can result from ancient Th+U-poor sources, resulting in low ^{4}He production with time, while low ^{3}He/^{4}He ratios can result from sources with ancient Th- and U-rich lithologies.

Despite these obvious considerations, the scientific literature is full of claims such as: "*Helium is a powerful tracer of primitive material in Earth's mantle. Extremely high ^{3}He/^{4}He ratios in some ocean-island basalts suggest the presence of relatively undegassed and undifferentiated material preserved in Earth's mantle*" (Jackson et al., 2010*); "Hot-spot magmas often have elevated values in the ratio of primordial helium to radiogenic helium (^{3}He/^{4}He), which indicates their source is in a part of the mantle that has not lost its dissolved gases to the atmosphere.*" (Humphreys and Schmandt, 2011); "*The existence of different ^{4}He/^{3}He ratios underpins the idea that there are at least two geochemical reservoirs in the mantle: a deep reservoir rich in gases and volatile compounds feeds material into an upper reservoir, which is the convecting part of the mantle that supplies magma to mid-ocean ridges*" (Ballentine, 2012); "*[...] the less-degassed mantle source traced by high ^{3}He/^{4}He. [...] He isotopes provide direct evidence for the preservation of relatively undegassed, primordial reservoirs in the present-day mantle.*" (Peters and Day, 2014).

755   More evolved views interpret both high ^{3}He/^{4}He and low ^{3}He/^{4}He ratios as being derived from

756 deep mantle plumes, the first representing the true plume matrix and the second representing the

757 "*subducted materials – oceanic crust, mantle lithosphere and sediments – which may also reside in*

758 *slab graveyards at the bottom of the mantle where plumes originate*" (Jackson et al., 2014). In other

759 words, whatever the ^{3}He/^{4}He ratios are measured in mantle melts (as low as 5 or as high as 50

760 R/Ra) they are considered to represent a proof for a deep mantle provenance.

761   Focusing on the elemental He content in basalt phenocrysts (mostly clinopyroxene and olivine) it

762 emerges that OIB have a much lower ^{3}He (typically around 10^{-14} to 10^{-11} cm^3/g) compared with

763 MORB (typically around 10^{-11} to 10^{-9} cm^3/g; Ozima and Igarashi, 2000; Hanyu et al., 2005; Mourao

764 et al., 2012; Hanyu, 2014). Despite this, it is commonly believed that "*The MORB source contains*

765 *less ^{3}He because it was degassed in Early Earth history*" (Moreira et al., 2012) and that high

766 ^{3}He/^{4}He ratios reflect lower mantle chemical signatures in continental settings (e.g., the Columbia

767 River Basalts; Camp, 2013). There is no reason to believe that MORB sources are depleted in ^{3}He

768 compared with postulated primitive and undegassed-plume-related OIB sources (Anderson, 1998,

769 2007; Ozima and Igarashi, 2000). On this basis, statements such as "*Large, long-lived, ^{3}He-rich*

770 *plumes, and especially those that have generated enormous volumes of oceanic or continental flood*

771 *basalts, are more likely to have come from the base of the lower mantle*" (Hofmann, 1997) need

772 rethinking. The actual very low ^{3}He content of postulated "plume magmas" (i.e., up to five orders of

773 magnitude less than what is recorded in MORB) has been related to the subaerial activity of OIB, a

774 characteristic that would favour preferential noble gas escape from magma compared with MORB,

775 erupted at high water depths (and therefore high pressures, preventing degassing). This solution is

776 not viable because OIB should also have much higher ^{3}He/^{36}Ar than MORB (the higher the mass of

777 the noble gas, the less its melt compatibility; e.g., Carrol and Draper, 1994), while actually MORB

778 are characterized by higher ^{3}He/^{36}Ar ratios, with no correlation between ^{3}He and ^{36}Ar (Ozima and

779 Igarashi, 2000). The fact that the highest ^{3}He/^{4}He ratios (~50 R/Ra) are recorded in Mg-rich, alkali-

780 poor picritic magmas (Baffin Island; NE Canada characterized by very low ^{87}Sr/^{86}Sr (~0.7031) and

781 very high ^{143}Nd/^{144}Nd (~0.5130; Stuart et al., 2003), indicate an important role of depleted mantle

782 sources in their petrogenesis. The depleted (i.e., not primitive nor undegassed) source is also

783 testified by low LREE/MREE ratios (LREE = Light Rare Earth Elements; MREE = Medium REE,

784 e.g., La/Sm <0.6).

The apparent conundrum of invoking undegassed sources in the petrogenesis of alkali-poor, Sr-unradiogenic and Nd-radiogenic basaltic melts is solved by proposing mixing between depleted upper mantle (responsible for all the geochemical characteristics of the Baffin Island picrites, also apparent in the mineral chemistry) and a gas-rich (^{3}He-rich) component (Stuart et al., 2003). The linear correlation between He-Sr and He-Nd isotopes should indicate a perfect He elemental distribution in the two mixing end-members, which is difficult to understand invoking DMM and primitive mantle regions (as a "plume head dispersed in the upper mantle") to represent these two end-members. The Baffin Island picrites are important because they are considered to be the first product of the proto-Icelandic mantle plume (e.g., Graham et al., 1998; Stuart et al., 2003; Jackson et al., 2010).

The mantle plume hypothesis has received support from the conclusions of many noble gas geochemists who have proposed a direct link between high ^{3}He/^{4}He ratios with high absolute ^{3}He and, as a consequence, a primitive and relatively undegassed source (White, 2010; Jackson et al., 2010; Ballentine, 2012; Class and Goldstein, 2005). Alternatively, the origin of a ^{3}He-rich lower mantle is considered not a primary feature, but, rather, related to accumulation of recycled oceanic basalts and hybrid pyroxenites rich in ^{3}He (Davies, 2011). The supposed high abundance in ^{3}He of oceanic crust recycled down to D" is based on the assumption that He is strongly partitioned to melts during shallow mantle melting beneath oceanic ridges. While this is certainly true, this model cannot explain: 1) the differences between MORB and "lower mantle-derived"-OIB; 2) the lower absolute abundance of ^{3}He in OIB compared to MORB and 3) the radiogenic ingrowth of ^{4}He due to the decay of U and Th isotopes that would decrease the ^{3}He/^{4}He in the mantle plume-related OIB.

In some cases ^{3}He/^{4}He ratios in the range 6.5-10.6 R/Ra and ^{3}He contents as low as 10^{-3} cm^3/g have been considered, together with other noble gas arguments, as sufficient proof for the presence of deep-rooted mantle plumes below Hawaii and the Louisville seamount chain (Hanyu, 2014). According to this view the U-Th-He isotopic system is related to the different compatibility of U+Th with respect to He, in rocks and magmas (degassing fractionation between U, Th, He and other noble gases being ignored). The two different approaches are reviewed by Parman et al (2005) (Fig. 8a,b). The continuous thick line evolving from ~130 R/Ra (at ~4.5 Ga) to ~50 R/Ra (Present) indicates the evolution of a Th+U-bearing undegassed mantle. Partial melts of this undegassed mantle should be characterized by relatively high R/Ra values, indicated with black dot 1 (representing the highest ^{3}He/^{4}He measured in igneous rocks; Stuart et al., 2003). A hypothetical

816 partial melting event at 2 Ga would produce a liquid and a mantle residuum. Both He and the U+Th

817 pair are strongly incompatible during mantle partial melting, but the standard model assumes

818 stronger incompatibility of He with respect to both U and Th. This means that partial melts have

819 higher He/(U+Th) than either the undegassed mantle or the mantle residuum. Such a partial melt

820 would be subject to degassing at shallow depths, allowing preferential escape of He from the melt

821 and resulting in a ~1000-fold reduction of the original He/(Th+U) ratio (Parman et al., 2005). The

822 isotopic evolution of this degassed melt is indicated with the dashed line in Fig. 8a. The mantle

823 residuum would be characterized by lower He/(Th+U) ratios than undegassed mantle and partial

824 melts. The evolution of this depleted (degassed) reservoir would evolve towards relatively low

825 ^{3}He/^{4}He (R/Ra ~8) like that recorded in present-day MORB (Fig. 8a). In the alternative model U

826 and Th are up to two orders of magnitude more incompatible than He during partial melting

827 ($D^{Th,U}<D^{He}$; Parman et al., 2005). The partial melt would evolve more or less in the same way as the

828 standard model, with shallow-depth magma degassing the controlling mechanism to produce He-

829 poor, He/(Th+U)-poor melts evolving with age towards very low ^{3}He/^{4}He ratios. The difference

830 from the standard model rests in the fact that in this case the degassed reservoir (mantle residuum)

831 would be characterized by higher ^{3}He/^{4}He than both partial melt and undegassed mantle, because it

832 is characterized by lower (Th+U)/He ratios (black dot 1 in Fig. 8b). The petrological implications

833 for this alternative model are particularly relevant. ^{3}He/^{4}He values as high as 50 R/Ra would reflect

834 not primitive (undegassed) mantle sources but derivation from depleted residua (Parman et al.,

835 2005). Partial melting effectively cannot decrease He/(Th+U) ratios in the mantle residuum and

836 high He/(Th+U) ratios can develop in mantle residua through large extents of melting, but at the

837 same time are associated with low He (and other noble gases) concentrations (Jackson et al., 2013).

838   In conclusion both high and low ^{3}He/^{4}He ratios can be associated with recycling processes. Low

839 ^{3}He/^{4}He requires the presence of an old U+Th-rich component (e.g., recycled crust or sediment),

840 while high ^{3}He/^{4}He ratios can be explained by recycling of refractory peridotite or olivine-rich

841 cumulates (rich in gas-filled bubbles or cracks; e.g., Natland, 2003; Anderson, 2007). In either case

842 recycling down to the lower mantle is not required.

843

4. Ink cartridges in the mantle isotopic printer

845   ^{87}Sr/^{86}Sr ratios of HiMu- and HiMu-like-OIB are all lower than BSE. This characteristic is at odds

846 with derivation from a primitive (i.e., never tapped by basaltic extraction) source. This conundrum

has been explained by derivation from a deep mantle source that interacted with low-$^{87}Sr/^{86}Sr$ recycled oceanic crust (e.g., Hofmann, 1997, 2003). The low $^{87}Sr/^{86}Sr$ characteristic is intrinsic of a partial melt generated from a depleted (DMM) source in which Rb, more incompatible than Sr during melt extraction, is preferentially transferred to the melt. If such a depleted, low Rb/Sr source partially melts again, the new liquid is characterized by low $^{87}Rb/^{86}Sr$, and consequentially evolves towards low $^{87}Sr/^{86}Sr$ isotopic ratios. Low Rb has also been postulated as a consequence of hydrothermal alteration of oceanic crust that concentrates this metal in secondary veins that are easily mobilized during the first stages of dehydration metamorphic reaction occurring at shallow depths below the supra-subduction lithospheric mantle wedge (e.g., Chauvel et al., 1992).

Ancient recycling (of the order of 2 Gyr and more) of MORB-like lithologies (characterized by low-to-very-low Rb/Sr and thus low-to-very-low $^{87}Sr/^{86}Sr$) would have reduced the $^{87}Sr/^{86}Sr$ of the primitive deep mantle from BSE to values indistinguishable from present-day MORB.

The EMI-EMII OIB $^{87}Sr/^{86}Sr$ ratios higher than BSE have been explained by derivation from a deep mantle that interacted with high $^{87}Sr/^{86}Sr$ lithologies in the form of subducted sediments (pelitic and terrigenous) and delaminated/eroded lower continental crust (e.g., Zindler and Hart, 1986; Lustrino and Dallai, 2003; Stracke et al., 2005; Jackson and Dasgupta, 2008; Willbold and Stracke, 2010; Stracke, 2012). What is interesting is that in some cases (e.g., HiMu-like basalts) the contribution of "normal" oceanic crust is dominant (low $^{87}Sr/^{86}Sr$) compared to the geochemical (and isotopic) budget of altered oceanic crust (characterized by much higher Rb/Sr ratios) or the thin sediment veneer (e.g., White, 2010; Stracke, 2012). In all these three cases, the HiMu, EMI and EMII components (actually isotopic "flavours") provide evidence of variable interaction with a shallow DMM-like mantle, producing the various "colors" recorded in intra-plate oceanic basalts.

In summary, the isotopic compositions of three of the main four "ink cartridges" of the mantle isotopic printer (HiMu, EMI and EMII) are essentially related to recycling of subducted lithologies (fresh vs. altered oceanic crust, pelitic vs. terrigenous sediments, plus variable contribution of metasomatically modified oceanic lithospheric mantle) or tectonic erosion of the base of the supra-subduction continental mantle wedge (e.g., Clift and Vannucchi, 2004; Willbold and Stracke, 2010). Alternative but similar views interpret these three "colors" as partial melts or ancient gases frozen in the shallow boundary layer (e.g., Natland, 2003; Anderson, 2007; Niu et al., 2011; Pilet et al., 2011; Pilet, 2014). These interpretations, albeit with several necessary distinctions and case-by-case peculiarities, are valid. The models explaining the significance of the geochemical mantle zoo

878   (Stracke et al., 2005) can be grouped into two categories. One considers that the most peculiar

879   isotopic characteristics of the mantle end-members reflect recycling (both directly, in the form of

880   subducted lithologies, or indirectly, in the form of tectonically eroded lithospheric sole) of material

881   once stored at shallow depths or at the Earth's surface (e.g., Hofmann, 2003; White, 2010; Stracke,

882   2012). The second considers that Na-K-H-C-rich partial melts infiltrating the shallow mantle can

883   metasomatize the lithospheric mantle and are not necessarily related to subduction tectonics (e.g.,

884   Niu and O'Hara, 2008; Pilet, 2014). Whichever is correct, the isotope systematics do not require

885   deep mantle sources nor temperature excesses. This means that any mantle plume hypothesis based

886   on geochemical arguments is fundamentally unsafe.

887   According to the standard geochemical model, the isotopic cartridges of the mantle printer are in

888   the deepest mantle because this is the only place not involved in vigorous convection (Fig. 1b). The

889   peculiar isotopic characteristics of the various mantle end-members are explained by isolation from

890   convection. This need for isolation actually applies more to the MORB source than to hypothetical

891   plume sources. What would be the difference if the recycled lithologies are stored not in the deeper

892   mantle, but in the upper thermal boundary layer (D" Fig. 1b, also known as Perisphere or LLAMA)?

893   There would be no difference at all. Having four ink cartridges close to the Earth's surface in the

894   shallowest mantle and the TZ also has the advantage that there is then no need to assume the

895   thermal state, chemical composition and rheological behaviour of the deep mantle, for which there

896   is little supporting evidence. Because of the low temperatures and high strength at the top of the

897   upper boundary layer, ionic diffusivities are very low and even ancient He isotope signatures can be

898   preserved.

899   What is necessary in the geochemical mantle plume model is the presence of regions in the Earth's

900   interior that escape continuous homogenization. In order to allow a given isotopic ratio to grow, the

901   source (isotopic color) must be placed somewhere (ink cartridge) and reside there until it is tapped.

902   Three of the four ink cartridges (as identified by different isotopic systematics) can certainly be

903   placed in the upper 150-250 km of the mantle.

904   As concerns the volume of magma production associated with postulated mantle plumes, it is

905   sufficient to consider the following. Assuming the presence of only 2% melt in a 100 km-thick

906   seismic Low Velocity Zone (e.g., the LLAMA volume of Anderson, 2011), the estimated amount of

907   melt there is of the order of 10^9 km^3. This amount is ample to explain the volumes erupted in

908   typical OIB or Large Igneous Province eruptions (e.g., Mahoney and Mahoney, 1997; Cañón-Tapia,
909   2010).

910

5. Concluding remarks

912   Various petrogenetic models have been proposed to explain the presence, the abundance, the
913   physical state and the origin of the four principal mantle end-members (DMM, HiMu, EMI and
914   EMII) in the oceanic mantle. These end-members, based on Sr-Nd-Pb isotope systematics represent
915   the most extreme compositions that can be found in the oceanic mantle. Extreme values
916   occasionally found in magmas emplaced in continental settings can be related to interaction of
917   mantle partial melts with isotopically extreme crustal lithologies.

918   We interpret these end-members using the analogy of printing, where four basic colors (black, red,
919   magenta, yellow), mixed in the appropriate amounts, can produce the full range of colors. Similarly,
920   assuming four isotopic mantle end-members, it is possible to produce the whole range of oceanic
921   basalt isotopic compositions. All the "colors" are present in a relatively restricted area east of
922   Australia, in the Polynesia-Melanesia-Micronesia region. In some cases they are virtually present in
923   the same volcanic district (e.g., Jackson et al., 2014), rendering the possibility of a provenance from
924   the D" Region (without complete mixing of the "colors") at least dubious. With the exception of
925   DMM, all the other mantle end-members require the involvement of olivine-poor lithologies. These
926   lithologies have been identified in upper/lower crustal rocks, recycled oceanic crust, terrigenous
927   and/or pelagic sediments, kimberlites, carbonatites, sulphides, oxides or frozen basaltic melts
928   crystallized at depth (e.g., Ivanov, in press; Pilet, in press; Smith, in press).

929   Geochemists and petrologists now generally agree on the origin of these colors. The great
930   differences in opinion lie in where the "isotopic cartridges" are considered to be located in the
931   Earth's interior. Thermal anomalies are not associated with these end-members, nor are they
932   required in any form. A small degree of melting is sometimes invoked to explain absolute trace
933   element contents or the trace element fractionation recorded in lavas. Shallow degassing and
934   contamination is implied in noble gas systematics. Helium isotopes cannot be used to constrain the
935   existence of an undegassed lower mantle or the physical conditions of deep mantle upwellings.
936   Extensive overlap of MORB and OIB in terms of Sr-Nd isotopic ratios and nearly complete overlap
937   in Pb isotopes indicate that the mantle sources are not necessarily very different in terms of depth or
938   insulated from each other.

Shallow anomalies are responsible for intra-plate volcanism. Mantle plumes and a fully convecting mantle are unproven assumptions. Physically realistic Earth models have a thick upper thermal boundary layer, characterized by superadiabatic thermal gradient, with a thickness of the order of 100-200 km. Three out of the four mantle "colors" (HiMu, EMI and EMII) can be drawn from this region of the Earth, which is also mobilised by shallow convection associated with plate tectonics. The fourth color, by far the most abundant, is represented by DMM probably comprises the shallow mantle matrix or, as recently proposed, passively updraft mantle from the TZ (Anderson and Natland, 2014). This thermodynamically self-consistent model eliminates the need for lower-mantle involvement in oceanic basalt petrogenesis and surface igneous activity in general. All the isotopic color cartridges can be placed at shallow depths and tapping of lower mantle is not required.

Acknowledgements

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1257   Figure captions:

1258   Fig. 1: (a) T-P simplified scheme of the classical view of Earth's shallow interior (modified from
1259   McKenzie and Bickle, 1988). Two geotherms for Archaean shield and old oceanic basin are
1260   shown. Dotted line indicates the solidus temperature (the temperature at which the first melt
1261   appears) for a pyrolite system. Pyrolite is an hypothetical chemical composition obtained by
1262   adding three parts by mass of depleted peridotite (dunite) + 1 part of tholeiitic basalt (Ringwood,
1263   1979). To the left of the solidus the temperature is too low for melting at any pressure. To the left
1264   of the solidus some melt is present. According to these geotherms, no melt should be present in
1265   the upper mantle. Dashed line indicates the adiabatic gradient, i.e., the temperature decrease per
1266   km of a solid rock. Partial melt can occur in the following cases: 1) the solid mantle adiabatically
1267   upwells (e.g., as a passive upflow following Anderson and Natland, 2014); 2) a temperature
1268   anomaly, e.g., from the deep mantle or 3), as follows. Mantle potential temperature (Tp) is a
1269   concept proposed by McKenzie and Bickle (1988) and corresponds to the temperature of magma
1270   at the Earth's surface. According to McKenzie and Bickle (1988) MORB Tp is slightly less than
1271   1300°C. (b) T-P simplified scheme of Earth's mantle. The thick line (1) schematically represents
1272   the classically accepted geotherm with two thermal boundary layers characterized by
1273   superadiabatic regimes, one close to the surface and the other at the top of the core, with the bulk

of the mantle characterized by an adiabatic geotherm. The thin line (2) is one possible geotherm

(Schubert et al., 2009) characterized by superadiabatic and subadiabatic geotherms and no

adiabatic gradients. In the first scheme the maximum T is reached at the base of the lithosphere

(~90-100 km in oceanic basins), with Tp as high as ~1300°C. Deeper mantle is hotter because

self-compressed, but when brought to the Earth's surface it is characterized by the same Tp

(~1300°C) as sub-lithospheric mantle. This temperature is considered to be ambient mantle Tp,

and recorded by MORB (e.g., McKenzie and Bickle, 1988). The most important differences

between the two type of geotherms are: a) the maximum Tp of geotherm (1) is lower than that of

geotherm (2); b) the maximum Tp of geotherm (1) is reached at shallower depths than geotherm

(2); c) after the thermal bump at ~200 km the Tp in geotherm (2) decreases with depth while the

Tp in geotherm (1) remains constant for nearly the entire mantle; d) D" in geotherm (1) is

characterized by higher Tp than the entire mantle, while in geotherm (2) much of D" is

characterized by lower Tp. The dashed lines represent the adiabatic upwelling of two samples of

the lowermost mantle starting at temperatures compatible with geotherm (1) (star) and geotherm

(2) (square). In the first case, which represents the classical mantle plume scheme, upwelling of

solid mantle from D" is characterized by higher Tp, recorded in high Tp magma (inferred on the

basis of high Mg/Fe ratios). In the second case (the fluid-dynamically and internally heated

compatible model) upwelling of solid mantle from D" is characterized by lower Tp. The highest

measurable Tp in this case is associated with mantle corresponding to the LLAMA mantle of

Anderson (2011), around 200-250 km depth, corresponding to the worldwide, well-defined Low

Velocity Zone (LVZ). A-B-C-D on the right of the figure represent the original seismological

zones into which the Earth was divided (modified from Anderson, 2011).

Fig. 2: Schematic evolution of the $^{87}Sr/^{86}Sr$ isotopic ratio with time. ^{87}Sr is continuously produced

by ^{87}Rb decay, while ^{86}Sr is the stable Strontium isotope. As a consequence $^{87}Sr/^{86}Sr$

continuously increases with time. Partial melting has the effect of increasing the isotopic ratio

rate in the melt and reducing it in the solid residuum.

Fig. 3: Rare Earth Elements (REE) normalized to primitive mantle estimates. The two curved lines

indicate simplified patterns of partial melts and mantle solid residua after anatexis. The

incompatibility of an element is its tendency to partition into the melt phase. Partial melts of a

primitive mantle source are characterized by relatively high Nd/Sm ratios, while mantle residua

are characterized by low Nd/Sm. With ageing these elemental ratios will evolve towards low

^{143}Nd/^{144}Nd and high ^{143}Nd/^{144}Nd, respectively.

Fig. 4: Schematic ^{143}Nd/^{144}Nd vs. ^{87}Sr/^{86}Sr isotopic diagram reporting Bulk Silicate Earth (BSE)

and Chondritic Uniform Reservoir (ChUR), which should represent the total average ^{87}Sr/^{86}Sr

and ^{143}Nd/^{144}Nd isotopic composition of the Earth. Starting from the initial composition, partial

melting produces isotopic differentiation into depleted (<BSE and >ChUR) and enriched fields

(>BSE and <ChUR) compositions.

Fig. 5: (a) ^{143}Nd/^{144}Nd vs. ^{87}Sr/^{86}Sr isotopic diagram for oceanic basalts. The background yellow

strip is referred to the Sr-Nd isotopic mantle array. DMM = Depleted MORB Mantle; HiMu =

High-Mu, where Mu = μ = ^{238}U/^{204}Pb; EMI = Enriched Mantle Type I; EMII = Enriched Mantle

Type II (from Stracke, 2012). (b) ^{143}Nd/^{144}Nd vs. ^{87}Sr/^{86}Sr isotopic diagram for continental rocks

from the circum-Mediterranean area (Lustrino and Wilson, 2007; Lustrino, 2011). In both cases

all the isotopic compositions can be defined in terms of relative abundance of four main

components, similar to computer printers where all the possible colors are produced using four

ink cartridges (black, yellow, magenta, blue).

Fig. 6: (a) ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb isotopic diagram showing the hypothetical evolution of the

Earth system starting at 4.56 Gyr with primordial (solar) ^{207}Pb/^{204}Pb = 10.29 and ^{206}Pb/^{204}Pb =

9.31, evolving with different μ values. Model lower continental crust from Bolhar et al. (2007).

Lower and upper continental crust fields from references reported in Lustrino (2005) and Bolhar

et al. (2007). References for oceanic basalt field are from Stracke (2012). (b) ^{207}Pb/^{204}Pb vs.

^{206}Pb/^{204}Pb isotopic diagram illustrating the effect of partial melt extraction (producing melts M1

and M2 and solid residua R1 and R2).

Fig. 7: (a) ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb isotopic diagram for oceanic basalts (references in Stracke,

2012). Worth noting is the nearly complete overlap of MORB with OIB and the position to the

right of the Geochron of nearly all the compositions. Also in this case, the Pb isotopic ratios of

oceanic basalts can be defined in terms of only four end-members (the isotopic colors of the

mantle printer). NHRL = Northern Hemisphere Reference Line (Hart, 1984) represents the average Pb isotopic composition of the Northern Hemisphere oceanic basalts. The vertical shift (negative or positive) from this line is defined by the parameter $\Delta 7/4$Pb. (b) ^{207}Pb/^{204}Pb vs. ^{206}Pb/^{204}Pb isotopic diagram for continental intra-plate volcanic rocks from the circum-Mediterranean area. References in Lustrino and Wilson (2007) and Lustrino (2011). The complete list of the analyses (>8000 rocks) is available on request to the first author.

Fig. 8: (a) Classical interpretation of isotopic evolution of ^{3}He/^{4}He system with age. The ^{3}He/^{4}He ratio decreases continuously because of progressive ^{3}He escape and ^{4}He production by Th-U decay into stable Pb isotopes. An undegassed Earth (i.e., primitive mantle composition) would today be characterized by ^{3}He/^{4}He around 50 R/Ra (black dot 1). R is the isotopic ratio measured in the rock and Ra is the same ratio measured in the present-day atmosphere. D is the bulk distribution coefficient in the melting assemblage and quantitatively indicates the tendency of an element to remain into the solid (high D, high compatibility) or to preferentially partition into the melt (low D, high incompatibility). According to this view, He is more incompatible than Th+U during partial melting, resulting in a ^{3}He/(Th+U)-poor mantle residuum (black dot 2). The melt will experience substantial degassing, resulting in strong ^{3}He depletion (dashed line). (b) alternative model of ^{3}He/^{4}He isotopic evolution, assuming stronger incompatibility of Th+U compared with He. In this case the solid residuum would be characterized by higher ^{3}He/(Th+U), leading to higher ^{3}He/^{4}He compared with undegassed melt. Modified from Parman et al. (2005).
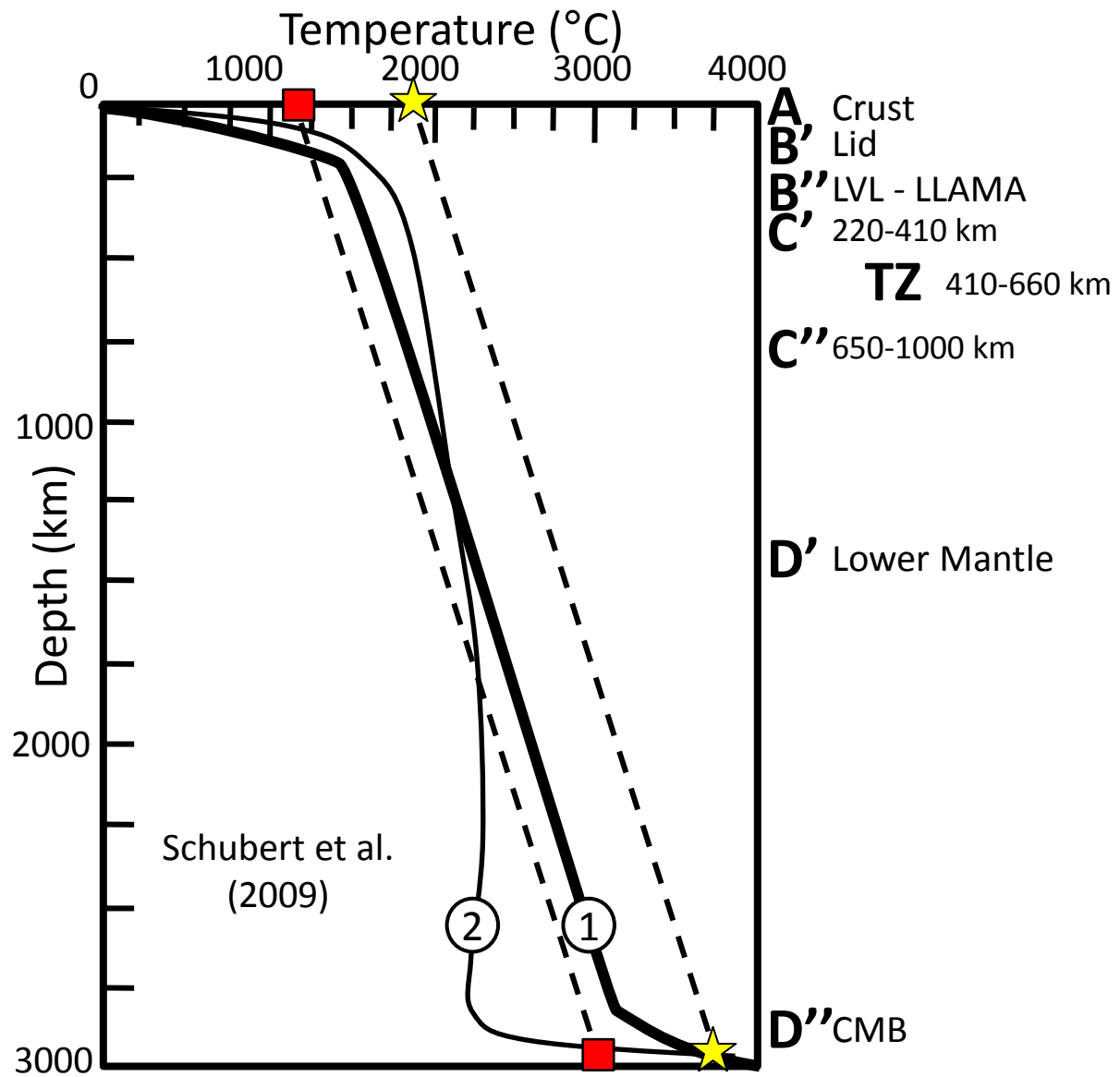
Table caption:

Table 1: Main parent-daughter isotopic characteristics of the systematics discussed in the text. The column "%" reports the mass abundance of that isotope compared to the remaining isotopic masses.
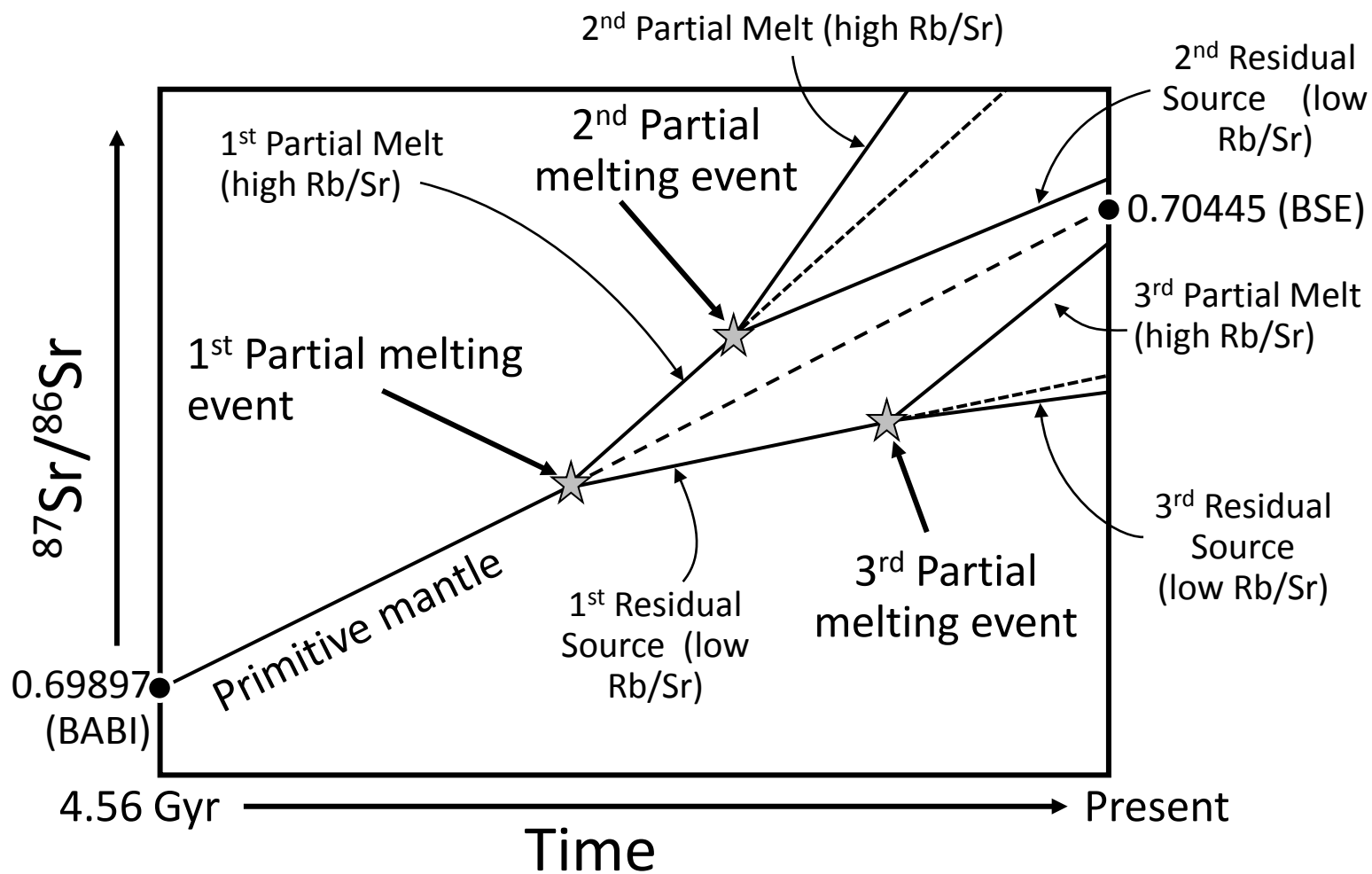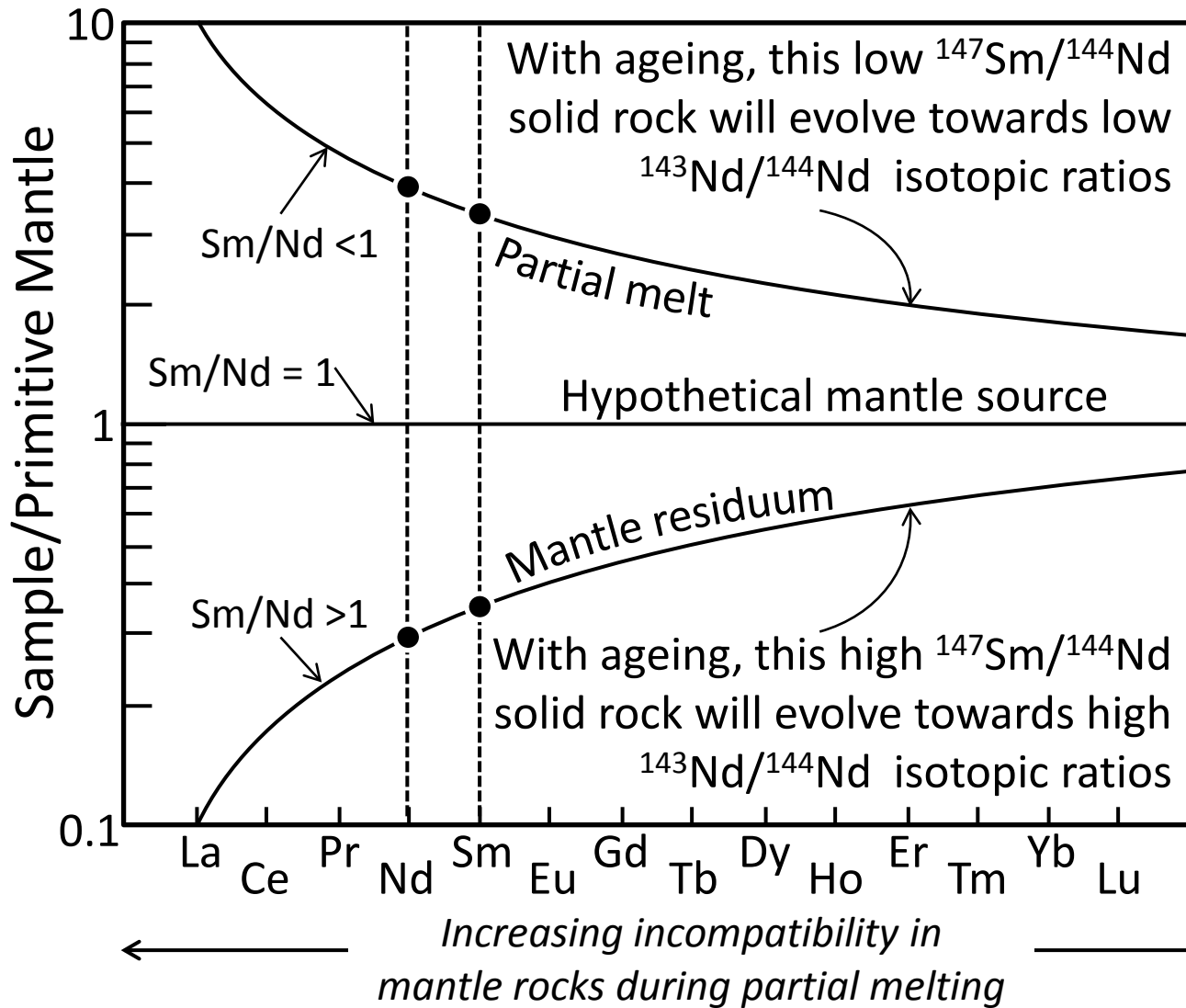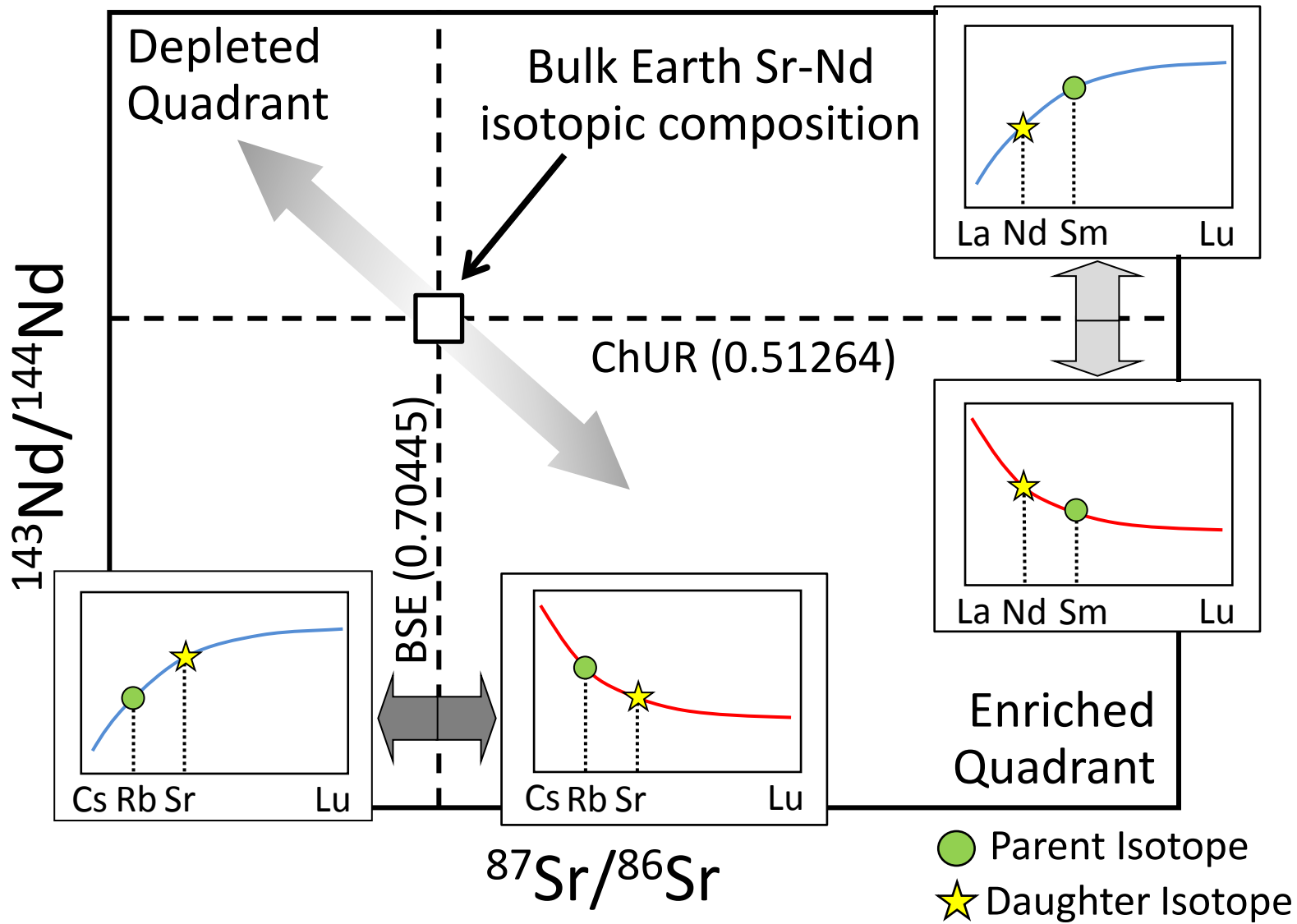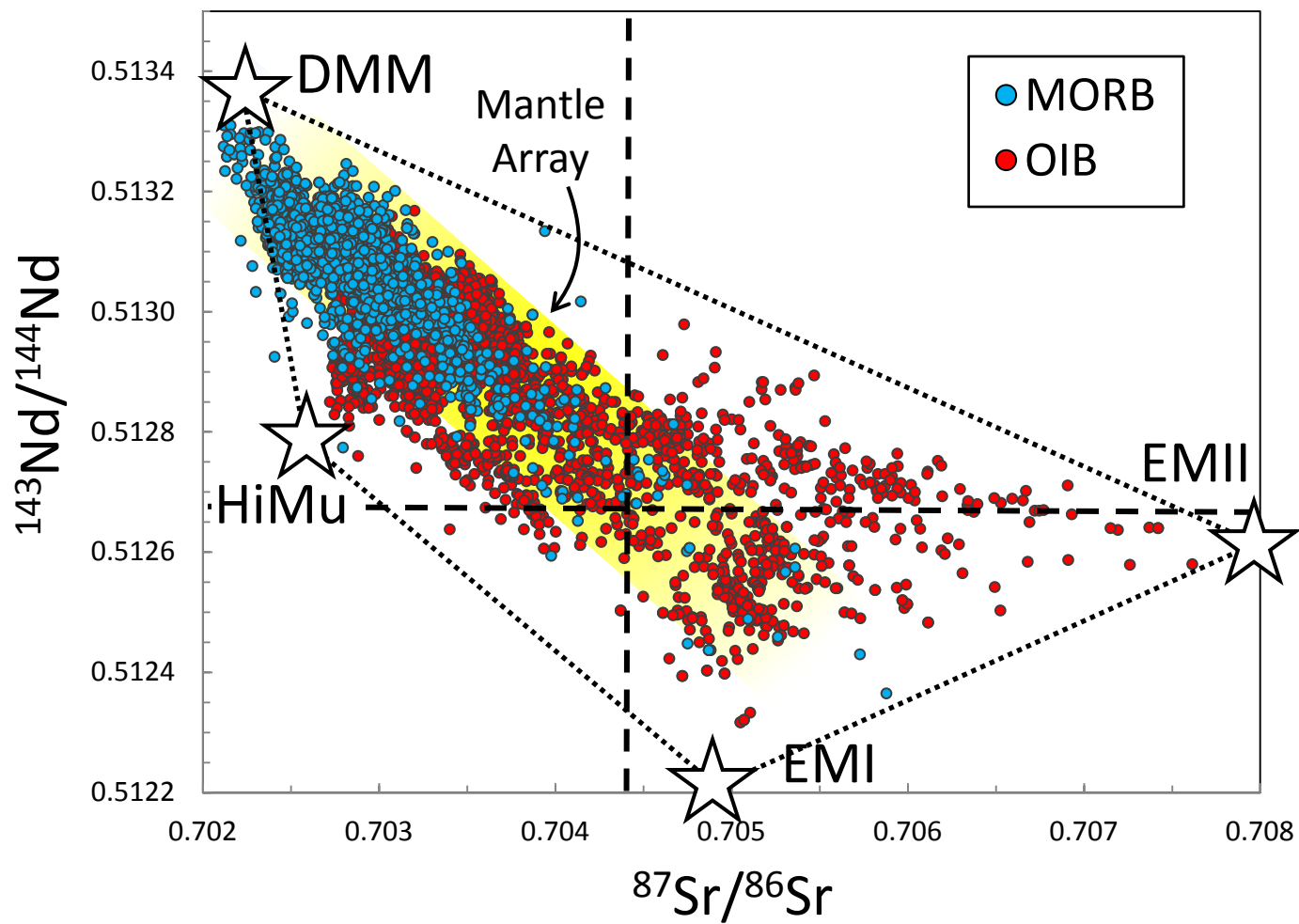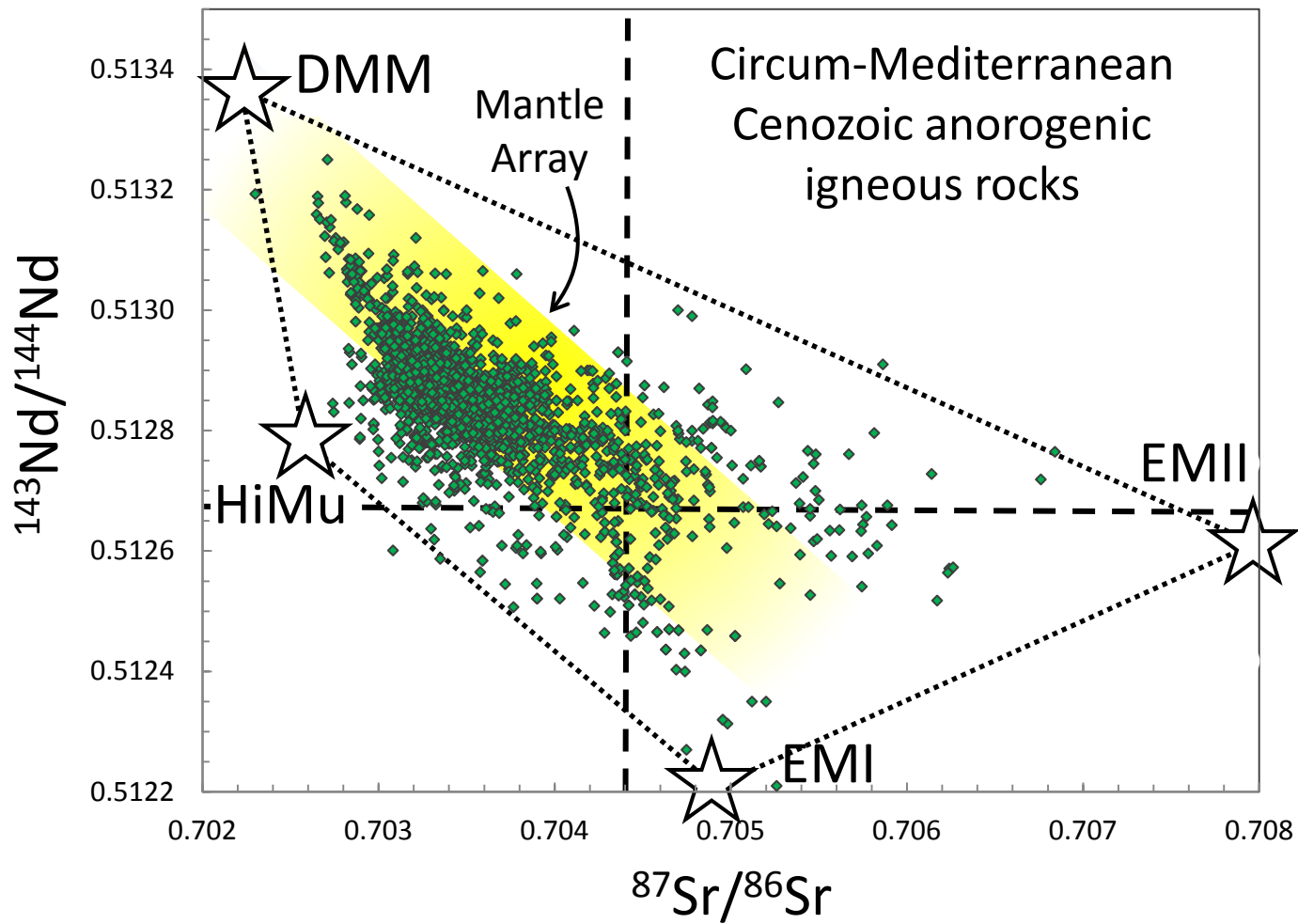
Fig. 1a
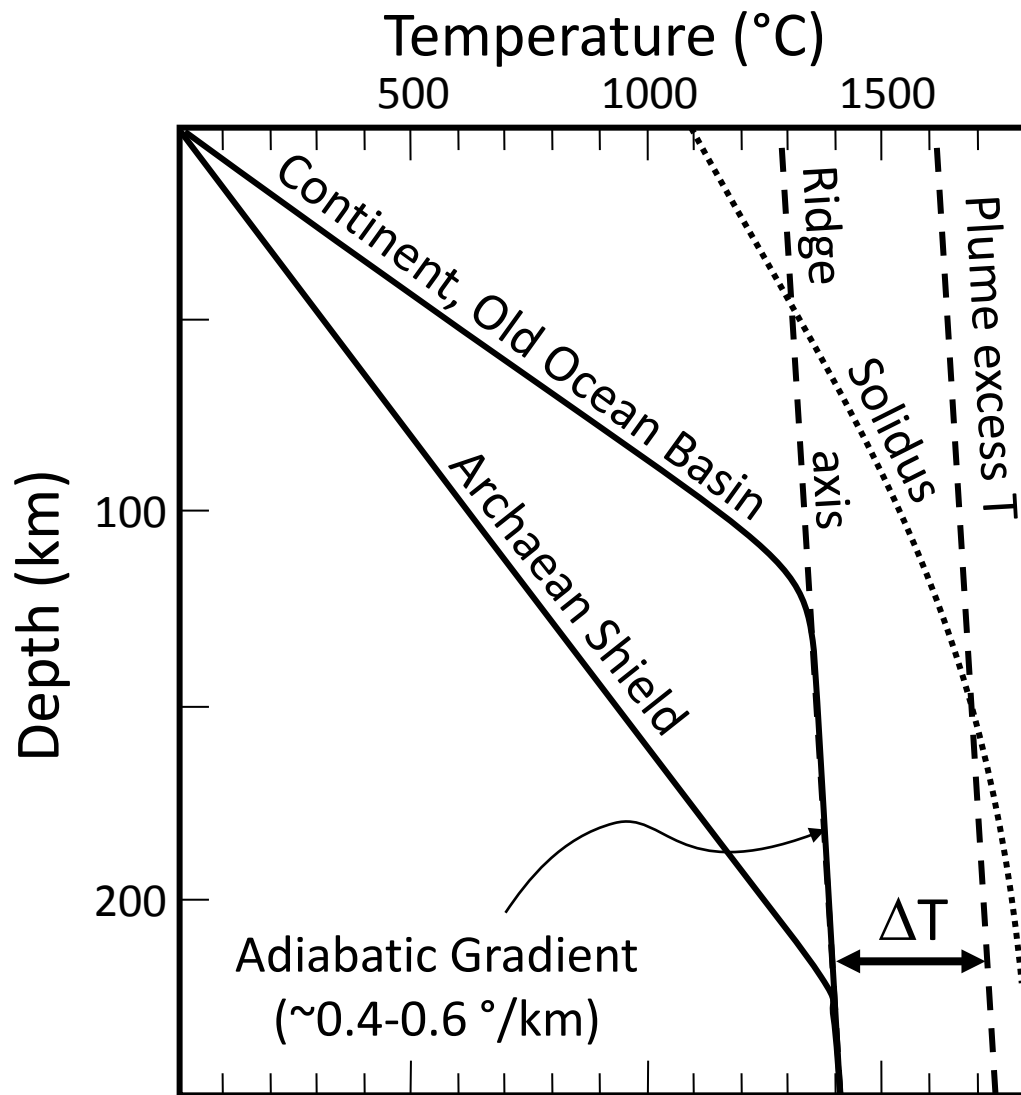
Lustrino and Anderson

Fig. 1b

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2nd Partial Melt (high Rb/Sr)

2nd Residual Source (low Rb/Sr)

1st Partial Melt (high Rb/Sr)

2nd Partial melting event

• 0.70445 (BSE)

1st Partial melting event

3rd Partial Melt (high Rb/Sr)

$^{87}Sr/^{86}Sr$

1st Residual Source (low Rb/Sr)

3rd Partial melting event

3rd Residual Source (low Rb/Sr)

Primitive mantle

0.69897 (BABI)

4.56 Gyr

Present

Time

Lustrino and Anderson

Fig. 2

With ageing, this low $^{147}Sm/^{144}Nd$ solid rock will evolve towards low $^{143}Nd/^{144}Nd$ isotopic ratios

Sm/Nd <1

Partial melt

Sm/Nd = 1

Hypothetical mantle source

Mantle residuum

Sm/Nd >1

With ageing, this high $^{147}Sm/^{144}Nd$ solid rock will evolve towards high $^{143}Nd/^{144}Nd$ isotopic ratios

Sample/Primitive Mantle

10

1

0.1

La Ce Pr Nd Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Increasing incompatibility in mantle rocks during partial melting

Lustrino and Anderson

Fig. 3

Depleted Quadrant

Bulk Earth Sr-Nd isotopic composition

ChUR (0.51264)

^{143}Nd/^{144}Nd

BSE (0.70445)

^{87}Sr/^{86}Sr

Enriched Quadrant

La Nd Sm Lu

Cs Rb Sr Lu

Parent Isotope

Daughter Isotope

Lustrino and Anderson

Fig. 4

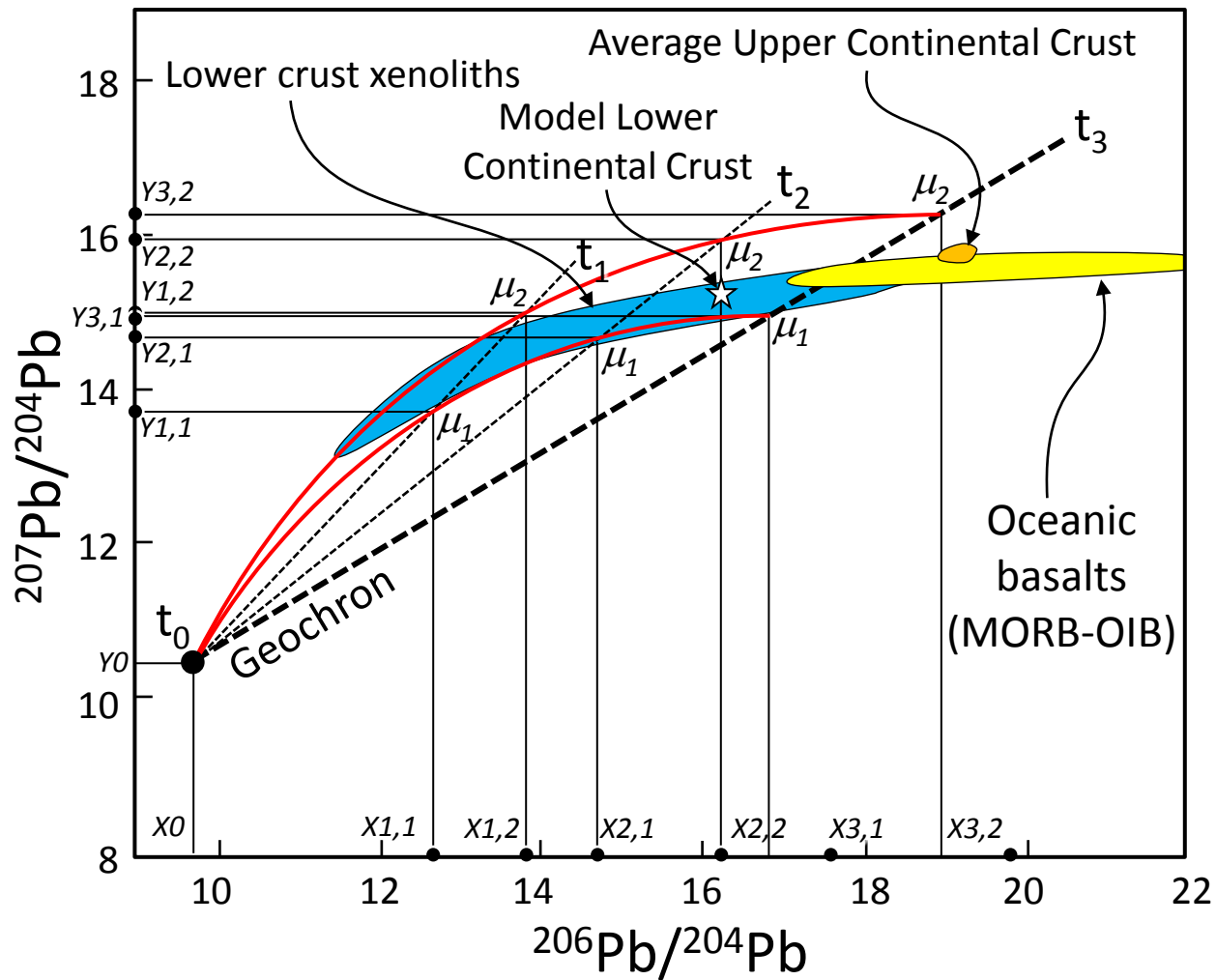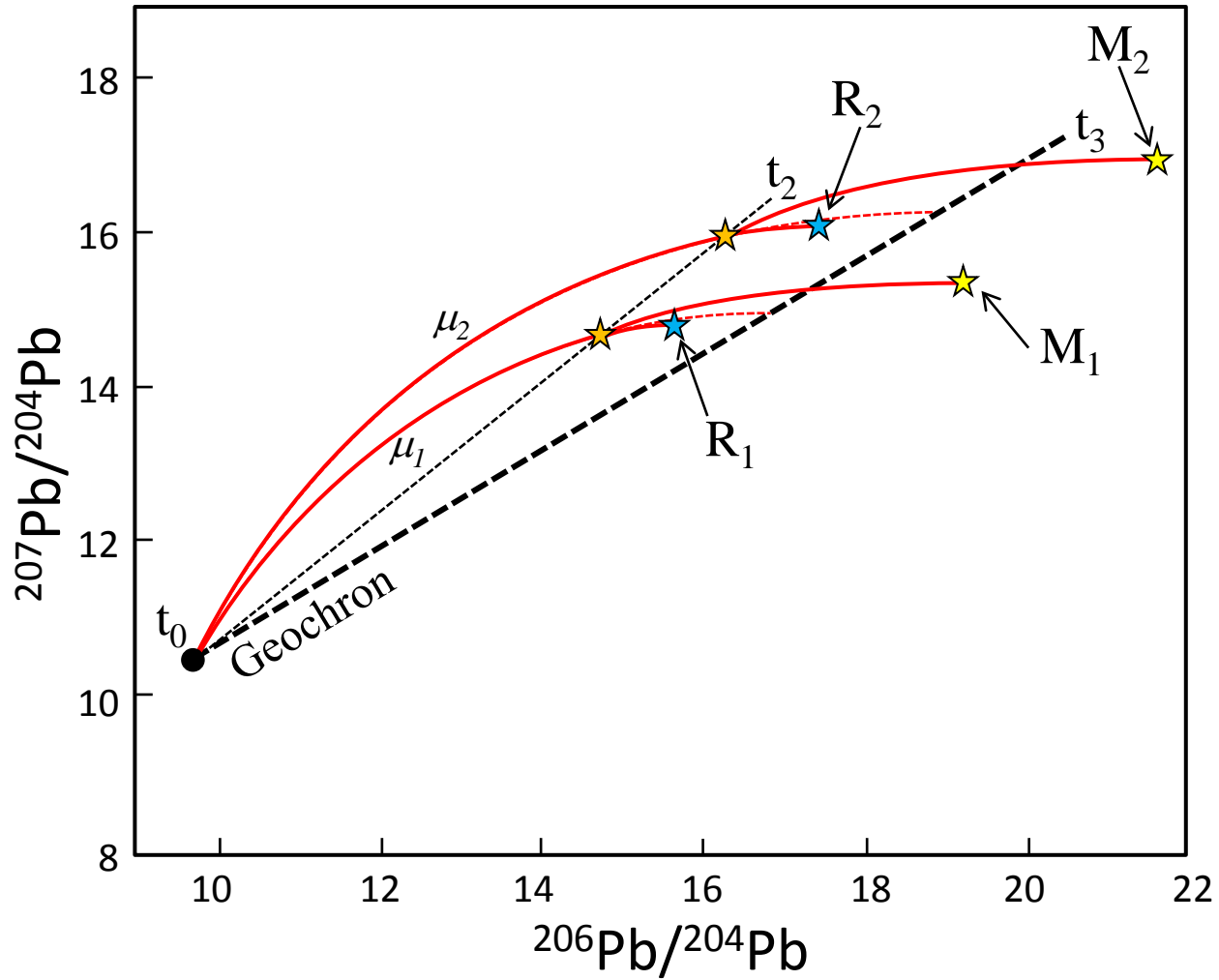Lustrino and Anderson   Fig. 5a
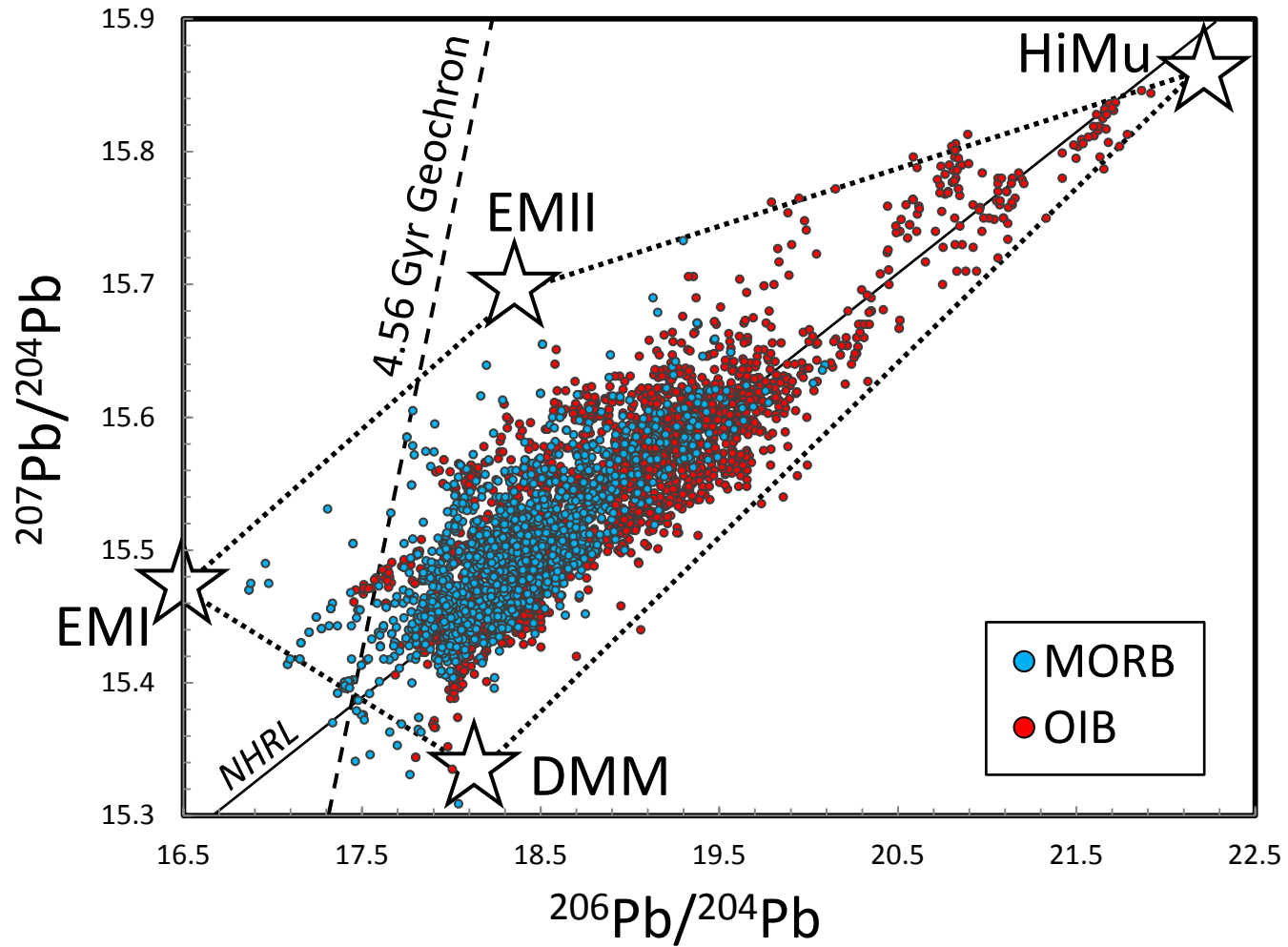
Lustrino and Anderson

Fig. 5b

Fig. 6a

Lustrino and Anderson

Lustrino and Anderson

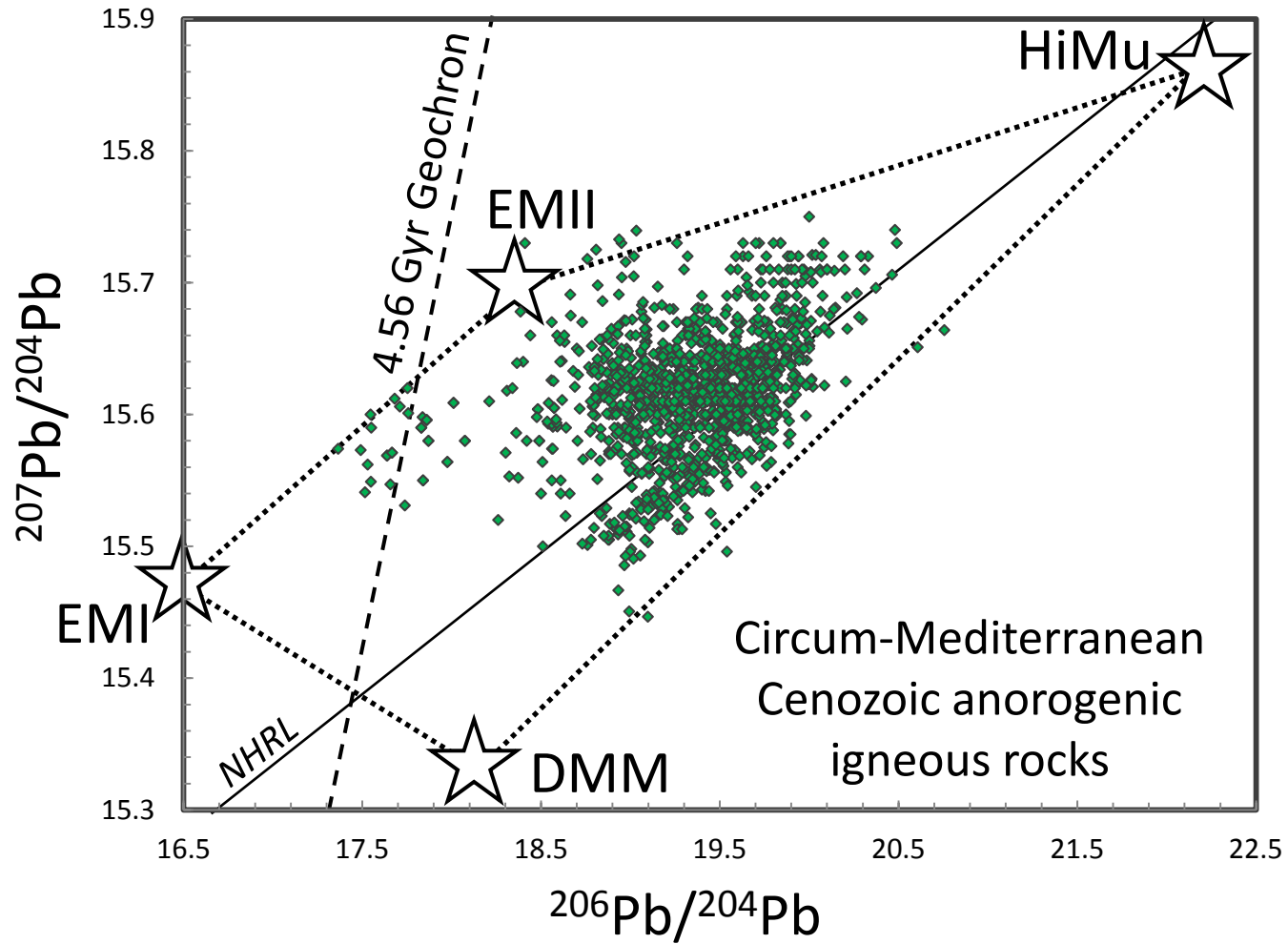Fig. 6b

Lustrino and Anderson
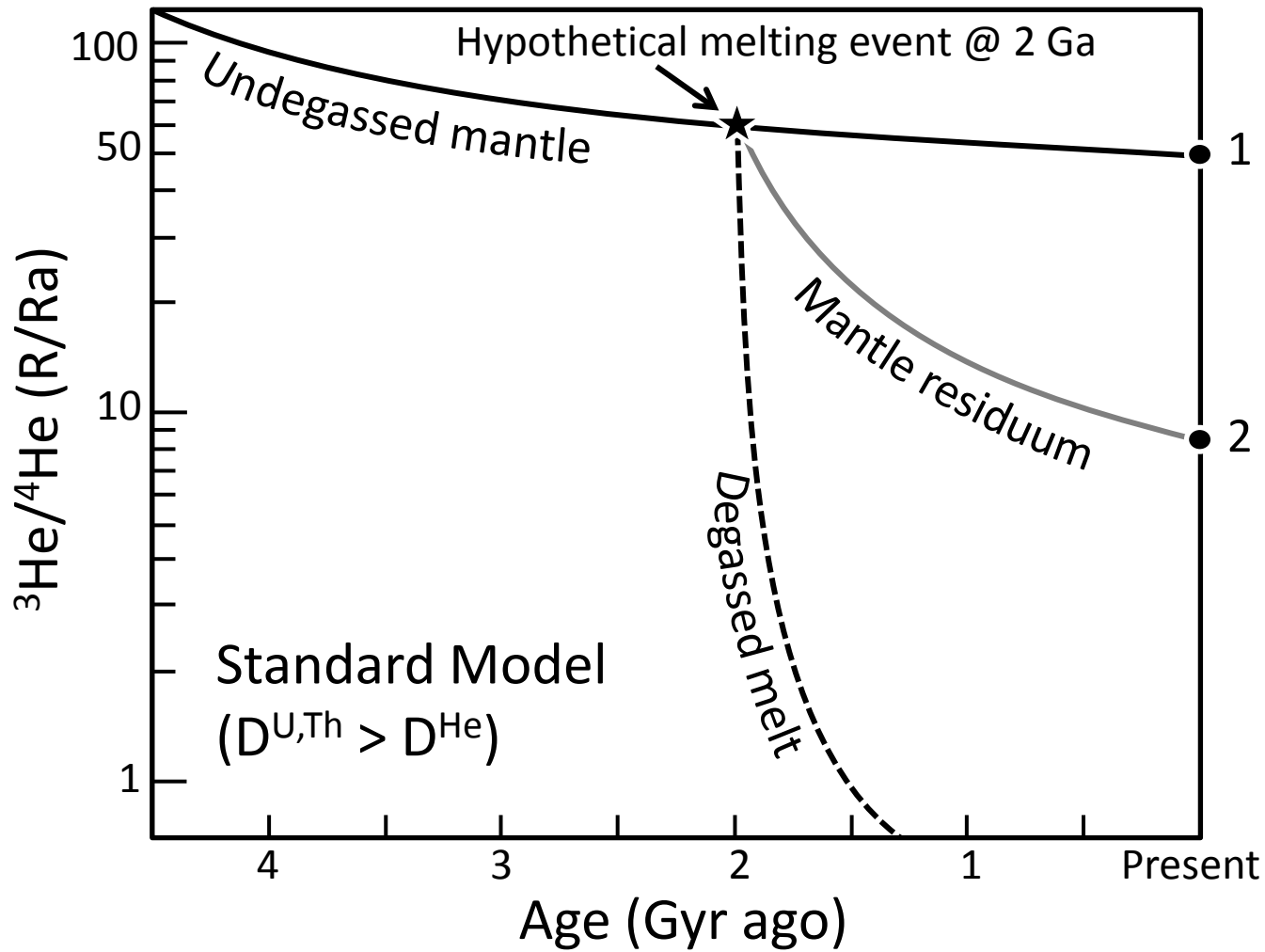
Fig. 7a

Lustrino and Anderson

Fig. 7b

Fig. 8a

Lustrino and Anderson
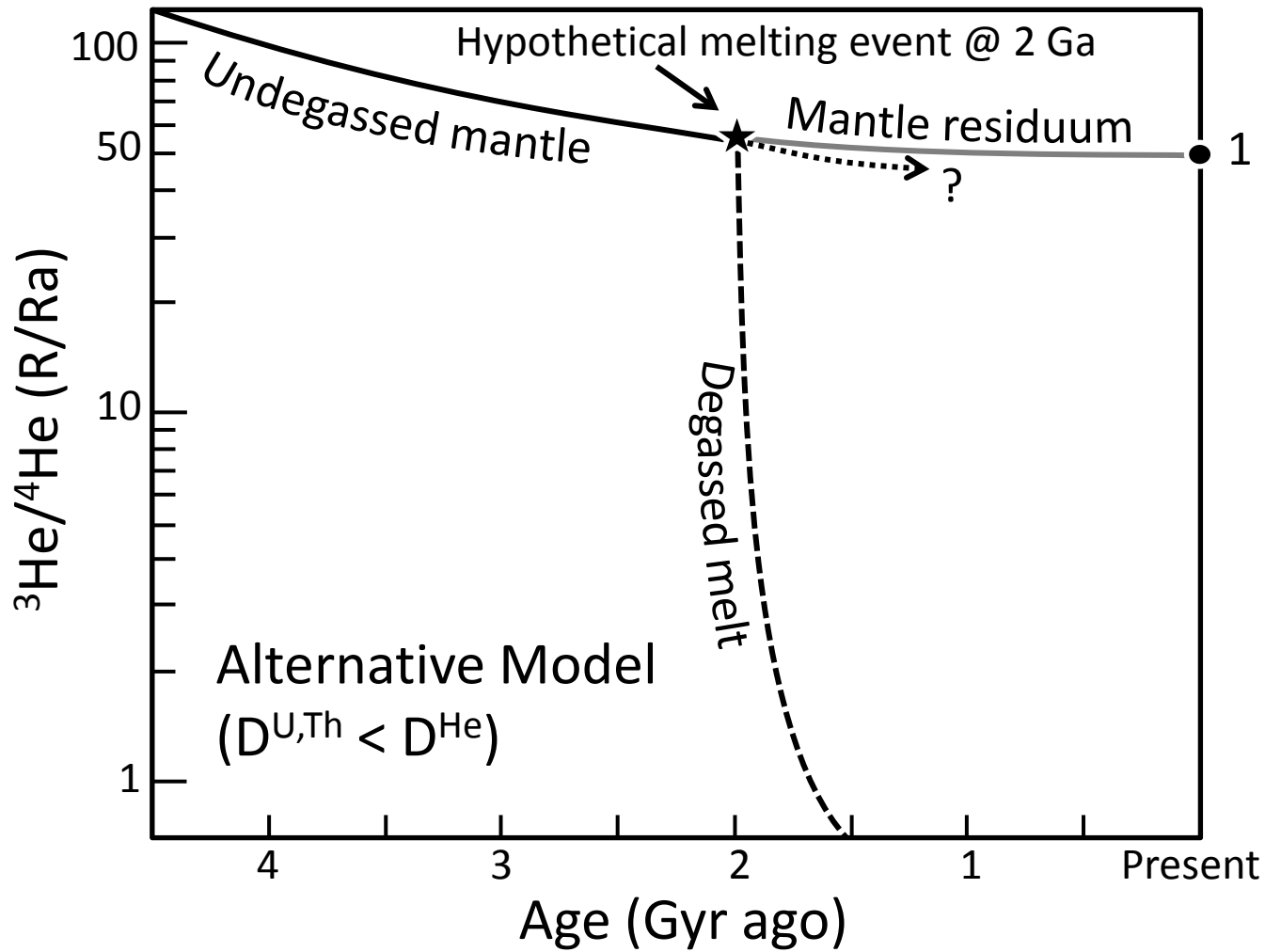
Fig. 8b

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Table 1
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Parent	%	Half-life	Daughter	Parent/Daughter Ratios	Present-day	Isotopic ratios	Initial	Present-day
^{87}Rb	27.8	$4.8*10^{10}$ yr	^{87}Sr	^{87}Rb/^{87}Sr	~0.072	^{87}Sr/^{86}Sr	0.69897	0.70445
^{147}Sm	15.0	$1.06*10^{11}$ yr	^{143}Nd	^{147}Sm/^{143}Nd	~0.202	^{143}Nd/^{144}Nd	0.506687	0.51264
^{232}Th	100	$1.4*10^{10}$ yr	^{208}Pb	^{232}Th/^{208}Pb	~36	^{206}Pb/^{204}Pb	9.31	
^{235}U	0.72	$7.07*10^{8}$ yr	^{207}Pb	^{235}U/^{207}Pb	~8.5	^{207}Pb/^{204}Pb	10.29	
^{238}U	99.28	$4.47*10^{9}$ yr	^{208}Pb	^{238}U/^{206}Pb	~0.06	^{208}Pb/^{204}Pb	29.48	