Lu-Hf ratios of crustal rocks and their bearing on zircon Hf isotope model ages: The effects of accessories

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ABSTRACT

All other factors being equal, the calculation of zircon Hf two stage model ages (T_{DM} Hf) depends on the particular Lu/Hf value assumed for the magmatic source, the effect being more pronounced as the age difference between zircon and magmatic source increases. It is generally considered that the Lu/Hf measured in the zircon-hosting rock does not represent the composition of the source because of potential garnet or zircon fractionation. Accordingly, most authors either assume a single fixed value for Lu/Hf$_{source}$, often Lu/Hf ≈ 0.079 to 0.108, or use two alternative models, one for felsic sources, often Lu/Hf ≈ 0.09, and the other for mafic sources, often Lu/Hf ≈ 0.165. In contrast with these opinions, however, here we show that partial melting of peraluminous sources causes little decoupling of Lu from Hf because of similar solubilities of zircon and monazite. Furthermore, the effects of residual garnet are largely compensated by the numerous zircon inclusions that garnet and other residual minerals almost always contain. Partial melting of metaluminous sources may significantly decouple Lu from Hf if allanite and/or titanite are not present in the source, but the effect decreases as the melt fraction increases. Similarly, fractional crystallization of metaluminous magmas may decouple Lu from Hf if amphibole or clinopyroxene begin to crystallize before zircon saturation. The Lu/Hf distribution in 4784 rocks from different regions and ages is lognormal rather than normal, and the calculated medians, i.e. the maximum of the probability density function for the logarithmically transformed Lu/Hf, are Lu/Hf$_{mafic\ rocks}$ ≈ 0.08, Lu/Hf$_{felsic\ rocks}$ ≈ 0.05, i.e. notably lower than the above-mentioned felsic and mafic magmatic source averages. Magmatic sources may be remarkably heterogeneous with respect to Lu/Hf. Our calculations show that fixed Lu/Hf$_{source}$ values translate the Lu/Hf heterogeneity of the source to the T_{DM} Hf thus producing an artificial distribution of model ages that may be erroneously interpreted as different episodes of crustal growth. Therefore, we propose that the best strategy to calculate two stage Hf model ages of zircon is to use the analytically determined whole-rock Lu/Hf ratio as a proxy of the source. In the case of detrital or inherited zircons, for which no whole-rock information is available, it is advisable first to determine whether they come from a mafic or felsic rock by interpreting cathodoluminescence images, Th/U ratios and other chemical parameters, and then venture an estimate of the Lu/Hf$_{source}$ from the SiO_2 average.

1. Introduction

As a result of the worldwide adoption of the LA-MC-ICPMS technique (e.g., Thirlwall and Walder, 1995; Griffin et al., 2002; Woodhead et al., 2004) the analysis of Hf isotopes in zircon has become increasingly popular for studying the formation of the crust and the petrogenesis of granite rocks. Unfortunately, many researchers often forget, or are unaware, that the proper interpretation of zircon Hf isotope data has several stringent requirements which, if not followed, may result in wrong conclusions (see Payne et al., 2016, and Vervoort and Kemp, 2016, for discussion). The calculation of two stage Hf model ages (T_{DM} Hf) has four main sources of uncertainty: (1) choice of the decay

constant (2) choice of mantle curve (3) estimation of the U-Pb zircon crystallization age (4) choice of the Lu/Hf of the crustal source. Several authors have debated points 1 to 3 quite thoroughly (e.g., Vervoort and Patchett, 1996; Blichert-Toft and Albarede, 1997; Blichert-Toft and Albarède, 2008; Patchett et al., 2004; Dhuime et al., 2011; Kemp et al., 2007; Dhuime et al., 2011; Vervoort and Kemp, 2016; Iizuka et al., 2017) but the Lu/Hf composition of potential crustal sources has rarely been discussed, particularly from the perspective of Lu and Hf residence in accessory minerals.

Two stage Hf model ages require assumption of a given crustal source Lu/Hf composition to trace the $^{176}Hf/^{177}Hf$ evolution from the zircon U-Pb crystallization age to interception with the selected mantle
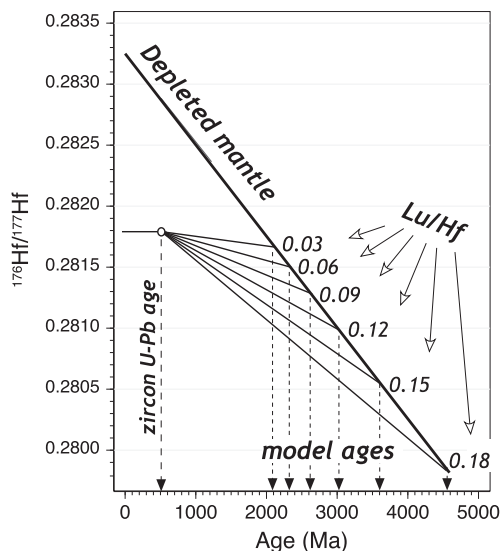
Fig. 1. Zircon Hf model ages are calculated in two steps: first, tracing the ^{176}Hf/^{177}Hf evolution from time = 0 to the zircon U/Pb crystallization age; second, tracing the ^{176}Hf/^{177}Hf evolution from this point until interception with the selected mantle curve. Note the dependence of T$_{DM}$ Hf from the Lu/Hf assumed for the magmatic source.
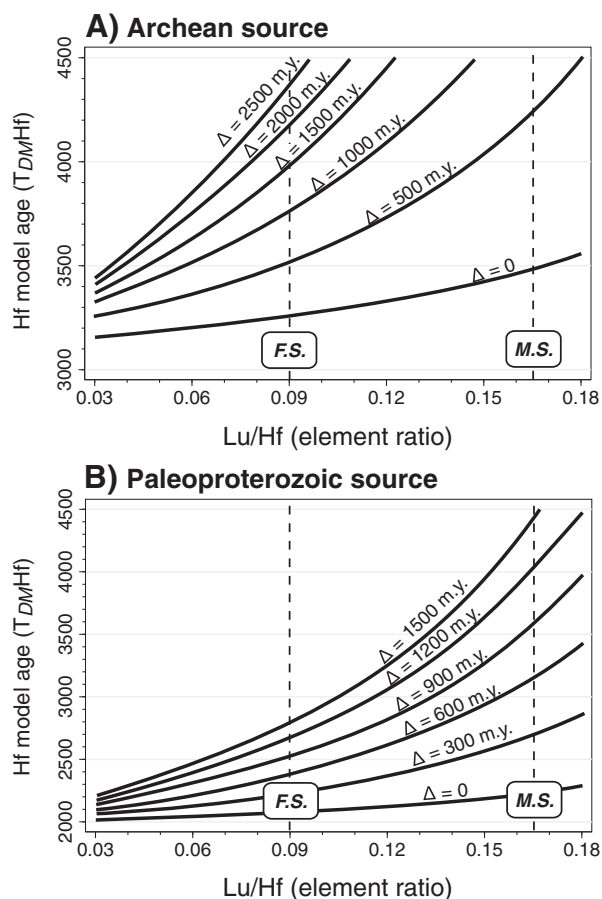

Fig. 2. Simulations of how the Lu/Hf selected for the source affects the T$_{DM}$ Hf of zircons with different U/Pb age from Archean (A) and Paleoproterozoic (B) sources. *F.S.* and *M.S.* represent the commonly used felsic source and mafic source averages, respectively. Δ represents the age difference between the zircon and its source. Note how the influence of Lu/Hf is greater as it and Δ increase.
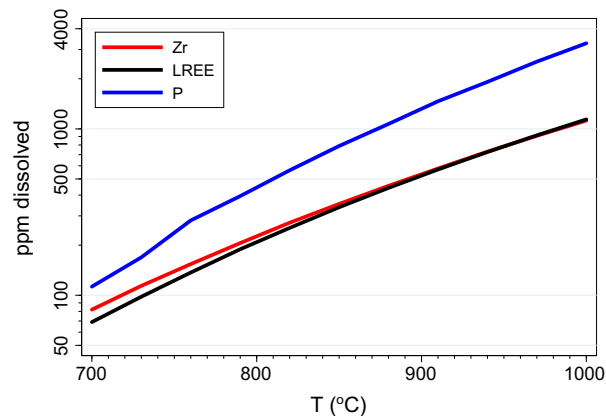

Fig. 3. Solubility curves of zircon (Boehnke et al., 2013), monazite (Stepanov et al., 2012) and apatite (Harrison and Watson, 1984, modified by Bea et al., 1992 for peraluminous melts) in felsic systems as functions of temperature represented by the concentration in the melt of Zr, LREE and P, respectively. The curves for monazite and zircon are nearly parallel and adjacent one to the other. The curve for apatite is steeper. Considering the concentrations of Lu and Hf in the three accessories, these curves explain the lack of significant Lu/Hf fractionation in peraluminous melts. See text.

curve (Fig. 1). This assumption is undoubtedly the weakest point of model age calculations because of the lack of a robust basis for choosing a particular Lu/Hf value and the strong influence of this on the resulting zircon Hf model ages (T$_{DM}$ Hf), particularly if zircons are much younger than the magmatic sources (Fig. 2). It is generally considered that the bulk composition of the zircon-hosting rock is not a suitable proxy for the Lu/Hf of the source because intracrustal differentiation processes involving garnet or zircon might significantly decouple the two elements (but see below). This consideration and the lack of evidence about the primary host-rock composition of inherited or detrital zircons have led many authors to assume a fixed Lu/Hf value supposed to represent the magmatic source. Such values include the average value for potential crustal protoliths (e.g., Amelin et al., 1999), the average upper continental crust (Bodet and Schärer, 2000; Iizuka et al., 2005) or the average bulk continental crust (Griffin et al., 2002; Hawkesworth and Kemp, 2006. However, given that Lu/Hf decreases significantly from mafic to felsic rocks (see Section 5), most authors now assume two values, one for felsic to intermediate magmatic sources: generally Lu/Hf ≈ 0.079 to 0.108 depending on the crustal model selected, and the other for mafic magmatic sources: generally Lu/Hf ≈ 0.13 to 0.21, Lu/Hf 0.165 is the most widely employed.

Nevertheless, these assumptions cannot be taken for granted and need more consideration. Firstly, it is not clear whether intracrustal granite magmatism may lead to large Lu/Hf variations. As discussed in Section 4 the similar behavior of Lu-rich and Hf-rich accessories during partial melting and crystallization tends to mutually cancel their effects on Lu/Hf. Secondly, the above-mentioned "magmatic source averages" are different from many published high-quality Lu/Hf data of crustal rocks from which abundant granite magmas have been formed. For example, Vervoort and Patchett (1996) studied Precambrian granites and found a distribution skewed to higher values with a mode of Lu/Hf = 0.025 and arithmetic mean of Lu/Hf = 0.066; Moyen and Martin (2012) compiled a database of Archean TTGs with an arithmetic mean of Lu/Hf = 0.035; Bea et al. (2003) found that the magmatic sources of Central Iberian granites cluster around Lu/Hf = 0.04, etc.

These considerations motivated us to study the variations of Lu/Hf in common crustal rocks and their influence on zircon Hf model ages, summarizing here the most important results. The strategy adopted was as follows: Firstly, we used available textural evidence and experimental data on the solubility of accessory phases in crustal melts to model the behavior of Lu and Hf during partial melting and melt segregation. Secondly, we compiled a large set of whole-rock analysis of Archean to Mesozoic igneous rocks from Eurasia, Africa, America, and
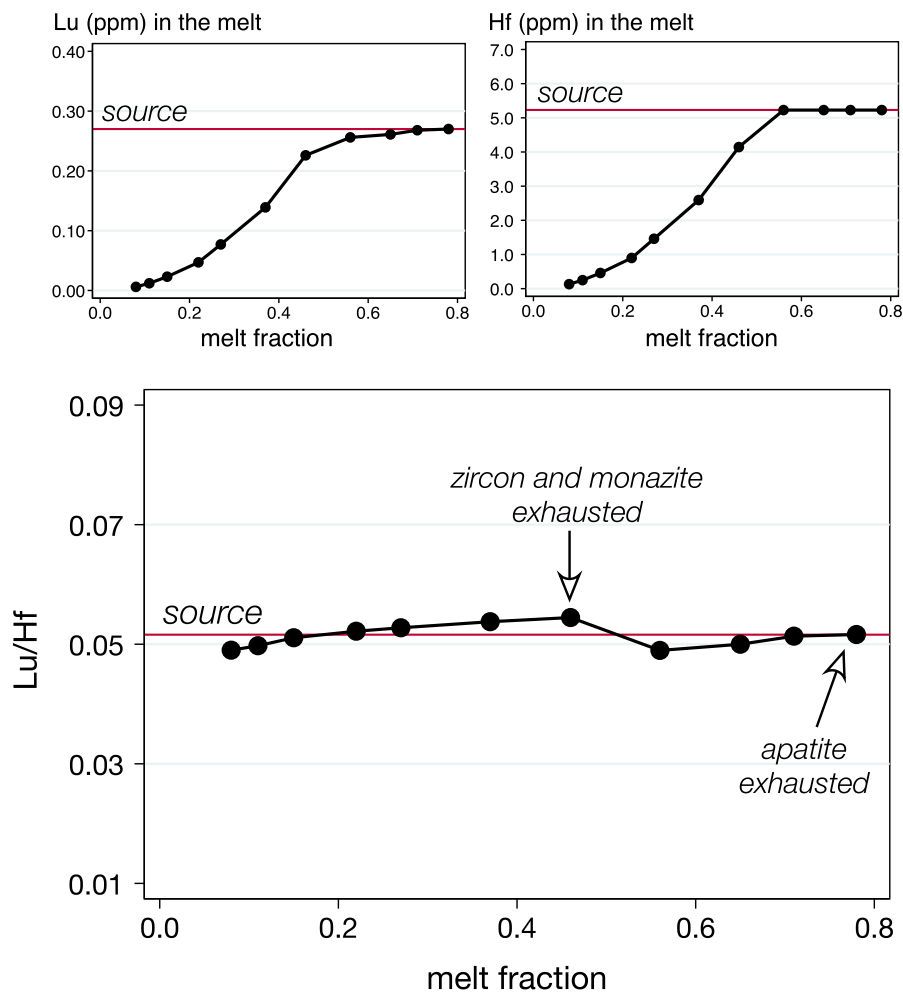
Fig. 4. Evolution of Lu and Hf and Lu/Hf as functions of the melt fraction in peraluminous systems (see Appendix for details). Despite the marked variations in the concentrations of the two elements, Lu/Hf_{melt} is nearly constant and close to Lu/H_{source}. because of the similar effect of temperature on the solubility of monazite (Lu main carrier) and zircon (Hf main carrier) as shown in Fig. 3.

Australia. Using the dataset we studied whether Lu/Hf varies systematically with rock type and silica contents, and which Lu/Hf values are likely to yield the most accurate T_{DM} Hf for a given rock type. Lastly, we checked the results against several well-studied natural examples and discussed the best approach to calculate zircon Hf model ages.

2. Samples and methods

The mineral dataset used here comprises the LA-ICP-MS analyses described in Bea (1996a) and Bea et al. (2006b). The whole-rock dataset comprises 4784 rocks analyzed with NAA or ICP-MS. About 80% of them were performed by the authors at the University of Granada on samples from Iberia, the Urals, Kola, Transbaikalia, Ivrea-Verbano, the Arabian-Nubian Shield, the Neoproterozoic to Archean inliers of the Egypt Western Desert, the Sanandaj-Sirjan zone in Iran, and the Archean to Proterozoic and Early Paleozoic terranes from the Reguibat and the Reguibat Promontory. The remaining 20% were collected from the literature and include the above-mentioned TTG database of Moyen and Martin (2012), as well as samples from the Cordilleran batholiths of America, the Leo Rise of the Western African Craton, the Hoggar, Amazonia, China, Tibet, and the Lachland Fold Belt. The datasets used are available from the authors upon request.

It is important to note that ICP-MS analysis may underestimate Hf concentrations depending on the sample solution method used (Hall and Plant, 1992; Totland et al., 1992; Park et al., 2013), hence producing erroneously high Lu/Hf ratios. Hydrofluoric evaporation at atmospheric pressure does not fully dissolves the zircon grains present in a sample. Hydrofluoric attack at elevated pressure either in Parr-type

bombs or high-pressure microwave reactors often dissolves all zircon; nonetheless, the ICP-MS Zr results must be compared with Zr XRF results before they may be accepted. Alkaline fusion prior to acid attack dissolves all zircon. To avoid outliers, therefore, the initial dataset was filtered to exclude: (1) samples analyzed with ICP-MS after low-pressure dissolution, (2) samples with Lu/Hf > 0.5 because these are likely caused by incomplete zircon dissolution or reflect ratio errors caused by extremely low Hf concentrations, (3) samples with Zr/Hf > 60 or Zr/Hf < 10 because they probably reflect anomalous rocks or wrong analyses (see Bea et al., 2006b), (4) samples with SiO_2 < 45 wt% or SiO_2 > 76 wt% to avoid oddities, metasomatic and extremely fractionated rocks.

To calculate the Hf isotope parameters, we used the following CHUR values $^{176}Lu/^{177}Hf = 0.0336$; $^{176}Hf/^{177}Hf = 0.282785$ (Bouvier et al., 2008), and λ $^{176}Lu = 1.867 * 10^{-11} y^{-1}$ (Scherer et al., 2001; Söderlund et al., 2004). We also assumed the mantle source was depleted and changed from chondritic ($\varepsilon Hf = 0$) at 4.56 Ga to $\varepsilon Hf_{0Ga} = +16$ today (but see Vervoort and Kemp, 2016; and references therein for discussion). To calculate the Nd isotope parameters we used the presently accepted CHUR Sm–Nd reference parameters, $^{147}Sm/^{144}Nd = 0.1966$ and $^{143}Nd/^{144}Nd = 0.512638$ (Jacobsen and Wasserburg, 1980, 1984), and assumed a depleted mantle that changed from chondritic ($\varepsilon Nd = 0$) at 4.56 Ga to $\varepsilon Nd = +10$ at the present day (Goldstein et al., 1984).

3. Crustal residence of Lu and Hf

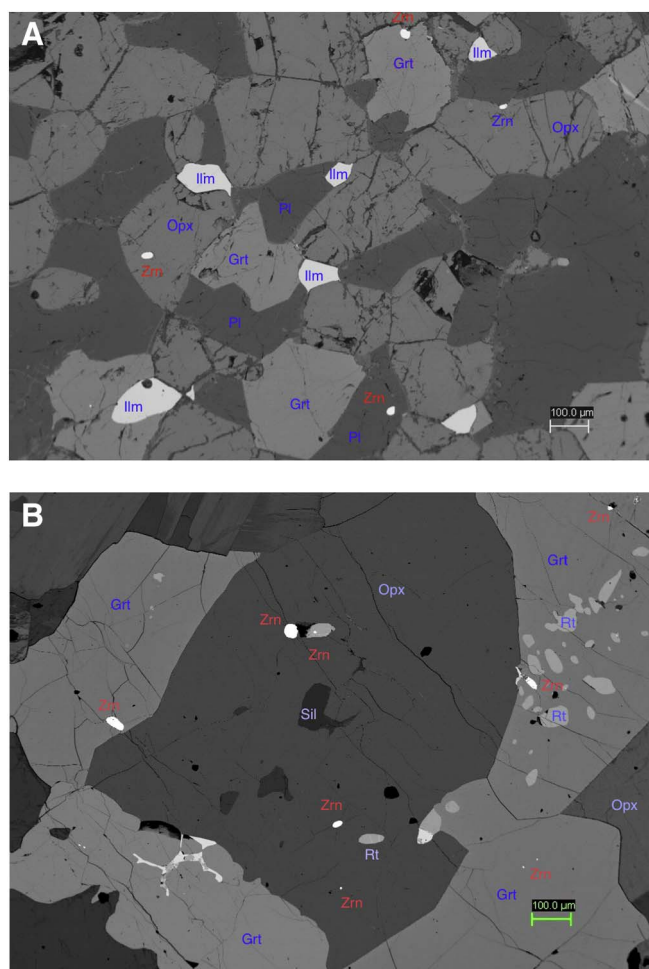The crustal geochemistry of Lu and Hf is mainly controlled by

Fig. 5. Textural aspect of granulites: (A) mafic granulite from Ivrea-Verbano, Italy (B) felsic granulite from the Lapland Granulite Belt, Russia. Note the abundance of zircon included in garnet, pyroxene, and plagioclase. If melts were extracted from these rocks, the effects of residual garnet on Lu/Hf ratios would be largely compensated by the retention of zircon; see Table 1. Mineral abbreviations are from Kretz (1983).

Table 1
Average concentrations and Lu/Hf in seven leucosome/melanosome pairs from the Ivrea-Verbano metapelitic granulites. Despite the melanosomes contain > 40 vol% modal garnet, the Lu/Hf in melanosomes and leucosomes is virtually identical. This happens because residual garnet contain numerous zircon inclusions that compensate the effects of garnet.

	Lu (ppm)	Hf (ppm)	Lu/Hf	95% conf. interval
Leucosomes	0.10	1.71	0.058	0.045–0.074
Garnet-sillimanite melanosome	0.43	7.01	0.061	0.048–0.078

accessory minerals (e.g., Bea, 1996a). Hafnium (Z = 72) is not an essential structural component of any mineral. The lanthanide contraction effect causes Hf^{4+} and Zr^{4+} to have nearly identical ionic radii (0.83 Å and 0.84 Å respectively in VIII fold coordination) so less abundant Hf is always sequestered in Zr minerals. The Zr/Hf chondritic ratio is 37 (McDonough and Sun, 1995) and changes little in crustal rocks, only decreasing to Zr/Hf ≈ 25–20 in heavily fractionated leucocratic segregates from granitoids (Bea et al., 2006b). Zirconium forms some 27 minerals, 7 oxides and 20 silicates. Ubiquitous zircon ($ZrSiO_4$) is the most abundant, followed, albeit distantly, by baddeleyite (ZrO_2), a scarce mineral found in carbonatites and extremely silica-undersaturated rocks. The other Zr-bearing minerals are very rare and mostly limited to agpaitic rocks (Vlasov, 1966). Zircon contains about 1 wt% of

Hf and is the main Hf reservoir in common crustal rocks (Bea et al., 2006b). Other major and accessory minerals such as titanite, amphibole, clinopyroxene and garnet may also contain several ppm of Hf (see below).

Lutetium (Z = 71) is the heaviest REE. It forms the trivalent ion Lu^{3+} with an ionic radius in sixfold coordination of 0.86 Å, similar to Y^{3+} (0.90 Å). Accordingly, yttrium minerals such as xenotime, yttrofluorite, gadolinite, kobeite, etc., and the Y-rich niobates of the fergusonite-formanite, euxenite-polycrase, aeschinite, pyrochlore, and samarskite groups also contain elevated concentrations of Lu and the other HREE (Vlasov, 1966). Most of these minerals, however, are only found in highly alkaline, often agpaitic, rocks. For this reason, the common crustal rocks' Lu budget is shared between accessories such as xenotime, monazite, allanite, zircon, titanite and thorite-huttonite, and rock-forming minerals such as garnet, amphibole and clinopyroxene.

The Lu/Hf ratios of common minerals can be tentatively summarized as follows:

- Xenotime, with 4000 to 7000 ppm Lu, has Hf ranging from 1–2 ppm in pure xenotime to 20,000 ppm in zircon-xenotime mixed phases, i.e., Lu/Hf from > 1000 to 0.1.
- Monazite contains no, or very little, Hf, and several hundred to a few thousand ppm of Lu; accordingly, Lu/Hf is always > 1000.
- Apatite contains no, or very little, Hf either. Lu is highly variable, from 0.2 to 25 ppm, albeit with the highest values resulting from contamination with minute monazite inclusions. Lu/Hf is always > 100.
- Thorite-huttonite often contains several hundred to a few thousand ppm Lu and negligible Hf, with Lu/Hf > 100.
- Allanite has between 15 and 50 ppm of Lu and no, or very little, Hf with Lu/Hf generally > 100, similar to monazite and apatite.
- Zircon is, after xenotime and monazite, the most important Lu reservoir, with concentrations often around 65–90 ppm. Its elevated Hf, however, results in Lu/Hf ≈ 0.06–0.08, the lowest values of any mineral.
- Primary titanite contains somewhat elevated concentrations of Lu (5–10 ppm) and Hf (30–50 ppm), with Lu/Hf ≈ 0.16.
- Amphibole often has Lu of around 0.25–0.35 ppm, and Hf 2–3 ppm, with Lu/Hf ≈ 0.12–0.13.
- Clinopyroxene often has Lu ranging from 0.07 to 0.1 ppm and Hf between 0.9 and 1.7 ppm, with Lu/Hf ≈ 0.06–0.07, i.e., about half that of amphibole.
- Garnet often contains about 1.8 to 2.7 ppm Lu and 0.4 to 0.6 ppm Hf, with Lu/Hf ≈ 3.5 to 5.7, the highest value of any silicate except allanite.

4. Effects of Lu and Hf minerals during intracrustal processes

Not all the above-mentioned minerals play a role during magma formation and segregation in the crust. Xenotime, for example, is present in medium grade metapelites but disappears quickly as the temperature increases, consumed in garnet-forming reactions (Bea and Montero, 1999). The two thorium orthosilicates, huttonite and thorite, are HREE-rich but contribute little to the Lu budget because of their very low modal fraction. Therefore, the minerals that generally influence the Lu/Hf distribution in crustal partial melts can be reduced to (i) monazite, apatite, zircon and garnet if the source is peraluminous, and (ii) apatite, zircon, allanite, titanite, amphibole and clinopyroxene if the source is metaluminous.

4.1. Lu/Hf in anatectic melts derived from felsic peraluminous protoliths

Kinetic effects aside, the dissolution of monazite, zircon and apatite in anatectic melts depends on their intrinsic solubility and the modal proportion of them available to the melt (Watson et al., 1989; Bea, 1996b). As melt fraction increases the relative amounts of each
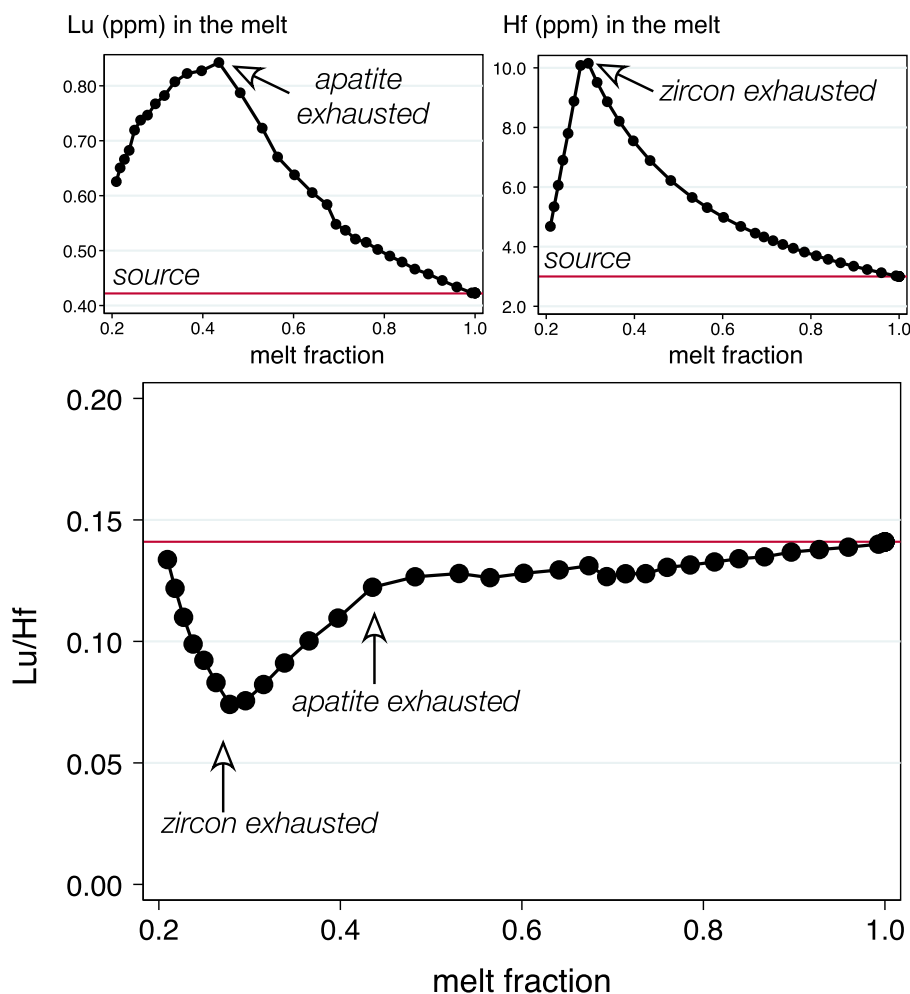
Fig. 6. Evolution of Lu and Hf and Lu/Hf as functions of the melt fraction in metaluminous systems with no allanite or titanite in the source (see Appendix for details). Lu/Hf$_{melt}$ decreases until zircon is exhausted from the source (m.f. ≈ 0.3) then increases quickly until all apatite is incorporated into the melt (m.f. ≈ 0.45) where Lu/Hf$_{melt}$ is slightly lower than Lu/Hf$_{source}$. Afterwards Lu/Hf$_{melt}$ converges slowly to Lu/Hf$_{source}$ as the temperature increases.

accessory "seen" by the melt are likely to approach the relative modal proportions. If so, the melt Lu/Hf composition would be a function of the modal proportion of the three accessories and the solubility of each accessory. In the absence of residual garnet, the last parameter determines the changes in Lu/Hf in the melt with respect to the source.

The solubility of zircon, monazite, and apatite in melts primarily depends on temperature. Fig. 3 shows the solubility of the three minerals calculated according to the models proposed by Boehnke et al. (2013) for zircon, Stepanov et al. (2012) for monazite, and Harrison and Watson (1984), modified by Bea et al. (1992) for apatite. Monazite and zircon solubility curves are nearly parallel but that of apatite is steeper. Given that monazite and zircon exert more influence on Lu$_{melt}$ and Hf$_{melt}$ than apatite, it seems that the differential solubility of accessories may hardly cause significant variations in the melt Lu/Hf. To check this, we modeled a peraluminous magmatic source using a rock from the Peña Negra Anatectic Complex, Central Spain, as an example (see Electronic Appendix for details). From the above-mentioned solubility curves and the Winther (1995) model for estimating the composition of partial melts, we calculated Lu$_{melt}$ and Hf$_{melt}$ assuming that no garnet was formed and all accessories were available to the melt proportional to their modal abundance. Fig. 4 shows how Lu$_{melt}$ and Hf$_{melt}$ increase with melt fraction (i.e., temperature) but Lu/Hf$_{melt}$ stays nearly constant with little scatter around Lu/Hf$_{source}$.

4.2. The effects of residual garnet

The effects of residual garnet and, especially, the permanence of accessories included in residual minerals cannot be modeled as above

but can be determined empirically. Most granulite rocks contain zircon included in residual garnet and orthopyroxene (Fig. 5), and this may compensate the effects of residual garnet retention on the Lu/Hf of segregated melts. A good example comes from the Kinzigite Formation of Ivrea-Verbano (Mehnert, 1975; Schmid and Wood, 1976) in which Bea and Montero (1999) studied the composition of spatially associated granitic leucosomes and granulitic melanosomes (modal garnet > 35–40%). Despite the Lu and Hf concentrations being lower in the leucosomes, the average Lu/Hf of these is 0.058, virtually identical to the average Lu/Hf of the melanosomes 0.061, so indicating that no significant variation Lu/Hf was produced despite the formation of garnet-rich residua (Table 1). This might explain the absence of high initial ^{176}Hf/^{177}Hf compositions in lower crustal granites and rhyolites that puzzled Vervoort and Patchett (1996).

4.3. Composition of anatectic melts derived from mafic metaluminous protoliths

In metaluminous protoliths an elevated proportion of Lu resides in amphibole, clinopyroxene, or garnet. The rest dwells in accessories: ubiquitous apatite and zircon, and rare allanite and titanite. This being the case, the Lu solid/melt partitioning must be treated (i) as henrian for the Lu that dwells in major minerals and, perhaps, apatite (ii) in terms of accessory solubilities for zircon, allanite, and titanite. The partitioning of Hf, on the other hand, must always be contemplated in terms of zircon solubility. Taking into account these considerations we modeled a metaluminous high-K calc-alkaline gabbro-dioritic source with apatite and zircon as the only accessories. The Lu$_{melt}$ and Hf$_{melt}$
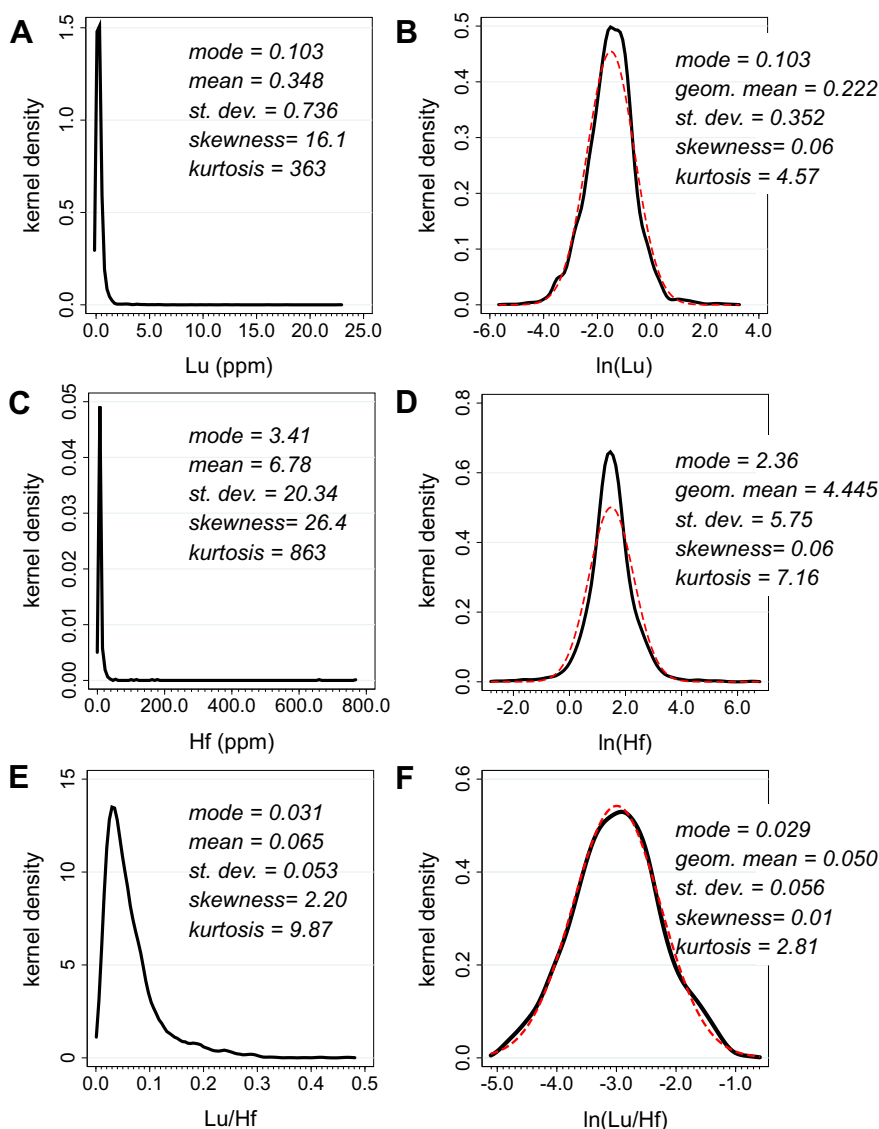
Fig. 7. Distribution of raw and logarithmic Lu, Hf and Lu/Hf in 4784 rock analyses (see text). The red dashed line in B, D, and F represents a gaussian distribution with the same mean and standard deviation. The three variables are lognormal so that their logarithms, especially ln(Lu/Hf), almost perfectly fit the theoretical gaussian distribution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

were determined by combining the MELTS software (thermodynamics from Ghiorso and Sack, 1995; Asimow and Ghiorso, 1998; front end from Smith and Asimow, 2005) and the above-mentioned accessory solubility models (see details in Electronic Appendix). Fig. 6 reveals that Lu/Hf$_{melt}$ decreases with melt fraction (m.f.) reaching a minimum at m.f. ≈ 0.3, then increases swiftly until all apatite is exhausted from the source (m.f. ≈ 0.45) at which point Lu/Hf$_{melt}$ is slightly lower than Lu/Hf$_{source}$. As the temperature increases further Lu/Hf$_{melt}$ also increases converging slowly to Lu/Hf$_{source}$. Little is known about the solubility of titanite and allanite in melts, but the few existing data (Prince, 1943; Broska et al., 1999) indicate that both minerals' solubility increase steeply with temperature. If so, the presence of these accessories in the source will tend to compensate the effect of zircon, hindering Lu/Hf partitioning between source and melt and so leading, once more, to Lu/Hf$_{melt}$ ≈ Lu/Hf$_{source}$.

If garnet remains in the source, its effects might be compensated by zircon inclusions in residual minerals (see Section 4.2). Nonetheless, if there is little or no zircon, or the bulk of this mineral is available to the melt, garnet in the residuum may cause partial melts to be notably depleted in Hf relative to Lu, i.e., low Lu/Hf$_{melt}$ and complementary high Lu/Hf$_{residuum}$ as proposed by Vervoort and Patchett (1996). Looking at the abundance and distribution of zircon in granulitic rocks, however, it seems that the permanence of zircon inclusions in residua,

and hence little melt/restite Lu/Hf fractionation, is more the rule than the exception.

4.4. Lu/Hf fractionation during magmatic fractionation

Experimental work indicates that mafic to intermediate magmas become saturated in zircon at much lower temperatures than required for the onset of crystallization of HREE-bearing rock-forming minerals such as clinopyroxene, amphibole and garnet (Hess et al., 1980; Dickinson and Hess, 1982; Watson and Harrison, 1983; Boehnke et al., 2013). Any fractionation of such minerals occurring before zircon saturation would thus decouple Lu from Hf and produce igneous rock series with Lu/Hf decreasing from the most mafic to the most felsic members. Peraluminous granitoids, on the other hand, which in most cases are saturated or nearly saturated in zircon and monazite, are likely to maintain nearly constant Lu/Hf during fractionation. Xenotime saturation, which only occurs in highly silicic melts, may increase the Lu/Hf ratios of the most silicic members. Evidence for this is given in the next section.

5. Distribution of Lu/Hf in crustal rocks

The "nugget effect" arising from residence in accessory phases

Table 2
Averages (medians) of Lu, Hf and Lu/Hf for the whole dataset and considered groups. See text for explanation.

SiO$_2$ range	Lu (ppm)	Hf (ppm)	Lu/Hf	95% conf. interval
Whole dataset (n = 4784)				
Total	0.222	4.445	0.050	0.049–0.051
45–50 wt%	0.225	2.720	0.082	0.076–0.090
50–55 wt%	0.308	4.227	0.073	0.068–0.078
55–60 wt%	0.303	5.132	0.059	0.056–0.063
60–65 wt%	0.247	4.687	0.053	0.051–0.055
65–70 wt%	0.195	4.698	0.041	0.040–0.043
70–74 wt%	0.184	4.621	0.040	0.038–0.041
> 74 wt%	0.207	4.509	0.046	0.042–0.050
M-type granitoids (n = 40)				
Total	0.234	1.800	0.130	0.096–0.176
45–50 wt%	0.186	1.295	0.143	0.078–0.264
50–55 wt%	0.167	1.314	0.127	0.050–0.321
55–60 wt%	0.274	2.889	0.095	0.060–0.150
60–65 wt%	0.363	3.369	0.108	0.036–0.325
65–70 wt%	0.310	3.263	0.095	0.064–0.141
70–74 wt%	0.216	2.640	0.082	0.033–0.200
> 74 wt%	0.282	2.863	0.098	0.084–0.115
I-type granitoids (n = 493)				
Total	0.192	4.180	0.046	0.042–0.050
45–50 wt%	0.266	2.146	0.124	0.097–0.157
50–55 wt%	0.350	3.603	0.097	0.072–0.131
55–60 wt%	0.267	4.914	0.054	0.040–0.073
60–65 wt%	0.235	4.162	0.056	0.050–0.063
65–70 wt%	0.179	4.583	0.039	0.035–0.043
70–74 wt%	0.116	3.973	0.029	0.025–0.034
> 74 wt%	0.270	4.406	0.061	0.051–0.073
S-type granitoids (n = 244)				
Total	0.137	3.423	0.040	0.037–0.044
60–65 wt%	0.189	4.662	0.041	0.022–0.076
65–70 wt%	0.238	4.870	0.049	0.042–0.056
70–74 wt%	0.098	2.935	0.033	0.029–0.038
> 74 wt%	0.103	2.458	0.042	0.033–0.053
A-type granitoids (n = 377)				
Total	1.034	13.30	0.078	0.073–0.083
50–55 wt%	0.484	5.506	0.088	0.070–0.110
55–60 wt%	0.527	13.392	0.039	0.022–0.071
60–65 wt%	0.795	13.252	0.060	0.053–0.068
65–70 wt%	0.866	13.608	0.064	0.050–0.081
70–74 wt%	1.276	17.400	0.073	0.067–0.080
> 74 wt%	1.053	11.453	0.092	0.082–0.103
TTG (n = 304)				
Total	0.100	3.601	0.028	0.026–0.030
60–65 wt%	0.141	3.601	0.039	0.033–0.047
65–70 wt%	0.112	3.894	0.029	0.026–0.032
70–74 wt%	0.086	3.414	0.025	0.022–0.029
> 74 wt%	0.058	3.106	0.019	0.014–0.025
Adakitic rocks (n = 602)				
Total	0.130	2.963	0.044	0.041–0.047
45–50 wt%	0.273	1.459	0.187	0.138–0.253
50–55 wt%	0.281	2.283	0.123	0.090–0.168
55–60 wt%	0.189	3.566	0.053	0.043–0.066
60–65 wt%	0.146	3.184	0.046	0.043–0.049
65–70 wt%	0.108	3.234	0.033	0.031–0.036
70–74 wt%	0.089	3.175	0.028	0.025–0.032
> 74 wt%	0.146	2.907	0.050	0.033–0.075

causes the distributions of Lu and Hf to be markedly asymmetric towards their highest values, with elevated skewness of 16.1 and 26.4, respectively (Fig. 7A and C). Logarithmic concentrations, on the other hand, yield nearly normal low-skewness distributions with some excess kurtosis (Fig. 7B and D). The distribution of individual Lu/Hf ratios is also skewed (Fig. 7E), albeit not so much as the individual elements, and the logarithm of Lu/Hf fits a neat normal distribution (Fig. 7F). The three distributions are, therefore, lognormal. This poses various theoretical and practical problems when calculating the best average of the populations because the arithmetic mean of the lognormally distributed

variables is very sensitive to high values, outliers and mixed populations (e.g., Yamamoto and Wakita, 2013), and is a poor estimate of the most probable value of the population. Accordingly, we preferred to used the median because (i) it is far less affected by outliers (ii) it is equal to the geometric mean of the raw dataset if this is lognormally distributed (iii) it represents the maximum of the probability density function for the logarithmically transformed concentrations or ratios.

The averages (medians) for the whole dataset are 0.22 ppm Lu, 4.45 ppm Hf, and Lu/Hf = 0.050 (0.049–0.051 95% confidence interval) (Table 2) which are quite different from the averages for the bulk continental crust estimated by Wedepohl (1995), Rudnick and Fountain (1995), Taylor and McLennan (1995), and Rudnick and Gao (2003), although close to the Upper Continental Crust averages of these authors. More surprisingly, they are also different from the median of granite rocks from the GEOROC database (http://georoc.mpch-mainz.gwdg.de/georoc/) estimated by Hawkesworth et al. (2010) using 7135 samples (Lu/Hf = 0.086). The differences with the bulk continental crust estimates may arise because (1) our data only consist of surface samples, (2) we did not weight the representation of each rock type according to their crustal abundance, (3) we did not include unfertile sedimentary and metamorphic rocks such as quartzites, limestones, etc., (4) we reported median instead of arithmetic means. The reasons for the discrepancy with GEOROC data are not clear. Given that this database contains different samples from our data set, the difference may simply reflect the large heterogeneity of Lu/Hf in crustal rocks; however, we cannot exclude some influence of analytical artifacts due to incomplete dissolution of zircon for ICP-MS analyses (see Section 2).

To understand whether Lu/Hf changes with magmatic fractionation, we studied our whole data set split in seven groups depending on the silica content. Five groups were defined at 5% intervals from SiO$_2$ = 45 to 70 wt%: one group from 70 to 74 wt% SiO$_2$, and the last for SiO$_2$ > 74 wt%. Fig. 8 shows the variation of Lu/Hf in the whole data set by plotting the median of each group inside the 95% confidence band. It appears that Lu/Hf varies from about 0.082 in rocks with 45–50 wt% SiO$_2$, to Lu/Hf ≈ 0.041 for rocks with 65–70 wt% SiO$_2$, and increases slightly in the most silicic samples. The figure reveals that using the mafic and felsic source averages may cause large errors; it also suggests that using a single fixed Lu/Hf$_{source}$ value similar to the Upper Continental Crust average (as used by Bodet and Schärer, 2000; and Iizuka et al., 2005) is likely to yield the most accurate T$_{DM}$ Hf estimates.

Then, to characterize the Lu/Hf distribution in different rock series we divided each silica group in six subsets depending on the rock typology: M-type, I-type, S-type, A-type, Archean TTGs and adakites, note that this division neither attempts to be systematic, exhaustive or geochemically correct, nor pretends to legitimize these categories. We simply used it as a means to investigate whether magmatic rocks coming from different sources show meaningful differences in the Lu/Hf distribution. It must also be considered that the ascription of samples to a given category is the one made by the authors, and only when this is clearly stated; doubtful or unclear cases were not considered. Accordingly only 2065 out of 4784 samples were ascribed to groups. Fig. 9 and Table 2 show the differences between the rock types considered. M-type granitoids display the highest Lu/Hf, with averages close to the generally recommended values; however they also show a tremendous variation, likely caused by the scarce number of samples included in this group (Table 2). The I-type granitoids have Lu/Hf around 0.124 for the less silicic rocks, decreasing to about 0.056 for samples with 55–60 wt% SiO$_2$ and 0.03 for samples with 70–74 wt% SiO$_2$ then increasing to 0.06 in the most silicic samples. The S-type granitoids and anatexites have nearly constant values around Lu/Hf ≈ 0.04. The A-type granitoids have values from Lu/Hf ≈ 0.07 for rocks in the 50–55 wt% SiO$_2$ range to Lu/Hf ≈ 0.09 at the silicic end. The Archean TTGs show the lowest Lu/Hf ratios of all types of granitoids, in most cases around Lu/Hf ≈ 0.03. Lastly, the rocks classified as adakites have Lu/Hf = 0.187 for 45–50 wt% SiO$_2$; the ratio decreases to Lu/Hf = 0.053 for 50–55 wt% SiO$_2$ and Lu/Hf = 0.028 for 70–74 wt
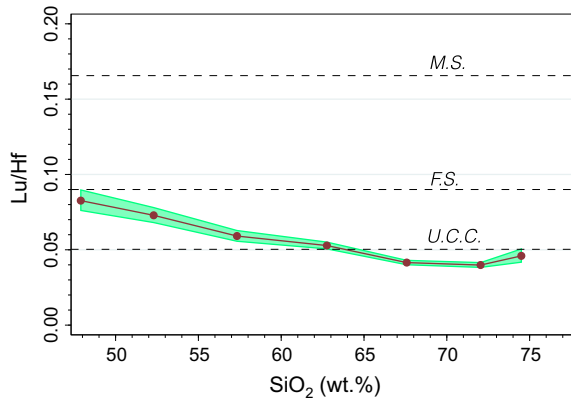
Fig. 8. Average and 95% confidence band of Lu/Hf vs SiO_2 for the whole data set. Rocks with $SiO_2 < 50$ wt% cluster around Lu/Hf = 0.082; rocks with SiO_2 between 60 and 65 wt% cluster around 0.053. The two values are much lower than the normally assumed mafic (M.S.) and felsic source averages (F.S.), but close to the upper continental crust average (U.C.C. ≈ 0.05; e.g., Rudnick and Gao, 2003).

% SiO_2, and increases slightly in samples with $SiO_2 > 75$ wt%.

6. Influence on zircon T$_{DM}$ Hf calculations

To check the correctness of the selected Lu/Hf value, in this section we compared the whole rock Nd and zircon Hf model ages. It should be noted that the Nd model ages do not need to be accurate estimates of mantle extraction ages; they can also represent mixed ages. If the particular Lu/Hf used in the zircon Hf model age calculation truly represents the source composition, the two model ages will approximate one another thus indicating that they reflect similar source components and that these mixed in similar proportions.

6.1. Fixed Lu/Hf crustal averages versus averages calculated depending on SiO_2

The medians calculated here are markedly different from the commonly used "mafic and felsic magmatic sources" Lu/Hf averages. Only the less silicic adakites (< 50 wt% SiO_2) have Lu/Hf comparable to, or even higher than, the "average mafic source" (Lu/Hf = 0.165); all other rocks with $SiO_2 > 55$ wt% have markedly lower Lu/Hf (Table 2). Similarly, most rocks with SiO_2 between 60 and 74 wt%, which are the
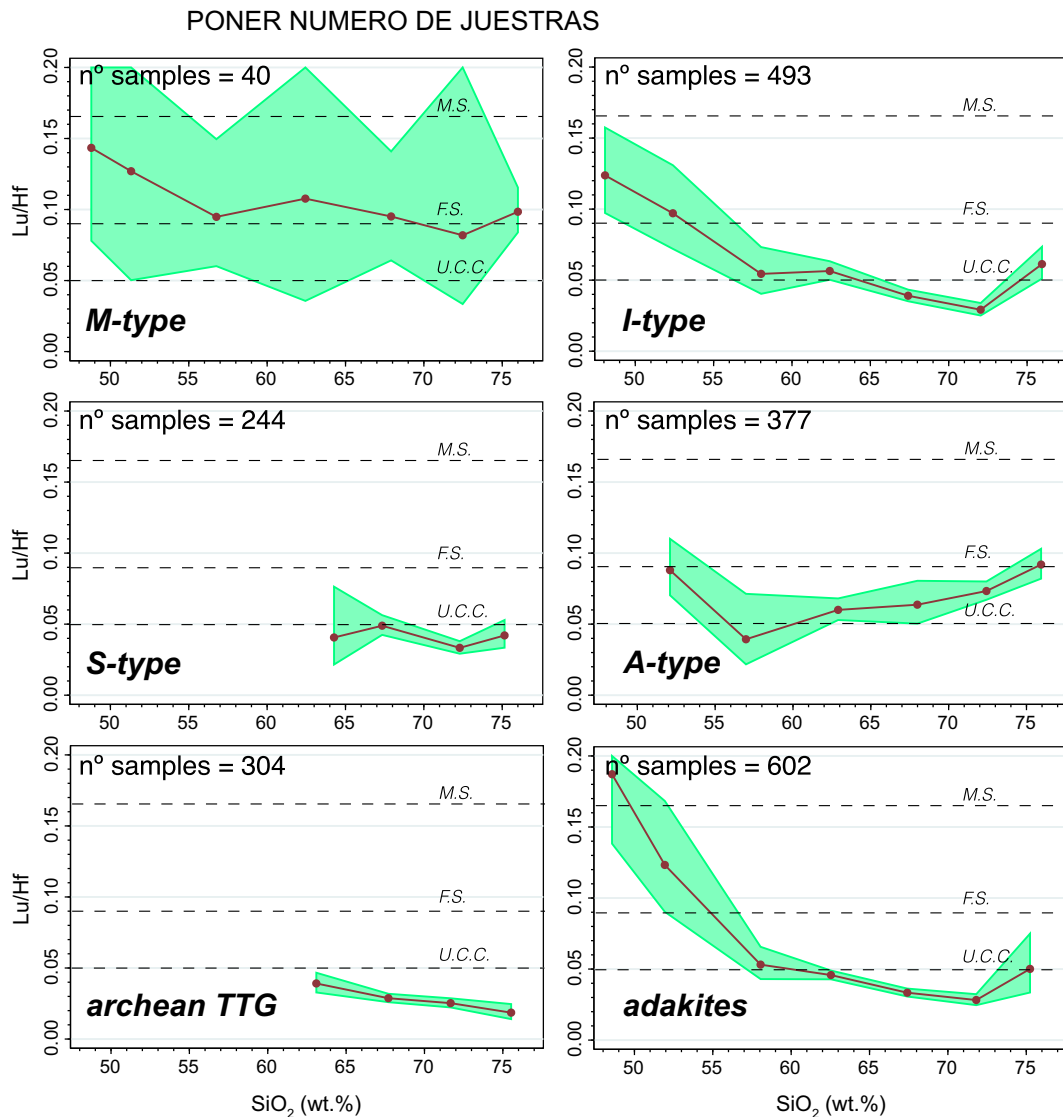
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Fig. 9. Average and 95% confidence band of Lu/Hf vs SiO_2 for different rock series. The large dispersion of M-type granitoids is caused by the scarce number of data included in this category (Table 1). See text for explanation.
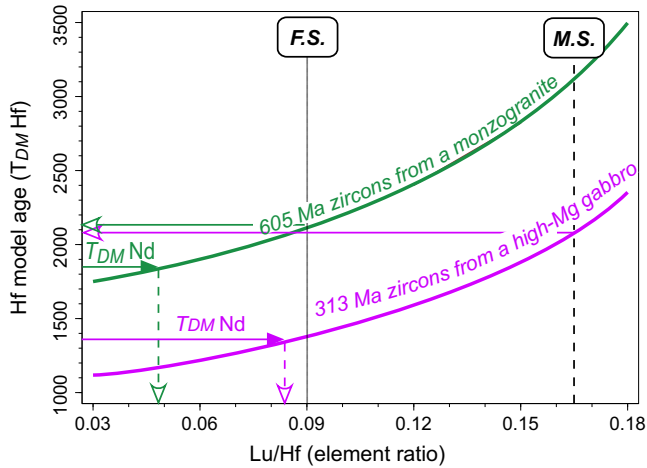
Fig. 10. Changes in Hf model age depending on the Lu/Hf assumed for the source for two real zircon populations: one from a Variscan high-Mg gabbro of central Spain (SiO_2 = 52.3 wt%); and the other from a Pan-African granite of western Egypt (SiO_2 = 70.6 wt%). *F.C.* and *M.C.* represent the felsic crust and mafic crust averages, respectively. To obtain zircon Hf model ages similar to the whole-rock Nd model ages it is necessary to assume a Lu/Hf = 0.055, for the granite and Lu/Hf = 0.083 for the gabbro. These values are much lower than *F.C.* (Lu/Hf = 0.09) and *M.C.* (Lu/Hf = 0.165) but almost exactly match the data set average for the 60–65 and 45–50 wt% SiO_2 intervals, respectively.

most probable source for crustal granites, have Lu/Hf of 0.05 or less, notably lower than the "average felsic magmatic source" used by most authors. The only exception is M-type granitoids, which have Lu/Hf ≈ 0.08–0.10 although with notable dispersion (Fig. 9).

To check whether the Lu/Hf ratios calculated here as a function of rock's silica concentration result in more accurate Hf model ages than the "mafic and felsic magmatic source" averages, we compared the zircon T_{DM} Hf to the whole rock T_{DM} Nd (see parameters in Section 2) in two cases of very different rocks: one Variscan high-Mg gabbro from the Arenal intrusive complex, central Spain (Bea et al., 1999), and a Pan-African granite from Bir Safsaf, Egyptian Western Desert (Bea et al., 2011).

Fig. 10 shows the variations of the mean T_{DM} Hf of the two zircon populations as a function of the Lu/Hf assumed for the calculation. In the case of the high-Mg gabbro the mean zircon Hf model age calculated assuming Lu/Hf = 0.165 is T_{DM} Hf = 2.08 Ga, about 700 Myr higher than the Nd model age. However, using Lu/Hf = 0.083 (equivalent to ^{176}Lu/^{177}Hf = 0.0116) which is nearly equal to the whole dataset median for the 45–50 wt% SiO_2 range (Table 2), the zircon Hf model age comes close to the Nd model age. Similarly, the mean zircon Hf model age of the Bir Safsaf granite calculated assuming the Lu/Hf value for a felsic crust (0.09) is T_{DM} Hf = 2.15 Ga, i.e., about 300 Myr higher than the Nd model age. Again, to obtain equal Nd and Hf model ages requires a lower value of Lu/Hf = 0.055 (equivalent to ^{176}Lu/^{177}Hf = 0.0076) which matches the calculated rock average for the 60–65 wt% silica range (Lu/Hf = 0.053, Table 2).

6.2. Fixed averages versus whole-rock Lu/Hf

Another example that may indicate the best strategy for selecting the most appropriate Lu/Hf values is illustrated in Fig. 11 which compares different calculations of T_{DM} Hf for a suite of Iberian mafic to intermediate rocks to whole-rock Nd model ages. Studied samples are seven gabbros (SiO_2 from 47.6 to 52.2 wt%), one quartzdiorite (SiO_2 = 59.3 wt%), and one tonalite (SiO_2 = 65.6 wt%); all of them have uniform zircon populations the ages of which range between 308 and 315 Ma (Montero et al., 2004; Bea et al., 2006a). Fig. 11A plots the zircon T_{DM} Hf calculated from the analytically-determined whole-rock Lu/Hf against the whole-rock Nd model ages; all data scatter around the
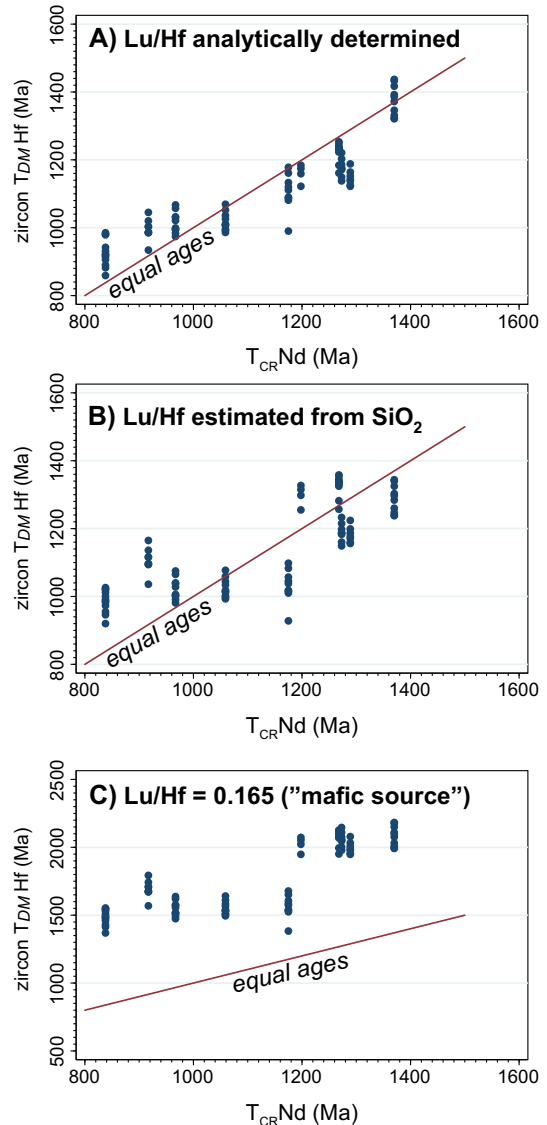

Fig. 11. Different calculations of zircon T_{DM} Hf for a suite of Iberian mafic to intermediate rocks compared to whole-rock Nd model ages. Analytically determined whole-rock Lu/Hf ratios produce the best coincidence. Lu/Hf estimated from the rock SiO_2 concentration produces worse, yet acceptable, results, but those using the "average mafic crust" seem unacceptable.

equality line and the maximum discrepancies are ~100 Myr. Fig. 11B plots the T_{DM} Hf calculated from the Lu/Hf ratio estimated according to the rock SiO_2 concentration as shown in Fig. 8. The two ages also scatter around the equality line but the discrepancies increase up to 200 Myr. Fig. 11C plots the T_{DM} Hf calculated from the "mafic crust value" of Lu/Hf = 0.165. In this case all zircon Hf model ages are greatly overestimated with respect to the Nd model ages, between 400 and 700 Myr. Despite common belief, therefore, the best agreement between zircon Hf and whole-rock Nd model ages arises when the analytically determined whole-rock Lu/Hf ratio is used in the calculations, at least in this case. Using the Lu/Hf estimated from the rock SiO_2 concentration produces worse, yet acceptable, results, but those calculated using the "average mafic crust" seem unacceptable.

6.3. Effects of fixed averages on rocks generated from heterogenous sources

The large Lu/Hf variation between the different granite types strongly suggests that crustal segments involved in orogenesis and anatexis are likely to be heterogeneous with respect to Lu/Hf. To
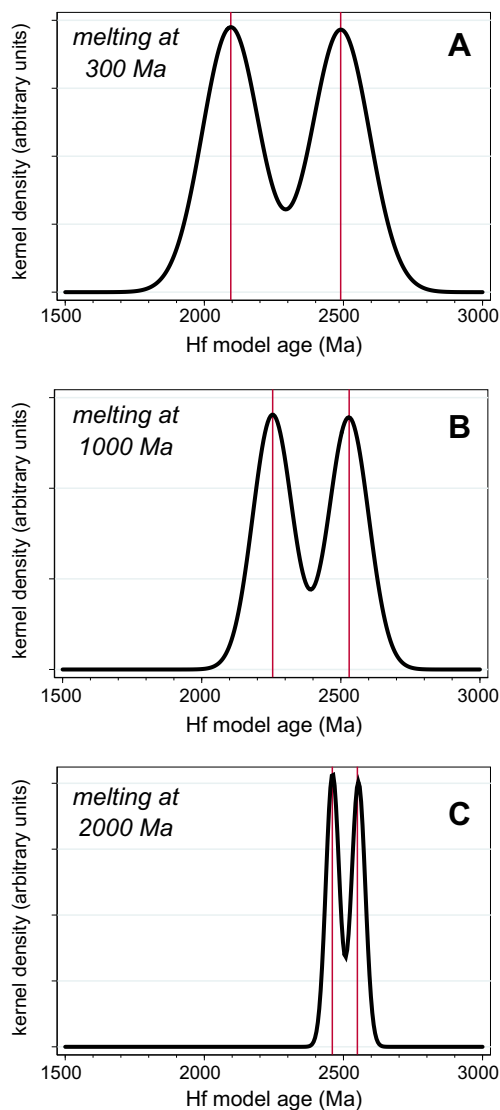
Fig. 12. Simulation of the distribution of Hf model ages in zircons crystallized from magmas generated at different times from a 2500 Ma source that was bimodal with respect to Lu/Hf. T_{DM} Hf was calculated assuming a fixed $Lu/Hf_{source} = 0.05$. Note how the Lu/Hf bimodality of the source translates in a bimodal distribution of T_{DM} Hf that might be erroneously interpreted as reflecting two episodes of crustal growth. See text for explanation.

understand the effects of assuming a fixed Lu/Hf_{source} value on the Hf model ages of zircons crystallized in magmas derived from heterogeneous sources, we undertook the following simulation (see details in the Electronic Appendix). Let us consider a crustal segment consisting of different igneous rocks generated at 2.5 Ga from an isotopically homogeneous source with $^{176}Hf/^{177}Hf = 0.281439$ and $\epsilon Hf = 8.9$, that is, close to the depleted mantle at that time. The magmas these 2.5 Ga rocks crystallized from were thus initially isotopically homogeneous but had different Lu/Hf as a result of fractionation processes during partial melting and emplacement. For simplicity we can assume that the 2.5 Ga rocks were bimodal, diorites and granites, with $Lu/Hf \approx 0.092$ and $Lu/Hf \approx 0.05$, respectively. These rocks remained stable in the crust until the Early Carboniferous, when they were eroded producing greywacke-like sediments that were metamorphosed and melted at 300 Ma to yield anatectic granites with newly crystallized zircons.

Given that the chemical composition of anatectic granites derived from metagreywackes would be broadly similar, i.e., peraluminous monzogranites or leucogranites (e.g., Montel and Vielzeuf, 1997), there is no reasons to presume they ultimately came from two sources with different Lu/Hf. Accordingly, we used a single fixed Lu/Hf_{source} value for all zircons separated from the granites, choosing Lu/Hf = 0.05 because the source is likely to be felsic. Fig. 12 A reveals that doing so results in a beautiful bimodal T_{DM} Hf distribution with maxima at 2.10 Ga and 2.49 Ga, respectively. If we displace the anatectic event to 1.0 Ga (Fig. 12B) or 2.0 Ga (Fig. 12C), the resulting T_{DM} Hf distributions are also bimodal but the two modes become closer as the age of anatexis approaches that of the source, merging when the two ages are equal. Remarkably, the bimodality appears independently of the particular Lu/Hf_{source} assumed; increasing this parameter simply modifies the position of the two modes towards higher ages and slightly increases distance between them.

Most geologists would be tempted to interpret Fig. 12 as evidence for two different pulses of crustal growth in this area, hardly imagining that it reflects a bimodal source formed during a single event. This illustrates how using a fixed Lu/Hf_{source} for calculating zircon Hf model ages risks translating the Lu/Hf heterogeneity of the source into a T_{DM} Hf distribution that may be erroneously interpreted as different episodes of crustal growth, in particular when dealing with zircons much younger than their sources.

7. Conclusions

Crustal rocks have highly variable Lu/Hf depending on the rock type and SiO_2 concentration. The highest Lu/Hf ratios are found in rocks with elevated proportion of juvenile mantle components, M-type granitoids and adakites, and the lowest in rocks with a protracted crustal history such as S-type granitoids and Archean TTGs. Except for A-type granitoids, the highest Lu/Hf of each rock type occur in the lowest SiO_2 range. Lu/Hf decreases, and the discrepancies between the rock series attenuate, as SiO_2 increases. The most silicic members of each rock series ($SiO_2 > 73$ wt%) often show a small increase in Lu/Hf which usually is related to the presence of modal xenotime.

The Lu/Hf distribution in 4784 igneous rocks of different ages from all over the world is lognormal rather than normal. Accordingly, the median instead of the arithmetic mean should be used for estimating rock averages if these are to reflect the maximum of the probability density function. The Lu/Hf averages for potential mafic and felsic magmatic sources calculated in this way are $Lu/Hf_{mafic} \approx 0.08$ and $Lu/Hf_{felsic} \approx 0.05$, much lower than customarily assumed in the calculations of the Hf model ages: $Lu/Hf_{mafic} \approx 0.165$ and $Lu/Hf_{felsic} \approx 0.09$. This may lead to huge overestimations of the zircon T_{DM} Hf, especially when there is a large difference between zircon and source ages.

Partial melting of peraluminous sources causes little decoupling of Lu from Hf because the solubility curves of monazite and zircon with increasing temperature are nearly parallel. Partial melting of metaluminous sources may decouple Lu from Hf at low melt fractions, especially if allanite and/or titanite are not present because the elevated solubility of zircon in hot low-silica melts may produce lower-than-source Lu/Hf_{melt} if the melt fraction is small, but Lu/Hf_{melt} quickly approaches Lu/Hf_{source} as the melt fraction increases. The presence of allanite or titanite in the source results in Lu/Hf_{melt} similar to Lu/Hf_{source} irrespective of the melt fraction. The effect of residual garnet on Lu/Hf melt/residuum partitioning is counterbalanced by the retention of zircon included in garnet and other residual minerals.

Fractional crystallization of peraluminous magmas hardly fractionates Lu/Hf because these magmas were either formed already saturated in zircon and monazite or became saturated in the two minerals at similar temperatures. Fractional crystallization of metaluminous magmas may decouple Lu from Hf if amphibole or clinopyroxene, in which HREEs are compatible, begin crystallizing before zircon saturation and the melt-solid segregation is efficient. If so, the less silicic rocks of the series will have higher Lu/Hf than the most silicic rocks.

Calculating Hf model ages using a fixed Lu/Hf_{source} value risks translating Lu/Hf_{source} heterogeneities into heterogeneities in the resulting T_{DM} Hf, and these can be erroneously interpreted as evidence for

different pulses of crustal growth.

For these reasons, and based on the above considerations, we suggest that the best strategy to calculate T_{DM} Hf is to use the analytically determined whole-rock Lu/Hf ratio as a proxy for the source Lu/Hf. The rock type and SiO_2 concentration dependent averages shown in Table 2 also are a good approximation if the source was homogeneous with respect to Lu/Hf. For detrital or inherited zircons, for which no whole-rock information is available, it seems advisable to determine first whether they crystallized in mafic or felsic rocks by interpreting cathodoluminescence images, Th/U ratios, etc…., and then estimate the Lu/Hf_{source} from the appropriate average in Table 2.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemgeo.2017.11.034.

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