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Catherine Chauvel[1,2], Marion Garçon[1,2], Sarah Bureau[1,2], Adeline Besnault[1,2*], Borming Jahn[3] and Zhongli Ding[4,5]

1: Univ. Grenoble Alpes, ISTerre, F-38041 Grenoble, France

2: CNRS, ISTerre, F-38041 Grenoble, France

3: Department of Geological Sciences, National Taiwan University, Taipei, 106 Taiwan

4: Key Laboratory of Cenozoic Geology and Environment, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beituchengxi Road 19, Chaoyang District, Beijing 100029, China

5: Chinese Academy of Sciences, Sanlihe Road 52, Xicheng, Beijing 100864, China

*: Now at INRA Orléans 2163 avenue de la Pomme de Pin CS 40001 45075 Orléans Cedex 02, France

Corresponding author: Catherine Chauvel, e-mail: Catherine.chauvel@ujf-grenoble.fr, tel: +334 76 63 59 12, address: ISTerre, Campus Universitaire, BP 53, F-38041 Grenoble Cedex 09, France.

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Abstract

Knowledge of the average composition of the upper continental crust is crucial to establish not only how it formed but also when. While well constrained averages have been suggested for its major and trace element composition, no values exist for its Nd and Hf isotopic compositions even though radiogenic isotopic systems provide valuable information on its average model age.

Here we present Nd and Hf isotopic data determined on a large number of loess deposits from several continents. We demonstrate that these deposits have very uniform Nd and Hf isotopic compositions. We obtain an average Nd isotopic composition that is similar to previous estimates for the upper continental crust (ε_{Nd} = -10.3±1.2 (1σ)) and we establish a new Hf average value at ε_{Hf} = -13.2±2 (1σ). This average falls on the "Terrestrial Array", demonstrating that the two parent-daughter ratios are not decoupled during crust formation. Trace element data acquired on the same set of samples allow us to calculate an average $^{147}Sm/^{144}Nd$ ratio for the upper continental crust: 0.1193±0.0026, a value slightly higher than previous estimates. Based on the relationship between Sm/Nd and Nd isotopes, we estimate the average Nd extraction age of upper continental crust from the depleted mantle at $T_{DM}(Nd)$ = 1.82±0.07 Ga. This model age is entirely consistent with previous suggestions made for example by Goldstein et al. [1984].

Assuming that for each individual sample, the Hf model age cannot be younger than the Nd model age, our new Nd-Hf isotopic data provide a value for the very poorly known $^{176}Lu/^{177}Hf$ ratio of the upper crust. Our estimate is $^{176}Lu/^{177}Hf$ = 0.0125±0.0018, a value significantly lower than commonly used values [0.0150 – 0.0159, *Griffin et al.*, 2002; *Goodge and Vervoort*, 2006; *Hawkesworth et al.*, 2010] but higher than Rudnick and Gao's [2003] estimate of 0.0083. The impact of our new $^{176}Lu/^{177}Hf$ ratio on crustal model ages of zircon populations is not simple to evaluate but the Hf model ages calculated with this new Lu/Hf ratio could be younger by up to 500 Ma.

1 - Introduction

The formation of the continental crust was certainly one of the most important events that affected the overall composition of the Earth, because the isolation at the surface of a light and enriched layer left behind a depleted residue in the mantle. This observation explains why so many studies concentrate on the processes that produce continental crust and on the timing of crustal growth [e.g., *Armstrong*, 1968; *McCulloch and Wasserburg*, 1978; *Armstrong*, 1981; *Allègre and Rousseau*, 1984; *Goldstein et al.*, 1984; *Taylor and McLennan*, 1985; *Condie*, 1993; *Wedepohl*, 1995; *Gallet et al.*, 1998; *Vervoort et al.*, 2000; *Griffin et al.*, 2002; *Rudnick and Gao*, 2003; *Harrison et al.*, 2005; *Hawkesworth and Kemp*, 2006; *Blichert-toft and Albarède*, 2008; *Belousova et al.*, 2010; *Hawkesworth et al.*, 2010; *Kemp et al.*, 2010; *Dhuime et al.*, 2011; *Garçon et al.*, 2011; *Iizuka et al.*, 2013]. In this study, we focus on the information provided by two isotopic systems, Sm-Nd and Lu-Hf. The two systems are strongly coupled during magmatic processes leading to the definition of the "Terrestrial array", an array along which all terrestrial magmas fall [*Vervoort et al.*, 1999; *Vervoort et al.*, 2011]. However, even though crustal magmas fall on the "Terrestrial Array" the location of the average composition of the continental crust remains unknown.

Knowing the position of present-day average crust on the Terrestrial array is important because it provides information not only on the processes active during the formation of the crust but also because the two isotopic systems record the past history of crustal materials and can be used to calculate an average extraction age of crust from the mantle. Finally, by using the constraints provided by the Sm-Nd isotopic system and those coming from the Lu-Hf isotopic system, we can evaluate the average crustal $^{176}Lu/^{177}Hf$ ratio, a very poorly known but crucial parameter necessary to calculate crustal residence ages of zircon populations [e.g.,*Griffin et al.*, 2002; *Harrison et al.*, 2005; *Kemp et al.*,

2007; *Blichert-toft and Albarède*, 2008; *Belousova et al.*, 2010; *Kemp et al.*, 2010; *Condie et al.*, 2011; *Yao et al.*, 2011; *Iizuka et al.*, 2013].

To address all these issues, we focus on a combined Nd and Hf isotopic study of a variety of recent loess deposits from several continents. Loess deposits result from the local accumulation of windblown dust coming from usually large continental areas. They represent natural mixtures of erosion products of continental surfaces and were therefore used by several previous workers to determine the average composition of the upper continental crust [e.g., *Taylor and McLennan*, 1981; *Taylor et al.*, 1983; *Taylor and McLennan*, 1985, 1995; *Barth et al.*, 2000]. We show that they are excellent proxies for the average composition of large areas of upper continental crust for both the Sm-Nd and the Lu-Hf isotopic systems. We then suggest an average value for the upper continental crust for the two systems and we determine an average model age. Finally, the combined Nd and Hf isotopic data allow us to suggest a value for the $^{176}Lu/^{177}Hf$ ratio of the upper continental crust.

2 - Source of samples

The samples in this study were collected from several locations around the world: Western Europe, Tajikistan, China and Argentina (see Figure 1). Most were previously studied by Gallet and co-workers [*Gallet et al.*, 1996; *Gallet et al.*, 1998; *Jahn et al.*, 2001] who reported major and trace element data as well as Nd and Sr isotopic compositions for loess samples from China, Western Europe and Argentina. The Tajikistan loess deposits come from the Chashmanigar section and were previously studied by Ding et al. [2002] and by Yang et al. [2006] who used sedimentological and major element data to constrain climate conditions during the past 1.8 Ma. However, they did not perform any trace element or isotopic analyses. Finally, two samples of Sahara dust collected in southern France were also analyzed.

The samples belong to two different types of loess deposits. The Western Europe Loess samples are periglacial deposits that were produced during the last glacial period by mechanical erosion of the crust followed by transport by wind over

limited distances [*Haase et al.*, 2007]. The situation is rather similar for the Argentinian loess deposits whose origin is mainly the Andes [*Smith et al.*, 2003]. The Chinese and Tajikistan loess deposits represent much larger volumes and have a very different origin: the materials come from large desert areas. For the Chinese loess, particles come mainly from the deserts located Northwest in Mongolia [*Sun*, 2002]; in southern Tajikistan, the particles originate from the Karakum and Kyzylkum deserts located northwest in Turkmenistan, Uzbekistan and Kazakhstan [*Ding et al.*, 2002]. In both cases, the deserts developed on continental crust that formed over large periods of geological time [e.g., *Lee et al.*, 2011; *Yoshida*, 2012] and particles were transported over long distances by high-energy winds to accumulate in protected areas [*Ding et al.*, 1999; *Ding et al.*, 2002; *Guo et al.*, 2002]. Consequently, they represent the average composition of much larger crustal areas than the periglacial deposits. Finally, the dust blown from the Sahara over Southern France does not constitute a real loess deposit [*Grousset et al.*, 2003], but it provides valuable information on the average composition of the largest desert area in the world.

3 - Analytical techniques

All samples were crushed using an agate mortar. Trace element concentrations were obtained after dissolution in a HF-$HClO_4$ mixture using Parr bombs. The complete procedure is that of Chauvel et al. [2011], but the dissolution time was increased to insure complete dissolution of the very resistant minerals, an issue particularly important when using the relationship between REE and Hf concentrations and when measuring Hf isotopes. Both accuracy and reproducibility of the data are estimated as better than 5% for most trace elements, as shown by the analyses of international rocks standards and duplicate analyses of samples (see Supplementary table).

Neodymium and hafnium were isolated from an aliquot of the solution prepared for trace element analysis and using standard ion-chromatography as described by Chauvel et al. [2011]. Total procedural blanks were less than 100 picograms for both Nd and Hf. The Nd and Hf isotopic compositions were measured using the Nu Plasma HR MC-ICP-MS at ENS Lyon. Mass bias corrections for Nd and Hf

isotopic compositions were performed using $^{146}Nd/^{144}Nd$ = 0.7219 and $^{179}Hf/^{177}Hf$ = 0.7325 respectively. Over the course of analyses, daily averages obtained for the Nd Ames-Rennes standard ranged between 0.511958±19 and 0.511976±14, while those obtained for the Hf Ames-Grenoble standard ranged between 0.282165±9 and 0.282168±19. All isotopic ratios reported in Table 1 are normalized to the reference values of 0.511961 and 0.282160 as published by Chauvel and Blichert-Toft [2001] and Chauvel et al. [2011]. Complete duplicate analyses of several samples show that the reproducibility of isotopic measurements is better than 100 ppm for both Nd and Hf isotopic ratios (Table 1).

4 - Results

New trace element data for the loess are provided in the Supplementary table. Some samples had been previously analyzed for their trace element contents by Gallet et al. [1998] and by Jahn et al. [2001] but these were reanalyzed because some key elements (e.g., Hf) were not measured in many of these older studies. The new values reported here are generally similar to those previously published but there are notable exceptions. For example, the new determinations of REE, Th, Zr and Hf concentrations are systematically higher than those reported by Jahn et al. [2001] suggesting that dissolution of samples in 2001 was incomplete, leaving some non-dissolved zircon and monazite grains (see supplementary figure).

Figure 2 shows the trace element patterns obtained for all loess samples. As previously shown by Gallet et al. [1996] and Jahn et al. [2001], the Chinese loess are remarkably homogeneous with normalized trace element concentrations close to the Upper Continental Crust values of Rudnick and Gao [2003] (see Figure 2b). The new Tajikistan data shown in Figure 2c display similar features. This is not the case, however, for the periglacial loess sampled in Western Europe and shown in Figure 2a. The latter samples have much more variable concentrations and they display large positive Zr-Hf anomalies, most probably due to the presence of excess zircon. Finally, the Argentinian loess samples and the two Sahara dust samples shown in Figure 2d have trace element patterns

generally parallel to the average upper continental crust (UCC) value, without positive Zr-Hf anomalies, but with more variability.

The Nd and Hf isotopic compositions of all loess samples analyzed in this study are listed in Table 1. The data are plotted in Figure 3 where they are compared to data published in the literature for MORB, OIB, oceanic sediments and crustal rocks. With the exception of the Argentinian samples, all loess define a restricted range of ε_{Nd} and ε_{Hf} values (-10.3±1.2 and -13.8±4.2) and lie on the terrestrial array of Vervoort et al. [2011] in the field of crustal materials. The Argentinian loess have less negative values (ε_{Nd} = -1.7 and ε_{Hf} = -2.8), a feature attributed to the abundance of Andean volcanic rocks in the source area [*Gallet et al.*, 1998; *Smith et al.*, 2003].

5 - Discussion

Constraining the average composition of the continental crust is a very active field of research [e.g., *Armstrong*, 1968; *McCulloch and Wasserburg*, 1978; *Armstrong*, 1981; *Allègre and Rousseau*, 1984; *Goldstein et al.*, 1984; *Taylor and McLennan*, 1985; *Condie*, 1993; *Wedepohl*, 1995; *Gallet et al.*, 1998; *Vervoort et al.*, 2000; *Griffin et al.*, 2002; *Rudnick and Gao*, 2003; *Hawkesworth and Kemp*, 2006; *Belousova et al.*, 2010; *Hawkesworth et al.*, 2010; *Dhuime et al.*, 2011; *Garçon et al.*, 2011]. Several studies have suggested average values for the upper continental crust but these mainly focus on its major and trace element composition (see Rudnick and Gao [2003] for a review). Knowing its radiogenic isotopic compositions is also important since it provides constraints on the timing of crust formation through geological time. Several Pb isotope compositions have been suggested for the upper continental crust [e.g., *Zartman and Doe*, 1981; *Newsom et al.*, 1986; *Rudnick and Goldstein*, 1990; *Garçon et al.*, 2013b] as well as some average Nd model ages [*Allègre and Rousseau*, 1984; *Goldstein et al.*, 1984; *Goldstein and Jacobsen*, 1988; *Jacobsen*, 1988]. These show that the continental crust formed, on average, about 1.8 to 2 Ga ago. Here, we will use loess as a proxy to more precisely constrain the Nd and Hf isotopic composition of average upper continental crust. We will then use these data to re-evaluate when the upper crust separated from the mantle and use the

combined Nd and Hf isotopic data to constrain the Lu/Hf ratio of upper continental crust. It could be argued that the sample set might not be representative of average upper crust and we will demonstrate that it is.

5.1 - Loess: an excellent proxy for the average upper continental crust Nd isotopic ratio

Loess has been widely used by Taylor and McLennan [1985] to establish the average REE composition of the upper continental crust because these sediments represent the average composition of large surface areas. Since the REE content is representative of the upper continental crust, loess can be used to evaluate its Nd isotopic composition [*McCulloch and Wasserburg*, 1978; *Taylor et al.*, 1983; *Gallet et al.*, 1998].

The measured Nd isotopic ratios of nearly 50 loess samples are remarkably uniform and define two groups (Figures 3 & 4). The first comprises only the Argentinian loess and is relatively radiogenic with an average ε_{Nd} of -1.7. Gallet et al. [1998] concluded that the unusual composition of these samples was due to the overwhelming presence of recent volcanic products coming from the Andes and could not be considered as representative of large areas of the upper continental crust. We concur with their conclusion. The second group of samples consists of all other analyzed loess samples (Figure 3). While the Chinese and Tajikistan loess have indistinguishable isotopic compositions (ε_{Nd} = -9.82±0.44 and ε_{Nd} = -9.46±0.36, respectively), the two Sahara dusts have lower ε_{Nd} at -12.4. Finally, the Western European loess are more heterogeneous and average at ε_{Nd} = -11.25±1.28. We attribute this larger range of isotopic compositions to processes acting during the formation of periglacial loess, when relatively small volumes of material were produced by erosion of proximal sources during the last glacial period. Such small volumes of glacial sediments were not well mixed by long distance transport and their composition is a function of the diversity of local terranes in Western Europe. In contrast, the Tajikistan and the Chinese loess are remarkably homogeneous, a feature consistent with their origin as dust blown from large desert areas [*Ding et al.*, 1999; *Ding et al.*, 2002]. Nevertheless,

taken together, all these samples define a well-constrained average at ε_{Nd}=-10.3±1.2 (1σ) (see inset of Figure 3).

Given the large number of Chinese and Tajikistan samples in our data set, it could be argued that our average ε_{Nd} value is only representative of the upper continental crust present in Russia and Central Asia. However, similar ε_{Nd} values have been reported for all sorts of other areas in the world: The Carpathian loess deposits in Eastern Europe have an average ε_{Nd} value at -10.21±0.34 [*Újvári et al.*, 2012] and a placer deposit that averages the area drained by the Rhone River in Western Europe has an ε_{Nd} value of -9.3 [*Garçon et al.*, 2011]. This suggests that most of the European continent has an ε_{Nd} value at about -10. The only two US loess samples analyzed for Nd isotopes have lower values at -13 and -15 [*Taylor et al.*, 1983] which might indicate that the American upper crust could have a different average value. However, the ε_{Nd} values reported by Goldstein et al. [1984] and Goldstein and Jacobsen [1988] for particulates collected on major rivers from the American continent do not confirm these low values but provide a range between -20.8 and -4.4. Worldwide aerosols can also be used to estimate the composition of exposed continental crust. Grousset and Biscaye [2005] compiled the existing data and showed that aerosols have much more variable compositions than loess or river particulates, but they could estimate that the world mean ε_{Nd} value was around -11 [*Grousset and Biscaye*, 2005]. Finally, Goldstein et al. [1984] analyzed a large number of river sediments and aeolian dusts from various continents and provided an average ε_{Nd} value at -11.4±4 for all these deposits. Given the similarity of all the values listed above, we suggest that our estimate (ε_{Nd}=-10.3) is probably accurate and representative of continental crust exposed today at the surface of the Earth. Estimating the uncertainty is more difficult. Here we use the 1σ error based on our data set (±1.2) but we acknowledge that with a larger set of samples, the value could change.

5.2 - Loess: also a good proxy for the average upper continental crust Hf isotopic ratio

Several authors have argued that the Zr and Hf contents of loess should not be used as analogues for their source [*Taylor et al.*, 1983; *Barth et al.*, 2000; *Rudnick and Gao*, 2003]. These arguments are based on the observation that the loess that they had studied had a very large excess of Zr and Hf relative to the REE, a feature attributed to the presence of excess zircons. All the samples that they studied, however, are periglacial loess sediments. Our Western European loess samples have the same large positive anomaly in Zr and Hf (see Figure 2) and we argue that many or all periglacial loess deposits contain this feature. In contrast, the Tajikistan, Chinese and Argentinian loess deposits as well as the Sahara dusts either have no anomaly or a slight negative anomaly (Figure 2). Since zircons are rich in Hf and have usually very unradiogenic Hf isotopes, their presence has strong impact on the whole rock Hf isotopic composition. As a result, the measured Hf isotopic ratios reported in the Table 1 for the Western European loess cannot be directly used to establish the average composition of the upper continental crust. It is, however, possible to correct for the "zircon effect" by using the relationship between Nd/Hf and $\Delta\varepsilon_{Hf}$ (the vertical deviation from the terrestrial array as defined by Carpentier et al. [2009]) as shown in Figure 4. Nd/Hf is well constrained in all estimates of upper continental crust, while $\Delta\varepsilon_{Hf}$ is a good measure of mineralogical sorting during sediment formation [*Carpentier et al.*, 2009; *Vervoort et al.*, 2011; *Garçon et al.*, 2013a]. In Figure 4, loess deposits define a positive correlation. The Western Europe loess have low Nd/Hf (i.e., positive Hf anomalies), lie below the terrestrial array of Vervoort et al. [2011] and have negative $\Delta\varepsilon_{Hf}$ values, as expected by the presence of excess old zircons. In contrast, the Tajikistan loess samples have relatively high Nd/Hf (i.e., slight negative Hf anomalies) and slightly positive $\Delta\varepsilon_{Hf}$ values, as expected for sediments deficient in zircon relative to their crustal source [*Carpentier et al.*, 2009; *Vervoort et al.*, 2011; *Garçon et al.*, 2013a]. The Chinese and Argentinian loess have compositions that plot in between these two end members. Using the values recommended for the Nd/Hf ratio of upper continental crust, we can therefore estimate the $\Delta\varepsilon_{Hf}$ value for average upper continental crust. The most recent estimation of $(Nd/Hf)_{UCC}$ provided by Rudnick and Gao [2003] constrains the $\Delta\varepsilon_{Hf}$ value for upper continental crust at +1.6 with an error of less than ±2, based on the range of estimated $(Nd/Hf)_{UCC}$ (see Figure 4).

This $\Delta\varepsilon_{Hf}$ value translates into an ε_{Hf} value of -13.2 ±2 (1σ) using the average ε_{Nd} value of -10.3 determined above and the terrestrial array equation of Vervoort et al. [2011] (ε_{Hf} = 1.55.ε_{Nd} +1.21). Such value is not identical to the average of all loess measurements (-13.8±4.2) but it is similar and the error on the average is smaller. These ε values correspond to a $^{143}Nd/^{144}Nd$ of 0.512102±67 and a $^{176}Hf/^{177}Hf$ of 0.282412±56 (see Table 2).

The combined Nd and Hf isotopic values for average upper continental crust define the point shown as a red star in Figure 3 at ε_{Nd} = -10.3±1.2 (1σ) and ε_{Hf} = -13.2±2 (1σ), an average that plots, within error, on the terrestrial array thereby supporting the long-standing observation that the parent-daughter ratios Sm/Nd and Lu/Hf are coupled during magmatic processes both in the mantle and the crust. It also provides a value for the average upper continental crust, a value that is very useful in modeling how the continents formed.

5.3 - Nd model age of upper continental crust

To model the average formation age of the upper continental crust, we need well-constrained values not only for Nd and Hf isotopic compositions but also for Sm/Nd and Lu/Hf ratios. Data listed in Table 1 show that both the loess Nd isotopic compositions and their $^{147}Sm/^{144}Nd$ ratios (0.1193±0.0026, recalculated using the Sm and Nd concentrations) are extremely constant. This feature arises from the uniform Sm/Nd ratio of most crustal minerals [*Taylor and McLennan*, 1981; *Goldstein et al.*, 1984; *Taylor and McLennan*, 1985; *Garçon et al.*, 2011]. When compared to the $^{147}Sm/^{144}Nd$ ratio recalculated from previously published UCC estimates [*Taylor and McLennan*, 1985; *Condie*, 1993; *Gao et al.*, 1998; *Rudnick and Gao*, 2003], our value is slightly higher (0.1193 vs. ≈0.1050) a feature that may be related to the poor precision of the Sm and Nd concentration estimates used in these publications (typically 10%, see Table 2). Our value is similar, however, to values proposed by Jahn and Condie [*Jahn and Condie*, 1995] and in studies when the $^{147}Sm/^{144}Nd$ was determined with better precision [*McCulloch and Wasserburg*, 1978; *Allègre and Rousseau*, 1984; *Goldstein et al.*, 1984]. Using this value for $^{147}Sm/^{144}Nd$ (0.1193±0.0026), our UCC estimate for

$^{143}Nd/^{144}Nd$, the depleted mantle values listed in Table 2 and the following equation,

$$T_{DM} = Log\left(\frac{(\frac{^{143}Nd}{^{144}Nd})_{UCC} - (\frac{^{143}Nd}{^{144}Nd})_{DM}}{(\frac{^{147}Sm}{^{144}Nd})_{UCC} - (\frac{^{147}Sm}{^{144}Nd})_{DM}} - 1\right)/\lambda$$

(with $\lambda=6.54*10^{-12}$ year^{-1}) we can calculate a model age for the extraction of the crust from the depleted mantle.

We obtain a Nd model age of 1.82±0.07 Ga (1σ) for the separation of crust from the mantle. Such value falls within the range of previous estimates based on Nd isotopes [e.g., *Allègre and Rousseau*, 1984; *Goldstein et al.*, 1984; *Hawkesworth and Kemp*, 2006], but has a much smaller error than previous estimates.

The calculated model age depends heavily on the chosen parameters for the depleted mantle source. Here, we consider that depletion started at the beginning of Earth history and we chose a very depleted mantle (see Table 2). Other authors prefer more subdued values. For example, Gale et al. [2013] recently provided an estimate based on the average composition of MORB while Dhuime et al. [2011] suggested that the source of newly formed continental crust was less depleted than the MORB mantle (see Table 2). When these references are used, we calculate that the Nd model age of upper continental crust would be 200 Ma younger. An extra complication has been introduced recently by Jackson and Carlson's [2012] suggestion that the Earth has a superchondritic composition. Gale et al. [2013] already discussed the issue and showed that a serious problem occurs because the present-day isotopic composition of a superchondritic Earth is identical to their estimate of present-day depleted mantle. Indeed, this leaves no space for the development of a mantle that had become depleted as a consequence of the extraction of enriched continental crust. If we accept that the Earth is superchondritic and that the depleted mantle is more depleted than suggested by Gale et al. [2013], with, for example, a Nd isotopic composition similar to our chosen estimate (see Table 2), then the entire mantle would have to be depleted to compensate for the extraction of the continental crust.

5.4 - $^{176}Lu/^{177}Hf$ ratio of upper continental crust and Hf model age

To establish the average Hf model age of the upper continental crust is not as straightforward as for Nd because the $^{176}Lu/^{177}Hf$ ratio of continental crust is poorly constrained, yet has a major impact on the calculations. In Table 2, we list estimates of $^{176}Lu/^{177}Hf_{UCC}$ that have been suggested in the literature. The $^{176}Lu/^{177}Hf$ values calculated using upper crustal Lu and Hf contents range mostly from 0.0057 to 0.0106 [*Shaw et al.*, 1967; *Shaw et al.*, 1976; *Taylor and McLennan*, 1985; *Condie*, 1993; *Wedepohl*, 1995; *Gao et al.*, 1998; *Rudnick and Gao*, 2003] but higher values have also been suggested: Goodge and Vervoort [2006] suggest a $^{176}Lu/^{177}Hf$ ratio of 0.0150 for new Proterozoic crust, while Hawkesworth et al. [2010] suggested a value of 0.0159 on the basis of over 7000 measurements of granitoids. Finally, Condie and co-workers [*Condie et al.*, 2011] suggest a value as high as 0.020. The range of suggested values is therefore very large.

Unfortunately, the measured $^{176}Lu/^{177}Hf$ ratios of the loess samples cannot be used to estimate the $^{176}Lu/^{177}Hf$ of the upper continental crust because loess deposits are affected by sedimentary processes that sort minerals eroded from crustal rocks. In contrast to their generally uniform $^{147}Sm/^{144}Nd$ ratios, all minerals do not have similar $^{176}Lu/^{177}Hf$ ratios, and their relative proportions strongly influence the whole-rock $^{176}Lu/^{177}Hf$ ratio, which might be quite different from that of the crustal precursor. One mineral, zircon, is particularly important because it dominates the whole-rock $^{176}Lu/^{177}Hf$ ratio with its very high Hf content and its extremely low $^{176}Lu/^{177}Hf$ ratio. In addition, it is very resistant to alteration processes and survives even extreme weathering. If a high proportion of old zircon is retained in a loess deposit, then the whole rock has low $^{176}Lu/^{177}Hf$ and unradiogenic $^{176}Hf/^{177}Hf$, as is the case with the Western European loess deposits (see Table 1 and Figure 4). In contrast, if the proportion of zircon is lower, as is the case for the Tajikistan loess samples, then the $^{176}Lu/^{177}Hf$ is higher and $^{176}Hf/^{177}Hf$ is more radiogenic. Thus, the large range of $^{176}Lu/^{177}Hf$ ratios reported in loess deposits is likely controlled by sedimentary sorting processes and these values cannot be considered as representative of the $^{176}Lu/^{177}Hf$ ratio of the crustal precursors. We therefore use a different

approach that combines the constraints provided by the Sm-Nd and Lu-Hf isotopic systems to determine the best estimate for the upper continental crust Lu/Hf ratio.

In Figure 5, we plot Hf model ages of individual loess samples as a function of their Nd model age. For each sample, we use the measured $^{147}Sm/^{144}Nd$ and $^{143}Nd/^{144}Nd$ ratios as well as the depleted mantle values shown with an asterisk in Table 2. To calculate the Hf crustal model ages, we used the measured $^{176}Hf/^{177}Hf$ ratios together with a range of $^{176}Lu/^{177}Hf$ ratios as published for upper continental crust, and the depleted mantle values shown with an asterisk in Table 2. Because the range of possible $^{176}Lu/^{177}Hf$ ratios in average upper crust (between 0.0057 and 0.0200, see Table 2) is very large, it introduces a very large range of possible Hf model ages $T_{DM}(Hf)$ (shown by vertical lines in Figure 5). If the upper crust has a high $^{176}Lu/^{177}Hf$ ratio of 0.0200, as suggested by Condie et al. [2011], then the T_{DM} (Hf) of all loess (excluding the Argentinian loess) averages 2.47±0.13 Ga, a value that is 600 Ma older than the average Nd model age (1.82±0.07 Ga); if the crustal $^{176}Lu/^{177}Hf$ ratio is 0.0159, as suggested by Hawkesworth et al. [2010], then the $T_{DM}(Hf)$ average at 2.05±0.11 Ga, still over 200 Ma older than the average Nd model age. In contrast, using a low $^{176}Lu/^{177}Hf$ ratio at 0.0057 provides much younger Hf model ages (1.45±0.08 Ga). Finally, a $^{176}Lu/^{177}Hf$ ratio of 0.0083, as suggested by Rudnick and Gao [2003], gives an average Hf model age of 1.57 ±0.09 Ga.

Considering the overall geochemical behavior of REE and Zr-Hf during magmatic and sedimentary processes [*Vervoort and Patchett*, 1996; *Vervoort and Blichert-Toft*, 1999; *Vervoort et al.*, 1999; *Chauvel et al.*, 2008; *Carpentier et al.*, 2009; *Vervoort et al.*, 2011], it seems unlikely that the Nd model age of upper continental crust should be older than its Hf model age. The opposite is, in fact, much more likely because most Hf present in crustal materials is sequestrated in zircon, a mineral phase that is extremely robust during alteration and reworking of continental crust.

To constrain the $^{176}Lu/^{177}Hf$ ratio of the upper continental crust, we assume here that $T_{DM}(Hf)$ and $T_{DM}(Nd)$ should be identical for each individual loess and dust sample and we calculate the necessary $^{176}Lu/^{177}Hf$ ratio for each individual

sample. Results of the calculation are shown in Figure 6 where they are also compared to the range of suggested values from literature. On average, we estimate that the $^{176}Lu/^{177}Hf$ ratio of upper continental crust is 0.0125±0.0018 (1σ).

In summary, the loess data suggest that the average model age of upper continental crust is 1.82±0.07 Ga (1σ) based on Nd isotopes. Assuming that Hf model ages cannot be any younger than Nd model ages, the loess data also provide constraints on the $^{176}Lu/^{177}Hf$ ratio of upper continental crust, which cannot be smaller than 0.00125 ± 0.0018, the value that corresponds to concordant T_{DM}(Hf) and T_{DM}(Nd) ages. Higher values, such as those suggested previously by other authors [*Goodge and Vervoort*, 2006; *Hawkesworth et al.*, 2010] are also plausible, but would result in an average upper crust T_{DM}(Hf) age over 200 Ma older than the T_{DM}(Nd) age.

6 - Conclusions

Our Nd-Hf isotopic study of a large number of loess samples provides new constraints on the average isotopic composition of the upper continental crust. We estimate that present-day upper continental crust has the following characteristics: $^{143}Nd/^{144}Nd$= 0.512101±60 and $^{176}Hf/^{177}Hf$=0.282412±60. Using the bulk silicate Earth values determined by Bouvier et al. [2008], these isotopic ratios translate into ε_{Nd}=-10.3±1.2 (±1σ) and ε_{Hf}=-13.2±2 (±1σ) and fall within error on the terrestrial array of Vervoort et al. [2011].

The uniform $^{147}Sm/^{144}Nd$ ratio (0.1193±0.0026) of loess deposits can also be considered as representative of the upper continental crust value. Combining the parent/daughter ratio with the average Nd isotopic composition, we calculate that the average Nd model age of upper continental crust is 1.82±0.07 Ga.

Finally, we constrain the $^{176}Lu/^{177}Hf$ ratio of the upper continental crust using the relationship between Hf and Nd isotopes. Our preferred estimate corresponds to 0.0125±0.0018, a value that is significantly higher than most previous estimates but lower than the ratio suggested by Goodge and Vervoort [2006] and Hawkesworth et al. [2010]. We emphasize that 0.0125 represents the

lower limit for $^{176}Lu/^{177}Hf$ because any lower estimate makes the Hf model ages younger than the Nd model ages, a very unlikely situation given the geochemical behavior of Hf and REE. The impact of this new $^{176}Lu/^{177}Hf$ ratio on crustal differentiation ages of zircon populations such as those calculated by numerous authors [e.g., *Griffin et al.*, 2002; *Harrison et al.*, 2005; *Kemp et al.*, 2007; *Blichert-toft and Albarède*, 2008; *Wang et al.*, 2009; *Belousova et al.*, 2010; *Kemp et al.*, 2010; *Yao et al.*, 2011; *Iizuka et al.*, 2013] is quite variable, but the ages can be younger by up to 500 Ma in the most extreme cases.

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724

725 **Table captions:**

726

727 **Table 1**: Nd and Hf isotopic results for all loess samples.

728 Footnotes: All ε_{Nd} and ε_{Hf} values were calculated using the BSE value suggested
729 by Bouvier et al. [2008]. Dup stands for complete duplicate analyses. The
730 $^{147}Sm/^{144}Nd$ and $^{176}Lu/^{177}Hf$ are calculated using the Sm, Nd, Lu and Hf
731 concentration data listed in the Supplementary table.

732

733 **Table 2**: Compilation of the parent-daughter ratios and Nd and Hf isotopic
734 compositions of various reservoirs.

735 Footnotes: Numbers in italics correspond to ratios recalculated using published
736 concentrations. *: values used to calculate T_{DM}. Data sources: Allègre and
737 Rousseau [1984], Bouvier et al. [2008], Chauvel et al. [2008], Condie [1993],
738 Condie et al. [2011], Dhuime et al. [2011], Gale et al. [2013], Gao et al. [1998],
739 Goldstein et al. [1984], Goodge and Vervoort [2006], Griffin et al. [2002],
740 Hawkesworth et al. [2010], Jahn and Condie [1995], McCulloch and Wasserburg
741 [1978], Rudnick and Gao [2003], Salters and Stracke [2004], Shaw et al. [1967;
742 1976], Taylor and McLennan [1985] and Wedepohl [1995].

743

744 **Supplementary table**: Trace element concentrations measured on all loess
745 samples as well as values published by Gallet et al. [1996] for the Luochuan loess.

746 **Supplementary figure**: Comparison between the new trace element data and
747 the data published previously by Jahn et al. [2001].

748

749 **Figure captions:**

750 **Figure 1**: Map of the world showing the location of loess deposits. The precise
751 locations of Western European, Chinese, Argentinian and Tajikistan loess
752 samples were provided by Gallet et al. [1996; 1998], Jahn et al. [2001] and Ding
753 et al. [2002]. The Sahara samples blown over Southern Europe were collected
754 close to Grenoble and at 2900 m altitude in the Alps. Latitudes and longitudes are
755 given in the Supplementary Table.

756

757 **Figure 2**: Trace element patterns of the loess samples. All concentrations are
758 normalized to the upper continental crust average of Rudnick and Gao [2003]. a)
759 Western European loess, b) all Chinese loess including data published by Gallet
760 et al. [1996], c) Tajikistan loess and d) Argentinian loess and Sahara dust.

761

Figure 3: Nd and Hf isotopic compositions of loess samples. ε_{Nd} and ε_{Hf} were calculated using the BSE value of Bouvier et al. [2008]. The terrestrial array corresponds to $\varepsilon_{Hf} = 1.55.\varepsilon_{Nd}+1.21$ as recently compiled by Vervoort et al. [2011]. Data for MORB and OIB were compiled using the PetDB and Georoc databases and also include some unpublished values of Chauvel. Oceanic sediments plotted here were published in the literature [*White and Dupré*, 1986; *BenOthman et al.*, 1989; *McLennan et al.*, 1990; *Godfrey et al.*, 1997; *Albarède et al.*, 1998; *Pearce et al.*, 1999; *Vervoort et al.*, 1999; *David et al.*, 2001; *Woodhead et al.*, 2001; *Vlastelic et al.*, 2005; *Prytulak et al.*, 2006; *van de Flierdt et al.*, 2007; *Carpentier et al.*, 2008; *Bayon et al.*, 2009; *Carpentier et al.*, 2009; *Chauvel et al.*, 2009; *Vervoort et al.*, 2011]. Data source for continental crust were published by Vervoort and Patchett [1996] and by Vervoort et al. [1999; 2000]. The inset shows how our estimated upper continental crust composition (red star) relates to the range of known isotopic values in the Earth.

Figure 4: Nd/Hf versus $\Delta\varepsilon_{Hf}$ for all the analyzed loess samples. The inset shows schematically how the $\Delta\varepsilon_{Hf}$ values are calculated for each sample. The terrestrial array used to calculate $\Delta\varepsilon_{Hf}$ values corresponds to $\varepsilon_{Hf} = 1.55*\varepsilon_{Nd}+1.21$ as recently reevaluated by Vervoort et al. [2011]. Shown by arrows along the horizontal axis are various estimates for Upper Continental Crust: Taylor and McLennan [1985], Shaw et al. [1967; 1976], Rudnick and Gao [2003], Condie [1993] and Gao et al. [1998].

Figure 5: T_{DM} (Nd) versus T_{DM} (Hf) for all loess samples.

The T_{DM} (Nd) are calculated using the $^{147}Sm/^{144}Nd$ ratio measured for each sample. They are well constrained with an error smaller than the horizontal bars. The T_{DM} (Hf) ages are calculated using a single stage Lu/Hf evolution for the samples coming from China, Tajikistan, Argentina and Sahara, and using a two stages evolution for the samples from Western Europe. For the latter, we assumed that the average crystallization age of the excess zircons was 0.9 Ga, an

age consistent with the Archean to Proterozoic materials that have been repeatedly reworked during the Cadomian and Hercynian orogenies [*Peucat et al.*, 1988]. For all samples, the vertical bar corresponds to the range of ages obtained with a $^{176}Lu/^{177}Hf$ ratio going from 0.0057 (the youngest ages) to 0.0200 (the oldest ages). The inset shows how the two-stages calculation operates. A "zircon stage" is calculated between present-day and a crystallization age T_{cryst} of 900 Ma, and using a $^{176}Lu/^{177}Hf$ ratio of 0.0001. Prior to T_{cryst}, the evolution follows the same range of UCC $^{176}Lu/^{177}Hf$ ratios as for all other samples. The inset also highlights how single stage crustal model ages become significantly too old if the zircons did not crystallize recently.

Figure 6: Measured $^{147}Sm/^{144}Nd$ versus calculated $^{176}Lu/^{177}Hf$ for all loess samples.

As in Figure 5, a single stage history is assumed for the Argentinian, Chinese, Tajikistan and Sahara samples and a two-stages history for the Western European samples. The grey field corresponds to the range of published values for the Lu/Hf ratio of upper continental crust [*Shaw et al.*, 1967; *Taylor and McLennan*, 1985; *Condie*, 1993; *Gao et al.*, 1998; *Griffin et al.*, 2002; *Rudnick and Gao*, 2003; *Goodge and Vervoort*, 2006; *Hawkesworth et al.*, 2010; *Condie et al.*, 2011]. The two red lines show our estimated averages and the orange fields correspond to the calculated error at 1σ.

Highlights

- First estimate of the average Nd-Hf isotopic composition of upper continental crust
- The average (ε_{Nd} = -10.3±1.2 and ε_{Hf} = -13.2±2) falls on the terrestrial array
- The average Nd model age of upper continental crust is 1.82±0.07 Ga
- The upper continental crust $^{176}Lu/^{177}Hf$ ratio is 0.0125±0.0018

Figure 1

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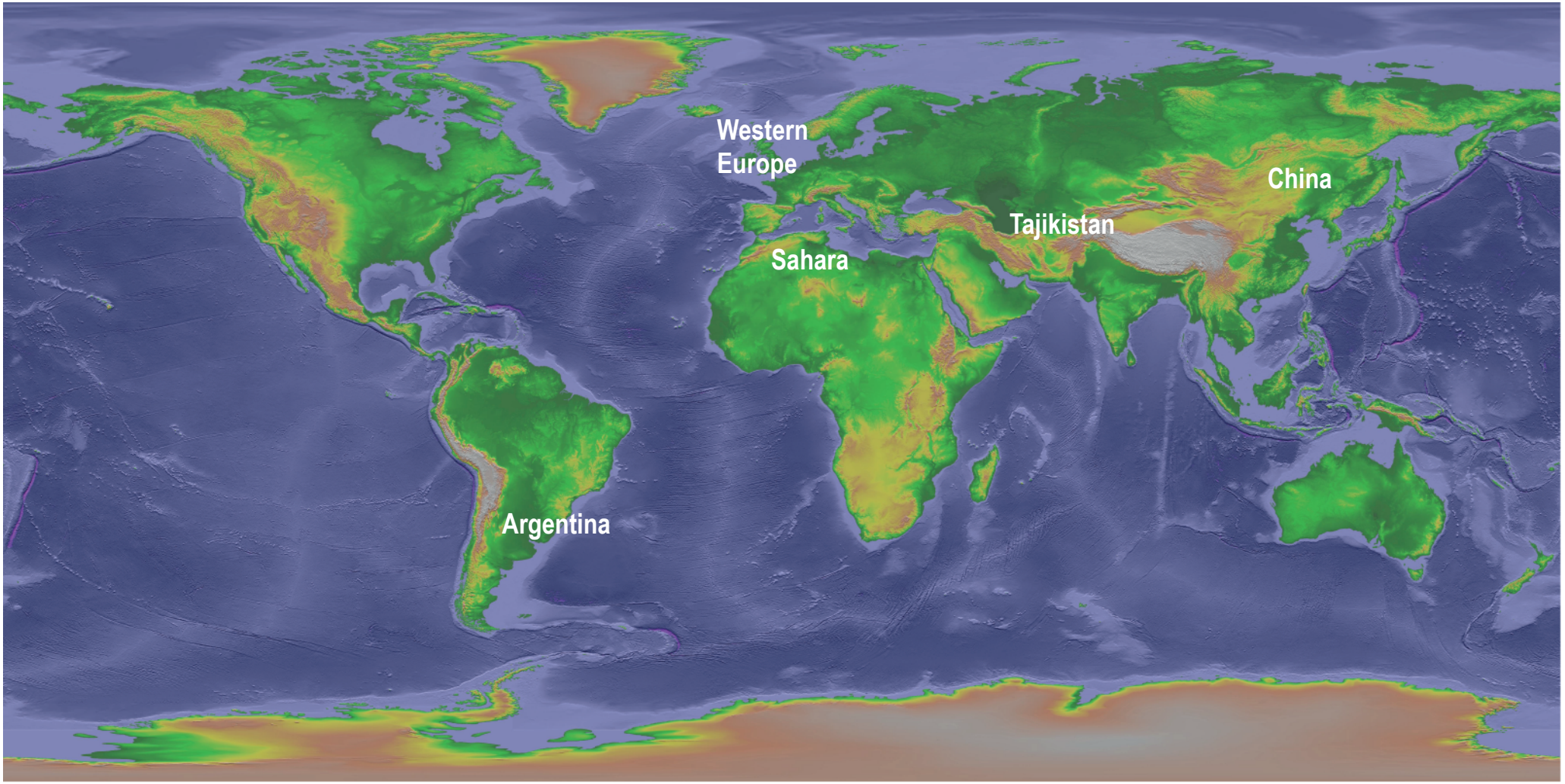

Figure 1

Figure 2

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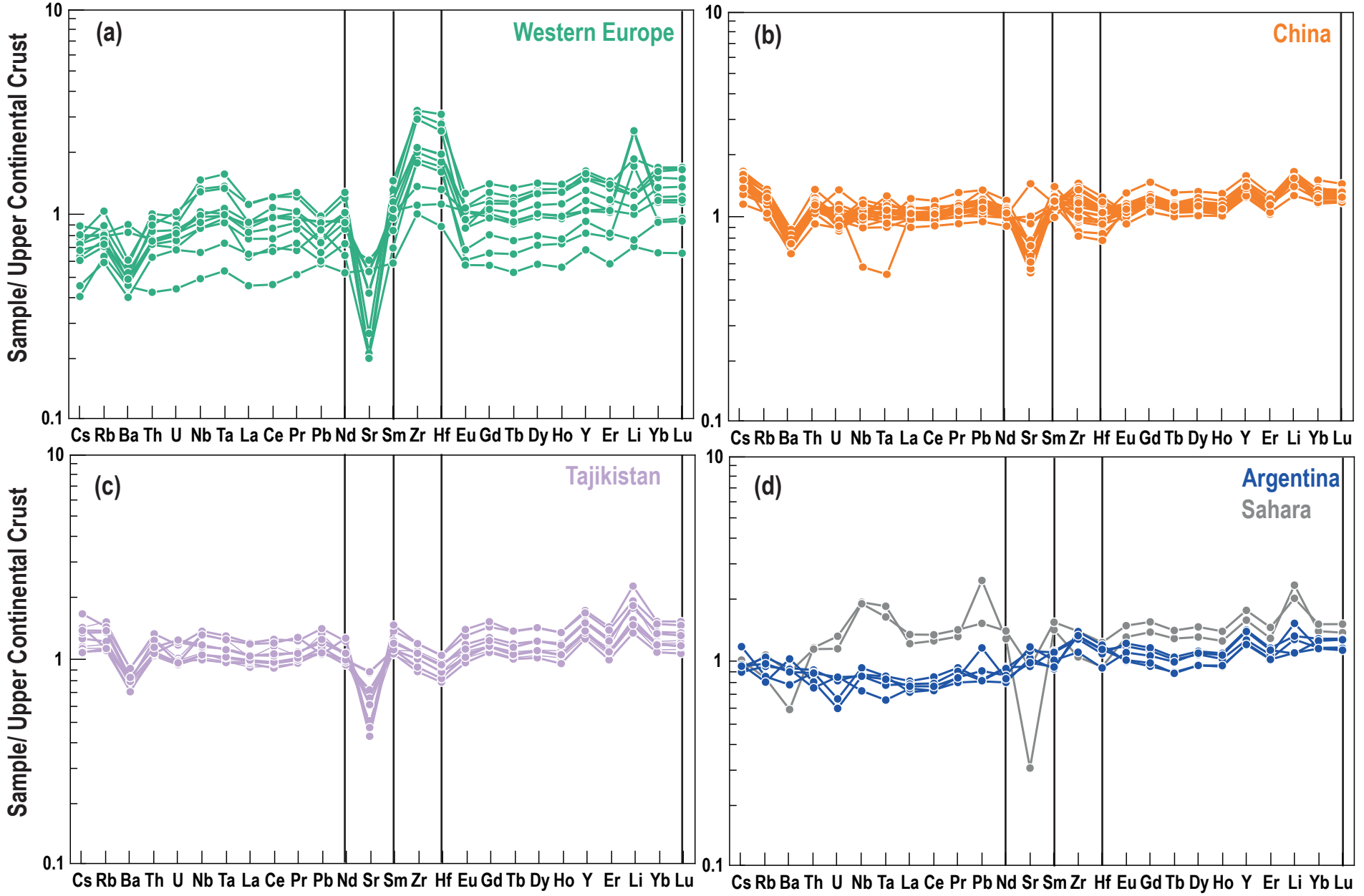

Figure 2

Figure 3

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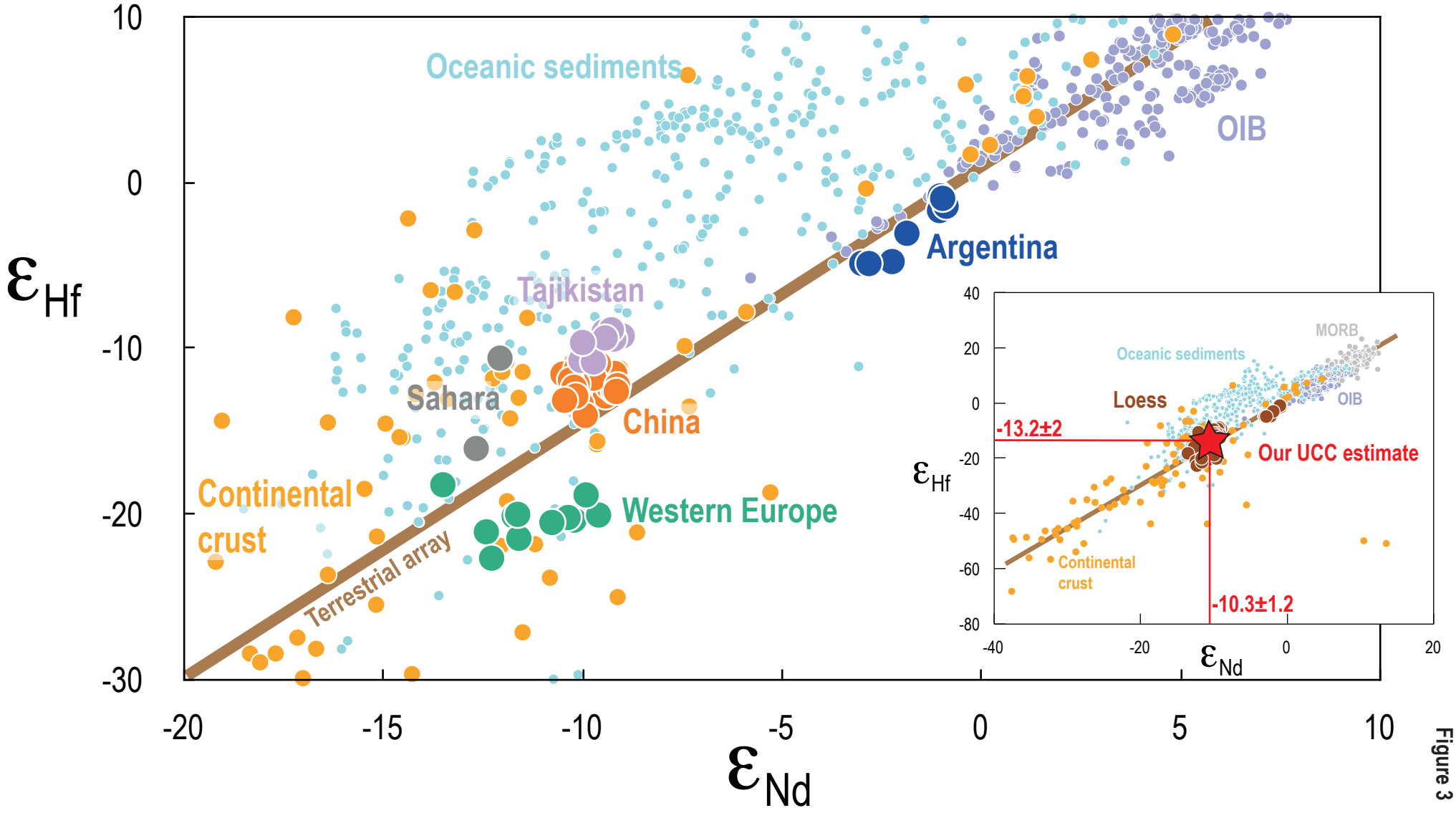

Figure 3

Figure 4

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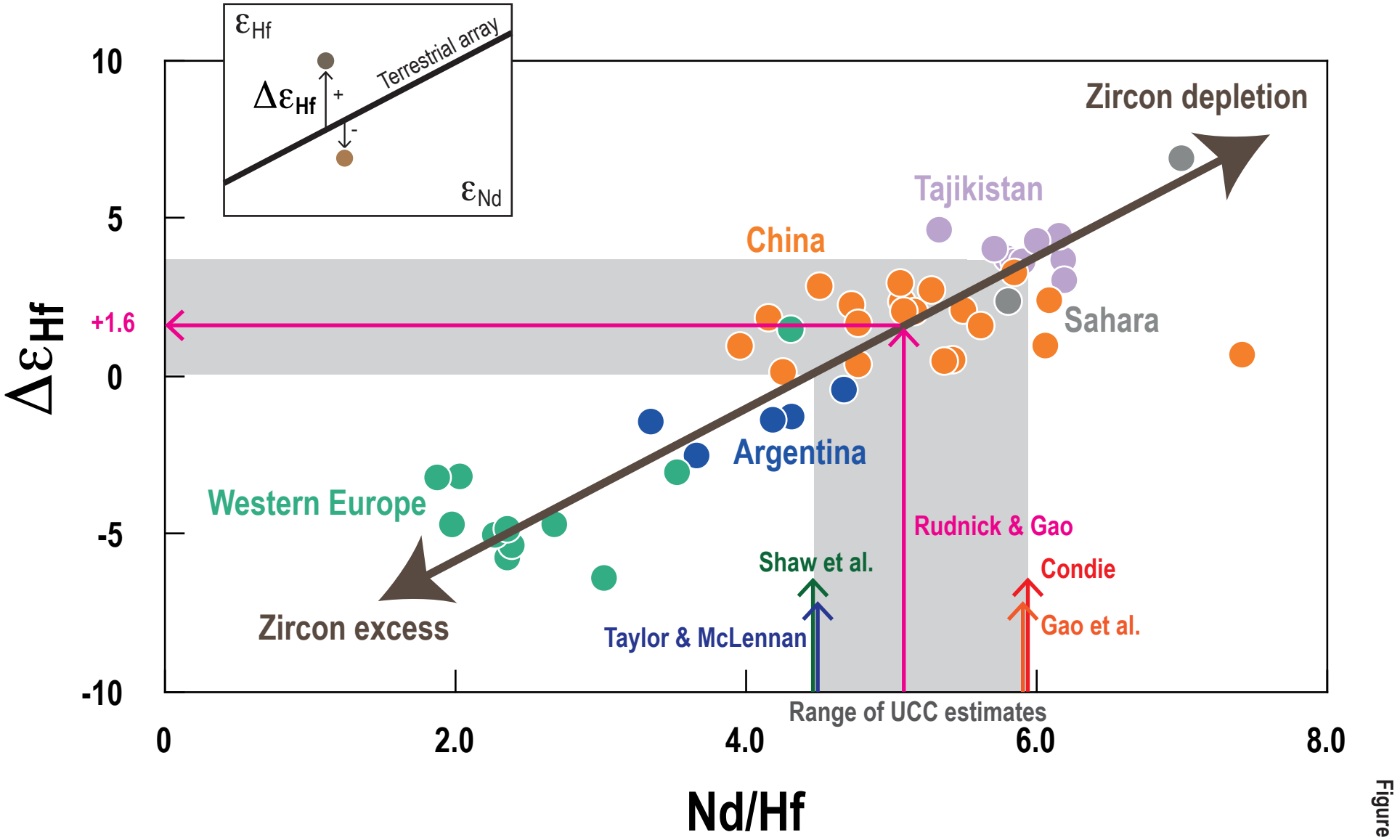

Figure 4

Figure 5

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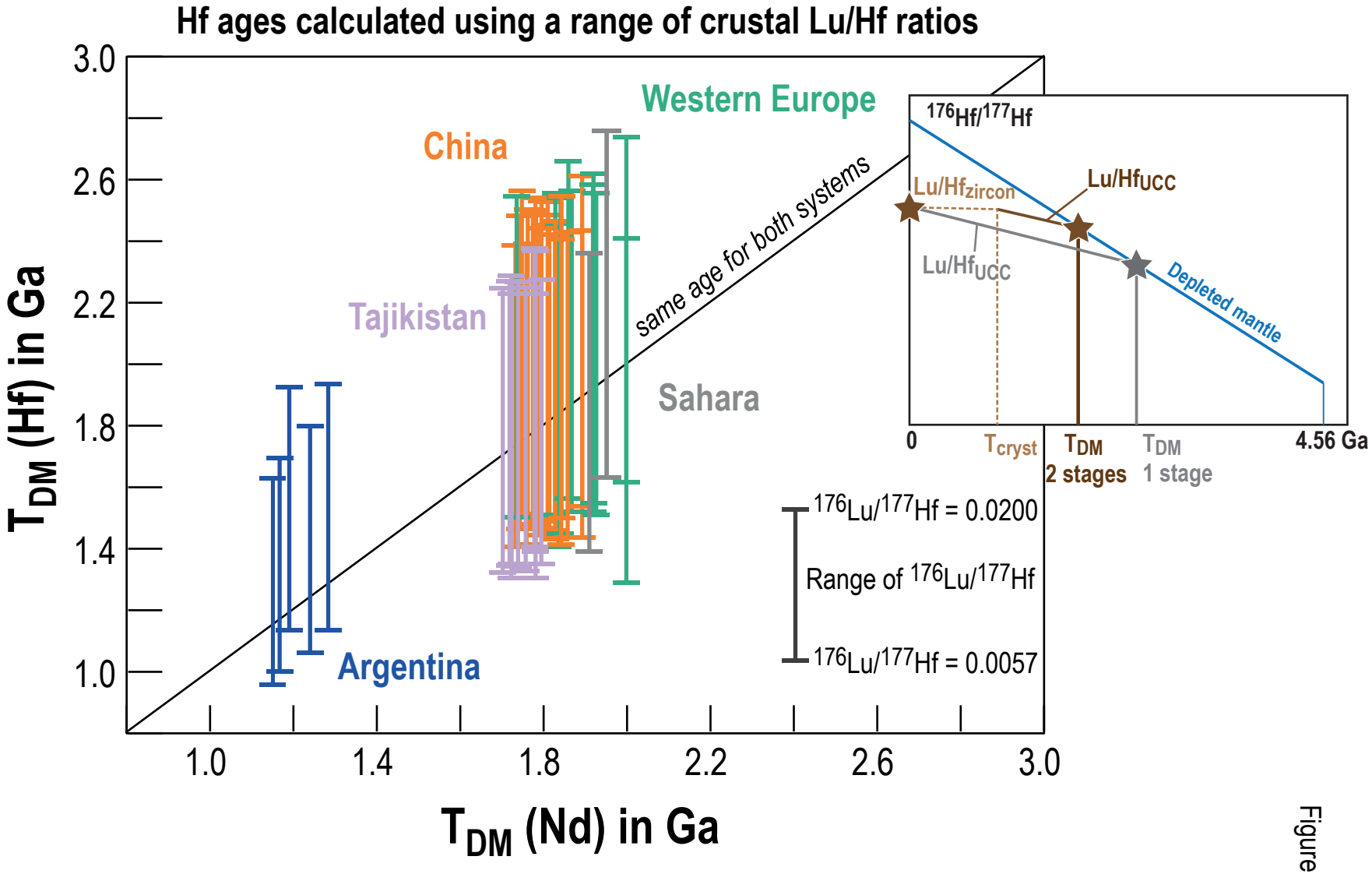

Figure 5

Figure 6

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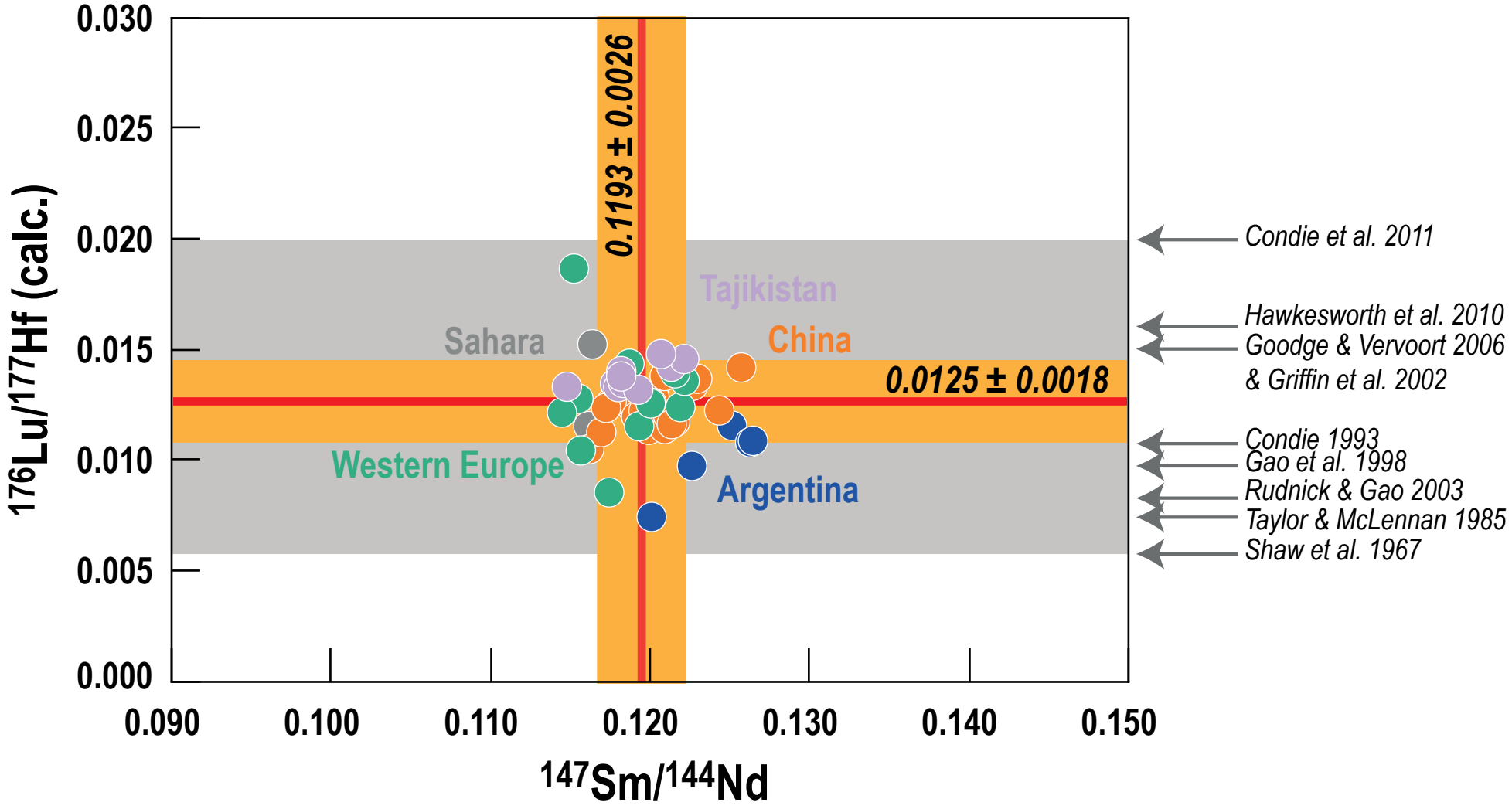

Figure 6

Table 1

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Table 1: Nd and Hf isotopic compositions of the loess samples

Sample	Location	$^{143}Nd/^{144}Nd$	2s	ε_{Nd}	$^{147}Sm/^{144}Nd$	$^{176}Hf/^{177}Hf$	2s	ε_{Hf}	$^{176}Lu/^{177}Hf$
Western Europe									
HOT1 whole rock	St Brieuc, France	**0.512106**	0.000009	**-10.2**	0.1219	**0.282209**	0.000008	**-20.4**	0.00574
HOT1 < 160 mm	St Brieuc, France	**0.512098**	0.000010	**-10.4**	0.1193	**0.282213**	0.000007	**-20.2**	0.00541
PR RT (whole rock)	Port Racine, Normandy, France	**0.512078**	0.000009	**-10.8**	0.1222	**0.282205**	0.000013	**-20.5**	0.00477
FOUG 3a<160 mm	Fougères, France	**0.512029**	0.000006	**-11.7**	0.1187	**0.282216**	0.000006	**-20.1**	0.00537
SAB 1a <160 mm	Sables d'or, France	**0.512138**	0.000009	**-9.6**	0.1174	**0.282218**	0.000015	**-20.1**	0.00613
NS 6 < 160 mm	Nantois, France	**0.512121**	0.000006	**-9.9**	0.1216	**0.282252**	0.000012	**-18.9**	0.00634
LO94	Spitsbergen (Svalbard)	**0.511937**	0.000010	**-13.5**	0.1152	**0.282269**	0.000010	**-18.2**	0.00905
P2E1	Spitsbergen (Svalbard)	**0.511993**	0.000009	**-12.4**	0.1155	**0.282189**	0.000013	**-21.1**	0.00717
K14	Kesselt, Belgium	**0.512000**	0.000011	**-12.3**	0.1200	**0.282144**	0.000006	**-22.7**	0.00509
R 11	Rocourt,Belgium	**0.512035**	0.000009	**-11.6**	0.1156	**0.282178**	0.000010	**-21.5**	0.00451
SCIL	Scilly Island, England	**0.512034**	0.000008	**-11.6**	0.1145	**0.282219**	0.000018	**-20.0**	0.00464
China									
JX-4	Jixian	**0.512110**	0.000008	**-10.1**	0.1203	**0.282442**	0.000011	**-12.1**	0.00987
JX-6	Jixian	**0.512101**	0.000015	**-10.3**	0.1188	**0.282448**	0.000013	**-11.9**	0.00855
JX-10	Jixian	**0.512115**	0.000009	**-10.0**	0.1162	**0.282406**	0.000011	**-13.4**	0.00843
JX-2	Jixian	**0.512106**	0.000007	**-10.2**	0.1189	**0.282435**	0.000008	**-12.4**	0.00976
XF-10	Xifeng	**0.512124**	0.000009	**-9.9**	0.1176	**0.282470**	0.000009	**-11.1**	0.01011
XF-6	Xifeng	**0.512131**	0.000011	**-9.7**	0.1201	**0.282451**	0.000013	**-11.8**	0.01010
XF-2	Xifeng	**0.512162**	0.000008	**-9.1**	0.1199	**0.282438**	0.000013	**-12.3**	0.01344
XF-4	Xifeng	**0.512160**	0.000010	**-9.2**	0.1209	**0.282429**	0.000014	**-12.6**	0.00948
XF-4 dup	Xifeng					**0.282443**	0.000008	**-12.1**	
XN-2	Xining	**0.512102**	0.000009	**-10.3**	0.1169	**0.282414**	0.000009	**-13.1**	0.01078
XN-4	Xining	**0.512120**	0.000011	**-9.9**	0.1243	**0.282388**	0.000010	**-14.1**	0.00880
XN-10	Xining	**0.512108**	0.000008	**-10.2**	0.1191	**0.282421**	0.000010	**-12.9**	0.00911
XN-6	Xining	**0.512094**	0.000008	**-10.5**	0.1196	**0.282413**	0.000008	**-13.1**	0.00835
L3	Luochuan	**0.512146**	0.000010	**-9.4**	0.1216	**0.282421**	0.000007	**-12.9**	0.01110
L4	Luochuan	**0.512138**	0.000010	**-9.6**	0.1257	**0.282457**	0.000014	**-11.6**	0.01082
L5	Luochuan	**0.512150**	0.000012	**-9.4**	0.1211	**0.282437**	0.000008	**-12.3**	0.01227
L6	Luochuan	**0.512158**	0.000009	**-9.2**	0.1213	**0.282429**	0.000005	**-12.6**	0.01114
L7	Luochuan	**0.512140**	0.000009	**-9.6**	0.1227	**0.282460**	0.000007	**-11.5**	0.01145
L7 dup	Luochuan	**0.512158**	0.000009	**-9.2**		**0.282459**	0.000009	**-11.5**	
L9	Luochuan	**0.512137**	0.000009	**-9.6**	0.1172	**0.282475**	0.000006	**-11.0**	0.01023
L1	Luochuan	**0.512125**	0.000010	**-9.9**	0.1229	**0.282456**	0.000014	**-11.6**	0.01194
L2	Luochuan	**0.512109**	0.000012	**-10.2**	0.1209	**0.282467**	0.000010	**-11.2**	0.01243
Argentina									
12-14	Argentina	**0.512515**	0.000009	**-2.2**	0.1201	**0.282650**	0.000005	**-4.8**	0.00821
24-26	Argentina	**0.512577**	0.000009	**-1.0**	0.1251	**0.282762**	0.000007	**-0.8**	0.01140
32RT	Argentina	**0.512576**	0.000008	**-1.1**	0.1263	**0.282737**	0.000006	**-1.7**	0.00984
32RT dup	Argentina	**0.512580**	0.000008	**-1.0**		**0.282758**	0.000006	**-1.0**	
40RT	Argentina	**0.512534**	0.000007	**-1.9**	0.1264	**0.282698**	0.000004	**-3.1**	0.00846
LUJA	Argentina	**0.512476**	0.000006	**-3.0**	0.1226	**0.282647**	0.000005	**-4.9**	0.00807
Sahara									
Sahara dust collected in Meylan	Meylan, France	**0.511980**	0.000007	**-12.7**	0.1161	**0.282331**	0.000008	**-16.1**	0.01020
Sahara dust collected at 2900m altitude	Alpes, France	**0.512011**	0.000007	**-12.1**	0.1164	**0.282485**	0.000005	**-10.6**	0.01220
Tajikistan									
TJK2772	Chashmanigar, Tajikistan	**0.512163**	0.000007	**-9.1**	0.1178	**0.282526**	0.000006	**-9.2**	0.01152
TJK2773	Chashmanigar, Tajikistan	**0.512168**	0.000011	**-9.0**	0.1213	**0.282523**	0.000005	**-9.3**	0.01206
TJK2930	Chashmanigar, Tajikistan	**0.512115**	0.000006	**-10.0**	0.1180	**0.282482**	0.000006	**-10.7**	0.01117
TJK3012	Chashmanigar, Tajikistan	**0.512154**	0.000006	**-9.3**	0.1221	**0.282517**	0.000004	**-9.5**	0.01163
TJK3070	Chashmanigar, Tajikistan	**0.512157**	0.000007	**-9.2**	0.1183	**0.282518**	0.000007	**-9.5**	0.01145
TJK3148	Chashmanigar, Tajikistan	**0.512145**	0.000006	**-9.5**	0.1207	**0.282530**	0.000006	**-9.0**	0.01189
TJK3179	Chashmanigar, Tajikistan	**0.512154**	0.000006	**-9.3**	0.1182	**0.282534**	0.000007	**-8.9**	0.01221
TJK3198	Chashmanigar, Tajikistan	**0.512131**	0.000008	**-9.7**	0.1192	**0.282479**	0.000006	**-10.8**	0.01146
TJK2814	Chashmanigar, Tajikistan	**0.512146**	0.000007	**-9.4**	0.1182	**0.282520**	0.000006	**-9.4**	0.01141
TJK3165	Chashmanigar, Tajikistan	**0.512117**	0.000009	**-10.0**	0.1148	**0.282512**	0.000007	**-9.7**	0.01056

Table 2

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Table2: Compilation of the parent-daughter ratios and Nd and Hf isotopic compositions of various reservoirs

Reservoir	Source	$^{143}Nd/^{144}Nd$	ε_{Nd}	Sm (ppm)	Nd (ppm)	$^{147}Sm/^{144}Nd$	$^{176}Hf/^{177}Hf$	ε_{Hf}	Lu (ppm)	Hf (ppm)	$^{176}Lu/^{177}Hf$
Bulk Silicate Earth	Bouvier et al. 2008	0.512630	-			0.1960	0.282785	-			0.0336
Most depleted MORB*	Chauvel et al. 2008	0.513270	12.48			0.2172	0.283381	21.08			0.0403
Depleted mantle	Salters and Stracke 2004			0.27	0.713	*0.2289*			0.063	0.199	*0.0449*
Average MORB	Chauvel et al. 2008	0.513072	8.62			0.2106	0.283208	14.96			0.0384
"	Gale et al. 2013	0.513074	8.66			0.2107	0.283000	7.6			0.0360
"	Gale et al. and Hf on terrestrial array	0.513074	8.66			0.2107	0.283199	14.63			0.0383
Source of new crust	)huime et al. 2011 and Nd on terrestrial arra	0.513027	7.74				0.283158	13.2			
Upper Continental crust											
	Rudnick and Gao TOG 2003			4.7	27	*0.1052*			0.31	5.3	*0.0083*
	Taylor and McLennan 1985			4.5	26	*0.1046*			0.32	5.8	*0.0078*
	Gao et al. 1998			5.09	30.4	*0.1012*			0.35	5.12	*0.0097*
	Shaw et al. 1967&1976			4.61	25.9	*0.1076*			0.233	5.8	*0.0057*
	Condie 1993			5.09	30.4	*0.1012*			0.32	4.3	*0.0106*
	Wedepohl 1995			4.7	25.9	*0.1097*			0.27	5.8	*0.0066*
	McCulloch and Wasserburg, 1978					0.1150					
	Goldstein et al. 1984					0.1150					
	Allègre and Rousseau 1984					0.1120					
	Jahn and Condie 1995					0.1180					
	Goodge and Vervoort 2006										0.0150
	Griffin et al. 2002										0.0150
	Hawkesworth et al. 2010										0.0159
	Condie et al. 2011										0.0200
Our estimate for Upper Continental Crust		**0.512101**	**-10.3**			**0.1193**	**0.282412**	**-13.2**			**0.0125**
uncertainity at one sigma		**±0.000060**	**±1.2**			**±0.0026**	**±0.000060**	**±2**			**±0.0018**

Supplementary table

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Supplementary figure

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