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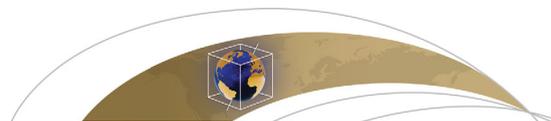
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RESEARCH ARTICLE

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Large-scale tectonic cycles in Europe revealed by distinct Pb isotope provinces

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Key Points:

- We have compiled and mapped out ~6800 Pb isotope measurements of lead ores and K-feldspars across Europe and the circum-Mediterranean
- Lead model ages define spatially distinct age provinces consistent with major tectonic events ranging from the Paleozoic to the Archean
- Time-integrated U/Pb and Th/Pb ratios are decoupled from the age provinces and suggest foundering of the lower crust in southern Europe

Supporting Information:

- Supporting Information S1
- Data Set S1

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Abstract Lead isotopic systematics of U-poor minerals, such as sulfides and feldspars, can provide unique insights into the origin and evolution of continents because these minerals “freeze in” the Pb isotopic composition of the crust during major tectonothermal events, allowing the history of a continent to be told through Pb isotopes. Lead model ages constrain the timing of crust formation while time-integrated U/Pb, Th/Pb, and Th/U ratios shed light onto key geochemical processes associated with continent formation. Using ~6800 Pb isotope measurements of primarily lead ores and minor K-feldspar, we mapped out the Pb isotope systematics across Europe and the Mediterranean. Lead model ages define spatially distinct age provinces, consistent with major tectonic events ranging from the Paleozoic to the Proterozoic and latest Archean. However, the regions defined by time-integrated U/Pb and Th/Pb ratios cut across the boundaries of age provinces, with high U/Pb systematics characterizing most of southern Europe. Magmatic influx, followed by segregation of dense sulfide-rich mafic cumulates, resulted in foundering of U- and Th-poor lower crust, thereby changing the bulk composition of the continental crust and leading to distinct time-integrated U-Th/Pb provinces. We show that the tectonic assembly of small crustal fragments leaves the crust largely undifferentiated, whereas the formation of supercontinents results in fundamental changes in the composition of the crust, identifiable in time and space by means of Pb isotope systematics. Observations based on Pb isotopes open up a new perspective on possible relationships between crustal thickness and geodynamic processes, in particular the role of crustal foundering into the mantle and the mechanisms responsible for the existence of cratons.

1. Introduction

How geological processes impart to continents their distinctive compositions is unclear. Crustal material is originally extracted from the mantle by magmatic processes to form “juvenile” crustal segments such as the Birimian of West Africa [Abouchami *et al.*, 1990], the Superior [Ludden and Hynes, 2000], and Grenville [Dickin, 2000] provinces of Canada, and the Pan-African of the Arabian-Nubian shield [Stein and Goldstein, 1996]. Continental crust is subsequently reworked by tectonic and magmatic processes at convergent plate boundaries through arc and continental collisions, which modify and obscure most of their original mantle signatures. Europe and the Mediterranean basin expose a large collection of diverse mountain-building processes, from Alpine tectonics through the vast expanses of granite-cored Variscan (=Hercynian) terranes to the Proterozoic and Archean orogenic belts of Scotland and the Baltic Shield [Cloetingh *et al.*, 2009]. Europe today represents an intricate patchwork of various continental blocks, such as Iberia, Adria, and Pannonia, brought together through the relative movements of large continents, first and foremost those of Gondwana, Laurussia, and, more recently, Africa [Cavazza, 2004; Stampfli *et al.*, 2013]. Understanding the extent to which the tectonics of continental assembly modify the composition of the crust is key to understanding the origin and evolution of continents.

Radiogenic isotope geochemistry provides parent/daughter ratios with a precision unparalleled by nonisotopic techniques and is therefore the method of choice for identifying lateral and temporal chemical

variations in crust composition. Chronometers, such as Sm-Nd, Lu-Hf, and U-Pb, provide “model ages” and time-integrated parent/daughter ratios (see supporting information). Because rare-earth elements and hafnium, for the most part, are immobile during weathering, metamorphism, and sediment transport, Nd and Hf model ages of granitic rocks and detrital sediments record the time at which the magmatic protolith of juvenile crust was extracted from the mantle, even if tectonic and sedimentary mélange may complicate the record. Only a few European geologic units, mostly in Finland [Huhma *et al.*, 2011], qualify as juvenile; Nd and Sr isotope compositions of granites and clays across most of the European crust attest to a long crustal history of their progenitors [Liew and Hofmann, 1988; Michard *et al.*, 1985].

In contrast to Nd and Hf model ages, which record crust formation events, Pb model ages signal large-scale thermal resetting and U-Th-Pb redistribution within the crust. The U- and Th-rich accessory minerals allanite and monazite are host to a large fraction of radiogenic Pb in the crust and are affected by metamorphic reactions at temperatures of 450–600°C [Budzyń *et al.*, 2011]. Uranium-poor sulfide ores, such as galena (lead sulfide PbS), as well as feldspars, are the main repositories of common or unradiogenic lead and their closure temperatures to Pb diffusion are ~350°C [Simkovich and Wagner, 1963] and ~550°C [Cherniak, 1995], respectively. When a crustal domain is heated above ~600°C, radiogenic Pb leaves U- and Th-rich minerals and gets incorporated into U-Th-poor sulfides and feldspars, “freezing in” the Pb isotopic composition of these U-Th-deficient minerals at the time the U-Th-Pb systems are reset. In high-grade metamorphic rocks, minerals like galena and potassium feldspar hence record the time-integrated U/Pb and Th/Pb values of the local crust as a function of time as given by the Pb model ages. The efficacy of U-Th-Pb systematics in mapping out compositional evolution of the crust is borne out by the remarkable geochemical provinciality of continents as displayed by the Pb isotope compositions of ore sulfide deposits. In particular, there have been some suggestions that Pb model ages and model U/Pb and Th/U ratios derived from Pb isotope data correlate with regional tectonic history in Europe [Kober and Lippolt, 1985; Michard-Vitrac *et al.*, 1981], Peru [Albarede *et al.*, 2012], and the Western USA [Bouchet *et al.*, 2014]. Although a high-resolution continent-wide seismic database as comprehensive and coherent as that produced by the US Array project remains to be completed for Europe and the Mediterranean, databases of ore Pb isotope compositions across Europe are already in use which allows archeological artifacts such as Greek and Roman coins, tools, weapons, and statues to be associated with specific mining districts [Stos-Gale and Gale, 2009]. The net size of these existing data sets is at least an order of magnitude larger than equivalent databases gathered on any other continent. The purpose of this work is to consolidate into one large database existing Pb isotope data sets on European and circum-Mediterranean ores in order to assess their geochemical provinciality and provide a first-order geodynamic framework for their interpretation.

2. The Lead Model Age Provinces of Europe and Their Geodynamic Significance

The global importance of early studies, while demonstrating proof of concept, was limited by modest numbers of samples and relatively small geographic coverage. To alleviate this restriction, we have assembled the largest and most geographically comprehensive Pb isotope data set to date using the Pb isotope compositions of sulfides and feldspars across the entirety of Europe, providing us with new insights into how the geodynamic and geochemical frameworks of continental assembly are linked. This data set comprises the Pb isotopic compositions of ~6800 samples (Figure 1) compiled from the literature, mostly from sulfide ores but also including 118 K-feldspars from granitic basement. The compilation predominantly consists of ores from the Oxford database OXALID [Stos-Gale and Gale, 2009], broadly used in archeology, and the national Swedish, Norwegian, and Finnish databases (supporting information) with additional post-2001 Pb isotope data sets added. All the data were geolocated using information from the original literature and Google Earth. Because sedimentary basins lack exposed sulfide ores and granitic intrusions, the Anglo-Paris, German, and Pannonian basins appear as data voids.

Radiogenic evolution of isotope ratios combines the effects of time and parent/daughter ratios. Different flavors of U decay at different rates, but strong correlations persist among radiogenic Pb isotopes (e.g., ^{207}Pb versus ^{206}Pb), which dominate and blur the effect of the parent/daughter factor. We therefore used parameters that carry information of both chronometric and geochemical value, namely the model age T_m , and the model $^{238}\text{U}/^{204}\text{Pb}$, $^{232}\text{Th}/^{238}\text{U}$, and $^{232}\text{Th}/^{204}\text{Pb}$ ratios. These parameters, which are derived from a reference two-stage model using the variables proposed by Stacey and Kramers [1975], map the 3-dimensional space of Pb isotope ratios ($^{206}\text{Pb}/^{204}\text{Pb}$, $^{207}\text{Pb}/^{204}\text{Pb}$, $^{208}\text{Pb}/^{204}\text{Pb}$) into a new space T_m ,

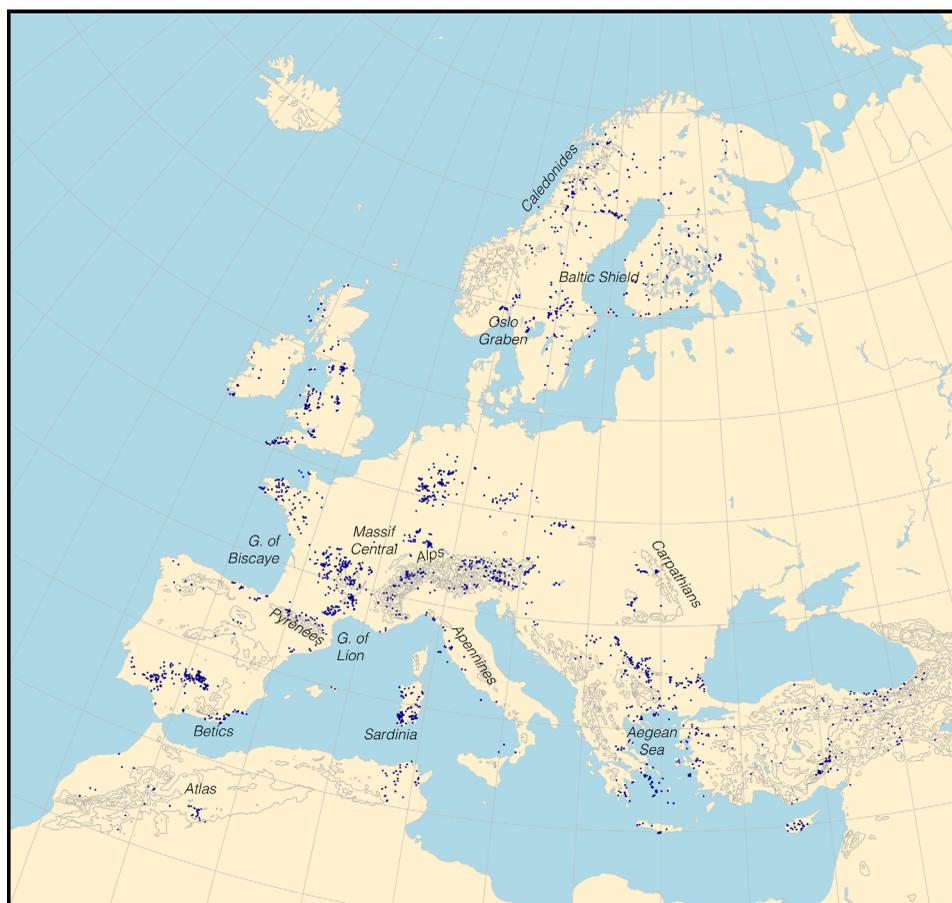


Figure 1. Geographic distribution of the 6735 samples analyzed for Pb isotopes and compiled and discussed in this work. Each black dot corresponds to one sample (which is contrary to Figures 3 and 4). Most samples (6617) consist of galena (PbS) with a minor contribution (118) of K-feldspars and were chosen for their very low U/Pb ratios. The complete sulfide ore and K-feldspar database of 6735 entries is provided in the supporting information and can also be obtained from the first author upon request.

$^{238}\text{U}/^{204}\text{Pb}$, and $^{232}\text{Th}/^{204}\text{Pb}$ (or $^{232}\text{Th}/^{238}\text{U}$) ratios. The new representation conserves the relative position of the samples and sample groups with respect to their position in the original space of raw isotopic ratios. These so-called geochemically informed parameters were calculated from the expressions detailed in the supporting information and displayed graphically on maps by averaging over 0.5×0.5 degree cells (0.25×0.25 for model ages).

The histogram of model ages T_m (Figure 2) shows that Europe and the Mediterranean domain record the impact of only four major tectonic cycles: the Alpine (81 Ma), Variscan (=Hercynian=Caledonian, 350 Ma), Pan-African (=Avalonian=Cadomian, 605Ma), and Svecofennian (1880 Ma), each corresponding to well-documented continental collisional events. Evidence of an additional Archean event (>2700 Ma) in the northeastern Baltic Shield, known as the Karelian, is faint because of the modest number of samples. The number of peaks in the histogram is robust: the ages given in parentheses were obtained by deconvolving the histogram for a mixture of normal or log-normal populations using Matlab software. Allowing for more peaks in an attempt to account for a more detailed tectonic history does not improve the fit of the population mixture: regional Alpine orogenic subevents (Alps, Pyrenees, Betics, Atlas, Aegean) do not define significantly distinguishable T_m peaks but instead merge into a broad ensemble referred to as the “Alpine” cycle. The Caledonides also do not stand out from the Variscides. Samples from the post-Variscan extensional system, which extends from the Oslo Graben through the German Eifel to the French Massif Central, are too few in the database to generate a visible peak. Likewise, samples from the Sveconorwegian (~ 1100 Ma) of Southern Norway and Sweden, which is commonly grouped with the Grenvillian of North America, are too scarce for this event to stand out in the histogram of Figure 2. This figure therefore shows that Pb isotopes reveal not the small regional orogenies, but the major tectonic cycles that laid the foundations for the

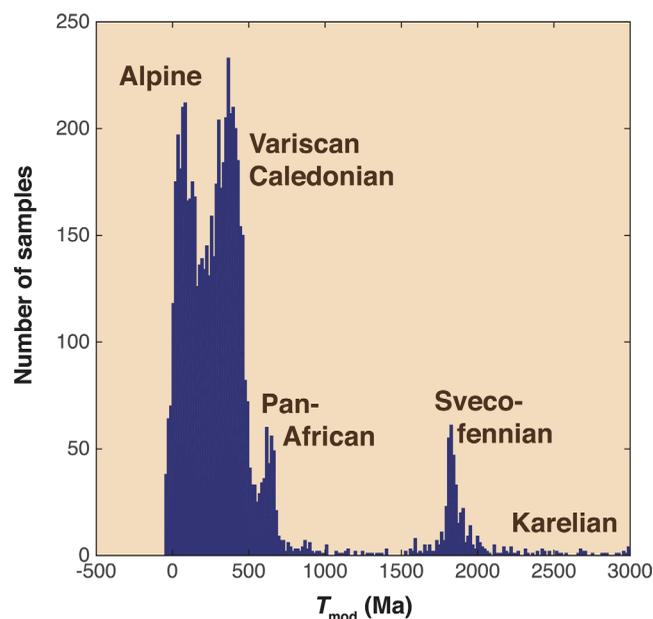


Figure 2. Histogram of Pb model ages showing that only long tectonic cycles dominate the overall age distribution. Ages T_m are calculated as in *Albarede et al.* [2012] (see also supporting information) using the crust evolution parameters of *Stacey and Kramers* [1975]. Only four modes can be distinguished: Alpine (85 Ma), Variscan (=Hercynian=Caledonian, 350 Ma), Pan-African (=Avalonian=Cadomian, 640 Ma), and Svecofennian (1850 Ma), while very old but more scattered model ages characterize the Karelain and Archean provinces. All Alpine orogenic subevents, such as those resulting in the formation of the Alps, the Pyrenees, the Betics, the Apennines, the Carpathians, and the Aegean, form a continuum, as do Variscan and Caledonian subevents, which both contributed to the amalgamation of Eurasia as part of Pangea. The samples from the Sveconorwegian of Southern Norway and Sweden (dark-green colored interval in Figure 3), which is commonly grouped with the Grenvillian, and from the Karelain (tan color in Figure 3), are simply too few to define conspicuous peaks. The model age histogram demonstrates that the thermal history of the European crust was controlled by major orogenic cycles and not by local tectonic events.

defined geographic provinces (Figure 4), but curiously their spatial boundaries cut across the Pb-model age provinces of Figure 3. The contrast between lower U/Pb and Th/Pb values of Northern Europe and Southwestern Iberia with higher values in Southern Europe is sharp. As best demonstrated by the localities where U/Pb and Th/Pb are less consistent (typically the Western Iberian Peninsula), model $^{232}\text{Th}/^{238}\text{U}$ values (supporting information Figure S1) show more scatter, but higher Th/U values occur in the south compared to the north. Based on the geological literature [e.g., *Stampfli and Borel*, 2004], it is likely that the boundary defined by model $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ is a prominent pre-Alpine marker of Variscan subduction of the Avalonia and Laurussia blocks beneath a Gondwana continent consisting mostly of Pan-African-aged material or beneath a long stretch of terranes detached from Gondwana [*Nance and Murphy*, 1994] (notably the Galatian terranes, *Stampfli et al.* [2013]).

A summary of the first-order features emerging from Figures 3 and 4 is provided in Figure 5. A striking feature is the presence of well-defined Pan-African (Cadomian) domains, which, once rotations of the Corsica-Sardinia block (opening of the Gulf of Lion) in Miocene times and Iberia (opening of the Gulf of Biscaye) in Cretaceous times are taken into account, somewhat discontinuously extend from the Ossa-Morena zone in the Southwestern Iberian Peninsula, through Corsica-Sardinia and into the Austro-Alpine region, further branching out towards the Cadomian block of Northwestern France. This inferred string of Pan-African blocks running through Europe has, as far as we know, never so far been recognized as a geodynamic feature of European tectonics and has only become visible now by the present approach of merging individual Pb isotope data sets into one large geolocated database.

Model ages not only correctly delineate crustal segments previously characterized by over a century worth of field and geochronological studies, but also demonstrate their distinctive thermal properties. The age

tectonic construction of Europe, namely the collision between Africa and Europe (the Alpine cycle), the Pangea-forming collision between Gondwana and Laurussia (the Variscan cycle), and the formation of Gondwana (the Pan-African cycle), along with Proterozoic and Archean events in the Baltic shield.

The map of Pb model ages T_m (Figure 3) defines coherent and well-delineated age provinces, which is particularly clear for the Baltic shield with its Svecofennian and Karelain nuclei. The contrast between the Alpine (Aegean, Betics) and the Variscan (Western Europe) domains is also rather sharp. Disregarding some young ages from the volcanic provinces of the Oslo Graben, German Eifel, and French Massif Central, which are unrelated to the Alpine orogeny, Western Europe seems surprisingly little affected by the various Alpine orogenies. Alpine ages are essentially restricted to the Betics, the Tunisian Atlas, the southern Apennines, and, most conspicuously, the broad Aegean and Turkish provinces. The relative scarcity of Alpine model ages in the European Alpine domain echoes the scarcity of Cenozoic granitic rocks (Adamello, Bergell, Elba, Kabylia).

Like Pb model ages, model $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ ratios also show well-

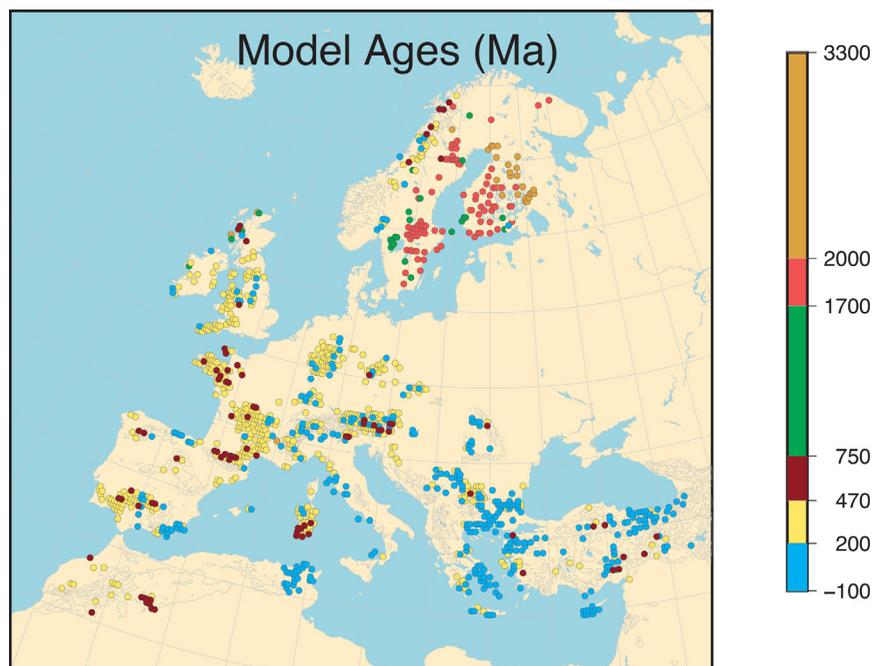


Figure 3. Map of Pb model ages in Europe and the circum-Mediterranean showing that the age provinces of model T_m in Western Europe and the circum-Mediterranean region are made of juxtaposed crustal segments in which ages were reset during different major tectonic events corresponding to supercontinent assembly. Maps drawn using the GMT software [Wessel and Smith, 1991]. Color-coding corresponds to time intervals. Data from the database have been averaged over 0.25×0.25 degree cells. Some intervals have been determined to separate the four major peaks of Figure 2 (Alpine in blue, Variscan in yellow, Pan-African in maroon, and Svecofennian in red).

histogram of Figure 2 carries additional geodynamic information. The dispersion of Pb model ages in a crustal segment around a peak indicates how long parts of this segment remained above the closure temperature of the relevant chronometric system, typically galena and K-feldspar. The characteristic time ΔT needed for a slab of thickness h to achieve thermal steady state is typically h^2/κ , with thermal diffusivity $\kappa \sim 25 \text{ km}^2 \text{ Ma}^{-1}$. A $\Delta T \sim 200 \text{ Ma}$ therefore signals that the Alpine and Variscan lithosphere was $\sim 70 \text{ km}$ thick, whereas the range of Pan-African and Svecofennian ages ($\sim 80 \text{ Ma}$) suggests a thinner $\sim 40 \text{ km}$ lithosphere probably made of arcs and small crustal terranes. The preservation of Pb isotopes of Pan-African timing within the vast Variscan expanses further attests to the accretion of cold fragments of crustal material during the Paleozoic orogenic cycle (Galatian terranes). These domains, which represent a string of fragments detached from the Gondwana margin, were later docked to Laurentia and Avalonia [Matte, 2001; Stampfli et al., 2013; Von Raumer et al., 2013]. An analog setting is the Peru-Chile margin, where preserved Proterozoic Pb model ages record the cold accretion of the Arequipa and Antofalla blocks to the Amazonia continent [Ramos, 2008]. These blocks are associated with an unusually deep Moho under the Andes, reminiscent of the thicker crust below the Eastern Alps and Eastern Pyrenees. Lead model ages therefore appear to be a robust tracer of cold, thick crustal fragments, another novel outcome of our large Pb isotope database.

3. The Origin of Geochemical U-Th-Pb Provinces of Europe and the Making of Continental Crust

Most noticeably, model $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ (Figures 4 and 5) provide insight into how vast expanses of continental crust can acquire distinctive geochemical signatures and evolve into geochemical provinces. Figure 6 shows that European crust has higher Th/U than both the planetary reference [Blichert-Toft et al., 2010] and average upper crust [Stacey and Kramers, 1975]. The Pb isotope signatures carried by the samples considered here are distinctly crustal and cannot be assigned to flushing of the crust by fluids rich in mantle Pb. The strong correlation ($r = 0.85$) of $^{238}\text{U}/^{204}\text{Pb}$ and $^{232}\text{Th}/^{204}\text{Pb}$ shows that Pb is fractionated from U and Th by up to ~ 15 percent. Fractionation of Pb from U and Th echoes the compatible behavior of Cu and Ag in arc magmas [Jenner et al., 2012; Lee et al., 2012]: dense sulfide minerals and immiscible sulfide melts

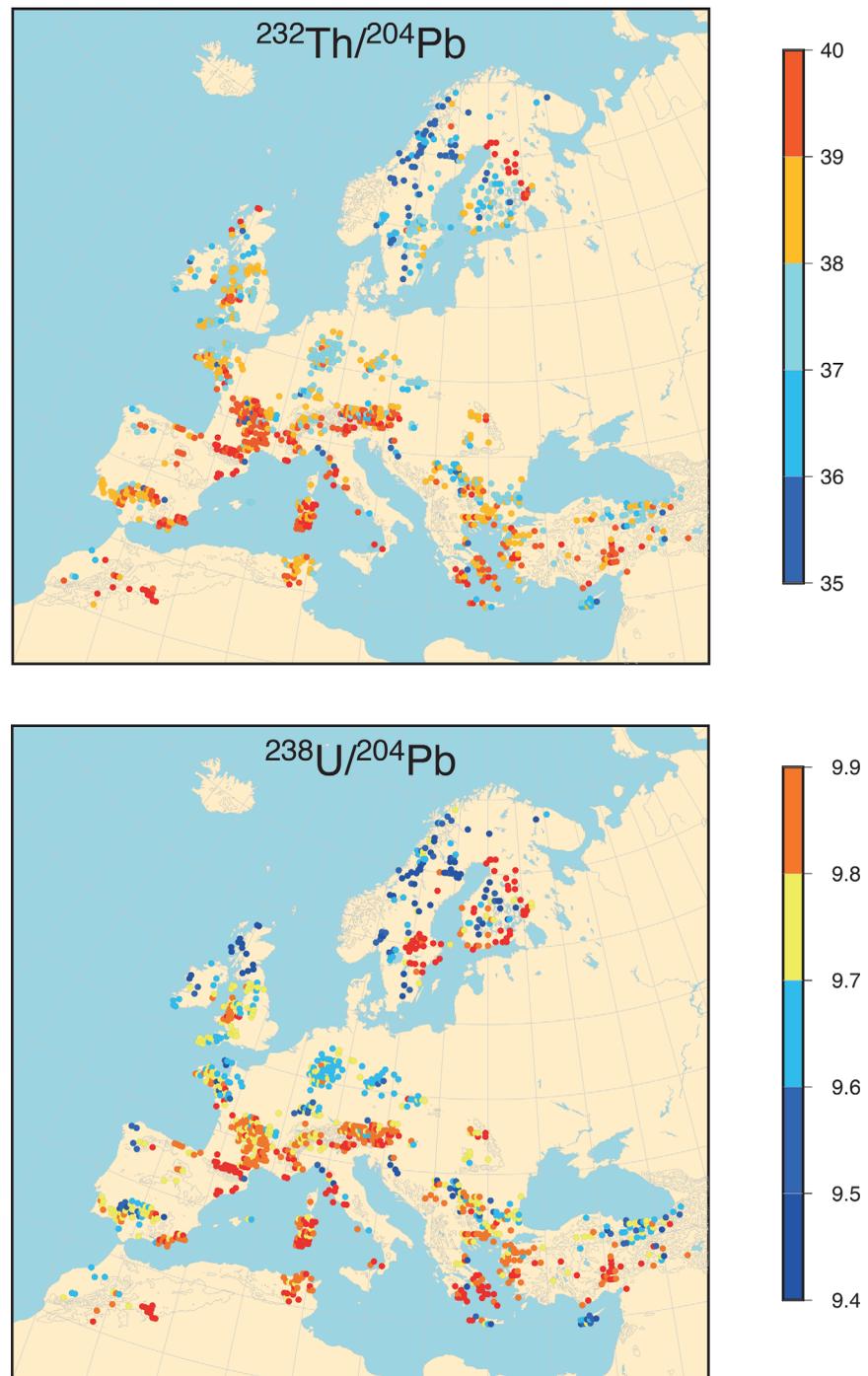


Figure 4. Compositional model $^{238}\text{U}/^{204}\text{Pb}$ (μ) (bottom) and model $^{232}\text{Th}/^{204}\text{Pb}$ (top) provinces in Western Europe and the circum-Mediterranean region do not coincide with the age provinces of Figure 3. For better readability, the data were averaged over 0.5×0.5 degree cells.

concentrate Pb, Cu, and Ag in lower crustal mafic cumulates. Low $^{238}\text{U}/^{204}\text{Pb}$ ratios (≤ 2) are actually known in mafic garnet-pyroxenite xenoliths [Lee *et al.*, 2007]. Although trace element partitioning studies suggest that monosulfide solid solution (MSS), the common form of sulfide in the source region of arc magmas, may not account for the bulk U/Pb fractionation [Li and Audétat, 2013], the subsequent separation of a fraction of a percent of a pyrrhotite (FeS) or immiscible sulfide melt with Pb partition coefficients between sulfide and silicate melt in the range of 20–50 [Kiseeva and Wood, 2015] can readily account for the 15 percent fractionation of Pb from U and Th inferred from Figure 6 (see supporting information).

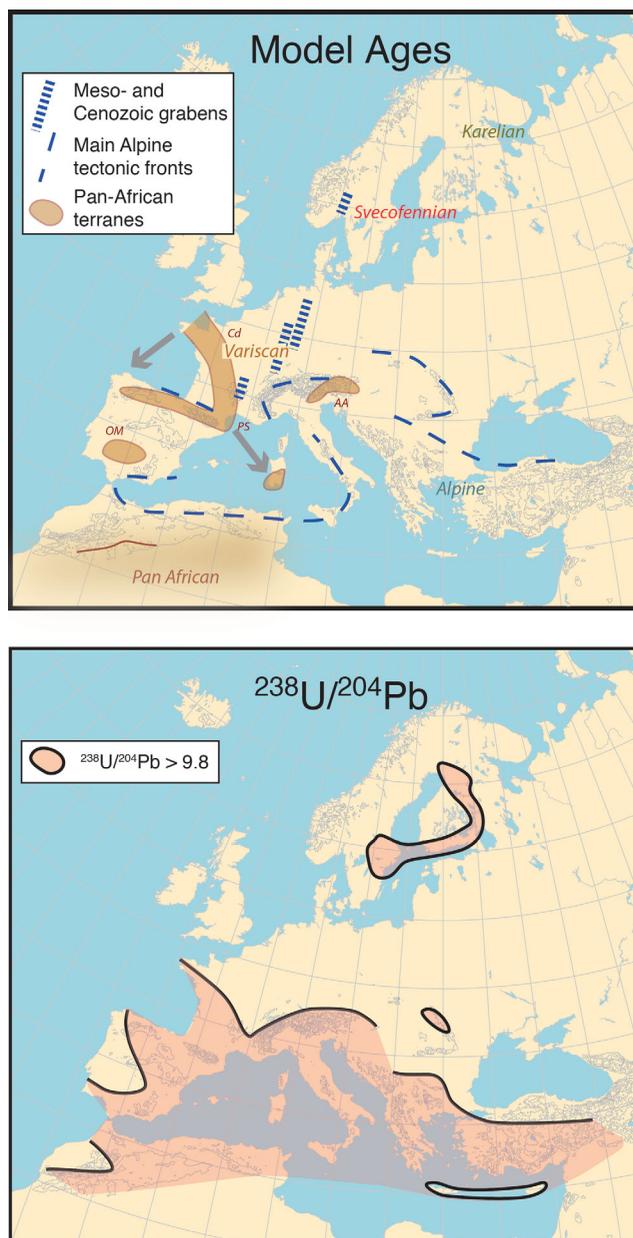


Figure 5. (top) Simplified interpretation of Figure 3. Thick gray arrows: Oligocene-Miocene rotation of the Sardinia-Corsica block (opening of the Gulf of Lion) and Lower Cretaceous rotation of the Iberian Peninsula (opening of the Bay of Biscaye). Thin blue-dashed lines: Main Alpine collision fronts of Western Europe (Alps, Pyrenees, Carpathians), the Mediterranean region (Betics, Atlas, Apennines), and Northern Aegean and Turkey. Striped blue bands: Post-Variscan rift systems, including the Oslo Graben, Eifel, Alsace, and Massif Central of France. Note that outside of these rifts, young model ages are relatively infrequent in Western Europe. In contrast, Alpine ages are the hallmark of the Aegean and Turkish areas, Southern Italy, and Tunisia. Western Europe largely remains a Variscan realm with Pan-African (Late Proterozoic-Early Paleozoic in tan color) nuclei preserved even within the core of Alpine mountain ranges. These domains are rifted fragments of the Southern Gondwana continent reaccreted during collision with Northern Europe. AA: Austro-Alpine; PS: Pyrenees-Sardinia; Cd: Cadomia; OM: Ossa-Morena. In the Baltic Shield, the Svecofennian and Karelian domains are extremely well delineated. (bottom) Simplified interpretation of Figure 4. The model $^{238}\text{U}/^{204}\text{Pb}$ ratios are visibly higher in Southern Europe than in Northern Europe, regardless of the Pb model ages T_m . This time-integrated U/Pb, as well as Th/Pb, gradient (Figure 4) signals massive and widespread loss of Pb by foundering into the mantle of sulfide-rich mafic cumulates from the lower crust south of the Gondwana Front.

Low U and Th contents of the lower crust have been acknowledged for several decades [Heier and Adams, 1965; Rudnick and Gao, 2003] as a feature of metamorphic origin enhanced by the presence of abundant mafic cumulates. In the Sierra Nevada [Brady et al., 2006], U and Th concentrations decrease by more than an order of magnitude over a range of paleodepths of about 30 km. Overall, lead isotopes in lower crustal xenoliths are unradiogenic, which reflects low time-integrated U/Pb [Rudnick and Goldstein, 1990]. In addition, the lower crust is also slightly more depleted in U than in Th. Figure 6 and supporting information Figure S1 shows that model Th/U in the source of ores and granites do not depart from the Solar System value of 3.88 [Blichert-Toft et al., 2010] by more than a few percent. The correlation between Th/U and U/Pb is relatively weak ($r = 0.5$) but still argues for incongruent dissolution of minor phases enriched in U and Th, such as apatite, monazite, epidote, and allanite. Detailed studies of the transition between amphibolite and granulite facies, such as in the Ivrea zone [Bea and Montero, 1999], show that the appearance of melt controls the redistribution of Th and U among accessories and major minerals. The stability relationships of accessory minerals in the presence of magmas are, however, complex and sensitive to magma composition [Budzyń et al., 2011], but Pb isotope evidence again helps clarifying the interpretation. Although the slow decay of ^{232}Th typically receives less

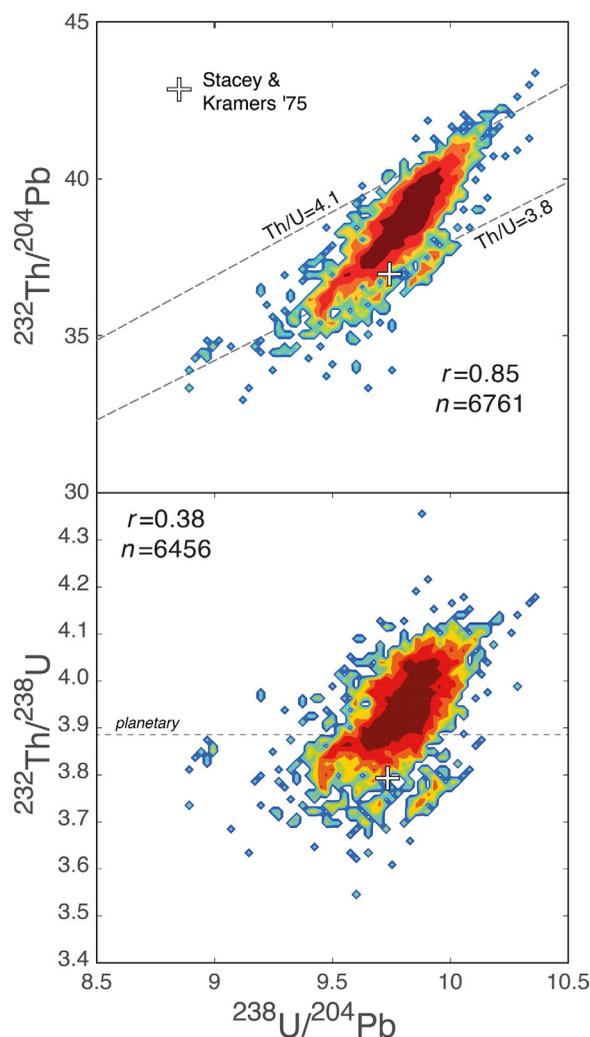


Figure 6. The strong correlation of (top) model $^{238}\text{U}/^{204}\text{Pb}$ (μ) with model $^{232}\text{Th}/^{204}\text{Pb}$ attests to the fractionation of both U and Th from Pb and reflects foundering into the mantle of sulfide-rich mafic cumulates from the lower crust. It contrasts with the much weaker but still positive correlation of (bottom) model $^{238}\text{U}/^{204}\text{Pb}$ (μ) with model $^{232}\text{Th}/^{238}\text{U}$ (κ), which reflects incongruent dissolution of apatite, monazite, and/or allanite during percolation of melts through the crust. Note the Th-rich character of European Pb isotopes relative to both chondrites [Blichert-Toft *et al.*, 2010] and the upper crust [Stacey and Kramers, 1975].

and ascent of Pb-depleted residual magmas. The extent of differentiation and generation of deep crustal cumulates is enhanced by crustal growth [Lee *et al.*, 2015]. During crustal thickening, elevation rises and erosion intensifies. At the same time, the dense mafic lower crust becomes poised to founder (a general term to describe gravitational instabilities such as delamination, detachment, or dripping off of the base of the crust or lithosphere). Eventual foundering leads to further uplift and erosion; what remains of the residual crust is less mafic and has elevated U/Pb and Th/Pb ratios. Where crust was not sufficiently thickened, generation of thick cumulate piles and foundering is less likely; the U/Pb and Th/Pb signature of this remaining crust does not change significantly. These concepts are illustrated in Figure 8. Such processes have been called upon to explain the thermal structure under the Sierra Nevada batholith in Western North America [Ducea and Saleeby, 1996] and Variscan Spain [Gutiérrez-Alonso *et al.*, 2011].

The crustal differentiation processes revealed by Pb isotopes have important implications. The generation of dense mafic lower crustal cumulates, rich in sulfides [Arndt and Goldstein, 1989; Behn and Kelemen, 2006; Kay and Mahlburg Kay, 1993], is likely an important process in continent formation and evolution. Loss of such mafic lower crust increases the U/Pb and Th/Pb of the remaining crust that makes up the continents.

attention in the literature than the faster decays of ^{238}U and ^{235}U , it stands out by variations in $^{208}\text{Pb}/^{206}\text{Pb}$ in Archean rocks. For example, granulite xenoliths and terranes from Isua, Greenland [Robertson, 1986], China [Liu *et al.*, 2004], and the Lewisian of Scotland [Moorbath *et al.*, 1969] all have model Th/U > 4.0, which confirms that high Th/U values tend to characterize lower crustal rocks.

Most (>98%) of the data reported in the present database are from epithermal and hydrothermal ores and hence represent fluids initially mobilized by regional metamorphism or magmatic intrusions. Most ore deposits therefore lie outside plutons themselves, implying that direct comparison between Pb isotope compositions of K-feldspar and galena at any given locality is rarely possible. However, the overall Pb model age and μ patterns inferred here from galenas and K-feldspars are consistent (Figure 7), which confirms that both types of material are equally useful for the present purpose.

4. Crustal Differentiation, Cratons, and Supercontinents

Lateral variations of crustal time-integrated U/Th/Pb systematics seem to result from a coherent combination of geological processes: vertical redistribution of U, Th, and Pb by downward segregation of sulfide-rich mafic cumulates in the lower crust and

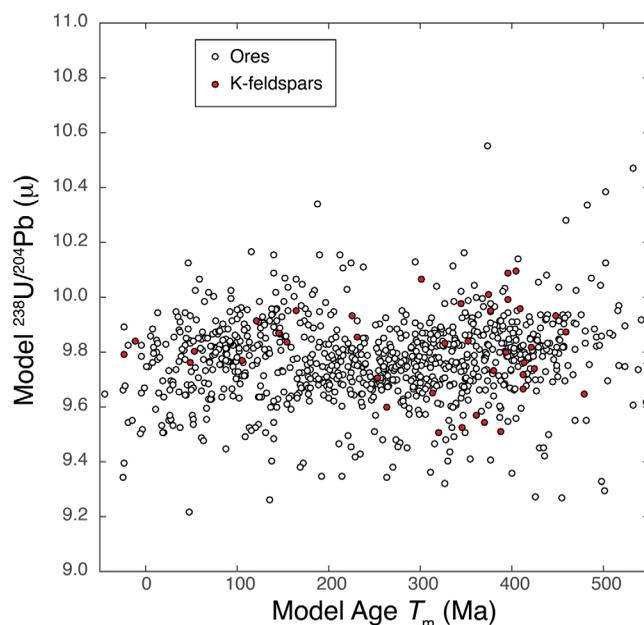


Figure 7. Comparison of the model $^{238}\text{U}/^{204}\text{Pb}$ (μ) and model ages T_m (Ma) calculated for 118 K-feldspars and 6617 galena and sulfide ores. A one-by-one comparison is difficult because in most cases ore deposits do not occur within granitic plutons but outside. The overall trend provided by K-feldspars, however, confirm that these low- μ minerals are an acceptable substitute for galenas [Kober and Lipolt, 1985; Michard-Vitrac et al., 1981].

Foundering of Pb-rich lower crust therefore explains the Pb “paradox” [Lee et al., 2007], which is the observation that the time-integrated U/Pb of both the crust and the upper mantle increases through time, requiring compensation by a low-U/Pb reservoir, which has proven elusive [Allègre, 1969]. Foundering also reduces the crustal Cu content, which explains why, although Cu is definitely incompatible with respect to silicates during melting [Lee et al., 2012], its average concentrations in the continental crust [Rudnick and Gao, 2003] and the upper mantle [McDonough and Sun, 1995] are similar.

We note that foundering of lower crust has been invoked to account for strong lateral heterogeneity in the structure of Europe: beneath the large Variscan domain, the crust is presently thin (30–35 km), whereas beneath the stable Baltic shield and East-European platform to the east, the crust is thicker [Artemieva and Thybo, 2013; Cloetingh et al., 2005; Grad and Tiira, 2009]. These two domains are separated by the Teisseyre-Tornquist Zone (TTZ), a sharp NW-SE trending structure running from the North Sea to the Black Sea (supporting information Figure S2). This strong contrast across the TTZ suggests that only the small fragments rifted off the edge of large cratons, such as the Avalonian and Galatian terranes, are efficiently processed geochemically and subjected to lower crustal foundering. In contrast, cratonic crust, underlain by thick and geochemically depleted mantle keels [Griffin et al., 2009; Herzberg, 2004], appear not to undergo chemical reprocessing and lower crustal foundering during collisional events, preserving their crustal compositions from the time of their initial formation. This suggests that the thick mantle keels underlying cratonic crust or their large areas serve to protect the crust from extensive tectonic and petrological reprocessing. Small lithospheric fragments may be

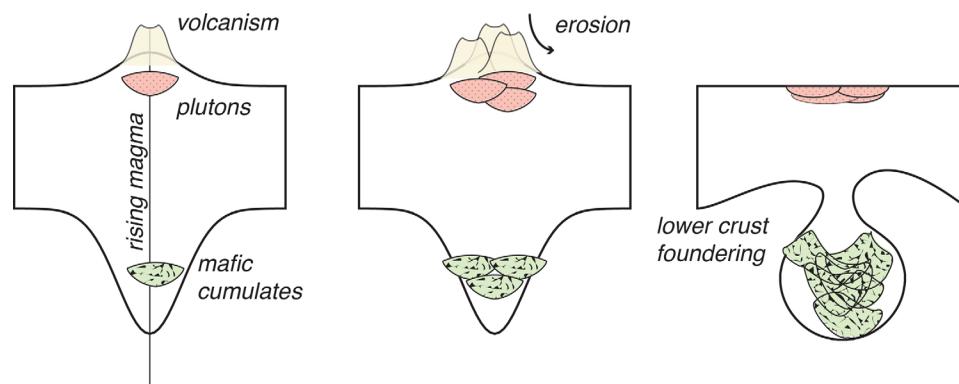


Figure 8. Cartoon describing the main processes leading to the vertical U-Th-Pb differentiation of continental crust. Mafic orogenic magmas rising in crust thickened by collision shed mafic cumulates in the lower crust. The residual melts, mixed with anatectic liquids, rise into the upper crust to form granitic batholiths and erupt as volcanoes. Excess density triggers foundering into the underlying mantle of the lower crust. Substitution of the dense lower crust by lighter upper mantle further enhances uplift and amplifies removal of the upper crust by erosion. Eventually, this continental crust ends up thinner than normal crust not involved in orogenic processes. Since Pb preferentially fractionates into the sulfide melts associated with mafic cumulates, the preserved middle and upper crust left after lower crustal foundering is characterized by higher U/Pb and Th/Pb than normal crust.

more sensitive to reworking simply because they are more easily thermally modified than large lithospheric blocks.

5. Concluding Remarks

In summary, our observations show that Pb isotope systematics of the continental crust are modulated by the depth of the continental lithosphere and the magnitude of tectonic events. Large tectonic events, such as supercontinent formation, can drive significant crustal reworking, whereas localized tectonic episodes appear not to. Superimposed on the effect of tectonics is the size of the continental lithosphere fragment; large ones with thick lithospheric keels may be less prone to crustal reworking than small ones with thin lithospheric keels. Extending our Pb isotope mapping study globally would go far in deciphering how the composition of the continental crust has changed with time.

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