

Perspectives from global modeling of terrestrial Pb and Nd isotopes on the history of the continental crust

Autor(en): **Kramers, Jan D. / Nägler, Thomas F. / Tolstikhin, Igor N.**

Objektyp: **Article**

Zeitschrift: **Schweizerische mineralogische und petrographische Mitteilungen
= Bulletin suisse de minéralogie et pétrographie**

Band (Jahr): **78 (1998)**

Heft 1

PDF erstellt am: **11.07.2024**

Persistenter Link: <https://doi.org/10.5169/seals-59282>

Nutzungsbedingungen

Die ETH-Bibliothek ist Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Inhalten der Zeitschriften. Die Rechte liegen in der Regel bei den Herausgebern. Die auf der Plattform e-periodica veröffentlichten Dokumente stehen für nicht-kommerzielle Zwecke in Lehre und Forschung sowie für die private Nutzung frei zur Verfügung. Einzelne Dateien oder Ausdrucke aus diesem Angebot können zusammen mit diesen Nutzungsbedingungen und den korrekten Herkunftsbezeichnungen weitergegeben werden. Das Veröffentlichen von Bildern in Print- und Online-Publikationen ist nur mit vorheriger Genehmigung der Rechteinhaber erlaubt. Die systematische Speicherung von Teilen des elektronischen Angebots auf anderen Servern bedarf ebenfalls des schriftlichen Einverständnisses der Rechteinhaber.

Haftungsausschluss

Alle Angaben erfolgen ohne Gewähr für Vollständigkeit oder Richtigkeit. Es wird keine Haftung übernommen für Schäden durch die Verwendung von Informationen aus diesem Online-Angebot oder durch das Fehlen von Informationen. Dies gilt auch für Inhalte Dritter, die über dieses Angebot zugänglich sind.

Perspectives from global modeling of terrestrial Pb and Nd isotopes on the history of the continental crust*

by Jan D. Kramers¹, Thomas F. Nägler¹ and Igor N. Tolstikhin²

Abstract

Transport balance modeling has been carried out to reconstruct present day Pb and Nd isotope data of the main accessible terrestrial reservoirs (upper mantle and continental crust). Models start from solar system initial ratios given by meteorite data and assume a start of Earth accretion at 4.55 Ga. The growth of the continental crust, as well as its partial recycling into the mantle, through geological time are sensitive parameter sets, which can therefore be constrained. The best fit solution shows the crust to grow from zero at 4.4 Ga to 75% of its present mass by 1.6 Ga, with slower net growth thereafter. A marked increase in the rate of crust-mantle recycling, from c. 10% of the crust production rate to c. 50%, is indicated to have occurred between 2 and 1.5 Ga. It is speculated that this results from increased erosion after sufficient atmospheric oxygen made an ozone layer, and therefore land life, possible.

Keywords: Pb, Nd, isotope, Earth accretion, continental crust, recycling rate, modeling.

Introduction

In efforts to reconstruct the history of the Earth, radiogenic isotopes are extremely useful, as initial isotope ratios can be derived from meteorite data, and the well known isotope abundances in the Earth's main reservoirs are time integrated functions of the complete geochemical history of those reservoirs. In forward modeling, the consequences of given scenarios are explored by describing their mass and trace species transport and fractionation processes as a set of balanced equations and then solving these while progressing through geological time. If present day data can be arrived at in any number of plausible ways, the system is underconstrained and the exercise is trivial. It is however useful if the range of resulting successful scenarios is limited. The larger the number of data, and the more types of data are used to constrain a model scenario, the better. A solution in forward modeling is a set of geologically realistic parameters that describes the evolution of a system from start to finish and allows to reproduce all

present day observations. In this paper the solution to forward modeling of the terrestrial Th–U–Pb and Sm–Nd parent-daughter sets, further constrained by siderophile element data, is considered.

Problems of global U–Th–Pb and Sm–Nd evolution

The two paradoxes of the Th–U–Pb trio are both well known. The first is the observation that the Pb isotope compositions of both MORB (representative of the depleted upper mantle) and pelagic sediments (proxies for the average eroded continental crust) plot to the right of the isochron defined by chondritic meteorites in $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ space, the "future domain"; hence it is often referred to as the "future paradox" (e.g. AL-LÈGRE, 1982). Unless the Earth as a whole was formed > 100 Ma later than meteorites this means that there is a significant Pb reservoir in the Earth with isotope ratios plotting to the left of the me-

¹ Mineralogisch-Petrographisches Institut (Isotopengeologie), Univ. Bern, Erlachstrasse 9a, CH-3012 Bern, Switzerland. <kramers@mpi.uni-be.ch>

² Geological Institute, Kola Scientific Centre of the Russian Academy of Sciences, Apatity 184200, Russia.

* Extended abstract of a contribution presented at the annual meeting of the Swiss Society of Mineralogy and Petrology, La Chaux-de-Fonds, October 9/10, 1997.

teoritic isochron. This could be the core, the lower mantle or the lower continental crust. The second Pb paradox concerns the $^{208}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ ratios of the MORB source mantle. These portray time integrated Pb isotope development in an environment with $\text{Th}/\text{U} \approx 3.8$, whereas the actual Th/U ratio of the upper mantle is 2.6–2.7 (O'NIONS and MCKENZIE, 1993). This means that the upper mantle is an open system with Pb derived from an external source. These paradoxes are both very fundamental, they cannot be considered in isolation from each other, and a solution for them must entail improved understanding of the history of the Earth.

Nd isotope evolution of the upper mantle-continental crust system in its broad sense has long been qualitatively understood and presents no apparent paradoxes. Through melt extraction leading to continental crust formation, the upper mantle acquired a high average Sm/Nd ratio which led to an ϵ_{Nd} value around 10.5 (BLICHERT-TOFT and ALBARÈDE, 1994) in today's upper mantle, whereas the continental crust is heterogeneous (mainly because of a lack of homogenization mechanisms and hence its heterogeneity in age) with ϵ_{Nd} values down to -50. While the present day situation is well established, the ϵ_{Nd} history of the upper mantle is a subject of controversy linked to varying views on the history of the continental crust. Indications for mantle ϵ_{Nd} values up to +4 at > 3.5 Ga (BENNETT et al., 1983; BOWRING and HOUSH, 1995) have been interpreted by some of these authors (BOWRING and HOUSH, 1995) as evidence that an amount of continental crust roughly equal to its present bulk had been formed on the early Earth within c. 200 Ma after its accretion, in agreement with the "freeboard" concept of ARMSTRONG (1981). The validity of these indications has been strongly contested by others (MOORBATH et al., 1997) who argue that the high apparent ϵ_{Nd} values in the early Archean are artefacts of later Sm–Nd mobilisation in the systems. Apart from its input into this controversy, a forward Nd model for the Earth should provide an ϵ_{Nd} evolution curve for the upper mantle, to serve as a reference in obtaining T_{DM} model ages.

Recent modeling and its results

Recently forward modeling of Earth history, targeting present day terrestrial data, was carried out by KRAMERS and TOLSTIKHIN (1997) for Th–U–Pb, and by NÄGLER and KRAMERS (1998) for Sm–Nd. The model used in both these efforts is identical. The reservoirs considered, and fluxes between them, are summarized in figure 1. The

Earth accretion – core formation scenario used is constrained by siderophile element data (KRAMERS, 1998). This includes a variable accretion flux during the first 100 Ma, accompanied by contemporaneous core formation, with a small core formation flux continuing for 50 Ma after accretion has effectively ceased. During accretion and the main core formation period, one silicate mantle reservoir exists in the model (a prerequisite for the removal of metal from the whole mantle), but after c. 150 Ma the upper and lower mantle are largely isolated from each other and have a mass ratio of c. 1 : 3. Oceanic crust is continuously generated from the upper mantle (melting zone *mf* in Fig. 1). Its destruction ("subduction") occurs in part as a bulk transfer back to the upper mantle, and in part via a mixing-fractionation zone (*sf*) in which the oceanic crust is mixed with a larger component of upper mantle, and proto-continental crust (of probably andesitic composition) is generated as a partial melt. This material is further fractionated (*cf*) into 50% "upper" and 50% "lower" crust. Melting and fractionation are treated as batch processes for simplicity. Recycling of continental material into the mantle can occur via

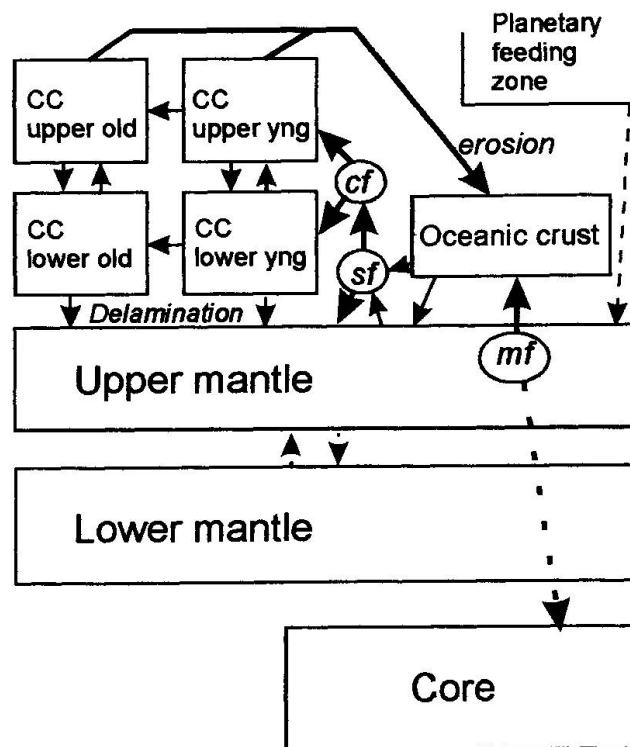


Fig. 1 Reservoirs and fluxes used in the Th–U–Pb and Sm–Nd modeling. *mf* = mantle melting zone giving rise to MORB (and core in early history). *sf* = mixing-fractionation ("subduction") zone. *cf* = Zone fractionating upper and lower crust. Thin arrows: Mass fluxes without fractionation; thick arrows: Mass fluxes with fractionation. Stippled arrows: fluxes only important during first 150 Ma of Earth history.

erosion, which transports mass and trace species from the upper crust into the oceanic crust reservoir, or via a delamination process, which transports lower crustal material directly into the upper mantle. Both processes are accompanied by mass fluxes designed to keep the upper and lower crust masses equal, and by corresponding trace species fluxes. Both processes also obey a law favouring destruction of younger over older continental crust, i.e. the erosion law of ALLÈGRE and ROUSSEAU (1984) which enables the reconciliation of Nd isotope data of crust and upper mantle. The upper and lower continental crust reservoirs are both divided into equal portions labeled "older" and "younger"; the operation of the erosion law then generates the age differences. Surface erosion is a chemically fractionating process, transferring U to the ocean floor in preference to Pb and Th once a sufficiently oxygenated atmosphere allows the mobile uranyl ion to exist (STAUDIGEL et al., 1995). Mass and species transport equations and details of intrinsic parameters such as effective partition coefficients used are given and discussed by KRAMERS and TOLSTIKHIN (1997), NÄGLER and KRAMERS (1998), and KRAMERS (1998).

The Th-U-Pb modeling, in conjunction with siderophile element work, shows that terrestrial Pb isotopes are surprisingly insensitive to the length of the Earth accretion – core formation interval (KRAMERS and TOLSTIKHIN, 1997), in contrast to the results of previous models (HALLIDAY et al., 1996; GALER and GOLDSTEIN, 1996) and that the Earth's core is a highly unlikely reservoir to account for the first Pb paradox. While the age histogram of the continental crust, with a mean age of 2 Ga, is approximately known and was used as a given parameter set, the total mass of continental crust existing at any time, $M_{cc}(t)$, turned out to be a critical free time dependent variable. Two aspects of the way in which crustal growth and recycling affect the fit achieved by the modeling are illustrated in figure 2. The $M_{cc}(t)$ curves shown in figure 2a reflect, from A to E, an increasing amount of continental crust present 150 Ma after the start of Earth accretion. Of these, variant E (the constant crust model) cannot provide any fit to terrestrial Pb and Nd isotope data (KRAMERS and TOLSTIKHIN, 1997; NÄGLER and KRAMERS, 1998). The reason is that the large amount of crustal recycling needed in this scenario to produce anything approaching the present day age distribution of the continental crust destroys the separate isotopic identity of the upper mantle. Variants A to D can reproduce isotopic data, but for B to D this is achieved at the cost of a progressively worse fit to geochemical data: The Th/U

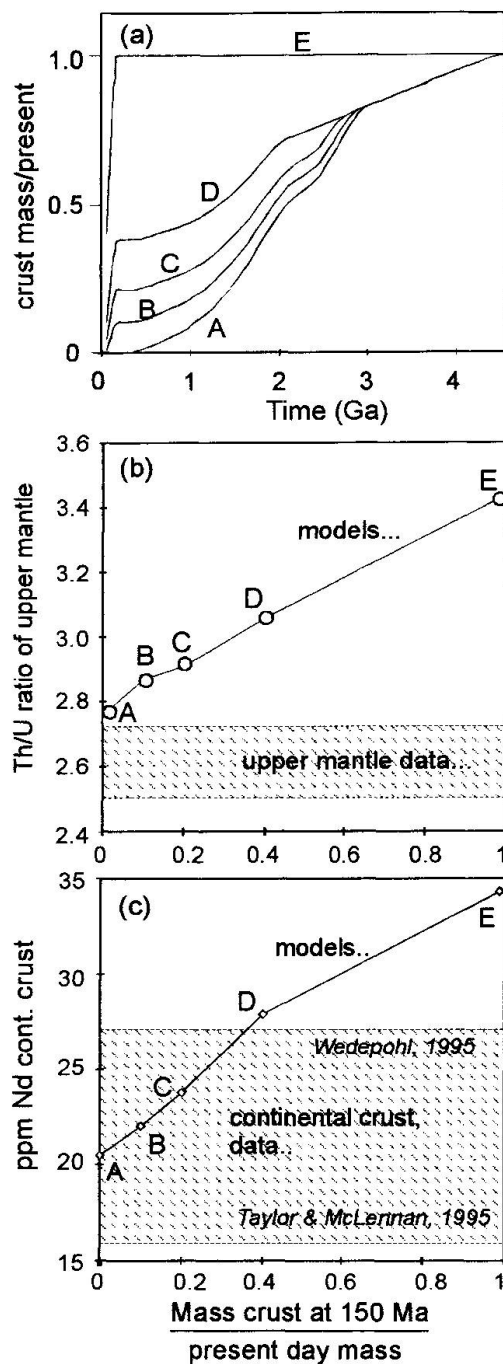


Fig. 2 (a) Five variants of $M_{cc}(t)$ (continental mass vs time) curves examined in modeling, which differ from each other principally in the amount of crust present at 150 Ma after the start of Earth accretion. Note that E (similar to the constant crust model of ARMSTRONG (1981) does not give isotope fits either for Pb or Nd. (b) Effect of early crust mass on present day Th/U ratio of the upper mantle for best fits of Pb isotope ratios in these reservoirs (in the case of A–E), compared to data (O'NIONS and MCKENZIE, 1993). (c) Similar for the Nd concentration of the continental crust resulting from fitting the Nd isotope composition of the upper mantle and crust reservoirs. Note large discrepancy between concentration estimates of TAYLOR and MCLENNAN (1995) and WEDEPOHL (1995).

ratio of the upper mantle (Fig. 2b) and the Nd concentration of the continental crust (Fig. 2c). Only variant A produces reasonably close fits to all geochemical as well as Pb and Nd isotope data of upper mantle and crust (see Fig. 3 for the case of Pb). The key to the solution of the first Pb paradox is the low U/Pb ratio of the "old lower crust" reservoir, which causes its Pb to plot well to the left of the meteoritic isochron. The second paradox is resolved through preferential transport of U over Th (and Pb) in the crust-to-mantle recycling process.

Thus Pb and Nd modeling have imposed similar constraints on the crustal history scenario:

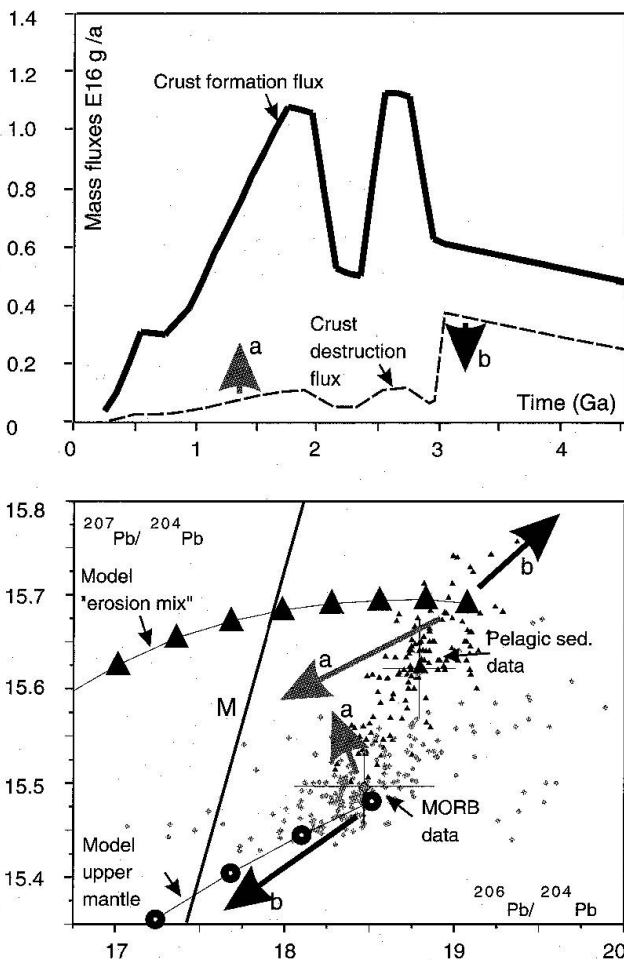


Fig. 3 Top: Crust formation and destruction fluxes for the best fit scenario (A in Fig. 2). Bottom: $^{207}\text{Pb}/^{204}\text{Pb}$ vs $^{206}\text{Pb}/^{204}\text{Pb}$ plot with MORB (grey diamonds) and pelagic sediment data (black triangles) and their averages and standard deviations. See KRAMERS and TOLSTIKHIN (1997) for data references. M: meteoritic isochron. Pb evolutions for upper mantle and "erosion mix" (consisting of older and younger upper crust) shown for best fit model with 200 Ma time intervals. Note "erosion mix" must plot above the mean of pelagic sediments because these contain a hydrothermal MORB Pb component. Large arrows explained in the text.

Very little sialic crust, or none at all, existed immediately after Earth accretion; the growth of continental crust was fast during the Archean and slowed down after c. 2.5 Ga ago. Further, in successful scenarios crust destruction takes place entirely or almost entirely through upper crust erosion; if delamination of lower crust amounts to more than 3% of the continent recycling flux all fits worsen dramatically, and it was concluded that lower crust delamination is unimportant (KRAMERS and TOLSTIKHIN, 1997). This conclusion does not affect ideas on the delamination of the sub-continental mantle.

The mass of continental crust at any time in Earth history is a function of both preceding crust formation and crust-mantle recycling, so that a given $M_{cc}(t)$ curve does not uniquely define crust history. The constraints on the "fine structure" of continent history from Pb isotope data and modeling (KRAMERS and TOLSTIKHIN, 1997) are sketched in figure 3. Fluxes in and out of the continental crust (pertaining to the best fit $M_{cc}(t)$ curve A of Fig. 2a) show continent recycling into the mantle in the early part of Earth's history amounting to no more than 10% of the rate of continent building, and a very much increased ratio of destruction to formation in the last 1600 Ma, with both fluxes agreeing with the estimates of REYMER and SCHUBERT (1984). How this history is constrained is shown qualitatively from the effect of deviations. Increased crustal recycling in the early part of the Earth's history (grey arrows [a] in Fig. 3) destroys the difference in $^{207}\text{Pb}/^{204}\text{Pb}$ between crust and upper mantle (which can only have been generated in the Archean, when the $^{235}\text{U}/^{238}\text{U}$ ratio was still sufficiently high) as well as the solution to the first Pb paradox. In contrast, reduced recycling in the last 1600 Ma (black arrows [b]) produces a highly radiogenic upper crust and an unradiogenic upper mantle. The small amount of crust-to-mantle recycling in the Archean found from the Pb modeling is a robust result, and is in accord with the conclusions from Lu-Hf studies (PATCHETT et al., 1984).

Geological perspectives: Internal or surface factors?

The solutions to the Th-U-Pb and Sm-Nd modeling outlined above are at variance with influential literature on the Archean, which stresses high rates of early crustal recycling (e.g. DE WIT et al., 1992; BOWRING and HOUSH, 1995). It is therefore necessary to assess the geological realism of these solutions. Two possible reasons why crust-mantle recycling rates could have increased sharply in the

mid Proterozoic are discussed below. The first is a suggestion that mountain belts were eroded less in the Archean and early Proterozoic than subsequently, and the second is related to the notion that the first extensive colonization of land by life forms occurred in the mid-Proterozoic.

On the basis of diminishing heat flow, SANDIFORD (1989) proposed that in the relaxation of orogenies, collapse and normal faulting played a more important role in the earlier history of the Earth compared to later, when erosion and uplift dominated (the latter is thought to be the more efficient means of exhuming rock units from great depths). It would be expected that an increase in the role played by erosion in exhumation since the Archean should be reflected by generally increasing peak P/T ratios in metamorphic terrains from the Archean to the present, accompanied by a change in retrograde P-T paths towards a more clockwise character. While it is true that no very high pressure rocks are found in Archean orogenic belts, a review of granulites by HARLEY (1989) does not reveal a significant or consistent difference in peak P-T conditions or the character of the retrograde path between provinces of different metamorphic age (Fig. 4). Further, metamorphic rocks are ubiquitous and clastic sediments abound in Archean and early Proterozoic provinces, pointing to uplift and mechanical erosion. It is therefore not clear how this could be a major factor to explain significantly less crust-mantle recycling in the Archean than at later times.

Rock weathering leading to soil formation and ultimate erosion of land surfaces (irrespective of relief) appears to be greatly enhanced by biological activity in the soil. The direct action of organisms in weathering as well as the important role of humic and fulvic acids in silicate mineral breakdown have been amply demonstrated in experiments and field studies (e.g. ROBERT and BERTHELIN, 1986; DREVER and VANCE, 1994). Various geomorphological observations also provide indications. First, the rate of subsoil rock weathering on slopes increases with decreasing soil thickness, while uncovered bedrock appears to weather very much more slowly than buried rock (HEIMSATH *et al.*, 1997); these variations coincide with differences in biological activity. Second, there are indications that denudation rates in arid environments are significantly slower than those in non-arid environments regardless of mean temperature (SMALL *et al.*, 1997).

A ready explanation why biologically-promoted erosion should be limited to the last 1500–2000 Ma is provided by the history of the atmosphere. Although life and photosynthesis may go back to the age of the oldest rocks, and there is evidence for some free oxygen in the atmosphere since 3 Ga ago (OHMOTO, 1996; WATANABE *et al.*, 1997), life on land requires a UV shielding ozone layer, and clear evidence for abundant atmospheric oxygen exists only for the time from c. 2 Ga onwards (KASTING, 1993). Interestingly, the solution of the second Pb paradox uses the same premise (see above).

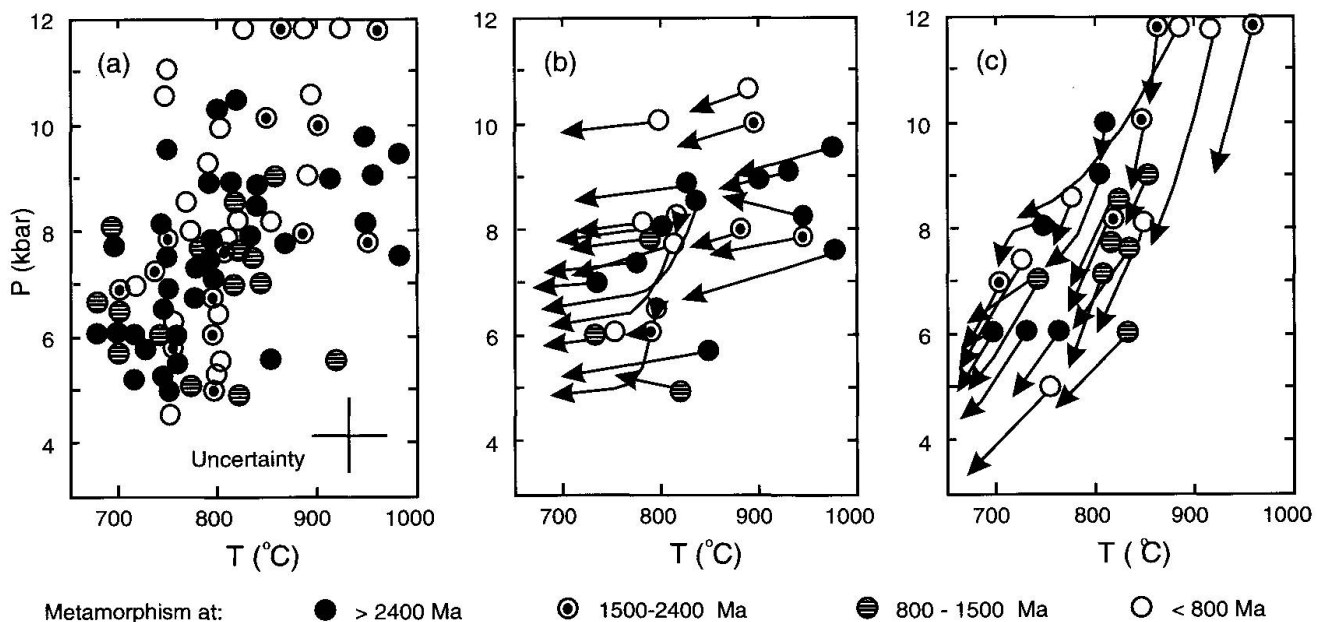


Fig. 4 Summary of peak p-T conditions and retrograde p-T paths of granulite occurrences reviewed by HARLEY (1989) broken down according to age categories. (a) Peak metamorphic conditions, (b) occurrences with near-isobaric cooling paths, (c) near-isothermal decompression paths. Note that different age groups do not appear to show significant overall differences in peak conditions or in the character of retrograde paths.

In summary, it appears likely that biological activity on land may be a more significant cause for a sharp increase in the rate of crust-mantle recycling in the last third of Earth history than tectonic factors. This highlights in a striking way the interaction between different parts of the Earth and, indeed, their interdependence, with surface processes and biological activity profoundly affecting mantle geochemistry and therefore, ultimately, heat flow and geodynamics.

Acknowledgements

Isotope geology research at Bern University is supported by the Swiss Nationalfonds, Grant 20-47157.96. Friedhelm von Blanckenburg and Igor Villa are thanked for discussions and constructive comments on the manuscript, and Viktor Köppel for a review.

References

- ALLÈGRE, C.J. (1982): Chemical geodynamic. *Tectonophysics*, 81, 109–132.
- ALLÈGRE, C.J. and ROUSSEAU, D. (1984): The growth of continents through geological time studied by Nd isotope analysis of shales. *Earth Planet. Sci. Lett.*, 67, 19–34.
- ARMSTRONG, R.L. (1981): Radiogenic isotopes: the case for crustal recycling on a near-steady-state no-continental-growth Earth. *Phil. Trans. royal Soc.*, 301, 443–472.
- BENNETT, V.C., NUTMAN, A.P. and McCULLOCH, M.T. (1993): Nd isotopic evidence for transient, highly depleted mantle reservoirs in the early history of the Earth. *Earth Planet. Sci. Lett.*, 119, 299–317.
- BLICHERT-TOFT, J. and ALBARÈDE, F. (1994): Short-Lived Chemical Heterogeneities in the Archean Mantle with Implications for Mantle Convection. *Science*, 263, 1593–1596.
- BOWRING, S.A. and HOUSH, T.B. (1995): The Earth's early evolution. *Science*, 269, 1535–1540.
- DE WIT, M.J., ROERING, C., HART, R.J., ARMSTRONG, R.A., DE RONDE, C.E.J., GREEN, R.W.E., TREDoux, M., PEDERBY, E. and HART, R.A. (1992): Formation of an Archaean continent. *Nature*, 357, 553–562.
- DREVER, J.L. and VANCE, G.F. (1994): Role of soil organic acids in mineral weathering processes: In PITMAN, E.D. and LEWAN, M.D. (eds): *Organic acids in geological processes*. Heidelberg, Springer-Verlag, 138–161.
- GALER, S.J.G. and GOLDSTEIN, S.L. (1996): Influence of accretion on lead in the Earth: in BASU, A. and HART, S.R. (eds): *Earth Processes – reading the isotopic code*. A.G.U. Geophys. Monograph 95, 75–98.
- HALLIDAY, A., REHKÄMPFER, M., LEE, D.C. and YI, W. (1996): Early evolution of the Earth and Moon: new constraints from Hf–W isotope geochemistry. *Earth Planet. Sci. Lett.*, 142, 75–89.
- HARLEY, S.L. (1989): The origins of granulites: a metamorphic perspective. *Geol. Mag.*, 126, 215–247.
- HEIMSATH, A.M., DIETRICH, W.E., NISHIZUMI, K. and FINKEL, R.C. (1997): The soil production function and landscape equilibrium. *Nature*, 388, 358–361.
- KASTING, J.F. (1993): Earth's early atmosphere. *Science*, 259, 920–926.
- KRAMERS, J.D. (1998): Reconciling siderophile element data in the Earth and Moon, W isotopes and the upper lunar age limit in a simple model of homogeneous accretion. *Chem. Geol.*, in press.
- KRAMERS, J.D. and TOLSTIKHIN, I.N. (1997): Two major terrestrial Pb isotope paradoxes, forward transport modelling, core formation and the history of the continental crust. *Chem. Geol.*, 139, 75–110.
- MOORBATH, S., WHITEHOUSE, M.J. and KAMBER, B.S. (1997): Extreme Nd-isotope heterogeneity in the early Archean – fact or fiction? Case histories from northern Canada and West Greenland. *Chem. Geol.*, 135, 213–231.
- NÄGLER, TH.F. and KRAMERS, J.D. (1998): Nd isotopic evolution of the upper mantle during the Precambrian: Models, data and the uncertainty of both. *Prec. Res.*, in press.
- OHMOTO, H. (1996): Evidence in pre-2.2 Ga palaeosols for the early evolution of atmospheric oxygen and terrestrial biota. *Geology*, 24, 1135–1138.
- O'NIONS, R.K. and MCKENZIE, D. (1993): Estimates of mantle thorium/uranium ratios from Th, U and Pb isotope abundances in basaltic melts. *Phil. Trans. R. Soc. Lond.*, A 342, 65–77.
- PATCHETT, P.J., WHITE, W.M., FELDMANN, H., KIELINCZUK, S. and HOFMANN, A.W. (1984): Hafnium/rare earth element fractionation in the sedimentary system and crustal recycling into the Earth's Mantle. *Earth Planet. Sci. Lett.*, 69, 365–378.
- REYMER, A. and SCHUBERT, G. (1984): Phanerozoic addition rates to the continental crust and crustal growth. *Tectonics*, 3, 63–70.
- ROBERT, M. and BERTHELIN, J. (1986): Role of biological and biochemical factors in soil mineral weathering. In HUANG and SCHNITZER (eds): *Interactions of soil minerals with natural organics and microbes*. SSSA spec. Publ. No. 17, Soil Science Society of America, Madison, Wisconsin, 453–495.
- SANDIFORD, M. (1989): Secular trends in the thermal evolution of metamorphic terrains: *Earth Planet. Sci. Lett.*, 95: 85–96.
- SMALL, E.E., ANDERSON, R.S., REPKA, J.L. and FINKEL, R. (1997): Erosion rates of alpine bedrock summit surfaces deduced from in situ ¹⁰Be and ²⁶Al: *Earth Planet. Sci. Lett.*, 150, 413–425.
- STAUDIGEL, H., DAVIES, G.R., HART, S.R., MARCHANT, K.M. and SMITH, B.M. (1995): Large scale isotopic Sr, Nd and O isotopic anatomy of altered oceanic crust: DSDP/ODP sites 417/418. *Earth Planet. Sci. Lett.*, 130, 169–185.
- TAYLOR and McLENNAN (1995): The geochemical evolution of the continental crust. *Rev. Geophys.*, 33, 241–265.
- WATANABE, Y., NARAOKA, H., WRONKIEWICZ, D.J., CONDIE, K. and OHMOTO, H. (1997): Carbon, nitrogen, and sulphur geochemistry of Archean and Proterozoic shales from the Kaapvaal Craton, South Africa. *Geochim. Cosmochim. Acta*, 61, 3441–3459.
- WEDEPOHL, K.H. (1995): The composition of the continental crust. *Geochim. Cosmochim. Acta*, 59, 1217–1232.

Received December 22, 1997; revision accepted January 13, 1998.