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Global modelling of continent formation and destruction through geological time and implications for CO_2 drawdown in the Archaean Eon

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Abstract: The possible drawdown of a massive CO_2 atmosphere in early Earth history is discussed using two working hypotheses: first, that this removal of CO_2 from the atmosphere occurred mainly via silicate weathering; second, that crust-to-mantle recycling rates found from forward modelling of crust–mantle history can be used to estimate rates of this ancient silicate weathering. Previous U–Th–Pb and Sm–Nd forward modelling efforts are reviewed, from which it was concluded that an insignificant amount of continental crust existed at 4.4 Ga, i.e. so-called 'no-growth models' for the continental crust appear untenable. New modelling carried out is based on a crustal growth curve starting with zero mass at 4.2 Ga and reaching 75% of the present crust mass by 2 Ga. It concerns variations in crust-to-mantle recycling rates through geological time. Best fits to isotope data are obtained if it is assumed that erosion rates (mass removal per unit surface) were approximately constant from early Archaean time to the present. From the results it can be estimated that drawdown of a massive CO_2 atmosphere by silicate weathering could have been completed by the end of Archaean time at the earliest, and about 1.5 Ga ago at the latest.

Silicate weathering on land surfaces was first suggested and studied by Ebelmen in 1845 (see Berner & Maasch 1996) as a mechanism that could have removed CO_2 from the atmosphere. Its importance as a major control on atmospheric CO_2 levels was highlighted by Urey (1952). Its effectiveness in lowering atmospheric CO_2 levels has been demonstrated by Berner *et al.* (1983) and Berner (1991) for Phanerozoic time and it is essential in models linking climate change to uplift of mountain belts (Raymo & Ruddiman 1992). The combined carbonate and organogenic carbon in sediments and metasediments amounts to at least 3.6×10^{21} moles (Ronov & Yaroshevskiy 1968; Wedepohl 1995). If all present as CO_2 this would form a *c.* 30 bar atmosphere, and there can be no doubt that all this carbon was once in the atmo-hydrosphere, although not necessarily all at the same time or all in the form of CO_2. This has important implications for the climate of the early Earth: Kasting & Ackermann (1986) found from 1D radiative–convective modelling that a dense (10–20 bar) CO_2 atmosphere in very early Archaean time could have produced a greenhouse effect that offset the 30% fainter solar irradiation at that time and prevented a wholly frozen Earth. However, Rye *et al.* (1995) concluded from mineralogical observations on palaeosols and
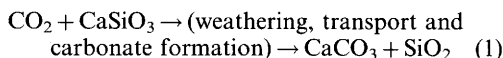
thermodynamic data that the partial pressure of CO_2 in the atmosphere between 2.5 and 2.2 Ga was less than *c.* 0.04 bar. They noted that CH_4 is also an effective greenhouse gas, and may have been abundant in the Archaean atmosphere. Alternatively, CO_2 that had made up a dense atmosphere in early Archaean time could already have been bound by silicate weathering at 2.5 Ga. Evidence of glaciation in the *c.* 2.9 Ga Mozaan Group, South Africa (Young *et al.* 1998) and in the early Proterozoic Huronian Supergroup, Canada (Nesbitt & Young, 1982) supports the latter view.

Thus estimates of weathering and erosion rates in Archaean time have a bearing on questions of the early evolution of the atmosphere and the climate of the young Earth. To make use of this connection to constrain early CO_2 drawdown potential, it must first be ascertained that chemical weathering was important in Archaean time. Then, Archaean weathering rates should somehow be estimated. This paper therefore consists of two parts. First, CO_2 drawdown is viewed in relation to continental weathering with specific reference to Archaean time. This leads to a minimum estimate for the amount of weathering and erosion needed to remove a *c.* 30 bar atmosphere. Second, an attempt is made to constrain erosion rates in Archaean time via forward global models

of continental crust growth and recycling, which correctly predict present-day Th–U–Pb and Sm–Nd isotope systematics of major terrestrial reservoirs (Kramers & Tolstikhin 1997; Nägler & Kramers 1998). In such modelling, rates of recycling continental crust into the mantle are critical. If the assumption is made that this recycling is a measure of erosion, and that erosion in turn is a measure of chemical weathering, the results of modelling allow us to place constraints on the potential for early CO_2 drawdown.

CO_2 drawdown and chemical weathering

Weathering of silicates occurs through many different hydrolysis reactions whereby CO_2 is converted to HCO_3^- ions and Si is either bound in alteration minerals or liberated as H_4SiO_4. Alkali and alkaline earth elements are progressively removed in solution. Of these, Ca and Mg are largely ultimately bound in carbonate, so that the whole process can be summarized in a generic way by the 'Urey reaction'

$$CO_2 + CaSiO_3 \rightarrow (\text{weathering, transport and} \\ \text{carbonate formation}) \rightarrow CaCO_3 + SiO_2 \quad (1)$$

(and analogously for Mg). The silicate weathering + carbonate precipitation process thus removes 1 mole of CO_2 out of the atmosphere per mole of Ca or Mg leached from a weathering silicate rock. A mass balance of organogenic and carbonate carbon in sediments can be made on the basis of their $\delta^{13}C$ values compared with that of juvenile emanations from the mantle (Schidlowski 1988). These data suggest that a mass ratio of carbonate to organogenic carbon of approximately $4:1$ has prevailed since about 3.5 Ga ago. As strong C isotope fractionation is a particular characteristic of photosynthesis, it is not possible that the mass balance merely reflects global redox balances. Thus silicate weathering has through geological time drawn down four times more CO_2 than photosynthesis. CO_2 is also bound by carbonate dissolution, but is then released again during the crystallization of new carbonate:

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2\,HCO_3^- \quad (2)$$
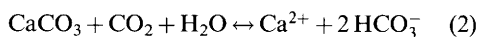
Therefore carbonate weathering and subsequent formation of new limestone cause no net removal of CO_2 and have, from the perspective of geological time, a transient effect on atmospheric CO_2 only.

The amount of carbonate rocks present on Earth is thus related to the release of cations by chemical silicate weathering over geological time. In the present-day world, silicate weathering

reactions are much enhanced by soil CO_2 partial pressures 10–100 times greater than atmospheric levels, and the presence of humic acids in soils, both of which are due to land plants and associated soil biota (Lovelock & Whitfield 1982; Schwartzman & Volk 1989; Berner 1997). In Archaean time, land vegetation was absent, and correspondingly larger inherent atmospheric concentrations of CO_2 were required for chemical weathering.

Present-day CO_2 drawdown rates can be estimated from the dissolved Ca^{2+} and Mg^{2+} load in rivers (Berner et al. 1983; Gaillardet et al. 1999). For estimating potential rates in the geological past, the counterpart of this dissolved load, i.e. Ca- and Mg-depleted palaeosols and clastic sediments, can be used. Evidence that intense chemical weathering occurred in Archaean and early Proterozoic time is provided by marked depletions in Na, K and Ca in palaeosols when compared with the corresponding unaltered rock (Rainbird et al. 1990), and also in Archaean shales and metapelites compared with average upper continental crust (e.g. Nesbitt & Young 1982; Fedo et al. 1996; Kreissig et al. 2000). In these studies, the immobile trace and major element geochemistry of the metasediments indicates provenance from ordinary Archaean granitoid crust, so that the mobile element depletion can be attributed with some confidence to chemical weathering in the source area. The amount of depletion in mobile elements in palaeosols or pelitic sediments is often expressed by the Chemical Index of Alteration (CIA, Nesbitt & Young 1982):

$$CIA = 100 \times Al_2O_3/(Al_2O_3 + CaO^* \\ + Na_2O + K_2O) \quad (3)$$

where

$$CaO^* = CaO_{(total)} - CaO_{(phosphates)} \\ - CaO_{(carbonates)}.$$

Fresh granitoid rocks have CIA values between 45 and 55. Average Mesozoic to recent shale values are between 70 and 75 (Nesbitt & Young 1982), and Archaean and Proterozoic shales and metapelites have values ranging from about 70 to an extreme of 99 for some shales from the Buhwa Greenstone Belt, Zimbabwe (Fedo et al. 1996). Losses of Ca and Na are mostly approximately equal, whereas K loss may be difficult to assess because of later metasomatism (Fedo et al. 1995). Mg depletion does not enter the CIA value. From metapelite geochemistry it is more difficult to quantify than K loss, because it is highly sensitive to the mafic rock content of the source area, and may also be enriched during

diagenetic metasomatism. Nevertheless, Mg is mobile in weathering, as well as being an important constituent of sedimentary carbonates, particularly in Precambrian time. Therefore it will be assumed below that Mg and Ca are released in proportion to their concentrations in chemical weathering of 'average upper continental crust'.

The upper continental crust contains close to 3% Ca and 1.4% Mg (Taylor & McLennan 1995; Wedepohl 1995). If mobilization of Ca and Mg is proportional, then the observed range of CIA values corresponds to a loss of between 1.5 and 3% Ca and between 0.7 and 1.4% Mg. This corresponds to between 650 and 1300 moles of Mg + Ca lost per tonne of rock weathered. Therefore between 650 and 1300 moles CO$_2$ would ultimately be bound as carbonate per tonne of average crustal silicate rock weathered. The total mass of carbon occurring as carbonate in sediments and metasediments is reliably estimated at 3.5×10^{22} g, or 2.91×10^{21} moles (Ronov & Yaroshevskiy 1968; Wedepohl 1995). Drawing this out of the atmosphere would thus have required chemical weathering of between 2.2×10^{18} and 4.5×10^{18} tonnes of upper-crustal silicate rock, i.e. between 10 and 21% of the present-day mass of the continental crust (2.1×10^{19} tonnes, Taylor & McLennan, 1995). Shales and metapelites, i.e. residua of chemical weathering, constitute at present $c.$ 4% of the continental crust (Ronov & Yaroshevskiy 1968; Wedepohl 1995). The difference is thus between 6 and 17% of the present continental crust mass. From a first-order estimate, this is the amount of such sediments that should have been recycled into the mantle over geological history to account for the present mass of carbonate in sedimentary rocks. This is a pure mass balance reckoning, which is not affected by consideration on the age distribution of sediments (e.g. Veizer & Jansen 1985).

There are, however, two main reasons why this must be a minimum estimate of the amount of sediment recycled into the mantle over geological time. These are, first, reintroduction of CO$_2$ into the atmosphere via arc volcanism, and second, the fact that purely clastic sediments are ignored in this mass balance. CO$_2$ is reintroduced into the atmosphere as a result of decarbonation reactions in calc-silicate rocks (the reverse 'Urey reaction'), requiring further weathering and photosynthesis to remove it. Fluxes associated with these processes over Phanerozoic time have been reviewed by Berner *et al.* (1983) and Berner (1991), who concluded that such addition of CO$_2$ by (mainly arc) volcanism and its drawdown by silicate weathering have been the major long-term fluxes over this period, and that drawdown has only slightly outstripped

supply. In other words, crust-to-mantle recycling that took place since early Phanerozoic time did not contribute significantly to net CO$_2$ drawdown, but merely helped to maintain a quasi steady state. Concerning the second reason, a significant portion of sediments recycled into the mantle over time was probably produced by mechanical erosion: greywackes are an abundant rock type throughout the geological record, and are often not strongly depleted in Ca and Mg relative to their source rocks.

Therefore it can be concluded that the total mass of sediment that must have been recycled into the mantle over geological time to account for CO$_2$ removal from the atmosphere is >6–17% of the present continental mass. Drawdown of most CO$_2$ before 2.5 Ga, as indicated by the Huronian glaciation (Nesbitt & Young 1982; Kasting 1993) indicates vast amounts of chemical weathering before that time. This cannot *a priori* be equated with sediment recycling into the mantle. However, Veizer & Jansen (1979, 1985) and McLennan (1988) have noted a comparative rarity of very ancient sediments and have shown that Archaean clastic sediments are mainly juvenile, i.e. they have model Nd 'crust formation' ages close to their depositional ages. This means, first, that young terrains were being weathered and eroded, and second, that little redeposition of sediments ('cannibalistic recycling') took place in Archaean time. Combined, these observations point to significant sediment recycling into the mantle before $c.$ 2.5 Ga. Below, the possibility of such Archaean recycling is considered from the global modelling point of view.

Models of crustal growth and recycling

Existing models of continental crust growth and recycling offer a perspective on the potential for CO$_2$ drawdown through geological time. There is a vast number of such models, reviewed, for example, by Reymer & Schubert (1984) and Taylor & McLennan (1995). They range from models that are based strictly on the age distribution of continental rocks observed today and thus imply minimal recycling or none at all (Hurley & Rand 1969; Condie 1990), to 'no-growth' models such as first put forward by Armstrong (1981) based on the principle that continental freeboard should have remained constant through geological time. In such models it is postulated that an amount of continental crust similar to that observed today was generated very early in Earth history (typically, in the first 500 Ma or less) and that since then, newly formed crust replaced old crust recycled into the mantle.

Although the 'no recycling' models appear incompatible with the above requirements for early CO_2 drawdown, the 'no growth' models require a very large amount of continental crust recycling to reproduce the observed crustal age distribution, and thus offer a huge excess capacity for CO_2 drawdown, probably allowing low atmospheric CO_2 levels to be attained in early Archaean time. This range of models thus has important consequences for the development of the Earth's early atmosphere and climate, and needs to be evaluated. One approach to do this has been a search for depleted mantle isotope signatures in the Archaean time, and another has been forward transport balance modelling.

The first approach was based on the observed complementarity with respect to Sm/Nd ratios of continental crust and depleted mantle. With time, the latter reservoir develops radiogenic $^{143}Nd/^{144}Nd$ ratios relative to the undifferentiated Chondritic Uniform Reservoir (CHUR; see Jacobsen & Wasserburg 1984), i.e. positive ε_{Nd} values, where $\varepsilon_{Nd} = [(^{143}Nd/^{144}Nd_{sample})/(^{143}Nd/^{144}Nd_{CHUR})-1] \times 10^4$. Positive initial ε_{Nd} values in ancient crustal provinces constitute evidence that a significant mass of continental crust existed before these ancient provinces were formed. Initial ε_{Nd} values were obtained on $c.\,3.7\,Ga$ rock suites from West Greenland (Bennett *et al.* 1993) and the $c.\,4\,Ga$ Acasta Gneisses from Northern Canada (Bowring & Housh 1995) by correcting measured Nd isotope ratios back using zircon U–Pb ages from the same rocks. The results showed large apparent initial ε_{Nd} variations with values up to four which were interpreted by Bowring & Housh (1995) as evidence that large amounts of crust had developed before $4\,Ga$, thus supporting no-growth models for the continental crust. The possibility that so large an amount of crust was formed very early was argued by Reymer & Schubert (1984) as follows. The melt fluxes required to form the core, and gravitation potential energy released, would be sufficient to generate the present amount of continental crust in $100\,Ma$ or less. After accretion and core formation had ceased, residual and radiogenic heat would support a much lower rate of melting in the mantle. However, the approach used by Bowring & Housh (1995) has been criticized by Moorbath *et al.* (1997). They showed that correlations of $^{143}Nd/^{144}Nd$ with $^{147}Sm/^{144}Nd$ in the ancient rock suites yield apparent ages much younger than those obtained from zircons (e.g. $3.4\,Ga$ in the case of the $4\,Ga$ Acasta Gneisses), indicating later resetting of Sm–Nd systematics. The apparent variations in initial ε_{Nd} values were reinterpreted by them as mere effects of this

resetting, which should therefore not be used as evidence for the pre-existence of continental crust. The debate about this is still continuing. Further, efforts to find Hf isotope effects in zircons from ancient sediments to substantiate the apparent source ε_{Nd} heterogeneity (Amelin *et al.* 1999) have been unsuccessful.

Transport balance or box models have been used by many workers in the past in efforts to understand the trace element and isotope characteristics of the Earth's major silicate reservoirs, i.e. continental crust, and upper and lower mantle (e.g. Jacobsen & Wasserburg 1979; Zartman & Haines 1988). Although simple mass balance calculations can be applied to present-day trace element concentrations and Pb, Nd and Hf isotope compositions of major reservoirs, e.g. continental crust and depleted mantle, to test the hypothesis that these reservoirs are complementary, transport balance models are needed to test ideas on their evolution in time. The reason is that the isotope ratio variations are the result of time-integrated trace element variations in the reservoir, modified by fluxes between them. Below, recent transport balance models in which the evolution of the continental crust is examined using Th–U–Pb (Kramers & Tolstikhin 1997) and
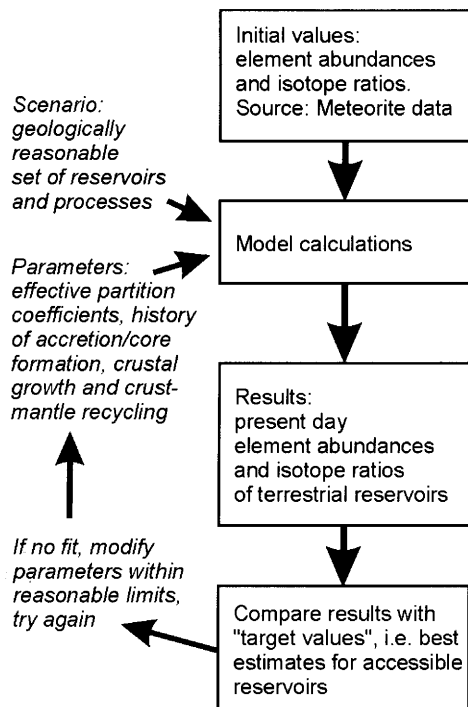

Fig. 1. Principle of forward transport balance modelling used.

Sm–Nd systematics (Nägler & Kramers 1998) are reviewed and then developed further.

Principles and methods of transport balance models; previous work

The principle of the procedure used in the work reviewed and the present study is illustrated in Figure 1. Target values of the modelling are present-day Pb and Nd isotope ratios as well as Th, U, Pb, Sm and Nd concentrations of the depleted mantle, as derived from mid-ocean ridge basalt (MORB) data (Blichert-Toft & Albarède 1994), and of the upper continental crust, for which pelagic sediments, atmospheric dust and river sediments are proxies (Goldstein *et al.* 1984; Ben Othman *et al.* 1989). Important sets of target values are summarized in Table 1b. The models include an accretion–core formation stage and therefore chondritic element abundance data are used as a starting point (Table 1a). Forward modelling also allows us to exclude scenarios that do not satisfy other constraints, e.g. accretion–core formation scenarios used were restricted to those that satisfied constraints from siderophile element abundances and Hf–W isotope systematics (Lee & Halliday 1996; Kramers 1998).

Th–U–Pb systematics and Sm–Nd systematics address in part different aspects of Earth differentiation. First, Th/Pb and U/Pb ratios are affected by core formation, whereas the Sm/Nd ratio is not. Second, in the silicate Earth Th/Pb

Table 1. *Input parameters and target values used in modelling*
(a) Input parameters and masses of reservoirs

Parameters, dimensions	Value
Initial reservoir: proto-terrestrial material	
Initial Th (ppm)	0.0607
Initial atomic $^{235}U/^{238}U$	0.31628
Initial atomic $^{232}Th/^{238}U$	2.4115
Initial atomic $^{238}U/^{204}Pb$	3.7628
$^{206}Pb/^{204}Pb$	9.308
$^{207}Pb/^{204}Pb$	10.294
$^{208}Pb/^{204}Pb$	29.440
Nd (ppm)	0.6
Initial $^{143}Nd/^{144}Nd$ ratio	0.506753
Initial atomic $^{147}Sm/^{144}Nd$ ratio	0.20264
Decay constants (Ga^{-1})	
$\lambda(^{238}U)$	0.155125
$\lambda(^{235}U)$	0.98485
$\lambda(^{232}Th)$	0.049475
$\lambda(^{147}Sm)$	0.00654
Masses of present-day reservoirs, 10^{25} g	
Continental crust	2.09
Depleted mantle	130

(b) Target values

Parameters	Depleted mantle	Upper continental crust (ucc)	Recent sediments; proxy for ucc
Th ppm	0.019 ± 0.004	10.5 ± 0.5	
U ppm	0.007 ± 0.002	2.6 ± 0.3	
$^{232}Th/^{238}U$	2.62 ± 0.14		
Pb ppm	0.05 ± 0.15	19 ± 2	
$^{206}Pb/^{204}Pb$	18.46 ± 0.41		18.80 ± 0.24
$^{207}Pb/^{204}Pb$	15.49 ± 0.04		15.64 ± 0.06
$^{208}Pb/^{204}Pb$	38.02 ± 0.37		38.68 ± 0.3
Sm ppm	0.28 ± 0.06	4.6 ± 0.1	
Nd ppm	0.77 ± 0.15	26 ± 2	
$^{147}Sm/^{144}Nd$	0.22 ± 0.02	0.107 ± 0.009	
ε_{Nd}	10.5 ± 0.5		-11.4 ± 4

See Kramers & Tolstikhin (1997) and Nägler & Kramers (1998) for a discussion and sources.

and U/Pb fractionation occurs in intracrustal processes rather than crust formation, because all three elements are so incompatible in mantle melting that their element ratios in the crust are *a priori* not very different from those in the mantle source. In contrast, Sm/Nd is strongly fractionated in mantle melting and thus in crust formation, and much less in intracrustal processes. The two sets of systematics have in common that parent and daughter species are both incompatible, strongly enriched in the continental crust and therefore Pb and Nd isotope ratios in the depleted mantle are highly sensitive to crust–mantle recycling.

The set of reservoirs used in the previous and present work is shown in Figure 2. Between reservoirs mass fluxes operate, to which concentrations of trace elements are assigned that can differ from the concentration in the 'source' of the flux depending on magmatic fractionation or weathering processes. Although the number of

reservoirs must be kept to a minimum to limit the number of free parameters in the model, the division of the continental crust reservoir into four subreservoirs (younger and older as well as upper and lower) is needed to portray age heterogeneity of the continental crust as well as chemical heterogeneity. The mass of each of these four subreservoirs is kept at one-quarter of the (variable) mass of the total continental crust. Whereas upper–lower crustal differences are brought about by magmatic fractionation, the distinct character of the older and younger crust reservoirs results from two factors. First, any continental crust newly produced is mixed into the younger part of the crust, and an equalizing flux transfers mass and trace species from the younger to the older reservoir to keep their masses equal. Second, an 'erosion law' (Allègre & Rousseau 1984; Jacobsen 1988) operates whenever continental mass is recycled by erosion: erosion rates for the subreservoir labelled 'old
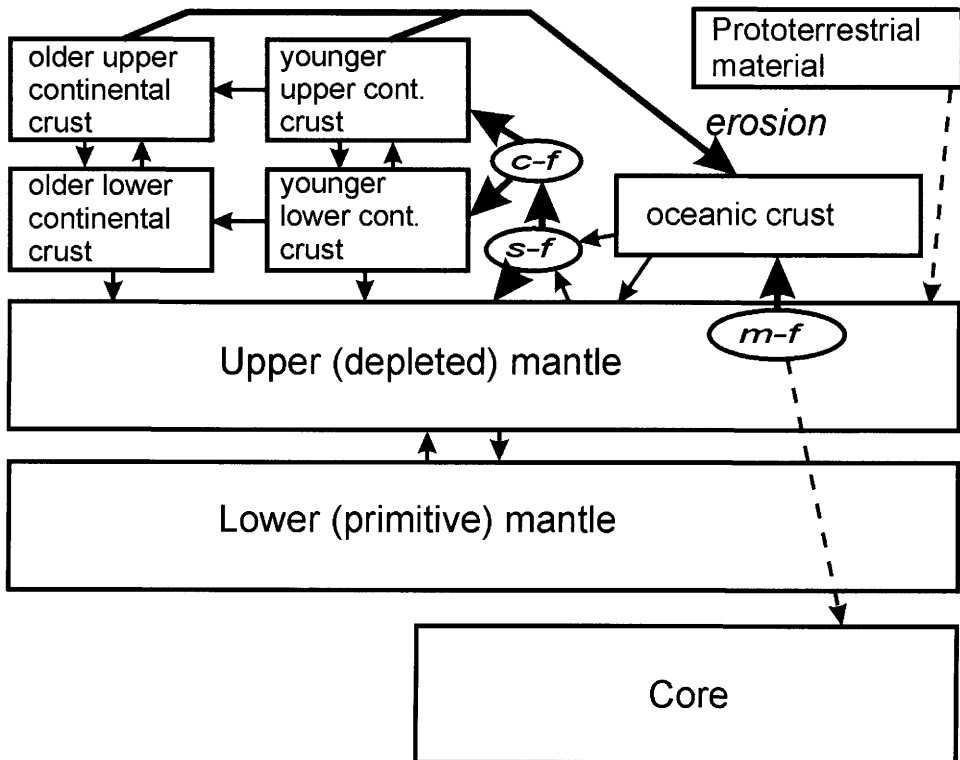

Fig. 2. Reservoirs and fluxes used in previous and present modelling work (not to scale). Rectangles used for reservoirs; ellipses for loci of fractionation by melt processes. *m-f*, depleted mantle melting, oceanic crust (MORB) formation; *s-f*, subduction zone melting leading to continental crust formation; *c-f*, intracrustal fractionation leading to upper and lower crust formation. Bold arrows, fluxes involving trace element fractionation; fine arrows: fluxes without trace element fractionation; stippled arrows, fluxes operating only during accretion and core formation.

upper crust' are set lower than those for that labelled 'young upper crust'. The erosion law factor K describes the disproportionality. If the amounts of older and younger crust are equal, then

$$K = \Phi_{erosion}(young)/\Phi_{erosion}(old) \qquad (4)$$
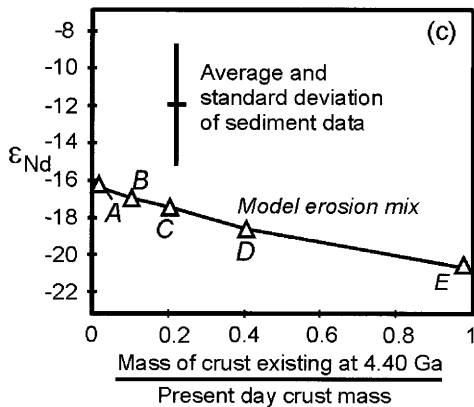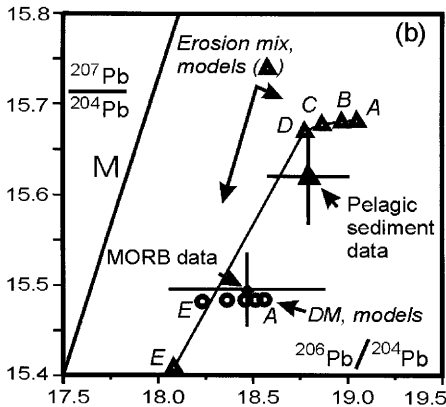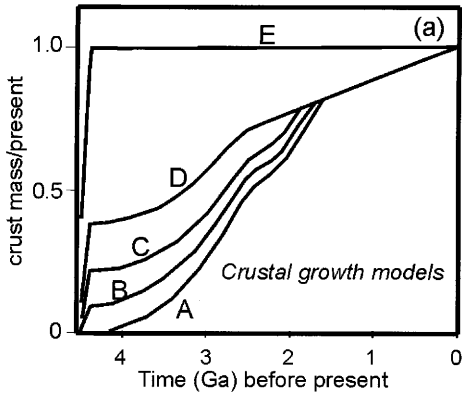
where $\Phi_{erosion}$ is the erosion mass flux. In forward modelling the application of this erosion law becomes a self-fulfilling prophecy, as the residence time of mass and species in the reservoir labelled 'older' becomes greater than that in the part labelled 'younger' because of the smaller fluxes into and out of the 'older' part. The division into younger and older crust thus exists throughout Earth history, and is alway relative. Erosion affects the upper crust and as it proceeds, fluxes are needed to transfer mass and trace species from the 'lower' to the 'upper' crust to keep their masses equal. Apart from erosion, destruction of continent can also occur by delamination of the lower crust, a process to which a 'delamination law' analogous to the erosion law can apply. Equations for the derivation of the mass fluxes between the reservoirs and their associated trace species fluxes have been given by Kramers & Tolstikhin (1997) and Nägler & Kramers (1998).

In both Th–U–Pb and Sm–Nd global modelling as outlined above, the crustal growth history has turned out to be a critical parameter set for producing fits to target values. With a given present-day age distribution for the continental crust that corresponds closely to that of Taylor & McLennan (1995), the main parameter varied by Kramers & Tolstikhin (1997) and Nägler & Kramers (1998) was the amount of crust generated during accretion and core formation, and surviving after those turbulent processes.

Fig. 3. Some results of previous modelling. (a) Crustal growth scenarios used (curves give crust mass existing at times in the past relative to present-day continental crust mass of 2.1×10^{15} g (Taylor & McLennan 1995). (b) $^{207}Pb/^{204}Pb$ v. $^{206}Pb/^{204}Pb$ plot showing modelling results for the depleted mantle (○) and average sediments (erosion mix) from the continental crust (△) for these scenarios, compared with data averages and standard deviations for MORB (proxy for depleted mantle) and for pelagic sediments (proxy for eroded continental crust). Data are from multiple sources quoted by Kramers & Tolstikhin (1997; see this reference also for details of modelling methods). M, 'Meteoritic' 4.55 Ga Pb/Pb isochron, drawn in for reference. Clearly no fit is achieved at all for the no-growth scenario E. (c) ε_{Nd} value of model erosion mix for these scenarios shown dependent on same parameter (Nägler & Kramers 1998), compared with data on recent sediments (Goldstein *et al.* 1984). In A, B, C and D models are forced to produce ε_{Nd} values of 10.5 ± 1 for the depleted mantle (Blichert-Toft & Albarède 1994), whereas in scenario E this value for the mantle could not be reached. In all this modelling $K = 2$ was used. Fits for ε_{Nd} in scenarios A, B and C (but not D and E) improve if $K = 3$. It should be noted that scenario A (no continental crust present at 4.4 Ga) gives the best fit to data in both cases.

Some results of these tests are summarized in Figure 3. From Figure 3b it is clear that no Pb isotope fit to pelagic sediment data is possible with a no-growth model (E in Fig. 3a). Figure 3c shows that fits for the erosion mix from the crust become progressively better as the amount of continental crust present at the end of the accretion and core formation period (c. 150 Ma after chondrite formation; 4.4 Ga ago) is reduced (models D, C, B and A). Both sets of results can be explained via the large amount of crust-to-mantle recycling needed in no-growth models or similar scenarios. Regarding Pb isotopes, the upper crust has a high U/Pb ratio, and has developed a radiogenic Pb signature whereby the $^{207}Pb/^{204}Pb$ ratio became particularly enhanced in early Earth history when ^{235}U was still abundant. This causes the observed Pb isotope difference between upper continental crust and depleted mantle. The explanation for the misfit of Pb isotope data in no-growth models is that the excessive crust-to-mantle recycling inherent in them brings large amounts of radiogenic Pb from the upper crust into the mantle, and therefore no Pb isotope difference similar to the observed one is predicted. With regard to Nd isotopes, in no-growth models large amounts of unradiogenic Nd from the crust are introduced into the mantle over time, so that the present-day ε_{Nd} value of the depleted mantle is only about three (Nägler & Kramers 1998) instead of the observed present-day value of around 10.5 (Blichert-Toft & Albarède 1994). This lower ε_{Nd} value for the mantle causes also the younger crust to have a lower average ε_{Nd} value, leading to the observed misfit.

Although the Pb isotope ratios on their own seem to allow scenarios B, C and D the fit for another parameter, the Th/U ratio of the mantle, worsens dramatically from scenario A to D (Kramers & Tolstikhin 1997). The conclusion, reached independently from Th–U–Pb and Sm–Nd modelling, was that only insignificant amounts of crust could have survived from the time of Earth accretion to become incorporated into the growing continental crust. This does not mean that no protocontinental crust could have been generated during Earth accretion and core formation (see Wilde *et al.* 2001) but this should have been destroyed rapidly in terms of geological time. Further, good fits for both Th–U–Pb and Sm–Nd systematics have resulted from models in which the average net growth of continental crust before 2 Ga was about twice that prevailing afterwards, so that the mass of crust in existence at 2 Ga was about 70% of present mass.

These main results of previous forward global modelling are in broad agreement with the estimate of continental growth by Taylor & McLennan (1995) and also with the mass balance obtained from Th/Nb ratios of mantle–derived volcanic rocks through time (Collerson & Kamber 1999). Further, if the lower crust is considered to be characterized by low Th/Pb and U/Pb ratios and unradiogenic Pb, a further result from the modelling to date is that crust destruction by lower-crustal delamination is insignificant compared with erosion of the upper crust. This result stems from the relatively radiogenic average Pb isotope composition of the upper mantle, and is fairly robust (Kramers & Tolstikhin 1997). Essentially, crust–mantle recycling thus depends on surface erosion. However, weathering and erosion rates (and therefore
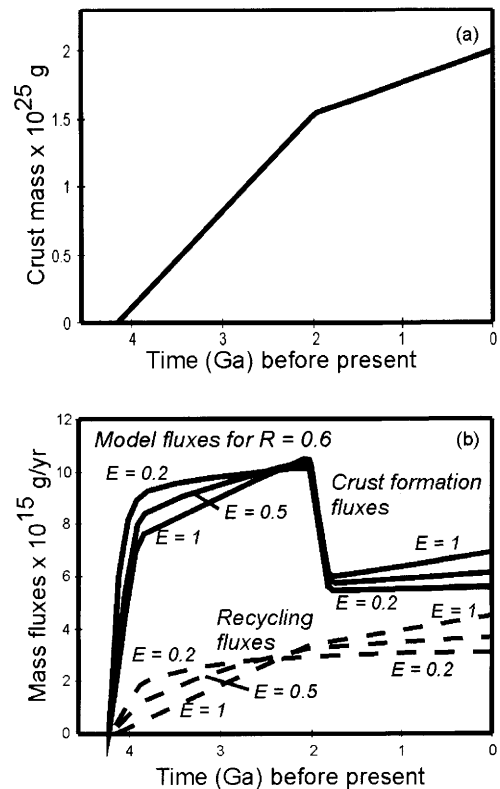

Fig. 4. (a) Crust mass v. time curve used in the present study, a simplified version of curve A in Figure 3a. (b) Bulk mass fluxes in and out of continental crust over time for three values of the geometrical parameter E and for $R = 0.6$ (see text). Continuous lines, fluxes into continental crust; dashed lines, fluxes out of continental crust. Pairs of curves for each value of E balance out to the crust mass v. time curve in (a).

potential CO$_2$ drawdown) in Archaean time cannot be assessed from net crust mass v. time curves alone: any curve giving the mass of crust in existence at any time in the past allows an infinite number of crust formation and crust destruction scenarios, whereby larger rates of crust formation can be compensated by larger rates of erosion to produce the same net crust mass v. time curve, as illustrated in Figure 4. Whereas the previous forward global modelling discussed above (Kramers & Tolstikhin 1997; Nägler & Kramers 1998) has examined the effect of varying very early continental crust mass, various scenarios of crustal growth and recycling rates based on a single crust mass v. time curve (Fig. 4a) are studied in the following section.

Variations on a theme: a single crust mass v. time curve

The single crust mass v. time curve in Figure 4a results from best fits of previous work (see Fig. 3), and the modelling described below explores different combinations of rates of crust formation and recycling, which all balance to this same net curve. To limit the number of unconstrained variables, the assumption is made that recycling is through erosion, with no lower-crustal delamination, as indicated by previous modelling. Two parameters, R and E (explained below), are introduced which, together with the erosion law factor K (see equation (4)), define crustal growth and recycling scenarios based on the curve of Figure 4a.

First, the total amount of crust-to-mantle recycling is defined by R, the time-integrated recycling mass flux over Earth history expressed as a fraction of present-day crust mass:

$$R = \frac{\int_{t=-4.55}^{\text{today}} \Phi_{\text{recycling}} \, dt}{M_{\text{crust}}(\text{today})}. \quad (5)$$

Second, it is assumed that the recycling mass flux and its ancillary trace species fluxes are at any time dependent on the amount of crust in existence at that time. This dependence can take the form of various functions, and a variable geometry parameter E is introduced, which describes the crust to mantle recycling flux $\Phi(t)_{\text{recycling}}$ as a function of crust mass in existence.

$$\Phi(t)_{\text{recycling}} = f M_{\text{crust}}(t)^E \quad (6)$$

where f is a constant proportionality factor with dimension mass$^{(1-E)}$time^{-1}. Its value is calculated for given values of R and E by integrating the flux over time (equation (5)) and adjusting.

The meaning of E is illustrated by the following examples. (1) If it is assumed that, through Earth history, the worldwide crust recycling flux is proportional to the land surface, and the thickness of continental crust is constant, then recycling is also at any time directly proportional to the crust mass in existence. In this case, $E = 1$. (2) If the assumption is that erosion takes place predominantly at continental margins, then the recycling flux is proportional to the length of these margins. If a smaller amount of continental mass in the geological past implies a larger margin to surface (or margin to mass) ratio, then the worldwide recycling flux through time would more probably be proportional to the square root of the continental mass: thus $E = 0.5$. Further, as total crust mass increases with time, $E < 1$ means more intense erosion in early Earth history, and $E > 1$ the opposite. Figure 4b illustrates the variation of bulk mass fluxes into and out of the continental crust as a function of E for the crust mass v. time curve used in this study.

For any given crust mass v. time curve, the two parameters R and E determine the bulk crust formation and the crust recycling (erosion) fluxes through time, as

$$\Phi_{\text{crust formation}}(t) - \Phi_{\text{recycling}}(t) = \frac{dM_{\text{crust}}}{dt}(t). \quad (7)$$

Further, the erosion law factor K, defined in equation (4), regulates the age distribution of eroded material relative to the age structure of the crust. Thus for a given crust mass v. time curve, the three parameters E, R and K fully describe the crust formation and erosion history. In the present modelling E was varied between 0.2 and 1, R from 0.3 to 0.7, and K from 1.5 to 3.5. The approach used and the effective partition coefficients, as well as initial (meteoritic) concentrations of the trace species are the same as those used by Kramers & Tolstikhin (1997) and Nägler & Kramers (1998).

The results of numerical modelling with the above range of parameter variations are summarized in Figures 5 and 6 and Table 2. Sm and Nd concentrations of the model reservoirs closely approximate target values (Table 1a). The same is true for Th, U and Pb concentrations in the depleted mantle. Model Th and U concentrations for the upper continental crust are somewhat low, and those for Pb are significantly lower than observed values. This problem, also encountered by Kramers & Tolstikhin (1997), may not be real, as the upper-crust Pb concentration estimates of Taylor & McLennan (1995) and Wedepohl (1995) are too high to be consistent with the average ^{238}U/^{204}Pb ratios of c. 10
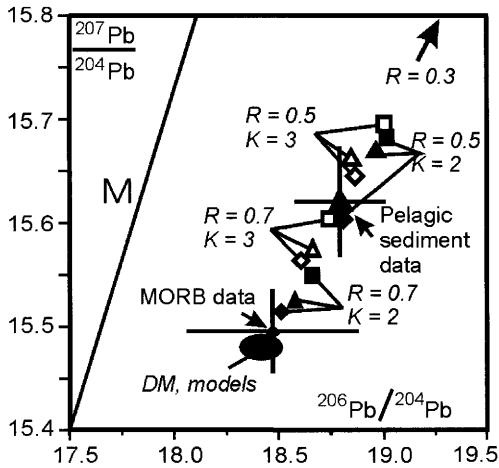
Fig. 5. Pb isotope results of present modelling compared with MORB and pelagic sediment data in $^{207}Pb/^{204}Pb$ v. $^{206}Pb/^{204}Pb$ diagram (for data source and 'M'; see caption to Fig. 3b). Filled ellipse below MORB data point is locus of depleted mantle Pb isotope compositions predicted by modelling. Also shown are present-day model isotope compositions for 'erosion mix'. Diamonds, $E = 1$; triangles, $E = 0.5$; squares, $E = 0.2$. Closed symbols, $K = 2$; open symbols, $K = 3$. Results shown for $R = 0.5$ and 0.7. Values from $R = 0.3$ are outside figure frame (arrow indicates direction) and clearly do not represent a fit. (Discussion in the text.)

Fig. 6. ε_{Nd} values of model erosion mix resulting from varying parameters R, E and K compared with recent sediment data of Goldstein *et al.* (1984). (**a**) Effect of K, modelled with $R = 0.7$ and $E = 1$. (**b**) Effect of R and E, modelled with $K = 3$. It should be noted that ε_{Nd} value for no-growth crust model are *c.* -21.5 (not shown; see Fig. 3c).

needed to generate observed average upper-crust Pb isotope ratios. Bearing in mind that between 1960 and 1985 the anthropogenic emission flux of Pb exceeded the crust–mantle recycling flux for Pb by more than an order of magnitude, it is not improbable that published estimates of upper-crust Pb concentrations are biased by contamination.

Regarding Th–U–Pb systematics, depleted mantle Th/U ratios around 2.9 and $^{208}Pb/^{204}Pb$ ratios around 37.8 result in all cases (Table 2). The latter is a near-perfect fit to data. The Th/U ratio is slightly too high compared with the best estimate of 2.62 ± 0.14 (O'Nions & McKenzie 1993) but nevertheless a fair fit. The relevant results from U–Pb isotope systematics modelling are summarized in Figure 5. Depleted mantle values for $^{207}Pb/^{204}Pb$ and $^{206}Pb/^{204}Pb$ ratios are closely reproduced, as in previous modelling, and those for the erosion mix all plot on a relatively narrow band through the average of pelagic sediment data. A measure of the goodnes of fit is how close the modelled erosion mix ratio results plot to the average of pelagic sediment data. Here a strong dependence on total recycling (parameter R) is apparent, with low
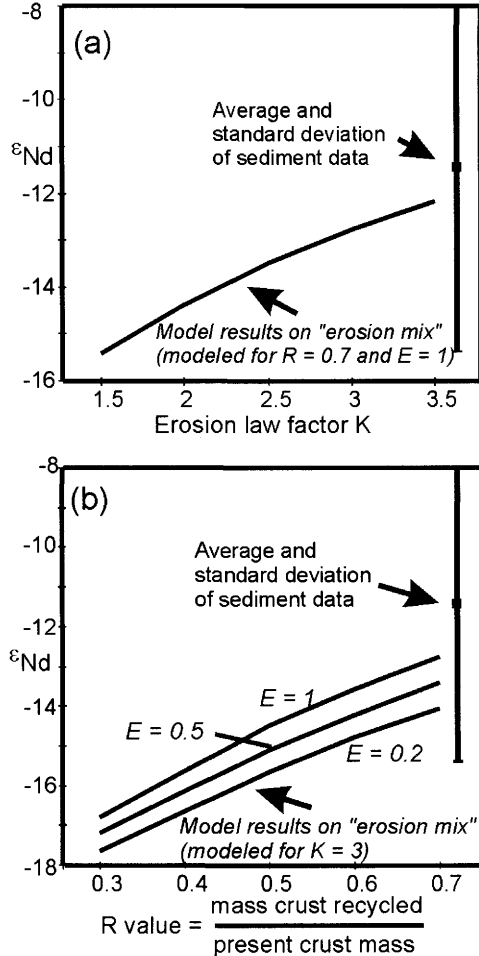
total recycling resulting in a strongly radiogenic erosion mix, and vice versa. The reason is twofold. First, a larger amount of recycling leads to more lower crust material becoming incorporated in the upper crust over time, and second, average eroded crust is younger if the recycling rate is high, and therefore less radiogenic. Although the value of the exponential parameter E is surprisingly uncritical for this Pb isotope modelling (the early and late effects of variations in this parameter counteract each other), the erosion law factor K is clearly important. With a value of $K = 2$ the Pb isotope difference between

Table 2. *Ranges of element concentrations and isotope ratios for reservoirs, resulting from present modelling*

Result	Depleted mantle	Upper crust (young)	Upper crust (old)	Erosion mix
Age (Ga)		1.1–1.6	2.7–2.9	
U (ppm)	0.006–0.0066	0.95–1.05	1.45–2.0	1.95–2.1
Th (ppm)	0.023–0.026	6.4–7.2	7.4–11	7.4–7.6
Pb (ppm)	0.036–0.04	6.3–6.9	9.4–11.1	7.52
Sm (ppm)	0.266	4.4–4.5	4.3–4.5	4.3–4.44
Nd (ppm)	0.677	21.8	24–25.5	22–23
$^{232}Th/^{238}U$	2.85–2.99	4.8–5.1	4.0–4.5	2.65–2.85
$^{238}U/^{204}Pb$	10.1–10.6	9.6–10.0	10–12	16.5–18
$^{206}Pb/^{204}Pb$	18.3–18.5	18.5–19.0	18.6–20.4	Fig. 6
$^{207}Pb/^{204}Pb$	18.65–18.8	15.5–15.7	15.51–16.2	Fig. 6
$^{208}Pb/^{204}Pb$	37.6–37.9	38.6–39.2	38.7–40.4	38.5–39.7
$^{147}Sm/^{144}Nd$	0.2375	0.1203	0.1085	0.1172
ε_{Nd}	9.5–11.5	−11 to −6.6	−34 to −30	Fig. 7

If no range is given for concentrations and element ratios, the variation is <1%.

the erosion mix and the depleted mantle almost disappears for high total recycling ($R = 0.7$). If $K = 3$ this difference is still discernible. As young crust is less radiogenic than old crust, this result is counter-intuitive and it is explained by enhanced retention of ^{207}Pb in the early continental crust if the K value is high. From Figure 5 it can be judged that a number of combinations of parameters would be possible. For instance, if $E = 1$ and $K = 2$ a good fit results for R $c. 0.5$. If $K = 3$ a value of R $c. 0.6$ gives a best fit.

In Sm–Nd isotope systematics the ε_{Nd} value of the erosion mix is used as a measure of the quality of the fits obtained (Fig. 6a and b). For all model variations, Sm and Nd concentrations are in the range of accepted values, and ε_{Nd} values between +10 and +11 were obtained for the depleted mantle (Table 2). Figure 6a shows a clear improvement of the fit with increasing K factor, as also noted by Nägler & Kramers (1998). This is intuitive, as a greater K factor means a greater proportion of younger crust in the erosion mix. Further, the quality of fit of erosion mix ε_{Nd} becomes progressively better as the values of E and/or R are increased (Fig. 6b). The effect of R is that (with constant E) greater time-integrated recycling reduces the average age of the present-day crust and therefore renders its ε_{Nd} value less negative. The effect of E is more subtle: for a fixed value of R, a lower value of E leads to a greater average age of the continental crust because erosion fluxes in the second half of geological history (see Fig. 4b) are reduced. The erosion law ultimately affects the average crust age more strongly if applied to late erosion than to early erosion, because the spread in ages in the crust becomes greater with time. Figure 6a and b shows that no perfect fit for model ε_{Nd} values of the erosion mix to recent

sediment data is achieved with the range of values of K, E and R investigated, although a reasonably close match is found if all three parameters are set high. Values of R lower than $c. 0.5$ and values of E lower than $c. 0.5$ appear highly unlikely.

It is useful to combine the results of U–Pb and Sm–Nd modelling, because they mutually constrain each other and together permit a narrow set of scenarios. If the lower limit of $c. 0.5$ for exponential parameter E imposed by Sm–Nd modelling is applied to U–Pb systematics, it is seen (Fig. 5) that values for R (total crust recycling) larger than $c. 0.6$ lead to model erosion mix Pb isotope compositions which are not compatible with data from pelagic sediments, even if $K = 3$. Thus $c. 0.6$ is an upper limit for parameter R from U–Pb systematics. As the lower limit for this parameter from Sm–Nd systematics is $c. 0.5$, this yields a rather well-constrained estimate for total crust recycling. $R \approx 0.6$ combined with $E \approx 1$ and $K \approx 3$ yields the best possible approximation of model erosion mix isotope compositions to sediment data for the combined sets of systematics.

Following this result, the total amount of crust recycled by erosion into the mantle would be about 60% of the present crust mass ($R \approx 0.6$). This is not in conflict with any known geochemical data. An apparent contradiction exists with a maximum value of 30% derived from the mass balance of Ar in the atmosphere and K in the continental crust by Coltice *et al.* (2000). The argument used by these workers was based on the assumption that the amount of ^{40}Ar in the atmosphere and the continental crust combined is equal to or greater than that generated over geological time by the amount of K that has ever been in the continental crust by (equation (3)

of Coltice *et al.* 2000). As they found an excess amount of ^{40}Ar in the atmosphere + crust of only 30% over what could have been produced by the equivalent amount of K at present in the crust, they concluded that not more than 30% of the continental crust mass can have been recycled into the mantle. In the basic assumption of this approach it is implied that the portions of mantle that melted to form continental crust are pristine and undegassed since the origin of the Earth. However, by far the most important degassing of Ar from the mantle occurs at mid-ocean ridges, and oceanic crust and mantle providing K in crust formation are already largely degassed (e.g. Tolstikhin & Marty 1998). Therefore the amount of Ar in the atmosphere and crust together cannot be used to place constraints on the amount of K that was added to the continental crust over time (and, by proxy, the total amount of continental crust formed over time).

The best fit result $E \approx 1$ means that the rate of recycling at any time in the past would have been approximately proportional to the mass of crust in existence at that time. If Archaean continental crust had the same thickness as today's, this implies an approximately constant rate of continent denudation per unit surface through geological time. It is interesting to compare predictions from this modelling with present-day denudation rates and oceanic sediment data. The combination $E = 1$, $R = 0.6$ yields a present-day erosion flux of $4.3 \times 10^{15}\,g\,a^{-1}$ (see Fig. 4b). Averaged over today's continental surface of $c.\,1.5 \times 10^8\,km^2$, and assuming an average density of 2.7 for the eroded material, this yields an average denudation rate of $c.\,10\,mm\,ka^{-1}$. Using cosmogenic nuclide abundances in river sediments, Schaller *et al.* (1999) have determined denudation rates over the last $10–20\,ka^{-1}$ of between 20 and $100\,mm\,ka^{-1}$ in Western European areas outside the Alps. Direct river load gauging data yield somewhat lower values, but have even more a snapshot nature. As much of the material eroded from continents is resedimented on continental shelfs and in deltas, measured denudation rates must be higher than those predicted by crust recycling models, which is true in this case. The mass flux of $c.\,4.3 \times 10^{15}\,g\,a^{-1}$ predicted by modelling can also be compared with estimated rates of oceanic sediment accumulation and sediment subduction. The Cenozoic (pre-anthropogenic) terrigenous oceanic sedimentation flux is estimated at $c.\,10^{16}\,g\,a^{-1}$ (Milliman & Syvitski 1992), whereas the flux of terrigenous pelagic sediments into subduction zones is at present $1.1 \times 10^{15}\,g\,a^{-1}$ (Rea & Ruff 1996). The difference between these

estimates illustrates the difficulty with estimating crust–mantle recycling over large time scales, as pointed out by Rea & Ruff (1996). For instance, a large portion of today's sediment flux to the ocean floor is represented by the Bengal Fan, which is an extremely short-lived phenomenon in Earth history. On the whole, predictions from the present modelling are comfortably within the range defined by estimates based on very different observations.

Implications for CO_2 drawdown in the Archaean time

By linking crust-to-mantle recycling via erosion and weathering to CO_2 drawdown, these modelling results can be used to provide a semi-quantitative estimate on net Archaean CO_2 drawdown rates and the length of time that might have been required to remove a massive CO_2 atmosphere. Such a venture can only be tentative. The Archaean crust–mantle recycling fluxes estimated from modelling provide minimum values for the total erosion rates, as resedimentation on continents is documented for Archaean time (Fedo *et al.* 1996; Hunter *et al.* 1998) and may have been significant. On the other hand, the relative importance of purely mechanical erosion leading to graywacke-type sedimentation is not well known for Archaean time, so that total erosion rates impose only a maximum limit on chemical weathering rates. Further, although the extensive loss of mobile cations from Archaean fine clastic sediments and metasediments (e.g. Eriksson 1995; Fedo *et al.* 1996) indicates that Archaean weathering and erosion were linked to CO_2 drawdown, the rate of reintroduction of CO_2 into the atmosphere by metamorphic decarbonation and (arc) volcanism in Archaean time are unknown. On the one hand, the freeboard criteria indicate that Archaean oceans were probably shallower than todays', increasing the likelihood of carbonate subduction. On the other hand, the calcite compensation depth (CCD) level must also have been shallower in Archaean time as a result of the high atmospheric CO_2 pressure, and this would make carbonate subduction less likely. Following this reasoning, chemical weathering rates can thus provide only a maximum estimate of net CO_2 removal from the atmo-hydrosphere. From this combination of maxima and minima it follows that no firm constraints on Archaean CO_2 drawdown can be imposed from this work.

However, the results do provide a perspective, which is summarized in Figure 7. Integrating the crust–mantle recycling fluxes of Figure 4b over
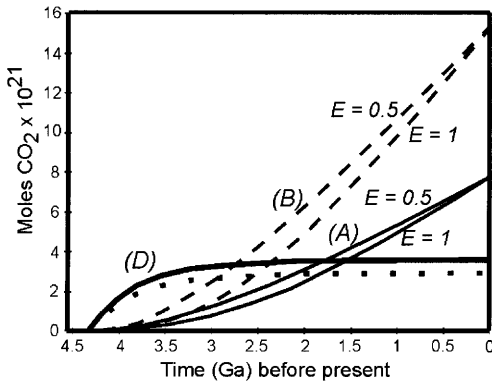
Fig. 7. Potential cumulative CO$_2$ drawdown capacity by weathering (curves A and B) compared with cumulative mantle CO$_2$ degassing (curve D) over geological time. A and B are derived from time integration of recycling curves in Figure 4b by assuming that erosion flux equals recycling flux, and drawdown of 650 moles of CO$_2$ per tonne of rock weathered (continuous curves, A) or 1300 moles (dashed curves, B). D is derived from upper-mantle melting flux of model of Kramers & Tolstikhin (1997), assuming MORB is fully degassed and no carbon goes back into the mantle, and is scaled to total carbon in sedimentary reservoirs (continuous curve) or to the portion in carbonate (dotted curve). D therefore depicts accumulation of carbon in atmo-hydrosphere and in sedimentary rocks. (Discussion in the text.)

time yields the total amount of crust recycled as functions of geological time. Such functions can be converted into cumulative CO$_2$ draw-down curves (indicating the total amount of CO$_2$ removed from the atmosphere, as a function of time) by assuming, first, that erosion equals crust–mantle recycling, and second, an amount of CO$_2$ removed from the atmosphere per unit mass of rock weathered. Curves A and B in Figure 7 are based in this way on recycling fluxes obtained for $R = 0.6$ (Fig. 4b). Curves for $E = 1$ represent the best-fit scenario for Th–U–Pb and Sm–Nd systematics, and those for $E = 0.5$ are added for comparison. Curves A give the cumulative CO$_2$ drawdown capacity for 650 moles CO$_2$ ton^{-1} of rock weathered, and curves B for 1300 moles CO$_2$ tonne^{-1}.

Curve D is one possible description of the amount of CO$_2$ accumulated in the atmo-hydrosphere and sediments as a function of time. It describes cumulative degassing of the upper mantle and is scaled to the amount of C that is in these reservoirs today (the stippled variant corresponds to the amount of C in carbonates). This curve is derived from the mantle melting flux (i.e. MORB production flux) inherent in the modelling of Kramers & Tolstikhin

(1997) and Nägler & Kramers (1998) using the assumptions that volatiles including CO$_2$ are completely lost from MORB, and that subducted oceanic crust returned to the mantle is free of CO$_2$. The late start of atmosphere accumulation in this model reflects a probable major atmosphere loss between 0.2 and 0.3 Ga as indicated by ^{129}Xe(I) and ^{136}Xe(Pu) systematics (Azbel & Tolstikhin 1993). This scenario for mantle degassing is slow compared with most others. For instance, Tolstikhin & Marty (1998) have modelled Ne, Ar and N$_2$ development of the atmosphere using a much greater degassing flux in early Earth history. For the purpose of estimating Archaean atmospheric conditions the differences are, however, insignificant, as even the slow degassing model used here leads to almost complete upper-mantle degassing by 3 Ga ago.

Following Figure 7 from the origin of the Earth towards the present, curve D is first above the cumulative drawdown curves A and B. The vertical difference between the sets of curves would roughly indicate the amount of free CO$_2$ (or more reduced species that can be oxidized to CO$_2$) in the atmosphere. This reaches between 1.8×10^{21} and 2.5×10^{21} moles, or 16 and 22 bar. At the intersection of curve D with curves A or B this large amount of CO$_2$ in the atmosphere could have been converted to carbonate. Later in time, when curves A or B are above curve D it would be expected that CO$_2$ levels will be kept low continuously by silicate weathering.

The question of which cumulative mantle degassing curve D is really relevant in this context is difficult to answer and depends on the relative rates of drawdown by photosynthesis and silicate weathering–carbonate formation in Archaean time. From the carbon isotope record, these are mainly considered to have remained constant (Schidlowski 1988), in which case the stippled lower curve D would be more appropriate. However, for the timing of drawdown derived from Figure 7 the choice of mantle accumulation curve is unimportant, given the tentative character of this whole consideration.

Following curves A and B for the best-fit scenario ($E = 1$), a massive CO$_2$ atmosphere could have been removed by about c. 2.5 Ga ago at the earliest, and by 1.5 Ga ago at the latest, provided that reintroduction of CO$_2$ by arc volcanism was of minor importance compared with drawdown. Bearing in mind that curves A and B represent minimum drawdown potential (resedimentation on continents must be added) and that CIA values for Archaean shales can be very high (Fedo *et al.* 1996) the earlier estimate is probably closer to the truth. This result would be consistent with the low atmospheric CO$_2$

content derived by Rye *et al.* (1995) for the age range 2.5–2.2 Ga, and also with the observed Huronian glaciation (Nesbitt & Young 1982). Given the low time resolution of the method, it is also not in serious conflict with the glaciation observed in the 2.9 Ga Mozaan Group (Young *et al.* 1998).

Notwithstanding the large uncertainties mentioned earlier, it can be concluded from the above argumentation that net surplus CO_2 drawdown capacity by continental weathering probably existed since early Proterozoic time. This leads to a scenario of the evolution of atmospheric CO_2 content in a three-stage history. In Phanerozoic time, silicate weathering takes place, in spite of very low atmospheric CO_2 contents, under CO_2 partial pressures enhanced by biological activity in soils (Lovelock & Whitfield 1982; Schwartzman & Volk 1989; Berner 1997). In Archaean time, it took place under an inherently high CO_2 pressure. Between these two regimes, during most of Proterozoic time, a lower limit on atmospheric CO_2 partial pressure was probably set in the first instance by the reaction equilibria associated with silicate weathering, i.e between 0.01 and 0.1 bar (Rye *et al.* 1995). The CO_2 levels of these three stages and the timing of changes between them coincide very closely with the atmospheric CO_2 history proposed by Kasting (1993) based on the increase of solar luminosity with time, and the variations in greenhouse effect this requires. The transitions between the three types of climate regime would have been relatively sharp: 'Snowball Earth' events (Hoffman *et al.* 1998) could have occurred in early Proterozoic time and, as recorded, in very late Proterozoic time, but not in Archaean or mid-Proterozoic time, as solar luminosity increased gradually, whereas atmospheric CO_2 levels decreased in a more stepwise manner.

Although global transport balance modelling thus provides some perspective on the rate at which CO_2 could have been removed from the atmosphere in early Earth history, the resolution of the method is inherently poor and it can provide only broad outlines. The large uncertainties and the problems encountered highlight the need to find independent constraints on weathering and erosion rates in Archaean time to understand the early evolution of the Earth's atmosphere, climate and life.

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