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Sm-Nd and Rb-Sr Chronology of Continental Crust Formation

Times of addition to continents of chemically fractionated mantle-derived materials are determined.

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One of the most obvious features of the outermost part of the earth is the difference between continents and ocean basins. This topographical duality is a reflection of major differences in the structure and the chemistry of the outer parts of the earth and of the dynamic interaction between the interior layers, the outer crustal layers, and the hydrosphere often biased and distorted, of the growth and evolution of the continents. They indicate that the continents have grown by addition of new material from underlying mantle sources, accretion of island arc volcanic systems to the continental margins, and interaction with ocean basins. In this article we present some data that may aid in identifying the times at which

Summary. Samarium-neodymium and rubidium-strontium isotopic systematics, together with plausible assumptions regarding the geochemical evolution of continental crust material, have been used to ascertain the times at which segments of continental crust were formed. Analyses of composites from the Canadian Shield representing portions of the Superior, Slave, and Churchill structural provinces indicate that these provinces were all formed within the period 2.5 to 2.7 aeons. It has been possible to determine the mean age of sediment provenances, as studies of sedimentary rocks suggest that the samarium-neodymium isotopic system is not substantially disturbed during sedimentation or diagenesis.

of the earth. The crust that occupies the ocean basins is only ~ 6 kilometers thick, is relatively uniform in chemical composition, and consists of very young materials less than ~ 0.2 aeon old [1 aeon (AE) = 10^9 years]. This young age reflects rapid recycling, which has almost completely destroyed all record of older oceanic crust within the present ocean basins. In contrast, continental crust is about 35 km thick, has a variable and distinctive chemical composition, and consists of materials ranging in age from 0 to 3.8 AE. These constituents of diverse age preserve a record, although SCIENCE, VOL. 200, 2 JUNE 1978

new materials were derived from the earth's mantle and added to the continental crust.

The ability to determine the time of formation of new crustal segments is of fundamental importance in attempting to understand the growth and evolution of continental crust. We consider "new crust" to be material that has not previously been present in the crust but is newly added during periods of continental growth and has its origin in the mantle. The decay of long-lived radioactive isotopes to stable daughter products has been used to obtain ages for a variety of rocks. However, because there have been multiple generations of crustal formation, metamorphism, remelting, and erosion, these ages may not be related to the actual times of formation of new crust. For example, it is often difficult to establish whether younger parts of continental crust (as defined by relative geologic age or by isotopic age determinations) represent the addition of new material, or are simply the product of metamorphism or remelting of preexisting crustal provinces or materials. This is particularly important in attempting to estimate the rate of development of continental crust through time. Hurley and co-workers (1), using whole rock Rb-Sr together with K-Ar age determinations, found crustal ages that indicated accelerated generation of crustal material from \sim 3.8 AE to the present. However, other workers, using U-Pb values in beach and river sands (2) and initial 87Sr/86Sr values in rocks of well-established age to identify remelted crust (3), concluded that major rock-forming events have been approximately episodic, with only relatively short periods of accelerated crustal growth.

In this article we will show that, by using the recently developed Sm-Nd isotopic technique together with Rb-Sr systematics and plausible assumptions regarding the geochemical evolution of crustal material from mantle sources, the times of formation of new crust can be obtained from both igneous rocks and metamorphic and sedimentary derivatives. In particular, we will show that by using Sm-Nd isotopic systematics, the times of formation of new continental crust can be obtained from a more diverse range of materials, including sedimentary and metamorphic rocks that have complex histories including erosion, deposition, and chemical alteration. To obtain formation ages of large segments of continental crust, we studied sediments that were probably derived from widespread source areas and composites consisting of a large number of igneous and metamorphic rock samples from the Canadian Shield (4, 5).

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This approach should yield further insight into questions related to the episodic or uniform growth of continental crust through time. In addition, it may be possible to identify source areas (provenances) of sedimentary rocks because the sediments retain information about the time of formation of the crustal segments that were their sources.

The general approach we used is to assume that each time new material is added to the continental crust, the dominant contribution comes from the emplacement of magmatic rocks derived from a mantle reservoir, and that the differentiation processes that produce the magmatic rocks occur with a marked chemical fractionation of the daughter and parent elements relative to the source region. It is these times of chemical fractionation that are dated; the values obtained are, of course, model-dependent.

The mantle reservoir that is taken to be the source of the new crust is assumed to have evolved through geologic time with the characteristic Sm/Nd ratio identified by DePaolo and Wasserburg (6, 7). These workers used the evolution of Nd through geologic time and the correlation of Nd and Sr isotopic variations in geologically young samples to identify the characteristics of the mantle reservoir. The arguments presented here are directly dependent on the validity of the mantle reservoir characteristics that they outlined. Such a simplified model will be subject to revision insofar as the Nd and Sr isotopic correlation is imprecise or not fully understood, and the mantle sources are chemically and isotopically complex regions.

Fig. 1. Evolution of initial 143Nd/144Nd in sources of crustal rocks, determined for a suite of rock samples of known ages from De Paolo and Wasserburg (6, 7)]. (Inset) Fractional deviation in parts in 104 of the initial 143Nd/ 144Nd ratio from the evolution to be found in a reservoir with a chondritic Sm/Nd ratio. The shaded area is for midocean ridge tholeiites and island arc volcanics. The initial 143Nd/144Nd ratio from the 2.64 ± 0.14 AE greenstone belt in Rhodesia (11) is coincident with the point WYWR (grandiorite Wind River from Mountains, Wyoming).

Sm-Nd and Rb-Sr Systematics

Although the Rb-Sr method has been in use for some time [for example, see (8)], application of the Sm-Nd method has only recently been made possible by the development of high-precision mass spectrometric techniques and chemical separation procedures (9). Lugmair *et al.* (10) first applied the Sm-Nd method to meteoritic and lunar samples, and De-Paolo and Wasserburg (6, 7), O'Nions and co-workers (11), and Richard *et al.* (12) subsequently studied terrestrial samples.

Both Sm and Nd are rare earth elements (REE), and ¹⁴⁷Sm decays to ¹⁴³Nd with a half-life of 1.06×10^{11} years. The ¹⁴³Nd/¹⁴⁴Nd ratio measured today for a rock derived *T* years ago from a source with an initial ¹⁴³Nd/¹⁴⁴Nd ratio I_8 is given by

 $(^{143}Nd/^{144}Nd)_{M} =$

$$I_{\rm S} + \left(\frac{{}^{147}{\rm Sm}}{{}^{144}{\rm Nd}}\right)_{\rm M} (e^{\lambda T} - 1)$$
(1)

where M denotes the ratio measured in the rock today and λ the ¹⁴⁷Sm decay constant.

Variations in I_s in terrestrial samples through geologic time were first studied by DePaolo and Wasserburg (6, 7), who showed that to a reasonable approximation the evolution of ¹⁴³Nd/¹⁴⁴Nd in the source of continental rocks implies a uniform ratio essentially equal to that found in chondrites. Figure 1 shows the initial ¹⁴³Nd/¹⁴⁴Nd values for a variety of igneous rock types as a function of age. The fractional deviations in parts in 10⁴ of $I_{\rm s}$ from ¹⁴³Nd/¹⁴⁴Nd in a reservoir with a chondritic Sm/Nd ratio $I_{\rm CHUR}(T)$ are shown in the inset of Fig. 1. The maximum deviation is less than 3 parts in 10⁴ and is at present recognized only in continental rocks younger than 1 AE. It is thus plausible to assume that the mantle reservoir which is the source of crustal rocks has an Sm/Nd ratio very close to the relative abundance found in a chondritic uniform reservoir (CHUR). The value of ¹⁴³Nd/¹⁴⁴Nd in CHUR today is defined as $I_{\rm CHUR}(0)$ and is given by

 $I_{\rm CHUR}(0) =$

$$I_{\rm CHUR}(T) + \left(\frac{{}^{147}{\rm Sm}}{{}^{144}{\rm Nd}}\right)_{\rm CHUR}(e^{\lambda T} - 1) \qquad (2)$$

where $I_{CHUR}(0) = 0.511836$ and $I_{CHUR}(T)$ is ¹⁴³Nd/¹⁴⁴Nd in CHUR at any time *T* in the past and (¹⁴⁷Sm/¹⁴⁴Nd)_{CHUR} = 0.1936 is that in CHUR (*I0*). A magma derived from the CHUR reservoir *T* years ago would have $I_s = I_{CHUR}(T)$. Then from Eqs. 1 and 2, assuming that a rock remains a closed system from the time of differentiation until today, the time of fractionation and concurrent derivation from the CHUR reservoir is given by

 $T_{\rm CHUR}^{\rm Nd} =$

$$\frac{1}{\lambda} \ln \left[1 + \frac{\epsilon_{\rm Nd}(0) I_{\rm CHUR}(0) \times 10^{-4}}{f_{\rm Sm/Nd}(^{147} {\rm Sm}/^{144} {\rm Nd})_{\rm CHUR}} \right]$$
(3)

where

$$f_{\rm Sm/Nd} = \left[\frac{(\rm Sm/Nd)_{\rm M}}{(\rm Sm/Nd)_{\rm CHUR}} - 1\right]$$
(4)

and

$$\boldsymbol{\epsilon}_{\mathrm{Nd}}(0) = \left[\frac{(^{143}\mathrm{Nd}/^{144}\mathrm{Nd})_{\mathrm{M}}}{I_{\mathrm{CHUR}}(0)} - 1\right] \times 10^4$$
(5)

It is apparent from Eq. 3 that T_{CHUR}^{Nd} is indeterminate for $f_{\rm Sm/Nd} = 0$. For precise determination of $T_{\rm CHUR}^{\rm Nd}$ ages, a relatively large fractionation of Sm/Nd from the chondritic ratio at the time of derivation from CHUR is required, along with a value of $\epsilon_{Nd}(0)$ distinct from zero. An example is shown schematically in Fig. 2 for a rock with an enrichment factor $f_{\text{Sm/Nd}} = -1$ [that is, $(\text{Sm/Nd})_{\text{M}} = 0$] and with the ratio of ¹⁴³Nd/¹⁴⁴Nd measured today (R_A) unchanged since the derivation from CHUR $T_{CHUR}^{Nd}(A)$ years ago. In this example for a closed system (no addition of Sm or Nd), remelting and metamorphic and sedimentary processes are assumed not to change (143Nd/144Nd)_M or Sm/Nd, and thus the T_{CHUR}^{Nd} age would be unaffected by these processes. A more SCIENCE, VOL. 200



general example is shown with $f_{\rm Sm/Nd} < 0$ and the (¹⁴³Nd/¹⁴⁴Nd)_M as measured today ($R_{\rm B}$) somewhat evolved since derivation from CHUR. Again, for a closed system, later metamorphic and sedimentary events shown schematically as $T_{\rm MET}$ and $T_{\rm SED}$, respectively, are assumed not to change the $T_{\rm CHUR}^{\rm Nd}$ age.

The classic REE distribution studies by Haskin et al. (13), Taylor (14), Ronov et al. (15), and Shaw et al. (16) have shown that for most crustal rocks $f_{\rm Sm/Nd} < 0$. This can be seen in Table 1, where estimates of $f_{\rm Sm/Nd}$ range from -0.26 to -0.46. Regardless of the particular model invoked for the formation of continental crust, the observation that in a wide variety of crustal rocks Sm/Nd is markedly fractionated with respect to the source (CHUR) value implies that this is an important characteristic of continental crust. Insofar as the CHUR reservoir is the source of new crustal materials, and if the major fractionation of Sm/Nd occurs when rocks are derived from this reservoir, the time of formation of new crustal segments is given by $T_{\rm CHUR}^{\rm Nd}$. To find $T_{\rm CHUR}^{\rm Nd}$ ages of the sources of metamorphic and sedimentary rocks also requires the assumption that no change in Sm/Nd and 143Nd/144Nd occurred during the secondary processes that formed these rocks. The validity of this approach is suggested by REE distribution studies which indicate that Sm/ Nd does not change with increasing metamorphic grade (17) and that many sedimentary rocks preserve the average Sm/Nd of their source (13, 14). However, the validity can be fully established only by the self-consistency of the $T_{\rm CHUR}^{\rm Nd}$ ages.

The samples we studied are composites of igneous and metamorphic rocks from the Canadian Shield, shales, graywackes, loess deposits, a schist, and a deep-sea sediment. These samples do not represent a single source, but almost certainly a mixture of a variety of sources. Although the isotopic systematics as outlined were for a single source, they are also applicable to a mixture of a number of sources. For example, it can be shown that a mixture of two rocks, A and B, with different T_{CHUR}^{Nd} ages $T_{CHUR}^{Nd}(A)$ and $T_{CHUR}^{Nd}(B)$ and enrichment factors $f_{\text{Sm/Nd}}(A)$ and $f_{\text{Sm/Nd}}(B)$, as in Fig. 2, would give a mean age

$$\langle T_{\text{CHUR}}^{\text{Nd}}(\mathbf{A} + \mathbf{B}) \rangle =$$

$$\underline{T_{\text{CHUR}}^{\text{Nd}}(\mathbf{A}) \text{Nd}_{\text{A}} f_{\text{Sm/Nd}}(\mathbf{A})}$$

$$\frac{1}{\mathrm{Nd}_{\mathrm{A}}f_{\mathrm{Sm/Nd}}(\mathrm{A}) + \mathrm{Nd}_{\mathrm{B}}f_{\mathrm{Sm/Nd}}(\mathrm{B})} + \frac{1}{\mathrm{Nd}_{\mathrm{A}}f_{\mathrm{Sm/Nd}}(\mathrm{B})}$$

$$\frac{T_{\text{CHUR}}^{\infty}(B)\text{Nd}_{B}f_{\text{Sm/Nd}}(B)}{\text{Nd}_{B}f_{\text{Sm/Nd}}(B) + \text{Nd}_{A}f_{\text{Sm/Nd}}(A)}$$
(6)
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Fig. 2. Schematic representation of the evolution of 143Nd/ 144Nd on the earth since it condensed at time $T_{\rm c}$. Assuming it to have a chondritic Sm/Nd, the growth rate of ¹⁴³Nd/¹⁴⁴Nd in a reservoir or a rock is proportional to Sm/Nd. Examples are shown of the evolution of 143Nd/144Nd with the Sm/Nd fractionated from CHUR. A rock derived from CHUR at time T(B) and enriched in Sm/ Nd by a factor $f_{\text{Sm/Nd}}$ will evolve subsequent to T(B)along the secondary trajectory to the ¹⁴³Nd/¹⁴⁴Nd ratio today, $R_{\rm B}$.

 R_{B} $f_{Sm/Nd} = 0$ $f_{Sm/Nd} = 0$ I_{C} R_{A} $f_{Sm/Nd} = -1$ I_{C} I_{C} I_{C} I_{TSED} I_{TMET} R_{A} I_{C} I_{C} I_{TSED} I_{TMET} R_{A} I_{C} I_{C} I_{TSED} I_{TAGE} I_{C} I_{C} I

Here Nd_A is the Nd contribution from rock A and Nd_B is the Nd contribution from rock B. From this equation it can be seen that $\langle T_{CHUR}^{Nd}(A + B) \rangle$ is simply the average of $T_{CHUR}^{Nd}(A)$ and $T_{CHUR}^{Nd}(B)$, weighted by the Nd concentrations and enrichment factors of the rocks. So, in general, the average $\langle T_{CHUR}^{Nd} \rangle$ is greater than the minimum T_{CHUR}^{Nd} and less than the maximum T_{CHUR}^{Nd} in any mixture.

From the correlation between Nd and Sr isotopic abundances in young igneous rocks, discovered by DePaolo and Wasserburg (7) and O'Nions and co-workers (11), it appears possible to estimate a characteristic Rb/Sr value of a standard unfractionated reservoir (UR) that is the source region of continental rocks. In a manner analogous to that discussed for Sm and Nd, Rb-Sr model ages can also be calculated, assuming that simple rules apply to Rb-Sr isotopic systematics. For this system

$$T_{\rm UR}^{\rm S\,r} = \frac{1}{\lambda} \ln \left[1 + \frac{\epsilon_{\rm Sr}(0)I_{\rm UR}(0) \times 10^{-4}}{f_{\rm Rb/Sr}(^{87}{\rm Sr}/^{86}{\rm Sr})_{\rm UR}} \right]$$
(7)

where $I_{\rm UR} = 0.7045$ is the ⁸⁷Sr/⁸⁶Sr ratio, (⁸⁷Rb/⁸⁶Sr)_{UR} = 0.084, and $\lambda = 1.39 \times 10^{-11}$ year⁻¹ in the source of continental rocks today (7, 11). Similarly

$$\epsilon_{\rm Sr}(0) = \left[\frac{({}^{87}{\rm Sr}/{}^{86}{\rm Sr})_{\rm M}^{\dagger}}{I_{\rm UR}(0)} - 1\right] \times 10^4$$
 (8)

and

$$f_{\rm Rb/Sr} = \left[\frac{(\rm Rb/Sr)_{\rm M}}{(\rm Rb/Sr)_{\rm UR}} - 1\right]$$
(9)

A relationship analogous to Eq. 6 for the mean Rb-Sr age of a mixture may also be derived. We have also carried out Rb-Sr studies on the samples for which Sm-Nd results are reported here. The major dif-

ference between the Rb-Sr system and the Sm-Nd system is that for most continental crustal rocks $f_{\rm Rb/Sr} >> 0$. This is also shown in Table 1, where estimates of the continental crustal $f_{\rm Rb/Sr}$ range from +10.3 to +11.3. In addition, the response of Rb and Sr to metamorphic and sedimentary processes is markedly different from that of Sm and Nd. In metamorphic processes redistribution of Rb and Sr between minerals has been well documented (18, 19). Rubidium-strontium isochrons have also been obtained from some sedimentary rocks (20-22), which suggests that large enrichments of Rb relative to Sr and reequilibration of ⁸⁷Sr/⁸⁶Sr have occurred, presumably during or subsequent to deposition of these rocks.

Experimental Results

Detailed descriptions of the experimental procedures are given by Papanastassiou and Wasserburg (23) for Rb and Sr and by Papanastassiou et al. (24) for Sm and Nd. Errors given for ¹⁴³Nd/¹⁴⁴Nd and ${}^{87}\text{Sr}/{}^{86}\text{Sr}$ are 2 σ_{mean} (two standard deviations of the mean) of about 200 ratios for Nd and 100 ratios for Sr. The Nd, Sm, Rb, and Sr concentrations were obtained by isotope dilution techniques. The errors in Rb/Sr and Sm/Nd are less than 1 percent and include an assessment of errors from gravimetry and measurement of isotopic ratios. The 2 σ_{mean} errors given for the T_{CHUR}^{Nd} and T_{UR}^{Sr} ages only allow for analytical errors and do not include uncertainties in the parameters used for the mantle sources. Table 3 summarizes the $\epsilon_{\rm Nd}(0)$, $f_{\rm Sm/Nd}$, $\epsilon_{\rm Rb/Sr}(0)$, and $f_{\rm Rb/Sr}$ values used to calculate $T_{\rm CHUR}^{\rm Nd}$ and $T_{\text{UR}}^{\text{Sr}}$ ages. With only a few exceptions, the $f_{Sm/Nd}$ values in Table 3 are

Table 1. Estimates of upper crustal Sm/Nd and Rb/Sr enrichment factors. The enrichment factors $f_{\text{Sm/Nd}}$ and $f_{\text{Rb/Sr}}$ are defined in Eqs. 4 and 9, respectively.

Composite	$f_{ m Sm/Nd}$	$f_{ m Rb/Sr}$	Reference		
Canadian Shield	-0.46	+11.3	Shaw et al. (5, 16)		
Upper crust	-0.45	+10.1	Taylor (40)		
Continental crust	-0.26		Ronov <i>et al.</i> (15)		
North American shales	-0.46	+30.1	Haskin et al. (57); this article		
Chondrites	0.0	+8.3	Haskin et al. (13); Urey (64)		
Model mantle reservoir	0.0	0.0			

Table 2. Lithologies of Canadian Shield composites.

Composite	Lithologic type	Reference (4)	
New Quebec* and Fort Enterprise	Banded gneisses, migmatites, and granitic gneisses		
Fort Enterprise	High-level granite and quartz monzonite	(4)	
North Quebec, Saskatchewan, Baffin Island, and Quebec	Quartzofeldspathic rocks including granite, granitic gneiss, pegmatite, rhyolite, arkose, sandstone	(5)	

*Area 12.

relatively constant. Hence, variations in the calculated T_{CHUR}^{Nd} age are mainly dependent on $\epsilon_{Nd}(0)$. For this reason, where appropriate, discussion of either $\epsilon_{Nd}(0)$ values or the calculated T_{CHUR}^{Nd} ages will be emphasized.

Canadian Shield Composites

The Canadian Shield is one of the better-studied Precambrian areas, and the results of these studies have been important in formulating theories of continental growth and evolution. Based on geologic evidence, derived primarily from field mapping and integrated with isotopic dating, a number of structural provinces have been recognized in the Canadian Shield. From areas within different provinces, we measured $\epsilon_{\rm Nd}(0)$, $f_{\rm Sm/Nd}$, $\epsilon_{\rm Sr}(0)$, and $f_{\rm Rb/Sr}$ values and calculated $T_{\rm CHUR}^{\rm Nd}$ and $T_{\rm UR}^{\rm Sr}$ ages. In an attempt to determine the average age of relatively large areas of continental crust without a prohibitive number of analyses, we analyzed composite samples. These composites, in some cases consisting of several thousand samples, were originally used by Eade and Fahrig (4) and Shaw et al. (5, 16) to estimate the average chemical composition of the upper continental crust of the Canadian Shield. The generalized provinces and the areas represented by the composites analyzed are shown in Fig. 3. From the composites prepared by Shaw et al. (5) we analyzed the "quartzofeldspathic" lithologic type (Table 2), which constitutes approximately 70 percent of the area sampled. Two different lithologies from the composites of Eade and Fahrig (4) were studied. These are the gneisses and the granite-quartz monzonites. As described in Table 2, the different lithologies of Eade and Fahrig (4) are comparable to those of Shaw et al. (5) and also constitute a significant portion of the sample area.

From Fig. 3 it can be seen that the New Quebec and a large portion of the



North Quebec composites are in the Superior Province. This province contains some of the older rocks in the Canadian Shield, where a major granodiorite-forming event has been recognized at ~ 2.5 to 2.7 AE (25). For New Quebec $\epsilon_{Nd}(0) =$ -29.4 ± 0.4 with a $T_{\rm CHUR}^{\rm Nd}$ age of 2.66 \pm 0.06 AE. The $T_{\rm UR}^{\rm S\,r}$ age is 2.73 \pm 0.03 AE and is in excellent agreement. The North Quebec composite, which includes a small proportion of younger material from the Grenville Province, gives $\epsilon_{\rm Nd}(0) = -28.9 \pm 0.3$, a $T_{\rm CHUR}^{\rm Nd}$ age of 2.50 ± 0.05 AE, and a $T_{\text{UR}}^{\text{sr}}$ age of 2.52 ± 0.03 AE. The striking agreement between the T_{CHUR}^{Nd} and T_{UR}^{Sr} ages for New Quebec and North Quebec composites is also fully consistent with previously determined radiometric ages (25) and confirms that the Superior Province consists predominantly of new crust that was first formed 2.5 to 2.7 AE ago.

The Fort Enterprise composites are in the Slave Province of northern Canada (Fig. 3). This province has some K-Ar (26) and Rb-Sr (27) dates of the same age (2.5 to 2.7 AE) as those found in the Superior Province, and the provinces are generally thought to be of similar age. For the gneissic composite the T_{CHUR}^{Nd} age is 2.62 \pm 0.05 AE and the $T_{\text{UR}}^{\text{sr}}$ age is 2.58 ± 0.03 AE. From the same area, the granite-quartz monzonite composite gives a $T_{\text{CHUR}}^{\text{Nd}}$ age of 2.49 \pm 0.04 AE and a $T_{\text{UR}}^{\text{Sr}}$ age of 2.56 \pm 0.03 AE. The $T_{\text{CHUR}}^{\text{Nd}}$ and $T_{\rm UR}^{\rm S\,r}$ ages for the two different lithologies are again in excellent agreement, indicating that lithologic type is not important in determining the time of formation of this crustal segment.

Composite samples from Baffin Island and Saskatchewan from different areas of the Churchill Province have been studied. For Baffin Island the T_{CHUR}^{Nd} age is 2.74 \pm 0.05 AE, and a $T_{\rm UR}^{\rm Sr}$ age of 2.56 ± 0.03 AE has been obtained. The Saskatchewan composite gives a $T_{\rm CHUR}^{\rm Nd}$ age of 2.68 \pm 0.06 AE and a somewhat lower $T_{\text{UR}}^{\text{Sr}}$ age of 2.43 \pm 0.03 AE. These crustal formation ages are much older than the K-Ar ages of ~ 1.8 to 1.9 AE that are most commonly found in these areas (26). In this province, the $T_{\rm UR}^{\rm S\,r}$ ages are slightly younger than the T_{CHUR}^{Nd} ages and may have been partially affected by the event or events that reset the K-Ar ages.

Adjacent to the eastern margin of the Superior Province is the Grenville Province. In the southwestern corner of the Grenville Province, the Quebec composite with $\epsilon_{\rm Nd}(0) = -7.1 \pm 0.3$ gives a $T_{\rm CHUR}^{\rm Nd}$ age of 0.80 \pm 0.04 AE and a $T_{\rm UR}^{\rm Sr}$ age of 1.01 \pm 0.01 AE. The $T_{\rm SR}^{\rm Sr}$ age is consistent with previously determined crystallization ages (19, 28), but the $T_{\rm CHUR}^{\rm Nd}$ age is approximately 0.2 AE

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younger. Although there is substantial evidence (19, 28) that some rocks in the Grenville Province are remobilized 2.5-AE rocks, particularly at the weld between the Grenville and Superior provinces, the results presented here indicate that the bulk of the area sampled is comprised of much younger crust.

The T_{CHUR}^{Nd} and T_{UR}^{Sr} ages of the Churchill Province are essentially identical to those obtained for the Superior and Slave provinces. Although this was suggested by some previous age determinations (29), there now appears to be compelling evidence that the Superior, Slave, and Churchill provinces were all formed as crustal segments within the same period from 2.5 to 2.7 AE. This now poses the problem of how these structural provinces, having relatively distinct boundaries and structural patterns but consisting of materials formed at nearly the same time, were juxtaposed. The good correlation between the K-Ar ages and the structural provinces (26) suggests that the K-Ar ages represent the time at which the different provinces were last metamorphosed and deformed and obtained their structural characteristics. If this is the case, the structural characteristics of the Superior and Slave provinces were imposed at the time of or within 0.2 AE of their formation, while those of the Churchill Province were obtained approximately 0.8 AE after its formation. It is not, however, apparent whether the last metamorphism and deformation of the Churchill Province occurred before, during, or after the time when the provinces assumed their present relative positions.

The $T_{\rm CHUR}^{\rm Nd}$ and $T_{\rm UR}^{\rm Sr}$ ages of ~0.8 to 1.0 AE for the Grenville Province composite show that it is markedly younger than the other Canadian Shield composites. This indicates the addition of younger material onto the preexisting Canadian Shield. However, from the T_{CHUR}^{Nd} and T_{UR}^{Sr} ages of the Superior, Slave, and Churchill composites, it is evident that the Canadian Shield contains only a relatively small amount of material that is substantially younger than 2.5 AE. Older structural units are manifest on the North American continent, where rocks of \sim 3.6 AE old have been found (30–32). Ancient cratonic components have also been found in Australia (33), Greenland (34), Africa (35), and possibly the Baltic (36) and Ukrainian (37) shields. However, considering the wide variety of materials and the distinctive areas that have been sampled, we must conclude that the period 2.5 to 2.7 AE was a major epoch of formation of new continental crust. This has been manifest from the studies of previous workers (3, 25), who observed the relatively high frequency of

radiometric ages in this period, but it can
now clearly be extended to a much
broader context. From our present
knowledge of the times of formation of
continental crust, it appears that the ac-
tivity around 2.5 to 2.7 AE ago has been
unique in geologic history. It also ap-
pears certain that some truly major peri-
ods of continental crustal growth are
sharply episodic. This raises the inter-
esting possibility that the dramatic de-
crease in the volume of continental crust
produced since 2.5 AE ago may have
been due to a change in the mechanism
rather than only in the rate of crustal for-
mation.

From heat flow data and the chemical composition of exposed lower crustal rocks, it is well known that the upper crustal composition represented by these composites cannot extend to a depth of more than 10 km (38). It has been inferred (38-40) that the Rb/Sr ratio in the lower crust is at least a factor of 2 smaller than in the upper crust. The $T_{\rm UR}^{\rm S\,r}$ ages indicate that this enrichment of Rb/Sr in the upper crust occurred during the period 2.5 to 2.7 AE. Thus the younger events that reset the K-Ar ages in the Churchill Province did not redistribute Rb or Sr over a scale greater than that sampled. Furthermore, the relatively good agreement between the T_{CHUR}^{Nd} and $T_{\text{UR}}^{\text{sr}}$ ages (that is, 2.5 to 2.7 AE) requires

Table 3. Provenance parameters for Nd and Sr.									
Sample	$\varepsilon_{\rm Nd}(0)$	$f_{ m Sm/Nd}$	$T_{ m CHUR}^{ m Nd}$ (AE)	$\varepsilon_{\rm Sr}(0)$	$f_{ m Rb/Sr}$	$T_{\mathrm{UR}}^{\mathrm{Sr}}$ (AE)	T _{geologic} (AE)		
Canadian Shield composites									
New Quebec	$-29.4 \pm 0.4*$ †	-0.444	$2.66 \pm 0.06^{*}$	$345.3 \pm 0.8*\dagger$	7.48	$2.73 \pm 0.03^{*}$	2.5 - 2.7§		
North Quebec	-28.9 ± 0.3	-0.464	2.50 ± 0.05	328.9 ± 1.1	7.74	2.52 ± 0.03	2.5-2.7		
Fort Enterprise Gneiss	-24.3 ± 0.4	-0.372	$2.62~\pm~0.05$	369.2 ± 0.8	8.47	2.58 ± 0.03	2.5-2.7		
Fort Enterprise Granite	-30.7 ± 0.2	-0.495	2.49 ± 0.04	344.5 ± 0.9	7.99	2.56 ± 0.03	2.5-2.7		
Baffin Island	-31.7 ± 0.3	-0.464	2.74 ± 0.05	802.8 ± 0.7	18.6	2.56 ± 0.03	1.8-1.9		
Saskatchewan	-32.5 ± 0.4	-0.486	2.68 ± 0.06	566.1 ± 0.9	13.8	2.43 ± 0.03	1.8-1.9		
Quebec	-7.1 ± 0.3	-0.361	$0.80~\pm~0.04$	164.8 ± 0.8	9.81	1.01 ± 0.01	0.9-1.2		
Sedimentary rocks									
Baja Shale	$+ 0.7 \pm 0.4$	-0.227	-0.12 ± 0.07	27.0 ± 0.8	55.2	0.030 ± 0.001	0.1		
San Gabriel Sand	-9.9 ± 0.4	-0.225	1.77 ± 0.09	59.5 ± 0.8	5.16	0.69 ± 0.02	0.2-1.7		
Figtree shale	-28.0 ± 0.4	-0.317	3.53 ± 0.06	4506.7 ± 1.0	90.6	2.94 ± 0.03	2.98		
Iowa loess	-14.1 ± 0.5	-0.411	1.38 ± 0.06	181.8 ± 0.7	15.3	0.710 ± 0.01	0.01		
Nanking loess	-10.2 ± 0.4	-0.410	1.00 ± 0.05	198.7 ± 1.0	34.3	0.350 ± 0.005	0.01		
North American shales	-14.4 ± 0.5	-0.380	1.52 ± 0.07	380.8 ± 1.1	30.1	0.76 ± 0.01	0.5		
Birch Creek Schist	-27.0 ± 0.3	-0.464	2.33 ± 0.05	811.8 ± 1.1	68.3	0.714 ± 0.008	0.5-1.8		
Deep-sea red clay	-3.3 ± 0.4	-0.212	$0.63~\pm~0.08$	53.7 ± 1.0	8.41	0.38 ± 0.01	0.01		
Australian sediments									
SC-5	-14.5 ± 0.4	-0.443	1.32 ± 0.05	2481.6 ± 0.7	293.0	0.509 ± 0.005	0.44		
AO-7	-16.8 ± 0.4	-0.433	1.56 ± 0.05	1130.0 ± 0.6	71.6	0.95 ± 0.01	0.8		
MI-1	-23.5 ± 0.3	-0.455	2.07 ± 0.05	6837.5 ± 0.8	264.0	1.55 ± 0.02	1.5		
K H44	-28.3 ± 0.5	-0.370	3.06 ± 0.08	$928.0~\pm~0.8$	18.2	3.01 ± 0.03	2.7-3.0		
Weathered Morton Gneiss									
Locality 3	-46.7 ± 0.4	-0.522	3.58 ± 0.03	3548.7 ± 3.0	98.7	2.14 ± 0.02	3.2-3.8¶		
Locality 5	-36.9 ± 0.3	-0.506	$2.92~\pm~0.03$	2099.4 ± 2.0	69.4	1.80 ± 0.02	3.2-3.8¶		
CHUR (Sm/Nd)	0.0	0.0							
UR (Rb/Sr)				0.0	0.0				

*Errors are 2 σ_{mean} . †Measured ¹⁴³Nd/¹⁴⁴Nd and ⁸⁷Sr/⁸⁶Sr values can be calculated from Eqs. 5 and 8, respectively, and the $\varepsilon_{Nd}(0)$ and $\varepsilon_{Sr}(0)$ values listed above. ‡For ¹⁴⁷Sm, $\lambda = 6.54 \times 10^{-12}$ year⁻¹; for ⁸⁷Rb, $\lambda = 1.39 \times 10^{-11}$ year⁻¹. §For the Canadian Shield composites, T_{geol} is the previously determined radiometric age from samples within the same province. ||For the sedimentary rocks, T_{geol} is the best estimate of the time at which the sediment was formed, based on the stratigraphic age or radiometric age determinations. ||For the sedimetric age of fresh Morton Gneiss.

that the fractionation of Sm and Nd was contemporaneous with that of Rb and Sr. From these data, the enrichment of Rb/ Sr in the upper crust appears to be a primary feature of continental crust, being associated with the formation of new crust, and does not reflect metasomatic or metamorphic processes at later times.

The enrichment factors $f_{\rm Rb/Sr}$ in the Churchill Province composites are approximately a factor of 2 greater than those in the Superior and Slave composites. This distinction may be attributable to more extensive erosion of the Superior and Slave provinces, exposing a greater proportion of a lower crust more depleted in Rb. Consistent with this is the relatively widespread occurrence in the Superior Province of granulite facies rocks (41), which are indicative of formation depths greater than ~ 20 km. An analogous variation of $f_{Sm/Nd}$ is not present in the same composites. Thus, although Sm and Nd were fractionated at the same time as Rb and Sr, their relative elemental distributions through the continental crust do not appear to be correlated

The Sm-Nd and Rb-Sr isotopic studies of composite samples can, of course, be applied to other continental segments to ascertain average times of formation with relatively few analyses. This approach may be particularly useful where there is little or no other radiometric age information indicative of formation times of new crust, or where complex metamorphic processes make the identification of primary magmatic crystallization ages difficult.

Sediments

In many respects, sedimentary rocks are similar to the Canadian Shield composites. They were originally derived from igneous and metamorphic rocks and often consist of materials from diverse sources. However, although sedimentary rocks cover approximately 80 percent of the continent's surface (42), attempts to characterize and identify their provenances by using isotopic tracers have not been extensively pursued (2, 43). This is mainly due to the disturbance of these systems by chemical processes during or after sedimentation. In particular, many trace elements are fractionated as a result of preferential weathering of specific mineral phases and of the formation of authigenic minerals such as clays. However, because of the geochemical coherence and short residence times of REE in seawater, the Sm-Nd isotopic system may be less susceptible to disturbance during sedimentation and diagenesis. This is apparent from Table 3, where the $f_{\rm Sm/Nd}$ values for the sediments are all approximately the same and are also similar to those estimated for the upper crust (Table 1). This suggests that the Sm-Nd isotopic system may remain closed during sedimentation and diagenesis, in which case the $T_{\rm CHUR}^{\rm Nd}$ age would represent the average time of formation of the crust from which the sediments were derived. The sediments could be derived from this crust either directly, or indirectly from recycled materials. In contrast, $f_{\rm Rb/Sr}$ is variable and in some sediments is up to a factor of 30 greater than the average upper crustal estimates in Table 1. These large $f_{\rm Rb/Sr}$ values show loss of Sr relative to Rb in the sediments, probably due to the formation of clay minerals such as illite and montmorillonite, within which Rb is strongly fixed relative to Sr (22, 44). Depending on the relative increase in $f_{\rm Rb/Sr}$ and the initial ⁸⁷Sr/⁸⁶Sr of the sediment, it would be expected that the $T_{\rm UR}^{\rm S\,r}$ age will be less than the time of formation of new crust and will approach the time of deposition or diagenesis of the sediment.

In an attempt to ascertain directly the effect of weathering on the Sm-Nd and Rb-Sr isotopic systems, we analyzed two samples from the weathered profile of the Morton Gneiss in the Minnesota River valley. These samples are the same as those used by Goldich (45) in his classic study of rock weathering. The profile consisting predominantly of quartz and kaolinite was developed during the Cretaceous in a humid tropical or subtropical climate by weathering of Precambrian gneisses and igneous rocks. The sample from Goldich's locality 3 has a $T_{\text{CHUR}}^{\text{Nd}}$ age of 3.58 \pm 0.03 AE and a distinctly younger $T_{\rm UR}^{\rm S\,r}$ age of 1.80 ± 0.02 AE. The sample from locality 5 has a $T_{\rm CHUR}^{\rm N\,d}$ age of 2.92 \pm 0.03 AE and a $T_{\rm UR}^{\rm S\,r}$ age of 2.14 ± 0.02 AE. The markedly younger $T_{\text{UR}}^{\text{S r}}$ ages and large $f_{\text{Rb/Sr}}$ values of 98.7 for locality 3 and 69.4 for locality 5 are probably due to loss of Sr relative to Rb during the weathering, or to earlier metamorphic events (32). The K-Ar and Rb-Sr ages of biotites were obtained from the same samples by Goldich and Gast (46). These ages are 25 to 75 percent lower than those obtained from biotites in the fresh Morton Gneiss and indicate preferential loss of radiogenic Sr and Ar. In addition, zircons analyzed from locality 3 (47) are highly discordant, with a minimum age of 0.455 AE, which has been attributed to bulk loss of lead by leaching (47). The T_{CHUR}^{Nd} age from locality 3 is within the age range of 3.2 to 3.8 AE found for fresh Morton Gneiss (32), indicating that the Sm-Nd system remained closed during weathering and

metamorphism. However, the T_{CHUR}^{Nd} age of 2.92 AE from locality 5 is difficult to interpret, as it could be attributed either to the presence of a large component of younger rocks, which are often associated with the Morton Gneiss (32), or to effects of weathering. This cannot be resolved in this geologically complex area and must be addressed by future studies in more carefully defined geologic settings.

To test this approach further, we chose an example of a sediment derived from a relatively young crustal source. We analyzed a shale from the Rosario Formation, Punta San Jose, western Baja California, Mexico (Baja Shale), which contains marine fossils of Maestrichtian age (~ 0.065 AE) and is isolated from older mainland material. Its source was most probably Jurassic or Cretaceous eugeosynclinal rocks, which are predominant in this region. No Precambrian terranes appear to be available as possible source regions. Its $\epsilon_{Nd}(0)$ value of $+0.7 \pm 0.4$ is clearly characteristic of a very young source and markedly different from the large negative $\epsilon_{ND}(0)$ for older sources. The $T_{\rm UR}^{\rm S\,r}$ age of 0.030 \pm 0.001 AE, although more reasonable than the T_{CHUR}^{Nd} age, is somewhat younger than the time of deposition. These results reflect the sensitivity of rocks with young sources to the detailed assumptions of their evolutionary history. However, both of these results clearly are compatible with the very young age of the crustal sources that constituted the provenance for this shale.

As an example of a young detrital sediment, derived from old source material, we analyzed sand (San Gabriel Sand), which was collected from the mouth of Santa Anita Canyon in the San Gabriel Mountains of Southern California. The rocks in this area are predominantly granitic rocks of Mesozoic age (48), although a wedge of Precambrian gneisses is present at the mouth of the canyon (49). This sample has $\epsilon_{\rm Nd}(0) = -9.9 \pm$ 0.4 and a relatively small value of $f_{\rm Sm/Nd} = -0.225$, giving a $T_{\rm CHUR}^{\rm Nd}$ age of 1.77 ± 0.09 AE. This suggests that most of the sample was derived from the older Precambrian gneisses. However, the $f_{\rm Rb/Sr} = 5.16$ together with the low value of $\epsilon_{\rm Sr}(0) = 59.5 \pm 0.8$ gives a calculated $T_{\text{UR}}^{\text{S r}}$ age of 0.69 \pm 0.02 AE. The $T_{\text{UR}}^{\text{S r}}$ age is markedly younger than the T_{CHUR}^{Nd} age, but the low $f_{\rm Rb/Sr}$ is not consistent with Sr loss or Rb fixation during weathering of this material. Further isotopic characterization of the possible sources of the San Gabriel Sand are required to resolve this problem.

To ascertain the self-consistency of this approach, sediments representing a SCIENCE, VOL. 200

range of depositional ages were studied. These sediments are from the Australian continent, and their locations are shown in Fig. 4. They were part of a REE distribution study by Nance and Taylor (50). The Australian sediment with the youngest depositional age is the Silurian State Circle Shale (SC-5). It has a measured $\epsilon_{Nd}(0) = -14.5 \pm 0.4$ and a resulting $T_{\text{CHUR}}^{\text{Nd}}$ age of 1.32 \pm 0.05 AE. However, the nearest exposed Precambrian rocks that could have acted as sources for this sediment are now approximately 720 km to the west. This suggests either that SC-5 was not locally derived or that it was derived from recycled older sedimentary material, which had in turn been derived from Precambrian sources. An exceedingly large enrichment of Rb relative to Sr is found in this sediment, which has $f_{\rm Rb/Sr} = 293$; together with the measured $\epsilon_{\rm Sr}(0)$, this gives a $T_{\rm UR}^{\rm Sr}$ age of 0.509 ± 0.005 AE. This age is only slightly greater than the age of 0.440 ± 0.009 obtained from an Rb-Sr isochron by Bofinger et al. (51). A shale (AO-7) from the Pertakaka Formation in the Amadeus basin, central Australia, has a depositional age of 0.8 AE (52) and $\epsilon_{\rm Nd}(0) = -16.8 \pm 0.4$, giving a $T_{\rm CHUR}^{\rm Nd}$ age of 1.56 ± 0.05 AE. The Musgrave-Mann and Arunta complexes that surround the Amadeus basin have Rb-Sr and K-Ar ages ranging from 1.1 to 1.8 AE (52). These ages are compatible with the $T_{\rm CHUR}^{\rm N\,d}$ age, which suggests that these complexes could have acted as the source of this sediment. For AO-7 $f_{\rm Rb/Sr} = 71.6$ which, together with the measured $\epsilon_{\rm Sr}(0)$, gives a $T_{\rm UR}^{\rm Sr}$ age of 0.95 ± 0.01 AE, compared with an age of 0.79 AE obtained previously from Rb-Sr studies (52). A shale (MI-1) from the Mount Isa Geosyncline, Mount Isa, Queensland, has $f_{\rm Rb/Sr} = 264$ and a $T_{\rm UR}^{\rm S\,r}$ age of 1.55 ± 0.02 AE. This is in good agreement with the estimated depositional age of approximately 1.5 AE (53), indicating that the massive enrichment of Rb relative to Sr occurred at this time. From the measured $\epsilon_{\rm Nd}(0) = -23.5 \pm 0.3$ a $T_{\text{CHUR}}^{\text{Nd}}$ age of 2.07 \pm 0.05 AE is calculated for MI-1. Zircon and Rb-Sr total rock ages of 1.86 and 1.84 AE, respectively, have been determined (54) from the oldest unit in the Mount Isa basement sequence, the Leichardt metamorphics. These ages, in conjunction with the T_{CHUR}^{Nd} age, suggest that the shale could have been derived mainly from this source, but with an additional component of substantially older age.

The application of Sm-Nd isotopic systematics to calculate the T_{CHUR}^{Nd} provenance age may also be particularly useful for older sediments, whose sources may no longer be preserved or recogniz-

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Fig. 4. Map of Australia showing the areas sampled (50). The approximate areas of outcrop of the sampled or related units are shaded.

able. An example is the graywacke KH44 from Coolgardie, Western Australia, which has a depositional age of approximately 2.6 to 3.0 AE and is part of the Archean granite-greenstone terrain prevalent in this area. The graywacke KH44 has $\epsilon_{\rm Nd}(0) = -28.3 \pm 0.5$, giving a $T_{\rm CHUR}^{\rm N\,d}$ age of 3.06 ± 0.08 AE. This is consistent with the younger age limit of 2.76 AE determined by Oversby (55) from granitic intrusives in the neighboring areas, but indicates a significant contribution of substantially older crust that has not yet been found, although there are other hints of it (55). The $T_{\text{UR}}^{\text{sr}}$ age of 3.01 ± 0.03 AE for KH44 is identical, within errors, to the T_{CHUR}^{Nd} age. This agreement may be explained by the fact that the $f_{\rm Rb/Sr}$ value of 18.24 is relatively low compared to those of other sediments.

Another example of a sediment from an Archean granite-greenstone terrain is the Figtree shale from the Swaziland system in South Africa. The Figtree Group conformably overlies the relatively well preserved Onverwacht Group, whose ages as summarized by Jahn and Shih (35) range from 3.2 to 3.5 AE. From the measured $\epsilon_{\rm Nd}(0) = -28.0 \pm 0.4$, a $T_{\rm CHUR}^{\rm Nd}$ age of 3.53 ± 0.06 AE is calculated for the Figtree shale. This is consistent with its derivation from the underlying Onverwacht Group, although at the upper limit of the proposed age range (35). Allsopp et al. (21) obtained an Rb-Sr isochron of 2.98 \pm 0.02 AE from the Figtree shale. Interpreted as the minimum age of the shale, the isochron clearly demonstrates that redistribution of Rb and Sr has occurred during sedimentation and diagenesis. The $T_{\text{UR}}^{\text{S}\,\text{r}}$ age of 2.94 \pm 0.03 AE that we obtained for a radiogenic sample with $f_{\rm Rb/Sr} = 90.6$, where the assumptions regarding the initial ⁸⁷Sr/⁸⁶Sr are relatively unimportant, is consistent with the age of Allsopp et al. (21). Thus

the $T_{\text{CHUR}}^{\text{Nd}}$ age indicates that the Figtree shale was derived from a source with a mean age of crustal formation of 3.53 AE, and the $T_{\text{UR}}^{\text{Sr}}$ age in conjunction with the large $f_{\text{Rb/Sr}}$ value suggests that the sediment was probably deposited ~ 2.94 AE ago.

For many sedimentary rocks the provenance is obscure or a complete enigma. Classic examples are the loess deposits that cover areas extending from northcentral Europe to eastern China and are found in the Mississippi Valley and the northwest United States. Their origin is still controversial (56), but they are generally believed to be eolian dust of Pleistocene age derived from desert surfaces, from alluvial valleys, or from unconsolidated glacial or glaciofluvial deposits. In an attempt to characterize their source regions, we analyzed loess deposits from Iowa, United States, and Nanking, China. The Iowa loess has $\epsilon_{\rm Nd}(0)$ = -14.1 ± 0.5 and $f_{\rm Sm/Nd}$ = -0.411, giving a T_{CHUR}^{Nd} age of 1.38 ± 0.06 AE. From these data, we infer that a major component of material from the older $[\epsilon_{\rm Nd}(0) = -30, T_{\rm CHUR}^{\rm Nd} \sim 2.6 \text{ AE}]$ Canadian Shield is prohibited. However, a composite of Paleozoic North American shales (NAS) of Haskin et al. (57) having $\epsilon_{\rm Nd}(0) = -14.5 \pm 0.5$ and $T_{\rm CHUR}^{\rm Nd} = 1.52$ \pm 0.07 AE (6) is almost identical to the Iowa loess. Hence the Paleozoic sediments, or a source similar to the source of Paleozoic sediments, could have provided materials for the Iowa loess. The penultimate source must, of course, be rocks with a mean crustal formation age of ~ 1.38 AE. Rocks of this approximate age are not widely exposed, although radiometric ages have been obtained (58) in the range 1.0 to 1.7 AE from numerous drill core samples of basement from the midcontinental region of the United States. These data suggest that a substantial component of the Paleozoic



NAS composite was probably derived from this Precambrian basement or from recycled materials derived from this basement. If the Nd isotopic composition $[\epsilon_{Nd}(0)]$ and $f_{Sm/Nd}$ of NAS is representative of the average from the midcontinental region of the U.S. crust, then the similarity with the Iowa loess suggests that loess deposits may also be good averages of large areas of continental crust. Hence the Nanking loess with $\epsilon_{\rm Nd}(0)$ = -10.2 ± 0.4 and $f_{\rm Sm/Nd}$ = -0.410, giving a $T_{\rm CHUR}^{\rm Nd}$ age of 1.00 ± 0.05 AE, may indicate that this part of the Asian continent is on the average approximately 0.40 AE younger than the North American continent. Only relatively moderate enrichments of Rb relative to Sr have occurred during the formation of these loesses, with $f_{\rm Rb/Sr} = 15.3$ for the Iowa loess and 34.3 for the Nanking loess. As a consequence, the $T_{\text{UR}}^{\text{S r}}$ ages of 0.71 ± 0.01 AE for the Iowa loess and 0.350 ± 0.005 AE for the Nanking loess are younger than the time of formation of their provenance as given by the $T_{\rm CHUR}^{\rm Nd}$ age and older than their time of deposition (Pleistocene).

Another example of a rock whose provenance is unknown is the Birch Creek Schist of the Alaska Range which, together with the correlated metasediments in the Yukon-Tanana Upland, constitutes a pervasive formation in this area. It is predominantly a quartz-sericite and quartz-sericite-calcite schist, and its metamorphic grade has been established as greenschist facies (59). No original sedimentary structures are preserved, the foliation within the formation being due to alignment of sericite flakes and segregations of quartz and sericite. The Rb-Sr and K-Ar age measurements on micas from the polymetamorphosed Birch Creek Schist indicate that it was locally metamorphosed at 0.12 to 0.18 AE (60). Total rock Rb-Sr ages from (60) range from 0.664 to 1.17 AE, but do not uniquely indicate a Precambrian age, as they are also compatible with a younger period of metamorphism. A sample of the Birch Creek Schist in the Healy D-4 Quad of Alaska has $\epsilon_{\rm Nd}(0) = -27.0 \pm 0.3$ and $f_{\text{Sm/Nd}} = -0.464$, giving a $T_{\text{CHUR}}^{\text{Nd}}$ age of 2.33 \pm 0.05 AE. This is definitive evidence that the Birch Creek Schist was derived predominantly from an ancient Precambrian source, which was probably the adjacent older portion of the Canadian Shield with a small component of younger crustal materials. The age of formation of the schist has not been established, although the $T_{\rm UR}^{\rm S\,r}$ age of 0.714 ± 0.008 AE is similar to the total rock Rb-Sr ages of Wasserburg et al. (60) and is suggestive of an early Paleozoic or late Precambrian depositional or metamorphic age for the schist.

"Red" clay is a sedimentary material predominant in the deeper parts of the ocean basis under surface waters of low biological productivity. The source of red clay is still open to dispute, its formation being attributed to eolian or currenttransported continental material and to decomposed volcanic ejecta and pyroclastics (61). We analyzed a sample of red clay obtained by the Deep Sea Drilling Project (leg V, hole 37, core 3, section 2, 22 to 24 cm, abyssal hill, northeast Pacific Ocean). For this sample $\epsilon_{\rm Nd}(0) = -3.3 \pm 0.4$ and $f_{\rm Sm/Nd} = -0.212$, giving a $T_{\text{CHUR}}^{\text{Nd}}$ age of 0.63 ± 0.08 AE, which is consistent with the idea that red clay is composed only of continental material with a mean age of 0.63 AE. This is much younger than the mean age of either the North American or the Asian continent as ascertained from the loess and shale results. It may be more reasonable to assume that the red clay consists of a mixture of oceanic basalt with $\epsilon_{\rm Nd}(0) \approx \pm 10$ and $f_{\rm Sm/Nd} \approx 0$ (7), island arc volcanics with $\epsilon_{Nd}(0) = +7$ and $f_{\rm Sm/Nd} \approx -0.28$ (62), and continental material such as the Iowa loess with $\epsilon_{\rm Nd}(0) = -14.1$ and $f_{\rm Sm/Nd} = -0.411$. For example, the Sm-Nd isotopic characteristics of this red clay could be accounted for by a mixture of approximately equal proportions of oceanic basalt, island arc volcanics, and Iowa loess. However, regardless of the proportions, the Sm-Nd results require a significant component of continental material. The Rb-Sr isotopic characteristics of the red clay $[\epsilon_{\rm Sr}(0) = +53.7 \text{ and } f_{\rm Rb/Sr} = 8.41] \text{ can al-}$ so be accounted for by similar proportions of oceanic basalt [$\epsilon_{sr}(0) \approx -25$ and $f_{\rm Rb/Sr} \approx -0.7$] (3), island arc volcanics $[\epsilon_{\rm Sr}(0) \approx -15 \text{ and } f_{\rm Rb/Sr} \approx 0.4]$ (62), and Iowa loess $[\epsilon_{\rm Sr}(0) = +181.1$ and $f_{\rm Rb/Sr} = 15.3$]. This agreement may, however, be fortuitous as the observed $\epsilon_{sr}(0)$ value of the red clay may also have been produced by exchange of Sr with seawater, which has $\epsilon_{sr}(0) = +65$.

For all the sediments that we studied, with only one exception (Baja Shale), the $T_{\rm CHUR}^{\rm N\,d}$ ages have been greater than the sedimentation age and less than the 'age'' of the earth (4.47 AE) (63). In addition, where known, the ages of crystallization or formation of likely source areas have been consistent with $T_{\rm CHUR}^{\rm Nd}$ ages. This self-consistency is also apparent in the $f_{\rm Sm/Nd}$ values, which are generally within the same range as those estimated for the upper crust (Table 1). This indicates that for the sedimentary rocks that were studied, the assumptions of no fractionation of Sm/Nd and no exchange of Nd since derivation from the CHUR reservoir are plausible. Possible exceptions may be the San Gabriel Sand and the Baja Shale, whose smaller enrichment factors may reflect fractionation of Sm from Nd during the sedimentary process. However, from previous REE distribution studies (13-15, 57) it appears more plausible to assume that these variations in Sm/Nd are simply a result of variations of Sm/Nd in the sediment source. In contrast, massive enrichments of Rb relative to Sr of up to a factor of 30 are often found in the sediments compared to their likely sources. As a consequence, the $T_{\rm UR}^{\rm S\,r}$ ages usually approach the time of sedimentation or diagenesis and are generally younger than the corresponding T_{CHUR}^{Nd} age. The calculated T_{CHUR}^{Nd} ages are interpreted to be the average ages of formation of the crustal sources from which the sediments were derived. These formation ages also appear to be retained in recycled sediments such as SC-5. Thus, $\epsilon_{\rm Nd}(0)$ and $f_{\rm Sm/Nd}$ parameters are characteristic of the sediment provenance and $T_{\rm CHUR}^{\rm Nd}$ is the provenance age.

Conclusions

The Sm-Nd and Rb-Sr isotopic systematics, together with plausible assumptions regarding the geochemical evolution of continental crustal materials, have been used to ascertain the times at which new segments of continental crust were formed. The general approach that has been used is to assume that the dominant contribution to the continental crust comes from the emplacement of magmatic rocks derived from a uniform mantle reservoir, and that the differentiation processes that produce the magmatic rocks occur with a marked chemical fractionation of the daughter and parent elements relative to the source region. It is the time of this chemical fractionation from the penultimate provenances that has been dated. These times of formation of new crust have been obtained from an extremely diverse range of rocks, including metamorphic and sedimentary rocks and composites of igneous and metamorphic rocks from different structural provinces of the Canadian Shield.

Analyses of composites representing portions of the Superior, Slave, and Churchill structural provinces indicate that these provinces were all formed within the period 2.5 to 2.7 AE. The times of formation of the Superior and Slave provinces are in agreement with previously determined K-Ar and Rb-Sr ages, but the time for formation of the Churchill Province, as represented by the Baffin Island and Saskatchewan composites, is approximately 0.8 AE greater than the K-Ar age. From our present knowledge of the times of formation of continental crust, it appears that the activity around the period 2.5 to 2.7 AE is unique in geologic history and that some truly major periods of continental growth are sharply episodic. A younger (1.0 AE) age obtained for the Grenville Province indicates the addition at this time of new crust onto the preexisting Canadian Shield.

Studies of sedimentary rocks indicate that the Sm-Nd isotopic systematics are not substantially disturbed during sedimentation or diagenesis, which has made it possible to determine the mean crustal formation age of their provenances. In contrast, Rb-Sr studies of these sediments have shown pronounced enrichments of Rb relative to Sr (up to a factor of 30). Depending on the relative enrichment, the Rb-Sr ages from the sediments are generally more compatible with the time of sedimentation or diagenesis. The Sm-Nd provenance ages have been used to characterize and, in particular cases, to identify the provenance of the sediment. This has enabled old crust that acted as the source for Archean sediments to be identified in the Yilgarn Block of Western Australia and in the Swaziland System from South Africa. The mean age of large areas of the North American and Asian continents has also been ascertained from the provenance ages of loess deposits. As an example of the characterization of sediment provenances by using Sm-Nd systematics, we showed that deep-sea red clay cannot be produced by only oceanic or island arc volcanism but also requires a significant component of continental material. In addition, a sample of widespread metasediment (Birch Creek Schist) from Alaska has a provenance age indicating derivation from the older portion of the Canadian Shield. Determinations of model crustal formation ages on sediments and on composite samples of welldefined lithologies with a broad distribution may prove to be useful as an aid to geologic mapping and to the better definition of geologic provenances.

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