Sm-Nd ISOTOPES IN FINE-GRAINED CLASTIC SEDIMENTARY MATERIALS: CLUES TO SEDIMENTARY PROCESSES AND RECYCLING GROWTH OF THE CONTINENTAL CRUST

Sam CHAUDHURI(*)
Department of Geology, Kansas State University
Manhattan, Kansas 66506 (USA)

Peter STILLE and Norbert CLAUER
Centre de Géochimie de la Surface
1 rue Blessig, 67084 Strasbourg (France)

Fine-grained clastic sedimentary rocks, which make up about 60 to 70 percent of the present-day sedimentary mass, almost always consist of large amounts of detrital minerals derived from multiple source rocks and some small amounts of diagenetic materials. Hence, the tracing of origin of the detrital particles to source rocks has been often extremely difficult. Age determinations by K-Ar and Rb-Sr isotopic methods have shown that many uncertainties attend the determination of source rocks for sedimentary materials by these isotopic methods, because the processes of weathering, erosion, transportation, and diagenesis for sedimentary rocks, and also the processes of metamorphism for metasedimentary rocks, cause unpredictable changes in the relations of parent-daughter isotopes of the clastic materials with respect to that of their sources.

The Sm and Nd elements which belong to a group of rare-earth

(*) Presently at the Centre de Géochimie de la Surface, Strasbourg (France)

elements (REE), have close chemical similarity. This behavior allows limited fractionation between them by intracrustal processes. Mantle-crust differentiation is the main process which produces significant differences in the Sm/Nd ratios among large terrestrial reservoirs. Little fractionation seems to occur in the crustal materials by intracrustal sedimentary processes, metamorphism, and even partial melting. As the Sm/Nd ratios seem to remain nearly unaffected against changes by intracrustal processes, the Sm-Nd isotopic systems of clastic sediments and sedimentary and metasedimentary rocks have become subjects of much studies in recent years following the work of McCulloch and Wasserburg (1978) which revealed that such analyses can provide much information about the history of the continental crust (DePaolo et al., 1983; Hamilton et al., 1983; O'Nions et al., 1983; Taylor et al., 1983; Allègre and Rousseau, 1984; Frost and O'Nions, 1984; Goldstein et al., 1984; Miller and O'Nions, 1984; Patchett et al., 1984; Clarke and Halliday, 1985; Davies et al., 1985; Heller et al., 1985; Michard et al., 1985; André et al., 1986; Frost and Winston, 1987; Huhma, 1987; Nelson and DePaolo, 1988; Goldstein and Jacobsen, 1988; McLennan et al., 1990; Nägler, 1990).

The approach to an understanding of the question of continental crustal history based on analysis of sedimentary materials requires that sediments or sedimentary rocks are approximately a good representative of the average composition of a large continental region. Coarse-grained clastic sediments and sedimentary rocks generally have a limited transportation history. The assemblage of detrital particles in these rocks is often biased by the effect of sorting during transportation. Also, the particles in these rocks have often derived by erosion of rocks from a limited continental area. Consequently, coarse-grained sediments and sedimentary rocks are generally not suitable for the Sm-Nd isotopic investigation of crustal evolutionary history. Carbonate sedimentary rocks may contain chemical sedimentary components with a history of differentiation between Sm and Nd and these rocks are generally low in total REE contents as compared to the clastic sedimentary rocks (Haskin et al., 1966; Piper, 1974; Elderfield et al., 1981; Shaw and Wasserburg, 1985). By contrast, fine-grained sediments and sedimentary rocks, in general, consist of large amounts of detrital particles with history of long transportation and well mixing of components derived from a large continental region. Fine-grained clastic sediments and sedimentary rocks generally have a limited range of Sm/Nd ratios (McLennan, 1989). The narrow range of the ratios is probably a reflection of well mixing of the fine particles by their long transport from the site of weathering and erosion in the continent to the site of deposition often in marine sedimentary basins. Because of the very common REE characteristics among vast numbers of fine-grained clastic sediments and sedimentary rocks, and their Sm/Nd ratios being very similar to that of granitoid rocks, the Sm/Nd ratios of the fine-grained materials are taken to be good representatives of average Sm/Nd ratio of large segments of continental crust from which the clastic particles derived. Hence the fine-grained clastic sedimentary materials have been the focus of a large number of Sm-Nd isotopic studies to obtain information about erosion and evolution of the continental crusts. This article summarizes the benefits of Sm-Nd isotopic studies on sediments and sedimentary rocks in understanding sedimentary processes and growth of the continental crust.

The understanding of continental crustal history by the analyses of Sm-Nd isotopes in sedimentary rocks requires an assumption that the two elements were do not significantly fractionated by intracrustal processes. We will briefly review the merits of such an assumption in the analyses of sedimentary materials. Calculations of Sm/Nd model ages are necessary to understand the evolutionary history of sediments and sedimentary rocks. For a non-specialist who is not altogether familiar with the manipulation of Sm-Nd model ages, we will define the meaning of these ages and discuss how different factors could influence the calculated model ages on sedimentary materials. Additional details are given by Faure (1986) and DePaolo (1988b).

MODEL AGES OF SEDIMENTS

The Sm-Nd model age of a sample of clastic sediment or sedimentary rock is calculated based on the comparison between the growth of the $^{143}Nd/^{144}Nd$ ratio of the sample and that of the upper mantle as a function of time. The calculated age relates to the time when the sample and the upper mantle had the same Nd isotopic composition, or in other words, when the sample or its constituent particles appeared for the first time as an entity of the continental crust by differentiation from a depleted mantle source. In a vast majority of studies, the model age is neither the age of deposition of the sediments, nor, in the strict sense of provenance, the age of the source rock, because almost always clastic sedimentary rocks consist of particles of diverse origin. Even in the case of a derivation of a sedimentary rock from a single source rock, the Sm-Nd model age of the sedimentary components will not correspond to the age of formation of the source rock if that source rock itself derived from an older crust. Hence the meaning of a Sm-Nd model age of a sedimentary rock can be best described as an average time of the continental crust forming events of the constituent particles. But it must be clear in mind that the model age does not imply a specific crust forming event. That is why some have preferred to use the term average "crustal residence age," and not a crust-formation age, when referring to the Sm-Nd model age of a sedimentary rock (O'Nions et al., 1983).

The procedure for calculation of a Sm-Nd model age and the the expression of the Nd isotopic composition of a sample in terms of the $_{Nd}$ value can be found in Faure (1986), DePaolo (1988b), and also in the introduction of this volume. The choice of the source mantle for continental crustal rocks will influence the calculated Sm-Nd model age. Most consider a depleted mantle for the derivation of the continental crust, but difference exists as to presumed evolutionary characteristic of the depleted upper mantle and its specific Nd isotopic value, which may lead to a difference in the calculated age by about 200-300 Ma (DePaolo, 1981; Goldstein et al., 1984; Nelson and DePaolo, 1985).

In addition to the choice of appropriate parameters for a depleted mantle source for the evolution of the crustal materials, the Sm-Nd model age of sediments can be influenced by their evolutionary history during the time of their residence in the crust.

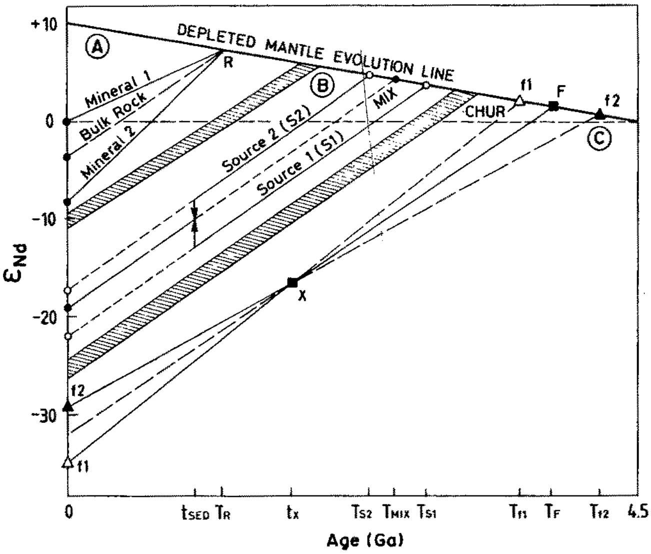

Figure 1: Illustration of the influence of sedimentary or intracrustal processes on the calculated Sm-Nd model age with respect to the crustal forming event. Part (A): transportation related sorting of different components from the same source; T_R is the age of a crust formation event R. Part (B): mechanical mixing of sediments of different sources; t_{sed} is the time of sedimentation, T_{s1} and T_{s2} are periods of crust formation events respectively for sources s1 and s2, T_{mix} is the calculated model age for the mixed sediments. Part (C): t_x is a time of differentiation between Sm and Nd due to diagenesis or metamorphism, T_{f1} is a calculated model age for a component whose Sm/Nd ratio is lower than that of the original source material, T_{f2} is a calculated model age for a component whose Sm/Nd ratio is higher than that of the original source material.

When components formed from a common source are seggregated due to sorting by transportation without having any significant modification of their respective Sm/Nd ratios, each component individually will still have the same model age, although the components will differ in their measured Nd isotopic compositions (Fig. 1 part A). The Nd isotopic evolution and Sm-Nd model age of sediments formed by mixing of materials derived from sources with different continental crustal histories are shown in part B of figure 1. Following the mixing, the Sm-Nd evolution of the mixed sample will occur at a rate intermediate between that of the two components and the resulting model age will be an intermediate value between the model ages of the two components, which is proportional to the relative amounts of each end member, weighted by the rare earth element (REE) concentrations in each end member. The interpretation of a model age can be complicated if the Sm-Nd of a system may be disturbed by an intracrustal process (weathering, diagenesis, and metamorphism) at some time which is much later than the time of formation of the system as a crustal entity, and the error in the calculated age is proportional to the difference of time between the crust formation and the intracrustal Sm-Nd fractionation (Fig. 1 part C). The material whose Sm/Nd ratio has been lowered by any disturbance will yield a lower Sm-Nd model age and the one whose Sm/Nd ratio has been elevated will yield a higher model age than the corresponding undisturbed material.

Sm-Nd FRACTIONATION DURING SEDIMENTARY PROCESSES

Sm-Nd Fractionation during Weathering

Balashov et al. (1964) concluded that subaerial weathering preferentially removes the heavy REE, but the quantity of the REE being removed is extremely small. They attributed this preferential removal of the heavy REE to the increased stability of carbonate complexes of the heavy REE as compared to the light REE. Recently, Goldstein and Jacobsen (1987) have shown that the Sm/Nd ratio of dissolved loads is higher than that of suspended loads in most rivers. Considerable evidence now exists that spring waters and streams selectively remove HREE from source rocks, although the absolute content of the dissolved REE in these waters, having concentrations of tens or few hundred parts per trillion, is extremely small as compared to that in solid source materials having a few hundred parts per million of the REE (Michard et al., 1987; Goldstein and Jacobsen, 1988). The evidence from analyses of dissolved loads of rivers and springs makes evident that in theory at least some difference can be expected in the relative abundances of Sm and Nd between weathered products and their source rocks. But the degree of changes in the Sm/Nd ratios from source materials to weathered products is difficult to document in the evolution of sediments and sedimentary rocks because of the potential for modification of the ratio by sedimentary processes subsequent to weathering. Nevertheless, evidence has been gathered that weathered products could differ substantially from their source materials in their Sm/Nd ratios.

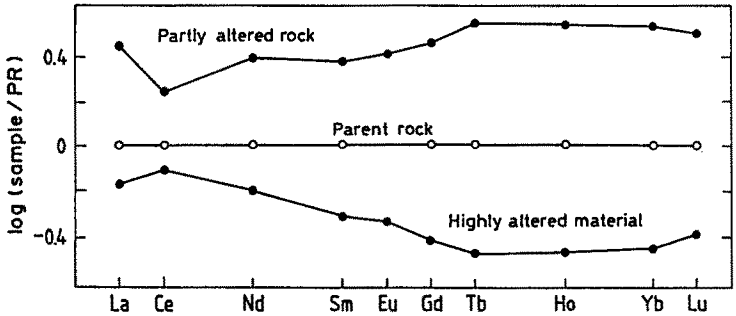

Figure 2: Concentrations of REE in partly and highly weathered material relative to parent unaltered material (after Nesbitt, 1979)

Studies are few which have carefully explored the paths of changes in relative and absolute contents of the REE between source rocks and their associated weathered products. Burkov and Podporina (1967) observed considerable preferential mobilization of the light REE in the formation of kaolinite from weathering of granite and granodiorite in an acidic environment. Roaldset and Rosenqvist (1971b) noted that considerable amounts of REE can be removed from weathered micas by leaching with EDTA, suggesting that the REE can be quite mobile in a weathering environment. Balashov and Girin (1969) also found from experimental work that as much as 95% of the REE in clays can be leached by acid, which suggests that the REE can be mobilized during weathering and subsequent processes.

Nesbitt (1979) compared the absolute and relative abundances of the REE between a parent granodiorite and its associated weathered products. Incipiently to moderately altered parent materials consisted dominatly of vermiculite and Fe-Ti oxyhydroxide with minor amounts of kaolinite and illite as the weathered products, whereas the most altered products consisted essentially of kaolinite and illite with small amounts of Fe-Ti oxyhydroxide and no vermiculite. He observed that while incipiently to moderately altered parent granodiorite became enriched in the absolute REE content and relatively enriched in the heavy REE, the most altered residual product became depleted both in the absolute REE and in the relative abundance of the heavy REE relative to the parent material (Fig. 2). Nesbitt explained that the mobilization of the REE from the most altered zone to partially altered zone was due to increase in pH, but the fractionation of the REE elements was due to mineralogical controls. This study showed that the Sm/Nd ratio of the most altered clayey-residual product was as much as 20% lower than that of the parent rock.

Clauer et al. (1982), who investigated the effects of natural weathering on the REE pattern of biotite, observed general increase in the heavy REE relative to the light REE with increase in the degree of weathering of biotites. The weathered biotites experienced on the average an increase in the Sm/Nd ratio by about 50%, compared to unweathered biotite. Also, the absolute contents of both Sm and Nd, like the other REE, increased in the weathered biotites relative to the fresh biotite.

Middelburg et al. (1988), who investigated the mobilization and redistribution of the REE during weathering of granitic rocks, found that the REE were significantly mobilized and fractionated only during advanced stages of weathering. They concluded that selective leaching of the REE from both stable and unstable minerals and subsequent concentration in secondary phases may account for the observed fractionation.

The preceding discussion makes evident that a measurable degree of remobilization of Sm and Nd and fractionation between the two elements occur in the transformation from parent materials to weathered products. The pattern of these changes is apparently controlled by both minera-logy of the weathered products and chemistry of the transporting fluids being involved.

Sm-Nd Fractionation during Transportation and Deposition

Transportation related differentiation in the Sm/Nd ratio between fine-grained sediments and their source rocks could potentially arise from two effects, one by sorting of weathered and eroded particles having different Sm/Nd ratios and the other by differential amounts of adsorption of Sm and Nd by clay particles from waters due to changes in the pH or alkalinity and changes in the relative abundances of Sm and Nd in the waters. Stordal and Wasserburg (1986) noted a difference of as much as about 23% in the Sm/Nd ratios between two very small clay fractions of a suspended load from a river, but the actual cause of the difference is not known. Study is needed to determine the extent and cause of inter-particle variations in the Sm/Nd ratios among fine suspended loads of rivers.

Cullers et al. (1975) noted that kaolinites can have as much REE as illites and smectites, but, unlike illites and smectites, whose REE patterns approach close to that of average shale, kaolinites have widely varied light enriched REE patterns. Differential transport of clay particles in depositional basin has been known for long times. Kaolinite is often more abundant than other clay minerals in near shore sediments, suggesting that some differences in the Sm/Nd ratio could arise due to differential transport of the clay minerals in a sedimentary basin. Schieber (1986) made a suggestion based on the REE data of sediments from Belt Supergroup in Montana that the length of the transport of clays could have some influence on the relative distribution of the REE in these sediments. Thus, potential preferential sorting of clay minerals in ocean environments could make some degree of difference in the relative abundances of Sm and Nd between fine-grained nearshore sediments and equivalent offshore sediments. The study of Stordel and Wasserburg (1986) has already shown that estuarine entrapment of sediments can have some effect on the Sm-Nd differentiation of sediments that are being delivered by streams from the continents to the oceans.

Sm-Nd Fractionation during Diagenesis

From an investigation of bulk clay-sized fractions in samples of sediments from a deep well in the Gulf Coast, Chaudhuri and Cullers (1979) concluded that diagenesis caused no significant modification in the Sm/Nd ratios of these sediments. Recently, Awwiller and Mack (1991) claimed that diagenesis could have influenced the Sm-Nd model ages of Tertiary sandstones and shales from the Texas Gulf Coast. These ages increased with increased depth of burial. Ohr et al. (1991) found an evidence of diagenetic Nd isotopic equilibrium at depths below the smectite to illite transition zone for very fine particles ($<0.1\mu m$) in sediments from a deep well in the Texas Gulf Coast. They observed a spread in the Sm/Nd ratios between leachates and insoluble residues after acid leaching of the very fine clay particles, although the Nd isotopic compositions between the two phases were nearly identical for about eighty per cent of the cases. They concluded that these isotopic similarities reflected diagenetic isotopic equilibrium and the spread in the Sm/Nd ratio is due to fractionation related to illitization and concurrent precipitation of phosphate minerals. This explanation may not be entirely correct, which has been discussed later in this paper. Even by considering that the isotopic equilibriation occurs during diagenesis of very fine clay particles, the effect of such a process on the model age of fine-grained sediments in general appears to be small, because the amounts of such fine-grained materials in bulk clay sediments or shales are often extremely small.

Potential diagenetic Sm-Nd differentiation has also been suggested by both Stille and Clauer (1986) and Bros et al. (1992) based on Sm-Nd isotopic data defining isochrons. As explained later in this article, these isochrons, although yielding ages which are either the same or less than that of the deposition of the sediments, do not necessarily signify isotopic equilibriation at a post-depositional time.

Integrated Effect of Sedimentary Processes

An individual process may cause some differentiation in the Sm/Nd ratio between sediments and their source rocks, but this effect may be balanced by subsequent processes in the history of sediments. To document competing or complementary influences of weathering, transportation, deposition, and diagenesis in the Sm-

Nd history of sedimentary rocks is extremely difficult or may be impossible, because the effect of these different influences on the Sm/Nd ratios of sediments cannot be easily distinguished from effects due to differences in the provenance or in the mineralogy of what is weathered in a single provenance. Detailed information about the differentiation of the REE are given by Fleet (1984) and McLennan (1989).

What is clearly evident from the REE data on fine-grained sediments and sedimentary rocks and granitoid rocks is that their Sm/Nd ratios are very similar. The Sm/Nd ratios of many different granitoid rocks are commonly between 0.14 and 0.23, an average being about 0.19 (Haskin et al., 1966; Othman et al., 1984; Nelson and DePaolo, 1985; DePaolo, 1988a, DePaolo et al., 1991). Ratios as high as about 0.41 have been found for some granitoids, but they are considered to be few (Cullers and Graf, 1984). Clastic sediments and sedimentary rocks, like the common granitoid rocks, have also a similarly narrow range of Sm/Nd ratios. A large number of studies on clay minerals of sedimentary origin and on fine-grained clastic sedimentary rocks, especially those of continental platforms, have shown that the Sm/Nd ratios very often range between 0.15 and 0.21 with an average of about 0.19 (Haskin et al., 1966; Haskin and Haskin, 1966; Cullers et al., 1975, 1979; Dypvik and Brunfelt, 1976, 1979; Nance and Taylor, 1976; Fleet et al., 1980, Fleet, 1984; O'Nions et al., 1983; Taylor et al., 1983; Goldstein et al., 1984; Miller and O'Nions, 1984; Patchett et al., 1984; Michard et al., 1985; Bhatia, 1985; Nelson and DePaolo, 1988; Goldstein and Jacobsen, 1988; McLennan et al., 1989; Dia et al., 1990; Nägler, 1990). Whereas sediments of the continents and continental shelves have an average Sm/Nd ratio of about 0.19-0.20, those from deep oceans have an average value of about 0.21-0.22 (Patchett et al., 1984). The small difference in the Sm/Nd ratio between the two types of sediments is probably a reflection of the presence of some amounts of products of weathering of basalts or hydrothermal activities in the deep sea sediments. Nevertheless, the close similarity in the Sm/Nd ratios between fine-grained clastic sediments and sedimentary rocks and continental crystalline rocks is a sufficiently justifiable reason to assume that the Sm-Nd ratios are changed little by intracrustal processes of weathering, erosion, deposition, and diagenesis.

Sm-Nd ISOTOPES OF MODERN CONTINENTAL EROSIONAL PRODUCTS

Studies of Goldstein and Jacobsen (1987, 1988) and Goldstein et al. (1984) on river loads have considerably advanced our understanding of the Sm-Nd isotopes of modern erosional products and have given a bedrock knowledge for the interpretation of Sm-Nd isotopic data of sedimentary rocks. The Sm and Nd contents of many present-day river suspended loads range respectively between 3 and 11 $\mu g/g$ and between 12 and 59 $\mu g/g$. The Sm/Nd ratios are between 0.15 and 0.21 and the $^{143}Nd/^{144}Nd$ ratios are between 0.50967, or ϵ_{Nd} value of about -42, and 0.51160, or ϵ_{Nd} value of about -4, for suspended loads of rivers draining primarily Archean, Proterozoic and Paleozoic terrains, whereas the Sm/Nd ratios are as high as 0.28 and the $^{143}Nd/^{144}Nd$ ratios are as high as 0.51221, or ϵ_{Nd} value of about +7, for suspended loads of rivers draining young island or continental arcs, the high values being for the dominant presence of detrital components from a depleted mantle source.

Goldstein and Jacobsen (1988) found a close agreement in the Sm-Nd model ages between suspended loads and their apparent source rocks in the drainage basins underlain by Archean and island or continental arc rocks. But relating the suspended loads of many North American rivers to any clearly definable source rocks is not easy. The authors assumed a close correspondence between basement crystalline rocks in the drainage basin and the suspended loads. Based on this assumption, they found that the Sm-Nd model ages of the suspended loads are on the average 350 Ma younger than the Sm-Nd model ages of the basement rocks in the drainage basin. On the whole, the Sm-Nd model ages agreed reasonably well between the suspended loads and their presumed source rocks (Fig. 3).

The study of Goldstein and Jacobsen (1988) on river suspended loads also revealed an inverse relationship between the Sm/Nd ratios of the river loads and their Sm-Nd model ages (Fig. 4). The

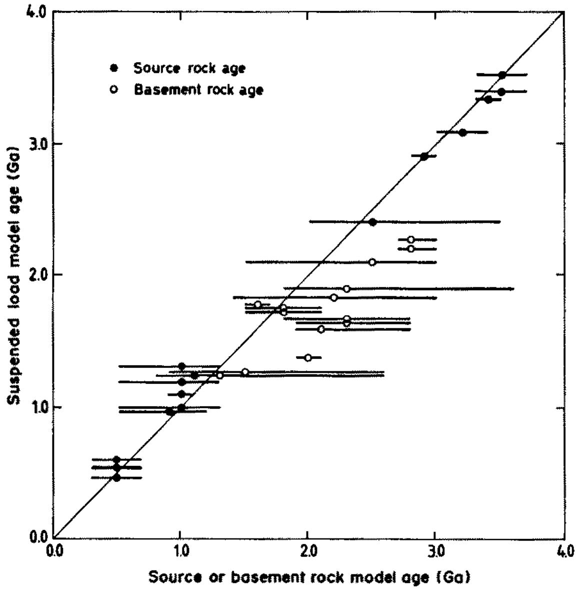

Figure 3: Comparison of depleted mantle based Sm-Nd model ages between river loads and their presumed source rocks (after Goldstein and Jacobsen, 1988)

authors suggested that the Sm/Nd age trend could be due to a progressive change in the Sm/Nd ratios of new additions of crust, possibly reflecting progressive depletion of incompatible elements in the mantle through time. DePaolo (1988a) also inferred a decrease in Sm/Nd ratio with increase in model age for the crust, based on evidence from granitic rocks. The results on modern river suspended loads are not in agreement with the observation made by Taylor and McLennan (1985) who claimed that Archean sedimentary rocks tend to have less fractionated light REE patterns than post-Archean sedimentary rocks. The study by Dia et al. (1990), on the other hand, showed no change in Sm/Nd ratio with depositional age for shales and greywackes ranging in age from 0.2 to 3.3 Ga. Isotopic studies focusing on morphology, mineralogy, and chemistry of the suspended loads are needed to understand the actual cause of the Sm-Nd age trend for modern river loads.

Based on the data on suspended loads of modern rivers, Goldstein and Jacobsen (1988) estimated that the average Sm-Nd model age for the flux of present-day river load from the North

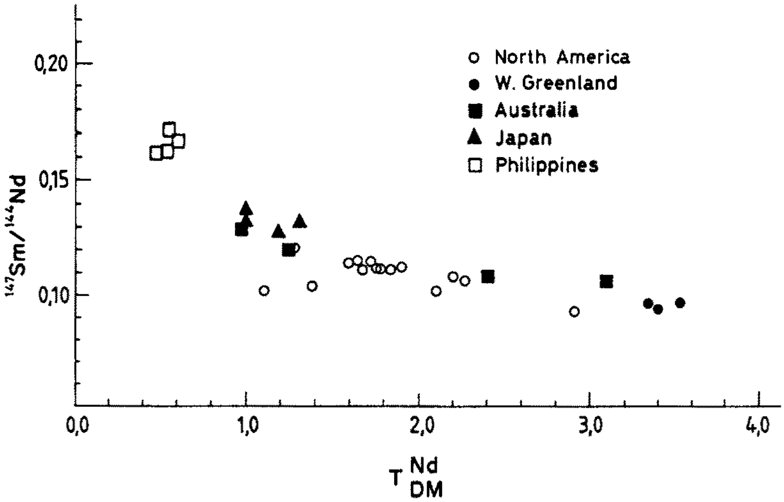

Figure 4: Variation of Sm/Nd ratio relative to the model age for the suspended loads of some major rivers in the world (after Goldstein and Jacobsen, 1988)

American continent to the oceans is about 1.8 Ga. By contrast, the estimated average Sm-Nd model age for the basement rocks of the North American continent is about 2.36 Ga, which makes the model age of the river load to be about 24% lower than that of the basement rocks. The authors explained that the discrepancy in the Sm-Nd model age between the river load and the basement rock reflects a large contribution of suspended material derived from young orogenic areas.

The weighted average Sm-Nd parameters for the loads of all rivers were used by Goldstein and Jacobsen (1988) to calculate the parameters for the upper crust presently exposed to weathering. The average values of different parameters for global river load are: Sm/Nd ratio of about 0.188, ϵ_{Nd} of about -10.6, and Sm-Nd model age of about 1.63 Ga. Based on the age relationship obtained between the river load and the basement rocks for the North American continent, Goldstein and Jacobsen estimated that the present-day upper crust exposed to weathering has an average Sm-Nd model age of about 2.1 Ga. Assuming that the average Sm/Nd of the upper crust exposed to weathering is approximately equal to that of the river load, the authors inferred the average ϵ_{Nd} of the continental upper crust to be about -17.

Sm-Nd isotopic information about the upper continental crust based on data of the present-day river suspended loads should be taken with some caution. Drainage basins of major rivers are mostly in trailing edge and continent-collision tectonic settings, whereas those of many small rivers are in arc-type tectonic settings. But, collectively, the suspended loads from these small rivers can make up a considerable fraction of the total loads removed from continents. Since the Sm-Nd model ages of sediments associated with trailing edge and continent-collision tectonic settings are much higher than those of sediments associated with arc-type settings, as noted by McLennan et al. (1990), a bias in the sampling of the river loads may not allow a reasonably correct estimation of the Sm-Nd isotopic characteristics of the continental upper crust based on the data of the river loads.

Sm-Nd ISOTOPIC VARIATIONS IN A SEDIMENTARY SEQUENCE

The Sm-Nd isotopic data of fine-grained clastic sedimentary rocks and their constituent particles in a sequence of deposition potentially can be of much significance to increased understanding of the depositional and post-depositional history of the sequence. The potential benefits about the latter have been pointed out by Awwiller and Mack (1991) and Ohr et al. (1991) who analyzed Tertiary sediments from the Gulf Coast area.

The data of Ohr et al. (1991) for rocks from a stratigraphic interval of about 3.5 km make evident that the Sm-Nd model ages of untreated bulk samples are higher than that of the corresponding insoluble residues by as much as 250 million years. Also, the dispersion in the model ages for the untreated bulk samples appears to be slightly higher than that for the acid-leached bulk samples. Similar degree of dispersion in the Sm-Nd model ages also exists between untreated and acid-leached clay fractions of $<0.1\mu m$. These disparities in the model ages reflect the presence of varied amounts of Sm and Nd in the acid removing phase or crystal sites which also differ to some extent in the Nd isotopic compositions.

The acid leachate contains Sm and Nd which are mobile, the origin of which could be different from that of the relatively inert REE in the residue. Hence, acid insoluble fraction may be preferable to untreated samples for the Sm-Nd isotopic studies on sediments.

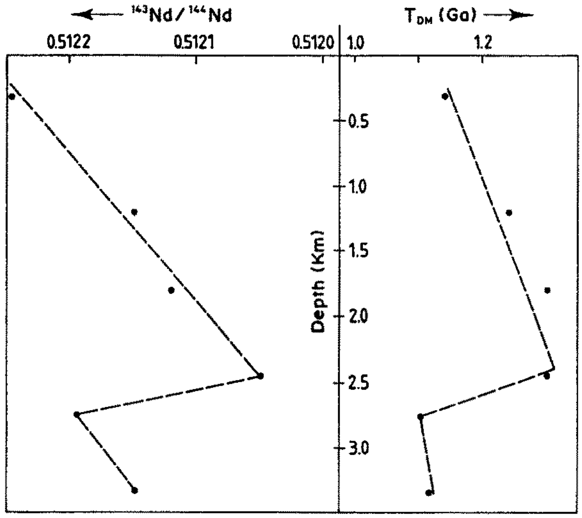

Figure 5: Changes in the Nd isotopic compositions and model ages with depths for HCl insoluble bulk materials of sediments from the Tertiary sequence in the Gulf Coast of Texas (modified from Ohr et al., 1991)

As suggested by the data of Ohr et al. (1991), the Nd isotopic composition decreases and the Sm-Nd model age increases with increase in depth for acid-insoluble bulk materials from the top 2.4 km of the sequence (Fig. 5). Awwiller and Mack (1991) also noted more radiogenic Nd toward the surface. Although some changes in the Sm/Nd ratios occur, no trend with depth could be established. The more radiogenic Nd toward the surface within the top 2.4 km of the sequence naturally reflects increasing input of younger crustal materials as deposition continued. This can be related to several factors such as changes in continental erosion related to sea level changes, slow epirogenic uplift of the land exposing more and more of the young crustal granitoid rocks, erosional order of an older stratigraphic sequence, and possibly some others. Additional studies are needed to determine the cause of such isotopic trends within a sequence of sediments.

The acid-leached bulk samples collectively do not define any discernable trend between the Nd isotopic compositions and the

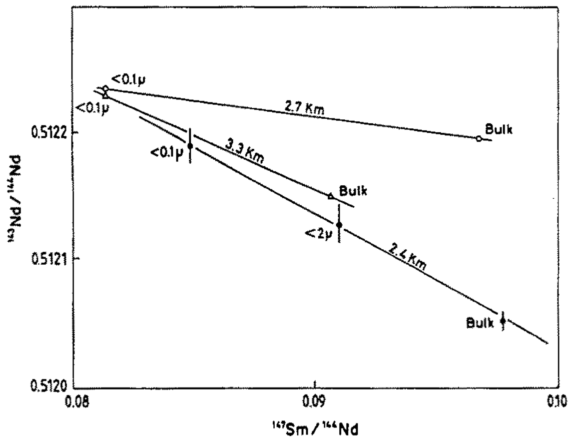

Figure 6: Changes in the Sm/Nd ratios vs. Nd isotopic ratios for acid leached bulk samples and corresponding clay fractions for sediments at three different depths (km) within the Tertiary sequence in the Gulf Coast area of Texas (reconstructed from Ohr et al., 1991)

Sm/Nd ratios. The scatter in this relationship is largely a reflection of varied provenances for the Tertiary sediments in the Gulf Coast area. We have reconstructed some of the data given by Ohr et al. (1991) and come to the conclusion that Sm-Nd isotopic data of each acid-leached bulk sample may be described in terms of mixing of two end-member components (Fig. 6). It is evident from the data on the sample at a depth of about 2.4 km that the Sm/Nd ratio decreases and the ^{143}Nd/^{144}Nd ratio increases from the bulk sample to the <2μm clay fraction to the very fine clay fraction. The linearity of the data among the two clay fractions and the bulk material for the sample collected at a depth of about 2.4 km probably represents a mechanical mixing between two end-member components. Similar two-component mixing lines with different slopes potentially exist also for the samples at depths of about 2.7 km and 3.3 km. The compositions of the end-member components may be defined based on some reasonable assumptions. As can be seen from the data presented in figure 6, the three mixing lines appear to have one common end-member component, but with a different second end-member component. The average Sm/Nd ratio of bulk sedimentary rocks is about 0.19, or ^{147}Sm/^{144}Nd ratio of about 0.115, which is about the same as that of many granitoid rocks. Assuming that each bulk sample contained a component with a Sm/Nd ratio of about 0.19, the three mixing lines may be extended to this average Sm/Nd ratio to obtain the corresponding Nd isotopic value of the component. The Sm-Nd model ages of the component with the average Sm/Nd ratio of 0.19 in the bulk samples are calculated to be about 2.0 Ga (2.4 km), 1.5 Ga (2.7 km), and 1.8 Ga (3.3 km). The other component which is common to all three samples represents a very fine clay fraction of diagenetic origin. The common end-member component for all three samples appears to have a Sm/Nd ratio about 0.13, or a $^{147}Sm/^{144}Nd$ ratio of about 0.08. By taking the corresponding Nd isotopic value from the extrapolation of the mixing line, the Sm-Nd model age for the common end-member component is calculated to be 1.0-1.1 Ga. The significance of this young model age is not clear, especially in view of the strong diagenetic overprint on the origin of this component.

Sm-Nd ISOTOPIC SIGNATURES AS TRACERS OF DIAGENESIS

The role of diagenesis on the Sm-Nd isotopes of sediments is poorly understood. Analyses of bulk samples of sediments or even <2μm clay fractions have not generally provided any convincing evidence that diagenesis plays any important role in the Sm-Nd chemical fractionation of sediments. Frost and Winston (1987) found in their study of the Middle Proterozoic sedimentary sequence in western North America that the average crustal residence age of fine grained sediments is nearly similar to that of some coarse grained sediments, in spite of wide variations in Sm/Nd ratios of coarse-grained samples. The similarity in the ages suggests that the total effect of weathering, erosion, transportation, and diagenesis is minimal as far as the Sm-Nd model age is concerned. Nelson and DePaolo (1988) observed from a study of Tertiary sediments deposited in a rift basin in north-central New Mexico that the Nd isotopic characteristics of a mudstone are identical to that of sandstones with which the mudstone is interlayered. They suggested that the data on the mudstone and the sandstone argue against any significant fractionation between Sm and Nd due to the combined effects of weathering, erosion, deposition and diagenesis. The results of the studies by Frost and Winston (1987) and by Nelson and DePaolo (1988) are in agreement with that of Chaudhuri and Cullers (1979) who found almost no change in the REE patterns of samples of clays from the deeply buried Tertiary sediments of the Gulf Coast area.

Any variation in the REE contents and Sm-Nd isotopic values among fine-grained sediments or sedimentary rocks can be due to difference in source rocks for the detrital particles, intensity of weathering, depositional environment, burial diagenetic reactions, or a combination of any of these factors. Some studies in about the last five years have either implied or underscored the importance of diagenesis as a major factor in determining the Sm-Nd isotopic characteristics of fine-grained sediments.

Stille and Clauer obtained a Sm-Nd isochron for four whole rock samples of argillite and a clay fraction from one of the whole rock samples of the Proterozoic Gunflint Formation, which yielded an age of 2.08 $\pm$ 0.59 Ga and initial ϵ_{Nd} value of about -2.1. The authors interpreted the age as being close to the depositional age of the sediments and suggested that the isochron could have resulted from near equilibrium of Nd isotopes during diagenesis shortly after deposition. A Sm-Nd isochron was also observed by Nägler (1990) who analysed whole rock samples of argillites from Spain, but the calculated age of 1524 $\pm$ 173 Ma is obviously geologically meaningless because the age of sedimentation for the argillites is about 490 Ma. As Nägler noted, the isochron for the argillites definitely represents a mixing line.

Recently Bros et al. (1992) analyzed the Sm-Nd isotopic compositions of different size fractions from two different samples about 60 m apart in a stratigraphic column of Lower Proterozoic black shales in southeastern Gabon. The two fine clay fractions of <0.2μm and 0.2-0.4 μm sizes for each of the samples were also leached with dilute HCl for determining the Sm-Nd isotopic compositions of the mobile REE relative to that of the inert REE in the mineral structures. The Sm-Nd isotopic data of the untreated, the acid insoluble and the soluble materials of each of these two fine clay fractions from individual samples independently defined isochron ages of 2099 ± 115 Ma and 2036 ± 79 Ma with very similar initial Nd isotopic compositions. The authors interpreted these dates to be a period of Nd isotopic homogenization related to illitization. The finer clay particles have higher Sm/Nd ratios than the coarser counterparts. Based on mineralogical and chemical evidence, the change in the Sm/Nd ratios suggests that diagenetic mineralization occurred with varied Sm/Nd ratios of the fluids.

The data point of the shale which was richest in the organic content (about 13% kerogen) plotted between the two isochrons defined by the clay fractions of the two other samples which were relatively less enriched in organic C. The agreement between the organic C rich shale, the leached clay particles and the leachates, indicates that it reached a Nd isotopic equilibrium with respect to diagenetic fluids. A fracture-filling bituminous sample showed the highest $^{147}Sm/^{144}Nd$ ratio (about 0.15) and the highest $^{143}Nd/^{144}Nd$ ratio of all materials analyzed. The data of this bituminous material also conform to the isochron trends defined by the silicate minerals. The Sm-Nd isotopic enrichment for the bituminous sample can be assumed to have been related to its migration history, as suggested by Manning et al. (1991) who also observed, as shown in this study, isotopic homogenization between source-rock kerogen and silicate phases of reservoir rocks.

The Sm-Nd isochron from data on clays must be interpreted with caution. The calculated date from an isochron can become much less than, or even approximately close to, that of the age of sedimentation, but this alone is not a good enough reason to assume that the isochron date relates to a diagenetic event. A mixing line with a negative slope at the time of sedimentation could evolve into an isochron with a positive slope, whereby the calculated date becomes less than, or nearly equal to, that of the age of deposition. The Sm-Nd isotopic data of clay fractions and bulk material of a sample of the Gulf Coast sediments of Tertiary age provide clear evidence that such a mixing line with negative slope can exist (Fig. 6).

Geochemical and mineralogical data obtained from analyses of Tertiary sedimentary deposits of the Gulf Coast area in the U.S.A.

have produced a paradigm for clay mineral diagenesis accompanying deep burial of sediments. The most attractive feature of the diagenetic history of these Gulf Coast sediments is the increase in illite content with increase in depth (see companion paper of Clauer et al. in this volume for details). Two recent studies have addressed on the relation of diagenesis to the Sm-Nd isotopic compositions of sediments from the Gulf Coast area (Awwiller and Mack, 1991; Ohr et al., 1991).

The Sm-Nd isotopic analyses by Awwiller and Mack (1991) on bulk samples of sandstones and shales in the Oligocene Frio Formation from south Texas, which consist of detrital particles derived largely from the Tertiary volcanic fields of west Texas and northern Mexico, showed a trend in decrease of the $^{143}Nd/^{144}Nd$ ratio with increase in depth for both types of sedimentary rocks. Their study of sandstones and shales from the Paleocene-Eocene Wilcox Group of south-central Texas indicated a similar trend, but of poorer quality, in the Nd isotopic ratio with depth. The sandstones of the Frio Formation were found to have the Sm-Nd model ages increase with increasing depth, but the shales within the same stratigraphic interval did not have such a record of change. Rather the Sm-Nd model ages of the shales remained nearly similar through much of the stratigraphic interval. Considering the entire stratigraphic interval of about 3.5 km within the Paleocene-Eocene Wilcox Group, from which the bulk samples were taken for the analyses, the Sm-Nd model ages were poorly correlated. Awwiller and Mack's (1991) claim that Sm-Nd model ages increase with increasing depth does not appear to be convincing. The authors suggested that, although the trends in ϵ_{Nd} and the Sm-Nd model ages in sandstones and shales of the Tertiary sequence are possibly due to a detrital control, diagenetic changes in the rocks could have influenced the modifications in the ages. They concluded that the model ages could have been modified by diagenetic reactions involving loss of radiogenic Nd from the sediment and mineralogic fractionation of Sm and Nd during mobilization of the REE. Awwiller and Mack noted that in the Frio sandstones late diagenetic ankerite cement with ϵ_{Nd} value of about -10 contained less radiogenic Nd than early diagenetic calcite cement with a ϵ_{Nd} value of about -6, which suggested early mobilization of Nd from volcanic materials. They also reported that the Sm/Nd ratios of clay fractions of <0.5μm size, which ranged from about 0.15 to 0.17, were lower than that of the equivalent bulk samples whose Sm/Nd ratios were between 0.17 and 0.23.

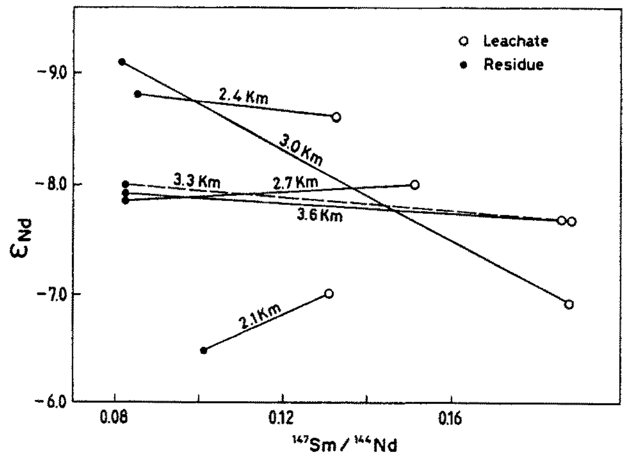

Figure 7: Relationships of Nd isotopic composition and Sm/Nd ratio between acid leachate and corresponding insoluble very fine clay fraction for samples at different depths within the sequence of Tertiary sediments in the Gulf Coast area of Texas. The zone of illitization includes the sequence at 2.4 km depth and lower in the colums (after Ohr et al., 1991)

Ohr et al. (1991) also observed that Sm/Nd ratios of fine clay fractions <0.1μm were lower than that of corresponding bulk samples from the zone of illitization in deeply buried sediments. Since these fine clay fractions consist of large amounts of diagenetic illites, mineralogical fractionation of Sm from Nd might have occurred during diagenetic formation of illites. Analyzing HCl-leached bulk samples and their leachates, and also a coarse clay fraction of one of the samples and its leachate, from the illitic zone, Ohr et al. found considerable disparity in the Nd isotopic composition between an acid insoluble residue and its corresponding leachate. This is expected because such materials consist of particles of diverse origin. But in analyzing the fine clay fractions, they found that, for four out of five fractions from different depths, the Nd isotopic composition of the insoluble residue was identical to that of the corresponding leachate. But for one sample, the leachate and the residue differed in their Nd isotopic compositions. Furthermore, for all five samples they analyzed, the Sm/Nd ratio of the leachate was higher than that of the corresponding insoluble residue (Fig. 7). The similarities in the Nd isotopic compositions between the acid insoluble residue and the corresponding leachate for most of these fine clay fractions suggest isotopic homogeneity during diagenesis. What is also clear from the data is that neither the insoluble residues of the very fine clay fractions themselves nor the leachates themselves are isotopically homogeneous. This indicates that if diagenesis produced isotopic homogeneity, it had to occur only within a limited scale.

We would like to draw attention to the low Sm/Nd ratios of about 0.13-0.14 for the fine clay fractions. These values are lower than the average value of about 0.18 which have been reported in the literature for many illitic, smectitic and glauconitic minerals (Cullers et al., 1975; Fleet et al., 1980). The reason for the difference could be a result of difference in the maturity of evolution between them, but research is needed to determine the real cause. Nevertheless, the Sm/Nd ratio of about 0.13-0.14 for the very fine clay fraction is about the same as that for many K-feldspar minerals in granitoid rocks, which may suggest that these very fine illitic minerals in the Gulf Coast sediments formed from the alteration of K-feldspar minerals. If we assume an approximate conservation of the proportion between Sm and Nd during the transformation of the precursor to the very fine-grained illitic clay minerals, then the average crustal residence age of the precursor for these clay minerals was about 1.0-1.1 Ga.

Undoubtedly, evidence already exists that mineralogical fractionation of Sm from Nd could occur during diagenesis. The question remains about the actual mechanism by which it occurs and the significance of this diagenetic silicate mineralization on the Sm-Nd model ages of the sediments.

Nd ISOTOPES AS POTENTIAL TRACERS FOR OROGENIC EVENTS AND PALEOGEOGRAPHICAL RECONSTRUCTION

The role of the mantle-derived components in the growth of the continent has been a subject of much investigation during the last two decades. Major subduction related orogenic events potentially involve additions of juvenile crust differentiated from a mantle source. The additions of any new mantle component during the orogenic episodes should theoretically be evident in the ϵ_{Nd} values of weathered and erosional products from the orogenic belts. Michard et al. (1985) noted several maxima of ϵ_{Nd} values in a relationship between Nd isotopic compositions and stratigraphic ages for Phanerozoic sediments from France (Fig. 8). The maxima of ϵ_{Nd} values generally coincide with known orogenic events in central Europe, suggesting addition of subduction related crust during these events. The data in this figure also make evident that the effect of the contributions of young mantle Nd is overshadowed in few tens of million years by contributions of relatively non-radiogenic Nd from older crustal rocks, as the Nd-isotope signatures of the sediments are quickly restored to the pre-orogenic background level. In other words, the young crust was uplifted which caused the isotopic signature of the detritus from the uplifted young crust to overwhelm the signature of the detritus from the ancient crust, but the influence of the young crust was soon reduced due to its rapid erosion from uplift. One conclusion which can be made from the study of Michard et al. (1985) is that a prominent maximum of the ϵ_{Nd} values in the spectrum of Nd isotopic compositional variation with the depositional age of sediments may be used for identification and dating of a subductional related, mantle source differentiated crust forming event.

Studies of sedimentary sequence spanning at least several tens of million years of depositional history may reveal a general increase, but without any discernible maximum, in the ϵ_{Nd} values with decreasing ages of the sediments. Such a trend may signify either continuous small additions of new crust produced by a series of short duration subduction or a slow and long duration subduction, or a slow epeirogenic uplift of the crust continuously exposing mantle source derived crystalline rocks to weathering and erosion, or a progressive decrease in the influence of the older tectonic province in the erosion of the continent. Independent evidence is required to explain the cause for a trend of increase in Nd isotope ratio with decrease in stratigraphic age.

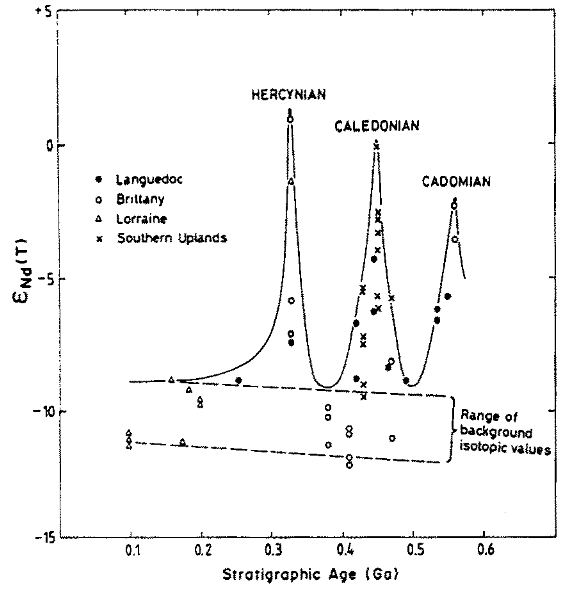

Figure 8: Relationship between stratigraphic age and Nd isotopic composition at the time of sedimentation for samples of Phanerozoic shales and siltstones from central Europe (after Michard et al., 1985)

The Nd isotopic records may reveal regional differences in the responses of sedimentary systems to additions of subduction related crusts. Miller and O'Nions (1984) noted contrasts in Nd isotopic composition among sedimentary rocks between the two sides of the Iapetus suture. They concluded that the Nd isotopic compositions of shales could be a useful tracer in paleogeographical investigations.

Crustal Recycling History

Taking the inventories of all sedimentary and metasedimentary rocks since the Archean time, Garrels and MacKenzie (1971) remarked that the half-life of global sedimentary rocks is about 600 million years. The preponderance of very young sedimentary rocks in the existing continental crust with the long evolutionary history has spurred many different investigations and debates about the crustal erosion and the growth of the continental crust. Different factors relating to intracrustal processes (such as rates of erosion and sedimentation, metamorphism, anatexis, and magmatism) and addition of new mantle differentiated material external to the continental internal cycle are important components in the evolutionary history of the continental crust with its present distribution of rock types exposed to the surface. Contentious views about the crustal growth can be found in the article by Veizer and Janssen (1985). The history of continental crust formation remains a controversial issue. The evolution has been variously explained ranging from a continuous formation (Hurley et al., 1962; Hurley and Rand, 1969; O'Nions and Pankhurst, 1978; Gurnis and Davies, 1986) to an episodic formation (Moorbath, 1977; Patchett et al., 1981; Page et al., 1984; Nelson and DePaolo, 1985; DePaolo et al., 1991), to increased continental mass trough time (Veizer and Janssen, 1979; Dewey and Windley, 1981; McLennan and Taylor, 1982), to steady continental mass (Patterson and Tatsumoto, 1964; Tatsumoto and Patterson, 1964; Armstrong, 1981), and to even decreased continental mass (Fyfe, 1978).

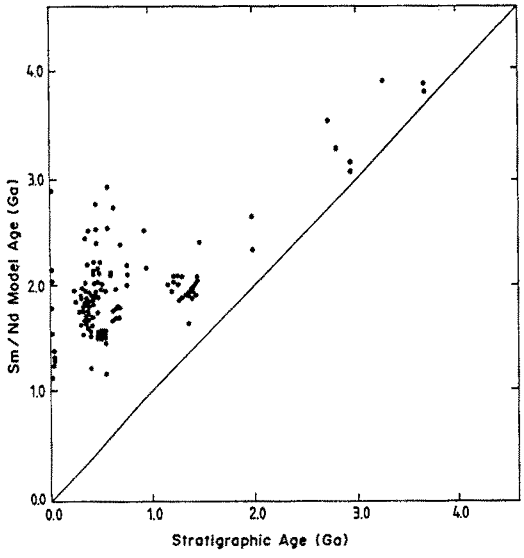

Figure 9: Relationship between stratigraphic age and the Sm-Nd model age for sedimentary and metasedimentary rocks ranging in age from Archean to Recent, including the data for modern river loads

The long term continental crustal growth history has been examined from the Sm-Nd isotope analyses of fine-grained sediments of different geologic ages. But this requires that the continental sedimentary mass should be rapidly recycled so that the records in the sedimentary mass reflect continuous evolution of the average composition of the continental crust. The long-term growth history of the continental crust should be studied only from analyses of well mixed, multi-cycled sedimentary systems, the criteria of which can be based on the REE distribution patterns. Several studies (Allègre and Rousseau, 1984; Frost and O'Nions, 1985; Michard et al., 1985; Frost and Winston, 1987; Dia et al., 1990) have brought attention to the relationship between the Sm-Nd model ages and the stratigraphic ages of sedimentary and metasedimentary rocks from different sedimentary basins in the world and the implication of the relationship concerning the growth of continents through the geologic time. Figure 9 is an illustration of the relationship between the model ages and stratigraphic ages of sedimentary rocks. The progressively greater difference between the crustal residence age and the stratigraphic age for sedimentary rocks younger than about 2.0 Ga suggests an increasing role of intracrustal recycling of older continental crustal materials since about the Proterozoic. The Nd isotopic data can be used to explain the evolution of the continental upper crust, provided the sedimentary rock records are not biased toward specific tectonic settings such as trailing edge and continental collision. Many are inclined to believe in such a bias in sedimentary-rock records (Veizer and Janssen, 1979, 1985). They provide an alternative explanation which suggests that the sedimentary mass essentially consists of reworked sediments and sedimentary rocks and old upper crustal crystalline rocks. They are in agreement with the results of early studies of Patterson and Tatsumoto (1964) and Tatsumoto and Patterson (1964) on Pb isotopes of detrital feldspars, which suggest that a very large segment of the continents was accreted before the Proterozoic, followed by a slow growth during the Proterozoic and the Phanerozoic.

CONCLUSION

The analyses of the Sm-Nd isotopes in sediments and sedimentary rocks have proved useful in reconstructing provenances of sediments, erosional history of the continent, tectonic evolution of the earth, and recycling of sediments. Recent studies have shown that considerable promise lies ahead in understanding diagenesis of sediments by analyses of the Sm-Nd isotopes in very fine-grained clays.

Evidence is sketchy about mineralogical fractionation of Sm from Nd in weathering environment, but considerable degree of fractionation seems possible. Nothing is known yet about the magnitude of change in the Sm-Nd model age which can occur due to weathering. Reports about the effect of sorting of detrital particles on the model ages are limited, but they point to conflicting results between no change and measurable differences in the systematics of Sm-Nd isotopes due to sorting. Influence of depositional environment on the systematics of Sm-Nd isotopes in fine-grained sediments needs investigations. Diagenetic reactions can cause mineralogical fractionation of Sm from Nd, but its real impact on the long-term changes in the Sm-Nd model ages of sedimentary rocks has not been examined. Present evidence shows that the diagenetic records in fine-grained sediments are limited to very fine clay fractions. We have yet to know what happens to the Sm-Nd isotopic systematics of these very fine clays when they mature in their evolutionary history subsequent to the growth in the diagenetic environment.

The comparison between stratigraphic ages of sedimentary rocks and their crustal residence ages estimated from analyses of systematics of the Sm-Nd isotopes has convincingly demonstrated that only small amounts of mantle-differentiated juvenile crust have been added to the continents since about 2.0 Ga ago. Changes in the Nd isotopic compositions of sedimentary rocks through time may provide clues for identification of subduction related crustal forming events and also tectono-eustatic related erosional history of the continent. A future research would be to determine the nature of the relationship between orogeny related Nd isotopic maxima as recorded in the sedimentary rocks and temporal variations in the Nd isotopic compositions of oceans which derived their Nd in large part from the continents.

ACKNOWLEDGEMENTS

This manuscript greatly benefited from review by Bruce K. Nelson (University of Washington at Seattle). We sincerely thank him for this immense help, as well as Mr. C. Hammel who made the draftings.

REFERENCES

Allègre C.J. and Rousseau D. (1984) The growth of the continent through geological time studied by Nd isotope analysis of shales. Earth Plan. Sci. Lett., 67, 19-34.

André L., Deutsch S. and Hertogen J. (1986) Trace element and Nd isotopes in shales as indexes of provenance and crustal growth: the early Paleozoic from the Brabant Massif (Belgium). Chem. Geol., 57, 101-115.

Armstrong R.L. (1981) Radiogenic isotopes: the case for crustal recycling on a near-steady-state no-continental-growth earth. Philos. Trans. Roy. Soc. london, Ser. A 301, 443-472.

Awwiller D.N. and Mack L.E. (1991) Diagenetic modification of Sm-Nd model ages in Tertiary sandstones and shales, Texas Gulf Coast. Geology, 19, 311-314.

Bhatia M.B. (1985) Rare earth element geochemistry of Australian Paleozoic graywackes and mudrocks: Provenance and tectonic. Sediment. Geol., 45, 97-113.

Balashov Y.A., Ronov A.B., Migdisov A.A. and Turanskaya N.V. (1964) The effect of climate and facies environment on the fractionation of the rare earths during sedimentation. Geochem. Intl., 10, 995-1014.

Balashov Y.A. and Girin Y.P. (1969) On the reserve of mobile rare earth elements in sedimentary rocks. Geochem. Intl., 7, 649-659.

Bros R., Stille P., Gauthier-Lafaye F., Weber F. and Clauer N. (1992) Sm-Nd isotopic dating of proterozoic clay materials: an example from the Francevillian sedimentary Series (Gabon). Earth Plan. Sci. Lett., in press.

Burkov V.V. and Podporina Y.K. (1967) Rare earths in granitoid residuum. Doklad. Acad. Nauk Sci., 177, 691-694.

Clarke D.B. and Halliday A.N. (1985) Sm/Nd isotopic investigation of the age of and origin of the Meguma zone metasedimentary rocks. Can. Jour. Earth Sci., 22, 102-107.

Clauer N., O'Neil J.R. and Bonnot-Courtois C. (1982) The effect of natural weathering on the chemical and isotopic compositions of biotites. Geochim. Cosmochim. Acta, 46, 1755-1762.

Chaudhuri S. and Cullers R.L. (1979) The distribution of rare-earth elements in deeply buried Gulf Coast sediments. Chem. Geol., 24, 327-338.

Cullers R.L., Chaudhuri S., Arnold B., Lee M. and Wolf C.W. Jr. (1975) Rare earth distributions in clay minerals and in the clay-sized fraction of the Lower Permian Havensville and Eskridge shales of Kansas and Oklahoma. Geochim. Cosmochim. Acta, 39, 1691-1701.

Cullers R.L., Chaudhuri S., Kilbane N. and Koch R. (1979) Rare-earth in size fractions and sedimentary rocks of Pennsylvanian-Permian age from the mid-continent of the U.S.A. Geochim. Cosmochim. Acta, 43, 1285-1301.
Cullers R.L. and Graf J.L. (1984) Rare earth elements in igneous rocks of the continental crust: Intermediate and silicic rocks - ore petrogenesis. In: Rare Earth Element Geochemistry, P. Henderson (ed.), Elsevier, New York, 275-316.
Davies G., Gledhill A. and Hawkesworth C. (1985) Upper crustal recycling in southern Britain: evidence from Nd and Sr isotopes. Earth Plan. Sci. Lett., 75, 1-12.
DePaolo D.J. (1981) Nd isotopic studies: some new perspectives on earth structure and evolution. EOS, 62, 137-140.
DePaolo D.J. (1988a) Age dependence of the composition of continental crust: evidence from Nd isotopic variations in granitic rocks. Earth Plan. Sci. Lett., 90, 263-271.
DePaolo D.J. (1988b) Neodymium Isotope Geochemistry: An Introduction, Springer-Verlag, New York, 187 p.
DePaolo D.J., Kyte F.J., Marshall B.D., O'Neil J.R. and Smit J. (1983) Rb-Sr, Sm-Nd, K-Ca, O, and H isotopic study of Cretaceous-Tertiary boundary sediments, Caravaca, Spain: Evidence for an oceanic impact site. Earth Plan. Sci. Lett., 64, 356-373.
DePaolo D.J., Linn A.M. and Schubert G. (1991) The continental crustal age distribution: methods of determining mantle separation ages from Sm-Nd isotopic data and application to the southwestern United States. Jour. Geophys. Res., 96, 2071-2088.
Dewey J.F. and Windley B.F. (1981) Growth and differentiation of the continental crust. Philos. Trans. Roy. Soc. London, Ser. A 301, 189-206.
Dia A., Allègre C.J. and Erlank A.J. (1990) The development of continental crust through geological time: the South African case. Earth Plan. Sci. Let., 98, 74-89.
Dypvik H. and Brunfelt A.O. (1976) Rare-earth elements in Lower Paleozoic epicontinental and eugeosynclinal sediments from the the Oslo and Tronheim regions. Sedimentology, 23, 363-378.
Dypvik H. and Brunfelt A.O. (1979) Distribution of rare earth elements in some North Atlantic Kimmeridgian black shales. Nature, 278, 339-341.
Elderfield H., Hawkesworth C.J., Greaves M.J. and Calvert S.E. (1981) Rare earth element geochemistry of oceanic ferromanganese nodules and associated sediments. Geochim. Cosmochim. Acta, 45, 513-528.
Faure G. (1986) Principles of Isotope Geology. J. Wiley and Sons, New York, 589 p.
Fleet A.J. (1984) Aqueous and sedimentary geochemistry of the rare earth elements. In: Rare Earth Element Geochemistry, Henderson P. (ed.), Elsevier, Amsterdam, 343-373.
Fleet A.J., Buckley H.A. and Johnson L.R. (1980) The rare earth element geochemistry of glauconites and celadonites. Jour. Geol. Soc. London, 137, 683-688.
Frost C.D. and O'Nions R.K. (1984) Nd evidence for Proterozoic crustal development of in the Belt-Purcell Supergroup. Nature, 312, 53-56.
Frost C.D. and Winston D. (1987) Nd isotopic systematics of coarse- and fine-grained sediments: examples from the Middle Proterozoic Belt-Purcell Supergroup. Jour. Geol., 95, 309-327.

Fyfe W.S. (1978) The evolution of the Earth's crust: modern plate tectonics to ancient hot spot tectonics? Chem. Geol., 23, 89-114.

Garrels R.M. and Mackenzie F.T. (1971) Evolution of Sedimentary Rock. W.W. Norton Company, Inc., New York, 379 p.

Goldstein S.L., O'Nions R.K. and Hamilton P.J. (1984) A Sm-Nd isotopic study of atmospheric dusts and particulates from major river systems. Earth Plan. Sci. Lett., 70, 221-236.

Goldstein S.J. and Jacobsen S.B. (1987) The Nd and Sr isotopic systematics of river-water dissolved material: implications for the sources of Nd and Sr in seawater. Chem. Geol. (Isot. Geosc. Sect.), 66, 245-272.

Goldstein S.J. and Jacobsen S.B. (1988) Nd and Sr isotopic systematics of river water suspended material: implications for crustal evolution. Earth Plan. Sci. Lett., 87, 249-265.

Gurnis M. and Davies G.F. (1986) Apparent episodic crustal growth arising from a smoothly evolving mantle. Geology, 14, 396-399.

Hamilton P.J., O'Nions R.K., Bridgwater D. and Nutman A. (1983) Sm-Nd studies of Archean metasediments and metavolcanics from West Greenland and their implications for the Earth's early history. Earth Plan. Sci Lett., 62, 263-272.

Haskin M.A. and Haskin L.A. (1966) Rare earth in European shales: a redetermination. Science, 154, 507-509.

Haskin L.A., Wildeman T.R., Frey F.A., Collins K.A., Keedy C.R. and Haskin M.A. (1966) Rare earths in sediments. Jour. Geophys. Res., 71, 6091-6105.

Heller P.L., Peterman Z.E., O'Neil J.R. and Shafiqullah M. (1985) Isotopic provenance of sandstones from the Eocene Tyee Formation, Oregon Coast Range. Geol. Soc. Am. Bull., 96, 770-780.

Huhma H. (1987) Provenance of Early Proterozoic and Archean metasediments in Finland: a Sm-Nd isotopic study. Prec. Res., 35, 127-143.

Hurley P.M., Hughes H., Faure G., Fairbairn H.W. and Pinson W.H. (1962) Radiogenic strontium 87 model of continental formation. Jour. Geophys. Res., 67, 5315-5334.

Hurley P.M. and Rand R.J. (1969) Pre-drift continental nuclei. Science, 164, 1229-1242.

Manning L.K., Frost C.D. and Branthaver J.F. (1991) A neodymium isotopic study of crude oils and source rocks: potential applications for petroleum exploration. Chem. Geol., 91, 125-138.

McCulloch M.T. and Wasserburg G.J. (1978) Sm-Nd and Rb-Sr chronology of continental crust formation. Science, 200, 1003-1011.

McLennan S.M. (1989) Rare earth elements in sedimentary rocks: influence of provenance and sedimentary processes. Rev. Min., 21, 169-200.

McLennan S.M. and Taylor S.R. (1982) Geochemical constraints on the growth of the continental crust. Jour. Geol., 90, 347-361.

McLennan S.M., McCulloch M.T., Taylor S.R. and Maynard J.B. (1989) Effects of sedimentary sorting on neodymium isotopes in deep-sea turbidites. Nature, 337, 547-549.

McLennan S.M., Taylor S.R., McCulloch M.T. and Maynard J.B. (1990) Geochemical and Nd-Sr isotope composition of deep sea turbidites: crustal evolution and plate tectonic associations. Geochim. Cosmochim. Acta, 54, 2015-2050.

Michard A., Gurriet P., Soudant M. and Albarede F. (1985) Nd

isotopes in French Phanerozoic shales: external vs; internal aspects of crustal evolution. Geochim. Cosmochim. Acta, 49, 601-610.
Michard A., Beaucaire C. and Michard G. (1987) Uranium and rare earth elements in CO_2-rich waters from Vals-les-Bains (France). Geochim. Cosmochim. Acta, 51, 901-909.
Middleburg J.J., van der Weijden C.H. and Woittiez J.R.W. (1988) Chemical processes affecting the mobility of major, minor and trace elements during weathering of granitic rocks. Chem. Geol., 68, 252-273.
Miller R.G. and O'Nions R.K. (1984) The provenance and crustal residence ages of British sediments in relation to paleogeographic reconstructions. Earth Plan. Sci. Lett., 68, 459-470.
Miller R.G. and O'Nions R.K. (1985) Source of Precambrian chemical and clastic sediments. Nature, 314, 325-329.
Moorbath S. (1977) Ages, isotopes and evolution of Precambrian continental crust. Chem. Geol., 20, 151-187.
Nägler T. (1990) Sm-Nd, Rb-Sr and common lead isotope geochemistry of fine-grained sediments of the Iberian massif. Ph.D. Thesis, Swiss Feder. Inst. Tech., Zürich, 141 p.
Nance W.B. and Taylor S.R. (1976) Rare earth patterns and crustal evolution. I: Australian post-Archean sedimentary rocks. Geochim. Cosmochim. Acta, 40, 1539-1551.
Nelson B.K. and DePaolo D.J. (1985) Rapid production of continental crust 1.7 to 1.9 b.y. ago: Nd isotopic evidence from the basement of the North American mid-continent. Geol. Soc. Am. Bull., 96, 746-754.
Nelson B.K. and DePaolo D.J. (1988) Comparison of isotopic and petrographic provenance indicators in sediments from Tertiary continental basins of New Mexico. Jour. Sedim. Petrol., 58, 348-357.
Nesbitt H.W. (1979) Mobility and fractionation of rare earth elements during weathering of a granodiorite. Nature, 279, 206-210.
Ohr M., Halliday A.N. and Peacor D.R. (1991) Sr and Nd isotopic evidence for punctuated clay diagenesis, Texas Gulf Coast. Earth Plan. Sci. Lett., 105, 110-126.
O'Nions R.K. and Pankhurst R.J. (1978) Early Archean rocks and geochemical evolution of the Earth's crust. Earth Plan. Sci. Lett., 38, 211-236.
O'Nions R.K., Hamilton P.J. and Hooker P.J. (1983) A Nd isotope investigation of sediments related to crustal development in the British Isles. Earth Plan. Sci. Lett., 63, 229-240.
Othman D.B., Polvé M. and Allègre C.J. (1984) Nd-Sr isotopic composition of granulites and constraints on the evolution of the lower crust. Nature, 307, 510-515.
Page R.W., McCulloch M.T. and Black L.P. (1984) Isotopic record of major Precambrian events in Australia. Prec. Geol., 27th Int. Geol. Congr., 5, 25-72.
Patchett P.J., Kuovo O., Hedge C. and Tatsumoto M. (1981) Evolution of continental crust and mantle heterogeneity: evidence from Hf isotopes. Contrib. Miner. Petrol., 78, 279-287.
Patchett P.J., White W.M., Feldmann H., Kielinczuk S. and Hofmann A.W. (1984) Hafnium/rare earth element fractionation in the sedimentary system and crustal recycling into the Earth's mantle. Earth Plan. Sci. Lett., 69, 365-378.
Patterson C.C. and Tatsumoto P. (1964) The significance of lead isotopes in detrital feldspar with respect to chemical diffe-

rentiation within the earth's mantle. Geochim. Cosmochim. Acta, 28, 1-22.
Piper D.Z. (1974) Rare earth elements in the sedimentary cycle: a summary. Chem. Geol., 14, 285-304.
Roaldset E. and Rosenqvist I.T. (1971a) Unusual lanthanide distribution. Nature, Phys. Sci., 231, 153-154.
Roaldset E. and Rosenqvist I.T. (1971b) Rare earth elements in vivianite from Lake Asrum. Lithos, 4, 417-422.
Schieber J. (1986) Stratigraphic control of rare-earth pattern types in Mid-Proterozoic sediments of the Belt Supergroup, Montana, USA: implications for basin analysis. Chem. Geol., 54, 135-148.
Shaw H.F. and Wasserburg G.J. (1985) Sm-Nd in marine carbonates and phosphates: implications for Nd isotopes in sea water and crustal ages. Geochim. Cosmochim. Acta, 49, 503-518.
Stille P. and Clauer N. (1986) Sm-Nd isochron-age and provenance of the argillites of the Gunflint Iron Formation in Ontario, Canada. Geochim. Cosmochim. Acta, 50, 1141-1146.
Stordal M.C. and Wasserburg G.J. (1986) Neodymium isotopic study of Baffin Bay water: sources of REE from very old terranes. Earth Plan. Sci. Let., 77, 259-272.
Tatsumoto P. and Patterson C.C. (1964) Studies of zircon and K-spar concentrates in Precambrian sands and their significance with respect to continental growth. Jour. Geol., 72, 232-242.
Taylor S.R., McLennan S.M. and McCulloch M.T. (1983) Geochemistry of loess, continental dust composition and crustal model ages. Geochim. Cosmochim. Acta, 47, 1897-1905.
Taylor S.R. and McLennan S.M. (1985) The Continental Crust: its Composition and Evolution. Blackwell, Oxford, 312 p.
Veizer J. and Jansen S.L. (1979) Basement and sedimentary recycling and continental evolution. Jour. Geol., 87, 341-370.
Veizer J. and Jansen S.L. (1985) Basement and sedimentary recycling - 2: Time dimension to global tectonics. Jour. Geol., 93, 625-643.