Review

Potential uses of stable isotope ratios of Sr, Nd, and Pb in geological materials for environmental studies

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(Communicated by Eitaro WADA, M.J.A.)

Abstract: The ratios of stable isotopes of certain elements in rocks and minerals have strong regional characteristics that are reflected in atmospheric components, in water, and in the living organisms that form Earth’s surface environment as well as in agricultural and fishery products. Geologically derived stable isotope ratios can be used as a tracer for the source of many kinds of substances, with current geochemical techniques allowing the precise determination of numerous stable isotope ratios in both natural and manmade objects. This review presents examples of the use of stable isotopes as tracers within diverse dynamic ecosystems, focusing on Sr isotopes but also including examples of Nd and Pb isotopic analysis, and reviewing the potential of this technique for a wide range of environmental research, including determining the geographic origin of food and archeological materials.

Keywords: stable isotopes, strontium, neodymium, lead, traceability indexes, environment

1. Introduction

Some 80 of the 92 naturally occurring elements on Earth are stable, with 54 of these having two or more stable isotopes. The fact that stable isotopes differ in mass number but not in atomic number means that the different stable isotopes of a given element differ slightly in their physicochemical behavior.1)–4) Consequently, the relative abundances of the various stable isotopes that compose matter can act as fingerprints that enable the tracing of the origin (or source) of the elements in a substance.

The stable isotope ratios of individual elements are affected by two main factors, namely isotopic fractionation and radioactive decay. Isotope fractionation occurs during physicochemical processes when atoms of an element are involved in chemical reactions, diffusion, and transformation between solid, liquid, and gaseous phases. The degree of fractionation is generally dependent on the relative difference in mass between the stable isotopes of a given element and the temperature at which the fractionation process occurs. Light elements, such as hydrogen (H), carbon (C), nitrogen (N), oxygen (O), and sulfur (S), are present in a wide variety of chemical forms and phases. These light elements have large isotopic fractionations that reflect the large relative difference in mass between their various isotopes. Consequently, the ratios of the stable isotopes of these elements have been used for a wide range of research into the processes that operate in Earth’s surface environment, including ecosystem research.1)–4)

Radioactive decay affects certain isotopes at a steady rate, including the decay of radioactive elements into stable isotopes of other elements. This has led to the development of techniques for the dating of rocks and minerals using the radioactive isotopes of parent elements and the corresponding stable isotopes of their daughter elements, as exemplified by the rubidium–strontium (Rb–Sr), samarium–neodymium (Sm–Nd), uranium–lead (U–Pb), and thorium–lead (Th–Pb) methods of dating (Table 1), where 87Rb decays into 87Sr by beta emission, 147Sm decays into 143Nd by alpha emission, and 238U, 235U, and 232Th ultimately decay into 206Pb, 207Pb, and 208Pb, respectively, by a cascade of alpha and beta emissions. These daughter
elements also include stable isotopes with primordial origins (187Sr) or radioisotopes with very long half-lives (144Nd and 204Pb). This means that the relative abundances of isotopes of Sr, Nd, and Pb within rocks and minerals (87Sr/86Sr, 143Nd/144Nd, 207Pb/206Pb, etc.) are considered to be constant in environmental studies on time scales of <10^4 years, but can vary significantly depending on their age of formation and the ratios of parent and daughter elements (e.g., Rb/Sr or Sm/Nd). In addition, 206Pb, 207Pb, and 208Pb isotopic ratios vary as a result of differing Pb, U, and Th ratios. 2)\end{itemize}

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2. Stable isotopes of Sr, Nd, and Pb

The factors that control the Sr, Nd, and Pb stable isotopic ratios of geologic materials include the age of the material, and the ratio of parent to daughter elements (e.g., Rb/Sr, Sm/Nd, U/Pb, Th/Pb), where higher parent:daughter ratios lead to a higher abundance of radiogenic Sr, Nd, or Pb. Alkaline elements such as K and Rb show a positive correlation with each other but a negative correlation with alkaline earth elements such as Ca and Sr. This leads to large differences between rock Rb/Sr ratios and the ratios in soils and sediments produced by the weathering of these rocks, a factor that in turn leads to wide variations in the 87Sr/86Sr ratios of crustal materials.

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released from metal ores by human activities making an enormous contribution to the total Pb within water and in ecosystems. The fact that metal ores generally contain negligible amounts of U and Th means that they have Pb isotope ratios that are a function of their age and the U/Pb and Th/Pb ratios of the geological materials responsible for ore formation. In addition, the fact that granites contain elevated concentrations of U and Th means that they are also enriched in radiogenic lead, especially when compared with radiogenic lead-depleted basalt and island arc volcanic rocks.2),5)

Strontium isotopic ratio measurements involve the simultaneous measurement of four stable isotopes (84Sr, 86Sr, 87Sr, and 88Sr; Table 1): 87Sr is the only one of these isotopes that is radiogenic, and it forms as a result of the beta decay of 87Rb. This means that the ratios of non-radiogenic 84Sr, 86Sr, and 88Sr only change as a result of isotope fractionation, with the isotopic fractionation of 87Sr relative to 86Sr almost half that of 87Sr relative to 88Sr. Setting the 86Sr/88Sr ratio at a fixed value (0.1194) enables an approach that allows compensation for changes in the 87Sr/86Sr ratio due to isotope fractionation and the precise determination of the abundance of radiogenic 87Sr in geological materials.

Neodymium has five stable isotopes (142Nd, 143Nd, 145Nd, 146Nd, and 148Nd) and two radioisotopes (144Nd and 150Nd) with half-lives of 2.29 × 10^15 and 6.7 × 10^18 years, respectively. These very long half-lives means that 144Nd and 150Nd are regarded as stable isotopes in both geological and environmental studies. The alpha decay of 147Sm forms 148Nd, and Nd isotopic comparisons are expressed in terms of the 143Nd/144Nd ratio. Neodymium isotopes are corrected in a similar fashion to the correction of 87Sr/86Sr measurements by setting the 86Sr/88Sr ratio to 0.1194, with Earth-derived materials having 143Nd/144Nd ratios that are corrected to a 148Nd/144Nd ratio of 0.7219, the chondritic uniform reservoir (CHUR) value.2),5) The fact that the range of 143Nd/144Nd ratios is small compared with that of 87Sr/86Sr ratios means that the 143Nd/144Nd ratio of a sample R ((143Nd/144Nd)_R) is often expressed in epsilon notation (i.e., ɛ(R)), where the Nd isotopic composition of the sample is evaluated by comparison with the present-day CHUR isotope ratio, as follows:

\[
\varepsilon^0(\text{Nd}) = \left\{ \frac{\frac{143\text{Nd}}{144\text{Nd}}}{(144\text{Nd})_{\text{CHUR}}} R \right\} \times 10^4
\]
where the superscript zero refers to the present time (t = 0) and $\frac{^{144}Nd}{^{143}Nd}$ = 0.512638.

Lead has four isotopes, and environmental studies use six Pb isotope ratios as traceability indices. The relative abundance of Pb isotopes in natural materials is generally in the order $^{208}$Pb, $^{206}$Pb, $^{207}$Pb, and $^{204}$Pb from highest to lowest abundance. Lead isotope ratios are expressed in forms comparing the respective ratios of $^{206}$Pb, $^{207}$Pb, and $^{204}$Pb with both primordial and radiogenic origins to primordially derived $^{208}$Pb ($^{206}$Pb/$^{204}$Pb, $^{207}$Pb/$^{204}$Pb, and $^{208}$Pb/$^{204}$Pb), and the ratios of the former three isotopes ($^{206}$Pb/$^{208}$Pb, $^{207}$Pb/$^{208}$Pb, $^{204}$Pb/$^{208}$Pb, or $^{206}$Pb/$^{207}$Pb).

3. Sr isotopes in freshwater ecosystems

Nearly all of the Earth’s surface water (97.3%) is seawater, which contains elevated concentrations of Sr (~8 ppm) and has an extremely homogenous $^{87}$Sr/$^{86}$Sr ratio.\(^2\),\(^5\) The $^{87}$Sr/$^{86}$Sr ratio of benthic foraminifera collected from the western Pacific Ocean and in corals from shallow seas and dated to the past 30,000 years is 0.709175 ± 0.000005,\(^1\) with the range in this value less than twice the uncertainty on these measurements. In contrast, large variations are present in freshwater $^{87}$Sr/$^{86}$Sr ratios.\(^2\),\(^12\)

3.1. Groundwater and river water. Groundwater, lake water, and river water resources contain \(22.3\%, 1.5\%, \) and \(0.016\%\) of the world’s freshwater, respectively. The quality of groundwater and spring water (i.e., groundwater appearing at the Earth’s surface) is strongly buffered by subterranean rocks and is generally stable. One example of the geochemistry of groundwater, from Saijo in southwestern Japan and the Kanto region have $^{87}$Sr/$^{86}$Sr ratios higher than seawater, including sandstone and shale units within Jurassic accretionary complexes. The sandstone and shale of the Shimanto Belt, a Cretaceous to Paleogene accretionary complex on the Pacific side of southwestern Japan, and the Mesozoic granites of the Chubu and Kinki regions of Japan also have high $^{87}$Sr/$^{86}$Sr ratios.\(^1\)\(^3\) This in turn has generated river water and groundwater in these areas that typically have higher $^{87}$Sr/$^{86}$Sr ratios than seawater. This is further exemplified by the Lake Biwa basin in the interior of southwestern Japan, which is generally underlain by Triassic and Jurassic sandstone and shale, and Cretaceous granite and rhyolite units. The water within the majority of rivers in this basin has $^{87}$Sr/$^{86}$Sr ratios higher than seawater, primarily as a result of the Sr derived from these rocks.\(^1\)\(^5\)\(^6\) The $^{87}$Sr/$^{86}$Sr ratios of river water also change according to variations in the contributions from tributaries with different $^{87}$Sr/$^{86}$Sr ratios. This is also demonstrated by studies of Lake Biwa, where $^{87}$Sr/$^{86}$Sr ratios at a given spot show temporal changes that are larger than the uncertainty on the Sr isotopic analysis (Fig. 3). However, these changes in river water are very small compared with the variations in $^{87}$Sr/$^{86}$Sr ratios caused by changes in atmospheric precipitation in inland Japan, which exceed 0.002 in most cases (Fig. 4).

3.2. Lake and marsh ecosystems. Lakes and marshes represent areas of mixing of river water and groundwater of variable water quality, yielding water with uniform isotope ratios. The $^{87}$Sr/$^{86}$Sr ratios of water in freshwater lakes and marshes in Japan have a characteristic and relatively narrow range of values (Fig. 5a). The $^{87}$Sr/$^{86}$Sr ratio of Lake Biwa water is characteristically high, reflecting the generally high $^{87}$Sr/$^{86}$Sr ratios of the river water within the watershed. Conversely, the watersheds of Lake Towada and Lake Suwa are dominated by volcanic materials with low $^{87}$Sr/$^{86}$Sr ratios, yielding lake waters with similarly low $^{87}$Sr/$^{86}$Sr ratios.

The range of geographic variations in lake water $^{87}$Sr/$^{86}$Sr ratios also differs depending on the lake. For example, the variation in $^{87}$Sr/$^{86}$Sr ratios in Lake Towada is only several times the uncertainty on the analysis, whereas the variations in Lake Biwa are several dozen times the uncertainty on the analysis (Fig. 5b). The factors involved in this variation include physical processes (e.g., the velocity of lake water circulation) and differences in the $^{87}$Sr/$^{86}$Sr ratios of inflowing river water and groundwater. Caldera lakes such as Lake Towada have low volumes
Fig. 3. Comparison of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in river water flowing into Lake Biwa in the summer of 2003 and the winter of 2004.16) Water quality data are provided for four areas (north, south, east, and west) that differ according to topography, geology, and the level of human activity. Sampling sites for baseflow observations in individual rivers are shown in the geological map in the lower right part of the figure, where red = granite, pink = rhyolite, yellow–green = Triassic–Jurassic sandstone and shale, pale blue = limestone, and white = Pliocene–Quaternary sediments.

Fig. 4. Time series of monthly $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in wet precipitation at three locations in Japan (Kawakami, Morioka, and Toyama) and a small island to the north of Taiwan (Peng–Chia–Yu).28–30,53) Dotted line (SS) indicates the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of seawater and brown bars (SMC) show the range of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for evaporitic (salinization) minerals in desert sand and loess within northern China.31,32)
of inflowing river water that generate small variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and low amounts of Sr isotopic heterogeneity. In comparison, the large surface area of Lake Biwa and the significant variations in Sr isotopic composition of inflowing river water have led to the development of Sr isotopic heterogeneity.

The food web in aquatic systems starts with phytoplankton and leads through zooplankton to predators and decomposers. Phytoplankton incorporates carbon dioxide and water containing Sr and other dissolved elements, meaning that phytoplankton and other organisms in aquatic environments should have similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios to the ambient water in which they are hosted. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of lakes and marshes coincide with the isotopic composition of sedentary organisms such as water grasses (measured in leaves and stems) and freshwater snails (measured in shells; Fig. 5). However, closer examination indicates that the variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of lake and marsh water, and in sedentary organisms are greater than the uncertainties on these analyses, as shown in an example from Lake Biwa (Fig. 5b). The water and water grasses or mollusk shells have very similar $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are generally higher in the North Basin of the lake compared with the South Basin. This finding is consistent with the higher $^{86}\text{Sr}/^{88}\text{Sr}$ ratios (>0.712) of rivers entering the North Basin (west and east areas in Fig. 3) compared with those entering the South Basin. However, some areas, for example where river water enters the lake, have water $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that differ from the Sr isotopic composition of organisms within the same area. The fact that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of organisms reflect the composition of the ambient lake water during their growth means that this disagreement is ascribed to temporal variations in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the lake water. In addition, brackish lakes where freshwater and seawater mix have water and organism $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that can vary significantly. This heterogeneity of Sr isotope ratios in water and organisms could be used to trace relationships between material dynamics and the organisms of these lakes in even greater detail.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of bones from great cormorants (*Phalacrocorax carbo*) collected from two different sites at Lake Biwa are identical to the composition of the lake water, indicating that these birds are eating fish and drinking water from the lake. The fractionation of Sr isotopes occurs during metabolic processes, although unlike N or C the mass-dependent fractionation of Sr can be corrected during data reduction by normalizing to $^{86}\text{Sr}/^{88}\text{Sr}$. This means that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of water and organisms, both of which reflect the regional geology of an area, can be used as a geologic index. The same is true for Nd isotopes, although these isotopes have only limited uses in environmental and ecological applications.
compared with Sr isotopes as a result of the generally very low concentrations of Nd in these environments.

3.3. Application to fish studies. Both marine and land areas are habitats for sedentary and sessile organisms with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are identical to the associated ambient water. However, fish that migrate in the aquatic environment, particularly anadromous fish, have behavioral histories that are reflected by their body tissues. In particular, otoliths that grow sequentially in fish provide an excellent archive that can help reconstruct the history of the aquatic environment in which the fish lived.

The Sr/Ca ratio of seawater (0.02) is approximately twice that of freshwater. This difference may be reflected in otoliths and can thereby be used to provide information on the living environment within both marine and land areas. However, freshwater Sr/Ca ratios are generally invariant between river systems, and the Sr/Ca ratios of otoliths change with temperature and vital effects. This means that otolith Sr/Ca ratios cannot be used to distinguish between rivers, for instance when attempting to identify the habitats or tracking the migration history of freshwater fish. For example, the Sr/Ca ratios of salmon or trout otoliths from fish migrating upstream will not reveal whether the fish in question are returning from the sea to their natal streams where they were spawned. However, river water (unlike seawater) shows large geographic variations in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, meaning that differences in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between water and biological material can be ignored. As such, otolith Sr isotope ratios enable the reconstruction of the history of a salmon’s behavior, even to the extent of determining whether the fish had returned to its natal stream.

Freshwater fish otolith $^{87}\text{Sr}/^{86}\text{Sr}$ ratios can also provide a good index of water mass movement, primarily as the narrow range of living conditions of these fish generates $^{87}\text{Sr}/^{86}\text{Sr}$ ratio variations that are no greater than the Sr isotopic variations in sedentary organisms. This is exemplified by threespined sticklebacks (Gasterosteus aculeatus) living in springs with small changes in water quality, which yield $^{87}\text{Sr}/^{86}\text{Sr}$ fluctuations no greater than the uncertainty of the analysis.

4. Forest ecosystems: atmosphere, plants, and soil

Forest is a complex ecosystem composed of macroorganisms (plants and animals) and soil, with the latter containing air, water, and microorganisms in addition to soil minerals. Mountain forests free of human inhabitants have plant and soil ecosystems containing elements derived from the atmosphere and the underlying geology. Recent deterioration of ecosystems has accompanied changes in the atmospheric environment, including warming or pollution by nitrogen oxides and heavy metals. As such, evaluation of the influence of atmospheric deposition on ecosystems requires the discrimination of elements with atmospheric and geological origins.

The analysis of the stable isotopic composition of material derived from rocks and minerals is an effective method of demonstrating the movement of elements between plants and soil or within the soil. For example, the decline of forests as a result of acid rain was a serious problem in many countries during the late 20th century. One of the causes of forest decline may be loss of Ca, an essential plant nutrient, from the soil due to leaching by acid rain. Both Sr and Ca are geochemically similar because they are divalent elements with similar ionic radii, meaning that Sr can be used as a proxy for Ca. This in turn means that Sr isotope ratios enable the quantification of the relative contributions of Sr and Ca from atmospheric deposition and basement rock sources.

4.1. Yakushima World Natural Heritage Site. The Yakushima World Natural Heritage Site is an island far from the Japanese mainland that has experienced minimal local anthropogenic influence on the natural environment (Fig. 1). The island receives two to five times more precipitation (2,700–8,600 mm/year) than the average for Japan (1,700 mm/year), but this precipitation contains large amounts of air pollutants originating from the Asian continent. In fact, precipitation on Yakushima is acidic (annual average pH is 4.7) and contains large amounts of non-sea salt sulfur (SO$_4^{2-}$: 22–93 µeq/L$^{-1}$), nssSO$_4^{2-}$/SO$_4^{2-}$: 0.6–0.8) that is derived from transboundary pollution. The granite that forms the majority of the island has a small acid neutralization capacity, meaning that concern is growing about the effect of this air pollution on the island’s ecosystem. Wet precipitation is also rich in components derived from sea salt particles that have a relatively constant $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.70917–0.70935) throughout the year. In contrast, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of stream waters on the island differs markedly between watersheds draining granitic and sedimentary rocks, indicating that 70%–80% of the Sr$^{2+}$ and Ca$^{2+}$ in stream waters is derived from basement rocks.

A detailed study conducted in the granitic Yotsuse area of northwestern Yakushima yielded
been leached from this granitic substrate. This 90% of the Ca, 80% of the Sr, and 70% of the P has dominated by weathered granite, and approximately the lower soil layers on Yakushima island are marked in Asian dust in sur quently, the predominance of minerals derived from speci acids having isotopic compositions more similar to minerals that have $^{87}\text{Sr}/^{86}\text{Sr}$ ratios variations that are smaller than the precision of the analyses, indicating that the basement rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in areas dominated by young volcanics (e.g., Japan) can be regarded as constant.

The Sr and Nd isotopic composition of soil in the Yotsuse area varies with depth, indicating a greater abundance of Asian dust-derived silicates near the ground surface (Fig. 6). Soils at different depths plot in the mixing zone between silicate minerals with local and Asian origins, and the stable isotopic ratios of these two components enable quantification of the relative contributions of these two sources. In particular, the fine-grained nature of particles in the atmosphere means that a more precise evaluation of soil components can be obtained by measuring different grain-size fractions, with fine-grained minerals having isotopic compositions more similar to Asian dust and the uppermost layers of soil in this area containing up to ~80% fine-grained mineral.

Smaller grainsize soil minerals have larger specific surface areas, meaning they play a significant role in determining soil-exchange capacity. Consequently, the predominance of minerals derived from Asian dust in surfi cal soils suggests that this dust has a marked influence on material exchange with plants. The lower soil layers on Yakushima island are dominated by weathered granite, and approximately 90% of the Ca, 80% of the Sr, and 70% of the P has been leached from this granitic substrate. This suggests that the supply of essential plant nutrients (e.g., Ca and P) on Yakushima island is strongly dependent on atmospheric deposition.

4.2. Kawakami Experimental Forest Site, Yatsugatake, Japan. The contribution of atmospheric deposition to forest ecosystems varies with the volume of rainfall, the properties of the basement rock, and other factors. Soils in Japan contain large amounts of easily weathered volcanic material. It is therefore assumed that basement-rock-derived components play a larger role in forest ecosystems in Japan than in similar ecosystems in Europe and Eastern North America, which host soils containing less volcanic material. In addition, the volcanoes in Japan are relatively young. Volcanoes that formed approximately one million years ago produce volcanic minerals that have $^{87}\text{Sr}/^{86}\text{Sr}$ ratio variations that are smaller than the precision of the analyses, indicating that the basement rock $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in areas dominated by young volcanics (e.g., Japan) can be regarded as constant.

The Kawakami Experimental Forest of the University of Tsukuba is located far from the sea in the southern Yatsugatake Mountains of central Japan (Fig. 1). This forest is located in a mountainous headwater area of 0.14 km$^2$ with elevations from 1,500 to 1,680 m above mean sea level and is located in an area dominated by early Pliocene andesite volcanic rocks. The vegetation in this area is dominated by dwarf bamboo (Sasa nipponica) and Mongolian oak (Quercus crispula) that is spaced at about 5 m intervals. Although the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of both plant species (measured in oak buds and bamboo leaves) are nearly the same in hillside localities, the ratio changes with distance from the valley bottom (Fig. 7a). Japanese oak buds and bamboo leaves have almost the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as soil water in this area (Fig. 7b), and they have the same $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as bulk soil NH$_4$Cl and H$_2$O$_2$ leachates. This means that this area is the same as the soils on Yakushima island in that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of soil-exchangeable components at individual sites are almost identical to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of organic matter and soil water.

The bulk soil in the Kawakami Experimental Forest is dominated by silicate minerals but has higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than the underlying andesitic bedrock (0.7039) and associated weathering products (0.7044). This indicates that the Kawakami soil, like the soils on Yakushima island, contains silicates derived from Asian dust. The variation in bulk soil $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.7051–0.7084) indicates that Asian dust plays a complex role in these soils that is
partially dependent on the location of the soil in the valley. As is the case on Yakushima, the Sr isotopic data from the Kawakami Experimental Forest provides evidence of material exchange between water, organic matter, and exchangeable components, although Sr and other elements in soil minerals are not involved in these exchanges.

The concentrations of Sr$^{2+}$ in soil solutions in the Kawakami Experimental Forest correlate with both Ca$^{2+}$ and NO$_3^-$ ions. This result suggests that nitrogen deposition from the atmosphere is linked to the leaching of components from soil and basement rocks within the forest ecosystem. The soils in this small watershed become thinner with increasing height above the valley floor, and the $^{87}$Sr/$^{86}$Sr ratios in plants, soil organic matter, and soil water increase with increasing height on the valley slope, indicating a positive correlation between decreasing distance...
from the valley floor and increasing proportions of Sr derived from basement rocks. This area contains swarms of train millipedes (*Parafuntaria laminata*) that emerge every 8 years; these millipedes congregate in the soil until they reach the 8th instar, when they leave the soil and migrate. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in 8th instar millipedes differ from the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in plants and soil organic matter at the same spot, indicating that the millipedes feed at different sites along the slope (Fig. 7a). However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in millipedes collected from the lower part of a slope are lower than those of millipedes from the upper part of the same slope. This indicates that individual millipedes travel no more than a few dozen meters along the slope, providing clear evidence of how the distribution of Sr isotope ratios can provide insights into the material dynamics of ecosystems, including animals.

5. Interaction between the atmospheric environment, and glacier and forest ecosystems

Stable Sr, Nd, and Pb isotopic ratios of atmospheric aerosols have been used as tools in atmospheric environmental research, primarily as these ratios differ according to the sources of aerosols within marine and terrestrial areas.\(^2,\!^3,\!^{10}\) These geologically sourced stable isotopes are also useful for elucidating interactions between the atmosphere and terrestrial ecosystems.

5.1. Effect of Asian dust minerals on the atmospheric environment and ecosystems. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of precipitation in Japan and Taiwan change seasonally, with values tending to be high in spring and low in summer and autumn.\(^28\)\(^{-30}\) Asian dust generated from desert areas in northern China is active in spring. Both desert soils in northern China and the loess derived from these soils are associated with evaporitic minerals that are dominated by calcium carbonate (CaCO$_3$) with high concentrations of Ca and Sr but also contain sulfates and chlorides. These evaporitic minerals are soluble in water and weak-acids and have distinct $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (0.710–0.713), which are lower than that of associated silicates (0.720 ± 0.003).\(^31,\!^{32}\) In many places, the higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of springtime precipitation than that of seawater (Fig. 4) is ascribed primarily to the input of Asian dust from China’s desert regions.

Soil containing evaporitic minerals is alkaline whereas rainwater is generally acidic, and the CaCO$_3$ in Asian dust has a neutralizing effect on the rainwater that transports the dust. Spring rain at the Kawakami site has a $^{87}\text{Sr}/^{86}\text{Sr}$ ratio close to that of evaporites, and ~70% of the Ca in precipitation at the Kawakami site is derived from the CaCO$_3$ in Asian dust.\(^28\)

Inland areas located far from the sea, and high mountain regions have low influxes of airborne sea salt particles and greater contributions from materials derived from inland regions. High mountain regions of the Asian continent contain a combination of algae and windblown minerals called cryoconite within ablation zones near the lower terminations of glaciers. The fact that the presence of cryoconite lowers the local albedo, causing an increase in heat absorption and an acceleration in glacial melting, means that investigating the origin of this material is important.\(^30\) Large amounts of cryoconite containing cyanobacteria are present in ablation zones within mountain glaciers in the Tian Shan and Kunlun mountains of China. In contrast, cryoconite is less abundant on glaciers in the Altai Mountains to the north of China and the Himalaya to the south of China, both of which also contain green algae instead of cyanobacteria.

The Sr and Nd isotope ratios of the silicate minerals that dominate cryoconite vary because the mineral sources differ from one glacier to another.\(^34,\!^{35}\) Silicate materials within Chinese glaciers have Sr and Nd isotope ratios that are similar to those of desert soils within western and northwestern China that produce Asian dust. In comparison, organic material (e.g., cyanobacteria) has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios that are nearly identical to those of evaporitic minerals within desert soils (Fig. 8). This indicates that the abundant cryoconite present within mountain glaciers in China is dominated by dust sourced from nearby deserts. This dust contains evaporitic minerals (mainly CaCO$_3$ minerals) that form the main source of nutrients for the cyanobacteria that thrive in alkaline environments.

Mount Tateyama (Fig. 1) in central Japan faces the Sea of Japan and is associated with precipitation that has seasonal changes in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar to those recorded in the Kawakami area. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (0.7099) of the Japanese stone pine (*Pinus pumila*) in this alpine region is higher than that of either the basement rock or seawater, indicating that these trees uptake a significant amount of Sr derived from evaporitic minerals within Asian dust.\(^36\) Transboundary materials from the Asian continent are rich in ammonia and nitrogen oxides, both of which tend to be deficient in forest environments. Asian dust is also considered to be a
Therefore, airborne pollutants from Far East Asia may act as nutrient sources for forests and other ecosystems, especially in environments such as glaciers and alpine areas.

### 5.2. Interaction between rain and plants.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of precipitation in Japan and Taiwan commonly decrease during summer and autumn (Fig. 4) owing to increased amounts of airborne material derived from cement and road dust. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of limestone, a raw material in cement manufacture, is 0.7080 ± 0.0012. However, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of precipitation is sometimes lower than that of seawater or limestone; this is even the case in forest areas that are distant from urban areas, indicating that this Sr is derived from other sources. The Earth’s mantle and mantle-derived volcanic rocks have low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, with Japanese volcanic rocks having $^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.703–0.706. The low $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (≈0.7065) of autumn rain in the Kawakami area suggests that this rainfall has been affected by contributions from Sr ultimately derived from volcanic rocks around the precipitation area.

Clarifying the interaction between precipitation and plants is important in assessing the impact of atmospheric deposition on ecosystems, including acid rain. Rainfall in forest areas is termed ‘incident precipitation’, with rain passing through forest canopies termed ‘throughfall’, and rain flowing along tree trunks termed ‘stem flow’. Research in the Kawakami area indicates that stem flow $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are nearly identical to plant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, with neither varying significantly from season to season. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of throughfall is the same as that of incident precipitation in winter, when there is little or no foliage, and is closely correlated with the Sr isotopic ratio of plants in summer when foliage is abundant (Fig. 9). The $^{87}\text{Sr}/^{86}\text{Sr}$ concentration in throughfall strongly correlates with $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ concentrations in throughfall. This result, combined with the fact that these cations are present in high concentrations in throughfall that has $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to the Sr isotopic ratios of plants in this area, indicates that these elements are sourced from plants locally.

Calcium, Sr, and other elements within plants are eluted in reactions with rainwater, suggesting that the introduction of aerosol particles derived from plants to the atmosphere may influence the quality of precipitation. In fact, wet precipitation in forests of northern Europe contains plant-derived $\text{Ca}^{2+}$, $\text{Sr}^{2+}$, and other elements, but the presence of plant-derived aerosols in this region remains unclear. The average annual precipitation in Japan is 1700 mm, and evapotranspiration from forests is ~800 mm, indicating that approximately half of the...

![Frequency diagram of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in organic matter in cryoconite on Chinese mountain glaciers (Grigoriev ice cap, Urumqi Glacier no. 1, and Miaoergou Glacier in the Tien Shan, and Qyi Glacier in the Qillian Shan), and evaporitic (salinization) minerals in desert sand and loess in northern China.](image-url)
precipitation returns indirectly through the plants in these forests to the atmosphere. The formation of microscopic particles on plant surfaces by the evapotranspiration of rain has also been found in atmospheric aerosols, indicating that these plant-derived particles can also influence the water quality of incident precipitation, as well as throughfall.

Rain $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Japan reach maximum values (0.7105) that are similar to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of evaporitic (salinization) minerals within Asian dust (Fig. 4). In contrast, the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are associated with summer and autumn rainfall but are area-dependent. For example, areas dominated by volcanic rocks (e.g., the Kawakami site) have low rain $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and similarly low plant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Other areas also record a correlation between the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of summer and autumn precipitation and plant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, with precipitation $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in South Korea and Japan correlating with plant $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in these areas (Fig. 10). The possible influence of plant-derived Sr on precipitation $^{87}\text{Sr}/^{86}\text{Sr}$ ratios has also been identified in tropical forests of central Africa. The fact that land surfaces in forest areas are widely covered with vegetation means that Sr isotope ratios can be used as a traceability index to evaluate the influence of terrestrial materials on the atmospheric environment in these regions.

### 5.3. Links between Pb isotope ratios in precipitation and ecosystems

The water quality of precipitation in Japan varies seasonally, reflecting areal differences in source materials such as water vapor and dissolved components. In contrast to Sr isotope ratios, precipitation in Japan has deuterium excess values (d) that are high in winter and low in summer, reflecting changes in water vapor sources. Nitrogen compounds, sulfur oxides, heavy metals, and other components are also present in higher concentrations in winter precipitation (snowfall) and in lower concentrations in summer precipitation. In particular, the water quality of precipitation on the Sea of Japan side of Japan differs markedly between summer and winter, primarily as a result of the presence of pollutants from the Asian continent in winter.

The concentration of heavy metals in the atmosphere has been increasing since the Industrial Revolution. In particular, a rapid increase in Pb within the atmosphere occurred during the period of high economic growth following Second World War as a result of the use of leaded gasoline, resulting in serious environmental pollution in many regions. The banning of leaded gasoline in the 1970s caused a rapid decrease in atmospheric Pb concentrations within industrialized nations, although heavy metals (including Pb) are still present in ash and particulate matter emitted from sources such as fossil-fuel-fired power plants and refuse incinerators.

The stable isotope ratio of atmospheric Pb differs greatly from country to country. The ores that are the ultimate source of atmospheric Pb have stable isotope ratios that differ substantially with the time of ore formation. Ancient Precambrian ore deposits such as those in Canada and Australia are generally deficient in radiogenic Pb. The use of Australian ores in Australia and the United Kingdom means that atmospheric aerosols in these countries are characterized by low $^{206}\text{Pb}/^{207}\text{Pb}$ and $^{208}\text{Pb}/^{207}\text{Pb}$ ratios. The Pb isotope ratios of precipitation in Japan also have regional and seasonal differences that reflect changes in the relative contributions from differing sources. Winter rain in Japan contains large amounts of Pb derived from China, with rain on the Sea of Japan side of Japan containing Pb originating in China, whereas rain in northern Japan contains Pb derived from Russia and Mongolia, and rain in urban areas in the Kanto and Setouchi areas contains Pb sourced from Japan.

Although river water Sr isotope ratios strongly reflect the underlying geology of a region, research in the mountains of South Korea and the Tsukuba region of central Japan indicates that river water Pb isotope ratios are identical to the isotopic composition of atmospheric Pb and clearly differ from the Pb isotopic compositions of local rocks or river sediments (Fig. 11). This result is primarily due to feldspar minerals, as plagioclase feldspar is more susceptible to chemical weathering but contains low concentrations of Pb, and K-feldspar contains more Pb but is resistant to chemical weathering. This mineralogical factor means that mineral-derived Pb is unlikely to be discharged into the environment.

Plants also have Pb isotope ratios that are similar to those of atmospheric Pb. The fact that heavy metal elements are strongly adsorbed onto soil particle surfaces means that they are difficult to desorb except in acid environments, a fact that is compounded for Pb as this element is especially strongly adsorbed onto soil particles. Soil Pb isotope ratios indicate that heavy metal elements originating in the atmosphere accumulate in exchangeable pools within the soil before being taken up into the ecosystem material cycle. The majority of
heavy metals in aerosols are ultimately derived from the manufactured products formed from ores. This means that Pb stable isotopes are a useful monitoring tool to identify atmospheric deposition, primarily as the source of ore metals utilized in a given nation changes as a result of responses to socioeconomic changes that affect the trading of ores.

6. Relationships to human society

6.1. Anthropogenic impacts on land ecosystems: the example of Lake Biwa. Human activities add a wide variety of materials into the natural environment, as exemplified by modern agriculture, which uses large amounts of chemical fertilizers and water, meaning that the environmental impact of agriculture is reflected in water quality and by organisms within associated ecosystems. The water quality in Lake Biwa has changed with the expansion of human activities since the 1960s. Research based on Sr, N, and S stable isotopes indicates that agricultural activity has contributed to this change.15),16),44)

Intensive rice farming takes place on the eastern plain of Lake Biwa, with water quality components of the rivers flowing from the mountains (particularly Ca^{2+}, Mg^{2+}, Sr^{2+}, and SO_{4}^{2-}) increasing in concentration within stream waters as they pass through...
this area. Sulfur isotope ratios indicate that increases in $SO_4^{2-}$ concentrations are the result of the sourcing of sulfur from agricultural fertilizers such as ammonium sulfate. Rice paddy areas also produce acids such as carbonic acid, organic acids, and sulfuric acid during the decomposition of organic matter and the dissolution of nitrogenous fertilizer, although nearby rivers are mildly alkaline, indicating that this acid generation is neutralized in this area.

The concentrations of divalent ions such as $Ca^{2+}$, $Mg^{2+}$, and $Sr^{2+}$ in inland waters tend to increase downstream from river headwaters, primarily as the minerals containing these elements are subjected to chemical weathering during transport within the river system. Increases in $Ca^{2+}$, $Mg^{2+}$, and $Sr^{2+}$ within stream waters flowing through rice paddy areas are caused either by the decomposition of soil minerals containing these elements or by the desorption of these elements from sediment particles through the action of various acids under rice paddy areas. The eastern plain of Lake Biwa is dominated by Kobiwako Group sediments that are derived from volcanic rocks of intermediate to felsic composition. This means that plagioclase is most likely the ultimate source of $Ca^{2+}$ and $Sr^{2+}$ in the water, whereas $Mg^{2+}$ is most likely derived from minerals such as amphibole and biotite.

Tributaries of the Mississippi River in the United States have alkalinity and $Ca^{2+}$ concentrations that increase during flow from forest into agricultural lands. This increase in alkalinity indicates that carbon dioxide ($CO_2$) from the atmosphere is being dissolved in the water, where it is converted into carbonic acid and bicarbonate ions. The corresponding increase in acid ($H^+$) is thought to accelerate the increase in $Ca^{2+}$ concentrations within the river water. Chemical weathering on land is driven by acids, including carbonic acid, nitric acid, sulfuric acid, and organic acids. Although human activity contributes to the generation of these acids, freshwater is generally mildly alkaline, suggesting that anthropogenic acid contributions accelerate the chemical weathering of basement rocks. This in turn means that the analysis of geologically derived stable isotopes can add a new perspective to the dynamic analysis of C, N, S, and other elements. Changes in the N, S, and Sr stable isotopic composition of lake water can be reconstructed using data obtained from organisms. The analysis of first-year isaza ($Gymnogobius isaza$), an endemic species of goby fish in Lake Biwa, yielded $\delta^{15}N$ values that increased over time with coincident decreases in $\delta^{34}S$ values and $^{87}Sr/^{86}Sr$ ratios as a result of an increase in human population within the watershed. These comparisons between temporal changes in lake water quality and geographic variations in the water quality of contributing rivers suggest that a recent increase has occurred in the contribution of rivers in the eastern plain to Lake Biwa. The accuracy of this type of environmental diagnosis can be improved by the use of different samples together with stable light and heavy isotopic analysis.

6.2. Isoscapes: application to agricultural and marine products, and to archeology. The $Sr$, Pb, and Nd isotope ratios of marine and agricultural products strongly reflect the isotopic composition of marine water, which varies geographically. This means that these isotope ratios provide an excellent traceability index because they reflect the isotopic composition at a precise sampling point. Bottled mineral water derived from groundwater has a strong regionality in terms of water quality, and Sr isotope ratios can be utilized as a forensic traceability index for the characterization of the production areas of bottled water and wine.

Maps of stable isotope ratios for water, agricultural products, and marine products make it easy to identify their production areas. These geographic patterns of isotopic distributions in environmental materials have been called isoscapes. Such isoscapes are useful in conducting global environmental research and have become increasingly frequently used in a wide variety of research. This is especially evident in Japan, where it has become increasingly important to be able to distinguish between food produced in Japan and food produced elsewhere. Isoscapes have also been used in archeological research, with various forms of ritual tooth extraction, perhaps related to coming-of-age ceremonies, identified in human skeletal remains from the Late and Final Jomon periods of Japan. Research into the Yoshigo and Inariyama skeletal remains at a site in southeastern Aichi Prefecture indicates that several types of tooth extraction were practiced during these times. In addition, although the $^{87}Sr/^{86}Sr$ ratios of marine products match seawater ratios, the $^{87}Sr/^{86}Sr$ ratios of terrestrial resources show regional variations. Plant $^{87}Sr/^{86}Sr$ ratios correlate strongly with geological conditions, reaching high values in the northern part of the granitic Ryoke Belt and values close to that of seawater in the coastal zone of Japan (Fig. 12). Plants near the archaeological site have $^{87}Sr/^{86}Sr$ ratios that are almost the same as seawater, indicating that teeth with $^{87}Sr/^{86}Sr$ ratios differing
from this value are most likely from immigrants, although this research did not show a clear relationship between tooth extraction and whether an individual was a native or an immigrant.52) Isotope maps of environmental substances such as water and plants can be used to trace the origin of these substances as well as providing a store of basic information concerning the life histories of animals and dynamic interactions between environmental substances. These maps are gaining attention not only in global environmental research but also in forensic studies aimed at identifying places of food production and the local certification of agricultural and marine products. Other implementations of such maps, including fingerprint maps for criminal investigations and other applications, will also be beneficial for society.

7. Conclusions

Stable Sr, Nd, and Pb isotopic ratios show wide geographical variations that reflect changes in the geological sources of these elements. These elements have smaller degrees of isotope fractionation than is the case for light stable isotopes, which enables the mass-dependent fractionation of Sr and Nd to be removed by analysis of multiple isotopes of these elements. This paper reviewed the application of these geologically derived stable isotopes in research into Earth environments, focusing mainly on the use of Sr isotope techniques.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of precipitation in Japan show seasonal and geographic variations that reflect mixing of Sr source materials, which include sea salt particles, water-soluble minerals within Asian dust, and geological materials at the site of precipitation. Strontium and Nd isotopic analysis indicates that insoluble minerals in Chinese desert soils are also present in glaciers in the surrounding mountains, whereas water-soluble minerals are decomposed and their elements are utilized by cyanobacteria. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of soil and surface waters are relatively stable over time but vary with the underlying basement and watershed rocks. This geographic variation is reflected in plants, agricultural products, aquatic organisms, and human bodies, indicating the usefulness of $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as traceability indices.

The integrated use of stable Sr, Nd, and Pb isotopes is an effective approach that allows the tracing of interactions within and between the atmosphere, pedosphere, hydrosphere, and biosphere. Human activities supply huge amounts of carbon, nitrogen, and sulfur into the environment as a result.
of the use of fossil fuels and agricultural and fishery products, generating acids in water that accelerate the chemical weathering of geologic materials. This in turn indicates that combining stable light and heavy elements is a powerful approach that enables the development of multiple traceability indices within Earth environments.

Acknowledgements

This report summarizes stable isotope research undertaken in collaboration with numerous scientists and students at the University of Tsukuba and the Research Institute for Humanity and Nature, Kyoto, Japan, and I gratefully acknowledge their participation in this study. This work was supported in part by a Grant-in-Aid for Scientific Research Projects from the Ministry of Education, Culture, Sports, Science and Technology (18201004) and the JST–CREST project, “Development of Multi-tracer Techniques for Diverse Functions of Coastal Ecosystems”.

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Profile

Takanori Nakano was born in 1950 and graduated from the Tokyo University of Education in 1974. He was Research Associate and Assistant Professor, Institute of Geoscience, University of Tsukuba, 1982–2003 and Professor of Research Institute for Humanity and Nature (RIHN) 2004–2015, and is Emeritus Professor of RIHN and Visiting Professor of Waseda University 2016–.