

Strontium isotope composition of sedimentary rocks and its application to chemostratigraphy and palaeoenvironmental reconstructions

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ABSTRACT

Strontium isotope composition of seawater is homogenous in all oceans and marginal seas but has varied through time with changing strontium fluxes. Strontium isotope ratio of ancient seawater may be reconstructed from well-preserved authigenic minerals and used for dating marine sediments. Because of a change in the strontium isotope ratio between sea- and freshwaters it can also be employed for the determination of palaeosalinities or the reconstruction of diagenetic processes of marine limestones. A review of methodology and practical hints concerning the utilization of strontium isotopes in geological studies of both marine and brackish sediments are presented in the current article.

1. INTRODUCTION

Strontium has four stable isotopes. Their natural concentrations on Earth average: ^{84}Sr – 0.56%; ^{86}Sr – 9.86%; ^{87}Sr – 7.0% and ^{88}Sr – 82.58%. The ^{87}Sr is radiogenic and forms continuously during decay of ^{87}Rb isotope. Because of the decay of ^{87}Rb isotope the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of Earth crust have increased from the initial value of ca. 0.6989. A change in the strontium isotope ratios is dependent on the rock Rb/Sr ratio. Since the continental crust is enriched in rubidium its $^{87}\text{Sr}/^{86}\text{Sr}$ ratios become increasingly higher and more and more dissimilar from the ratios of the oceanic crust and the mantle (Fig. 1).

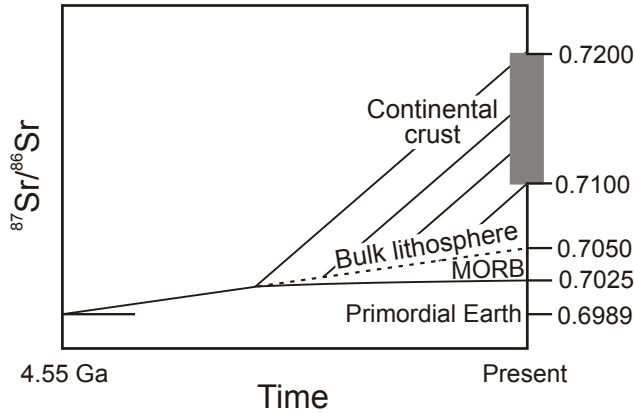


Fig. 1. Evolution of strontium isotope ratios in Earth's crust and mantle.

The seawater strontium isotope composition is uniform across modern oceans due to relative long residence time of strontium ($1-5 \cdot 10^6$ years) and the short mixing time of water masses (10^3 years; [1-5]). The modern seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is ca. 0.709175 [4]. The seawater strontium isotope composition has changed through geologic history of the Earth owing to changing inputs of strontium. Three major input sources influence the strontium isotope composition of seawater. Strontium of low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~ 0.703) is derived from hydrothermal circulation at mid-oceans ridges, strontium of high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~ 0.711) is derived from continental weathering, and strontium of intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (~ 0.708) originates from submarine dissolution and recrystallization of carbonate sediments (cf. [1-4]). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of continental strontium may have varied with changing proportions of various types of rocks exposed to weathering (granites, basalts or marine carbonates; cf. [6]). Changing areas of weathered rocks do not, however, appear to have had a considerable effect on seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in the Mesozoic [3]. The dependence of the seawater strontium isotope ratio on the changing inputs of strontium may be represented as a model diagram (Fig. 2).

Based on actualistic assumption of the low flux of diagenetic strontium ($\sim 6\%$; cf. [4, 7]) one can deduce from Fig. 2 that the strontium isotope ratio of seawater, which ranged from 0.7068 to 0.7092 during the Phanerozoic [5, 8, 9], mainly depended on changing inputs of hydrothermal and continental strontium.

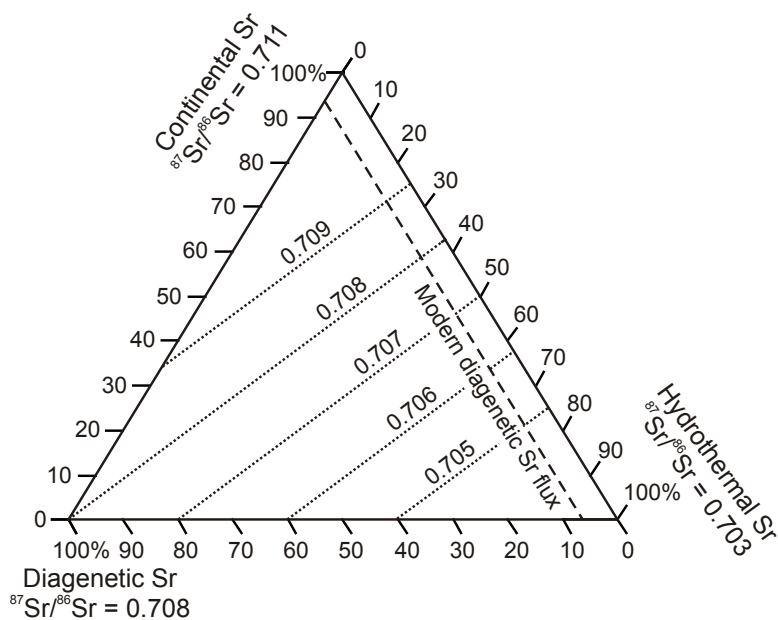


Fig. 2. Model of seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio regarded as a mixture of strontium contributed by the weathering of continents, strontium contributed by the hydrothermal activity of the seafloor and diagenetic strontium derived from dissolution and recrystallization of carbonates. Dotted lines represent different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of seawater. Dashed line represents modern diagenetic strontium flux (cf. [4, 7]).

The temporal seawater strontium isotope curve is characterized by several maxima and minima (two deepest minima occur in the Late Permian and at the Middle–Late Jurassic transition), which shows the changing inputs of strontium. An almost continuous increase of the seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratio has occurred since the Late Cretaceous (Fig. 3).

The seawater strontium isotope curve may be used to date marine sedimentary rocks (cf. [1, 5, 9]). The strontium isotope composition of fossils derived from brackish environments is an indicator of palaeosalinity (cf. [10]). The variation in the isotope composition of strontium may also be an indicator of diagenetic alteration of marine rocks and may allow quantifying fluid-rock interactions (cf. [11–14]).

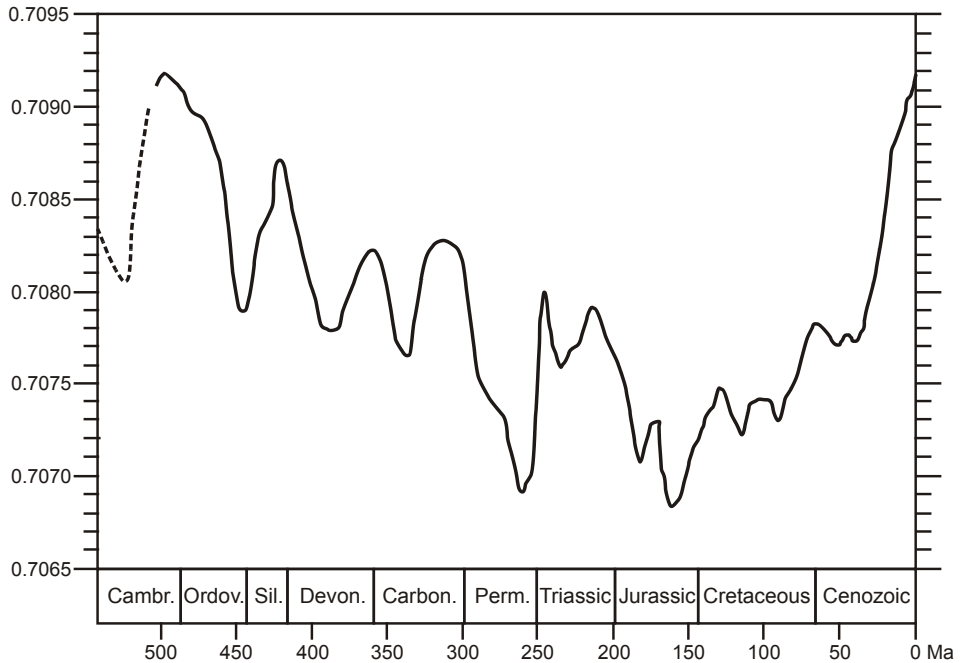


Fig. 3. Variation of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the Phanerozoic seawater (after [5]; modified).

The aim of the present contribution is not to repeat information and interpretation of the $^{87}\text{Sr}/^{86}\text{Sr}$ data given elsewhere but focus on practical aspects of using strontium isotope for dating of marine rocks, and the reconstruction of ancient salinities of brackish environments as well screening of diagenetic processes.

2. METHODOLOGY

Strontium concentration in seawater is $90 \mu\text{mol}/\text{kg}$, its concentrations in river waters are nearly 100 times lower averaging $0.89 \mu\text{mol}/\text{kg}$ [15, 16]. Strontium rarely forms pure minerals (e.g. celestine or strontianite) and is co-precipitated, especially with carbonates, and incorporated into detritic sediments or organic matter. Strontium content in marine sediments is high because of the high seawater concentration. The concentration of strontium in modern marine carbonates ranges from 200 to 10 000 ppm (cf. [17, 18]). Strontium isotope composition of ancient waters may be studied based on analyses of strontium preserved in authigenic minerals – carbonates, phosphates or evaporates. Carbonates are especially useful for strontium isotope studies because they are ubiquitous in all sedimentary rocks.

Analytical methods involve sample dissolution, evaporation to dryness, subsequent dissolution and separation of strontium on cation exchange resins (cf.

[19-22]). Selective dissolution techniques in weak acids (e.g. acetic acid) are recommended by some authors for impure samples to avoid dissolution of clay contaminants or diagenetic mineral phases [3, 23, 24].

Strontium isotope composition is traditionally reported as $^{87}\text{Sr}/^{86}\text{Sr}$ ratio because the ratio is measured directly by thermal ionization mass spectrometers. Before reporting measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized to a standard $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of 0.1194 to allow for the fractionation between ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr isotopes during mass-spectrometry analysis. In order to correct for interlaboratory bias, which is caused by instrumental effects, measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratios are normalized to the recommended ratios of isotope standards analysed along with studied samples. For the strontium isotope stratigraphy the recommended ratios of NIST-987 (=SRM-987) and EN-1 standards are given as 0.710248 and 0.709174, respectively [3, 5, 25, 26]. As strontium isotope ratios were normalized in older studies to different ratios of the isotope standards, the data need recalculation. The normalization does not, however, remove all the bias, which is pronounced for some old data (cf. [3]). This scatter may result from various preparation techniques. Whereas the external precision of the measurement of $^{86}\text{Sr}/^{88}\text{Sr}$ ratio of $\pm 2 \cdot 10^{-5}$ is attested in older studies [25] new laboratory and mass-spectrometry techniques allow better precision of replicated strontium isotope analyses of $\pm 3 \cdot 10^{-6}$ [5].

3. DIAGENETIC ALTERATION

Strontium isotope composition of sedimentary rocks may be affected by diagenetic alteration. Marine rocks are susceptible to exposure and alteration by meteoric waters due to their low strontium concentration and, as a rule, high strontium isotope ratios (cf. [11, 12, 27-29]). Good preservation state of investigated samples is therefore *condicio sine qua non*¹ for all chemostratigraphy applications and palaeoreconstructions based on strontium isotope data.

Skeletal calcites can be screened for the state of preservation using chemical analyses, cathodoluminescence studies and staining techniques. Diagenetic alteration often causes an increase in Fe and Mn contents of calcite and a decrease in its Sr contents as concentrations of these elements drastically differ between seawater and diagenetic fluids in reduced or freshwater environments [11, 12, 27-29]. The comparison between measured element concentrations and concentrations found in modern marine shells or predicted for intact marine calcites permits an assessment of diagenetic alteration. Some problems may arise because various authors indicate different threshold levels of element concentrations in well-preserved skeletons of extinct or ancient organisms (see Tables 1, 2).

¹ "a needed condition"

Table 1. Published threshold levels of element concentrations in well-preserved belemnite rostra

	Mn (ppm)	Fe (ppm)	Sr (ppm)
Veizer [27]	-	-	≥800
Jones et al. [30]	≤50	≤150	-
Veizer et al. [8]	-	-	≥800
Price et al. [31]	≤100	≤250	-
Rosales et al. [32]	≤32	≤250	≥950
Gröcke et al. [33]	≤100	≤200	-
Rosales et al. [34]	≤150	≤250	≥900
Price and Rogov [35]	≤100	≤150	-
Nunn and Price [36]	≤100	≤150	-
Wierzbowski et al. [37]	≤100	≤200	≥800

Mn²⁺ ions are also an activator of orange-red cathodoluminescence that is distinctive of diagenetically altered calcites but high Fe²⁺ contents may quench their luminescence [29, 38]. Since primary shell calcite is not precipitated in reducing environments where Mn²⁺ is available, the luminescence is indicative of the shell recrystallization (Fig. 4). Barbin and Gaspard [39] showed, however, that luminescent bands may occur in modern brachiopod shells in areas of slow growth rate characterized by distortion of crystal lattice. Some authors additionally recommend staining thin sections made from calcitic fossils with potassium ferricyanide and alizarine red-S to screen for the replacement of Ca²⁺ by Fe²⁺ (cf. [36, 40]). This is because of the fact that calcite zones with higher iron contents due to its quenching properties cannot be observed using cathodoluminescence studies.

Table 2. Published threshold levels of element concentrations in modern and well-preserved brachiopod shells

	Mn (ppm)	Fe (ppm)	Sr (ppm)
Morrison and Brand [41]	≤450	≤550	≥200
Joachimski et al., [41], van Geldern et al. [43]	≤100	≤400	≥500
Korte et al., [44-46]	≤250	-	≥400
Armendáriz et al. [47]	≤60	≤300	-

Low-magnesium calcite is relatively insoluble therefore shows high potential for the preservation of original stable isotope ratios [29]. Well-preserved belemnite rostra, oyster, inoceramid and brachiopod shells, all of which are composed of low-magnesium calcite, have been successfully used for measurements of the strontium isotope ratios of ancient waters (e.g. [19, 20, 22, 30, 43, 48, 49, 50, 51]; Fig. 5). Less certain results, albeit still within the range of $^{87}\text{Sr}/^{86}\text{Sr}$ predicted for pristine marine rocks, were obtained from bulk chalk, foraminifers or mudstones [23, 52-54]. Care should be taken in such cases to avoid clay contamination or diagenetically altered samples. Pre-leached techniques, elemental analysis, microstructure observation and comparisons to the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of coeval samples from different sites and localities were employed to increase the reliability of bulk rock data (cf. [23, 52, 53]). Reliable Cenozoic strontium isotope data are derived from foraminifers from deep ocean drilling sites, which have not been affected by meteoric diagenesis (cf. [55-58]).

Fossil biogenic apatites can be recrystallized during early or late stages of diagenesis. Diagenetically altered fish teeth are reported to show altered microstructure [59], strong enrichment in intermediate rare earth elements (“bell-shaped REE patterns”; [60, 61]) or elevated Fe, Mn, Si, Al and Ba concentrations [62]. The REE enrichment is also reported to activate orange-brown cathodoluminescence of teeth [63]. Conodonts can be screened for the state of preservation by studying microstructure and conodont alteration index (CAI), which varies with changing degree of thermal maturation (cf. [21, 59, 64-65]). As phosphates can easily exchange Sr isotopes with pore waters the reliability of conodont and fish tooth $^{87}\text{Sr}/^{86}\text{Sr}$ data is disproved by some authors (cf. [21, 66]). Despite this strontium isotope composition of well-preserved dental apatites is also found to be a proxy for ancient water chemistry (cf. [63, 67-69]).

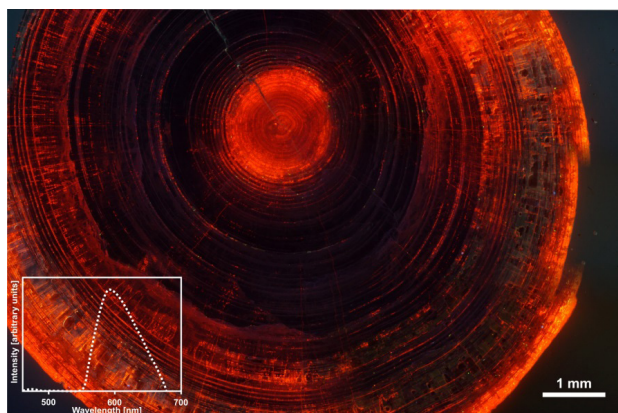


Fig. 4. Orange-red cathodoluminescence of diagenetically altered belemnite rostrum of *Hibolites* sp. from the Upper Oxfordian (Upper Jurassic) of the Kraków-Wieluń Upland. The luminescence is activated by Mn^{2+} ions with emission peak at ~ 600 nm.

4. STRONTIUM ISOTOPE STRATIGRAPHY

Since seawater strontium isotope composition has varied through time (Fig. 3) the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of well-preserved samples may be used to date and correlate marine sediments. Comparison of measured $^{87}\text{Sr}/^{86}\text{Sr}$ ratio to previously constructed temporal calibration curves can yield stratigraphical or numerical ages. The precision of the strontium isotope dating depends on the analytical precision of an isotope measurement, confidence limits of a calibration curve and its slope (Figs. 3, 5). Best results may be obtained for well-documented parts of the strontium isotope curve of sufficient slope including some early Jurassic intervals, Late Cretaceous and Late Paleogene to Recent (Fig. 3). The precision of strontium isotope dating will be not better than ± 0.1 Ma [5].

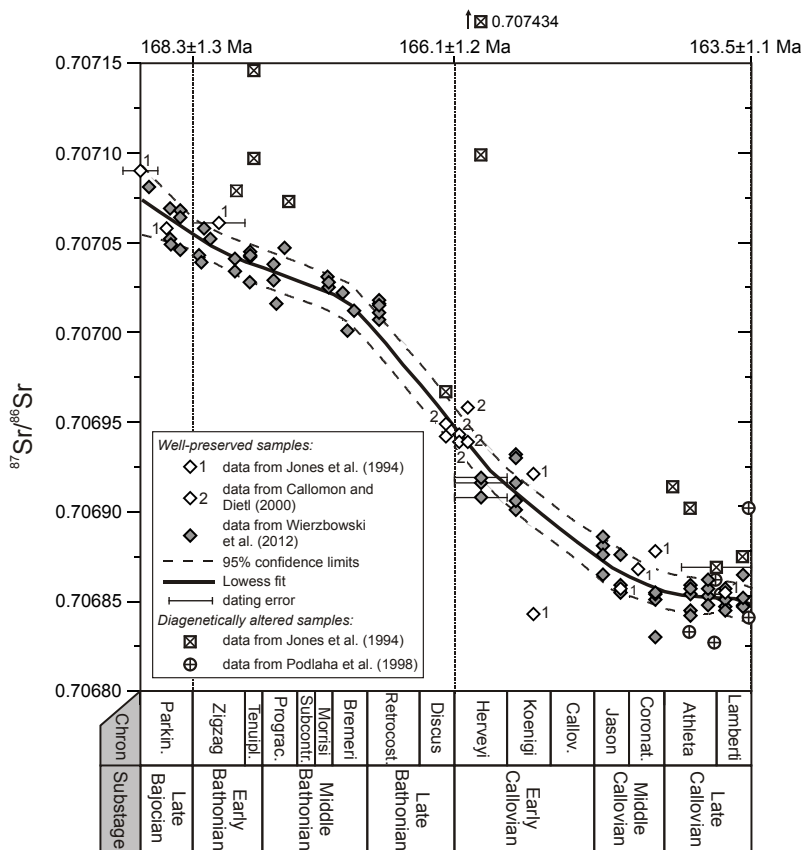


Fig. 5. Strontium isotope variations in Late Bajocian–Callovian seawater (after Wierzbowski [22]; modified). The strontium isotope curve is produced using a statistical Lowess method and based on well-preserved samples (with element contents: $\text{Mn} \leq 50$ ppm, $\text{Fe} \leq 150$ ppm, $\text{Sr} \leq 950$ ppm). Altered samples show higher and scattered $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. All values are normalized to the SRM 987 $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.710248.

Seawater strontium isotope curves have been constructed for several stratigraphical intervals by various authors (e.g. [19, 20, 22, 23, 26, 30, 43, 48, 50-52, 54-57, 68, 70]). Universal strontium isotope curves for the whole Phanerozoic are presented by Veizer et al. [8], McArthur et al. [5, 71], and McArthur and Howarth [9]. Improved strontium isotope curves are produced by using statistical methods (cf. [71, 72]). Reliable curves are based on samples stratigraphically well-dated and carefully screened for the state of preservation (see Fig. 5).

The seawater curves produced by McArthur et al. [5, 71] and McArthur and Howarth [9] are recommended for chemostratigraphic dating. They are available on request for scientific purposes from j.mcarthur@ucl.ac.uk in electronic format with fitted 95% confidence intervals. The principal disadvantage of the McArthur's trends is, however, the use of an absolute time scale which introduces remarkable uncertainty of dating of older rocks (Palaeozoic to Jurassic). This is also a reason for the necessity of updating the trends with amended time scales published.

5. VARIATION IN STRONTIUM ISOTOPE COMPOSITION OF BRACKISH WATER

Strontium isotopes can be used to determine palaeosalinities of ancient brackish waters owing to differences in strontium isotope ratios and concentrations between end-members – seawater (modern $^{87}\text{Sr}/^{86}\text{Sr} = 0.709174$, modern $C_{\text{Sr}} = 90 \mu\text{mol/kg}$; [16, 26]), and freshwaters (modern average $^{87}\text{Sr}/^{86}\text{Sr} = 0.711922$, modern average $C_{\text{Sr}} = 0.89 \mu\text{mol/kg}$; [7, 15]). The riverine strontium input depends on the type of weathered rocks. River that drain old continental shield have relatively high $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, and low strontium concentrations (Fig. 6; [7, 15]). Rivers draining young volcanic arcs show low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and high strontium concentrations, whereas rivers draining continental basins, filled with sedimentary silicates and limestones, show intermediate $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and intermediate to high strontium concentrations. Exceptionally high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and significant strontium concentrations of Brahmaputra and Ganges result from rapid erosion of Himalayas (Fig. 6; [7, 15]).

The strontium isotope composition of brackish waters forms a hyperbolic relationship to salinity, and the salinity can normally be resolved in the lower part of the mixing range only (Fig. 7; see also Bryant et al. [10] and Holmden et al. [73]).

The construction of the mixing trend, which is given as an eq. (1) needs the knowledge of the chemistry of freshwater and seawater end-members.

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{BW}} = \frac{[(\frac{^{87}\text{Sr}}{^{86}\text{Sr}})_{\text{SW}} C_{\text{SW}} SF_{\text{BW}} + (\frac{^{87}\text{Sr}}{^{86}\text{Sr}})_{\text{FW}} C_{\text{FW}} (1 - SF_{\text{BW}})]}{[(C_{\text{SW}} SF_{\text{BW}}) + C_{\text{FW}} (1 - SF_{\text{BW}})]} \quad (1)$$

where $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{BW}}$, $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{SW}}$, $(^{87}\text{Sr}/^{86}\text{Sr})_{\text{FW}}$ are strontium isotope ratios of brackish water, seawater and freshwater, respectively. C_{SW} and C_{FW} concentrations of strontium in seawater and freshwater, respectively.

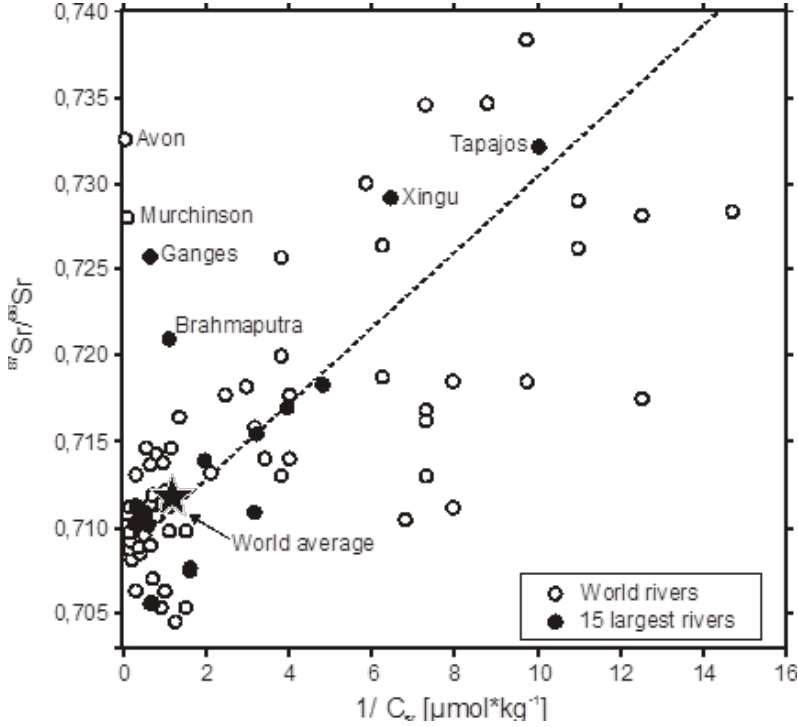


Fig. 6. Inverse relationship between strontium isotope compositions and strontium concentrations in world rivers. The strontium isotope composition and concentration depends on the type of rocks in draining area. Anomalously high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations of Avon and Murchinson rivers result from evaporative concentration of strontium. High $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and Sr concentrations in Ganges and Brahmaputra result from large sediment load from Himalaya Mountains (after Jones and Jenkyns [4]).

SF_{BW} is a salinity factor of brackish water calculated as a fraction of freshwater and seawater from absolute salinities according to an eq. (2).

$$SF_{\text{BW}} = (S_{\text{BW}} - S_{\text{FW}}) / (S_{\text{SW}} - S_{\text{FW}}) \quad (2)$$

S_{BW} , S_{FW} and S_{SW} from the eq. (2) are absolute salinities (in per mil) of brackish, fresh- and seawater, respectively.

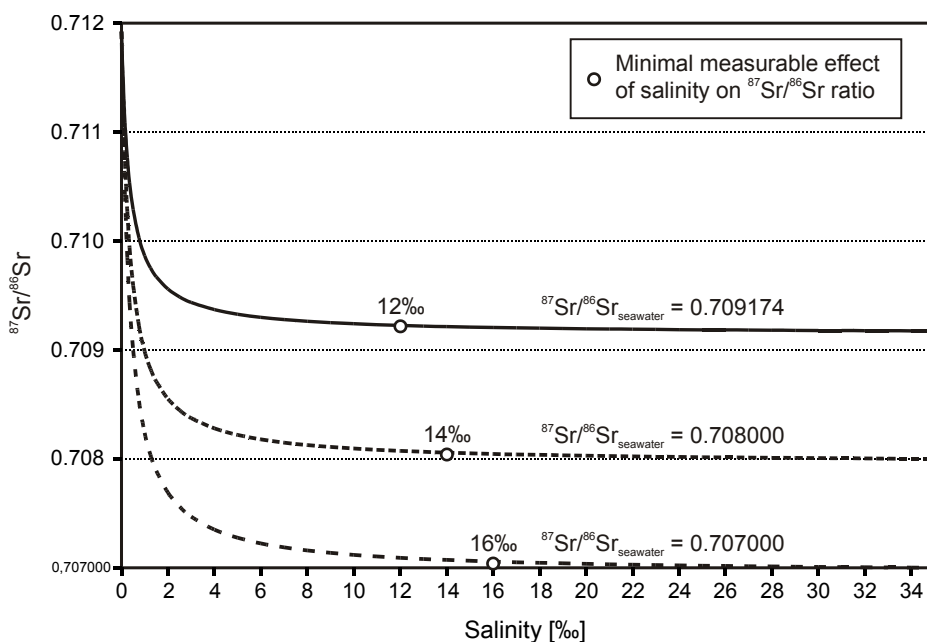


Fig. 7. Calculated effects of mixing of river water (average river water: $^{87}\text{Sr}/^{86}\text{Sr} = 0.711922$; $C_{\text{Sr}} = 0.89 \mu\text{mol/kg}$) and seawaters ($^{87}\text{Sr}/^{86}\text{Sr} = 0.709174, 0.708000, \text{ and } 0.707000$, $C_{\text{Sr}} = 90 \mu\text{mol/kg}$) on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of brackish water. Measurable effects (at $\Delta^{87}\text{Sr}/^{86}\text{Sr}$ of 0.0004) occur at salinities below 12-16‰.

The chemistry of end-members may be assumed as similar to modern analogues for relatively young sediments [74, 75], and be reconstructed from the composition of coeval freshwater and seawater calcareous fossils [49, 73]. It can also be tentatively calculated from sedimentary and river transport models [37, 76-78]. Measurable effects of salinity on $^{87}\text{Sr}/^{86}\text{Sr}$ ratios do not allow precise reconstruction of salinity in polyhaline or euhaline environments (with salinity $\geq 16\text{‰}$) unless river waters are characterized by high strontium load and radiogenic strontium ratios (cf. Fig. 7; see also Wierzbowski et al. [37]). The simple two-end members mixing models are also not valid in evaporation-dominated basins due to the evaporative increase in water salinity [78, 79].

6. STRONTIUM ISOTOPES AS A TRACER OF DIAGENETIC PROCESSES

Since $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of marine carbonates is affected by diagenetic fluids it can be used as tracer of their alteration. Diagenetic interactions between pore fluids and marine rocks lead to the re-equilibration of original element and isotope com-

positions. Changes in the element and the isotope composition of marine limestones at given water:rock ratios may be modelled using mass-balance equations [11, 12]. Although $\delta^{18}\text{O}$ values of marine limestone are most easily affected by freshwater diagenesis, a change in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the rocks (along with a change in element contents) can be used to trace the degree of limestone alteration and the mixing ratio of pristine and diagenetically altered carbonates ([11, 12]; see Fig. 8).

$^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be more reliable than other diagenesis tracers (such as Mn, Fe or Sr contents) due to the lack of fractionation by organisms – any change in $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of carbonates is, therefore, an unambiguous indicator of the alteration of the original marine rock.

An increase in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of aragonite ammonite shells was reported to be caused by the adsorption of diagenetic strontium on aragonite with minor alteration of the original shell chemistry [80]. Depletions in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of marine carbonates resulting from the non-typical alteration by hydrothermal fluids have been observed in belemnite rostra from Canada and New Zealand [13, 14]. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the belemnite rostra have also been used as a precise and independent diagenesis tracer in the micro- or macroscale [13, 14].

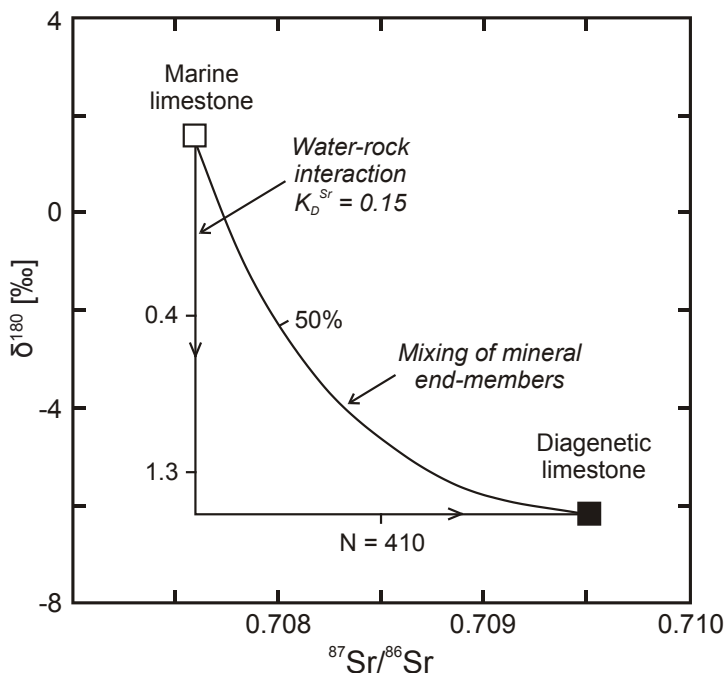


Fig. 8. Modelled oxygen and strontium isotope variations during recrystallization of a marine limestone by freshwater. Water:rock ratios (N) are shown at given stages of the interaction paths. The original limestone is assumed to have $\delta^{18}\text{O} = 1.5\text{‰}$ VPDB, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7076$, $C_{\text{Sr}} = 300$ ppm, porosity = 20%; the freshwater composition is $\delta^{18}\text{O} = -1\text{‰}$ VSMOW, $^{87}\text{Sr}/^{86}\text{Sr} = 0.7095$, $C_{\text{Sr}} = 0.6$ ppm. $T_{\text{recrystallization}} = 40^\circ\text{C}$ (after Banner [12]).

7. CONCLUSIONS

The present study aims to present the most popular applications of strontium isotopes in chemostratigraphy, salinity reconstruction or screening of diagenetic processes in marine or brackish sediments. The summary of the methods, analytical problems and the interpretations may be helpful for PhD students and geologists. It may also contribute to the wider use of strontium isotopes in Earth sciences to solve dating and palaeoenvironmental problems.

Further less common aspects of strontium isotope geochemistry in marine rocks, i.e. its use to decipher global weathering and hydrothermal fluxes, to analyse water exchange in isolated basins, to trace migration of diadromous fishes, and to determine the sedimentation rate are beyond the scope of this presentation.

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