Sues and W. Munk, *Palaeontol. Z.* **70**, 213 (1996)].
7. The new skeleton was collected from the Kupferschiefer of Ellrich, Thuringia (Germany), and is now housed in the Staatliches Museum für Naturkunde Karlsruhe (SMNK 2882 PAL). It is almost complete and mostly articulated. The vertebral column is coiled, presumably due to postmortem desiccation.
8. S. E. Evans, *Zool. J. Linn. Soc.* **76**, 97 (1982); S. E. Evans and H. Haubold, *ibid.* **90**, 275 (1987).
9. T. H. Pettigrew, *Nature* **281**, 297 (1979).
10. J. Weigelt, *Nova Acta Leopold.* **6**, 625 (1930).
11. R. L. Carroll, *Palaeont. Afr.* **21**, 143 (1978).
12. G. Schaumberg, *Palaeontol. Z.* **60**, 319 (1986). Schaumberg first questioned the interpretation of the rods as rib elements proposed by Evans (*8*), but, with the fossils of *C. jaekeli* known at that time, he could not establish the arrangement and true nature of the rods.
13. The Bauhaus specimen is housed in the private collection of W. Simon, Cornberg (Germany), and the Bodental skeleton in the collection of P. Bürger, Bad Hersfeld (Germany). High-fidelity casts of these fossils have been deposited in the collections of the Staatliches Museum für Naturkunde Karlsruhe and the Royal Ontario Museum.
14. A. P. Russell, *Zool. J. Linn. Soc.* **65**, 233 (1979).
15. We thank the Royal Ontario Museum Foundation and Staatliches Museum für Naturkunde Karlsruhe for financial support, the authorities of the Sunderland Museum for permission to examine the Eppleton specimen, and P. Bürger and W. Simon for access to material in their private collections. B. Herkner, C. McGowan, and an anonymous reviewer provided constructive comments on a draft of the manuscript. U. Greiner and B. Boyle assisted with photography.

5 December 1996; accepted 16 January 1997

Strontianite in Coral Skeletal Aragonite

Robert B. Greegor, Nicholas E. Pingitore Jr.,* Farrel W. Lytle

An x-ray spectroscopic study of scleractinian coral skeletons indicated that, although some strontium substitutes for calcium in the aragonite structure, at concentrations of about 7500 parts per million, as much as 40 percent of the strontium resides in strontianite ($SrCO_3$). A doublet peak in the Fourier transform of the extended x-ray absorption fine structure of the coral corresponded to six metal and 13 oxygen neighbors surrounding strontium at about 4.05 angstroms in strontium-substituted aragonite and at about 4.21 angstroms in strontianite. Thus, the mechanism of the temperature-sensitive partitioning of strontium between seawater and coral skeleton used for paleothermometry is unexpectedly complex.

Strontium/calcium ratios in scleractinian corals have been used to reconstruct past sea surface temperatures (SSTs) on the basis of the observed temperature dependence of Sr partitioning between seawater and coral skeleton (*1*). However, in some cases SSTs derived from Sr/Ca ratios differ from those derived by other techniques (for example, oxygen isotopes), and the origins of these differences are not clear (*2*). Because $SrCO_3$ is isomorphous (*3*) and shows at least partial solid solution with aragonite (*4*), it generally has been thought (*4, 5*) that Sr substitutes for Ca in biogenic and inorganic marine aragonites, although there is recent evidence to the contrary (*6*).

To characterize the site of Sr in aragonite scleractinian corals, we used x-ray absorption near-edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopy. In these experiments, an intense, monochromatic beam of x-rays, usually from a synchrotron source, is tuned gradually across the energy of a specific absorption edge of the element of interest, in this case Sr. Excitation and backscattering of Sr K-edge electrons provide information about the local environment (out to several nearest-neighbor shells) of the Sr atoms, at Sr concentrations as low as 1000 parts per million (ppm).

We analyzed four *Montastrea annularis* (MA) corals (one of Holocene age, one collected live, one collected live and then bleached, and one collected dead; all had ~7000 ppm of Sr), three *Acropora palmata* (AP) corals (one of Pleistocene age and two collected live; all had ~7500 ppm of Sr), and an aragonitic pelecypod bivalve (with ~1500 ppm of Sr) (*7*). We used calcite, inorganic aragonite, $SrCO_3$, SrO, and SrO_2 as standards for structural comparison and extraction of EXAFS phase shifts and scattering amplitudes. Measurements were conducted at the Stanford Synchrotron Radiation Laboratory (SSRL) using XAS techniques (*8*).

The aragonite and calcite XANES (Fig. 1) were taken at the Ca K-edge (4038.5 eV), whereas the other spectra were taken at the Sr K-edge (16104.6 eV). In calcite, Ca and Sr are distinguished from the other structural sites by a distinctive doublet at the top of the absorption rise for calcite and Sr in calcite. Fourier transforms of the K^3-weighted EXAFS data (from ~3.5 to 12 $Å^{-1}$) at the K-edges corresponding to the XANES, along with the appropriate phase shift (Ca-O or Sr-O), yielded peaks close to the expected crystallographic distances (Table 1). The measured metal-metal distances are also close to the reference distances established by x-ray diffraction (XRD) (*9*).

The Sr K-edge XANES of the different coral species and ages appear identical at the resolution presented in Fig. 2. The absence of the doublet at the top of absorption rise indicates that Sr is not in the calcite form of $CaCO_3$. The XANES features resemble Sr in $SrCO_3$, SrO_2, and SrO, and to a lesser extent, Ca in aragonite (Fig. 1).

Table 1. Summary of Fourier transforms, XRD, and least-squares fits to EXAFS data. N_f, coordination number (±20%) from least-squares fit; R_f, bond length (±0.05 Å) from least-squares fit; $\Delta\sigma^2$, mean-squared relative displacement (with respect to SrO standard) from least-squares fit; E_0, inner potential (treated as arbitrary parameter) from least-squares fit; SD, standard deviation of least-squares fit to data; R_t, bond length from peak of Fourier transform; XRD, x-ray diffraction data for coordination number and bond length; Sr, strontium in aragonite sample; MA, *M. annularis* coral; AP, *A. palmata* coral; PEL, pelecypod bivalve; H, Holocene age; P, Pleistocene age; l, collected live; d, collected dead; b, bleached. Calcite (rhombohedral) and aragonite (orthorhombic) are polymorphs of $CaCO_3$; $SrCO_3$ is isomorphous with aragonite.

Sample	N_f	R_f (Å)	$\Delta\sigma^2$ (Å^2)	E_0 (eV)	SD	R_t (Å)	XRD (Å)
Calcite						2.36	VI-2.36
Aragonite						2.53	IX-2.53
SrO						2.58	VI-2.58
SrO_2	10.6	2.57	0.0030	1.17	0.187	2.57	X-2.61
Strontianite	9.0	2.59	0.0006	0.44	0.189	2.64	IX-2.64
Sr (MA l)	8.8	2.55	−0.0004	0.00	0.225	2.57	
Sr (MA l, b)	8.6	2.56	−0.0006	0.17	0.274	2.57	
Sr (MA d)	9.3	2.56	−0.0002	0.56	0.202	2.57	
Sr (MA H)	8.8	2.56	−0.0008	1.01	0.273	2.60	
Sr (AP l-14)	8.8	2.56	−0.0007	0.29	0.294	2.57	
Sr (AP l-15)	8.9	2.55	−0.0003	0.30	0.286	2.57	
Sr (AP P)	8.9	2.55	−0.0004	−0.31	0.284	2.60	
Sr (PEL)	9.6	2.55	0.0007	0.14	0.253	2.52	

R. B. Greegor, The Boeing Company, Seattle, WA 98124, USA.
N. E. Pingitore Jr., Department of Geological Sciences, University of Texas at El Paso, El Paso, TX 79968–0555, USA.
F. W. Lytle, The EXAFS Co., Pioche, NV 89043, USA.

*To whom correspondence should be addressed. E-mail: nick@geo.utep.edu

Fourier transforms of the K^3-weighted EXAFS coral data (Fig. 3) show a first peak at ~2.56 Å, which corresponds to the nearest oxygen neighbors, and a double peak at ~4 Å, which corresponds to the coordination shells with six metal and 13 oxygen atoms. This doublet is not prominent in the lowermost two AP corals.

Least-square fits of the Fourier back transforms of the first peak (*10*) provide estimates of the coordination number, bond length, and relative disorder at the Sr site (Table 1). We made the fits using an experimental scattering amplitude from SrO and a single-bond length averaging all the bonds actually present. The determined Sr coordination of IX is consistent with Sr in aragonite or $SrCO_3$ but not in calcite (coordination VI).

Comparison of Sr K-edge Fourier transforms of EXAFS data for $SrCO_3$, two corals, and Sr in aragonite with the Ca K-edge data for aragonite indicates that Sr is present both at the Ca site in the aragonite structure and at a distinct $SrCO_3$-like site (Fig. 4). A double peak in the Fourier transforms at ~4 Å, which corresponds to six metal and 13 oxygen neighbors, verifies the presence of both phases. These atoms are closer to the central atom in aragonite (~4.05 Å) than in $SrCO_3$ (~4.21 Å), thereby producing the doublet when the Sr is present in both arrangements in a sample. The Ca-Ca shell at ~4 Å in the low-Sr aragonite pelecypod is slightly expanded because the larger Sr cation [Sr^{2+} VIII = 1.39 Å, Sr^{2+} X = 1.46 Å, Ca^{2+} IX = 1.32 Å (*11*)] substitutes at the Ca site. In $SrCO_3$ (bottom Fourier transform) the Sr-Sr shell is at an even greater distance than the Ca-Ca shell or the Sr-Ca shell in the aragonite pelecypod. Therefore, when a mix of both Sr-Ca and Sr-Sr shells is present in the corals, we see the characteristic double peak in the ~4 Å metal-metal shell. The peaks in the Fourier transforms are not at their exact expected positions because of phase-shift effects and disorder arising from the accommodation of atoms having different radii.

Linear combinations of the Fourier transforms of the Sr K-edge EXAFS for Sr in aragonite and $SrCO_3$ can be used to estimate the $SrCO_3$ content of our corals (Fig. 5). We assumed that the relatively small amounts of Sr in the pelecypod substitute randomly for Ca in the aragonite structure and do not appreciably cluster into domains of a $SrCO_3$-like phase. This supposition is reasonable because the pelecypod Sr-Ca peak at ~4 Å is shorter than that for Sr-Sr in $SrCO_3$ (Fig. 4), and the shoulder, corresponding to Sr-Sr neighbors in $SrCO_3$, was barely or not observable to

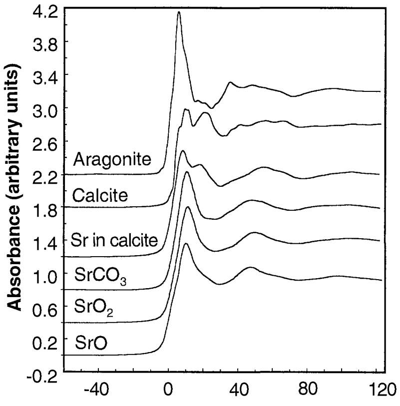

Fig. 1. The Ca K-edge XANES for aragonite and calcite polymorphs of $CaCO_3$, and the Sr K-edge XANES for Sr in calcite (1500 ppm), $SrCO_3$, SrO_2, and SrO. Note the doublet at the top of the absorption rise for calcite and Sr in calcite.

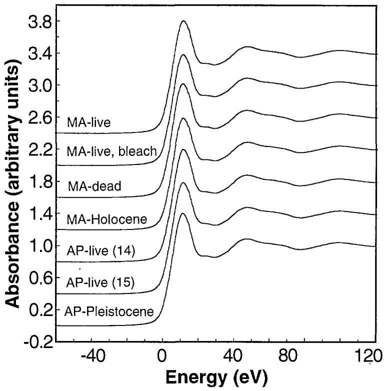

Fig. 2. The Sr K-edge XANES for all corals (~7500 ppm of Sr) investigated in this study. None of the corals exhibited the doublet at the top of the absorption rise, which is characteristic of calcite. MA stands for *M. annularis*, and AP stands for *A. palmata*.

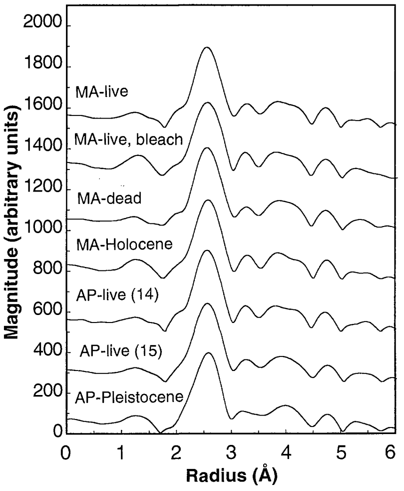

Fig. 3. Phase-corrected (using SrO) Fourier transforms of Sr K-edge EXAFS from ~3.5 to 12 $Å^{-1}$ for all corals (~7500 ppm of Sr) investigated in this study. Note the double peak for most of the samples at ~4 Å. MA stands for *M. annularis* and AP stands for *A. palmata*.

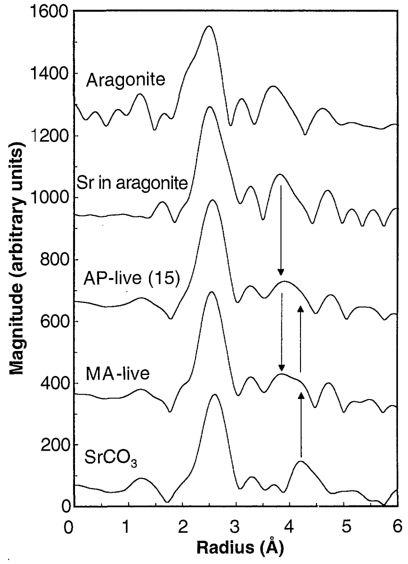

Fig. 4. Comparison of phase-corrected Fourier transforms of K-edge EXAFS for aragonite, Sr in aragonite (1500 ppm of Sr, pelecypod), corals, and $SrCO_3$. All of the data are at the Sr K-edge except for the aragonite, which was taken at the Ca K-edge (in electron yield). Note (at ~4 Å) that the Ca-Ca shell distance is shorter than the Sr-Ca distance in aragonite, and both of these are shorter than the Sr-Sr distance in $SrCO_3$. The presence of both a Sr-Ca shell and a Sr-Sr shell in the corals is noted by the arrows.

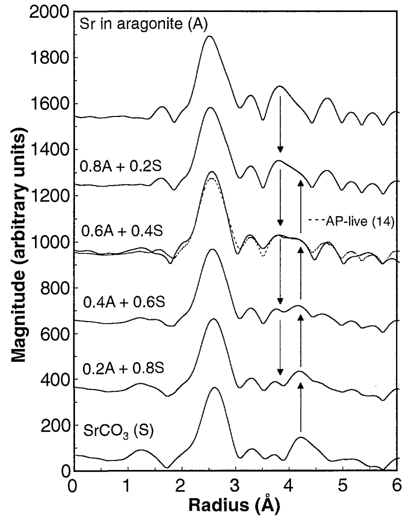

Fig. 5. Linear combinations of phase-corrected Fourier transforms of Sr K-edge EXAFS for Sr in aragonite (A) (1500 ppm of Sr, pelecypod) and $SrCO_3$ (S). Note that a mix of 60% A + 40% S is a close approximation of the double peak at ~4 Å in the AP-14 coral collected live (denoted by dashed line).

the right on the Sr-Ca peak. This sample was determined to be pure aragonite by XRD (7). The dashed line in Fig. 5 is the Fourier transform of the Sr K-edge EXAFS spectrum for coral AP-14. A linear combination of ~60% Sr substituted in aragonite and ~40% Sr in a $SrCO_3$ phase approximates (±15%) the EXAFS of AP-14 and all of the MA corals. The remaining two AP corals did not show as large a $SrCO_3$ shoulder on the doublet at ~4 Å, suggesting a more homogeneous distribution of their Sr in the aragonite structure.

Plummer and Busenberg (6) showed that there was a wide miscibility gap in the aragonite-$SrCO_3$ solid solution from a $SrCO_3$ mole fraction of 0.0058 ± 0.0003 to 0.875 ± 0.011 at 25°C. Aragonite with more than ~5000 ppm of Sr substituted for Ca is therefore metastable. For the two-phase corals, our estimate of 4500 ppm of Sr at the Ca structural sites in aragonite (60% of 7500 ppm) and 3000 ppm in the $SrCO_3$ (40% of 7500 ppm) agrees with thermodynamic analysis of the laboratory aragonite-$SrCO_3$ system (6). Most scleractinian corals grow between 25° and 29°C, a temperature range close to the 25°C of the synthetic system (6). The two AP corals exhibiting smaller $SrCO_3$ shoulders apparently formed as metastable high-Sr aragonite.

It seems reasonable that the $SrCO_3$ domains are primary features that formed during biomineralization. The domains are present in specimens that were collected live, and solid-state diffusion or dissolution-reprecipitation is difficult or slow in seawater at ambient temperatures. The size and distribution of the $SrCO_3$ domains is not known, and neither is the mechanism by which corals sequester more Sr in aragonite skeletons than expected at equilibrium with seawater, although Plummer and Busenberg (6) suggest that precipitation kinetics cause nonequilibrium incorporation of Sr in many marine carbonates.

These findings indicate that Sr does not substitute solely for Ca at its structural sites in MA and AP, species that have not been directly calibrated for Sr/Ca SST paleothermometry. Further investigation of the $SrCO_3$ in these and other species will advance our understanding of the mechanisms of Sr incorporation into scleractinian coral.

REFERENCES AND NOTES

1. J. Weber, *Geochim. Cosmochim. Acta* **37**, 2173 (1973); S. V. Smith, R. W. Buddemeier, R. W. Redalje, J. E. Houck, *Science* **204**, 404 (1979); T. P. Guilderson, R. G. Fairbanks, J. L. Rubenstone, *ibid.* **263**, 663 (1994); M. T. McCulloch, M. K. Gagan, G. E. Mortimer, A. R. Chivas, P. J. Isdale, *Geochim. Cosmochim. Acta* **58**, 2747 (1994); M. T. McCulloch *et al.*, *Earth Planet. Sci. Lett.* **138**, 169 (1996); T. Lee, C.-C. Shen, C.-Y. Chen, C.-H. Wang, C.-F. Dai, *Eos* **76**, 180 (1995).
2. S. De Villiers, G. T. Shen, B. K. Nelson, *Geochim. Cosmochim. Acta* **58**, 197 (1994); D. J. Barnes, R. B. Taylor, D. S. Miller, *J. Exp. Mar. Biol. Ecol.* **194**, 251 (1995); S. R. Hart and A. L. Cohen, *Geochim. Cosmochim. Acta* **60**, 3075 (1996).
3. J. P. R. De Villiers, *Am. Mineral.* **56**, 758 (1971).
4. H. D. Holland, M. Borcsik, J. Munoz, U. M. Oxburgh, *Geochim. Cosmochim. Acta* **27**, 957 (1963).
5. R. G. C. Bathurst, *Carbonate Sediments and Their Diagenesis* (Elsevier, New York, 1971); A. J. Amiel, G. M. Friedman, D. S. Miller, *Sedimentology* **20**, 47 (1973); J. A. Speer, in *Carbonates: Mineralogy and Chemistry*, R. J. Reeder, Ed. (Mineralogical Society of America, Washington, DC, 1983), pp. 145–190; J. W. Morse and F. T. Mackenzie, *Geochemistry of Sedimentary Carbonates* (Elsevier, New York, 1990).
6. L. N. Plummer and E. Busenberg, *Geochim. Cosmochim. Acta* **51**, 1393 (1987).
7. Samples were powdered and scanned from $10^\circ < 2\theta < 70^\circ$ on an x-ray powder diffractometer. All major aragonite peaks were present and identified. No other peaks were encountered, implying a purity in excess of 98% aragonite. Strontium and calcium were determined in these samples by direct current plasma atomic emission spectroscopy.
8. The materials for XAS analysis were ground to fine powders of 300 to 400 mesh size. The standards were mixed in Duco cement, and spread as a thin layer on Al foil. Beam line 4-1 at SSRL was used with a Si(111) (for Ca) and Si(220) (for Sr) monochromator. The stored electron beam energy was 3 GeV at a current of 50 to 90 mA. The monochromator was detuned to reduce harmonics, and the slits were set at 1 mm by 20 mm to give ~1- and 4-eV resolution at the Ca and Sr K-edges, respectively. The data were gathered in fluorescence mode for the corals and in absorption mode for the standards. The Ca K-edge experiment was performed in the electron yield mode, as noted in the data where appropriate.
9. The Fourier transform peaks were identified with the use of the software Shells for EXAFS-Interactive (B. Rupp, Lawrence Livermore National Laboratory) to calculate bond distances and coordination numbers. Unit cell parameters are available in R. W. Wyckoff, *Crystal Structures* (Interscience, New York, 1963), vol. 1, for all compounds except SrO_2, for which we made an estimate for the fractional parameter *u* of 0.391.
10. F. W. Lytle, in *Applications of Synchrotron Radiation*, H. Winick, D. Xian, M. Ye, P. Huang, Eds. (Gordon and Breach, Luxembourg, 1989), pp. 135–223.
11. R. D. Shannon, *Acta Crystallogr. A* **32**, 751 (1976).
12. The research of R.B.G. was supported by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences, under grant DE-FG06-84ER45121. For user support and synchrotron beam time, we thank SSRL, which is funded by DOE, Office of Basic Energy Sciences, and NIH, Biotechnology Resource Program, Division of Research Resources. N.E.P. thanks T. Pogue for laboratory assistance at the University of Texas at El Paso, El Paso, and L. N. Plummer and P. D. Glynn of the U.S. Geological Survey, Reston, VA, for discussions. We thank J. R. Greegor for help in data preparation and handling.

7 October 1996; accepted 14 January 1997

Pulses of Rapid Ventilation in the North Atlantic Surface Ocean During the Past Century

Ellen R. M. Druffel

The Suess Effect is a gradual decrease of the $^{14}C/^{12}C$ ratio in tree rings from 1870 to 1950 that is attributed mostly to the burning of ^{14}C-free fossil fuels for energy. In contrast, pre–nuclear bomb high-precision measurements of $^{14}C/^{12}C$ ratios in banded corals from the North Atlantic Ocean do not exhibit the expected Suess Effect. Instead, large biennial-to-decadal shifts in the $^{14}C/^{12}C$ ratios appear throughout the coral records. This pattern indicates that rapid pulses of increased mixing between surface and subsurface waters occurred in the North Atlantic Ocean during the past century.

Since the late 19th century, humans have burned substantial amounts of fossil fuels for energy. As a result of this combustion, the concentration of CO_2 in the atmosphere has increased by at least 25% (*1*). This increase represents about half of the CO_2 that has been emitted into the atmosphere; most of the other half is in the oceans. The decline in $\Delta^{14}C$ (*2*) values of atmospheric CO_2, due to CO_2 release from fossil fuels and to cosmic ray flux variability, has been measured in tree rings [−20 per mil (*3*)] and is known as the Suess Effect (*3*, *4*). Because atmospheric CO_2 exchanges with dissolved inorganic carbon (DIC) in the surface ocean, $\Delta^{14}C$ measurements in the upper ocean can be used to quantify the main sink for fossil-fuel CO_2. Coralline aragonite has been shown to accrete calcium carbonate with the same $\Delta^{14}C$ signature as that in DIC in the surrounding seawater (*5*, *6*). The $\delta^{18}O$ (*7*) values in banded corals have been shown to correlate inversely with sea surface temperature (SST) (*8*–*10*) and to correlate directly with the salinity and $\delta^{18}O$ of seawater (*11*, *12*). Here I report high-precision $\Delta^{14}C$ measurements of banded corals from three sites in the North Atlantic Ocean and use the results to calculate the water mass renewal (or ventilation) rate in the North Atlantic over the past 100 years.

Cores of *Diploria strigosa* were collected from surface waters (at a depth of 5 m) near North Rock (32°29′N, 64°41′W; 14 km north of Bermuda), and *Montastrea annularis* corals were cored from Pickles Reef off Key Largo, 100 km south of Miami, and from The Rocks Reef (24°57′N, 80°33′W), 1 km south of Plantation Key in Florida. Biennial (2-year) bands were cut from the

---

Department of Earth System Science, University of California, Irvine, Irvine, CA 92697-3100, USA.