

# Data report: $^{87}\text{Sr}/^{86}\text{Sr}$ in pore fluids off Shimokita, Japan<sup>1</sup>

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## Abstract

We report the strontium isotope ratios ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) from pore water collected during Integrated Ocean Drilling Program Expedition 337 off Shimokita peninsula, Japan. We use the ratios to track the origin of pore water between 1289 to 2405 meters below seafloor at Site C0020. Strontium isotope ratios measured from the samples collected by conventional sediment squeezer and the Quick-silver probe are in good agreement and suggest the success of the latter sampling technique. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios in the pore water range from 0.7086 to 0.7061, suggesting the mixing between ancient seawater and fluids derived from volcanic material alteration, a process also confirmed by onboard smear slide observations.

## Introduction

Integrated Ocean Drilling Program (IODP) Expedition 337 aims to understand the relationship between a deep-seated (~1950 meters below seafloor [mbsf]) hydrocarbon reservoir off Shimokita peninsula (northeast Japan) and the microbial community at such depth. Understanding the sources and pathways of fluids is one of the primary objectives of the expedition (see the “**Expedition 337 summary**” chapter [Expedition 337 Scientists, 2013a]). Migration of fluid supports the deep microbial community as well as the shallow-dwelling organisms through delivery of critical nutrients and elements. To this aim, we use the strontium (Sr) isotope ratios from pore water to identify the sources and migration pathway of the deep fluid.

Radiogenic Sr isotope ratio,  $^{87}\text{Sr}/^{86}\text{Sr}$ , is known to be free from biological fractionation (Mook, 2001), which makes it a valuable and conservative tracer for fluid from different sources (Torres et al., 2004; Teichert et al., 2005; Joseph et al., 2012, 2013). Possible sources include modern seawater ( $^{87}\text{Sr}/^{86}\text{Sr} \cong 0.7092$ ; McArthur et al., 2012), continental felsic and basaltic rocks ( $<0.7180$ ; Faure and Powell, 1972), biogenic calcite ( $\sim 0.7075$ – $0.7092$ ), volcanic material ( $\sim 0.7065$ ), and oceanic crust ( $\sim 0.703$ ; Veizer, 1989). Whereas some of the dissolved constituents measured in the pore water samples show significant contamination by drilling fluid, Sr is considered to be relatively free from such contamination due to the low Sr concentration in drilling fluid ( $<30 \mu\text{M}$ ) (see the “**Methods**” chapter [Expedition 337 Scientists, 2013b]).

<sup>1</sup>Moen, N., Hong, W.-L., and Haley, B., 2015. Data report:  $^{87}\text{Sr}/^{86}\text{Sr}$  in pore fluids off Shimokita, Japan. In Inagaki, F., Hinrichs, K.-U., Kubo, Y., and the Expedition 337 Scientists, *Proceedings of the Integrated Ocean Drilling Program, 337*: Tokyo (Integrated Ocean Drilling Program Management International, Inc.).

doi:10.2204/iodp.proc.337.201.2015

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## Materials and methods

Most of the pore water samples were collected by the conventional sediment squeezer, whereas four of the samples were collected by the Quicksilver probe (Fig. F1). The Quicksilver water samples were extracted from the formation under in situ pressure and temperature. All pore water samples were recovered and treated under standard IODP protocol (see the “Methods” chapter [Expedition 337 Scientists, 2013b]). Sr concentration was measured on board by inductively coupled plasma–atomic emission spectroscopy (ICP-AES). We used preserved samples for onboard alkalinity titration for our Sr isotopic analyses. All samples were kept below  $\sim 4^\circ\text{C}$  before analyses.

For all pore water, 75  $\mu\text{L}$  of sample was loaded onto Eichrom “Sr-spec” chromatographic columns (Horwitz et al., 1992). Four samples from Sections 337-C0020A-11R-5, 13R-2, 13R-8, and 15R-7 were processed through cation columns using Eichrom cation-exchange (AG50 8X) resin (Cohen et al., 1988) prior to Sr isolation to reduce the high concentrations of rubidium (Rb) in these samples. This initial reduction of Rb increased the efficiency of the Sr isolation, thus reducing isobaric interference from  $^{87}\text{Rb}$ . Pure solutions at 20–30 ppb Sr were then analyzed using the Nu Plasma multicollector inductively coupled plasma–mass spectrometer (MC-ICPMS) in the W.M. Keck Collaboratory for Plasma Spectrometry in the College of Earth, Ocean, and Atmospheric Science at Oregon State University (OSU-CEOAS; USA). Instrument mass bias was corrected using  $^{88}\text{Sr}/^{86}\text{Sr}$  of 8.375209, and all data were normalized to an  $^{88}\text{Sr}/^{86}\text{Sr}$  value for the NBS987 standard of 0.710245 ( $2\sigma = 0.000050$ , which is 91). Replicate analyses of an in house standard (an EMD Millipore Sr standard solution) defines the long-term  $2\sigma$  external reproducibility, which was 0.000060 ( $n = 79$ ). We used the same protocols for sample pretreatment and analyses as Joseph et al. (2013). All data and the associated analytical error can be found in Tables T1 and T2.

## Results

Results of the samples collected by the conventional sediment squeezer and Quicksilver probe are in close agreement, suggesting the success of the later sampling technique (Fig. F1). Strontium concentration increases from 1278 to 1989 mbsf with two distinct peaks at 1765 and 1939 mbsf (see the “Site C0020” chapter [Expedition 337 Scientists, 2013c]) (Fig. F1A). Accordingly, the isotope ratios decrease from 0.7086 at 1278 mbsf to 0.7062 at 1958 mbsf (Fig.

F1B) and are slightly elevated around 1944 mbsf, which corresponds to the concentration peak at the same depth. Although the lack of measurements between 1959 and 2406 mbsf limits our interpretation, similar Sr concentration and isotope ratios between these two depths suggest a similar fluid source below 1959 mbsf.

To further investigate the source of pore water Sr, we plot the isotope ratios against the reciprocal of concentration in Figure F2. Seawater younger than middle Miocene, the age of our first measurement at 1278.1 mbsf based on the onboard biostratigraphy reconstruction (see the “Site C0020” chapter [Expedition 337 Scientists, 2013c]), has Sr isotope ratios that range from  $\sim 0.7088$  to 0.7092 (McArthur et al., 2012). The Sr isotope ratios for volcanic materials from northeast Japan range from  $\sim 0.7059$  to 0.7029 (Oba et al., 1983; Kurasawa et al., 1986; Ohki et al., 1994), a range very close to our measurements at 1978 mbsf. The trend in Figure F2 suggests mixing between seawater younger than middle Miocene and fluid derived from volcanic material alteration. Volcanic glass was commonly observed in cuttings and sediment cores. Smear slide observations confirm the existence of volcanic material (Fig. F1C, F1D). At 1940.44 mbsf, 1 m below the highest Sr concentration with the slightly elevated isotopic signature, a smear slide observation confirms weathered volcanic material (Fig. F1E) (see the “Site C0020” chapter [Expedition 337 Scientists, 2013c]).

Alteration of volcanic material can release various cations, bicarbonate, and silicate into pore water (Wallmann et al., 2008; White et al., 2011). These excess cations and anions not only stimulate the precipitation of authigenic minerals but may also provide the necessary nutrient for microbial life (Torsvik et al., 1998; Izawa et al., 2010). Both the elevated cell count and the geochemical signatures infer the active methanogenesis around the  $\sim 1950$  mbsf coalbed (see the “Site C0020” chapter [Expedition 337 Scientists, 2013c]), where the Sr concentration and isotope ratios suggest active volcanic material alteration. Solute released during volcanic material decomposition may also be an important controlling factor for the microbial life at such harsh environment.

## Acknowledgments

The authors would like to thank the captains, crew members, and laboratory technicians on board the D/V *Chikyu* for core recovery and sample collection. Samples were provided by the Integrated Ocean Drilling Program (IODP). Funding was provided by

Post-Expedition Activity (PEA) award. The authors also appreciate the critical comments from one anonymous reviewer.

## References

- Cohen, A.S., O'Nions, R.K., Siegenthaler, R., and Griffin, W.L., 1988. Chronology of the pressure-temperature history recorded by a granulite terrain. *Contrib. Mineral. Petrol.*, 98(3):303–311. <http://dx.doi.org/10.1007/BF00375181>
- Expedition 337 Scientists, 2013a. Expedition 337 summary. In Inagaki, F., Hinrichs, K.-U., Kubo, Y., and the Expedition 337 Scientists, *Proc. IODP, 337*: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). <http://dx.doi.org/10.2204/iodp.proc.337.101.2013>
- Expedition 337 Scientists, 2013b. Methods. In Inagaki, F., Hinrichs, K.-U., Kubo, Y., and the Expedition 337 Scientists, *Proc. IODP, 337*: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). <http://dx.doi.org/10.2204/iodp.proc.337.102.2013>
- Expedition 337 Scientists, 2013c. Site C0020. In Inagaki, F., Hinrichs, K.-U., Kubo, Y., and the Expedition 337 Scientists, *Proc. IODP, 337*: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). <http://dx.doi.org/10.2204/iodp.proc.337.103.2013>
- Faure, G., and Powell, J.L., 1972. *Strontium Isotope Geology*: New York (Springer-Verlag). <http://dx.doi.org/10.1007/978-3-642-65367-4>
- Horwitz, E.P., Chiarizia, R., and Dietz, M.L., 1992. A novel strontium-selective extraction chromatographic resin. *Solvent Extr. Ion Exch.*, 10(2):313–336. <http://dx.doi.org/10.1080/07366299208918107>
- Izawa, M.R.M., Banerjee, N.R., Flemming, R.L., Bridge, N.J., and Schultz, C., 2010. Basaltic glass as a habitat for microbial life: implications for astrobiology and planetary exploration. *Planet. Space Sci.*, 58(4):583–591. <http://dx.doi.org/10.1016/j.pss.2009.09.014>
- Joseph, C., Torres, M.E., and Haley, B., 2013. Data report:  $^{87}\text{Sr}/^{86}\text{Sr}$  in pore fluids from NanTroSEIZE Expeditions 322 and 333. In Saito, S., Underwood, M.B., Kubo, Y., and the Expedition 322 Scientists, *Proc. IODP, 322*: Tokyo (Integrated Ocean Drilling Program Management International, Inc.). <http://dx.doi.org/10.2204/iodp.proc.322.207.2013>
- Joseph, C., Torres, M.E., Martin, R.A., Haley, B.A., Pohlman, J.W., Riedel, M., and Rose, K., 2012. Using the  $^{87}\text{Sr}/^{86}\text{Sr}$  of modern and paleoseep carbonates from northern Cascadia to link modern fluid flow to the past. *Chem. Geol.*, 334:122–130. <http://dx.doi.org/10.1016/j.chemgeo.2012.10.020>
- Kurasawa, H., Fujinawa, A., and Leeman, W.P., 1986. Calc-alkaline and tholeiitic rock series magmas coexisting within volcanoes in Japanese island arcs: strontium isotopic study. *Chishitsugaku Zasshi*, 92(4):255–268. <http://dx.doi.org/10.5575/geosoc.92.255>
- McArthur, J.M., Howarth, R.J., and Shields, G.A., 2012. Strontium isotope stratigraphy. In Gradstein, F.M., Schmitz, J.G.O.D., and Ogg, G.M. (Eds.), *The Geologic Time Scale*: Boston (Elsevier), 127–144. <http://dx.doi.org/10.1016/B978-0-444-59425-9.00007-X>
- Mook, W.G., 2001. Application to low temperature systems. In Geyh, M. (Ed.), *Environmental Isotopes in the Hydrological Cycle: Principles and Applications* (Vol. 4): *Groundwater: Saturated and Unsaturated Zone*: Vienna (Int. At. Energy Agency), 49–118. [http://www-naweb.iaea.org/napc/ih/documents/global\\_cycle/vol%20IV/IV\\_Ch5.pdf](http://www-naweb.iaea.org/napc/ih/documents/global_cycle/vol%20IV/IV_Ch5.pdf)
- Oba, Y., Katsui, Y., Kurasawa, H., Ikeda, Y., and Uda, T., 1983. Petrology of historic rhyolite and dacite from Usu Volcano, North Japan. *J. Fac. Sci., Hokkaido Univ., Ser. 4*, 20(4):275–290. <http://hdl.handle.net/2115/36722>
- Ohki, J., Shuto, K., and Kagami, H., 1994. Middle Miocene bimodal volcanism by asthenospheric upwelling: Sr and Nd isotopic evidence from the back-arc region of the Northeast Japan arc. *Geochem. J.*, 28(6):473–487. <http://dx.doi.org/10.2343/geochemj.28.473>
- Teichert, B.M.A., Torres, M.E., Bohrmann, G., and Eisenhauer, A., 2005. Fluid sources, fluid pathways and diagenetic reactions across an accretionary prism revealed by Sr and B geochemistry. *Earth Planet. Sci. Lett.*, 239(1–2):106–121. <http://dx.doi.org/10.1016/j.epsl.2005.08.002>
- Torres, M.E., Teichert, B.M.A., Tréhu, A.M., Borowski, W., and Tomaru, H., 2004. Relationship of pore water freshening to accretionary processes in the Cascadia margin: fluid sources and gas hydrate abundance. *Geophys. Res. Lett.*, 31:L22305. <http://dx.doi.org/10.1029/2004GL021219>
- Torsvik, T., Furnes, H., Muehlenbachs, K., Thorseth, I.H., and Tumyr, O., 1998. Evidence for microbial activity at the glass-alteration interface in oceanic basalts. *Earth Planet. Sci. Lett.*, 162(1–4):165–176. [http://dx.doi.org/10.1016/S0012-821X\(98\)00164-2](http://dx.doi.org/10.1016/S0012-821X(98)00164-2)
- Veizer, J., 1989. Strontium isotopes in seawater through time. *Annu. Rev. Earth Planet. Sci.*, 17(1):141–167. <http://dx.doi.org/10.1146/annurev.earth.17.050189.001041>
- Wallmann, K., Aloisi, G., Haeckel, M., Tishchenko, P., Pavlova, G., Greinert, J., Kutterolf, S., and Eisenhauer, A., 2008. Silicate weathering in anoxic marine sediments. *Geochim. Cosmochim. Acta*, 72(12):2895–2918. <http://dx.doi.org/10.1016/j.gca.2008.03.026>
- White, R.J., Spinelli, G.A., Mozley, P.S., and Dunbar, N.W., 2011. Importance of volcanic glass alteration to sediment stabilization: offshore Japan. *Sedimentology*, 58(5):1138–1154. <http://dx.doi.org/10.1111/j.1365-3091.2010.01198.x>

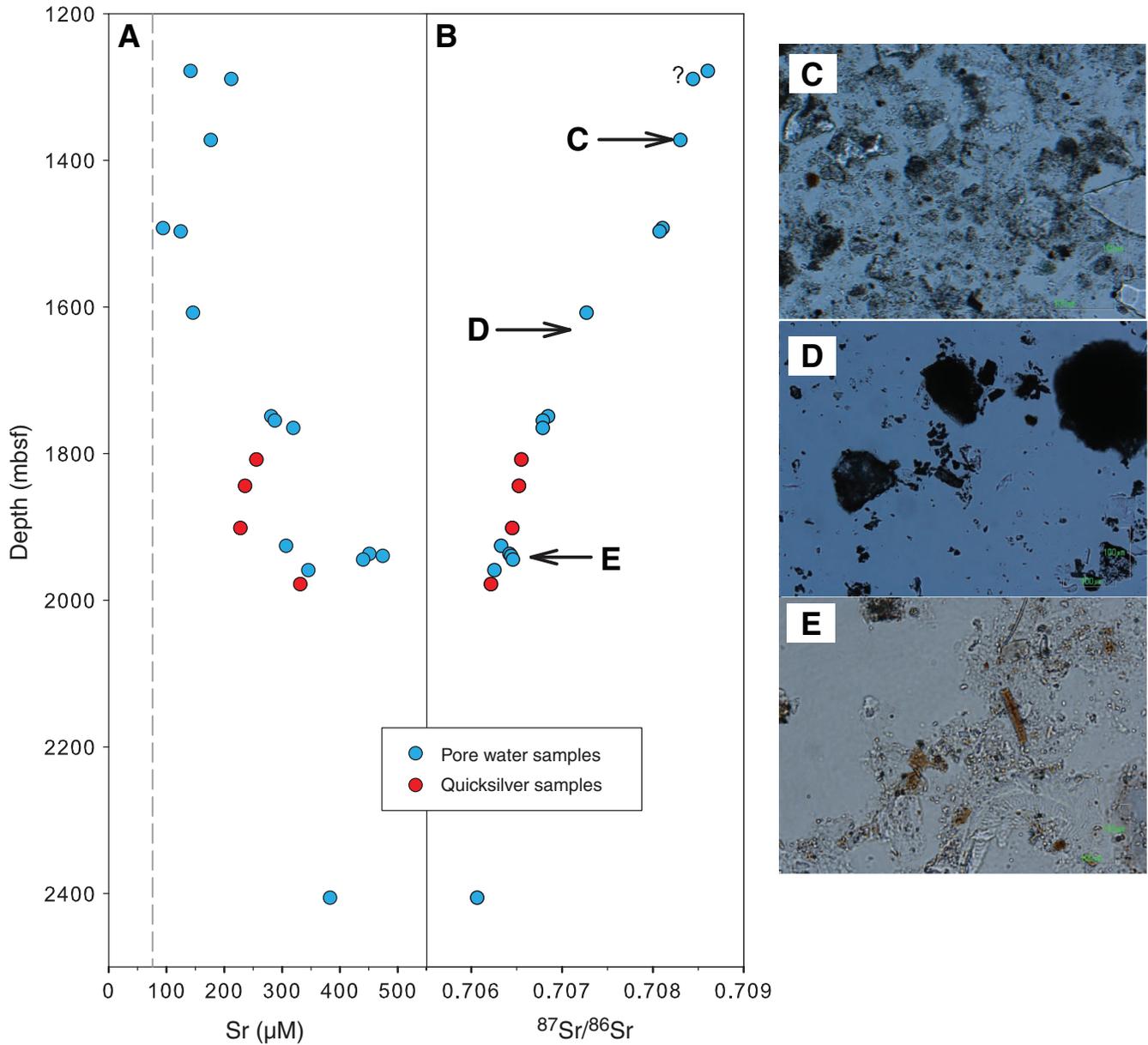
**Initial receipt:** 14 January 2015

**Acceptance:** 18 August 2015

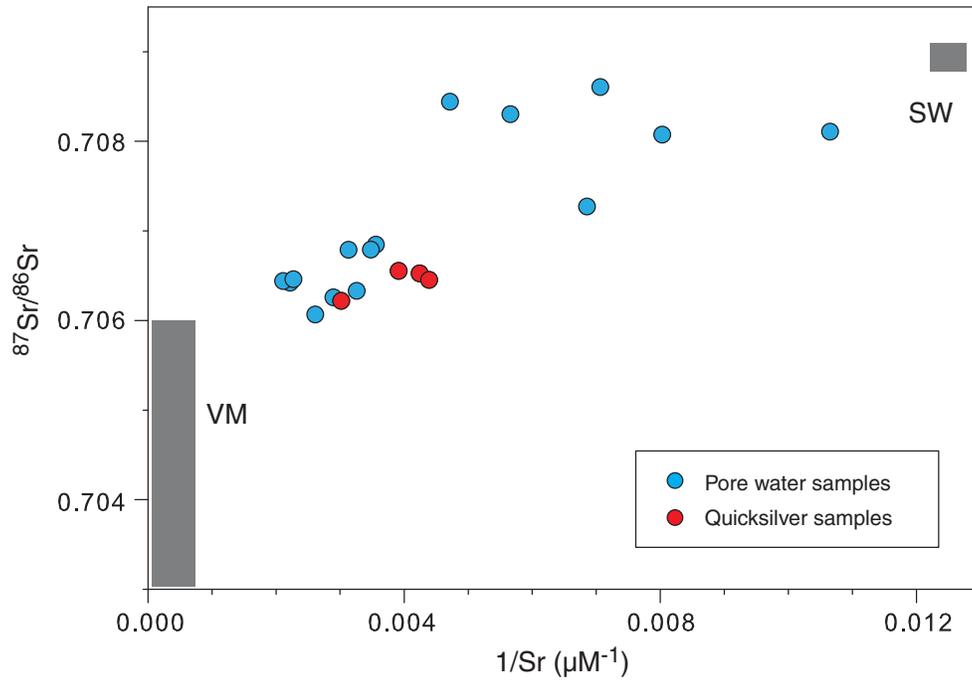
**Publication:** 3 November 2015

**MS 337-201**

**Figure F1.** (A) Strontium concentration and (B) isotope ratios of all analyzed pore water samples, Site C0020. Concentrations are from the “Site C0020” chapter (Expedition 337 Scientists, 2013c). All data can be found in Tables T1 and T2. Analytical error of the isotopic ratios is smaller than the symbol size. Shipboard thin section observations (C–E) confirm the appearance of altered volcanic material.



**Figure F2.** Sr isotope ratios versus the reciprocal of Sr concentration in the pore water samples, Site C0020. The end-member Sr isotope ratios for seawater (SW) are from McArthur et al. (2012) assuming the ratios for seawater younger than middle Miocene (0.7092–0.7088). The volcanic material (VM) end-member covers the Sr isotope ratios reported for northeast Japan (Oba et al., 1983; Kurasawa et al., 1986; Ohki et al., 1994). The mixing line clearly shows the contribution of Sr from both sources.



**Table T1.** Pore water Sr concentration and isotopic ratio from whole-round cores, Site C0020.

Unit	Core, section, interval (cm)	Depth CSF-B (m)		Sr ( $\mu\text{M}$ )	$^{87}\text{Sr}/^{86}\text{Sr}$	$1\sigma$
		Top	Bottom			
337-C0020A-						
II	1R-2, 0–65	1277.77	1278.42	141.61	0.70860	1.14E–05
II	2R-3, 0–60	1288.79	1289.39	212.10	0.70844	9.08E–06
II	3R-3, 0–60	1371.99	1372.59	176.68	0.70830	1.06E–05
II	5R-3, 39–85	1492.24	1492.70	93.90	0.70811	8.00E–06
II	6R-2, 15–76	1496.56	1497.17	124.54	0.70807	1.21E–05
II	8L-5, 35–93	1607.67	1608.09	145.90	0.70727	1.58E–05
II	12R-2, 53–75	1748.97	1749.19	281.15	0.70685	7.15E–06
II	12R-7, 30–50	1754.84	1755.04	287.31	0.70679	9.08E–06
II	13R-8, 27–60	1764.81	1765.12	319.24	0.70679	7.88E–06
III	15R-7, 18–33	1925.65	1925.80	306.82	0.70633	1.31E–05
III	17R-1, 60–100	1936.60	1937.00	450.86	0.70642	1.11E–05
III	17R-4, 65–85	1939.35	1939.55	473.94	0.70644	1.42E–05
III	17R-9, 25–51	1944.39	1944.65	440.18	0.70646	8.16E–06
III	19R-9, 30–60	1958.83	1959.11	345.36	0.70626	1.10E–05
IV	29R-6, 0–76	2405.30	2406.06	382.94	0.70607	1.06E–05

$1\sigma = 1$  standard deviation of analyses.

**Table T2.** Interstitial water Sr concentration and isotopic ratio from Quicksilver probe, Site C0020.

Unit	Section	Sample number	Depth (mbsf)	Sr ( $\mu\text{M}$ )	$^{87}\text{Sr}/^{86}\text{Sr}$	$1\sigma$
II	LWL	396	1808	255.45	0.70655	1.02E–05
III	LWL	395	1844	235.78	0.70652	1.09E–05
III	LWL	394	1901.5	227.78	0.70645	1.60E–05
III	LWL	393	1978	331.32	0.70622	1.12E–05

$1\sigma = 1$  standard deviation of analyses.