Teagle, D.A.H., Wilson, D.S., Acton, G.D., and Vanko, D.A. (Eds.)
Proceedings of the Ocean Drilling Program, Scientific Results Volume 206

10. DATA REPORT: COMPOSITIONS OF CALCIUM CARBONATE VEINS FROM SUPERFAST SPREADING RATE CRUST, ODP LEG 206[1]

Rosalind M. Coggon,[2] Damon A.H. Teagle,[2] Matthew J. Cooper,[2]
Tina E.F. Hayes,[2] and Darryl R.H. Green[3]

INTRODUCTION

Drilling a complete deep crustal section has been a primary yet elusive goal since the inception of scientific ocean drilling. In situ ocean crustal sections would contribute enormously to our understanding of the formation and subsequent evolution of the ocean crust, in particular the interplay between magmatic, hydrothermal, and tectonic processes. Ocean Drilling Program (ODP) Leg 206 was the first of a multileg project to drill an in situ crustal section that penetrated the gabbroic rocks of the Cocos plate (6°44.2′N, 91°56.1′W), which formed ~15 m.y. ago on the East Pacific Rise during a period of superfast spreading (>200 mm/yr) (Wilson, Teagle, Acton, et al., 2003).

During Leg 206, the upper 500 m of basement was cored in Holes 1256C and 1256D with moderate to high recovery rates. The igneous rocks recovered are predominantly thin (10 cm to 3 m) basalt flows separated by chilled margins. There are also several massive flows (>3 m thick), although their abundance decreases with depth in Hole 1256D, as well as minor pillow basalts, hyaloclastites, and rare dikes. The lavas have been slightly (<10%) altered by low-temperature hydrothermal fluids, which resulted in pervasive dark gray background alteration and precipitation of saponite, pyrite, silica, celadonite, and calcium carbonate veins.

Calcium carbonate is a common secondary precipitate that fills veins and cements breccias in the upper basement as the ocean crust spreads

---

[1] Coggon, R.M., Teagle, D.A.H., Cooper, M.J., Hayes, T.E.F., and Green, D.R.H., 2006. Data report: compositions of calcium carbonate veins from superfast spreading rate crust, ODP Leg 206. *In* Teagle, D.A.H., Wilson, D.S., Acton, G.D., and Vanko, D.A. (Eds.), *Proc. ODP, Sci. Results,* 206: College Station, TX (Ocean Drilling Program), 1–6. doi:10.2973/odp.proc.sr.206.002.2006

[2] School of Ocean and Earth Science, National Oceanography Centre, Southampton, University of Southampton, European Way, Southampton SO14 3ZH, United Kingdom. Correspondence author: rmc01@noc.soton.ac.uk

[3] Challenger Division for Seafloor Processes, National Oceanography Centre, Southampton, European Way, Southampton SO14 3ZH, United Kingdom.

Initial receipt: 29 April 2005
Acceptance: 9 December 2005
Web publication: 16 October 2006
Ms 206SR-002

away from the ridge axis. The carbonate veins record the compositions of the fluids from which they precipitate. Coggon et al. (2004) demonstrated how calcium carbonate veins that precipitated in the upper basement accurately predict the chemistry of ridge flank hydrothermal fluids, with increasing temperature, across the eastern flank of the Juan de Fuca Ridge. Here we present a geochemical analysis of the $CaCO_3$ recovered from cores. The compositions of ridge flank fluids within superfast spreading crust will be determined from these data, following the approach of Hart et al. (1994), Yatabe et al. (2000), and Coggon et al. (2004).

Calcium carbonate was identified in only 2.3% of the 5839 veins recovered from Site 1256 basement cores and is concentrated in two intervals, 250–350 and 450–550 meters below seafloor (mbsf) (Wilson, Teagle, Acton, et al., 2003). $CaCO_3$ typically occurs as a minor constituent of composite veins, forming the cores of 0.5- to 1-mm-wide saponite + $CaCO_3$ ± pyrite veins, or 1-mm-wide rims to wider (2–4 mm) quartz veins. Occasionally, $CaCO_3$ is the principal component of 1-mm-wide veins.

ANALYTICAL METHODS

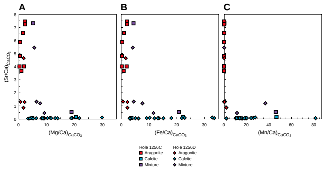
Thirty-seven basalt samples containing thin (<1 mm wide) carbonate veins were chosen for analysis. Carbonate vein samples were handpicked and prepared for compositional analysis. Stable isotope compositions ($\delta^{18}O$ and $\delta^{13}C$) were analyzed on a Europa GEO 20-20 spectrometer with a CAPS preparation system using Carrera marble standards that were calibrated to National Institute of Standards (NIST) reference material NIST-19. The errors for this instrument are better than ±0.1‰ for both C and O isotopes. The Ca, Mg, Sr, Fe, and Mn concentrations of the carbonates were measured on a PerkinElmer 4300 DV inductively coupled plasma–atomic emission spectrometer (ICP-AES) using synthetic standards prepared from ARISTAR ICP–mass spectroscopy (MS) primary standards. The precision of elemental ratios is 0.2%, whereas elemental concentration errors are 0.5%.

Strontium was isolated with 80-µL Sr-Spec columns and eluted with 3-M HNO_3. Sr samples were loaded onto out-gassed Ta filaments using a Ta activator solution and analyzed in a multidynamic mode using a VG sector 54 thermal ionization mass spectrometer. The average $^{87}Sr/^{86}Sr$ ratio for NIST-987 on this instrument was 0.710249 ± 0.000025 (2σ) for the period of the analyses (N = 83) and Sr-Spec column blanks were <0.15 ng.

RESULTS

The calcium carbonate polymorphs aragonite and calcite have distinct trace element concentrations because their structures allow for preferential incorporation of different cations (Deer et al., 1992). The mineralogy of the Site 1256 carbonate veins is therefore determined from their Sr/Ca and Mg/Ca ratios, which reveal two distinct groups (Fig. F1; Table T1). The compact calcite structure can incorporate the small Mg cation, whereas aragonite has a larger cation site and favors accommodation of the larger Sr cation (Deer et al., 1992). Samples with Sr/Ca ratios less than ~0.2 mmol/mol are classified as calcite, and those with Mg/Ca ratios of less than ~2.5 mmol/mol are classified as arago-

F1. Sr/Ca concentrations vs. Mg/Ca, Fe/Ca, and Mn/Ca, p. 5.



T1. Geochemistry of $CaCO_3$ samples, p. 6.

nite (Table **T1;** Fig. **F1**). The remaining samples, with intermediate compositions (Sr/Ca >0.2 mmol/mol and Mg/Ca >2.5 mmol/mol), are interpreted to be aragonite-calcite mixtures, which were homogenized during hand-picking.

Fe and Mn are similar in diameter to Mg and are therefore also preferentially incorporated into calcite, with Fe/Ca ranging from ~3 to ~35 mmol/mol and Mn/Ca ratios up to ~80 mmol/mol (Fig. **F1**). The aragonite veins have lower Fe/Ca ratios (<2.5 mmol/mol), and their incorporation of Mn is extremely limited, with Mn/Ca ratios ranging from ~0.01 to ~2 mmol/mol.

The carbonate veins have ^{87}Sr/^{86}Sr ratios ranging from ~0.70804 to 0.70872. The majority of the aragonite veins have Sr isotopic compositions between ~0.7087 and ~0.7086, whereas the calcite veins precipitated from fluids with ^{87}Sr/^{86}Sr ranging from ~0.7086 to ~0.7080. The strontium isotopic composition of the oceans ~15 m.y. ago was ~0.70875 (Hodell et al., 1991), and it has increased progressively since then. All the carbonate veins precipitated from fluids with ^{87}Sr/^{86}Sr ratios lower than the seawater ^{87}Sr/^{86}Sr ratio has been since the eruption of the host basalt. The veins therefore all contain a discernible component of basalt-derived Sr (^{87}Sr/^{86}Sr ~0.7027). The carbonate δ^{13}C and δ^{18}O compositions range from –3‰ to 4‰$_{\text{VPDB}}$ (Vienna Peede belemnite) and 20‰ to 32‰$_{\text{VSMOW}}$ (Vienna standard mean ocean water), respectively, within the range previously established for hydrothermally altered mid-ocean-ridge basalt–hosted calcite breccia cements and veins (Stakes and O'Neil, 1982).

ACKNOWLEDGMENTS

This research was supported by Natural Environmental Research Council (NERC) Ph.D. Studentship NER/S/A/2001/063 to R.M. Coggon. Laboratory costs were covered by a NERC UK ODP Rapid Response Award to D.A.H. Teagle and R.M. Coggon. This research used samples and/or data provided by the Ocean Drilling Program (ODP). ODP is sponsored by the U.S. National Science Foundation (NSF) and participating countries under management of Joint Oceanographic Institutions (JOI), Inc.

REFERENCES

Coggon, R.M., Teagle, D.A.H., Cooper, M.J., and Vanko, D.A., 2004. Linking basement carbonate vein compositions to porewater geochemistry across the eastern flank of the Juan de Fuca Ridge, ODP Leg 168. *Earth Planet. Sci. Lett.,* 219:111–128. **doi:10.1016/S0012-821X(03)00697-6**

Deer, W.A., Howie, R.A., and Zussman, J., 1992. *An Introduction to the Rock-Forming Minerals* (2nd ed.): Harlow, United Kingdom (Longman Scientific Technical).

Hart, S.R., Blusztajn, J., Dick, H.J.B., and Lawrence, J.R., 1994. Fluid circulation in the oceanic crust: contrast between volcanic and plutonic regimes. *J. Geophys. Res.,* 99:3163–3174. **doi:10.1029/93JB02035**

Hodell, D.A., Mueller, P.A., and Garrido, J.R., 1991. Variations in the strontium isotopic composition of seawater during the Neogene. *Geology,* 19:24–27. **doi:10.1130/0091-7613(1991)019<0024:VITSIC>2.3.CO;2**

Stakes, D.S., and O'Neil, J.R., 1982. Mineralogy and stable isotope geochemistry of hydrothermally altered oceanic rocks. *Earth Planet. Sci. Lett.,* 57:285–304. **doi:10.1016/0012-821X(82)90151-0**

Wilson, D.S., Teagle, D.A.H., Acton, G.D., et al., 2003. *Proc. ODP, Init. Repts.,* 206 [Online]. Available from World Wide Web: <**http://www-odp.tamu.edu/publications/206_IR/206ir.htm**>. [Cited 2005-04-24]

Yatabe, A., Vanko, D.A., and Ghazi, A.M., 2000. Petrography and chemical compositions of secondary calcite and aragonite in Juan de Fuca Ridge basalts altered at low temperature. *In* Fisher, A., Davis, E.E., and Escutia, C. (Eds.), *Proc. ODP, Sci. Results,* 168: College Station, TX (Ocean Drilling Program), 137–148. [**HTML**]

Figure F1. Sr/Ca concentrations of $CaCO_3$ veins vs. (**A**) Mg/Ca, (**B**) Fe/Ca, and (**C**) Mn/Ca. The $CaCO_3$ veins are classified as calcite, aragonite, or calcite-aragonite mixtures on the basis of Sr/Ca and Mg/Ca concentrations. Errors are less than the width of data points.

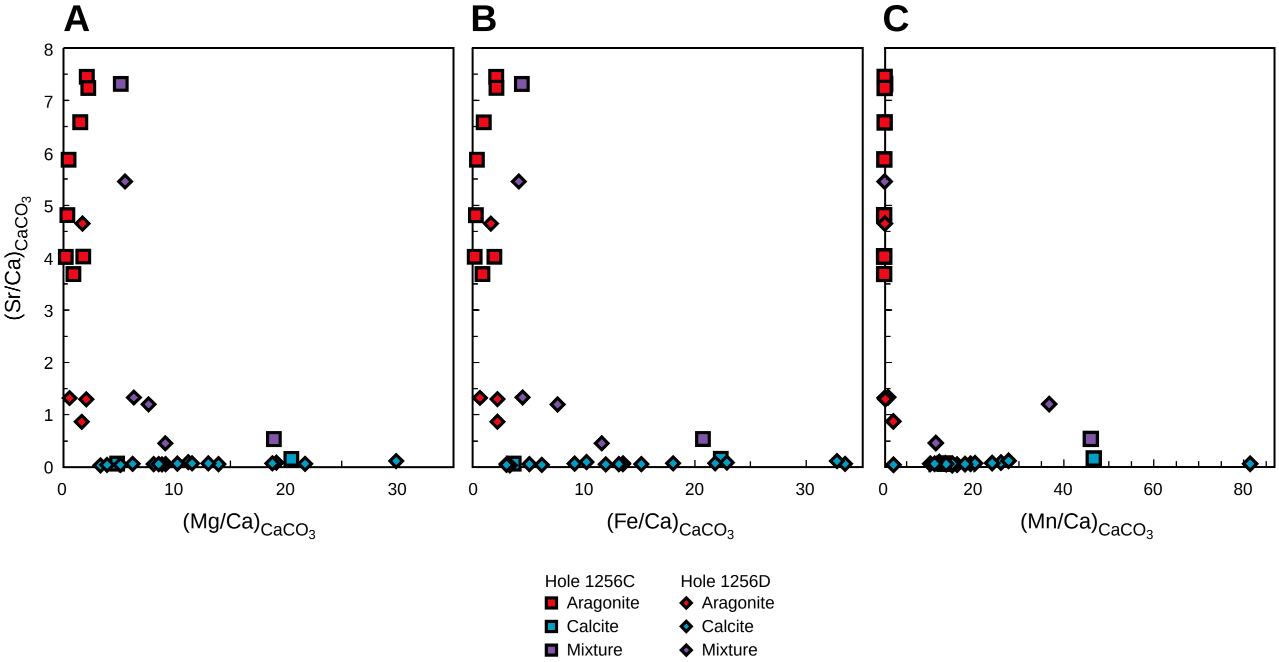


Table T1. Geochemistry of $CaCO_3$ samples.

Core, section, interval (cm)	Depth (mbsf)	Depth within basement (m)	$CaCO_3$ mineral	δ^{13}C (‰$_{\text{VPDB}}$)	δ^{18}O (‰$_{\text{VSMOW}}$)	Mg (ppm)	Sr (ppm)	Fe (ppm)	Mn (ppm)	^{87}Sr/^{86}Sr	±2σ E
206-1256C-											
5R-3, 14–18	255.4	5.4	A	0.58	27.66	429	3,520	1,130	15	0.708638	±0.000011
5R-3, 27–30	255.6	5.6	A	1.37	26.45	217	3,230	528	10	0.708632	±0.000013
6R-3, 109–112	260.8	10.8	A	1.58	26.89	47	3,520	140	5	0.708623	±0.000011
6R-4, 107–111	262.1	12.1	AC	0.61	25.48	4,590	471	11,600	25,300	0.708572	±0.000011
7R-3, 50–55	269.8	19.8	C	0.32	25.17	4,970	140	12,500	25,600	0.708566	±0.000013
8R-1, 56–60	276.1	26.1	A	0.66	27.28	84	4,210	209	12	0.708658	±0.000010
8R-4, 20–23	279.8	29.8	C	0.42	21.87	1,170	59	2,100	7,390	0.708216	±0.000093
8R-4, 32–35	279.9	29.9	A	3.47	30.76	508	6,520	1,210	70	0.708691	±0.000010
8R-4, 64–67	280.2	30.2	A	3.29	30.52	541	6,340	1,230	51	0.708701	±0.000011
8R-4, 72–75	280.3	30.3	AC	2.54	30.61	1,250	6,400	2,500	124	0.708684	±0.000011
8R-6, 21–23	281.7	31.7	A	3.11	31.50	366	5,760	590	79	0.708553	±0.000011
13R-1, 10–12	322.1	72.1	A	3.23	28.92	110	5,140	249	36	0.708719	±0.000011
206-1256D-											
7R-1, 46–49	304.4	54.4	C	0.36	22.99	1,240	40	3,510	8,900	—	—
7R-6, 39–41	311.1	61.1	C	–0.93	22.64	2,720	86	5,740	6,700	—	—
8R-3, 67–68	316.2	66.2	A	3.61	29.45	415	4,070	950	86	0.708614	±0.000011
8R-4, 111–116	317.4	67.4	AC	1.93	26.35	1,860	1,050	4,280	20,200	0.708437	±0.000011
12R-5, 76–81	347.1	97.1	C	–0.35	25.92	1,970	53	2,890	44,700	0.70823	±0.000013
12R-6, 93–95	348.8	98.8	C	1.07	23.59	807	29	1,910	8,310	0.708086	±0.000047
12R-8, 27–33	350.8	100.8	AC	2.29	28.43	1,340	4,770	2,350	67	0.708675	±0.000011
13R-1, 82–85	351.1	101.1	C	0.06	23.08	1,510	53	1,760	8,340	—	—
26R-5, 104–105	445.0	195.0	C	0.30	22.23	3,380	52	8,490	10,600	0.708341	±0.000024
27R-1, 23–27	445.6	195.6	C	–1.34	22.27	3,160	63	10,100	11,100	0.708296	±0.000014
27R-1, 29–32	445.7	195.7	C	–0.57	22.09	4,650	76	12,800	14,300	0.708446	±0.000016
27R-2, 28–31	447.1	197.1	C	0.53	22.29	2,490	60	5,140	6,720	0.708308	±0.000011
28R-1, 121–123	452.1	202.1	C	–0.44	22.04	4,560	65	7,580	13,200	0.708408	±0.000018
32R-1, 98–99	476.2	226.2	A	0.00	22.11	133	1,160	404	52	0.708365	±0.000010
32R-1, 124–126	476.4	226.4	C	–3.11	21.59	2,230	50	7,560	9,890	0.708286	±0.000011
32R-2, 44–46	477.1	227.1	A	–1.23	21.77	398	759	1,290	1,110	0.708259	±0.000011
32R-4, 2–4	479.3	229.3	AC	–1.49	21.60	2,220	398	6,500	6,320	0.70825	±0.000011
33R-3, 15–17	484.0	234.0	C	0.07	21.45	5,270	53	18,700	5,660	—	—
34R-1, 0–3	484.4	234.4	C	–0.34	21.35	2,800	62	12,200	7,480	0.708268	±0.000013
36R-1, 42–45	494.4	244.4	C	–0.99	22.02	7,260	102	18,300	15,200	0.70849	±0.000016
38R-1, 91–93	505.2	255.2	AC	–0.37	21.60	1,540	1,160	2,540	480	0.708295	±0.000011
41R-2, 117–118	527.2	277.2	C	–1.84	21.01	2,150	48	6,700	7,570	0.708269	±0.000011
41R-3, 6–10	527.5	277.5	A	–1.43	21.32	495	1,130	1,290	171	—	—
42R-1, 33–35	529.7	279.7	C	–2.28	20.97	2,080	51	7,360	6,170	—	—
59R-1, 27–31	659.3	409.3	C	0.80	20.02	950	37	1,740	1,160	0.708043	±0.000016

Notes: A = aragonite, C = calcite, AC = aragonite-calcite mixture. VPDB = Vienna Peedee belemnite, VSMOW = Vienna standard mean ocean water. ^{87}Sr/^{86}Sr for NIST-987 was 0.710248 ± 0.000027 for the period of the analyses (*N* = 80). — = not determined.