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59. *DATA REPORT:* ELECTRON MICROPROBE ANALYSES OF CRETACEOUS LIMESTONES FROM MIT GUYOT[1]

Robert J. van Waasbergen[2] and Janet A. Haggerty[2]

INTRODUCTION

We analyzed samples from Site 878, stratigraphic Unit V (Shipboard Scientific Party, 1993), which comprised part of the lower carbonate platform of the section drilled at MIT Guyot. This work is part of an ongoing project to relate some of the surface features of the guyot to the diagenetic history of the limestone. Of particular interest is whether the observed irregular surface topography (Shipboard Scientific Party, 1993; van Waasbergen and Winterer, 1993) can be attributed to removal of soluble deposits, such as evaporites, from the subsurface.

METHODS

Polished thin sections of available sample material were made and analyzed with blue-violet fluorescence microscopy to reveal details of cement stratigraphy and other microstructures. Under blue-violet light, dolomite rhombs typically remained darker (nonfluorescent) than the surrounding calcite matrix. Variable fluorescence in cements, related to slight variations in mineralogy, trace-element chemistry of the crystals, or the abundance of fluid or solid inclusions (van Gijzel, 1979), allows the observation of the detailed growth history of individual cement generations.

Electron microprobe analysis was used to determine variations in the chemical composition of the dolomite rhombs and calcite cements. Polished thin sections were coated with silver following the method of Smith (1986). Microprobe analysis of carbonates coated with silver differs from analysis of carbonates with conventional carbon for several reasons (Smith, 1986; Daniel and Haggerty, 1988; Haggerty and Smith, 1988).

1. During electron bombardment, the silver coating inhibits thermal decomposition of carbonates better than carbon coating.
2. This enhanced stability of the carbonate mineral during electron bombardment permits the use of higher sample currents, a focused beam, and longer counting times.
3. A more focused beam on silver-coated carbonates than the diffuse beam (typically 250 µm) used on carbon-coated carbonates enhances the spatial resolution.
4. The longer counting times lowers the detection limits for trace elements in carbonate rocks.

A Cameca 3-spectrometer electron microprobe was used, with a focused beam of 4 to 6 µm in diameter. We used an accelerating potential of 20 kV, and a sample current of 20 nA (dolomite) and 12 nA (calcite). Counting times on peak and background for each analysis for calcite were 60 s for Ca and Mg and 360 s for Fe, Mn, Sr, Na, and S. For analyses on dolomite, counting times were 10 s for Ca and Mg and 300 s for Fe, Mn, Sr, Na, and S.

K_α-peaks were used for all elements analyzed, with the exception of Sr. Sr-LMçα was analyzed using a thallium acid phthalate (TAP) crystal rather than the conventional pentaerythritol (PET) crystal. The Sr-L_α peak on a TAP crystal occurs near the lower limit of the wavelength spectrometer, which provides maximum intensity of X-rays and lowest detection limits. The Sr-L_α peak on the PET crystal occurs on the upper limit of the wavelength spectrometer, which causes the intensity of the X-rays to be extremely attenuated.

Detection limits for each of the elements were calculated using the equation

$$L = X \times \frac{3\sqrt{C}}{S},$$

where X = weight fraction of the element in the standard, C = background counts measured on the unknown, and S = peak counts of the element in the standard, all corrected for the counting time. Detection limits for each of the elements in calcite were as follows: Ca = 180 ppm, Mg = 110 ppm, Fe = 110 ppm, Mn = 100 ppm, Na = 60 ppm, Sr = 93 ppm, and S = 128 ppm. Detection limits in dolomite were as follows: Ca = 290 ppm, Mg = 225 ppm, Fe = 86 ppm, Mn = 81 ppm, Na = 55 ppm, Sr = 92 ppm, and S = 86 ppm.

Five areas were microprobed from four separate thin sections.

RESULTS

Sample 144-878A-75R-1, 32–37 cm (693.8 mbsf)

This sample consists of a porous wackestone containing small skeletal fragments of foraminifers, thin-shelled gastropods, and echinoderms in a dense micrite matrix. Moldic porosity is common, with pores frequently filled with anhedral equant calcite cement. Several large stylolite structures cross this interval. These form up to 0.5-mm-thick horizons commonly very rich in fibrous siliceous minerals such as clay or mica. Dolomite occurs in this sample as massive, unzoned euhedral rhombohedra dispersed throughout the matrix, and as zoned (in blue-violet fluorescence microscopy) euhedral rhombohedra, many of which are concentrated in the stylolites.

Two microprobe transects were made, one in an unzoned dolomite rhombohedron (Table 1) and one in a zoned rhombohedron (Table 2). The unzoned rhombohedra commonly contain irregular patches that show greater fluorescence and contain less Mg.

Sample 144-878A-75R-1, 126–130 cm (694.7 mbsf)

This sample consists of fine-grained packstone with rather large bioclasts of algae and coral that are poorly preserved. Much of the material has neomorphosed to euhedral rhombic crystals up to 0.1 mm in diameter. A microprobe transect of a euhedral crystal that was nonfluorescent under blue-violet light showed a uniformly low Mg content and some variation in trace elements. This particular crystal was interpreted, from its petrographic characteristics, to be dolomite before the microprobe analyses. Hence, the analyses were conducted using the operating conditions for dolomite. Two of the analyses resulted in distinct spikes in concentrations of Mg, Na, S, and Sr (Table 3).

[1] Haggerty, J.A., Premoli Silva, I., Rack, F., and McNutt, M.K. (Eds.), 1995. *Proc. ODP, Sci. Results,* 144: College Station, TX (Ocean Drilling Program).

[2] Department of Geosciences, University of Tulsa, Tulsa, OK 74104, U.S.A.

Table 1. Microprobe transect across an unzoned dolomite rhombohedron in Sample 144-878A-75R-1, 32–37 cm.

Point	Ca	Mg	Fe	Na	Mn	S	Sr
1	22.13	1.29	145	83	BD	333	BD
2	22.20	13.97	71	313	BD	401	BD
3	24.39	14.70	143	154	BD	364	BD
4	23.66	15.58	71	151	BD	152	BD
5	25.12	11.73	83	138	BD	317	BD
6	25.14	11.71	BD	114	BD	405	BD
7	24.77	11.60	95	137	BD	356	BD
8	25.27	11.59	BD	161	BD	233	BD
9	25.50	11.73	BD	115	74	270	BD
10	25.22	11.50	BD	BD	BD	245	BD
11	24.96	11.27	BD	184	BD	245	BD
12	25.63	11.21	BD	162	BD	244	BD
13	25.32	11.31	BD	184	BD	281	BD
14	25.06	11.50	71	252	74	307	BD
15	25.01	11.49	107	229	BD	306	BD
16	25.68	11.55	72	207	BD	318	BD
17	26.84	10.24	251	213	BD	349	BD
18	25.60	11.18	BD	230	BD	354	BD
19	29.98	6.91	BD	202	BD	346	BD
20	25.02	8.34	BD	286	BD	371	BD
21	24.82	13.65	BD	242	BD	401	BD
MP	24.89	12.31	BD	205	BD	308	BD

Notes: Values for Ca and Mg are reported as weight percent (wt%); other elements as parts per million (ppm). Point "MP" refers to an isolated analysis in the center of the crystal. BD = below detection limit.

Sample 144-878A-71R-1, 119–123 cm (656.1 mbsf)

This sample consists of coarse grainstone to rudstone of bioclasts of mollusks, echinoderms, and algae. Primary pore space is generally occluded with bladed fringing spar, followed by a pore-filling blocky cement with banded fluorescence. The results of a short microprobe transect into a late-stage cement crystal that varies from dull fluorescence to no fluorescence is shown in Table 4.

Sample 144-878A-73R-1, 14–19 cm (674.3 mbsf)

This sample consists of coarse grainstone to rudstone of bioclasts of primarily fragmented mollusks and algae. Abundant primary pore space is occluded with several generations of cements, which include fringing, inclusion-rich bladed spar, as well as clear, fine-grained equant spar, and coarse, clear, void-filling blocky spar. Results of a microprobe transect through several generations of cements, across an entire pore, are listed in Table 5.

DISCUSSION

The first three transects have similarities in trace element composition: they show little Fe, Mn, or Sr throughout. Mg-poor areas in unzoned dolomite rhombohedra may be representative of partial dolomitization. The third transect (Sample 144-878A-75R-1, 126–130 cm) was in a crystal that had similar petrographic characteristics as dolomite (euhedral, little fluorescence). Results from this sample show distinct spikes in the concentration of Mg, Na, S, and Sr; this suggests the presence of sulfate mineral microinclusions. Daniel and Haggerty (1988) also noted distinct spikes in the trace element concentrations, especially S, in Upper Jurassic/Lower Cretaceous dolomites from the Galicia margin. Haggerty and Smith (1988) subjected these dolomites to mineral pyrolysis and showed that the microinclusions were sulfate minerals.

The fourth sample (144-878A-71R-1, 119-123 cm) shows much lower levels of Na and a relatively higher and more consistent concentration of Fe, which might be related to a fresh-water burial influence. More data, including stable isotopic analyses, will be needed to substantiate this possibility.

The last sample (144-878A-73R-1, 14–19 cm) has a quite different trace-element composition. The Sr concentration is consistently higher. There is a general decrease in Sr content toward the center (dull fluorescence), whereas the Fe concentration is highest in the fluorescent tips of the bladed fringing spar cement.

Any of the above interpretations are very preliminary and further work will be needed before more conclusive statements about the diagenetic history of the materials can be made.

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*Abbreviations for names of organizations and publications in ODP reference lists follow the style given in *Chemical Abstracts Service Source Index* (published by American Chemical Society).

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Table 2. Microprobe transect across a zoned dolomite rhombohedron in Sample 144-878A-75R-1, 32–37 cm.

Point	Ca	Mg	Fe	Na	Mn	S	Sr
1	23.97	12.13	262	183	BD	295	BD
2	24.76	11.46	BD	185	BD	244	BD
3	24.78	11.43	72	231	BD	281	BD
4	24.63	11.53	72	230	BD	245	BD
5	24.56	11.47	BD	253	BD	318	BD
6	24.48	11.57	143	207	BD	330	BD
7	24.56	11.48	BD	138	BD	110	BD
8	24.66	11.63	BD	115	99	257	BD
9	24.39	11.64	BD	115	BD	208	BD
10	24.39	11.60	BD	92	BD	306	BD
11	23.66	12.03	322	136	BD	210	BD
12	24.91	11.50	72	116	BD	171	BD
13	24.80	11.59	143	161	BD	208	BD
14	24.61	11.47	BD	115	BD	269	BD
15	24.67	11.63	72	46	BD	171	BD
16	25.04	11.55	119	92	BD	85	BD
17	24.68	11.48	95	69	BD	232	BD
18	24.93	11.30	72	162	BD	256	BD
19	24.93	11.23	107	162	BD	317	BD
20	25.38	11.06	83	140	BD	279	BD
21	24.91	11.10	72	162	BD	414	BD

Notes: Values for Ca and Mg are reported as weight percent (wt%); other elements as parts per million (ppm). BD = below detection limit.

Table 3. Microprobe transect across a euhedral calcite crystal from Sample 144-878A-75R-1, 126–130 cm.

Point	Ca	Mg	Fe	Na	Mn	S	Sr
1	40.64	0.16	BD	BD	BD	BD	BD
2	40.56	0.37	BD	BD	BD	253	BD
3	40.65	0.19	BD	57	89	284	BD
4	39.30	0.67	BD	1201	BD	3841	575
5	40.13	0.22	BD	141	76	399	BD
6	40.16	0.23	BD	85	BD	242	BD
7	40.89	0.25	84	85	BD	431	BD
8	41.20	0.29	145	57	BD	537	BD
9	40.54	0.26	97	141	BD	599	BD
10	43.30	0.32	BD	198	76	705	162
11	40.40	0.35	BD	85	BD	263	BD
12	40.14	0.07	145	BD	139	178	BD

Notes: Values for Ca and Mg are reported as weight percent (wt%); other elements as parts per million (ppm). Note the high trace element values in Points 4 and 10, which are interpreted to contain microinclusions of sulfate. BD = below detection limit.

Table 4. Microprobe transect in a late-stage calcite cement in Sample 144-878A-71R-1, 119–123 cm.

Point	Ca	Mg	Fe	Na	Mn	S	Sr
1	38.99	0.33	169	BD	177	BD	BD
2	39.48	0.20	133	BD	BD	116	BD
3	39.74	0.14	133	85	BD	210	BD
4	39.56	0.14	BD	BD	BD	168	BD
5	40.32	0.16	157	28	BD	BD	BD

Notes: Values for Ca and Mg are reported as weight percent (wt%); other elements as parts per million (ppm). BD = below detection limit.

Table 5. Microprobe transect across calcite pore-filling cement from Sample 144-878A-73R-1, 14–19 cm.

Point	Ca	Mg	Fe	Na	Mn	S	Sr
1	42.15	0.33	96	141	BD	369	410
2	41.88	0.31	BD	170	BD	221	311
3	41.63	0.34	BD	BD	BD	548	224
4	42.84	0.22	BD	56	BD	116	BD
5	41.84	0.55	BD	BD	BD	316	348
6	42.76	0.40	BD	BD	89	147	249
7	42.54	0.22	BD	BD	89	158	BD
8	42.28	0.33	229	BD	BD	242	162
9	42.03	0.26	109	BD	139	126	149
10	41.98	0.42	BD	BD	BD	158	124
11	42.23	0.21	BD	BD	BD	147	BD
12	43.16	0.32	BD	141	BD	337	BD
13	43.03	0.16	133	BD	89	211	186
14	40.35	0.28	BD	BD	BD	147	BD
15	41.53	0.32	BD	85	127	BD	BD
16	42.52	0.24	217	BD	BD	168	721
17	41.79	0.58	BD	BD	BD	579	373
18	41.13	0.47	BD	56	BD	642	820
19	42.79	0.28	133	113	BD	BD	174
20	42.65	0.26	265	BD	76	242	99
21	43.22	0.48	BD	85	BD	274	709
22	42.24	0.23	BD	BD	BD	158	87

Notes: Values for Ca and Mg are reported as weight percent (wt%); other elements as parts per million (ppm). BD = below detection limit.