the possibility of its formation in pure $MgSiO_3$ garnet at high pressures and high temperatures. Ringwood and Major[13] have reported the synthesis of garnet with a composition of $Fe/Fe + Mg = 0.25$ and $Al_2O_3 = 1.3$ mol % at 1,000 °C and above 25 GPa. Akaogi and Akimoto[14] found that, in the enstatite $(MgSiO_3)$-pyrope $(Mg_3Al_2Si_3O_{12})$ system below 1,200 °C, at least 5 mol % Al_2O_3 is required to stabilize garnet. We have confirmed the expected formation of alumina-free garnet of $MgSiO_3$ at much higher temperatures than the previous studies. The synthesized garnet is not cubic but of lower symmetry. In some meteorites, cubic majorite garnet occurs in association with glass and high-pressure phases of orthosilicate (spinel and modified spinel)[15], suggesting that crystallization involves melting at high pressures. This phase assemblage suggests that pressure and temperature conditions of majorite formation are close to those of the present experiment. The only difference between majorite garnet and the present non-cubic phase is the composition of $Fe/Mg + Fe$. Therefore, we anticipate the future finding of non-cubic aluminium-free garnet instead of cubic majorite in shocked enstatite chondrites (E) and bronzite chondrites (H), which have low $Fe/Mg + Fe$ in silicate phases. The detailed relationship between the cubic and non-cubic garnets is an important problem to be studied in order to clarify quantitatively the conditions prevailing in majorite-bearing meteorites.

The pressure-induced phase transitions in magnesium silicates $(Mg_2SiO_4$ and $MgSiO_3)$ have been extensively studied because of their importance for investigating the nature of the Earth's mantle[16]. The transition in $MgSiO_3$ at ~1,000 °C is: orthopyroxene (OPx) → clinopyroxene (CPx) → modified spinel (MS) + stishovite (St) → spinel (Sp) + St → ilmenite (Il) → perovskite (Pv), and it possesses a gap between CPx and Il in polymorphic transition. In contrast, the transition in Mg_2SiO_4 shows a simple mode: two steps of polymorphic transition followed by a disproportionation reaction: olivine → MS → Sp → Pv + St. The disproportionation reaction of CPx involving stishovite, followed by the recombination reaction to Il, is poorly understood. The stability field of the new non-cubic garnet borders those of CPx and Il, all in the polymorphic relation, and the non-cubic garnet fills the gap between CPx and Il in the polymorphic transition of $MgSiO_3$ at high temperature. Therefore, $MgSiO_3$ has five polymorphic phases, OPx → CPx → Gt* → Il → Pv, in continuous sequence with increasing pressure (Gt* denotes non-cubic garnet). The presumed phase relation for $MgSiO_3$ composition is shown in Fig. 3, which summarizes the latest experimental data[17-20]. The two phase assemblages involving stishovite (stippled area in Fig. 1) at the lower temperatures may be interpreted as a result of the abnormally high density and low entropy of stishovite.

We note several important implications of the present result for the constitution of the Earth and planetary interiors. The congruent melting of $MgSiO_3$ persists continuously from pyroxene to perovskite through non-cubic garnet, so that the pyroxene-stoichiometric phase remains as a major solid phase in the partial melting process throughout the mantle, regardless of the alumina and other minor elemental concentrations of the candidate material. Because the density of garnet is expected to be larger than the silicate melt throughout the upper mantle[21], it may sink, thereby constituting the bottom of the upper mantle. The fractionation of garnet could have an important role in the formation of the layered structure in the mantle.

1. Kumazawa, M. & Endo, S. in *Material Science of the Earth's Interior*, (ed. Sunagawa, I.) 587-603 (Terra Scientific, Tokyo, 1984).
2. Ohtani, E. *J. Phys. Earth.* 79, 189-208 (1979).
3. Sawamoto, H. *Phys. chem. Miner.* (in the press).
4. Kato, T. & Kumazawa, M. *Phys. Earth planet. Inter.* (submitted).
5. Fujino, K., Momoi, H. & Sawamoto, H. *Abstr. Miner. Soc. Jap. A. Meet.* (in Japanese) (1981).
6. Prewitt, C. T. & Sleight, A. W. *Science* 163, 386-387 (1969).
7. Akaogi, M., Matsumoto, I., Akimoto, S. & Suzaki, J. *Abstr. Miner. Soc. Jap. A. Meet.* (in Japanese) (1981).
8. Smith, J. V. & Mason, B. *Science* 168, 832-833 (1970).
9. Coleman, L. C. *Can. Miner.* 15, 97-101 (1977).
10. Sawamoto, H. & Kozaki, M. *Abstr. seism. Soc. Jap.* (in Japanese) No. 2, 135 (1984).
11. Jeanloz, R. *J. geophys. Res.* 86, 6171-6179 (1981).
12. Moore, R. K. *Am. Miner.* 56, 54-71 (1971).
13. Ringwood, A. E. & Major, A. *Earth planet. Sci. Lett.* 12, 411-418 (1970).
14. Akaogi, M. & Akimoto, S. *Phys. Earth planet. Inter.* 15, 90-106 (1977).
15. Price, G. D., Putnis, A. & Agrell, S. O. *Contr. Miner. Petrol.* 71, 211-218 (1979).
16. Ringwood, A. E. *Compositions and Petrology of the Earth's Mantle*, (1975), 618 (McGraw-Hill, New York).
17. Boyd, F. R., England, J. L. & Davies, B. T. C. *J. geophys. Res.* 69, 2101-2107 (1964).
18. Ito, E. *Geophys. Res. Lett.* 4, 72-74 (1977).
19. Suito, K. in *High Pressure Research Application in Geophysics* (eds Manghani, M. H. & Akimoto, S.) 405-420 (Academic, New York, 1977).
20. Ito, E. & Yamada, H. in *High Pressure Research in Geophysics* (eds Akimoto, S. & Manghani, M. H.) 255-266 (Center of Academic Publication, Tokyo, 1982).
21. Ohtani, E. *Earth planet. Sci. Lett.* 67, 261-272 (1984).

Neogene history of the calcite compensation depth and lysocline in the South Pacific Ocean

David K. Rea

Oceanography Program, Department of Atmospheric and Oceanic Science, The University of Michigan, Ann Arbor, Michigan 48109, USA

Margaret Leinen

Graduate School of Oceanography, The University of Rhode Island, Narragansett, Rhode Island 02882-1197, USA

The depth–time pattern of calcite accumulation recorded at Deep Sea Drilling Project (DSDP) sites beneath the oligotrophic subtropical gyre in the south-east Pacific Ocean allows us to define here both the calcite compensation depth (CCD) and the lysocline. The Neogene CCD history is one of shoaling before 15 or 20 Myr and subsequent deepening to the present level of 4,100 m. A broad zone of increased calcite dissolution, 600 m thick, formed during early to middle Miocene time and has remained. This zone, the lysocline, denotes an important change in ocean chemistry and may reflect either an increase in the volume of more corrosive deep water beginning about 18 Myr and reaching steady state by 14 Myr, the time of rapid ice build-up in Antarctica, or an increase in calcite rain rate caused by an increase in surface-water productivity.

Early workers in marine geology realized that throughout most of the deep ocean the calcium carbonate microfossil tests generated in surface waters dissolved before they could be incorporated into the sediments[1]. Experiments in the Pacific by Peterson[2] and Berger[3,4] showed that calcite dissolution did not increase linearly with depth but that little dissolution occurred above about 3,500 m and rapid dissolution occurred at greater depths. This depth zone of rapidly increasing dissolution rate is the lysocline[4,5] and that depth at which the dissolution rate of calcite matches the supply rate, and below which there is no net $CaCO_3$ accumulation, is the CCD[6,7].

Studies of piston cores[8] and surface sediments[9] from the South Pacific have shown the present CCD to be at ~4,100 m depth, and the top of the lysocline near 3,500 m. Heath[10] studied calcium carbonate deposition in the equatorial Pacific and inferred changes in the CCD through Cenozoic time. Berger[11] first incorporated seafloor subsidence history into Pacific CCD studies, using an empirical age-depth curve similar to that compiled by Sclater et al.[12] Results of this study of equatorial Pacific sediments gave the first reasonable estimate of the equatorial Pacific CCD history. An important event in this history was the rapid deepening of the CCD from ~4,000 to 4,800 m at 35–40 Myr. Van Andel and co-workers used empirical subsidence curves and DSDP data to determine the CCD histories of the equatorial and non-equatorial Pacific[13-15]. Their results refined those of Berger for the equatorial Pacific and
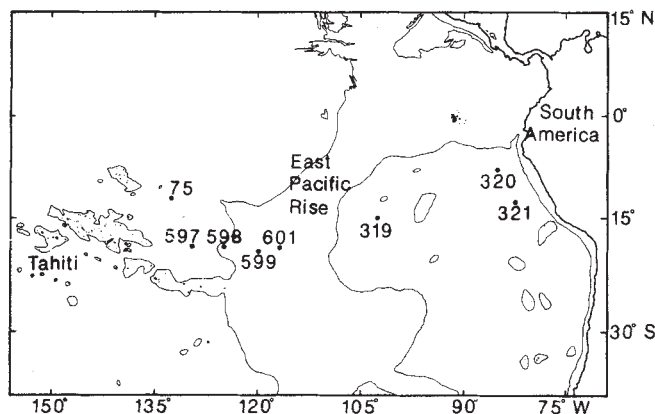
Fig. 1 Index map of the South Pacific showing sites used to construct the subsidence, CCD, and lysocline history of the region.

Fig. 2 $CaCO_3$ accumulation record plotted on age–depth curves for each site. Squares are 1 Myr × 100 m and provide an indication of accuracy. The shaded region indicates the depth zone of the lysocline. Solid line, CCD; dashed line, lysocline.

showed that CCD has been ~600 m shallower (4,000–4,200 m) since the early Oligocene in areas 10° or more north and south of the Equator.

We have determined the history of $CaCO_3$ deposition in the South Pacific based on data from the site chapters in the Leg 8 (ref. 16), Leg 34 (ref. 17) and Leg 92 (ref. 18) DSDP Initial Report volumes, converting the other data to the Leg 92 biostratigraphy. For each of the eight sites analysed (Fig. 1) we determined intervals of $CaCO_3$ deposition at rates typical of oligotrophic oceans, intervals over which there was an order-of-magnitude reduction in the mass accumulation rate of $CaCO_3$-rich sediments, and the times at which $CaCO_3$ accumulation stopped[19]. The latter is a functional definition of the sedimentary CCD[9]. We presume that the large decrease in rate records the influence of the lysocline. The times of these changes are plotted along the subsidence curves[19] and produce the first reconstruction of separate histories of the CCD and lysocline in the Pacific (Fig. 2).

The eight sites chosen for this study provide a generalized history of the lysocline and the CCD. Site 601 has always been above the lysocline. Sites 598 and 599 are now below the lysocline and above the CCD; Sites 319 and 597 have passed through both the lysocline and the CCD. The two oldest sites, 75 and 321, passed through the CCD abruptly with no evidence of reduced calcite accumulation rates before reaching the CCD. Site 320 was spot-cored; the youngest calcareous sediments recovered there are 15 Myr old. Nonetheless, the reasonably good agreement between the CCD from Site 597 and the maximum age of the transition through the CCD at 320 suggests that these sites passed through the CCD at about the same time.

The CCD in the South Pacific was at ~4,200 m in late Oligocene time, shoaled ~500 to a depth of 3,700 m in the middle-early Miocene, and has deepened since then to the present depth of ~4,100 m (Fig. 2). This history is similar to that determined by van Andel et al.[15] for the subtropical and temperate Pacific.

The absence of a zone of decreased preservation[20] or reduced $CaCO_3$ accumulation above the CCD at Sites 75 and 321 suggests that the lysocline was not well developed before 20–17 Myr. It then developed and shoaled to 600 m above the CCD by 13.5 Myr. This 600-m dissolution zone (shaded in Fig. 2) has been present ever since. Linear sedimentation rates for $CaCO_3$-rich sediment above the lysocline at Sites 597, 598, 599 and 601 and above the CCD at Sites 75 and 321 are all ~3–10 m Myr^{-1}. Site 319 had higher rates: 11 m Myr^{-1} just above the CCD and 35 m Myr^{-1} for older, shallower sediments[19].

All investigations of the Cenozoic history of the CCD have shown a shoaling of the CCD from the middle Oligocene to middle or late Miocene time, followed by a younger deepening, broadly similar to the information shown in Fig. 2[15,21–23]. A rise in the CCD must reflect some combination of (1) increased CO_2 content, hence corrosivity, of deep waters, reflecting either
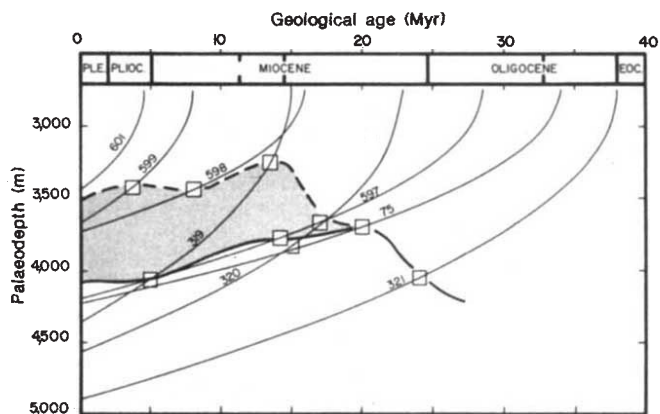
stagnation or enhanced input of organic carbon, and (2) reduced input of biogenic $CaCO_3$ to the deep ocean. The ultimate causes of changes in these parameters have been related to: the rate of formation of oceanic bottom water; the nature of shelf/basin depositional fractionation which depends largely on sea level; and sea-surface biological productivity of calcium carbonate and organic carbon. Oxygen isotope data suggest that the middle Cenozoic is characterized by constant or perhaps even declining ice volume[24,25], hence only minor changes in the production rate of bottom water may have occurred then. Sea level rose gradually from the mid-Oligocene to the mid-Miocene[26], consistent with a shoaling CCD, but as the sudden, large mid-Oligocene sea-level fall does not affect the CCD, it seems inappropriate to invoke the ensuing gradual rise of sea level. We therefore agree with the view[15,22,23] that, during times of constant ice volume, sea-surface biological productivity exerts the dominant control of the CCD. The problem remains complex, however, because factors such as total carbonate supply to the sea floor[15], the amount of non-calcareous, siliceous productivity[27], and how or why productivity changes during times of relatively uniform oceanic and atmospheric circulation, are not well understood on a global scale.

Van Andel et al.[15] have suggested that the lysocline may be related to the volume of corrosive deep water. If this is the case, our data suggest an increase in this volume which, within the accuracy of our data, occurred during the same time span as the inferred ice build-up on Antarctica, 16.0–12.4 Myr (oxygen-isotope stratigraphy from ref. 28; foraminifer zonation and timescale from ref. 29). We note, however, that the present lysocline does not correspond to any water mass boundaries in the Pacific. More recently, Broecker and Peng[30] have suggested that the thickness of the zone of rapid $CaCO_3$ dissolution between the lysocline and the CCD varies directly with the downward flux of calcite. If so, the early Miocene separation of the lysocline and CCD may be related to increased surface-water productivity. There exists ancillary evidence supporting increased equatorial productivity of both calcareous[15] and siliceous[27] organisms then.

1. Murray, J. & Renard, A. F. *Challenger Expedition Reports*, London (1891).
2. Peterson, M. N. A. *Science* **154**, 1542–1544 (1966).
3. Berger, W. H. *Science* **156**, 383–385 (1967).
4. Berger, W. H. *Mar. Geol.* **8**, 111–138 (1970).
5. Berger, W. H. *Deep Sea Res.* **15**, 31–43 (1968).
6. Bramlette, M. N. *Am. Ass. Adv. Sci. Pub.* **67**, 345–366 (1961).

7. Heath, G. R. & Culberson, C. *Bull. geol. Soc. Am.* **81**, 3157-3160 (1970).
8. Broecker, W. S. & Broecker, S. *Soc. Econ. Paleont. Miner., Spec. Publ.* **20**, 44-57 (1974).
9. Berger, W. H., Adelseck, C. G. Jr & Mayer, L. A. *J. geophys. Res.* **81**, 2617-2727 (1976).
10. Heath, G. R. *Bull. geol. Soc. Am.* **80**, 689-694 (1969).
11. Berger, W. H. *Bull. geol. Soc. Am.* **84**, 1941-1954 (1973).
12. Sclater, J. G., Anderson, R. N. & Bell, M. L. *J. geophys. Res.* **76**, 7888-7915 (1971).
13. van Andel, Tj. H. & Bukry, D. *Bull. geol. Soc. Am.* **84**, 2361-2370 (1973).
14. van Andel, Tj. H. & Moore, T. C. Jr *Geology* **2**, 87-92 (1974).
15. van Andel, Tj. H., Heath, G. R. & Moore, T. C. Jr *Mem. geol. Soc. Am.* **143** (1975).
16. Tracey, J. I. *et al. Init. Rep. DSDP* **8** (1971).
17. Yeats, R. S. *et al. Init. Rep. DSDP* **34** (1976).
18. Leinen, M. *et al. Init. Rep. DSDP* **92** (in the press).
19. Rea, D. K. & Leinen, M. *Init. Rep. DSDP* **92** (in the press).
20. Bukry, D. *Init. Rep. DSDP* **34**, 715-735 (1976).
21. van Andel, Tj. H., Thiede, J., Sclater, J. G. & Hay, W. W. *J. Geol.* **85**, 651-698 (1977).
22. Heath, G. R., Moore, T. C. Jr & van Andel, Tj. H. in *The Fate of Fossil Fuel CO₂ in the Oceans* (eds Andersen, N. R. & Malahoff, A.) 627-639 (Plenum, New York, 1977).
23. Hsu, K. J., McKenzie, J. A., Oberhansli, H. & Wright, R. C. *Init. Rep. DSDP* **73**, 771-785 (1984).
24. Savin, S. M. *A. Rev. Earth planet Sci.* **5**, 319-355 (1977).
25. Kennett, J. P. *J. geophys. Res.* **82**, 3843-3860 (1977).
26. Vail, P. R., Mitchum, R. M. Jr & Thompson, S. III *Mem. Am. Ass. petrol. Geol.* **26**, 83-97 (1977).
27. Leinen, M. *Bull. geol. Soc. Am. Part II* **90**, 1310-1376 (1979).
28. Woodruff, F., Savin, S. M. & Douglas, R. G. *Science* **212**, 665-668 (1981).
29. Kennett, J. P. & Srinivasan, M. S. *Neogene Planktonic Foraminifera, A Phylogenetic Atlas* (Hutchinson Ross, Stroudsburg, 1983).
30. Broecker, W. S. & Peng, T.-H. *Tracers in the Sea* (Lamont-Doherty Geological Observatory, Palisades, 1982).
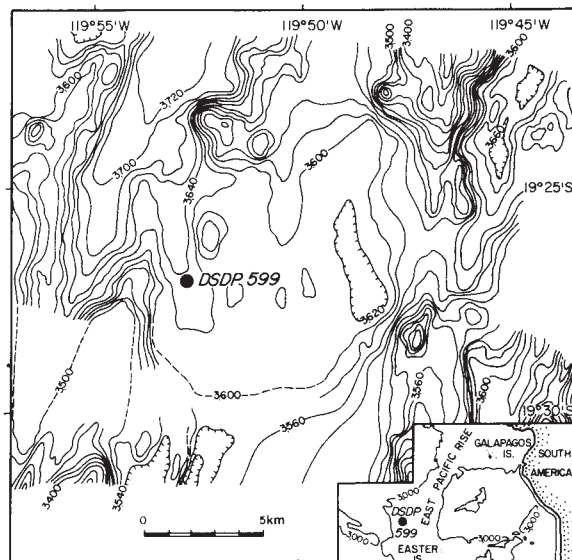
Downslope transport of metalliferous sediments along the East Pacific Rise during the late Miocene

Stephen Knüttel*, David K. Rea†
& Sherwood W. Wise Jr*

* Department of Geology, Florida State University, Tallahassee, Florida 32306, USA
† Department of Atmospheric and Oceanic Science, University of Michigan, Ann Arbor, Michigan 48109, USA

The distribution of metalliferous sediments next to active spreading centres has scientific and economic interest[1]. Although metal-rich waters emanating from active hydrothermal vents have been traced in intermediate level water masses far beyond the ridge crest[2], the greatest concentrations of metal oxides in sediments occur near the vents[3]. There, however, it is conceivable that the oxides may be redistributed and possibly further concentrated by redeposition, resulting in misconceptions of the age and relative timing of hydrothermal pulses. Here, we document microfossil evidence of stratigraphical inversion and redeposition of Upper Miocene (Messinian) sediments cored at Deep Sea Drilling Project (DSDP) Site 599 on the East Pacific Rise (EPR). This suggests that where reworking can be confirmed, care should be taken not to correlate directly the occurrences of the metalliferous sediments with apparent coeval pulses of hydrothermal activity or enhanced sea-floor spreading rates.

Hole 599 (19°27.09' S, 119°52.88' W; water depth = 3,654 m), located ~600 km west of the present ridge crest, was drilled in a small basin surrounded by a region of low relief with abyssal hills ranging from 200 to 300 m in height (Fig. 1). This site yielded some 41 m of mostly Upper Miocene clay-bearing to clayey calcareous oozes with a basement age of 8.1-8.6 Myr (ref. 5). The lower 31 m of the section is strikingly layered, consisting of alternating light (mostly yellowish brown to dark yellowish brown) and dark (mostly dark reddish brown) coloured layers tens of centimetres thick (Figs 2, 3). The colour variations are the result of changes in the relative amounts of calcium carbonate (70-80% in light coloured sediments, 55-70% in dark coloured sediments[5]) and a noncarbonate fraction which is primarily clays and ferruginous grains. The clays are mixtures of poorly crystalline smectites and amorphous oxides. The ferruginous grains, which range in size from 10 to 100 μm, are a metalliferous hydrothermal component which has been described by Leg 34 scientists as red-brown to yellow-brown, semi-opaque oxides (RSOs)[6].

The strongly layered portion of the section is dated between

Fig. 1 Bathymetry (from seabeam swath-mapping[4]) and location of Deep Sea Drilling Site 599 on the west flank of the East Pacific Rise. This site, along with the other DSDP Leg 92 sites, was the first on the East Pacific Rise to be drilled using the hydraulic piston corer, which minimizes sediment disturbance during the coring process.
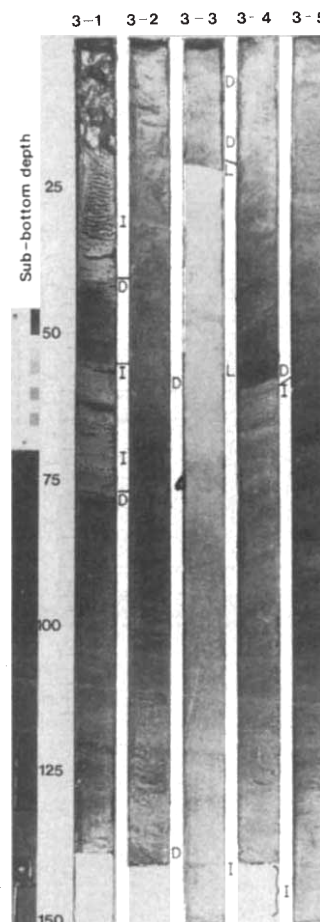
Fig. 2 Sections 1-5 of DSDP Core 599-3 showing alternations of light (L), dark (D), and intermediate (I) coloured lithologies within the Messinian clayey nannofossil ooze sequence (see key in Fig. 3 for detailed colour descriptions). The darker lithologies contain less carbonate and more hydrothermal metalliferous components than do the lighter lithologies. Note the sharp contact (dark over light) at 21 cm in section 599-3-3.