chloride as the only anion. The solution compositions, and the cationic composition of sea water from reported data (*3*), as well as the electrode-potential measurements, appear in Table 1. The electrode measurements were repeated several times; reproducibility was within 0.3 mv.

We have attempted to make the calibrating solutions so like the sea water that we can assume that calcium ion has the same activity coefficient in the several solutions. Then, using an empirical electrode equation written in terms of concentrations rather than activities, we determine from the data in Table 1 the ionized calcium in this sea water to be $0.0086 \pm 0.0002M$.

The total calcium in sea water of this chlorinity being $0.0102M$, we compute that about 84 percent of the calcium in sea water is ionized and that about 16 percent is presumably complexed with sulfate, carbonate, and bicarbonate. This result is in fair agreement with Garrels and Thompson's (*2*) value of 91 percent ionized calcium. Their chemical model for sea water made use of individual-ion activity coefficients and thermodynamic dissociation constants for a number of quantitatively important ion pairs or complex ions. They used an activity coefficient for calcium ion of 0.28, calculated from mean salt activity-coefficient data for KCl and $CaCl_2$ by use of data from Latimer (*4*) and Harned and Owen (*5*).

For purposes of comparison with the results of Garrels and Thompson, we may compute the activity of calcium ion in this sea water, using their activity coefficient and our measurement of the percentage of ionized calcium. Because calcium is $0.0106M$ in sea water of 19.373-ppt chlorinity, the activity of calcium is

$$(0.0106)(0.84)(0.28) = 0.00249$$

a value slightly lower than Garrels and Thompson's calculation—0.00264 for sea water of 19.00-ppt chlorinity.

Another activity coefficient for calcium ion in sea water has been reported by Berner (*6*), who measured the *p*H of sea water in equilibrium with calcite or aragonite at known pressures of carbon dioxide. His experiments yielded a *total*-activity coefficient, relating the activity of calcium ion to the total concentration of calcium in the sea water. For standard artificial sea water of 19.00-ppt chlorinity Berner determined the total-activity coefficient for calcium at 0.203 ± 0.010.

Because the products of total concentration and total-activity coefficient and of ionic-activity coefficient and ionic concentration equal the same activity, our measurement of concentration of ionized calcium may be combined with Berner's total-activity coefficient and with the known total concentration to evaluate the ionic-activity coefficient of calcium in sea water. The small difference in chlorinities is neglected, and the ionic-activity coefficient is found to be 0.24 ± 0.02—somewhat lower than the value used by Garrels and Thompson, but within the range of results from mean-salt data, depending on whose mean salt activity-coefficient data are used (*7*). With this smaller activity coefficient, the activity of calcium in this sea water is

$$(0.0106)(0.84)(0.24) = 0.00214 \pm 0.00023$$

We conclude, as did Berner, that these results, together with the recently reported (*8*) electrode measurement of magnesium in sea water, affirm the essential validity of the sea-water model of Garrels and Thompson. Their assumptions that individual-ion activity coefficients are, to a first approximation, dependent only on ionic strength, and that major deviations may be attributed to ion-pair or complex-ion formation, are useful as long as too much accuracy is not expected. As more ion-specific electrodes become available one should be able to establish the distribution of the chemical species in sea water with somewhat greater precision.

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References and Notes

1. By Orion Research, Inc., Cambridge, Mass.; a complete description of the electrode and its properties is in preparation.
2. R. M. Garrels and M. E. Thompson, *Amer. J. Sci.* **260**, 57 (1962).
3. H. U. Sverdrup, M. W. Johnson, R. H. Fleming, *The Oceans* (Prentice-Hall, New York, 1942), p. 173.
4. W. M. Latimer, *Oxidation Potentials* (Prentice-Hall, New York, 1952), p 354.
5. H. S. Harned and B. B. Owen, *Physical Chemistry of Electrolyte Solutions* (Reinhold, New York, 1958), p. 498.
6. R. A. Berner, *Geochim. Cosmochim. Acta* **29**, 947 (1965).
7. Using other data compiled by Harned and Owen (*5*, pp. 731, 735) and the method of computation used by Garrels and Thompson, and obtaining by graphical extrapolation the mean-salt data at an ionic strength of 0.7, we find

   $$\gamma_{Ca^{++}} = (\gamma \pm CaCl_2)^3 / (\gamma \pm KCl)^2 = (0.460)^3 / (0.626)^2 = 0.248$$

   Moreover, activity coefficients obtained in this way for calcium change very little, if at all, in this region of ionic strength.
8. M. E. Thompson, *Science* **153**, 866 (1966).
9. Aided by NIH grant WP-0065-03.

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Lower Cretaceous Rocks (Neocomian-Albian) Dredged from Blake Escarpment

Abstract. *Algal calcarenites, Neocomian to Aptian in age, dredged from 3000- to 5000-meter depth on Blake Escarpment, are the oldest rocks yet obtained from deep-sea outcrops. Five thousand meters of post-Aptian subsidence of the Blake Plateau is thus established. Aptian-Albian calcilutites obtained from depths of less than 3000 meters mark the establishment of an offshore environment.*

The semiconsolidated Upper Cretaceous and Tertiary coastal-plain sediments that underlie Blake Plateau have been cored where they outcrop on the upper part of Blake Escarpment (*1*, *2*, *3*). Below 2500 m the escarpment is precipitous, and the high seismic velocity (5.1 km/sec) of the material implies a well-consolidated rock that could not be sampled by normal techniques for deep-sea coring (*4*).

Dredging was first attempted from Blake Escarpment in March 1966 (*5*). Of ten dredge lowerings near 29°N in depths of 2300 to 4800 m, three hauls (No. 3, 4, and 7) were productive (Fig. 1). From three more lowerings in the area of Blake Nose (Fig. 1), a fourth successful haul (No. 12) was taken in 4800-m depth from near the base of the steep north face of this feature.

All rocks recovered are carbonates resembling the formations of the coastal-plain sequence of Florida and the Gulf Coast. That each dredge haul recovered in-place rocks is suggested by the relatively large size of the fresh angular fragments; by the broken surfaces (Fig. 2); by the uniform lithology of the contents of any one haul; and by the strong pulls on the cable, measured by the accumulator (5500 to 6000 kg) (*6*). Bottom-photographs of

Table 1. Details of four samples dredged from Blake Escarpment. Bracketed velocities were determined from the same sample; comp, comparable with.

Haul (No.)	Source	Wire out on release (*6*) (m)	Lithology	Velocity (*7*) (km/sec)	Fauna, flora	Age
E-9-66-7	28°57.5′N 76°45′W	2375	Gray and tan very-fine-grained calcilutite; hard where more recrystallized and soft and chalky where not, and with some pyrite flakes and pyrite filling the foraminiferal chambers	{3.34 3.44} 5.03	*Thalmanninella* sp.* comp *T. multiloculata*, *?Globigerina* sp. comp *G. Washitensis*, *Conicospirillina* sp., *Cadosina* sp., ophthalmidiids, few ostracods, *Nannoconus* sp.† comp *N. truitti*, *Nannoconus* sp. comp *N. minutus*, *Nannoconus* sp. comp *N. elongatus*	Aptian-Albian (after Percival)
4	28°59′N 76°43.5′W	3130	Gray, thin-bedded calcarenite, with a disrupted framework of medium-grained ooliths and fossil debris in a fine-grained calcilutite matrix	4.68 5.38	*Textularia* sp., miliolids	Aptian?
3	28°59.5′N 76°45′W	3200	Massive, vuggy, fine-to-very-coarse-grained dolomitic algal calcarenite, with some algal fragments reaching pebble size and with euhedral dolomite rhombs distributed throughout	{3.04 3.02 3.70}	*Textularia* sp.,* *Trocholina* sp., *?Conispirillina* sp., few miliolids, *Cayeuxia* sp. comp *C. kurdistanensis*	Neocomian-Aptian*
12	30°15′N 76°21′W	4800	Massive, fine-to-very-coarse-grained algal calcarenite, with some algal fragments reaching pebble size	4.50 5.24 5.68	*Trocholina* sp.* comp *T. infragranulata*, *Textularia* sp., *?Quadrimorphina* sp., few miliolids, *Cayeuxia* sp. comp *C. kurdistanensis*, few *Thaumatoporella parvovesiculifera*, *Salpingoporella* sp., few *Bouenia* sp., gastropods, few echinoid spines	Neocomian-Aptian*

* Fauna and age after N. K. Brown, Jr., Esso Production Research Co. † Nannoconids identified and aged by S. F. Percival, Jr., Mobil Oil Corp.

the escarpment reveal that the limestones outcrop both as ledges of bedded strata and as massive rocks. The steepness of the slope is apparent in the compass-oriented photographs, which show the bottom dropping off sharply to the east (Fig. 2).

The shallowest dredge haul (No. 7) contained soft, chalky calcilutite and hard, recrystallized, thin-bedded calcilutite from the very top of the prominent bench at 2500 m (Fig. 3). The apparently interbedded nature of this part of the section suggests a gradational contact, from soft calcilutite above to the hard limestones of higher velocities that form the 5.1-km/sec seismic layer below. Haul 4, from below the 2500-m bench at 3130 m, recovered hard, thin-bedded oolitic calcarenites having velocities of 4.68 and 5.38 km/sec (*7*).

On the basis of the microfossil assemblage, the age of the rocks from haul 7 is considered Aptian to Albian; planktonic Foraminifera dominate the very-fine-grained calcilutite, suggesting a more-offshore facies than the calcarenites found below 3100 m on the escarpment. The pyrite in the calcilutites also implies an environment of quiet waters contrasting with the agitated environments in which the calcarenites must have been deposited. Thus, in the area of the escarpment, a transgression to a more-offshore facies apparently occurred before the Aptian-Albian. The horizon forming the bench at 2500 m falls within the upper part of the Lower Cretaceous (Fig. 3).

The calcarenite facies recovered in hauls 3 (Neocomian-Aptian) and 4 (Aptian?) (*8*), including the oolitic grains, algal fragments, miliolids, and arenaceous Foraminifera, originated in shallow water and is similar to the normal

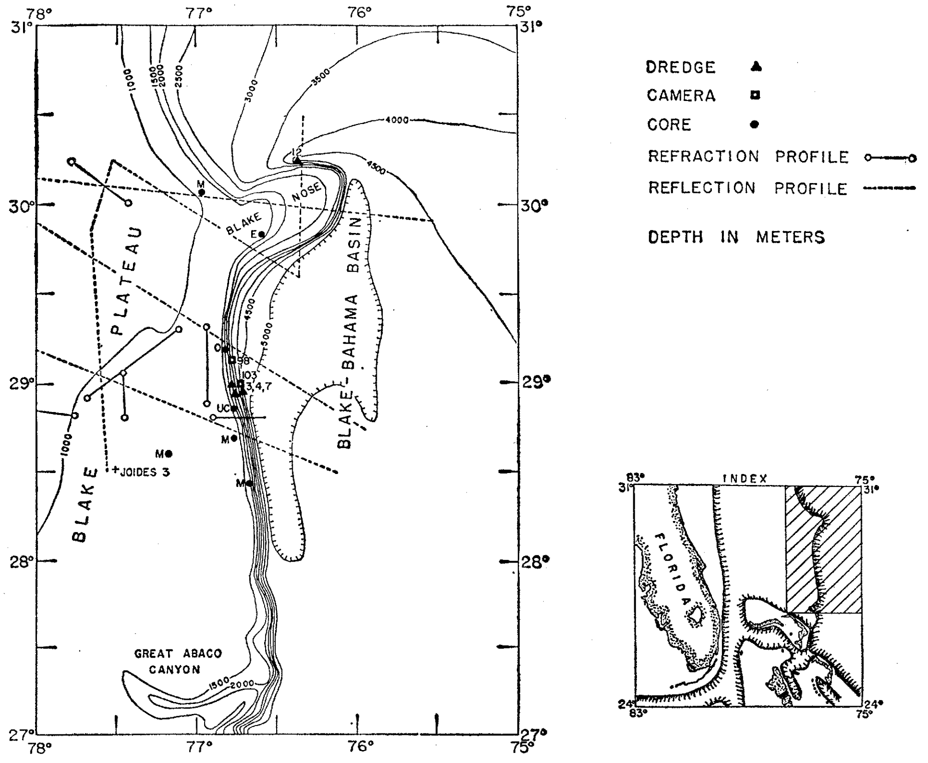

Fig. 1. Sites of dredge and camera lowerings from R.V. *Eastward*. Seismic-reflection and refraction lines (*3, 4*), a JOIDES core hole that penetrated to Lower Eocene (*2*), and several cores taken from the upper part of the escarpment (*2*) are located. Ages of the unconsolidated Tertiary and Upper Cretaceous sediments cored are indicated by initial letters (*M*, Miocene; *O*, Oligocene; *E*, Eocene; *UC*, Upper Cretaceous).

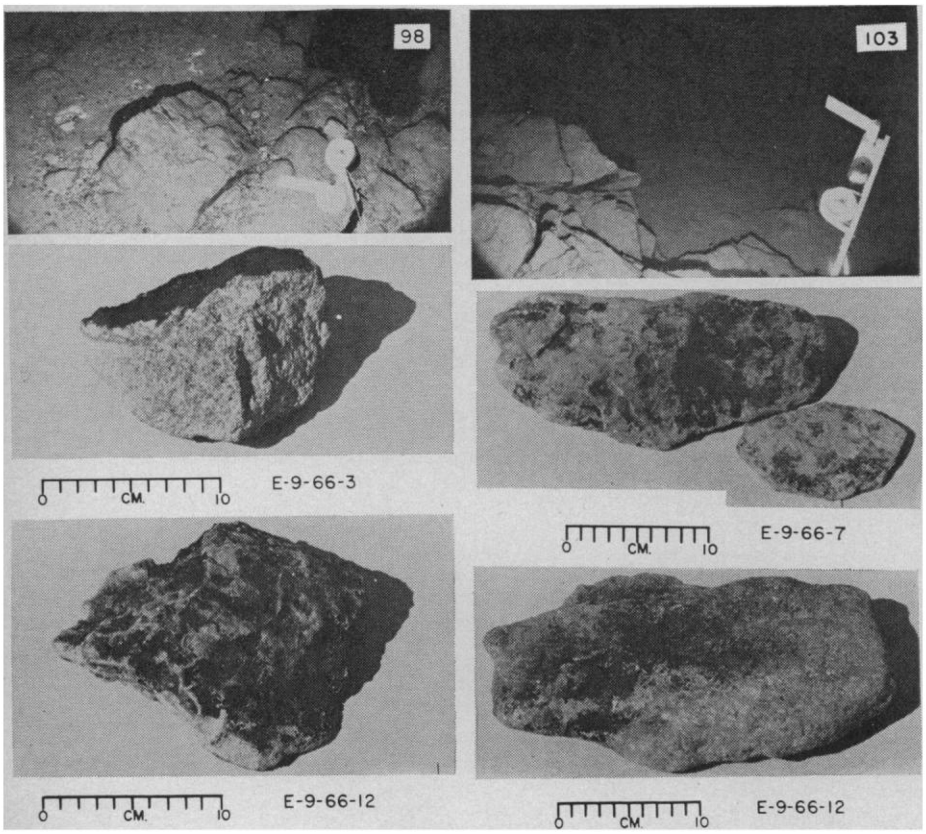

Fig. 2 (top left.) The sea floor and dredged rocks. Photograph *98*, from station E-9-66-98 (29°09′N,76°45′W), shows massive boulders outcropping and the escarpment dropping off to the east. Photograph *103*, from station E-9-66-103 (28°50.3′N, 76°42.2′W), shows ledges of platy rocks and the escarpment dropping off to the east. The compass in the photographs is 10 cm in diameter. The freshly broken surface (*E-9-66-3*, Fig. 3) contrasts markedly with the older manganese-coated surface. The platy, angular rocks from haul *E-9-66-7* are comparable with the platy rocks in photograph *103*.

facies of the early Trinity (Aptian) and the Fort Pierce (Late Jurassic?-Neocomian) formations of southern Florida (*9*).

Haul 12, from the base of Blake Nose in 4800 m, included calcarenites in which Foraminifera and algal fragments abound and the matrix is thoroughly recrystallized. Velocities measured in samples from haul 12 were 4.5 to 5.7 km/sec, resembling those measured at these depths in nearby refraction profiles. The fauna in haul 12 imply Neocomian to Aptian age for these rocks. The similarity of the calcarenites in hauls 3, 4, and 12 from depths of 3100 m and greater suggests the outcropping of a continuous horizon of calcarenitic limestone along the lower part of the escarpment.

The similarity of the lithologies and fauna of the dredged rocks to the Lower Cretaceous of southern Florida suggests that the same shallow-water environment extended as far east and north as Blake Nose. The abundance of algal fragments in the calcarenites requires a nearby source. During the Lower Cretaceous, algal and perhaps coral banks apparently formed a barrier-reef structure extending north of the Bahamas (*10*).

The rocks from the base of the escarpment (5000-m depth) represent sediments laid near sea level, whereas the rocks from 2000- to 3000-m depth represent sediments laid down at depths approaching those at which Blake Plateau now lies. Thus 5 km of slow, uniform subsidence over a wide area of the continental margin is well substantiated, both by the wells in the Bahamas and Florida and by the dredging from Blake Escarpment. This area is a continuation of the continental-rise trough found along the continental margin to the north (*11*).

In addition to these dredged rocks of subsided shallow-water facies, many cores of pre-Pleistocene deep-sea sediment have been obtained from all the oceans (*12*). The oldest so far reported from the Pacific are Albian; from the Atlantic, Upper Cretaceous. The Neocomian-Aptian algal limestones recov-

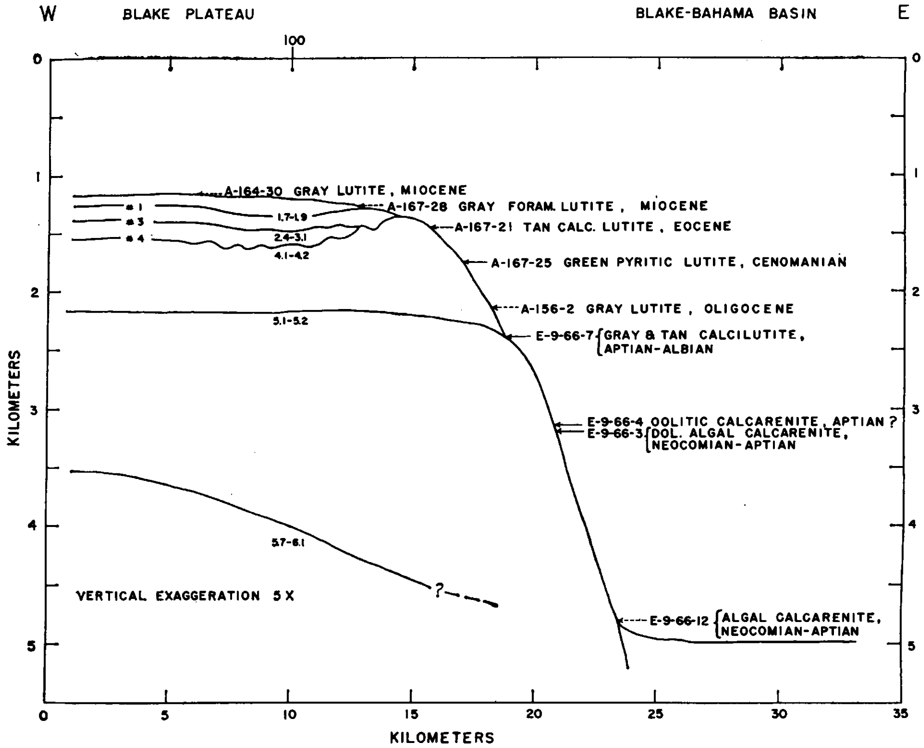

Fig. 3 (bottom left). Outcrops on Blake Escarpment at 29°N. Prominent reflecting horizons are labeled #1, #3, and #4 (*3*); deeper layers are indicated by the velocity range observed (kilometers per second) (*4*). Dashed arrows indicate data-extrapolated significant distances. Unconsolidated sediments (*A*) sampled by coring (*2*); rocks below 2300 m sampled by dredging (*E*).

ered from Blake Escarpment are the oldest in-place rocks yet dredged from the floor of the deep Atlantic; they may even be older than the shallow reefal deposits of Lower Cretaceous age dredged from the Pacific guyots (*13*).

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References and Notes

1. B. C. Heezen, M. Tharp, M. Ewing, *The Floors of the Oceans* (Geol. Soc. Amer., New York, 1959); R. M. Pratt and B. C. Heezen, *Deep-Sea Res.* **11**, 721 (1964).
2. D. B. Ericson, M. Ewing, B. C. Heezen, *Amer. Assoc. Petrol. Geologists Bull.* **36**, 489 (1952); D. B. Ericson, M. Ewing, G. Wollin, B. C. Heezen, *Geol. Soc. Amer. Bull.* **72**, 193 (1961); A. R. Loeblich, Jr., and H. Tappan, *Micropaleontology* **7**, 257 (1961). The discovery in 1949 and subsequent exploration of the unconsolidated Tertiary and Upper Cretaceous sediments are reported. JOIDES drill hole No. 3 bottomed in Eocene 178 m below the sea floor, 90 km west of our hauls 3, 4, and 7; *Science* **150**, 709 (1965).
3. J. Ewing, M. Ewing, R. Leyden, *Amer. Assoc. Petrol. Geologists Bull.* **50**, 1948 (1966).
4. R. E. Sheridan, C. L. Drake, J. E. Nafe, J. Hennion, *ibid.*, p. 1972.
5. During a training cruise by Duke University's R.V. *Eastward*.
6. Each time the dredge bucket soon became snagged; in 12 instances, pulling at strains of 5500 to 6000 kg for from 10 minutes to 2 hours broke it free. Tension and "wire-out" were logged continuously. Wire angles on release were less than 5 degrees; wire-out (Table 1) closely approximated the true depth.
7. Unrefined velocity measurements, reliable to within 5 percent, were carried out on dry samples at room temperature and 1 atm pressure by a method similar to that of G. H. Sutton, H. Berckhemer, J. E. Nafe, *Geophysics* **22**, 779 (1957). The measured velocities compare favorably with those determined in nearby refraction profiles (*4*). A mixture of the 3.34-km/sec soft limestone and the dense 5.03-km/sec limestone of haul 7 might be observed seismically as a layer of intermediate velocity, similar to the 4.1-km/sec layer observed in refraction profiles.
8. Haul 4, taken in only slightly shallower water than haul 3, contained a fauna characterized by abundant miliolids and textularids, tentatively dated as Aptian, that is distinctly different from the Neocomian to Aptian fauna of haul 3.
9. P. L. Applin and E. R. Applin, *U.S. Geol. Surv. Profess. Paper* **447** (1965), 86 pp. The coarse bioclastic calcarenites, with algal fragments, found on Blake Escarpment resemble oil-reservoir rocks of southern Florida. The arch structures in the three deepest seismic horizons, along the eastern edge of Blake Plateau, may provide traps for any oil present.
10. N. D. Newell, *Nat. Hist.* **1959**(March), 119; **1959**(April), 227 (1959).
11. C. L. Drake, M. Ewing, G. H. Sutton, *Physics and Chemistry of the Earth* (Pergamon, London, 1959), vol. 3, pp. 110–98.
12. M. Ewing, T. Saito, J. I. Ewing, L. H. Burckle, *Science* **152**, 751 (1966); J. I. Ewing, J. L. Worzel, M. Ewing, *Trans. Amer. Geophys. Union* **47**, 122 (1966).
13. E. L. Hamilton, *Geol. Soc. Amer. Mem.* **64**, 97 (1956).
14. We thank Duke University Marine Laboratory for the use of R.V. *Eastward* on cruise E-9-66 in the Cooperative Oceanographic Program. This program, directed by R. J. Menzies, is supported through NSF grant G17669 to Duke University. The work at sea was greatly aided by Capt. R. Craig and Party Chief J. Cason. C. Bertelsen, J. Conally, D. Folger, P. J. Fox, H. Haring, T. Holcombe, M. Schneck, A. Lowrie, Jr., D. Needham, W. Ruddiman, and E. D. Schneider assisted at sea. N. K. Brown, Jr. (Esso Production Research Co.), S. F. Percival, Jr., L. Jones, K. Keller, L. R. Tucker (all of Mobil Oil Corp.), and T. Saito (Lamont Geological Observatory) assisted in stratigraphic paleontology. W. Ruddiman assisted in many ways both at sea and in the laboratory. A. McGarr assisted in measuring the compressional wave velocities. Report aided by grants from ONR (Nonr 266-48) and NSF (GA 580). Lamont Geological Observatory contribution 1009.

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Garnet Zoning: An Interpretation Based on the Rayleigh Fractionation Model

Abstract. *Manganese zoning in almandine garnet is interpreted by the use of calculations based on the Rayleigh fractionation model. A close similarity of a measured manganese zoning profile and a calculated profile indicates that the assumptions used in the calculations are good. These assumptions are: complete removal of garnet from a homogeneous reservoir as the garnet crystallizes, and a nearly constant manganese fractionation factor between garnet and reservoir.*

Compositional zoning in almandine garnet, as measured with the electron microprobe, appears to be the rule rather than the exception; and it is most clearly characterized by decreasing Mn outward from the garnet center (*1*). This report offers a semiquantitative interpretation of zoning in garnets.

In a study of mineral growth histories and metamorphic reactions in the Kwoiek area of British Columbia 80 miles (130 km) northeast of Vancouver (*2*), it was recognized that zoned almandine garnets are ubiquitous; Mn, Fe, and Mg zoning patterns of most of the garnets are similar to those shown in Figs. 1a and 1c. The Mn pattern of Fig. 1b is an exception, discussed below. The bell-like shape of the Mn profiles suggests that the cause of the zoning might be progressive depletion of Mn from the rock surrounding an individual garnet as the garnet grows. Because the garnet is zoned, successive layers are not in mutual chemical equilibrium, and they cannot be in equilibrium with the rock external to the garnets. In fact, only the infinitesimally thin outer layer of the garnet can possibly be in equilibrium with the rest of the rock at any stage of garnet growth. The model proposed below is consistent with a concept of garnet growing from a reservoir of minerals which internally reequilibrate with changing conditions and which are therefore individually homogeneous.

Rayleigh (*3*) derived a mathematical expression for the composition of a liquid as it condensed and was continuously removed from a multicomponent vapor. This system is analogous to a garnet growing from a homogeneous reservoir and zoning as it grows. Neumann *et al.* (*4*) and McIntire (*5*) used a similar approach in considering the theoretical distribution of trace elements in crystals crystallizing from a magma as well as the concentration of trace elements in the magma during crystallization. Based on the basic method of Rayleigh (*3*), the following is a derivation of the formula used for the present work, which gives the weight percent of an element at the garnet edge as a function of the weight of garnet crystallized from the rock. The terms used are:

M_G = weight fraction of element in garnet edge;

$W_M{}^R$ = weight of element in rock external to crystallized garnet;

W_R = weight of rock external to garnet;

M_R = weight fraction of element in rock excluding that in garnet;

λ = fractionation factor, M_G/M_R;

W^0 = initial weight of rock, prior to garnet crystallization;

$W_M{}^0$ = initial weight of element in rock, prior to garnet crystallization;

M_0 = initial weight fraction of element in rock, prior to garnet crystallization;

W^G = total weight of crystallized garnet.

$$M_G = \frac{-dW_M{}^R}{-dW_R} \qquad (1)$$

Equation 1 is a statement of the assumption of removal of garnet from the rock as the garnet crystallizes.

$$M_G = \lambda\, M_R = \lambda \frac{W_M{}^R}{W_R} \qquad (2)$$

Equation 2 states that the weight fraction of Mn in garnet is proportional to that in the rest of the rock; λ may be an equilibrium fractionation factor