chalcopyrite will be presented elsewhere (*8*).] At a pressure of 16 kb the pyrrhotite spectrum, shown in Fig. 2B, is a single peak (or broadened quadrupole doublet) with an isomer shift of 0.36 mm/sec. A trace of the outermost magnetic peaks remain, in the same positions as at 1 atm. If the applied pressure is reduced to only 5 kb as in Fig. 2C, a partial reversal to the ordered state takes place; if the pelletized material is chopped up to remove any locked-in strain, a complete reversal to the magnetic spectrum occurs (Fig. 2D).

The changes observed in the Mössbauer spectra of chalcopyrite and pyrrhotite as a function of pressure can be interpreted as evidence of a transition from the antiferromagnetic state to the paramagnetic state for chalcopyrite and a transition from the ferrimagnetic state to the paramagnetic state for pyrrhotite. These transitions are apparently totally reversible and take place over a range of pressures from 5 to $16+$ kb. The proportion of the magnetically ordered material decreases with increasing pressure over this range, whereas the chemical nature of the ordered and disordered phases, as shown by their Mössbauer parameters, remains the same.

In both chalcopyrite and pyrrhotite, the magnetic transition could be accompanied by a change in crystal structure. A high-pressure polymorph of troilite has been reported by Taylor and Mao (*9*), but it does not exist below a pressure of 55 kb and a temperature of 25°C. The magnetic transition in troilite occurs below 36 kb (*1*) and therefore appears to be distinct from the structural change. It is probable that in pyrrhotite, which is closely related to troilite (*10*), the magnetic transition occurs before any structural change. However, there is a large change in isomer shift between the magnetic and nonmagnetic phases [from $\sim$ 0.80 mm/sec (average value) to 0.36 mm/sec] which could be produced by a transition from a high-spin to a low-spin state associated with the magnetic change. In chalcopyrite, the isomer shift is already very small (0.24 mm/sec) at atmospheric pressure and shows no appreciable change at higher pressures, but the quadrupole splitting changes at the magnetic transition (from 0.03 to 0.72 mm/sec). Here again, a structural or spin-state change is possible, probably the latter.

Goodenough (*11, 12*) has discussed the behavior of electrons in solids in terms of localized and collective electrons. At a critical value of the energy required to transfer an electron from one atom to another, the electrons are either localized and give rise to spontaneous magnetism (for example, antiferromagnetism or ferrimagnetism) or collective and exhibit Pauli paramagnetism (*12*). Such energies are strongly dependent on the interatomic distance. The transitions we observe in chalcopyrite and pyrrhotite may represent changes from localized to collective electron behavior resulting from a reduction in the distances between the metal and sulfur atoms. Conversely, the transition to paramagnetism at the Curie temperature results from increased interatomic separations and thermal displacements. In addition, our results for chalcopyrite and pyrrhotite suggest that similar changes in magnetic properties occur in other magnetically ordered sulfides at elevated pressures.

Troilite is an important phase in meteorites and in the lunar rocks. Moreover, several investigators have suggested that sulfur, as well as iron, may be a major component of the earth's core (*13*). It is probable, therefore, that iron sulfides exist at depth in planetary interiors. The metal-deficient pyrrhotite is one of the very few minerals which exhibit ferrimagnetism or ferromagnetism. As an accessory mineral in many rocks and as a major phase in many sulfide ore deposits, it contributes to geomagnetic anomalies and has been used in paleomagnetic investigations. This study shows that, at the pressures encountered in high-grade metamorphism or in subduction zones at continental margins, the magnetism of pyrrhotite would be partially or completely eliminated and that deep-seated pyrrhotite ore bodies may produce no surface magnetic anomalies. Alternatively, if the temperature approaches the Curie point, the effects of increasing temperature and pressure may prove to be competing and ordering may be retained. Furthermore, the physical and chemical properties of the iron sulfides are very different at pressures only slightly above those of planetary surfaces.

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Red Sea Drillings

Abstract. *Recent drilling in the Red Sea has shown that much of the basin is underlain by evaporites of a similar age to that of evaporites found in the Mediterranean Sea. These evaporites and their structural positions indicate that other brine areas are present—and, indeed, several others have been discovered.*

Leg 23B of the Deep Sea Drilling Project (DSDP) aboard the R.V. *Glomar Challenger* was devoted to scientific drilling in the central and southern Red Sea. The major shipboard findings include the following. (i) The Red Sea appears to be underlain by Late Miocene evaporites, including rock salt, at relatively shallow depths throughout most of its extent. The evaporites are absent only in the central rift valley. These data are not consistent with a model of continuous sea-floor spreading since Miocene time. (ii) The Miocene age of the evaporites in the Red Sea is similar to that of an evaporite sequence found by drilling in the Mediterranean Sea. (iii) The interstitial waters of the cores continuously increase in salinity with depth, with values approaching saturation with sodium chloride as the evaporites were neared. These data and the coincidence of brines with evaporate outcrops suggest that brine deeps can be found nearly anywhere in the Red Sea where structural dislocations expose evaporitic rocks at or near closed depressions in the sea floor. (iv) Shipboard spectrographic analyses (*1*) have made possible the discovery of two widespread suites of metalliferous shales, one enriched in vanadium and molybdenum and the other enriched chiefly in zinc [up to 5 percent (by weight)]. (v) In the Atlantis II Deep, a known site of hot brine and heavy metal deposition (*2*), basalts associated with the heavy metal–rich sediments were similar to deep ocean tholeiites and showed no significant mineralogical alteration or abnormal metal content.

The hot brine area consists of three depressions (Atlantis II, Chain, and Discovery deeps) overlain by waters of high salinity and temperature (*3*). The source of these waters is generally accepted to be in the Atlantis II Deep with occasional overflows filling the other deeps (*4*). The sediments underlying the deeps, and especially those of the Atlantis II Deep, are enriched in many heavy metals. The in situ value of the zinc, copper, lead, silver, and gold in the top 10 m (the maximum depth of previously taken samples) is about $2.4 billion based on 1968 smelter prices (*5*).

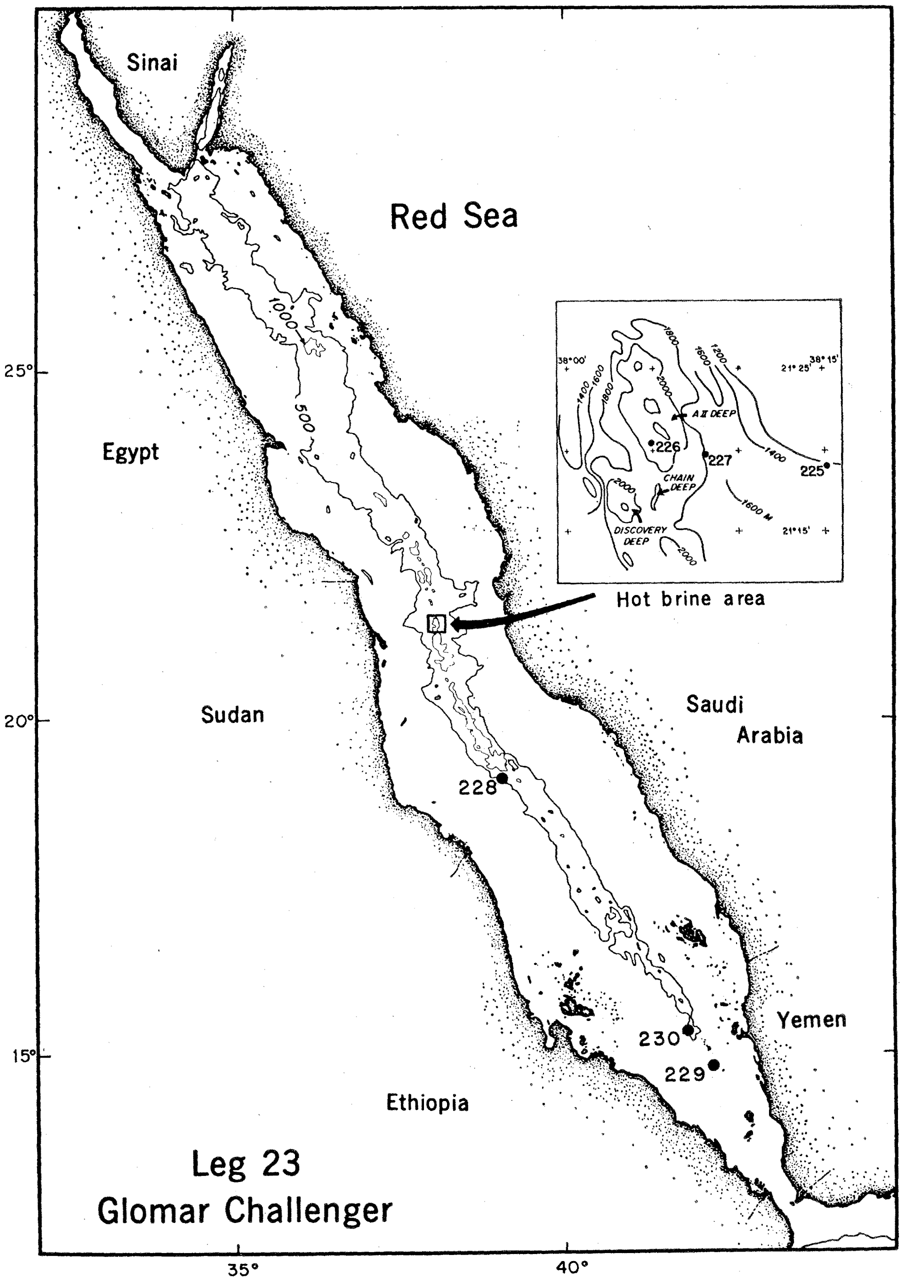

Fig. 1. Location of drilling sites in the Red Sea (*12*).

Site 225 is 10 miles (16 km) east of the Atlantis II Deep (Fig. 1). At this site we wanted to determine the nature of a subsurface acoustic reflector (reflector S) which had been mapped throughout much of the Red Sea (*6*). A total of 177 m of Late Miocene to Late Pleistocene clayey silt and ooze overlie 53 m of anhydrite and halite. Reflector S correlates with the top of the evaporite sequence. Its sonic velocity is 4.4 km/sec, whereas the overlying sediments have a velocity of 1.6 to 1.7 km/sec. Because the evaporites (dated by fossils found within interbedded shales) in the Red Sea are the same age as those found by deep-sea drilling in the Mediterranean Sea (*7*), reflector S in the Red Sea must be the same age as reflector M observed in the Mediterranean.

Dark shales recovered at this site often contain appreciable amounts of organic matter and more than 5 percent iron, partly combined as pyrite. Vanadium and molybdenum are present in amounts [1000 parts per million (ppm) of vanadium and 500 ppm of molybdenum] typical of classical black shale deposits, such as the Mansfelder Kupferschiefer (*8*). Minor enrichments of copper (200 ppm) are found in thin shale layers within the evaporite sequence.

The salinity of the interstitial waters increased as the evaporite sequence was approached, forming a typical diffusion gradient to values approaching a saturated sodium chloride solution (Fig. 2). Measurements of diffusive permeability showed that the anhydrite overlying the rock salt has a much lower diffusional permeability than shales and siltstones but still retains some ability to transmit salt ions by molecular diffusion.

Drilling at site 226 in the southwestern part of the Atlantis II Deep was essentially unsuccessful because of a shallow basalt sequence which could not be penetrated. Fourteen meters of heavy metal–rich sediments similar to those previously reported (*2*) were obtained, together with chips and fragments of basalt and anhydrite. Mineralogically, the basalts are similar to deep oceanic tholeiitic basalts. Neither glassy chilled borders nor more crystalline fragments, evidently from inner zones, showed indications of alteration from contact with the hot brine. The metal concentrations of the basalt are

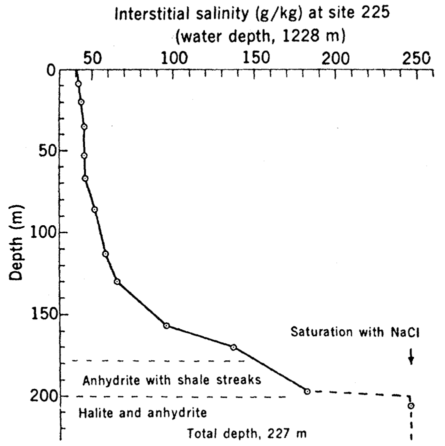

Fig. 2. Interstitial salinity of sediments from site 225. We determined the "salinity" by measuring the index of refraction on the extracted pore fluids, using the salinity-refractivity relationship valid for seawater. This relationship does not hold strictly for the brines in question. For example, the saturation concentrations of sodium chloride are closer to 260 g/kg, instead of less than 250 g/kg, as shown.

not significantly higher than those of ordinary basalts. It is, however, conceivable that heavy metal–rich sediments may occur below the basalts.

Site 227 is about 2 miles east of the edge of the Atlantis II Deep. A 359-m section of Quaternary to Late Miocene sediments was cored, including 133 m of Late Miocene and possible older anhydrite and halite. As at site 225, high concentrations of vanadium and molybdenum occurred in mud and shale layers, and an interstitial salt gradient was similar to that shown in Fig. 2. In addition, copper concentrations were as high as 700 ppm. These values suggest that these or similar sediments could be a source for some of the metals in the hot brine deposits. The coincidence in depth of the acoustic reflector (the top of the Miocene evaporite sequence) and that of the brine interface (Fig. 3) also may be significant. It may suggest that, wherever the Miocene evaporite sequence crops out in or near an enclosed basin, a brine occurrence is possible. If so, other brine areas should be present in the Red Sea, but, prior to this cruise, no verified ones had been reported. However, while in the brine area, we had a rendezvous with the German R.V. *Valdivia*, under contract to the Preussag Mining Company. The shipboard staff (*9*) indicated that, using sophisticated navigational systems and a narrow-beam echo sounder to detect acoustic reflections from the dense brine, they had located some brine areas. We crossed two of these areas, the Valdivia Deep (21°21′N, 37°56′E) and the Suakin Deep 19°22′N, 39°05′E), during our passage. We located another brine deep area (which conceivably could already have been found by the *Valdivia*) at 20°21′N, 38°56′E and suggest the name Glomar Challenger Deep for this depression.

An interesting aspect of the drilling at site 227 was the discovery of rocks as old or older than the Late Miocene (about 5 million years) within 1 or 2 miles of a supposedly active spreading center. One interpretation of the magnetic anomaly pattern from this area (*10*) indicates that rocks no older than about 2 million years should be present. This interpretation is based upon the assumption that a continuous Tertiary spreading history exists for the Red Sea. A more reasonable interpretation is that spreading resumed only recently (less than 2 million years ago) in the Red Sea following a period of quiescence that may have extended back into the Early Miocene.

Site 228, near the axial valley, provided sediment sequences similar to those described for sites 225 and 227. Evaporites (anhydrite) were encountered at a depth of about 280 m below the sea floor. The evaporites here, as in some other holes, showed relatively steep dips possibly due to folding or flowage. Seismic profiles showed diapiric structures in this area. Owing to drilling difficulties, the hole had to be abandoned before we reached rock salt, but estimates based on the extrapolation of the interstitial salinity gradient to expected saturation values of sodium chloride indicated that the hole terminated only a few tens of meters above the halite deposits. Tectonism at this site was indicated both by the absence of sediment of Lower Pliocene age and by extensive fracturing and brecciation in the lowermost rocks. Here, black shales contained high concentrations of zinc, ranging from 0.5 to 5 percent, as determined by the semiquantitative spectrographic analyses. Layers containing discrete sphalerite and pyrite crystals also were observed under the petrographic microscope. As at other sites, some of the shales contained abundant cristobalite, possibly the product of ash decomposition in waters having high ionic strength.

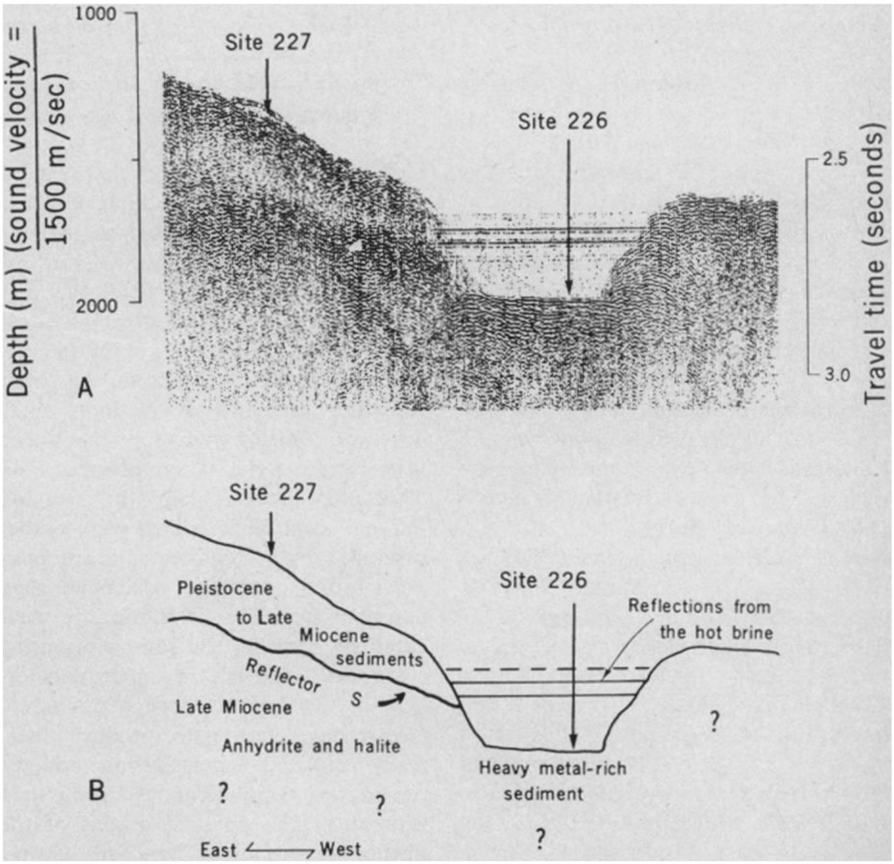

Fig. 3. Seismic profile record (A) and interpretation of general stratigraphy (B) near sites 227 and 226. The travel time is the two-way travel time.

Site 229 was in the southernmost extension of the Red Sea rift system. The Late Quaternary section contained carbonate ooze with volcanic glass fragments and occasional ringing-hard welded tuff beds. The site was abandoned at 212 m after we had encountered increasingly gassy cores.

Only one core was recovered from site 230, owing to the inability of the *Glomar Challenger* to maintain position in adverse weather conditions at this record shallow depth (850 m). However, a 50 percent increase in the interstitial salinity at this very shallow depth allows us to conclude that the acoustic reflector here was the top of the Late Miocene evaporites as in previous sites. Previous DSDP drillings (*11*) showed that interstitial salinity gradients of the type observed here are accurate predictors of halite and other evaporites at depth beneath sediments.

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Radiation Dosimetry by a New Solid-State Effect

Abstract. *Ionizing radiation can induce strong electrical polarization phenomena in dielectic solids. These radiation-induced thermally activated depolarization (RITAD) effects are quite different from radioelectret effects. For nominally pure calcium fluoride samples, the RITAD signals show a signal-to-noise power advantage of 40 decibels over that of thermoluminescence signals measured under the same experimental conditions. Ease of measurement, very high radiation sensitivity, and simple sample fabrication requirements give the RITAD phenomena a great potential for use as a new solid-state dosimetry technique.*

It has been reported (*1*) that a stable electrical polarization is induced when high-purity LiF is exposed to ionizing radiation in the presence of an externally applied electric field. We now report a much stronger effect observed in a variety of dielectrics; in the absence of any external field during either radiation exposure or readout, small doses of ionizing radiation produce a very intense polarization phenomenon. This effect occurs along the sample's internal local fields, which were earlier produced by a high-temperature bias-polarization procedure, which we shall describe later. The effect is easily measured by shorting the sample's sensing electrodes through a picoammeter, heating the sample through a characteristic temperature to produce thermally activated depolarization, and recording the depolarization current thus generated. The physical origins of the phenomena reported here are clearly different from those responsible for various radioelectret effects (*2*–*4*) such as occur in thermal electret-forming materials, for example, in Teflon or carnauba wax. We have been unable to detect any thermal electret-like activity in our unirradiated samples in the temperature ranges characterizing the activated depolarization subsequently induced by irradiation. Consequently, we call the effects we report here by the general description "radiation-induced thermally activated depolarization" (RITAD). External RITAD phenomena are generated in an externally applied electric field and differ from the more sensitive local RITAD phenomena generated in the sample's local fields.

Local RITAD shows very high radiation sensitivities. For example, although CaF$_2$ is used (*5*) as one of the most sensitive thermoluminescence (TL) dosimetry phosphors, we have observed RITAD signals in CaF$_2$ showing, to our astonishment, at least a 40-db advantage in the signal-to-noise power ratio over that of the TL signals mea-