Immediately overlying the epsilon cross-strata are the horizontally bedded, argillaceous sands and silts of the upper unit. The ichnofossil suite, although somewhat more abundant, is essentially similar to the one described for the middle McMurray but is characterized more by a bioturbated texture in which individual burrow forms are difficult to recognize. The intensity of the burrowing is such that primary sedimentary structures and bedding are commonly indistinct. Two notable exceptions to this pattern have been recognized near the top of the unit. The first consists of a distinct sand horizon (approximately 120 cm thick) grading from bioturbated argillaceous sands at the base to more well-sorted sand at the top characterized by parallel laminations, wave ripples, contorted bedding, and ball-and-pillow structures. The ichnofossil suite at the top of this unit (Fig. 3C) consists of ?*Dolopichnus*, *Bergaueria*, and vertical escape structures (a single specimen of a possible *Rosselia* has also been found). *Dolopichnus* and *Bergaueria* have been interpreted as the dwelling burrows of sea anemones (*7*), which are often associated with low-energy beach deposits. Second, at the top of the upper unit, near the contact with the overlying Clearwater Formation (Wabiskaw Member), there is a highly bioturbated unit containing profuse numbers of the wall-like, feeding burrow *Teichichnus* (Fig. 3D), which is generally considered to be a marine form. The retrusive nature of the associated spreiten generally is indicative of low sedimentation rates.

At present there is some controversy about the depositional interpretation of the epsilon-dominated McMurray Formation, with different investigators suggesting environments ranging from fluvial to estuarine to deltaic (*2–4*). Although Mossop and Flach (*5, 6*) have shown that sedimentation was dominated by deep channel and associated depositional processes, the physiographic setting of the channels remains enigmatic. Mossop and Flach envisage a basically fluvial channel system associated with, and in places prograding into, a mosaic of lakes and fresh to brackish bays with limited links to the sea. Although the indigenous palynofloral assemblage is dominantly continental, with local brackish water dinoflagellates (*8*), the overall trace fossil assemblage presents strong evidence that marine environments were also involved, particularly in the deposition of the upper McMurray sediments. The distribution of the trace fossils is consistent with a channel origin for the epsilon-dominated sequence, but shows that saltwater conditions must have been important at least locally, perhaps as salt wedges in the channels or as marine to brackish interchannel bays. In any event the trace fossil assemblage demonstrates that, at the time of deposition of the channel sequence, the marine shoreline must have been very close.

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Magnetostratigraphy of Sediments in Mammoth Cave, Kentucky

Abstract. *Clastic sediment deposits found within the caves of Mammoth Cave National Park have yielded a magnetostratigraphic pattern of magnetic polarity reversals which indicates that they were deposited over a range of at least 1 million and most likely 2 million years.*

Caves, being voids, are peculiarly difficult to date. As far as the cave passage itself is concerned, about the only technique that offers much hope for success is correlation with river terraces (*1*), although the ages of the terraces may not always be reliably determined. Dating the contents of the cave passages is more promising, but this provides only a lower bound.

Dating techniques which have been applied to cave sediments include faunal correlation (*2*), uranium disequilibrium series dating of calcitic deposits (*3, 4*), and magnetostratigraphy. Most cave sediments distant from an entrance are paleontologically sterile, while the uranium isotope methods yield satisfactory results back to no more than 350,000 years before present.

The chronology of polarity reversals of the earth's magnetic field during the past several million years has been worked out in considerable detail and precision during the past two decades (*5*). Although reversely magnetized clastic cave sediments were reported (*6*) as early as 1969, interest in the magnetic remanence record of these ubiquitous sediments has been fairly recent.

Previous studies (*7–11*) have been concerned with the correlation of minor changes in the direction and magnitude of the local magnetic vector (termed secular variation) with regional reference curves, derived mainly from lake sediments. As a result, previous magnetostratigraphic studies of cave sediments have not addressed ages much greater than about 20,000 years.

The first reversely magnetized clastic sediments from Mammoth Cave were discovered in late 1978, and intensive sampling from caves in the National Park has been carried out since then, yielding a regional pattern of striking consistency. More than 500 oriented sediment samples have been collected to date. A cubical pedestal was carved into the sediment and a 2-cm plastic box was then pressed over the pedestal. After orienting the base and one edge of the box, the pedestal was cut off at its base and the box was capped. Measurements were made with a cryogenic magnetometer at the University of Pittsburgh rock magnetism laboratory.

Nearly all the cave sediments collected have proved to be amenable to magnetic measurement. Only dry loose sands and powders have given erratic results, due to mobility of the grains within the sample boxes. Almost without exception, clay, silt, and sand samples

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which are moist and physically stable respond well to the standard "magnetic cleaning" technique of progressive alternating-field demagnetization (*12*).

A surveying altimeter (readings reproducible to 2 feet) was used to record the elevation of each site. Corrections for temperature and barometric pressure changes were facilitated by the presence of two recording microbarographs, maintained within Mammoth Cave by the National Park Service. The presence of U.S. Geological Survey bench marks along tour routes in Mammoth Cave also aided in maintaining vertical control. Subsequent visits to the same sites showed that we could reproduce corrected elevations to within 10 feet. Measurements taken at bench marks showed similar absolute accuracy.

Individual sections range in thickness from a few inches up to 20 or more feet and in some places fill the cave passage up to the ceiling. Descriptions of numerous sediment sections throughout the caves of the park have been given by Davies and Chao (*13*) and Carville and Hawkinson (*14*).

Figure 1 shows polarity zonation as a function of elevation of the sediment section. Interpretation of the polarity change at approximately the 560-foot elevation is straightforward if we regard the sediments as resulting from fluvial action and ponding near the local hydrologic base level. This occurs at and above the elevation of the Green River and of the Echo River, its subterranean tributary. As the Green River cuts down into its narrow valley, the hydrologic base level is lowered and formerly submerged cave passages are now exposed to free-surface stream action. At this stage, the coarse gravels and sands are deposited fluvially. At some point the cave stream is pirated to lower levels of the cave, and now the passage receives sedimentation only during times of flood. This relatively gentle periodic ponding deposits the fine laminar silts and clays characteristic of the upper portions of the sediment sections.

If the hydrologic base level is always lowering (*15*), then the resulting magnetostratigraphic relations are inverse to those usually encountered; that is, the youngest sediment sections are at the lowest elevations (although, of course within any given sediment section, the youngest sediment is found at the top of the pile). Thus sediments are currently being deposited within the historically observed flood zone extending from low water at 423 feet to 479 feet, an interval of nearly 60 feet. All sediments found within the interval from 423 feet to 550 feet are normally magnetized, while a predominately reversed magnetozone extends from 560 feet to 650 feet (*16*). Data are sparse and of mixed polarity above 660 feet.

I interpret the polarity change at 550 feet as that of the most recent (Brunhes-Matuyama) reversal of the magnetic field 730,000 years ago. At that time the low water line of Echo River would have been at that elevation and the top of the flood zone would have been some tens of feet above that. So the age of the sediments can yield a sort of operational "age" for the cave passage in the sense of dating the emergence of the passage from the phreatic zone and the initiation of fluvial activity through to the cessation of all deposition of clastic sediments.

The elevation of the 730,000-year magnetochron appears to be remarkably constant throughout the 80-km^2 area under study, further indicating that the fine-grained sediments resulted from broad-scale subterranean ponding during times of high floods.

Interpretation of the magnetic record at elevations above 560 feet is more difficult. There are two possibilities. (i) If we assume that the zone from 550 to 590 feet represents the Brunhes-Matuyama transition smeared out due to the height of the flood zone, then the next normal interval (above 650 feet) should be the Jaramillo normal. This would date the sediments in the highest cave levels within the park at about 1 million years ago. (ii) If the transition zone from 550 to 590 feet contains the unresolved Jaramillo normal as well as the Brunhes-Matuyama transition, then the mixed polarity zone from 650 to 710 feet corresponds to the Olduvai and Reunion normal intervals, extending from 1.67 million to 2.13 million years ago.

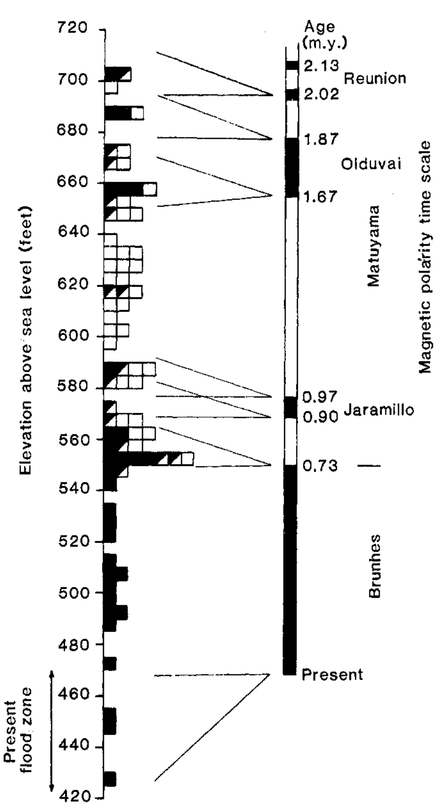

Fig. 1. Magnetic polarities of sediment sections are shown on the left, arranged by elevation. The magnetic polarity scale on the right (*5*) is positioned according to interpretation (ii), discussed in the text.

There are several reasons for preferring option (ii). Option (i) requires rapid downcutting of the Green River from 1.0 million to 0.73 million years ago (1500 years per foot) and slower downcutting from 0.73 million years ago to the present (7300 years per foot). Option (ii) yields more even rates of downcutting (8500 and 8000 years per foot, respectively) and provides a chronology for the cave levels that is more compatible with that proposed by Miotke and Palmer (*1*) on the basis of correlation of passage levels with Pleistocene river terraces.

Continuing work within the cave system promises a resolution of this question as the details of the actual polarity transitions recorded within individual sediment sections become known. Each section appears to contain a fairly high-resolution record of the magnetic field behavior spanning a time interval of perhaps a few thousand years. Several sites within the elevation range 550 to 580 feet appear to record portions of polarity transitions, and preliminary results obtained to date indicate that at least one of these is a normal-to-reverse transition. If this should prove to be the case, then this must mark the end of the Jaramillo normal interval and option (i) would be ruled out.

A calcite chip from a thin layer of flowstone atop a sediment section in Collins Avenue (elevation, 600 feet) was analyzed by the uranium-thorium method (*17*). The apparent age of the sample exceeded the range of the method (350,000 years).

We may conclude that the clastic sediments in the caves of Mammoth Cave National Park at an elevation of 550 feet were deposited 730,000 years ago. Sediments in passages at higher elevations are older, and those in the highest cave passages within the park are at least 900,000 years old and may well be closer to 2 million years old. Many of the larger passages found on the main tourist routes (the Rotunda, the Main Cave, Kentucky Avenue) would fall into the

800,000-year range under interpretation (i) or into the 1-million-year range under the preferred interpretation (ii).

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15. This may not always be the case. Miotke and Palmer (*1*) argue for fluctuations in the level of the Green River due to downcutting during interglacial periods and partial filling with alluvium during glaciations.
16. Two sites show mixed polarity at about 620 feet. Of four samples taken at one of the sites, three showed reversed polarity and only one showed a weak intermediate direction. These samples were dry and powdery and may have been unreliable. The two samples from the other site gave consistent directions located about 45° from the mean reversed pole. It is not known whether this site represents an actual magnetic field excursion or reflects some external influence such as slumping in the sediment.
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Selenium in Reducing Waters

Abstract. *The analysis of selenium species in reducing waters provides important insight into the element's biogeochemical cycle. The absence of selenate and selenite in reducing waters suggests that some removal mechanism could be operative, but the presence in these waters of about 1 nanomole per liter of dissolved organic selenide indicates that the regeneration of selenium in the form of organic species may be the dominant process. The data demonstrate that the regenerative and biogeochemical cycles of selenium are quite complex.*

In recent years attention has been paid to those elements that have multiple oxidation states in seawater [for example, arsenic (*1*), iodine (*2*), chromium (*2*), antimony (*3*), and selenium (*4*)]. This matter is of interest to environmentalists because certain elemental oxidation states may be more toxic than others. In addition, determining the concentrations of individual members of an oxidation-reduction couple may provide information on the oxidation-reduction potential of seawater. Dissolved selenium has three oxidation states: selenate, +6; selenite, +4; and selenide, −2. Thermodynamic calculations (*5, 6*) lead to the prediction that selenate should be the exclusive oxidation state in oxic seawater. These same calculations lead to the prediction that the ratio of selenate to selenite should be unity at an ambient pE of 6.1 (*7*), whereas in anoxic reducing systems selenide should become the stable dissolved form.

These calculations should be considered with caution since they ignore the apparent stability of thermodynamically unstable species as a result of kinetic effects as well as the biologically mediated production of unstable species. Indeed, data obtained by Measures *et al.* (*4*) show that approximately 35 percent of the total selenium found in oxygenated deep seawater is selenite. By examining the speciation of selenium in areas with extreme oxidation-reduction conditions (that is, anoxic basins and fjords), it may be possible to observe both biological and thermodynamic effects and in the process to illuminate details of selenium's biogeochemical cycle. This report presents what I believe are the first data on selenium species in reducing and anoxic waters.

Samples were taken in the Saanich Inlet, an intermittently anoxic fjord located along the southeastern portion of Vancouver Island, Canada, aboard the R.V. *Alpha Helix* in May 1981. The station (48°32.2′N, 123°32.7′W) has a water depth of 196 m. The interface between H_2S and O_2 was at approximately 175 m. A suboxic zone, characterized by low O_2 values (< 10 μM) and nitrate reduction (nitrite maximum of 0.5 μM at 130 m), extended from approximately 110 to 170 m. Waters above this depth were considered oxic.

Samples for selenite, selenate, and dissolved organic selenide analysis were passed through 0.4-μm Nucleopore filters and stored in borosilicate bottles at pH 1.5 (HCl). Analyses were completed within 3 months of sampling. Other workers (*8*) have demonstrated that this storage method does not alter the concentration or identity of selenate and selenite over this time period. The method of analysis for selenite and selenate consists of hydride generation, liquid nitrogen–cooled trapping, and atomic absorption detection (*9*). Analysis for total dissolved selenium, which includes dissolved organic selenide, is performed by boiling a 50-ml sample acidified to 4M with HCl, to which 1 ml of a 2 percent (weight-volume) potassium persulfate solution has been added, for 1 hour. The resultant solution is analyzed as selenite. The characterization of the dissolved organic selenide entails analyzing 50-ml samples by means of a method developed for free and combined (peptide) amino acids [see (*10*) for an example of its usage with seawater samples]. The seawater is acid-hydrolyzed, rotary-evaporated to dryness, taken up in distilled water with pH adjustment to 9.0, and passed through a copper sulfate–treated Chelex 100 column. This column chelates free amines, which can then be eluted with NH_4OH. The column flow-throughs and elutions are treated as for total selenium.

In order to sample for hydrogen selenide ($HSe^- + H_2Se$), water from the anoxic region was anaerobically transferred into a 1-liter stripping vessel. Helium purged the vessel and was routed into two gas impingers in series, each filled with 20 ml of 7M HNO_3. Upon acidification of the sample to 1M HCl, H_2Se evolved and was oxidized in the impingers to selenite. This method has been shown to be 100 percent efficient for hydrogen selenide concentrations up to 100 ng per liter. The HNO_3 solutions were taken to dryness, and distilled water portions analyzed for selenite. Samples from the anoxic region were also analyzed for dimethyl selenide. In the procedure one uses the gas stripping vessel with 1 liter of seawater, 90 minutes of helium stripping and liquid nitrogen–cooled trapping, gas chromatographic separation, and photoionization