

## Paleomagnetism of the Upper Silurian and Lower Devonian carbonates of New York State: evidence for secondary magnetizations residing in magnetite

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Paleomagnetic directions for the Upper Silurian and Lower Devonian carbonates of the Helderberg escarpment (New York State) differ from expected Late Silurian and Early Devonian directions for cratonic North America. The mean direction ( $D = 165^\circ$ ,  $I = -10^\circ$ ; paleopole at  $50^\circ\text{N } 129^\circ\text{E}$ ) is similar to Late Carboniferous and Early Permian results. Negative fold tests, and a lack of reversals, suggest that the magnetization is secondary. However, low coercivities, low blocking temperatures, the thermomagnetic curves ( $T_C$  near  $570^\circ\text{C}$ ) and the acquisition of isothermal remanent magnetizations all suggest that the remanence is carried by magnetite. If a detrital origin of these magnetites is assumed, the secondary nature of the remanence would argue for thermal resetting as a result of deep burial of the rocks. However, no evidence for such thermal resetting is seen in the alteration of conodonts. More likely perhaps is a chemical or thermochemical origin of the remanence; this would require the magnetites to be authigenic.

### 1. Introduction

The Siluro–Devonian portion of the North American apparent polar wander path is not well known. The polar wander path is presently defined by a few Middle Silurian poles (French and Van der Voo, 1979; Wilkinson et al., 1981), a single late Silurian pole (Roy et al., 1967), a recently described Early Devonian pole from the Canadian Arctic (Dankers, 1982) and several Late Devonian poles, tabulated by Van der Voo (1981). A pole has been determined for the Middle Devonian Onondaga limestone (Kent, 1979); however, a negative fold test indicates that the magnetization was acquired later in the Paleozoic. Additional Late Silurian or Devonian poles have been published from maritime Canada and New England,

as well as from the Alexander terrane of southeastern Alaska (e.g., Kent and Opdyke, 1980; Van der Voo et al., 1980); however, these results are certainly from allochthonous terranes and should not be included with the results from the craton.

Paleomagnetic evidence for cratonic North America suggests that from the Late Silurian to the Late Devonian, North America moved from a subtropical to an equatorial position. The timing of this transition, especially in relation to the positions of Gondwana and Baltica, has important biogeographic and paleoclimatic implications (Ziegler et al., 1980). In order to resolve the time of this movement better, a paleomagnetic study of Upper Silurian and Lower Devonian carbonates of the Helderberg escarpment was undertaken.

Another important aspect of this study is that

the results are obtained entirely from carbonate rocks. Although numerous paleomagnetism investigators have studied carbonates in the past, the nature and acquisition of the remanence is still not well understood (Lowrie and Heller, 1982).

## 2. Geological setting and sampling

During the Early Devonian, the seas retreated from North America and the resulting emergence

and erosion stripped much of the Upper Silurian and lowermost Devonian rock record from the central areas of the craton. Much of what remains is now preserved in the marginal basins of the Appalachians, Ouachitas, and western Cordillera, as well as in the Franklinian basin of the Canadian Arctic. One of the best exposures of Upper Silurian and Lower Devonian rock occurs along the northern margin of the Appalachian basin in upstate New York. Carbonate units crop out along a continuous belt which stretches east from Lake

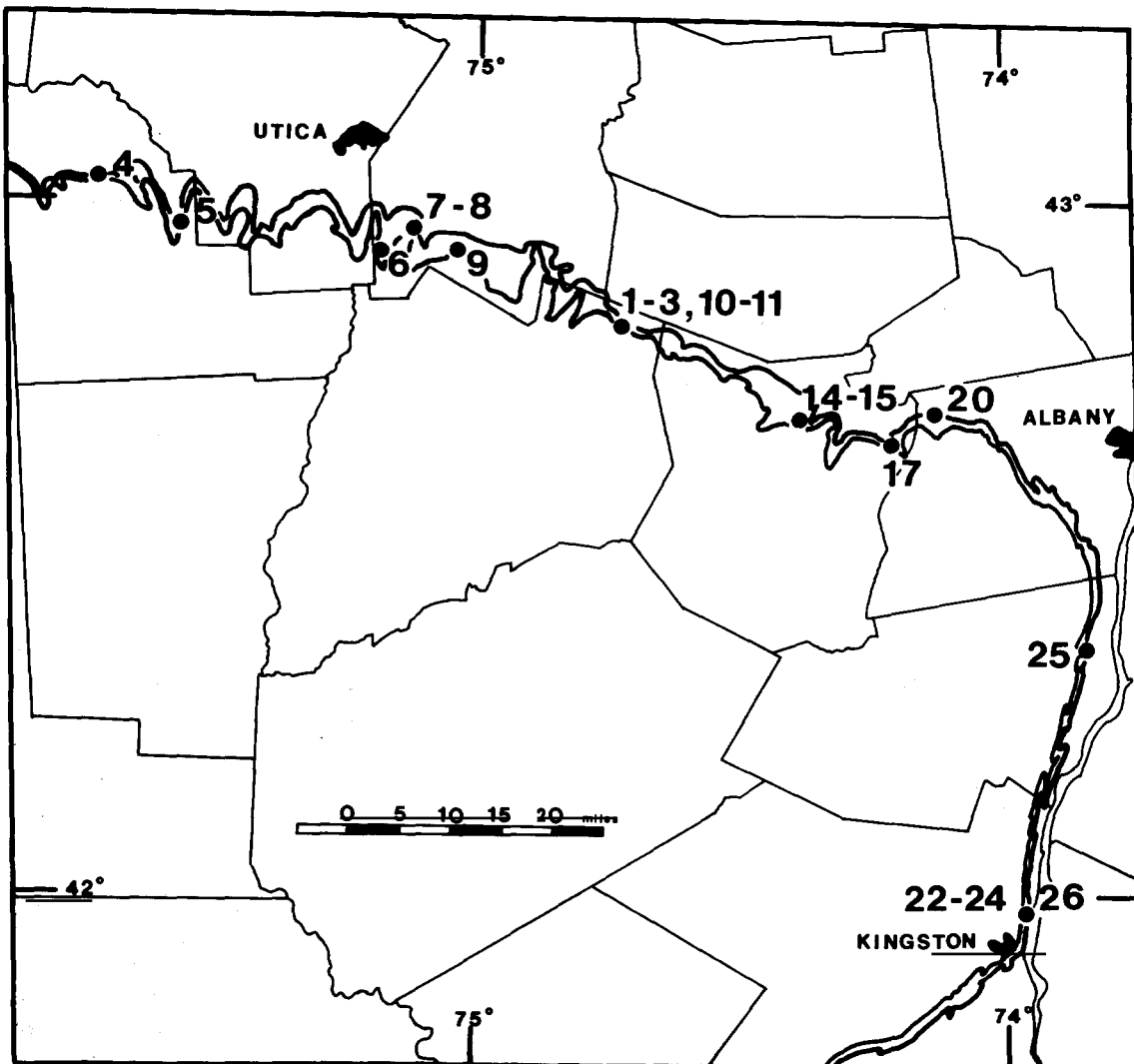


Fig. 1. Outcrop belt of Helderberg limestones and location of sites (after Rickard (1962), Fig. 10).



Cayuga, across to Utica and Albany, and south down the Hudson River valley (Fig. 1).

The Late Silurian (Cayugan) in this area consists of shales and shaly dolomites. The dolomites, which are often thin-bedded and eurypterid-bearing (Fiddler's green limestone), are succeeded gradationally by Lower Devonian limestones of the Helderberg group. The name Helderberg comes from the Dutch words "helder" meaning bright, and "berg" meaning mountain, and locally refers to the hills and escarpments southwest of Albany. Several facies have been recognized in the limestones of the Helderberg group, from which lagoonal (Thacher limestone), nearshore neritic (Dayville and Ravena limestones) and deeper neritic environments (Kalkberg and New Scotland formations) have been inferred (Rickard, 1962).

The stratigraphy of Upper Silurian and Lower Devonian rocks of New York State has been described extensively (Oliver et al., 1967; Head, 1969, 1974; Barnett, 1970). A study and correlation of more than 175 measured sections by Rickard (1962) provided the stratigraphic framework for the present study.

Twenty-five sites were sampled along the Helderberg escarpment during the summer of 1979 by C.R.S. An additional site was added by C. McC. in 1980. In total, 120 samples of Upper Silurian and Lower Devonian carbonates were collected from 18 sites along a 150-mile traverse from Utica south to Kingston (Fig. 1). Eight additional sites in Middle Silurian and Middle Devonian sandstones were also sampled. However, because these rocks have different (noncarbonate) lithology and because they did not reveal stable, characteristic directions of magnetization, the results from these sites will not be described. Figure 2 illustrates the stratigraphic position and diachronous relationships of the formations which were sampled. The vertical bars indicate the stratigraphic range of the samples collected at each site.

At sites 1–20, the beds are flat-lying, or dip gently to the S-SW. Only one site exhibits dips greater than 5°. In contrast, the beds at sites 22–26 along the Hudson River are strongly folded. The fold axes are aligned nearly N–S, with limbs dipping 20–45°. The youngest beds affected by the folding are Middle–Late Devonian in age,

although it is not clear whether the folding was the result of the Acadian (Middle–Late Devonian) or Alleghenian (Late Carboniferous–Early Permian) orogeny (Rodgers, 1970, p. 68).

### 3. Laboratory techniques

The magnetization of the samples was measured using the Superconducting Technology (ScT) magnetometer at the University of Michigan. All samples were demagnetized in stepwise fashion using either thermal or alternating-field (AF) techniques. The direction of magnetization remaining after each treatment was plotted using the demagnetization diagrams described by Zijderveld (1967). Directions of magnetization were determined in all cases by vector subtraction for straight-line demagnetization trajectories defined by three or more points.

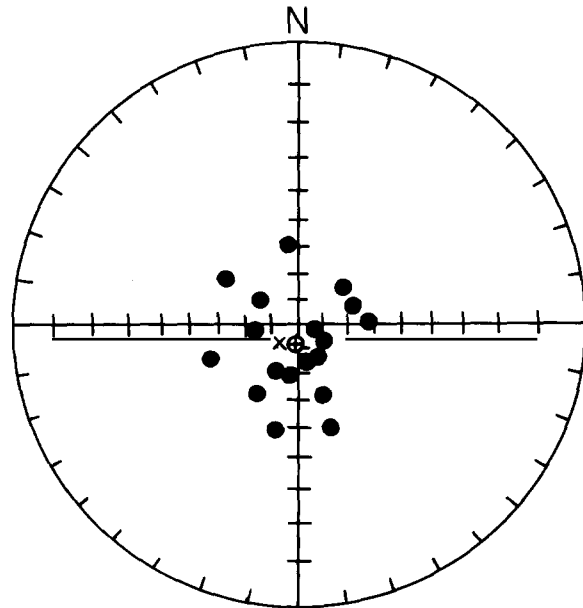


Fig. 3. NRM directions (site means) plotted on in situ coordinates:  $\oplus$  = mean of site means,  $\otimes$  = mean NRM direction for Onondaga limestone (Kent, 1979); solid circles indicate positive (downward) inclinations; open circles, negative (upward) inclinations. Directions plotted in stereographic polar projection.

#### 4. Natural remanent magnetization

Upper Ordovician, Upper Silurian and Lower Devonian carbonate rocks from upstate New York were first studied paleomagnetically by Graham (1954). Seven samples were collected from the Cayugan dolomites of upstate New York as part of a broader study of Paleozoic rocks from cratonic North America. His work, based on undemagnetized samples, revealed that Paleozoic rocks ranging in age from Ordovician to Permian were characterized by an extremely stable natural remanent magnetization (NRM). NRM directions, in general, were consistently southerly and very steeply inclined.

Similar NRM directions were obtained from the Cayugan and Helderberg carbonates in this study. The site mean NRM directions plotted in Fig. 3 show the same pattern as obtained by Graham. The mean NRM direction for the Onondaga limestone (Kent, 1979), which lies strati-

graphically just above the Helderberg group, is also plotted in Fig. 3.

#### 5. Characteristic directions and viscous magnetizations

Subsequent investigation of some of the same units studied by Graham, namely the Trenton limestone (McElhinny and Opdyke, 1973) and the Onondaga limestone (Kent, 1979), have demonstrated that the steep NRM direction is actually a composite of two directions. These directions are revealed by stepwise thermal or AF demagnetization.

The two demagnetization plots shown in Fig. 4 are typical thermal-demagnetization diagrams. Two components of magnetization can be clearly identified. The first component has a relatively low blocking temperature and is completely removed at 350°C. This component is steeply inclined to

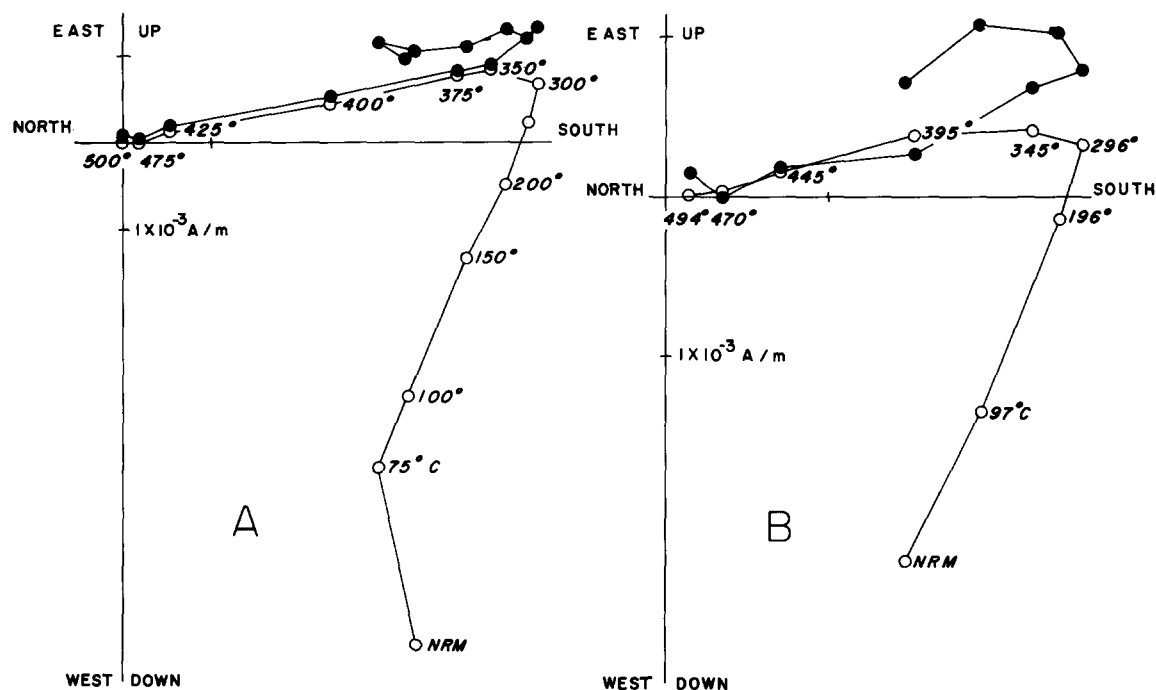
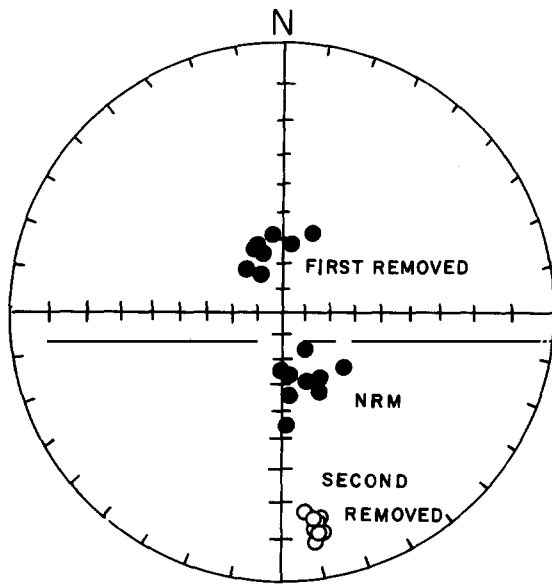


Fig. 4. Thermal demagnetization diagrams for (A) Cayugan dolomite (site 7-A) and (B) Helderberg limestone (site 26-E) plotted on in situ coordinates: solid circles represent vector endpoints projected onto the horizontal plane; open circles, vector endpoints projected onto the N-S vertical plane.



the north, and is nearly coincident with the present-day field direction for upstate New York. Similar behavior was observed by Kent (1979) for the Onondaga limestone. In that study, viscous remanent magnetization (VRM) experiments demonstrated the presence of a viscous component aligned with the present-day magnetic field.

The second component, which is revealed at temperatures above 350°C, decays linearly to the origin and is completely eliminated at ~500°C. Its southerly direction and shallow negative inclination are characteristic of Middle-Late Paleo-

Fig. 5. NRM directions and component directions of magnetization for samples from site 26, plotted on in situ coordinates. The first component removed is a viscous magnetization of recent origin. The second direction removed is the characteristic direction. Same plotting conventions as in Fig. 3.

TABLE I  
Characteristic directions and VGP's (in situ coordinates)

Site	Section	Site	$n_1/n_2$	Characteristic direction				Pole		
				$D$ (deg.)	$I$ (deg.)	$k$	$\alpha_{95}$ (deg.)	Latitude (deg.)	Longitude (deg.)	
		Latitude (deg.)	Longitude (deg.)							
3	94	42.8	-74.7	6/6	160	-9	9	23	-47.8	-44.2
4	142	43.0	-75.7	4/5	158	-7	58	12	-45.9	-43.2
5	137	43.0	-75.6	8/8	164	-10	71	7	-49.5	-50.6
6	126B	43.0	-75.2	4/4	169	-6	36	16	-48.8	-58.4
7	<sup>a</sup>	43.0	-75.1	7/7	166	-13	345	3	-51.6	-52.4
8	<sup>a</sup>	43.0	-75.1	2/2	164	-15	—	—	-51.9	-48.8
9	122A	42.9	-75.0	8/9	163	-8	32	10	-48.3	-49.0
10	94	42.8	-74.7	8/8	163	-10	55	8	-49.3	-48.1
11	94	42.8	-74.7	4/4	171	-8	11	29	-50.4	-60.5
14	74	42.7	-74.4	8/8	164	-8	47	8	-48.8	-49.7
15	74	42.7	-74.4	3/3	161	-11	233	8	-49.2	-44.7
17	67	42.6	-74.2	8/8	164	-20	49	8	-54.8	-46.1
20	64	42.7	-74.1	7/7	164	-16	79	7	-52.7	-47.3
22	<sup>b</sup>	42.0	-74.0	7/7	168	-3	8	23	-48.1	-55.9
23	<sup>b</sup>	42.0	-74.0	9/9	165	-8	103	5	-49.7	-50.5
24	<sup>b</sup>	42.0	-74.0	8/9	167	-13	100	6	-52.8	-52.3
25	47	42.3	-73.8	7/7	168	-1	3	39	-46.8	-56.1
26	<sup>a</sup>	42.0	-74.0	9/9	170	-13	842	2	-53.5	-57.1
Means				117/120	165	-10	200	2.4	-50.1	-50.8
									(50.1)	(129.2) <sup>c</sup>

<sup>a</sup> Treesh (1972).

<sup>b</sup> Waines (1967). All other sections, Rickard (1962).

<sup>c</sup>  $k = 395$ ,  $\alpha_{95} = 1.7$ .

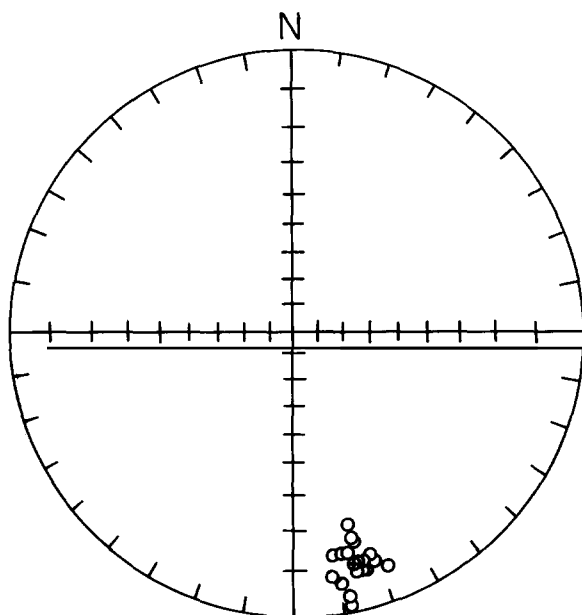


Fig. 6. Characteristic directions (site means) plotted in situ coordinates:  $\oplus$  = mean of site means ( $D = 165^\circ$ ,  $I = -10^\circ$ ). Same plotting conventions as in Fig. 3.

zoic directions for North America. The characteristic directions for samples from site 26, together with the viscous components and NRM directions, are plotted in Fig. 5.

The results of thermal demagnetization for all sites are listed in Table I. The site mean characteristic directions are plotted in Fig. 6. The mean characteristic direction for all sites is  $D = 165^\circ$ ,  $I = -10^\circ$ , with  $k = 200$  and  $\alpha_{95} = 2.4^\circ$ .

Although the samples were also demagnetized using AF treatment, the results were found to be less satisfactory. A comparison of thermal and AF demagnetizations for specimens taken from the same core indicated that the AF treatment may not completely remove the viscous component. Two samples from site 17 showed an average inclination of  $-17^\circ$  after thermal demagnetization, compared with an inclination of  $+12^\circ$  after AF treatment. Altogether, the nine samples from four sites that were AF-demagnetized had an average inclination of  $+8^\circ$ , compared with an inclination of  $-10^\circ$  for all thermal samples. Because the directions during demagnetization changed within a nearly N-S vertical plane, declinations were not

affected. Because of this disparity in inclination, samples that had been AF-demagnetized were not included in the calculation of the site means.

## 6. Evidence of secondary nature of remanence

The characteristic directions listed in Table I were obtained from beds spanning  $\sim 15$  My and covering 140 m of section. If the results for the Onondaga limestone are included, these ranges are nearly doubled. Yet, from formation to formation the direction of magnetization is remarkably constant. Furthermore, there is no record of magnetic reversals. Both of these observations suggest that the remanence of the Late Silurian and Early Devonian carbonates may be secondary.

In order to determine conclusively whether this magnetization is primary or the result of a secondary overprint, a fold test was carried out at five sites in the tectonically disturbed areas along the west bank of the Hudson River (sites 22–26). Four of these sites are located in road cuts along Route 199, 0.5 miles west of the Kingston–Rhinebeck bridge (Waines, 1967). There, a continuous section of Helderberg limestones and younger strata is exposed in a series of N–S-trending synclines and anticlines.

Although the limbs of the folds are steeply dipping, the directions of the fold axes are, unfortunately, nearly coincident with the characteristic direction. As a result, within-site dispersion does not significantly change after tilt corrections have been applied.

In each case, however, after unfolding, the inclination of the site means becomes more positive, moving away from the tight cluster of directions obtained from the flat-lying beds (Fig. 7). An argument may be made that the remanence is secondary because the characteristic directions from the folded sites without tilt correction cluster better with the directions from the flat-lying sites. This argument is strengthened by the observations that the directions are uniform throughout the section, that there are no reversals, and that the Onondaga limestone, which stratigraphically overlies the Helderberg group, fails the fold test (Kent, 1979).

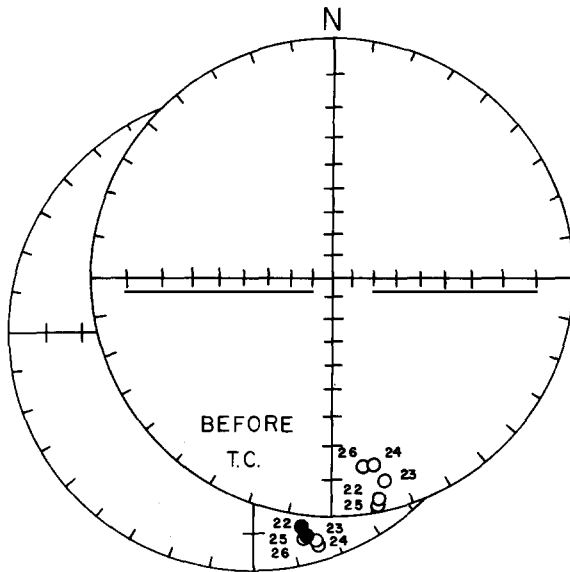


Fig. 7. Fold-test results (sites 22–26): all site mean inclinations become more positive (less negative) after application of the tilt correction (T.C.); before tilt correction  $k = 193$ , after tilt correction  $k = 106$ . Same plotting conventions as in Fig. 3.

If the remanence is secondary, when was it acquired? The folding in the Hudson River valley has been attributed to the Acadian or the Alleghenian orogeny (Rodgers, 1970). At present, neither alternative can be eliminated.

#### 7. Rock magnetism: magnetite as the carrier of remanence

Several rock magnetic experiments were carried out to ascertain the nature and mode of occurrence of the remanence carrier(s). All these experiments indicated fine-grained, relatively pure magnetite in the limestones as the only carrier of NRM. It is of interest to note that these findings are entirely similar to those of Kent (1979) for the Onondaga limestone.

Perhaps the most convincing are the thermomagnetic measurements made using a vibrating-sample magnetometer on a sample chip, which yielded a Curie temperature of  $\sim 565^\circ\text{C}$  (Fig. 8). The field applied was 1.8 T, the vacuum was  $10^{-4}$  torr, and the weight of the sample chip was  $\sim 30$

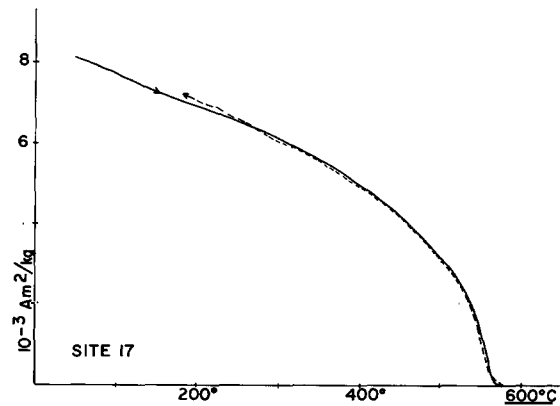


Fig. 8. Thermomagnetic curve for sample from site 17, indicating single Curie temperature of  $\sim 565^\circ\text{C}$ .

mg. The smooth, reversible, and convex-upward nature of the curve suggests relatively pure (titanium-free) magnetite, and shows no indication of maghemite inversions or of pyrrhotite, despite the presence of abundant pyrite in our samples.

In Fig. 9 the acquisition of isothermal remanent magnetization (IRM) is plotted for several representative samples, versus the applied field produced in a cryogenic solenoidal magnet constructed at the University of Michigan. Almost all samples reach saturation rapidly, well below 0.3 T (3000 gauss), again suggesting that magnetite is the only iron compound capable of carrying remanence.

In order to ascertain whether the magnetites undergo the magnetocrystalline transition at

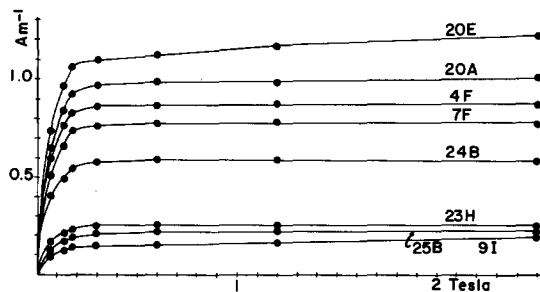


Fig. 9. Acquisition of isothermal remanent magnetization (IRM) by several representative samples, identified by site (number) and sample identification (letter), and showing rapid saturation generally reached by 0.3 T.



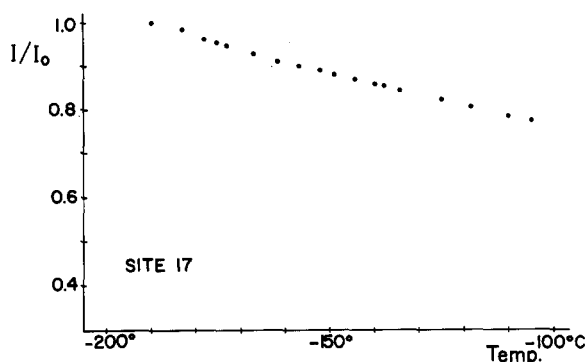


Fig. 10. Intensity of IRM, given at liquid-nitrogen temperature, measured quasi-continuously as a function of temperature as sample is allowed to warm up. No magnetic transitions are observed.

—160°C, a sample was given an IRM at liquid-nitrogen temperature and allowed to warm up to room temperature while the remanence was measured using a cryogenic magnetometer. The results (Fig. 10) do not reveal any transition in the Helderberg rocks, whereas several limestone samples from formations in other parts of North America did reveal marked transitions. This suggests that the magnetites are fine-grained and possibly possess shape-related or other anisotropies which predominate over the magnetocrystalline anisotropies.

We conclude from these bulk-rock experiments that no remanence carriers other than fine-grained, relatively pure magnetites are present in these rocks. Naturally, it would be of great interest to study the morphology, chemistry and mode of occurrence of these grains using microscopic techniques, in order to resolve the question of how these magnetites acquired their secondary magnetizations, which we elsewhere in this paper postulate to be chemical remanent magnetizations. Although authigenic magnetites are considered to be quite uncommon, occasional references to their occurrence have been made in the literature (e.g., Friedman, 1954).

Unfortunately, we have thus far been unable to dissolve the Helderberg carbonates and retain a magnetite-bearing residue. A simple experiment, involving IRM acquisition by the original rock sample as well as by the residue, revealed that the

dissolution process removed all iron oxides. Further dissolution experiments using different buffered acids are planned for the near future.

Another approach has been to examine thin sections using scanning and transmission electron microscopy (STEM) techniques, but no iron oxides have thus far been unambiguously identified. This is not surprising in view of the magnetic intensities of our samples, which predict iron oxides to constitute ~10 p.p.m. of the total rock.

## 8. Discussion

The paleomagnetic directions in the Upper Silurian and Lower Devonian rocks from the Helderberg escarpment give a paleopole at 50°N 129°E; this pole is very similar to that of the overlying Onondaga limestone (Kent, 1979) and falls in a group of Late Carboniferous–Early Permian poles for the North American craton (Van der Voo, 1981). The pole does not agree with North American Middle or Late Silurian poles obtained from the Bloomsburg redbeds (Roy et al., 1967), the Rose Hill formation (French and Van der Voo, 1979), the Wabash limestones from Indiana (Wilkinson et al., 1981), or a recently described Early Devonian pole from the Canadian Arctic, located at 25°N 99°E (Dankers, 1982). The position of our Helderberg pole suggests a remagnetization during Late Carboniferous–Early Permian time.

Support for this contention is found in the negative fold test for the Onondaga limestone (Kent, 1979) and the inconclusive fold test for our samples; although the age of the deformation is uncertain and could be related to either the Acadian or the Alleghenian orogeny, the available evidence precludes a primary age of the magnetization. Further study of equivalent strata in the Valley and Ridge Province in Pennsylvania is underway in order to settle the question concerning the age of magnetization, and preliminary fold tests have revealed a post-folding magnetization. It is worth noting that Late Devonian, Silurian and Ordovician formations of the Valley and Ridge Province all appeared to carry secondary (post-folding) Late Paleozoic overprints as well as pre-

folding characteristic magnetizations (Roy et al., 1967; French and Van der Voo, 1977; Van der Voo and French, 1977; Van der Voo et al., 1979; Watts and Van der Voo, 1979). Clearly, the whole area of the central Appalachians and adjacent plateaus in New York, Pennsylvania and further south, underwent some Late Carboniferous–Early Permian event that caused large-scale magnetic overprinting.

The interesting question then arises of whether this event was thermal, chemical, or a combination of the two. A purely thermal magnetic resetting, however, seems precluded by a combination of factors, such as the blocking temperatures of the overprints compared with the low paleo-temperatures in central and western New York State as indicated by the alteration of conodonts (Epstein et al., 1977), as well as the relatively low estimates for the depth of burial in that area. Instead, we prefer to argue for a chemical or thermochemical cause of the remagnetization, involving diagenetic growth of new (authigenic) minerals.

In the Helderberg escarpment, our study shows that this involves authigenic magnetites. Until conclusive electron-microscope evidence is obtained concerning the mode of occurrence, the morphology and chemistry of these magnetites, we cannot speculate about the mechanisms for remagnetization. Future work is planned to resolve this.

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