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U-PB AND TH-PB WHOLE ROCK STUDIES IN THE SOUTHERN APPALACHIAN PIEDMONT

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ABSTRACT

In this paper, reconnaissance results of U-Pb in zircon and U-Th-Pb in whole rocks and minerals are reported for several areas of the southern Appalachian Piedmont, and some geologic implications of the entire Piedmont Pb isotope data set are considered.

Zircons from the Vance County albite granodiorite of the Carolina slate belt in the Virgilina area are discordant, but define a cord with an upper intercept age of 571 ± 17 Ma. In contrast, a reconnaissance study of U-Pb in zircons from Haile-Brewer block (South Carolina) volcanoclastics and from the adjacent Great Falls Granite of the Charlotte belt indicates the presence of an inherited population.

Measured and inferred initial Pb isotope ratios in these and other Piedmont lithologies suggest four types of protolith histories: A. Rocks with MORB-mantle-like isotopic affinities; B. Rocks with volcanic arc-like, mixed "mantle-crust" isotopic trends; C. Rocks containing Pb that may have been derived from older volcanic arc materials; and D. Rocks that were derived from much older continental crust. Type A consists of a late Precambrian(?) amphibolite and the Hillabee greenstone in Alabama, and metatonalites and metavolcanics of the Kings Mountain belt. Volcanic arc-like Pb isotope trends (type B) are recognized from the central North Carolina and the Georgia-South Carolina border areas of the Carolina slate belt. Pb in the Vance County and Roxboro plutons of the Virgilina area, the Haile-Brewer block, and a Mesozoic diabase dike are thought to have derived their Pb from different generations of older volcanic arc-derived material (type C). Finally, the Great Falls Granite is characterized by an unusually high $^{207}Pb/^{204}Pb$, which indicates a protolith with a long history of crustal residence (type D).

INTRODUCTION

In the past few years, I have reported on U-Th-Pb isotope studies in several southern Appalachian areas. Three of these reports have primarily dealt with different parts of the Piedmont: 1) volcanogenic massive sulfides of the Piedmont (LeHuray, 1982); 2) rocks and ores of the Kings Mountain belt (LeHuray, 1986); and 3) volcanics and sulfides of the Haile-Brewer block of the Carolina slate belt (LeHuray, 1987). My purposes in this paper are to present additional data and to call attention to some geologic implications of the entire Piedmont data set that have not been fully addressed in previous papers. The new data are principally from the Vance County Pluton, associated with the Hamme tungsten district of the Virgilina area of the Carolina slate belt, but a few other data are included to facilitate comparison and discussion. The analytical techniques used to obtain the data reported in this paper have been described in the papers cited above and in LeHuray (1984) and will not be repeated here. Sample locations are listed in the

Appendix to this paper.

VANCE COUNTY PLUTON

The Hamme tungsten district, Vance County, North Carolina, has been the subject of a number of recent studies (Gair, 1977; Casadevall and Rye, 1980; Foose and others, 1980). The geology of the area around the district has been discussed by Espenshade (1947) and Parker (1963, 1968). The quartz-huebnerite veins at Hamme are associated with the emplacement of the Vance County pluton, which lies in the Carolina slate belt at the North Carolina-Virginia border (Figure 1). It intrudes metavolcanics of Carolina slate belt and is tectonically bounded on the east by the Nutbush Creek fault (Bobyarchik, 1981). The pluton has been called an "albite granodiorite" to emphasize its K-poor character, and could also be called a "plagiogranite". It is one of a suite of similar intrusions in the Virgilina area. One of these, the Roxboro granodiorite, has a U-Pb zircon upper intercept age of 575 ± 20 Ma, somewhat younger than the ≈620 Ma upper intercept age of the enclosing metavolcanic sequence (Glover and Sinha, 1973).

Tungsten mineralization in the Hamme district occurs on the western margin of the Vance County pluton, near the contact with slate belt rocks. In a stable isotope study of the Tungsten Queen vein, Casadevall and Rye (1980), found that premetamorphic stable isotope systematics were largely preserved. Hydrogen, carbon and sulfur isotopes indicate that a predominantly meteoric water component, some input of sedimentary organic carbon, and a magmatic source of sulfur contributed to the mineralizing hydrothermal fluids.
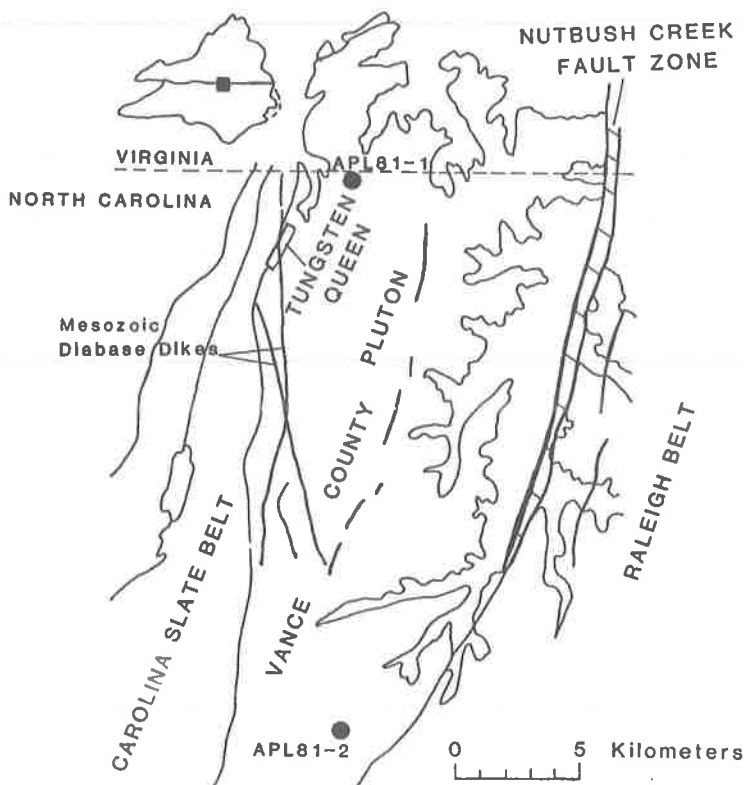

Figure 1. Index map of the Vance County pluton, showing locations of samples.

Table 1. U-Pb zircon results from various southern Appalachian Piedmont rocks, as discussed in the text.

| Sample Number	Fraction	Pb (ppm)	U (ppm)	^{204}Pb (atom %)	^{206}Pb (atom %)	^{207}Pb (atom %)	^{208}Pb (atom %)	$\frac{^{206}Pb}{^{238}U}$	$\frac{^{207}Pb}{^{235}U}$	$\frac{^{207}Pb}{^{206}Pb}$
									Ages (Ma)	
Great Falls Granite:										
HB-11	+200 NM	68.5	777	0.0293	79.54	5.085	15.34	502	511	551
HB-11	-325 NM	75.8	830	0.0176	80.51	5.485	13.98	527	576	773
HBB Metavolcanoclastic rock:										
HB-3	Bulk	35.8	300	0.0402	69.72	5.653	24.58	589	684	1010
Vance County pluton:										
APL81-1	+150 NM	19.4	237	0.1185	73.88	6.089	19.91	424	448	572
APL81-1	-325 NM	30.4	366	.0274	77.54	5.006	17.43	463	483	582
APL81-1	-325 M	38.8	598	0.0748	75.29	5.572	19.07	350	383	589
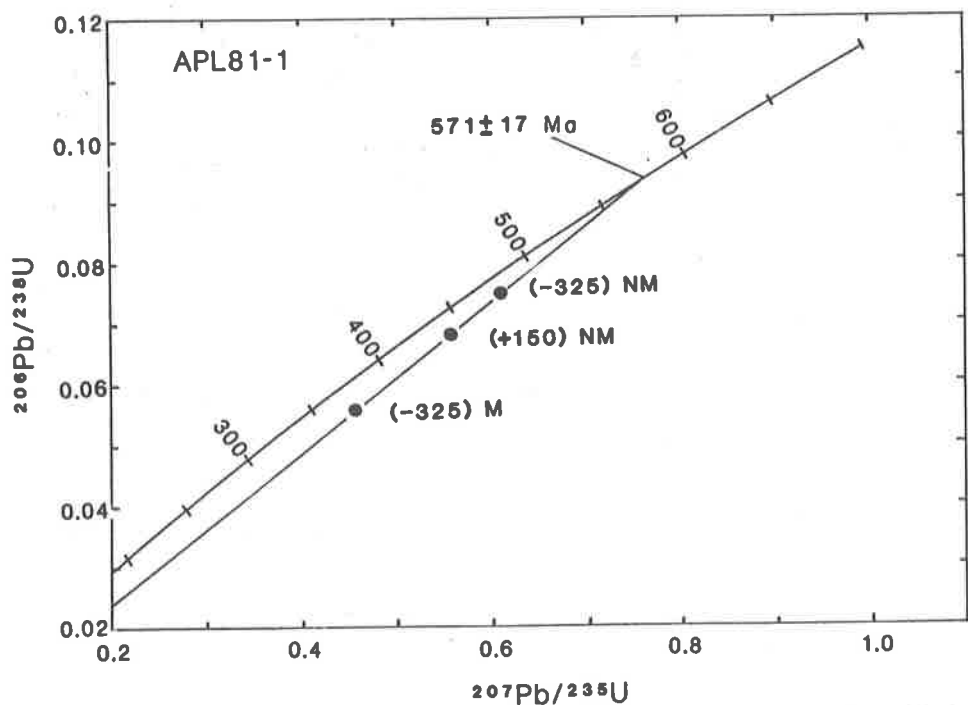
Figure 2. Concordia diagram showing results from three fractions of zircon separated from sample APL81-1 of the Vance County albite granodiorite. The upper intercept of the cord defined by the three fractions corresponds to an age of 571 ± 17 Ma, which is interpreted to be the crystallization age of the pluton.

U-Pb Zircon Age

Three size and magnetic fractions of zircon from a sample taken at the State Line Quarry (APL81-1 in Figure 1) were analyzed for U-Pb age determination. The three data points are discordant, but define a cord with an upper intercept at 571 ± 17 Ma (Table 1; Figure 2; unless otherwise indicated, errors are reported as

2σ). This is interpreted to be the crystallization age of the pluton. There is no significant difference between the 571 ± 17 Ma age of the Vance County Pluton and the 575 ± 20 Ma U-Pb age of the Roxboro Pluton (Glover and Sinha, 1973) which supports the view that the two K-poor granodiorites are part of the same intrusive suite.
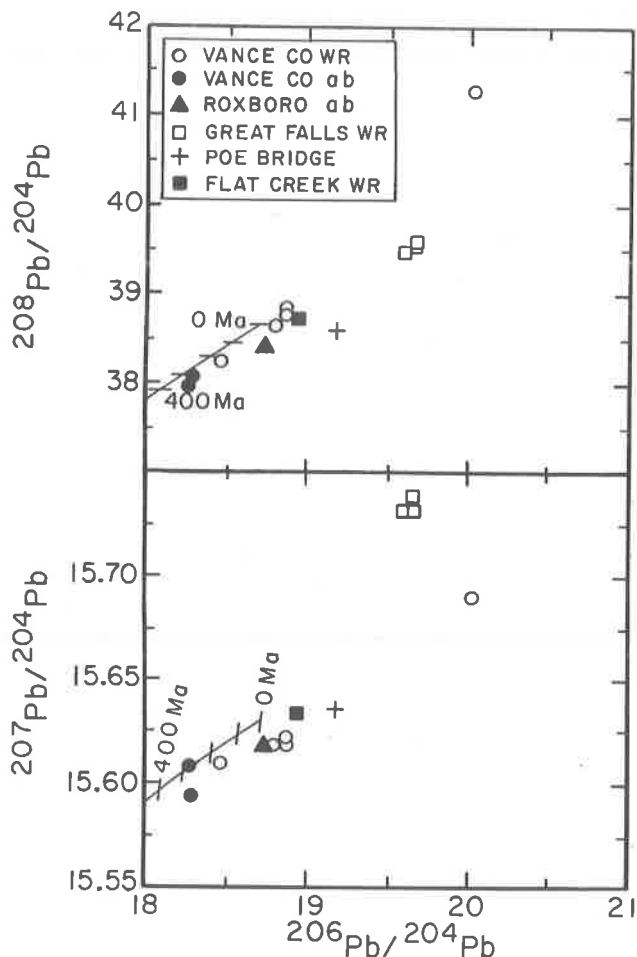

Figure 3. Lead isotope ratio diagrams showing results of whole rock (WR) and albite (ab) analyses reported in this paper. The data are discussed in the text. Growth curves from Stacey and Kramers (1975).

U-Th-Pb Systematics

In the study of Piedmont ore Pb (LeHuray, 1982) I reported that five galenas from the Tungsten Queen vein have homogeneous Pb isotope ratios, which is typical of deposits associated with intrusive magmatism (e.g. Doe, 1978). As illustrated in Figure 3 and Table 2, albite separated from samples taken at the northern and southern ends of the pluton have Pb isotope ratios similar to the galena data, indicating that the magma was the probable source of most of the Pb (and, presumably, other metals) in the tungsten veins. The galena data, however, has slightly but consistently higher $^{206}Pb/^{204}Pb$ than the feldspars, which may

Table 2. Lead isotope composition and U, Th and Pb concentrations of samples from the Vance County pluton.

Sample Number	Type[1]	$\frac{206Pb}{204Pb}$	$\frac{207Pb}{204Pb}$	$\frac{208Pb}{204Pb}$	Pb (ppm)	U (ppm)	Th (ppm)	$\frac{238U}{204Pb}$	$\frac{232Th}{238U}$	$\frac{232Th}{204Pb}$
HW-144U	WR	20.039	15.690	41.293	6.24	1.83	10.6	19.8	5.98	118.3
HW-181U	WR	18.800	15.618	38.647	15.4	1.67	6.36	6.94	3.93	27.3
HW-192U	WR	18.864	15.619	38.846	10.6	1.5	7.6	9.09	5.23	47.6
APL81-1	WR	18.865	15.621	38.765	12.2	1.27	5.49	6.68	4.47	29.8
APL81-2	WR	18.465	15.610	38.266	8.42	0.27	2.24	2.03	8.57	17.4
APL81-1	Ab-L	18.538	15.606	38.328						
APL81-1	Ab-R	18.292	15.595	38.076						
APL81-2	Ab-L	18.364	15.613	38.036						
APL81-2	Ab-R	18.271	15.608	37.967						
Roxboro	Ab-R	18.729	15.619	38.426						

1. WR = whole-rock; Ab = albite; L = leachate; R = residue.

indicate that some other source contributed a minor fraction of the ore Pb. This is consistent with the finding of Casadeval and Rye (1980) that some of the carbon in Hamme carbonates was derived from sedimentary sources.

Whole-rock data indicate that the U-Th-Pb system in the Vance County pluton has been disturbed. The whole rock data are shown in Figure 4 along with 300 Ma and 600 Ma reference isochrons constructed using galena (G) and albite (F) analyses as initial ratios. The data form an irregular pattern between the reference isochrons, and seem to have undergone variable losses of both U and Pb, relative to constant Th. The scatter of data on both the 238U/204Pb - $^{206}Pb/^{204}Pb$ and $^{232}Th/^{204}Pb$ - $^{208}Pb/^{204}Pb$ isochron diagrams indicate that the disturbance was more than simple loss of U during recent weathering, such as has been observed in other plutons (e.g. Rosholt and others, 1973).

Some effects of the hydrothermal event associated with W mineralization may be observable in the concentrations of Pb in the pluton. Samples with numbers beginning "HW" are part of a suite collected underground at the Tungsten Queen vein by Jacob Gair (USGS). The lowest number (HW-144U) is the closest to the vein, and has a Pb concentration that is about a factor of two lower than other samples in the northern part of the Vance County pluton (Table 2, Figure 5). Concentrations of U and Th may decrease away from the vein, however more analyses are required to verify the trends in the pluton away from mineralization. The Pb depletion in sample HW-144U, on the other hand, is evident in both its Pb concentration and its elevated $^{238}U/^{204}Pb$ and $^{232}Th/^{204}Pb$ ratios (Figure 5). The high U/Pb and Th/Pb ratios have resulted in radiogenic Pb isotope ratios in the whole-rock. The loss of Pb must have occurred shortly after emplacement of the pluton, because the model U-Pb and Th-Pb ages of HW-144U, calculated using the feldspar values as initial Pb isotope ratios, are approximately 550 Ma, close to the age given by the zircons. This is consistent with the magmatic association of the mineralizing event.

Without a more comprehensive study, it is difficult to determine how much other samples may have been effected by the hydrothermal event. Sample
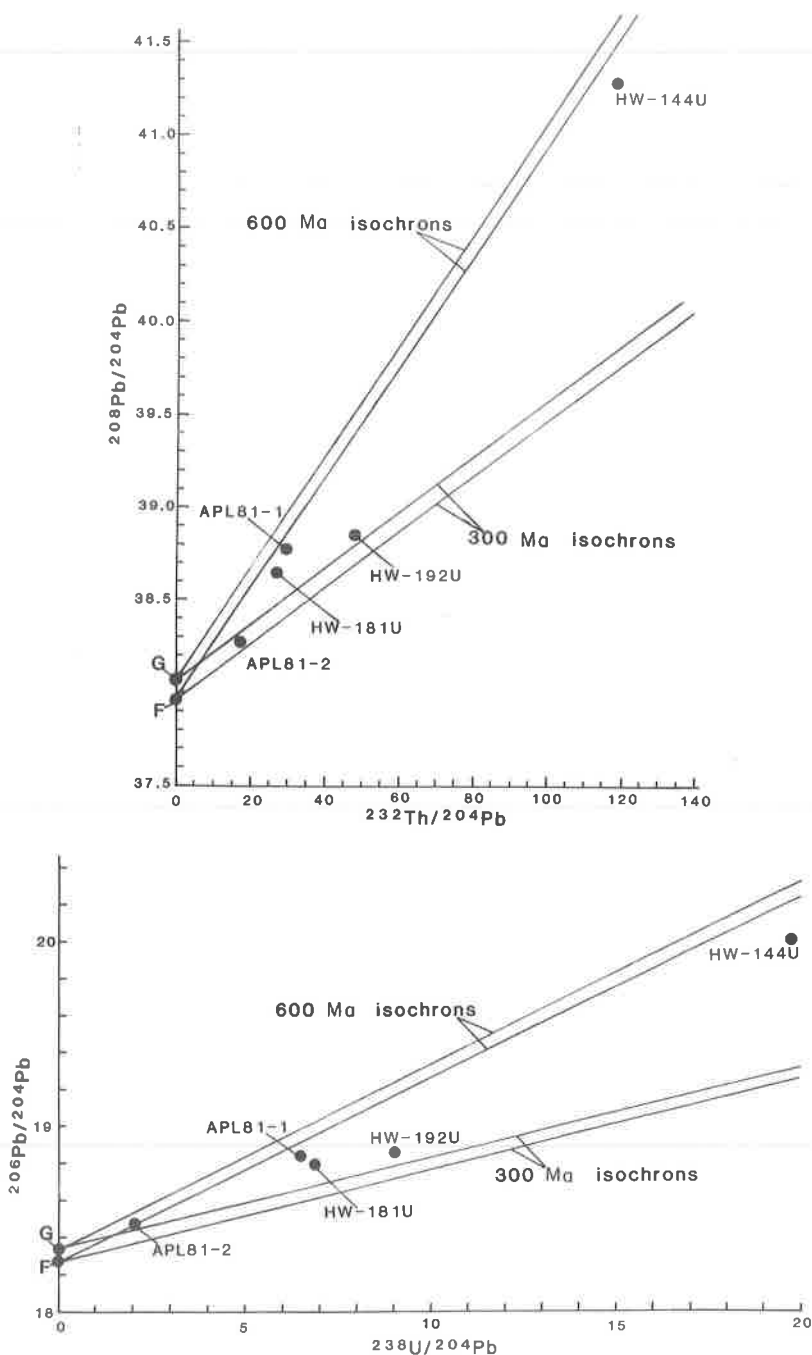
Figure 4. $^{208}Pb/^{204}Pb$ versus $^{232}Th/^{204}Pb$ and $^{206}Pb/^{204}Pb$ versus $^{238}U/^{204}Pb$ (isochron) diagrams showing whole rock data from the Vance County albite granodiorite. Reference isochrons are drawn for 600 and 300 Ma using the average of five galena (G) and two albite (F) analyses as initial ratios. The scatter of the data indicates that the U-Th-Pb system has been disturbed, probably through both U and Pb loss, but shows no evidence of Pb isotope homogenization during the Alleghanian ($\approx$300 Ma) event.

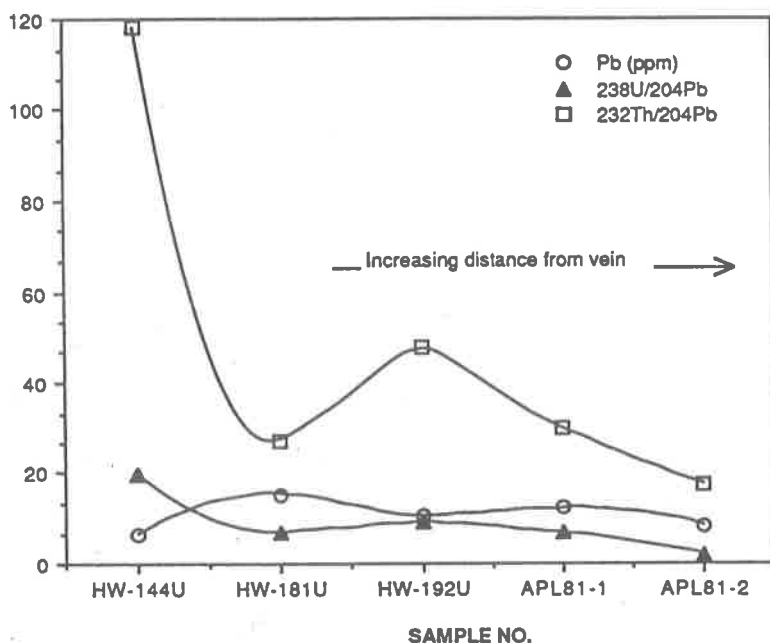Figure 5. Diagram showing changes in Pb concentration, $^{238}U/^{204}Pb$, and $^{232}Th/^{204}Pb$ with increasing distance from the Hamme tungsten vein. The samples with the prefix "HW" were collected along a perpendicular drift underground, with HW-144U being closest to the vein. The samples with the prefix "APL" were collected well away from any known mineralization (see Fig. 1). The scale of the distance axis, therefore, is relative only. The sample closest to the vein has apparently lost about half of its Pb.

APL81-2, collected from the southern part of the pluton and well removed from known mineralization has low U and Th concentrations for a rock of intermediate composition. The Th concentration has presumably not changed much, because of its immobile chemical behavior, so that low U and Th must be at least partially an original character of the rock. The current whole-rock data only allow us to say that some disturbance(s) has occurred.

RECONNAISANCE WORK IN OTHER AREAS

Additional Data From the Haile-Brewer Area

When the ≈465 Ma U-Pb and Th-Pb isochron ages of the metavolcanic rocks of the slate belt in South Carolina were found (LeHuray, 1987), samples on hand were processed for zircons in an attempt to verify the age. The results (Table 1, Figure 6) made it evident that U-Pb zircon systematics in the area are complex. Two fractions from the Great Falls Granite, an intrusive rock in the Charlotte belt adjacent to the Haile-Brewer block with a poorly-defined Rb-Sr isochron age of 543 ± 63 (1σ; Fullagar, 1971, 1981), and one fraction from a metavolcanoclastic unit of the Haile area are discordant and have three different $^{207}Pb/^{206}Pb$ ages: 551 Ma, 773 Ma, and 1010 Ma (Table 1, Figure 6).

Clearly, definitive age information will be difficult to obtain from this population of zircons by standard techniques. The data are, however, of interest
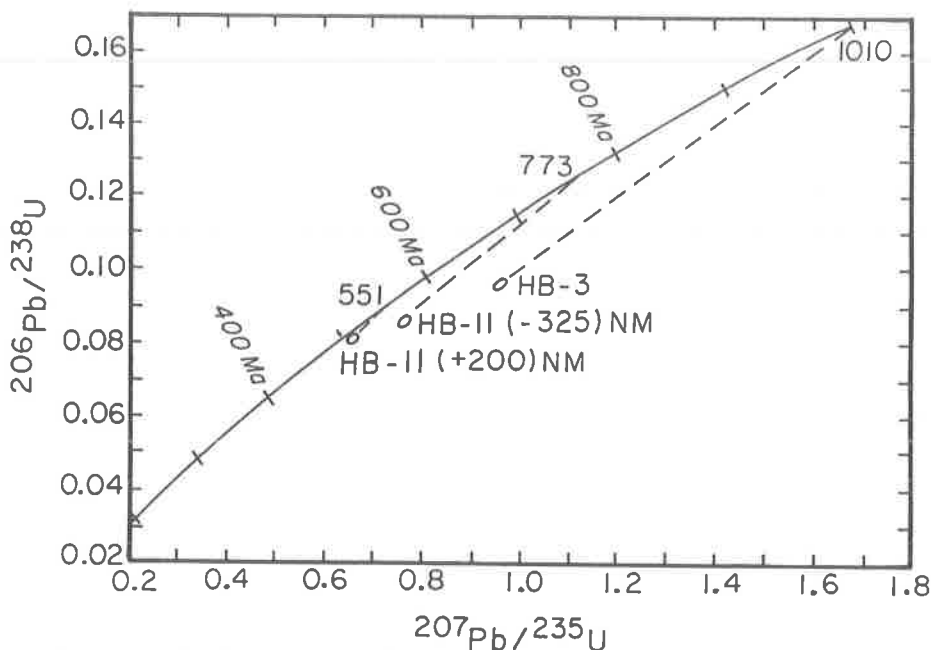
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Figure 6. Concordia diagram showing results of analysis of two fractions of zircon from the Great Falls Granite (HB-11) and one from a volcanoclastic unit in the Haile-Brewer block (HB-3). Dashed lines connect individual fractions with their $^{207}Pb/^{206}Pb$ ages (551, 773, and 1010 Ma). The presence of inherited fractions in both units is suggested by the old $^{207}Pb/^{206}Pb$ ages. The reconnaissance nature of these results, however, do not allow meaningful estimates of the actual ages of either the units analyzed of the inherited zircons.

because they indicate the presence of inherited zircons. Whereas the 551 Ma upper intercept age is not geologically unreasonable for the Great Falls Granite, 773 Ma is thought to be much too old for a Charlotte belt granite. The 1010 Ma upper intercept of the volcanic sample is entirely unreasonable as an age of the volcanics in the Haile area, but suggests the possible presence of Grenville age material in the magmatic source.

An additional indication of a continental character for the precursor of the Great Falls Granite is the high $^{207}Pb/^{204}Pb$ of whole-rocks analyzed from the unit (Figure 3, Table 3). These are the highest values known from any southern Appalachian rock, including the Mount Rogers Formation of the western Blue Ridge (LeHuray, 1984). Indeed, there are few Phanerozoic rocks anywhere in the world with whole rock $^{207}Pb/^{204}Pb$ higher than 15.7. Initial ratios calculated for an age of 500 Ma and measured U/Pb and Th/Pb (Table 4) indicate an initial $^{207}Pb/^{204}Pb$ of ≈15.70. No matter how disturbed the U-Th-Pb system may be in the Great Falls, or how incorrect the age used for calculation, it would be difficult to postulate anything but a very high initial $^{207}Pb/^{204}Pb$ for the granite, and, therefore, precursors with a very long term history of high U/Pb - i.e. old continental crust.

I would also like to note here that the U-Pb and Th-Pb isochron ages of 466 ± 40 Ma and 462 ± 53 Ma, respectively, reported in LeHuray (1987) have errors substantially greater than when the standard method of statistical error treatment (York, 1969) is used. The treatment used for the reported ages is designed to

Table 3. Lead isotope composition and U, Th and Pb concentrations of samples from the Great Falls granite and the Flat Creek diabase dike, South Carolina, and the Poe Bridge Mountain amphibolite, Alabama.

Sample Number	Type[1]	$\frac{206Pb}{204Pb}$	$\frac{207Pb}{204Pb}$	$\frac{208Pb}{204Pb}$	Pb (ppm)	U (ppm)	Th (ppm)	$\frac{238U}{204Pb}$	$\frac{232Th}{238U}$	$\frac{232Th}{204Pb}$
Great Falls Granite:										
HB-9	WR	19.657	15.739	39.557	17.6	2.02	12.8	7.53	6.55	49.3
HB-10	WR	19.665	15.732	39.591						
HB-11	WR	19.589	15.732	39.488	17.1	1.85	10.7	7.09	5.97	42.3
Flat Creek diabase dike:										
DD-201	WR	18.939	15.634	38.728	3.44	0.483	1.81	9.02	3.87	34.9
Poe Bridge Mountain amphibolite:										
DK-60	WR	19.170	15.636	38.602	1.15	0.166	0.506	9.28	3.15	29.2

1. WR = whole-rock.

Table 4. Initial Pb isotope ratios inferred for various pre-Alleghanian Piedmont rocks. Sources of data are this paper and LeHuray (1982, 1984, 1986, 1987).

Unit (age)	$\frac{206Pb}{204Pb}$	$\frac{207Pb}{204Pb}$	$\frac{208Pb}{204Pb}$	Method of determination
A. ROCKS WITH MORB-LIKE ISOTOPIC AFFINITIES				
Poe Bridge Mtn. (late pC ?)	17.92	15.53	37.64	Least radiogenic Stone Hill galena; supported by amphibolite whole-rock data
Hillabee greenstone (lower Pz)	17.93	15.55	37.72	Pyriton ore
KMB: metatonalite & metavolcanics (lower Pz)	18.04	15.53	37.62	Kings Creek barite mine galena, consistent with whole-rock data
B. ROCKS WITH ARC-LIKE, MIXED "MANTLE-CRUST" ISOTOPIC AFFINITIES				
Carolina slate belt [range] (≈550 Ma)	18.13	15.62	37.87	Average Cid district massive ore
	18.03	15.56	37.63	Least radiogenic galena (Dorn mine
Kings Mtn. belt [range]	18.32	15.63	38.32	Cameron mine galena
	18.04	15.53	37.62	Kings Creek barite mine galena
C. ROCKS CONTAINING PB POSSIBLY DERIVED FROM OLDER ARC MATERIALS				
Vance Co. pluton (≈570 Ma)	18.28	15.60	38.00	Average of two albite analyses
Haile-Brewer area (≈465 Ma)	18.37	≈15.61	38.05	Calculated from isochrons
Flat Creek Diabase (Triassic)	18.83	15.62	38.35	Calculated assuming no disturbance since 220 Ma.
D. ROCKS WITH UNEQUIVOCALLY CONTINENTAL ISOTOPIC AFFINITIES				
Great Falls Granite (Cambrian ?)	19.03	15.70	38.38	Calculated assuming age = 500 Ma

maximize errors (Ludwig, 1985). Calculated ages and errors for these data using the standard York (1969) treatment are: ^{238}U-^{206}Pb - 472 ± 27, MSWD = 1.43; ^{232}Th-^{208}Pb - 464 ± 33, MSWD = 1.09 (Model 1, including scatter). Thus, relative to the York model of error treatment, the whole rock data indicate that volcanism in the Haile-Brewer block could have occurred in the Ordovician. Full consideration of the meaning of the U-Pb and Th-Pb isochrons is given in LeHuray (1987).

Miscellaneous Whole-Rocks

Flat Creek diabase: The Flat Creek Mesozoic diabase dike, which intrudes the Haile- Brewer volcanics, has reasonable U/Pb and Th/Pb ratios (9.02 and 34.9, respectively; Table 3) for an igneous rock, suggesting that alteration and attendant U mobility have not been substantial. Using these values and an assumed age of 220 Ma, initial Pb isotope ratios are calculated to be ^{206}Pb/^{204}Pb = 18.63, ^{207}Pb/^{204}Pb = 15.62, and ^{208}Pb/^{204}Pb = 38.35. These values, especially the relatively high ^{207}Pb/^{204}Pb, indicate that the Pb in the diabase magmas was not derived from an ancient equivalent of the typical modern mid-ocean ridge basalt (MORB) source. It would be difficult to generate such high ^{207}Pb/^{204}Pb values in a typical MORB-like source, even if U was added to the diabase during some early alteration event and subsequently removed during recent weathering, because the amount of U that would need to be added and then removed in order to support the observed ^{207}Pb/^{204}Pb would have resulted in much higher present day ^{206}Pb/^{204}Pb ratios than observed. However, some of the extremely radiogenic values known from modern MORB can be projected back to compositions similar to calculated Flat Creek diabase initial ratios, and so a MORB-like source can not be unequivocally ruled out.

Poe Bridge Mountain amphibolite: The Poe Bridge Mountain Group of the late Precambrian(?) Ashland- Wedowee belt of Alabama (see Tull, 1978) is the host rock of the Stone Hill volcanogenic sulfide deposit. Whole-rock analysis of the amphibolite unit (collected from drill core kept at Ducktown) that encloses the ore is reported in Table 3 and shown relative to other whole-rock data in Figure 3. In this case, we can calculate model ages based on the measured U/Pb and Th/Pb ratios and the assumption that galenas in the Stone Hill deposit reflect initial Pb isotope ratios. The model ages so obtained are 812 Ma and 966 Ma for the ^{238}U-^{206}Pb and ^{235}U-^{207}Pb systems, respectively, and 652 Ma for Th-Pb. The Th-Pb age seems reasonable but, of course, is only a model age. The high U-Pb ages probably indicates that the U-Pb system has been disturbed but it is also possible that Stone Hill galenas do not reflect initial ratios. In either case, the Stone Hill galena values have Pb isotope ratios that are plausible for a typical MORB-like source material.

DISCUSSION

The locations of areas of the Piedmont for which Pb isotope data are available are shown in Figure 7. The numbers assigned locations in Figure 7 are explained in Table 4.

Sulfide minerals in deposits associated with volcanic and plutonic rocks of the southern Appalachian Piedmont have Pb isotope ratios that are thought to be
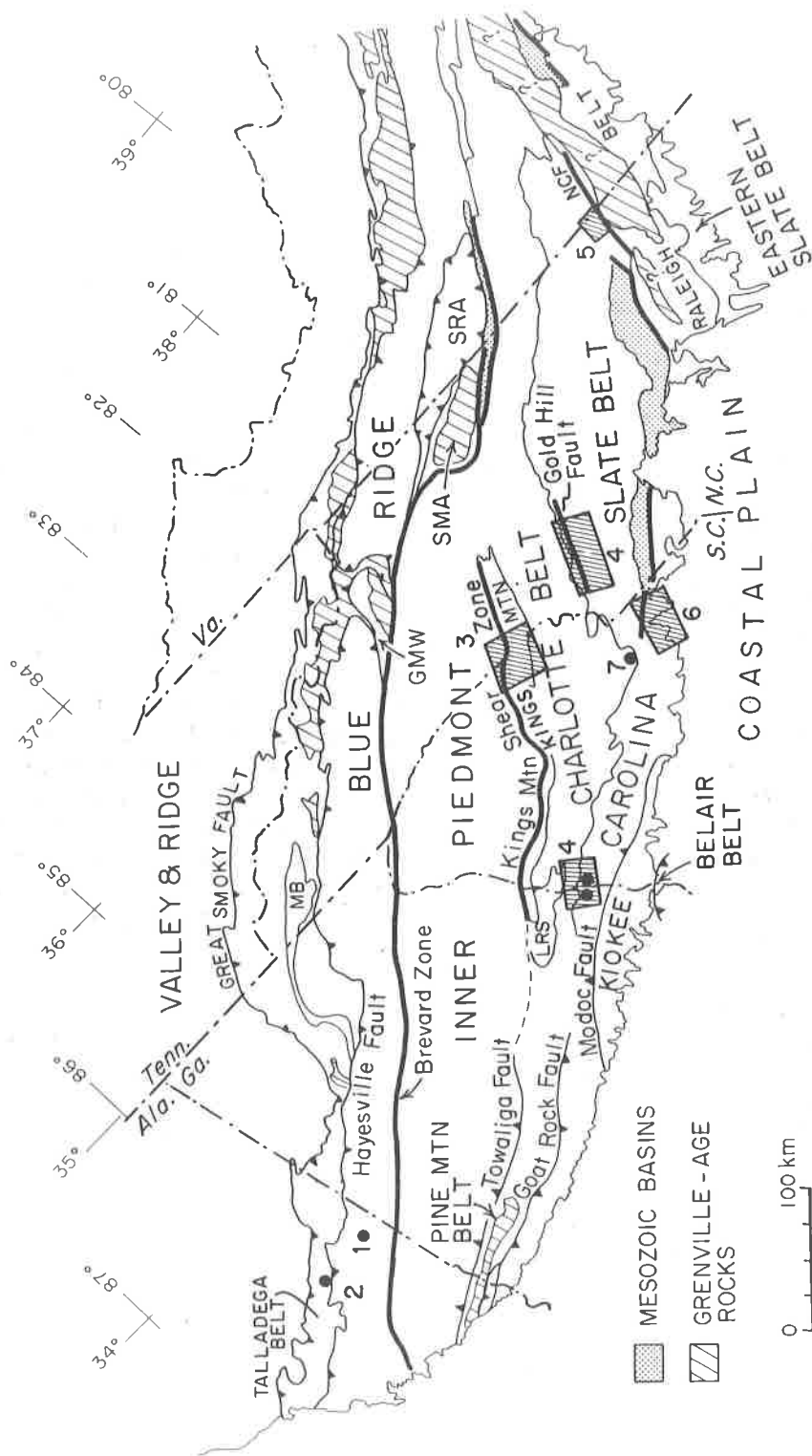
Figure 7. Index map of the southern Appalachians showing locations of rocks for which initial Pb isotope ratios can be inferred. Key to location numbers is in Table 4. Abbreviations: LRS - Little River Series; GMW - Grandfather Mountain window; MB - Murphy belt; NCF Nutbush Creek Fault; SMA - Sauratown Mountain anticlinorium; SRA - Smith River allochthon.

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representative of the initial ratios of their host rocks. In the case of the Hamme tungsten-Vance County pluton association (above) and the area around the Haile and Brewer mines in the "Carolina slate belt" of South Carolina (LeHuray, 1987), the sulfides have been clearly shown to approximate initial, local magmatic Pb. The Kings Creek barite deposit of the Kings Mountain belt has galena Pb isotope ratios that may reasonably be inferred to reflect the initials of the metatonalite-metavolcanic sequence (LeHuray, 1986), as may (based on the single whole rock analysis) the Stone Hill galenas reflect the protolith of the local amphibolite (above).

The polymetallic massive sulfide deposits of the slate belt are, in all likelihood, representative of the average Pb isotope ratios in the slate belt volcanic arc (LeHuray, 1982). The clue to this last point does not lie in Pb systematics of the slate belt volcanics themselves, because none have been analyzed. Rather, that the ores reflect the initial composition of the rocks may be inferred from comparison with examples in young volcanic arcs. The steep slope of the $^{207}Pb/^{204}Pb$ - $^{206}Pb/^{204}Pb$ trend seen in Cascades ore deposits has been shown to match that in Cascades basalts and andesites (Church and others, 1986), and the Cascades mantle-crust mixing trend, which is what the steep slope is interpreted to be, is virtually identical to trends reported for rocks from the Aleutians (Kay and others, 1978; Morris and Hart, 1983) and from the Marianas (Meijer, 1976; Woodhead and Fraser, 1985) and similar to trends in other volcanic arcs. Other than in regions underlain by very old, U-depleted granulites, such steep $^{207}Pb/^{206}Pb$ trends in rocks and ores are only observed in arc-related volcanics. Because there is no evidence that the Carolina slate belt proper (i.e. excluding the problematic Haile-Brewer block) is (or was) underlain by very old continental crust, and because of the general concensus that the slate belt was a marginal volcanic arc (Whitney and others, 1978; Rogers, 1982), we may be reasonably confident that the steep $^{207}Pb/^{206}Pb$ slope in slate belt volcanogenic massive sulfide deposits (Figure 8) is reflecting the ancient volcanic arc mixing trend. This is not to imply that the slate belt might not represent, at least in part, intra-arc rift volcanism (cf. Long, 1979). Indeed, comparisons of Carolina slate belt mineralization with the Kuroko deposits of Japan must lead to consideration of the implications for the Carolina slate belt of the evidence for an extensional setting for the Green Tuff region (Cathles and others, 1983; Ohmoto, 1983).

Whether the Kings Mountain belt slope also reflects an arc type mantle-crust mixing trend is less certain because of the ambiguity in the relationships among rocks and between rocks and ores (LeHuray, 1986; Horton and others, 1987). Based purely on the steep slope of the Pb isotopic trend, one could argue for a volcanic arc setting, but more evidence is required for definitive assignment of tectonic setting.

The initial Pb isotope ratios of the 571 ± 17 Ma Vance County Pluton have significantly more radiogenic $^{206}Pb/^{204}Pb$ that the values indicated for the volcanic sequence in the more southern parts of the slate belt (Figure 8), which generally have U-Pb zircon ages of ≈550 Ma (Wright and Seiders, 1980; Carpenter and others, 1982). A different mix of source materials can be inferred for the pluton. Partial melting of older pre-existing arc-derived materials, that is, of materials derived from a source with Pb isotope ratios lying along an arc-like "crust — mantle" mixing trend such as is preserved in slate belt ores (Figure 8), could adequately explain the high $^{206}Pb/^{204}Pb$ as well as the $^{207}Pb/^{204}Pb$, which is intermediate between MORB-like values and fully continental values.
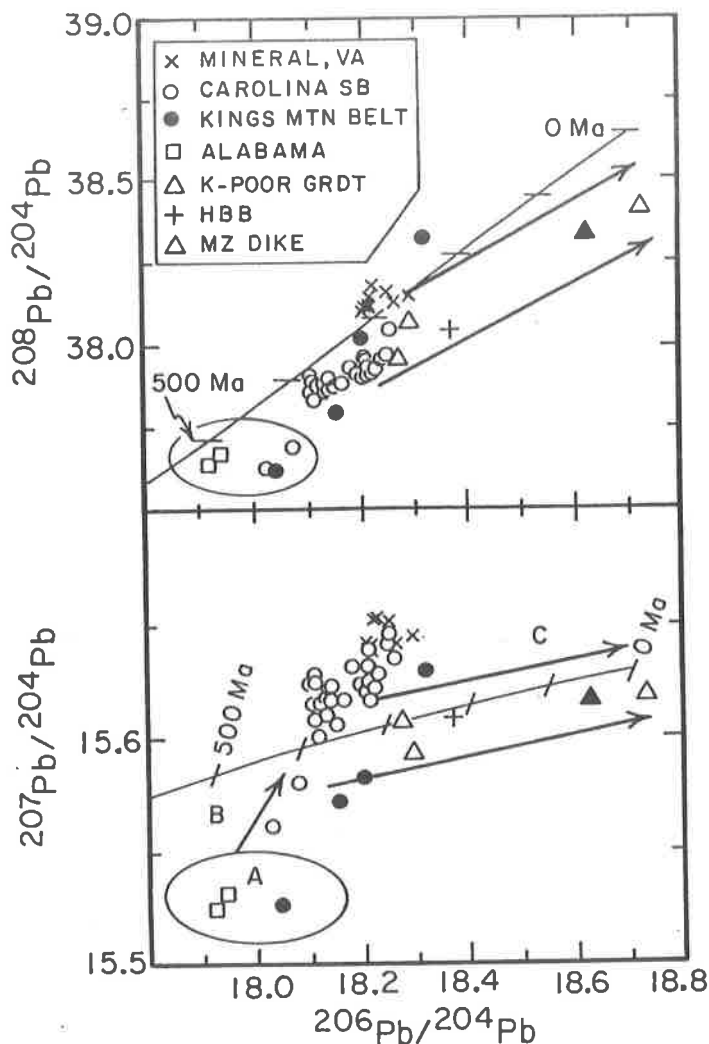
Figure 8. Lead isotope ratio diagrams showing calculated and inferred initial ratios for various rock units of the southern Piedmont, as well as galena ratios from Piedmont volcanogenic massive sulfide deposits that are believed to preserve the isotopic characteristics of their host rocks. Data are from this paper and LeHuray (1982, 1986, 1987). Data from the Great Falls Granite are not shown in order to maintain resolvability of other data.

The initial Pb isotope ratios of the Haile area volcanics, derived from U-Pb and Th-Pb isochrons, are $^{206}Pb/^{204}Pb = 18.37 \pm .08$, $^{207}Pb/^{204}Pb \approx 15.61$, and $^{208}Pb/^{204}Pb = 38.05 \pm .12$. These are also significantly different from the slate belt values indicated by polymetallic ores. Once again, a different mix of source materials can be inferred. Like the Vance County pluton, the Haile area initial ratios could be explained by derivation from sediments with provenance in an older arc. The presence of an inherited, possibly Grenville-age, fraction of zircons, however, could be taken as evidence of a more complex source history for Haile area volcanics.

Initial Pb isotope ratios inferred for the various pre-Alleghanian lithologies of

Figure 7 are listed in Table 4 and shown in Figure 8. The rationale for use of the Lincolnton (southern location 4 in Figure 7) and Arbemarle (northern location 4 in Figure 7) area sulfides as representative of their host Carolina slate belt rocks is, as discussed above, based on comparison with relationships between sulfides and host volcanics in young volcanic arcs. The rationale for the suggestion that sulfide Pb reflects the initial Pb in the Poe Bridge Mountain amphibolite (location 1) and the Hillabee greenstone (location 2), both of which likely formed in rift settings, lies in comparison of Pb isotope ratios in modern sulfides forming on active ridges, which have been shown to faithfully record the isotopic characteristics of their host rocks (LeHuray and others, 1988).

INITIAL RATIO VARIATIONS IN THE PIEDMONT

From the measured and inferred initial Pb isotope ratios we can discern four distinct "types" of isotopic trends in Piedmont rocks and ores. The four types may be described as those containing: A) Pb derived from a MORB-mantle like source; B) Arc-like "mantle-crust" mixing trends; C) Pb possibly derived from older arc-like source material; and D) unequivocal indications of long term continental residency of precursors.

A. Rocks and ores that can reasonably be described as reflecting derivation from a source resembling the MORB mantle (field A in Figure 8) include 1) metatonalites and the Battleground Schist of the Kings Mountain belt, whose initial ratio is preserved in galena from the Kings Creek barite deposit; 2) galena in the Stone Hill massive sulfide deposit, Alabama, which may reasonably be inferred to preserve the initial characteristics of the host Poe Bridge Mountain amphibolite; and 3) the Pyriton deposit, which is hosted by the Hillabee greenstone in the Talladega belt of Alabama. Each of these units has Pb isotope ratios that indicate probable derivation from the MORB-source mantle, with little or no crustal contamination. The $^{207}Pb/^{204}Pb$ ratios of these southern Appalachian representatives of ancient MORB are not as low as those found in the Elizabeth mine, Vermont (LeHuray, unpub.), the Central Mobile belt of Newfoundland (Swinden and Thorpe, 1984; Swinden, pers. comm.), or the Devonian West Shasta district of California (Doe and others, 1985), and thus could be interpreted as somewhat contaminated. However, from studies of modern MORB we know that $^{207}Pb/^{204}Pb$ in the MORB source mantle has a considerable range of values, and thus we can not be certain of the extent to which the southern Piedmont MORB ratios deviate from "pristine".

B. The arc-like "mantle-crust" mixing trend is represented in Figure 8 by the arrow labeled "B". Comparison with modern analogues indicate that this trend reflects mixture between the MORB-source mantle and penecontemporaneous oceanic sediments. In the southern Appalachians, one such trend is preserved in volcanogenic massive sulfide deposits of the Carolina slate belt and another, more speculatively, in Kings Mountain belt ores. The ores at Mineral, Virginia, probably represent a nearly "pure" oceanic sediment source of Pb. The Pb isotope ratios preserved in these deposits, based on comparison with young arc and ocean ridge hydrothermal systems, are believed to reflect the initial isotope systematics of their host rocks, and so may be used to characterize the terrane in which the deposits occur.

C. The trend labeled "C" in Figure 8, and marked by subparallel arrows, represents rocks that are interpreted as having derived their Pb from older volcanic

arc material (whether *in situ* or in sediments). That is, the precursors may have had Pb isotope ratios lying along a steep arc-like trend. As studies of modern analogues reveal, many arcs are dominated by such trends, and thus the precursors for the southern Appalachian rocks lying along trend "C" can not be definitely associated with any particular older arc by isotopic means. It seems likely, based on geologic relationships, that the precursor arc for the Virgilina area albite granodiorites was the underlying ≈620 Ma volcanics, and was distinct from the precursor arc for the Haile-Brewer block.

The apparent presence of an inherited component of zircons in Haile-Brewer block volcanics and the nearby Great Falls Granite is clearly in contrast with the slate belt in the Albemarle (Wright and Seiders, 1980), Lincolnton (Carpenter and others, 1982) and Virgilina (Glover and Sinha, 1973; this paper) areas. This preliminary zircon work seems to support the view expressed in LeHuray (1987) that the relationship between the Haile-Brewer block and the Carolina slate belt to the north and south needs clarification.

One way to reconcile the presence of inherited zircons and the "C" trend whole rock Pb isotope ratios in Haile-Brewer block volcanics would be to envision a precursor dominated by arc-derived sediments with a small component of continental detritus that contained most of the zircon. Another way would be to postulate that the zircons were added to the volcanoclastics during (by entraining non-volcanic wall rock) or after (by sedimentary processes) eruption.

D. The fourth isotopic trend consists of the Great Falls Granite, which can be unequivocally interpreted as having derived from old continental crustal material. This trend is not shown on Figure 8 so that the other data can remain resolvable.

At this early stage of our understanding of isotopic characteristics of the southern Piedmont, it is difficult to make more than general conclusions. The results described in this and previous papers may be outlined as indicating Pb isotope ratios with continental isotopic affinities to the west of the Kings Mountain shear zone (LeHuray, 1986), arc-like and MORB-like isotopic affinities in terranes east of the Inner Piedmont, and indications of continental influence reappearing towards the southeast. Although the currently available data base is scanty, the possible presence of Grenville-age zircons in volcanics of the Haile-Brewer block and the continental characteristics of Pb isotope ratios in the Great Falls Granite suggest that these units have been strongly influenced by continental crust.

ACKNOWLEDGMENTS

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APPENDIX: SAMPLE LOCATIONS

Vance County Pluton, Carolina slate belt

HW-144U, HW-181U, and HW-192U. From the vein NW of #6 shaft, 900 level, of Hamme Tungsten mine. Collected by J.E. Gair, U.S.G.S., Reston.

APL81-1. From "State Line" quarry. 36°32.5'N 78°26.5'W

APL81-2. From quarry in Crooked Run, NW of Henderson, N.C. 36°22'N 78°27.6'W.

Roxboro Pluton plagioclase was provided by S.A. Kish.

Haile-Brewer area, "Carolina slate belt" HB-3. Partially sericitized felsic volcanoclastic rock on strike with Haile mine, on County Road 221 about 1.2 km NW of Kershaw, S.C. 32°30.6'N 80°35.9'W. Photomicrographs of a thin section of this rock are published in LeHuray (1987).

Great Falls Granite, Charlotte belt

HB-9. Behind Rocky Creek hydroelectric plant. Same location as SC-150 of Fullagar (1971). 34°32.4'N 80°52.7'W.

HB-10. Same location as SC-151 of Fullagar (1971). 34°31.5'N 80°55.4'W.

HB-11. Same location as SC-107 of Fullagar (1971). 34°32.2'N 80°55.1'W.

Flat Creek diabase dike (intrudes Haile-Brewer area of "Carolina slate belt")

DD-201. On U.S. 601, NE of Midway, S.C. 34°38.9'N, 80°31'W.

Poe Bridge Mountain Group amphibolite, Northern Alabama Piedmont

DK-60. Collected from drill core of the Stone Hill deposit kept at Ducktown (Stone Hill d.d.h. 13, 139-143'). The Stone Hill copper mine is in Cleburne and Randolph Counties, Alabama, at 33°21.6'N 85°45.3'W (Sect. 35, T-17S, R-11E).

CHARACTERISTICS AND IMPLICATIONS OF A CONODONT FAUNA FROM A METAMORPHOSED CARBONATE SEQUENCE IN CHILTON COUNTY, ALABAMA

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ABSTRACT

A sequence of carbonate rocks of Ordovician age, approximately 1,500 feet thick in Chilton County, Alabama, is separated from Mississippian sedimentary rocks (Floyd Shale and Parkwood Formation) to the northwest by the Shelby Springs (reverse) fault. The carbonate sequence is structurally overlain to the southeast by a metamorphic sequence of slate and quartzite. Some authors have interpreted the latter boundary as a reverse fault also, and the age of the slate-quartzite sequence as Precambrian(?) or lowermost Cambrian (Waxahatchee slate of the Kahatchee Mountain Group). Others have considered the contact as an unconformity and the age of the slate-quartzite sequence as younger (Mississippian) than the subjacent carbonates. Radiometric dates obtained from rocks structurally (and stratigraphically?) higher in the Kahatchee Mountain Group suggest that metamorphism of the rocks occurred no later than Early Devonian.

Petrological characteristics and megafaunal assemblages suggest that the lower part of the carbonate sequence is Newala Limestone (Early Ordovician) and that the upper part is the Odenville facies of the Newala. Conodont assemblages from the upper part of the carbonate sequence confirm the latter assignment and limit the minimum age of the carbonate rocks to latest Canadian.

Affinities of the Newala and Odenville at this locality with the overlying metamorphic sequence, rather than with the Mississippian sedimentary rocks across the Shelby Springs fault to the northwest, are suggested by the following: 1) the color alteration index and surface textures of the conodonts suggest that the carbonate rocks have been subjected to a temperature of about 300° C. 2) Adjacent rocks on both sides of the Shelby Springs fault are severely folded, sheared, and veined with quartz and carbonate minerals. By contrast, the rocks adjacent to the contact between the carbonate and slate-quartzite sequences are markedly less deformed: bedding on either side of the contact is apparently parallel, the rocks are only mildly folded, and there is little mineral veining in the rocks. 3) Petrographic examination of the carbonate rocks reveals variable degrees of allochem strain, but no consistent pattern of change in degree of strain across the carbonate exposure belt, except for rocks adjacent to the Shelby Springs fault.

The contact is not considered to be a fault contact. Because of the common occurrence of a regional unconformity that elsewhere overlies rocks equivalent to the Newala and Odenville of this area, the contact is considered to be

unconformable, and the age of the slate-quartzite sequence at this locality as no older than Early Ordovician. The slate-quartzite sequence is therefore either 1) not part of the Precambrian(?) or lowermost Cambrian Waxahatchee slate of Kahatchee Mountain Group, or 2) the age of the lower part of the Kahatchee Mountain Group is misunderstood.

The Newala, Odenville, and the slate-quartzite sequence were, after metamorphism by Early Devonian, faulted northwestward onto the Floyd-Parkwood, probably during the Alleghenian orogeny.

INTRODUCTION

Purpose

Disagreement exists as to the structural and stratigraphic relationships between the largely unmetamorphosed Paleozoic rocks of the southeasternmost Valley and Ridge in Alabama and the low-rank metamorphic rocks that lie adjacent to the southeast. An Ordovician carbonate sequence occurs locally at the boundary between the two in Chilton County, Alabama, and an understanding of its relationships to the rocks on either side is considered to be critical to the resolution of the disagreement.

The carbonate sequence is separated from rocks of the Valley and Ridge to the northwest by a southeasterly dipping reverse fault. The nature of the similarly dipping contact between the carbonate sequence and the structurally superjacent metamorphic rocks to the southeast, on the other hand, is a matter of dispute. Whether this boundary is a reverse fault, an unconformity, or a normal depositional contact is important to the interpretation of the relative ages of the carbonate and metamorphic sequences. It was believed (TJC) that if conodonts were obtained from the carbonate sequence, the age(s) of the carbonate rocks could be better defined and in addition, the condition (color alteration index) of the conodonts might indicate the maximum temperature that affected the host carbonates since their deposition. Determination of the maximum temperature might in turn suggest affinities of the carbonate sequence with either the unmetamorphosed Paleozoic rocks to the northwest or with the metamorphic rocks lying to the southeast.

Location

The study area (Figure 1) lies southwest of the community of Minooka and northwest of the community of Ocampo (Montevallo 7.5-minute Topographic Quadrangle, U.S.G.S., 1980) in northern Chilton County, Alabama, about 35 miles south of Birmingham. The sequence of carbonates studied is exposed near and along Watson Creek and its tributaries, west of U.S. Highway 31.

Geologic Setting and Previous Work

The carbonate rocks of this study are bounded on the northwest by a generally northeast-trending, southeast-dipping high-angle reverse fault (Carrington, 1967, 1973) that separates the typically unmetamorphosed Floyd Shale and/or Parkwood Formation (Mississippian) of the Valley and Ridge on the northwest from carbonate rocks on the southeast (Figure 1). This fault, the Shelby Springs fault of McCalley (1897) and Guthrie (1985) [=? the Metamorphic Front fault of
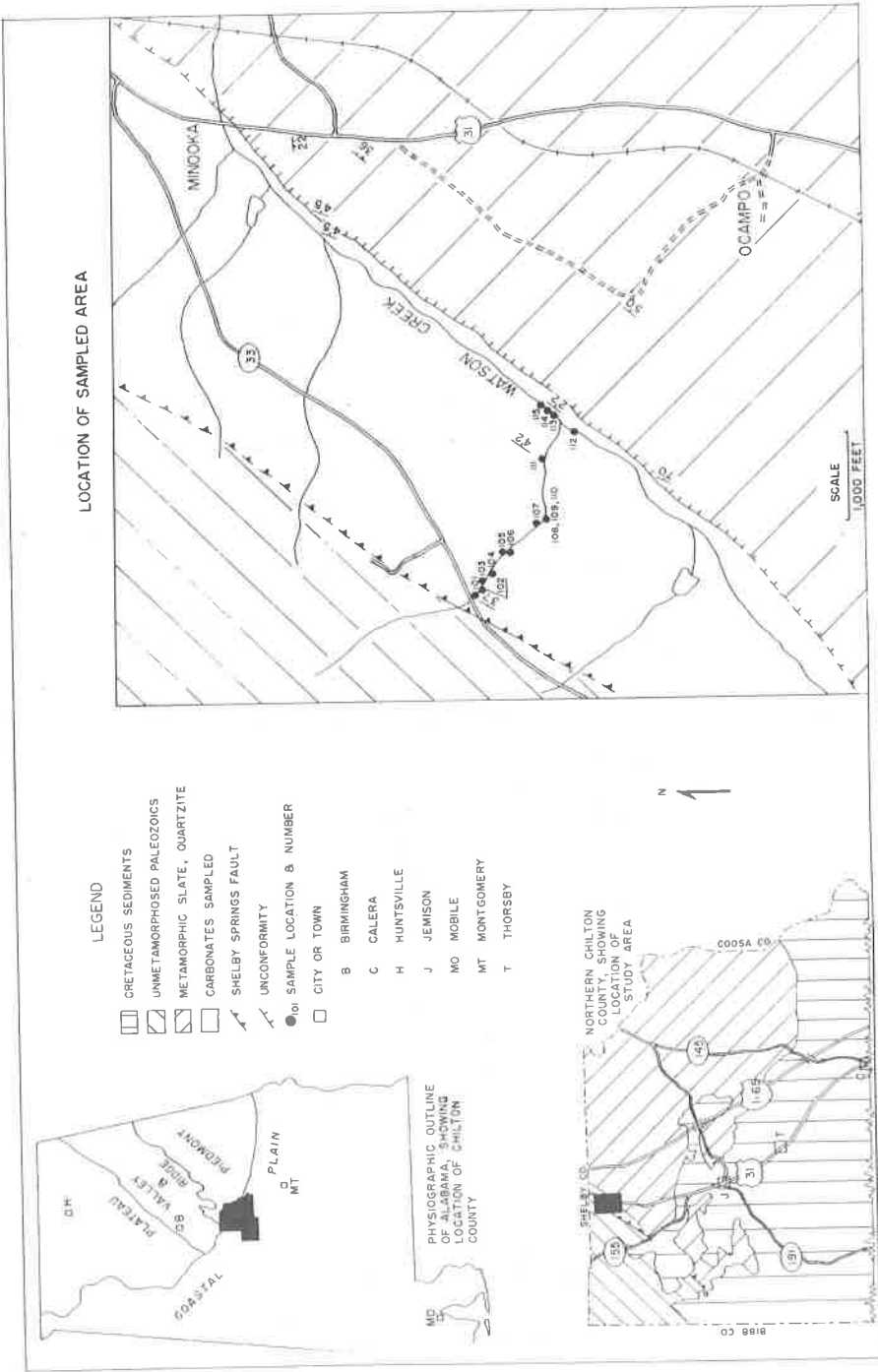
Figure 1. Location and general geology of the study area. Black areas show successively larger-scale map locations. Sampling locations are shown on the map at right.

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Carrington (1972a, 1972b), the Talladega Front fault of Thomas and Neathery (1980), and the Talladega-Cartersville fault of Tull (1982a, 1982b)], may presently be placed within a few feet where it is crossed by Alabama Highway 33 in the study area. The name "Shelby Springs fault" is preferred for this fault in Chilton and Shelby Counties because McCalley's use in 1897 has precedence.

Butts (1926, p. 203) apparently thought the carbonate sequence was part of the Floyd Shale, and therefore of Mississippian age. K. E. Richter (Alabama Geological Survey, written communication, 1967) considered the sequence to consist of Newala Limestone (Early Ordovician) overlain by either Odenville Limestone (Early Ordovician) or Lenoir Limestone (Middle Ordovician). Carrington (1972a, 1972b, 1973) mapped the sequence as Newala Limestone overlain (on the basis of lithologies present and the apparently mistaken identification of Maclurites) by Lenoir Limestone.

According to Butts (1926), the Newala Limestone was named for exposures in the vicinity of Newala post office, Shelby County, Alabama. He describes the formation as about 1000 feet thick in Cahaba Valley, and as consisting of predominant thick-bedded, compact, mainly pearl-gray limestone with relatively minor beds and interfingerings of dolostone. On the basis of fossil content, the Newala was interpreted as of Beekmantown (Early Ordovician) age.

Taylor (1971), in a study of a 140-foot cored sequence of the Newala near Lake Purdy (Cahaba Valley, approximately 8.5 miles southeast of Birmingham and about 28 miles north of the area of this study) described the lithotypes present, but not their stratigraphic positions in the formation. It is not clear that the cored section represents the entire thickness of the formation. Of 28 samples studied, the most predominant lithotype was pelletal lime packstone, followed in decreasing order of abundance by stromatolitic lime mudstone, intraclastic lime packstone, intraclastic-pelletal lime packstone, unfossiliferous laminated dolomite mudstone, intraclastic lime grainstone, and snail-bearing pelletal lime packstone. Based on sedimentary structures and textures, and on the dearth of fossils, he (Taylor, 1971) interpreted the depositional conditions as those of a tidal flat environment.

Roberson (1988) described the Newala Limestone in the Valley and Ridge as being about 500 feet thick and composed of "massive-bedded, compact, high-calcium limestone intercalated with discrete beds of dolostone", with the dolostone beds being more numerous and thicker near the base and top of the formation. The limestone ranges from "beige to medium dark gray, with an intermediate dove-gray being the most characteristic color". Lithotypes include a predominance of carbonate mudstone and peloidal packstone/ grainstone with minor quantities of intraclastic grainstone and algal-laminated mudstone. Extensive bioturbation is suggested by "vague, mottled zones". Fossis are generally uncommon, but are dominated by euryhyaline forms such as gastropods and ostracodes. Some cephalopods and brachiopods are present. The deposition of the Newala was interpreted to have been in a restricted, intertidal marine environment, and the age as late Early Ordovician (late Canadian).

As contrasted with Butts' (1926) description of a single exposed sequence of Odenville Limestone, "about 50 feet thick" near Odenville, St. Clair County, Alabama, Roberson (1988) found the Odenville Limestone to extend in a main outcrop belt in Cahaba Valley from the town of Odenville southwestward to the Gulf Coastal Plain overlap— a distance of about 54 miles. The Odenville is also repeated in the Cahaba Valley along the traces of the Cahaba Valley and Dry Creek faults, and apparently occurs outside the Cahaba Valley at Columbiana (Shelby

County) and "in a metamorphosed state in a thrust slice near Minooka in northwest Chilton County."

According to Roberson (1988), the Odenville reaches a maximum thickness of about 366 feet near Lake Purdy from which point it thins along strike to the southwest and northeast, and across strike to the northwest. The Odenville is gradational with the underlying Newala Limestone and the contact between the two was arbitrarily placed at the top of the highest dolostone bed characteristic of the subjacent Newala. The formation is divided into two members, the lower of which is dominated by burrow-mottled wackestone (medium gray lime mud laced by a network of dolomitic and argillaceous burrows). Oncoidal skeletal wackestone, high-calcium lime mudstone, and stylenonodular skeletal wackestone lithotypes constitute a minor proportion of the lower member. The thickness of the lower member ranges from 50 to 100 feet.

The upper member, which is as much as 275 feet thick, is dominated by stylenonodular wackestone, with subordinate amounts of burrow-mottled wackestone, sponge-dominated bindstone, back-reef breccia, and dolomitic algal stromatolite lithotypes. Near the middle of the upper member where the thickest section is exposed, Roberson (1988) recognized "Zone F" which marks the part of the upper member where there is the greatest faunal abundance, the greatest faunal diversity, the highest clay content, and the darkest color (black) in the Odenville Limestone. This zone is regarded as representing deposition during the greatest transgression of the shoreline, after which regressive conditions prevailed. Fossils (including conodonts) from "Zone F" suggest (Roberson, 1988) a very latest Canadian age, but at Leeds, Alabama, fossils from the highest beds (dolomitic algal stromatolite lithotype) of the Odenville suggest an even younger age [very latest Canadian (Lower Ordovician) or earliest Whiterockian (Middle Ordovician)].

The carbonate rocks of this study are overlain to the southeast by a 1,300- to 3,000-foot-thick sequence of gray slate— the Waxahatchee Slate (Butts, 1940) of the Precambrian(?) to Cambrian (Tull, 1982a, Tull and others, 1988, Guthrie and Tull, 1985) Kahatchee Mountain Group, the Cambrian Stumps Creek Formation (Guthrie, 1985), or metamorphosed Mississippian Floyd Shale (Carrington, 1973). Two K-Ar whole-rock analyses of samples collected about 8 to 10 miles to the southeast, and structurally (and stratigraphically?) higher [Wash Creek Slate (Butts, 1940) of the Kahatchee Mountain Group (Tull, 1982a)] than these basal metasedimentary rocks gave ages of 396 ± 8 m.y. and 417 ± 8 m.y., which are thought to represent ages of metamorphism (Kish and Harper, 1973; Tull, 1982a). If the metamorphic sequence overlying the carbonates of this study is stratigraphically continuous with the rocks providing the radiometric dates, a Mississippian age cannot be correct. White (5YR 8/1), tan (7.5YR 8/2), to gray (7.5YR 5/0) medium- to coarse-grained micaceous and feldspathic quartzites occur at or near the base and sporadically throughout the slate sequence. Thicknesses of quartzite beds range from 1 inch to 4 feet.

The contact between the carbonates and the quartzites at the base of the overlying slate sequence generally parallels Watson Creek and was mapped as a fault by Butts (1926, 1940), Tull (1982a, 1982b), and Guthrie (1985). The average strike and dip of the carbonates is N.35° E., 37° E., and average strike and dip of the rocks of the adjacent slate sequence is N.49° E., 48° SE. Few of the measurements resulting in these average attitudes were taken adjacent to the contact, because of poor exposures. In 1967, scouring along Watson Creek exposed the contact, which was examined on several occasions by Richter and the

senior author (TJC). The relative lack of shear and deformation in the rocks and the apparent parallelism of beds adjacent to the contact are in sharp contrast to the highly folded, fractured, and sheared rocks adjacent to the Shelby Springs fault, less than 0.6 mile away. The contact was therefore not believed to be a fault contact.

In this region, several unconformities present in the Paleozoic sequence at Birmingham merge irregularly to the south, southeast, and east (for details, see Copeland, Carrington, and Smith, 1965; Copeland and Carrington, 1965; Carrington, 1967, 1972a, 1972b, 1973; Thomas and Drahovzal, 1973; Thomas, 1982; and Benson, 1986). The lowest of these unconformities may be underlain by rocks ranging from Upper Cambrian [Copper Ridge Dolomite of the Knox Group (Butts, 1926; Benson, 1986)] to Middle Ordovician in age [Athens Shale (Decker, 1952; Copeland and Carrington, 1965)]. In the vicinity of Calera, about four miles to the north of the study area, rocks of Middle Ordovician age are overlain by a thin Middle Devonian sandstone, which is in turn overlain by Lower Mississippian chert. Because the lowest of these unconformities locally overlies rocks of equivalent age to the carbonate rocks of this study, the contact was interpreted (Carrington 1967, 1972a, 1972b, 1973) to be unconformable, rather than a normal one reflecting a change in depositional conditions.

Methods

Sample collection and examination of outcrops was by the senior author (TJC) and several colleagues. Conodonts were recovered (by TJC) using standard techniques with acetic acid, bromoform, and 16- and 150-mesh screen fractions. Conodont identifications and interpretation of the conodont assemblage was done by the second author (DER). Thin sections and polished and etched slabs were prepared from the samples by TJC and a colleague, whereas petrographic analysis of the thin sections and slabs was done by the junior author (JCP).

Samples were collected systematically from exposures along a tributary to, and along, Watson Creek (Figure 1). Samples 101 through 112 are numbered in ascending stratigraphic order, but the stratigraphic relationships of sample numbers 113 through 115 are uncertain because of the irregular occurrence of exposures and the undulatory nature of bedding contacts along the winding course of Watson Creek.

Colors used in the description of rocks are followed by a Munsell Color Charts (1975 Edition) hue and chroma designation.

RESULTS

General Description of the Carbonate Rocks

The thickness of the carbonate sequence, based on outcrop width and average dip, is between 1,440 and 1,600 feet. The lower part (about 890 feet) of the sequence is characterized by alternating beds (as much as 6 feet thick) of limestone and dolostone with sporadic thin, discontinuous beds, lenses, and nodules of light-gray to light-tan (7.5YR 7/2 to 2.5Y 6/2) chert. The limestone interbeds are light to medium gray (2.5Y 8/0 to 2.5Y 6/2), finely crystalline to micritic, and contain irregular patches of darker gray dolomite. The dolostone interbeds are light gray to medium brownish gray (7.5YR 8/0 to 10YR 5/1) and range from sucrosic to medium crystalline. "Floating" quartz grains and anastomosing silty laminae (stylolites)

occur sporadically. Both limestone and dolostone contain carbonate and (less commonly) quartz fracture fillings. Near the top (between Samples 108 and 109, Figure 1) are thin (as much as 2.5 inches thick) beds or concentrations of well-rounded and frosted silt- to sand-sized quartz grains. In the lower part of the sequence (adjacent to the Shelby Springs fault), the rocks are severely folded, fractured, joint-filled, and recrystallized.

The upper part (about 630 feet) of the carbonate sequence is characterized by light- to medium-gray (7.5YR 6/0 to 7.5YR 3/0), finely crystalline to micritic limestone in beds up to 5 feet in thickness. Locally, the beds exhibit abundant anastomosing silty layers, and light- to medium-gray (7.5YR 8/0 to 7.5YR 5/0) chert occurs in irregular beds and lenses. Rare orthocone cephalopods and several types of small brachiopods are present. Although bedding attitudes are variable throughout the sequence, no increase in the degree of deformation (folding, fracturing, or recrystallization) is present adjacent to the contact with the overlying slate sequence.

Petrographic Analysis of the Carbonate Rocks

All samples are composed of carbonate, or carbonate replaced by chert. The carbonate content ranges from greater than 90 percent calcite to greater than 90 percent dolomite. Fine-grained, bedded to lenticular chert replacing carbonate occurs sporadically. Allochems include pellets, bioclastic debris, rounded intraclasts, and quartz sand grains. No ooids were noted, but skeletal grains commonly exhibit micritic coatings. Although allochems are variably strained (stretched and/or fractured) through the sequence, no pattern of increase or decrease of strain across the exposed carbonate sequence was detected.

Pellets are the dominant allochem in samples from the lower part of the section (Samples 101 through 109), whereas skeletal debris predominates in the upper part (Samples 110-115). Sedimentary textures also are variable. Packstones are confined to the lower one-third of the section (Samples 101 through 104), but mudstones and wackestones characterize the upper two- thirds of the section (Samples 105-115). The mudstones and wackestones of Samples 111 through 115 are horizontally burrowed, resulting in a "swirled" appearance in slabs.

Megafossil assemblages also are divisible into two categories. Fossils in the lower part of the section (Samples 101-109) include small (2-6 mm) trilobites, gastropods, small (4-10 mm) brachiopods, and ostracodes. The upper part of the section (Samples 110-115) contains a more abundant and diverse faunal assemblage, characterized by echinoderms, brachiopods, pelecypods, trilobites, and sponge spicules (Sample 108). With the exception of echinoderms, fossils commonly are whole.

Micropaleontology

Five of the samples (110, 111, 113, 114, and 115), all from the upper part of the carbonate succession, yielded conodonts. The greatest number of conodont specimens was obtained from intensely stylolitized limestone samples. The conodonts recovered are black (color alteration index of 5, Epstein and others, 1977; Rejebian and others, 1987) and surfaces are pitted and grainy. Many specimens are in poor condition and are highly microfractured. Although many of

the fractures have been "healed", the specimens are fragile and easily broken during handling.

Species recovered (Table 1) comprise a primarily Midcontinent fauna characteristic of the upper part of Fauna E of Ethington and Clark (1971) and the correlative *Oepikodus communis* Zone (latest Canadian) of Ethington and Repetski (1984). Present correlations of Midcontinent and North Atlantic province faunas place this fauna in the *Oepikodus evae* Zone (upper lower Arenigian) of the latter province.

Table 1. Conodonts identified from limestone samples collected along Watson Creek and a tributary, northern Chilton County, Alabama.

Sample Number	Juanognathus jaanussoni	Juanognathus variabilis	Paltodus sp. s.f.	Protopanderodus gradatus	Oepikodus communis?	Reutterodus andinus?	Scolopodus carlae s.f.	Scolopodus rex paltodiformis s.f.	Scolopodus sp. s.f.
115					X				
114	X	X				X			
113	X	X		X		X			
112									
111		X	X				X	X	
110				X					X

Although records were not kept of the sizes of samples processed, *Juanognathus variabilis* Serpagli (Figure 2, Number 1a-c) and *J. jaanussoni* (Figure 2, Number 2) *Serpagli* (where present) are more numerous than other species (Table 1). Other identified species include *Protopanderodus gradatus* Serpagli, *Scolopodus rex paltodiformis* Lindström s.f., *Scolopodus carlae* Repetski s.f., *Reutterodus andinus*? *Serpagli*, and one possible element of *Oepikodus communis* (Ethington and Clark). Ethington and Repetski (1984) reported that *Juanognathus variabilis* and *Reutterodus andinus* are known only from the *Oepikodus communis* Zone, and therefore serve as important index fossils for the zone. *J. variabilis* has been reported previously from the San Juan Limestone of Argentina (Serpagli, 1974; the Lower Ordovician of Malaya (Igo and Koike, 1967); the Odenville Limestone and the Knox Group in Alabama (Repetski, 1982; Erickson, 1985); the Fillmore Formation of Utah (Ethington and Clark, 1971); the upper West Spring Creek Formation of Oklahoma (Potter, 1975); Nelson, New Zealand, and the Georgina Basin, Australia (Cooper and Druce, 1975); possibly the Mystic Conglomerate of Quebec (Barnes and Poplawski, 1973); and the upper part of the El Paso Group in Texas and New Mexico (Repetski, 1982).

Reutterodus andinus Serpagli has been reported from the San Juan Formation of Argentina (Serpagli, 1974) and possibly the El Paso Group in Texas and New Mexico (Repetski, 1982). Three elements (two unibranched and one conelike) assignable to *Reutterodus andinus*? were collected from samples 113 and 114 of this study. These specimens are almost identical to the conelike and unibranched elements reported by Repetski (1982, pl. 19, figs. 3 and 1, respectively) as

Reutterodus andinus?. The only difference is that the conelike element from the Watson Creek sample 114 has incipient denticulation along the basal part of the posterolateral costa. This element appears to be transitional between the conelike and unibranched elements figured by Serpagli (1974, text-figure 19).
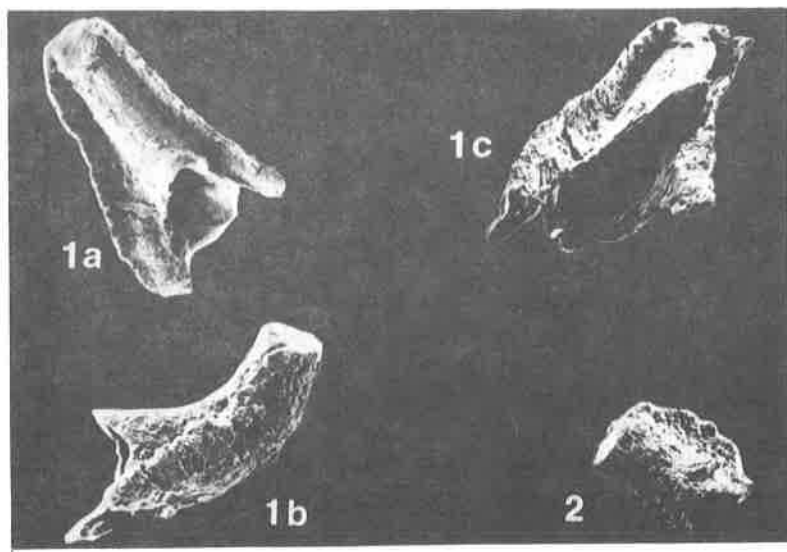
Figure 2. Number 1a-c. *Juanognathus variabilis* Serpagli 1a, posterior view. Sample 114. X100 1b, lateral view. Sample 114. X100 1c, posterior-basal view. Sample 114. X100
Number 2. *Juanognathus jaanussoni* Serpagli. Posterior view. Sample 113. X100

Juanognathus jaanussoni previously has been reported from the San Juan Limestone of Argentina (Serpagli, 1974), the Levis Formation of Quebec (Uyeno and Barnes, 1970), the uppermost part of the El Paso Group in Texas and New Mexico (Repetski, 1982) and the Knox Group in Shelby County, Alabama (Erickson, 1985). Serpagli (1974) concluded that *J. jaanussoni* is younger than and evolved from *J. variabilis* because *J. jaanussoni* occurs stratigraphically higher than *J. variabilis* in the San Juan Formation. Repetski (1982), however, reports that *J. jaanussoni* occurs with *J. variabilis*, although it is only present in the stratigraphically highest samples. *J. jaanussoni* therefore indicates the uppermost part of the *O. communis* Zone.
   J. jaanussoni occurs with *J. variabilis* in samples 113 and 114 from the Watson Creek locality. *J. variabilis* is also present in underlying strata (sample 111). Association of these two species and the presence of *Reutterodus andinus?* in samples 113 and 114 indicates that strata represented by samples 113 and 114 are assignable to the uppermost part of the *O. communis* Zone.
   Scolopodus carlae Repetski s.f. first occurs high within the range of Fauna D (Ethington and Clark, 1971) and does not extend above the *O. communis* Zone. Repetski (1982) reported occurrences of *S. carlae* s.f. in the Jefferson City Dolomite of Missouri, the Nine-mile Formation of Nevada, the West Spring Creek Formation of Oklahoma (Potter, 1975) and the El Paso Group in Texas and New Mexico. Only one specimen of this distinctive species was found in sample 111 of this study.

Protopanderodus gradatus Serpagli first appears within the *O. communis* Zone but also ranges into younger strata (Ethington and Repetski, 1984). Repetski (1982) reported that *P. gradatus* is present in the San Juan Limestone of Argentina (Serpagli, 1974), possibly the Marathon Limestone of Texas (Graves and Ellison, 1941) and the upper El Paso Group of Texas and New Mexico. *P. gradatus* was present in samples 110 and 113 of this study, indicating that the base of the *O. communis* Zone occurs just beneath strata from which sample 110 was taken. *P. gradatus* has been reported from faunas of both the Midcontinent and North Atlantic provinces.

Scolopodus rex paltodiformis Lindstrom s.f. ranges from Fauna D through Fauna E (Repetski, 1982). This species is known only from Sweden (Lindstrom, 1955), Nevada (Ethington, 1972) and Texas (Repetski, 1982). In Fauna D, *Scolopodus rex* characterizes a population (North Atlantic Province) that typically occurs in open-ocean deposits (Ethington and Repetski, 1984). *S. rex paltodiformis* s.f. was recovered from sample 111 of this study.

DISCUSSION

The carbonate sequence has conspicuous lithological and paleontological similarities to the upper part of the Knox Group (Longview and Newala Limestones) and overlying Lenoir Limestone in Alabama (Pruneau, 1987). The peloidal packstones and mudstones (Samples 101-109) contain a relatively impoverished fauna much like the peloidal grainstones-to-mudstones of the Longview and Newala of the upper part of the Knox Group. These lithologies are interpreted as shallow marine-shelf deposits on the basis of abundance of peloids and their relatively impoverished fauna (Enos, 1983). The fossiliferous mudstones and wackestones (Samples 110-115) contain a macrofaunal assemblage that closely resembles that of the Odenville facies of the Newala Limestone. These strata probably represent below-wave-base deposits in a marine environment that was well-circulated, as indicated by faunal diversity and the presence of stenohaline fossil types (*i.e.*, echinoderms).

Conodont assemblages suggest that Samples 110-115 may be correlated with the Odenville facies of the Newala Limestone, and the species present indicate assignment of these strata to the *O. communis* Zone (latest Canadian). On the basis of conodont affinities, deposition was probably in an open-shelf, normal marine environment, possibly in cooler or deeper water. The conodont fauna was indigenous to the outer part of the eastern and southern North American platform (Repetski and Shaw, *in* Erickson, 1985). Conodont faunas similar to the Watson Creek fauna have been obtained from the Odenville facies of the uppermost Newala in Jefferson and Shelby Counties, Alabama (Keith Roberson, personal communication, 1985), and from rocks mapped as the Knox Group in Shelby County, Alabama (Erickson, 1985).

The color alteration index (CAI) implies that the host carbonates were subjected to temperatures of about 300 degrees C. (Epstein and others, 1977; Rejebian and others, 1987). Microscopic examination reveals that the carbonates have been deformed to various degrees by fracturing and/or stretching of grains and by stylolitization, but no pattern of increase or decrease in strain across the outcrop belt is apparent. Limited exposures suggest that folding, fracturing, and fracture-filling are much more intense in the carbonates proximal to the Shelby Springs fault, but (even though special attention was given to examination of

exposures and samples near the contact with the overlying slate sequence) are much less intense elsewhere across the outcrop belt.

CONCLUSIONS

A carbonate sequence, faulted from the southeast onto Floyd Shale and/or Parkwood Formation (Mississippian) along the Shelby Springs fault, and overlain by a slate-quartzite sequence of the Kahatchee Mountain Group, is correlated with the Newala Limestone and its Odenville facies (latest Canadian) on the basis of lithologic and faunal similarities. Faunal and lithologic characteristics of the Newala Limestone suggest deposition in a shallow, marine-shelf environment wherein circulation was at times restricted. Faunal and lithologic characteristics of the Odenville facies of the Newala are interpreted to reflect deposition in an open, below-wave-base marine environment.

The color and condition of the conodonts and the degree of strain of the carbonate rocks suggest that the carbonates have been subjected to temperature and pressure conditions that were notably greater than those that affected the Floyd-Parkwood, but which approached the conditions that probably affected the overlying slate-quartzite sequence. Although deformation associated with faulting is evident in the rocks adjacent to the Shelby Springs fault, no evidence for faulting other than a moderate divergence of attitudes is found where the carbonates are overlain by the slate-quartzite sequence. Because several unconformities occur at or near this stratigraphic interval in the Paleozoic sequence in this region, the slate-quartzite sequence is therefore interpreted (by TJC) as lying unconformably above the Odenville facies of the Newala Limestone. The deviation of attitudes across the contact between the carbonate and the slate-quartzite sequences is interpreted as the result of the development of erosional relief (perhaps with local or regional tilting) prior to deposition of the muds and sands of the slate-quartzite sequence. The age of the slate-quartzite sequence at this locality is therefore no older than latest Canadian. The slate-quartzite sequence is either 1) not part of the Kahatchee Mountain Group, or 2) the age of the lower part of the Kahatchee Mountain Group is misunderstood.

After their metamorphism by Early Devonian time, the Newala, Odenville, and the slate-quartzite sequence were faulted (probably during the Alleghenian orogeny) to the northwest onto the Floyd-Parkwood sequence of Mississippian age.

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SINKHOLES DETECTED BY MICROGRAVITY SURVEY

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ABSTRACT

In the summer of 1987 dramatic sinkhole development and ground settlement occurred in and near the town of Fairmount, Georgia. Microgravity surveys were conducted to determine the magnitude of mass deficiencies near portions of buildings that were actively experiencing ground settlement associated with sinkhole development. These measurements were designed to assess the utility of microgravity surveys in detecting potential areas of sinkhole development and ground settlement. For comparison, a microgravity survey was performed near open sinkholes which had developed in the base of a sewage treatment pond. Negative Bouguer anomalies on the order of 0.100 mGal were observed in the areas of greatest structural damage in the town and adjacent to sinkholes in the sewage pond. Also, the areas of structural damage were characterized by greater variability in the gravity anomalies, suggesting that the density of the underlying soil and rock was non-uniform. Models for these non-uniform negative mass deficiencies suggested that the microgravity technique detected sinkholes and zones of anomalous low density which were less than five meters deep. In contrast, microgravity anomalies obtained near the undamaged portions of buildings were smooth. Deeper structures which may have been associated with sinkholes were not detected.

INTRODUCTION

At the beginning of the summer of 1987, several sinkholes developed in and near the town of Fairmount, Georgia. One of the most dramatic consequences of sinkhole development was the draining of a sewage treatment pond. At about the same time structural damage was also noted in some buildings, especially those near the town square. The damage consisted mainly of cracks in walls and subsidence of floors. The subsidence suggested an association of the damage with the development of sinkholes and the apparent underground erosion of near-surface soils by the ground water system. Because the underground erosion of soil prior to the development of a sinkhole represents a mass deficiency, a microgravity survey was undertaken to assess the value of gravity data in the early detection of sinkholes.

Fairmount is underlain by limestone and shale of the Conasauga group (Cambrian). Sinkholes have occurred in the past in and near the town, particularly in limestone areas. However, landforms commonly associated with karst terrains are rare in the Fairmount area. Instead, in the Fairmount area the landforms are determined by the thick residium which covers the limestones and most sinkholes

are characterized by surface soil residium and alluvium collapsing into soil voids.

The main objective of the gravity survey was to determine if there was a correlation between observed structural damage and negative gravity anomalies which could be attributed to shallow mass deficiencies beneath building foundations. For control, a microgravity survey was performed adjacent to surface sinkholes to confirm theoretical estimates of the magnitude of the negative gravity anomaly expected from a shallow sinkhole. Continued development of the sinkholes was of concern since cracks had recently developed along the floors and walls of several buildings. A microgravity survey could prove to be useful in predicting where damage might continue.

Previous microgravity surveys have successfully detected underground caverns and other mass deficiencies (Butler, 1984; Frohlich and Smith, 1977; and Smith and Smith, 1987). Butler (1984) found a correlation of observed gravity anomalies with known cavities. Furthermore, he found that density anomalies near the surface were indicated by short-wavelength vertical-gradient anomalies with large magnitudes. Butler's (1984) study areas were two known underground cave systems in Florida. Frohlich and Smith (1977) performed a microgravity survey in karst terrain near the Ellington Fault in southeast Missouri in an attempt to explain the disappearance of Logan Creek. The results of Frohlich and Smith (1977) showed gravity lows in the area in which the creek disappears. They also concluded that the density contrast between cavernous and compact limestone could explain the 0.5 to 1.0 mGal anomalies observed in their data and make gravity data useful in studying areas of intensive karstification. Smith and Smith (1987) used measurements of the vertical gradient of gravity to study a known underground cavern system in Florida's karst terrain. Their data suggested that voids six meters wide and three meters high were detected but smaller voids were hidden in the background noise.

DATA ACQUISITION

Three types of gravity surveys were conducted: a larger area survey to define the regional gradient, a control survey adjacent to surface sinkholes, and detailed line surveys near areas of structural damage. The regional survey (Figure 1) of 25 points with a spacing of 100 to 300 m in the town of Fairmount determined the magnitude of regional gradients in the gravity field. The control microgravity survey was conducted in a sewage pond which had been drained by the collapse of soils into several sinkholes. This survey allowed a comparison of negative anomalies with obvious mass deficiencies. Microgravity data with spacings of 1.5 and 3.0 m were observed along four lines in areas of structural damage. Two of these survey lines were located inside a building. At these spacings, density anomalies in the upper 5 m could be resolved. In some areas where structural damage was evident, one meter spacings were used.

The survey points were located using a tape measure for distance and a Brunton compass for direction. All readings were obtained with a LaCoste-Romberg (G-668) gravimeter and for each reading, the gravimeter was leveled and read at least twice to confirm a reading precision of 0.005 mGals. All survey points were leveled to a precision of 0.03 m, which corresponds to a precision of 0.006 mGal in gravity. The meter drift between base ties was measured and the gravity values at each point were corrected by assuming a linear drift. The tidal attraction of the Sun and Moon were computed and removed prior to removal of

meter drift. Variations in gravitational attraction due to changes in elevation and latitude were removed in the data reduction. The effects of uncertainty in meter reading, elevation, latitude, and drift give a combined precision of 0.01 mGal for closely spaced data. The uncertainty in the elevation control for the regional survey of Figure 1 gives an uncertainty of 0.2 mGal.

Figure 1. Regional gravity survey point locations in Fairmount, Georgia. The solid circles are locations of gravity observations. The open circle is the base station. The larger numbered circles are locations of the five line surveys: 1. Town Square, 2. Carpet Factory, 3. Dye House, 4. Open Fissure, and 5. Sewage Pond.

ANALYSIS

The size of the sinkholes which had recently collapsed in the sewage pond suggested that mass deficiencies associated with voids in the residium could be assumed to be up to three meters in diameter, and no more than a few meters below the surface (i.e. in the soil residium and alluvium). Such negative density zones near the surface give short-wavelength negative anomalies. In our theoretical

model, short-wavelength negative anomalies were assumed to be caused by shallow air-filled cavities or loosely packed soil. Such cavities might exist below a cement floor which was being undermined by a developing sinkhole. The limestones and shales in areas without cavities were expected to give relatively smooth anomalies.
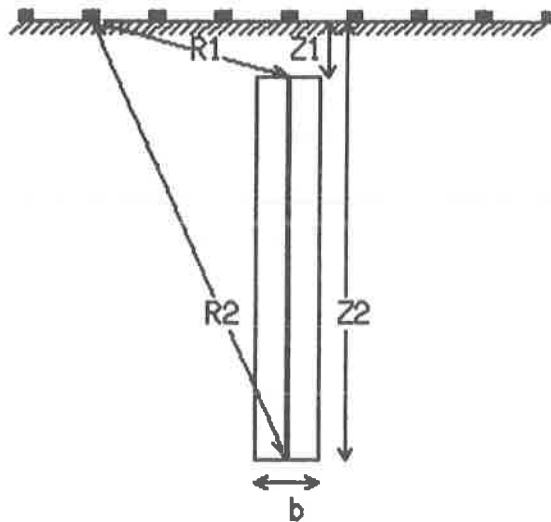
Figure 2. Two-dimensional model for a vertical sheet and the thin sheet approximation used to model the sinkholes as shallow mass deficiencies. The squares are observed gravity values along the line and the distances, R1 and R2, and depths, Z1 and Z2, are to the top and bottom of the sheet, respectively.

A two-dimensional vertical thin sheet, the shape of a dike, was chosen to model the mass deficiencies (Figure 2). Although a vertical cylinder would give similar results, the sheet was assumed to be a better approximation for the irregular and shallow mass deficiencies. Other direct modeling formulae, such as those for horizontal polygonal sheets, would also be appropriate for two-dimensional data but could not have been adapted as easily to the modeling technique. The top of the sheet was placed at a depth equal to or greater than the station spacing so that the approximation to a thin sheet would be valid. The base of the sheet was varied to fit the observed anomalies. The equation for the vertical component of the gravity anomaly for the thin sheet approximation is

$$g = 2\rho\gamma b \; Ln(R2/R1), \tag{1}$$

where b   = the width of the sheet,
  ρ = the density contrast, assumed to be –2.67 g/cm,
  γ = the universal gravitational constant, 6.67E–11 Nm /kg,
  R1 = the distance to the top of the sheet,
and   R2 = the distance to the bottom of the sheet.

The solution for the model is a non-linear process because the amplitude of the correction made during the modeling process depends on depth as well as on contributions from adjacent anomalies. For this reason, an iterative technique
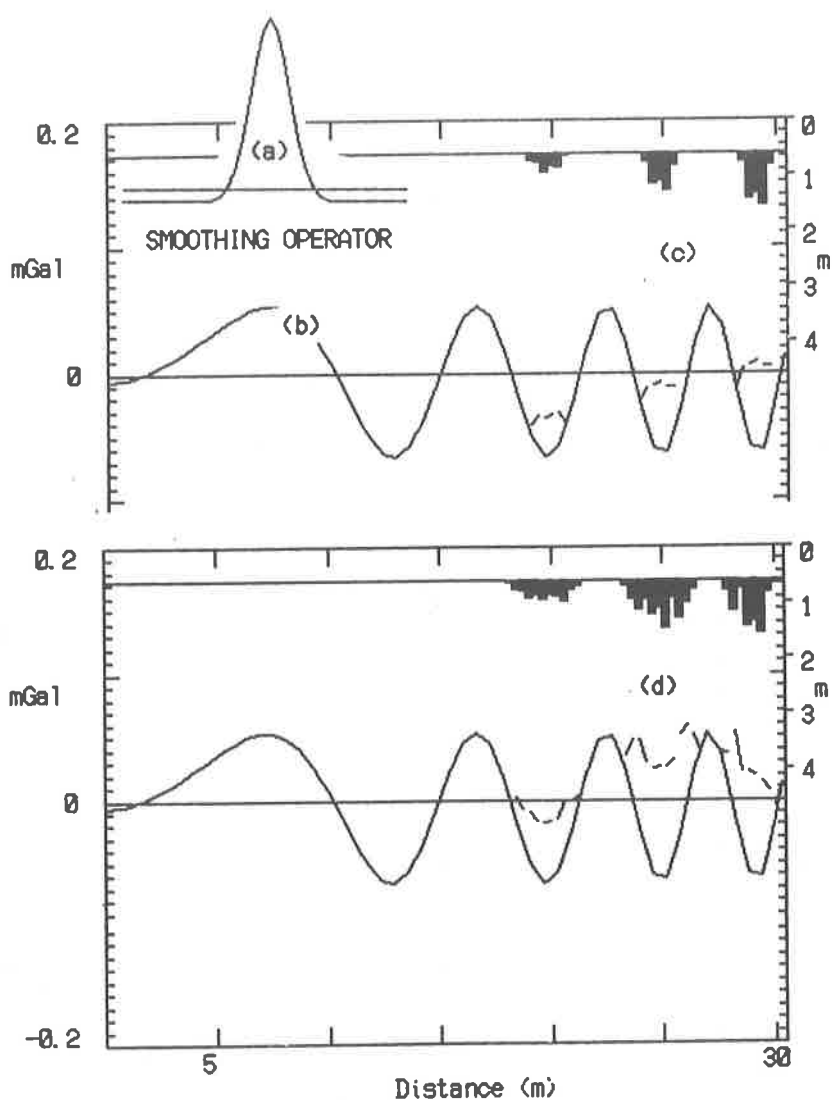
Figure 3. Example of the modeling procedure showing the influence of wavelength. (a) smoothing operator after 15 iterations, (b) sample observed gravity profile, (c) model (solid bars) and reduced profile (dashed) after the first approximation, and (d) after 10 approximations.

was necessary to compute the depth to the base of the sheet. The steps used to compute the depths of the anomalous mass are as follows:

1) A moving average (Shapiro, 1970), equivalent to a long-wavelength pass filter, was used to smooth the data. The moving average chosen is weighted (0.25, 0.5, 0.25) and is applied repeatedly for a smoother curve. The smoothing operator for 15 iterations, typical for this study, is shown in Figure 3.

2) The residual was then computed and used to approximate the distribution of anomalous density. Only the negative anomalies exceeding a threshold value were used to compute approximations to the anomalous densities, so that only the larger short-wavelength anomalies would be modeled.

3) Gravity anomalies computed from the model were then subtracted from the observed gravity profile. This reduced anomaly was, in turn, smoothed and its residuals used to update the model. For each subsequent smoothing, the approximate model was added to the previous model. This iteration was continued until the model converged to a stable solution.

The procedure, shown in Figure 3, is roughly equivalent to a downward continuation constrained to short-wavelength negative anomalies. The model represents the cross-sectional volume of cavity below a given depth required to explain the observed negative anomalies.
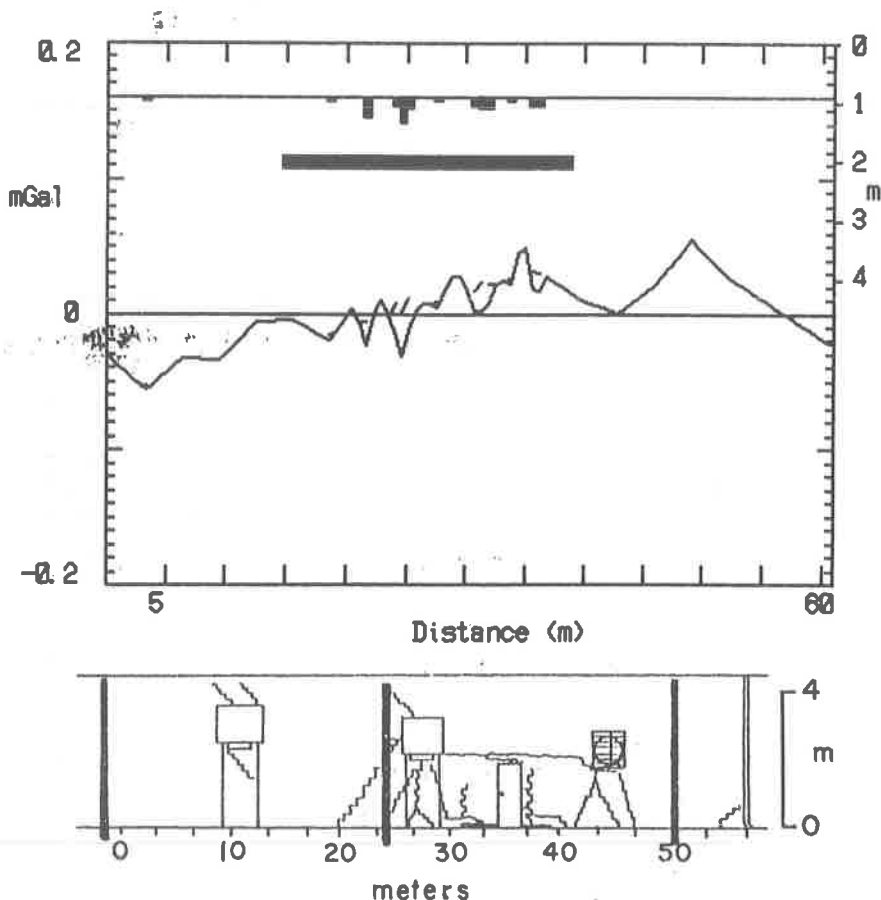
Figure 4. Town Square gravity profile (solid), reduced gravity profile (dashed) and model. The model represents the cross-sectional volume needed to explain the short wavelength negative anomalies. The depths to the top and bottom of the model can be read from the scale on the right. In this and subsequent profiles, the threshold anomaly was 0.005 mGals, and the smoothing operator was applied 10 times. The horizontal solid line indicates zones of observed damage.

THE SURVEYS

The Bouguer gravity anomaly map of Georgia (Long, 1974) indicates anomalies between –39 and –40 mGal in the Fairmount vicinity. The observed regional Bouguer gravity anomalies of this study (Figure 1) were consistent with

the Georgia gravity map. Over an area of 0.5 by 1.0 km in the town of Fairmount the Bouguer anomalies varied from −38.9 to −40.6 mGal. The lowest anomalies (<−39.5 mGals) were concentrated in a northeast trending zone centered on the intersection of Calhoun Street and highway US 411. This zone also included the areas of damage examined in this study. The variation of less than 1.5 mGal suggested that the gradient from regional anomalies would be less than 0.003 mGal/m.

The town square microgravity survey was performed along the north, outside wall of the carpet mill which is situated on the south side of the Fairmount town square. Station spacings of 3.3 m were used in this survey, except in areas of structural damage where one meter spacings were used. This location was selected because numerous, recent cracks run the height of the building and the floor and sidewalk along the side of the building have subsided approximately 0.025 m. The survey was conducted along the sidewalk about 0.85 m away from the wall. The gravity anomaly profile for this survey showed rough negative anomalies in the areas of structural damage and subsidence; whereas, smooth anomalies were observed where there was no damage (Figure 4).
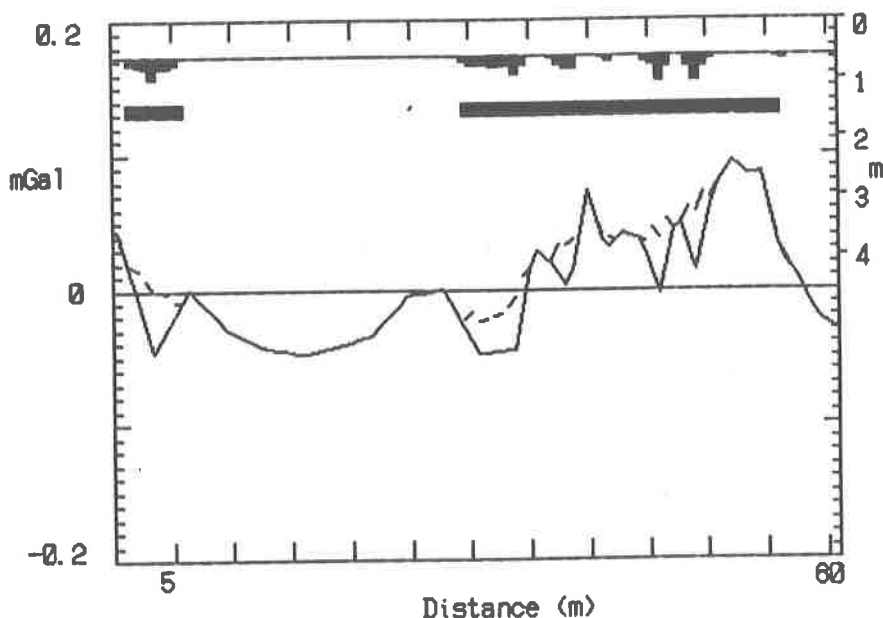

Figure 5. Carpet Factory gravity profile (solid), reduced anomaly (dashed) and model. The solid horizontal bar indicates zones of observed damage. (see Figure 4 for model parameters)

The carpet factory and dye house surveys were performed in a carpet mill located northeast of the town square. The carpet factory survey was carried out in a large portion of the building consisting of three storage rooms, a large room with a plywood floor approximately 0.3 m above a concrete floor, and a downward sloping hallway. Cracking was evident in the area covered by the survey, except for the part conducted on the plywood floor. A smooth negative anomaly was observed along the plywood floor and rough, negative anomalies were observed in the areas of cracking (Figure 5).
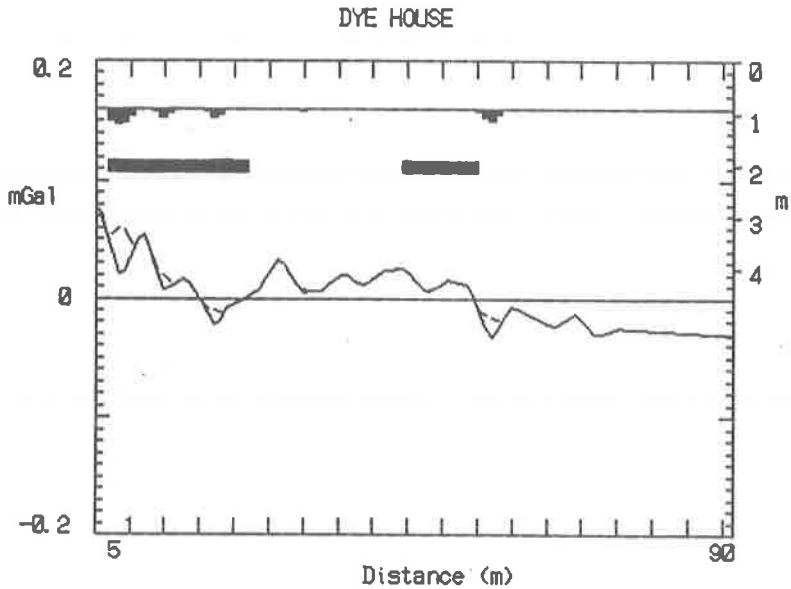
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DYE HOUSE

Figure 6. Dye House gravity profile (solid), reduced anomaly (dashed) and model. The solid horizontal bar indicates zones of observed damage. (see Figure 4 for model parameters)
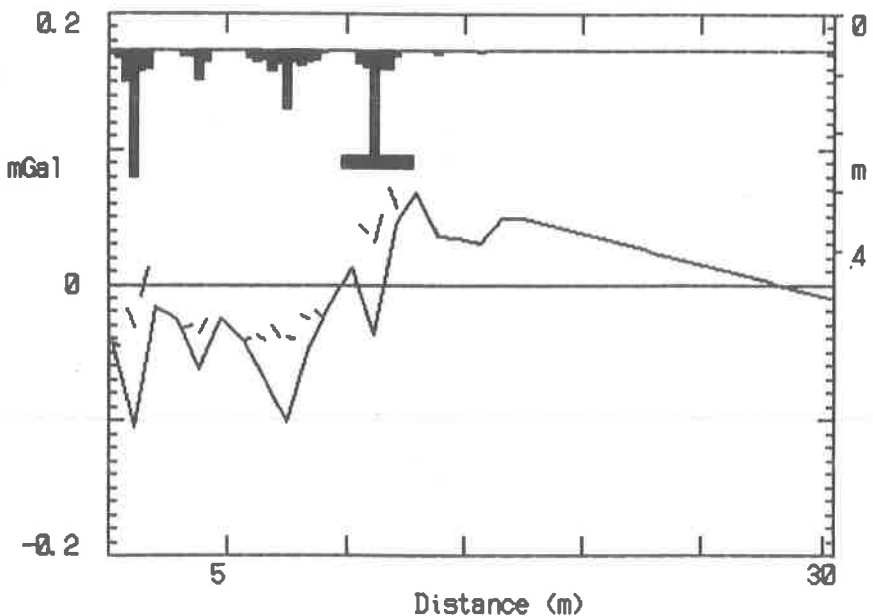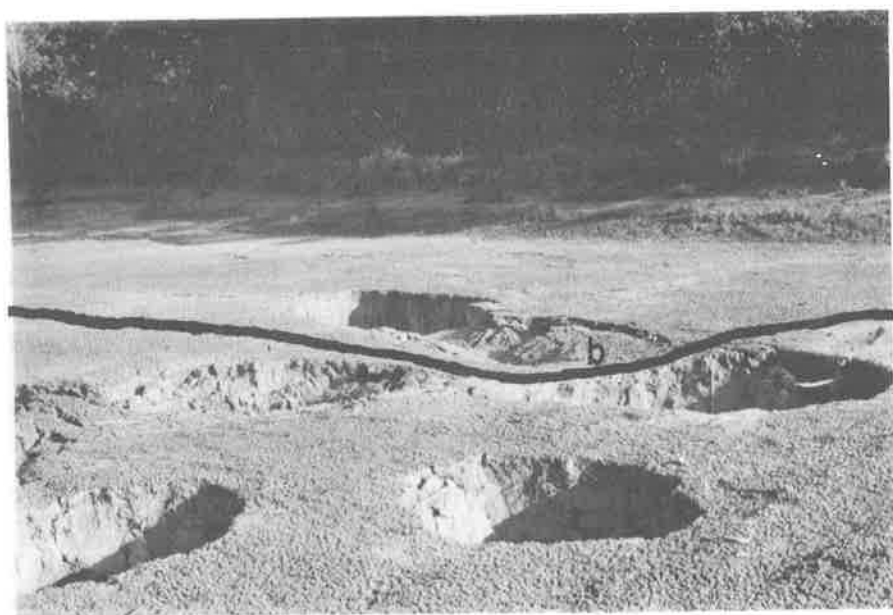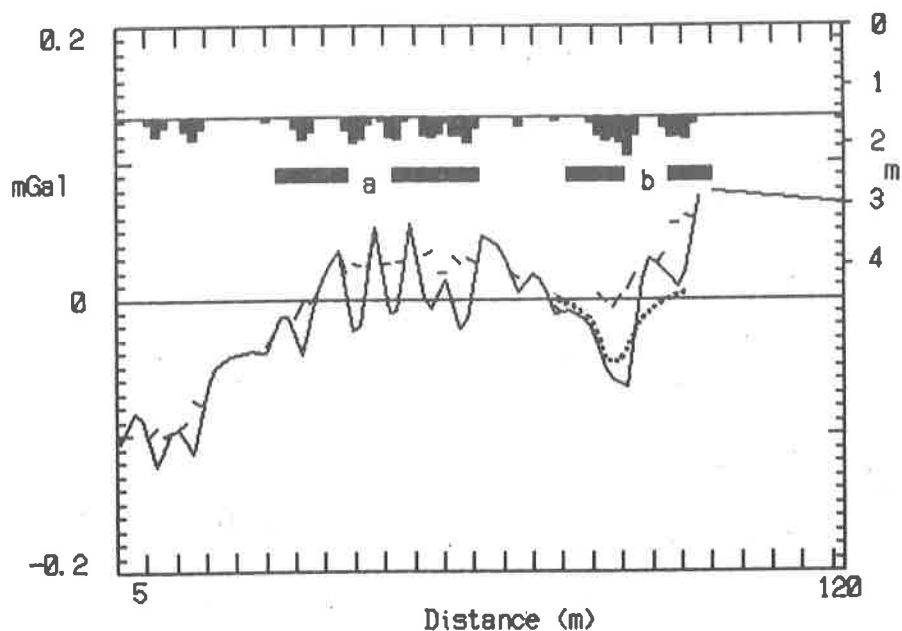

Figure 7. Open Fissure gravity profile (solid), reduced anomaly (dashed), and model. The solid horizontal bar indicates the site of the fissure. (see Figure 4 for model parameters)

The second part of this survey was performed adjacent to the most damaged part of this carpet mill, the dye house. Cracks in the walls were 0.02 to 0.03 m wide near a window. Lesser cracks extended from the floor to the ceiling and along the floor. The survey line was 70 m in length, continued outside the build-

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Figure 8. Sewage Pond gravity profile (solid), reduced anomaly, and model. The solid line (b) indicates area of open sinkhole shown in photograph below. The dotted line gives the anomaly expected for a model of the two holes in the photograph at "b". The solid line (a) indicates an area of similar surface disturbances.

ing, and consisted of 1.5 m station spacings. Rough, negative gravity anomalies were observed in the areas of the major cracking and in the other areas of cracking (Figure 6). Smooth anomalies exist where there was no apparent damage.

The open-fissure survey was performed in a gravel-paved alley just to the

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north of the town square. A 0.05 m wide open fissure of undetermined depth ran across this alley. Our profile consisted of a 19 m line running perpendicular to the fissure using station spacings of 1.0 m. The resulting gravity anomaly profile showed a sharp, negative anomaly in the vicinity of the fissure and also showed three other sharp, negative anomalies which suggest areas of mass deficiency and potential cavity development (Figure 7).

As a means of calibrating negative anomalies with observable mass deficiencies, a 100 m line was surveyed in a sewage treatment pond which had been drained by the collapse of ten to twelve sinkholes in the southwest end of the pond. The spacing used in this survey was 3.3 m and the line was oriented so that it would pass directly through the sinkhole area. The resulting profile showed the correlation between the actual sinkholes and the observed rough, negative anomalies (Figure 8). Depths of 0.5 to 1.0 m are suggested by the model; however, these two-dimensional gravity profiles can not distinguish between cavities below the line and larger cavities off to the side. The theoretical anomaly of 0.050 mGal for two holes (shown in Figure 8) agrees well with the observed anomaly.

DISCUSSION AND CONCLUSION

We concluded that microgravity surveys were useful in detecting mass deficiencies related to the development of sinkholes in the town of Fairmount, Georgia. The negative anomalies which were a result of the mass deficiencies could be modeled as vertical sheets extending to depth from near the surface. The areas of structural damage in Fairmount were characterized by rough, negative anomalies which were modeled by shallow density anomalies; whereas, areas of no observed damage were characterized by smooth anomalies which did not predict shallow density anomalies.

The model of negative density contrast near the surface was designed to fit a typical condition that poses a hazard to structures susceptible to damage. This condition was a cement floor or other ground surface being undermined by the development of a sinkhole. In the early stages, no damage would be evident, but a measurable mass deficiency might exist. The lack of negative anomalies and the existence of a smooth anomaly suggested a foundation of uniform density.

ACKNOWLEDGMENTS

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ANATASE PSEUDOMORPHS AFTER TITANITE
FROM FULTON COUNTY, GEORGIA
AND THEIR EXPERIMENTAL SYNTHESIS

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ABSTRACT

Weathering of titanite from lenticular pegmatites within the Wahoo Creek Formation in the southern Piedmont of Fulton County, Georgia transforms the red brown, euhedral crystals with adamantine luster into white pseudomorphs with dull luster. Analysis of the weathered crystals indicates that they are anatase pseudomorphs after titanite. Crystals of fresh titanite, from the Wahoo Creek Formation were used as seed crystals in low-temperature hydrothermal experiments conducted to synthetically produce anatase pseudomorphs after titanite. Anatase pseudomorphs were produced in HCl solutions of pH 1 (at 60° C) to 6.5 (at 250° C). The formation of anatase pseudomorphs is caused by the hydration of the titanite structure. Formed are Ca^{2+} and H_4SiO_4 ions and anatase. While the former substances are dissolved in solution, the anatase, TiO_2, remains as a solid that forms the pseudomorph. The results of this study are in agreement with the observed formation of anatase pseudomorphs after titanite forming during saprolite development in the southern Blue Ridge and Piedmont.

Synthetic titanite has been proposed as part of a ceramic containment system for the long term (100,000 to 1,000,000 years) storage of high level radioactive waste. The immobility of Ti is confirmed by this study; however, release of Ca and Si under even weak acid conditions indicates poor containment ability of radioactive materials by a synthetic titanite at the expected elevated temperatures of the containment system.

INTRODUCTION

Anatase pseudomorphs after titanite occur in Fannin County, Georgia (Cook, 1978); Henderson County, North Carolina; Roanoke County, Virginia (Mitchell, 1964) and we have collected similar pseudomorphs in Fulton County, Georgia. The latter pseudomorphs occur in a deeply weather road cut in the Palmetto Quadrangle. Deep unweathered road cuts in the same area have fresh titanite found in lenticular pegmatites surrounded by diopside gneiss of the Wahoo Creek Formation (Wallace, 1981). This report describes the chemistry of the titanite and its anatase pseudomorphs. Synthetic anatase pseudomorphs after

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titanite were synthesized to better understand the stability relationships of anatase, rutile and titanite. Previous studies include rutile, anatase and titanite by Schuiling and Vink (1967); titanite by Smith (1969); rutile by Corlett and McIlreath (1974); ilmenite and titanite by Zen (1974); rutile and titanite by Hunt and Kerrick (1977) and Hollabaugh (1980); perovskite and rutile by Myhra and others (1984); rutile, brookite, anatase and ilmenite by Morad (1986) and Morad and Aldahan (1986). The insoluble nature of Ti in groundwater and low-temperature hydrothermal solutions is also discussed. The proposed usage of synthetic titanite as part of a ceramic containment system for the long term storage of radioactive waste is also considered. Preliminary reports were given at the Georgia Academy of Science by Callaham (1985) and Warhurst (1988).

PREVIOUS STUDIES

Previous experimental studies on the stability of anatase and titanite have been at temperatures well above the conditions of soil formation where rutile rather than anatase is the stable TiO_2 polymorph. Schuiling and Vink (1967) and Hunt and Kerrick (1977) determined the stability limit of titanite in environments with high CO_2, using the following relationship;

(1) rutile + calcite + quartz = titanite + CO_2.

Hunt and Kerrick (1977) determined equilibrium temperatures of $500 \pm 5°$ C at $P_{(fluid)} = 2$ kilobars and $X_{(CO_2)} = 0.5$ and about $580°$ C at $P_{(fluid)} = 5$ kilobars and $X_{(CO_2)} = 0.5$.

A series of low-temperature leaching experiments on natural and synthetic titanite, titanite glass, and titanite-ceramic glass have been performed. Bancroft and others (1982) performed leaching experiments on titanite glass at $90°$ C for up to 8 days in deionized water. They found that after 12 hours the surface layer was largely depleted in Ca and Si, and after 8 days a surface coating of poorly crystalline anatase was formed. Hayward and others (1982) leached synthetic titanite crystallites in an aluminosilicate glass matrix mixed with 5-10g of crushed granite in deionized water and synthetic ground water (Ca = 15000 mg/L; Na = 5050 mg/L; Si = 15 mg/L; Sr = 20 mg/L; Mg = 200 mg/L; K = 50 mg/L; Cl = 34260 mg/L; $SO_2{}^{2-}$ = 790 mg/L; HCO_3^- = 10 mg/L; and NO_3^- = 50 mg/L) for 10 - 360 days at pH ranging from 6 to 8. Their results suggest that the glass matrix leaches more rapidly than the titanite and that the titanite surface is leached more at pH = 6 - 7 than at pH = 8 - 9. Hayward (1986; Hayward and others, 1987) reviews further leaching experiments from 25 - $100°$ C in deionized water and synthetic groundwater (brine) using a titanite ceramic containing simulated high level radioactive waste. These studies determined (1) that leaching in brine starts at $60°$ C; (2) leaching rate is not controlled by excessive concentrations of Ca, Na, and Cl; and (3) U is the only "impurity" ion that is released.

All of these studies deal with restricted pH ranges (6 - 8) and limited temperatures (25 - $100°$ C). Our experiments were designed to determine the stability of anatase and titanite from 25 to $250°$ C at a pH of .01 to 7.

GEOLOGIC SETTING

The titanite-bearing calc-silicate unit was first mapped by Cofer (1958) in

the Ben Hill area of southern Fulton County, Georgia. He described it as a microcline-plagioclase-diopside-epidote gneiss with minor biotite-epidote-microcline gneiss and feldspathic amphibolite. Crawford and Medlin (1974) extended the unit into Coweta County. Hinton and Williams (1975) conducted chemical and petrographic analyses of samples collected by Crawford and Medlin. They found the calc-silicate rocks were rich in orthopyroxene, clinopyroxene, actinolite, epidote, microcline, plagioclase and hornblende with minor quartz. O'Connor (1977) extended the calc-silicate unit northeast across Dekalb County into Gwinnett County, northwest of Tucker, as well as through southern Dekalb into Henry County. Atkins and Higgins (1980; Higgins and Atkins 1981) incorporated the calc-silicate gneiss into the Wahoo Creek Formation. They describe the calc-silicate gneiss as a locally present, thinly-layered epidote, calcite and diopside-bearing gneiss. Wallace (1981) did a petrographic and major element analyses of 25 samples from the Stone Mountain north Quadrangle, Georgia. She determined that units within the Wahoo Creek Formation consisted of (1) biotite and granitic gneisses derived from a felsic igneous rock, (2) amphibolite derived from a basalt, and (3) diopside gneiss formed from a calcareous subgraywacke or calcareous arkose. Wallace estimated that the diopside gneiss formed at approximately 600 ± 20° C and 4.3 ± 0.9 kilobars.

Fresh titanite was collected from a deep road cut along highway 154. The road cut is 4.3 km north of Palmetto and 300 meters north of where highway 154 crosses Bear Creek. The fresh titanite are wedge-shaped crystals with {001}, {110} and {111} faces. They are brown with adamantine luster and are 1-5 mm long. The anatase pseudomorph (same wedge-shape crystal form as fresh titanites of the first sample location) was collected from a weathered road cut along Ono Road 1.1 km east of where the fresh titanite was collected. The pseudomorph is white with a waxy luster. The part of the Wahoo Creek formation sampled for this study is an epidote-diopside gneiss surrounding a one to two meter thick lens of granite pegmatite to alkali feldspar-quartz syenite pegmatite. Titanite occurs in both the gneiss and pegmatite. Saprolite development in the study area is very extensive and anatase pseudomorphs could be formed from either the gneiss or pegmatite. Fresh bedrock outcrops are most abundant where streams have eroded through the saprolite (i.e. our sample area north of Bear Creek).

Table 1 presents chemical and petrographic analysis of four samples of the pegmatite rock and two samples of the diopside gneiss. Atomic absorption mass spectrophotometer analyses were performed on whole rocks. Standards were U.S.G.S. rocks. Standard point counts were done to determine thin section modal analyses.

METHODS

Experiments were performed on natural titanite crystals with the intended purpose of transforming them to anatase pseudomorphs and determining the range of pH and temperature conditions for this pseudomorph formation. The pseudomorph experiments were performed using 23 and 25 cc volume Parr teflon-lined acid digestion bombs. Vessels were heated from 40 to 250° C in pot furnaces or ovens with contact chromel-alumel thermocouples. Temperatures are accurate to ± 5° C and pressures were calculated from thermodynamic equations for nonideal gases. Experiments at room temperature (20-25° C) were conducted in Nalgene bottles with closures. Starting solutions were 2-16 ml of pure water,

Table 1. Chemical analyses of titanite and whole rock from Pelmetto Quandrangle, Georgia.

OXIDE	TITANITE*	PEGMATITE** (WHOLE ROCK)	DIOPSIDE GNEISS# (WHOLE ROCK)
SiO_2	30.80	64.80	51.60
TiO_2	37.44	0.49	0.35
Al_2O_3	2.16	14.98	10.38
Fe_2O_3##	0.70	3.49	4.68
MnO	0.09	0.06	0.07
MgO	0.06	0.55	1.84
CaO	28.16	3.38	26.22
Na_2O	0.15	2.34	2.48
K_2O	---@	8.75	1.64
Total	99.56	98.85	99.26

* Atomic absorption mass spectrophotometer analyses using U.S. Geological Survey Standard BCR-1 and synthetic titanite (Hollabaugh and Rosenberg, 1983) standards.

** Average of 4 samples. Thin section modal analyses of the same rocks yields; 58.90% microcline, 13.79% quartz, 8.34% myrmekite, 7.86% diopside, 3.89% titanite, 3.05% hornblende, 3.03% oligoclase, 0.71% epidote, 0.43% calcite and 0.01% pyrite.

Average of two samples. Thin section modal analyses of the same rocks yields; 34.03% quartz, 26.26% myrmekite, 25.40% diopside, 4.01% epidote, 3.03% titanite, 2.03% muscovite, 1.75% microcline, 1.69% calcite, 1.41% hornblende and 0.39% oligoclase.

All Fe as Fe_2O_3.

@ None detected.

oxalic acid, 0.0 to 6.5 pH solutions of HCl, 13 pH solution of NaOH, 0.6 to 1.7 mole solutions of NaCl and 0.8 mole solution of NaF. The non-HCl solution experiments were done to confirm that H^+ was the key cause of pseudomorph formation. One problem encountered with the teflon-lined vessels was retention of F by a liner after a vessel was used in an experiment involving HF. Later usage of a liner in a subsequent experiment with a HCl solution often resulted in formation of CaF_2. This problem was solved by using different liners for all HF experiments. Natural euhedral, unbroken crystals of titanite were employed as seed crystals. The titanite was from a pegmatitic zone of the Wahoo Creek Formation. Analysis of hand picked titanite crystals was done by atomic absorption. Standards for Si, Ti, and Ca were synthetic titanite from Hollabaugh and Rosenberg (1983); U.S.G.S. rocks were used as standards for Al, Fe, Mn, Mg, Na, and K (Table 1). All the titanites used in the experiments were from fresh unaltered pegmatite (i.e. no alteration observed in thin section of titanite, pyrite, pyroxene or feldspars). The titanite crystals were cleaned in acetone in an ultrasonic cleaner and weighed on an Ainsworth analytical balance. The weight recorded for each crystal (5-50 mg.) was that of successive weighings that gave identical results. Estimated surface area for a 20 mg seed crystal is 16 mm^2. Titanite to water ratios average 0.004. Scanning electron microscope examination of the surface of seed crystals indicated no details at 5000X. Experiments lasted from 12 to 88 days. Vessels were quenched by cooling in a sheet of flowing cold

water.   Analysis of several solutions was done by atomic absorption using standards prepared by dilution of 1000 ppm Fisher reference solutions of Ca, Ti, and Si. At the conclusion of each experiment the seed crystal was recleaned in acetone in an ultrasonic cleaner and reweighed. Seed crystals were analyzed by powder x-ray diffraction and scanning electron microscope with energy dispersive x-ray. Standard x-ray slides of anatase and titanite mixtures were prepared and used to determined the weight percent anatase and titanite in the crystals after each experiment using a Philips APD 3520 x-ray unit. Surface textures were examined with a Cambridge Mark 2A SEM (Figure 1) and semiquantitative chemical analysis was performed using an EDAX 707B system. Experimental results are given in Table 2.

RESULTS

The titanite from the pegmatite is usually 1-5mm and euhedral.   The structural formula for the titanite is:

$$(Ca_{0.984}Na_{0.009}Mg_{0.003}Mn_{0.003})(Ti_{0.920}Al_{0.083}Fe_{0.017})Si_{1.005}O_4(O,OH,F).$$
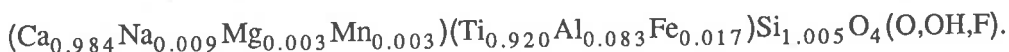
Two separate groups of experimental results appear in Table 2.   The titanite seed crystal remained unchanged if experiments were conducted using neutral or basic solutions (distilled water, .1m NaOH, .5 to 2m NaCl and .1m NaF) or HCl solutions below 55°C. Pseudomorphs were formed from HCl solutions above 55°C and in two oxalic acid solutions. In these solutions the dark brown seed crystals with adamantine luster were transformed into white to yellow pseudomorphs with dull, waxy luster. The different acid solutions produced a diversity of pseudomorphs. Pseudomorphs formed within the anatase and titanite field of Figure 2 were partial pseudomorphs with an unaltered titanite core surrounded by anatase. The boundary between the anatase and titanite was sharp. Strong HCl solutions (pH = 1 to 1.2) resulted in anatase if temperatures were above 125°C.   Still higher temperatures (>130°C) and stronger acid (pH = .1 to 1) produced rutile and anatase pseudomorphs with many solution voids or etch pits.

The natural pseudomorph was broken into two equal halves. The half that was x-rayed showed the pseudomorph was composed entirely of anatase. EDAX of its surface (Figure 1A) indicated Ti with minor Fe.   Scanning electron micrographs of natural and synthetic pseudomorphs are shown in Figure 1. Identical uniform surface features were observed on the 1) natural pseudomorph, 2) titanite seed crystals, 3) partial pseudomorphs produced in HCl solutions of pH = 2 to 6, and 4) unaltered titanite from solutions of NaF and NaCl.   Figure #1B shows the solution pits formed in HCl solutions of pH = 1. Inside the pits are clusters of microspheres (Figure #1C). Analysis of spheres with EDAX indicate they are composed of TiO_2. Figure #1D shows the surface of a seed crystal after being subjected to a HCl solution of pH = 0.6 for 20 days at 136°C. Solution pit development is so extensive that the original crystal outline is destroyed and a pseudomorph is not formed. The surface formed is an uneven surface covered with microspheres (Figure 1E) composed of TiO_2. Viewing the microspheres at higher magnification shows that the clusters consist of discrete tetragonal crystals. The acute bipyramidal anatase forms are very similar to SEM micrographs of interstitial anatase in the Proterozoic Visingso Group sandstones of Sweden (Morad, 1986). Two samples, H588 and H753, produced prismatic acicular crystals and clusters of

Table 2. Results of low temperature hydrothermal experiments on titanite seed crystals.

RUN NUMBER	TIME days	TEMP °C	pH	WEIGHT LOSS (%)	RESULTS
H651a	75	22	.2[#]	0	No change
H651g	75	22	0.7	0	No change
H1035	47	39	1	0	No change
H1036	47	39	6	0	No change
H1193	68	41	1	0	No change
H1071	60	43	1.2	0	No change
H1072	60	43	2	0	No change
H1077	55	44	0.7	0	No change
H1076	55	44	3.5	0	No change
H1192	68	47	1	0	No change
H726	71	55	1	0	No change
H725	71	55	3	0	No change
H724	71	55	5	0	No change
H1130	86	62	1.2	26	titanite + anatase
H1131	86	64	3.5	0	titanite + anatase
H1024	40	78	1	32	titanite + anatase
H1025	40	78	2	3	titanite + anatase
H1026	40	78	4	0	titanite + anatase
H1027	40	78	5	0	no change
H1028	40	78	6	0	no change
H1057	70	81	1	*	titanite + anatase
H1058	70	81	1.2	*	titanite + anatase
H1059	70	81	2	*	titanite + anatase
H1060	70	81	3	*	titanite + anatase
H1065	60	81	3.5	*	titanite + anatase
H1066	58	81	5.8	0	no change
H1067	58	81	6.5	0	no change
H1068	58	81	3.5	0	titanite + anatase
H1070	58	81	6.5	0	no change
H1074	53	81	5.8	6	no change
H1075	53	81	6.5	2	no change
H709	31	82	1	16	99% titanite + 1% anatase
H710	31	82	3	7	99% titanite + 1% anatase
H711	31	82	5	14	99% titanite + 1% anatase
H1191	68	109	1.2	67	titanite + anatase
H664	30	127	1	38	anatase
H706	30	132	5	28	60% titanite + 40% anatase
H707	30	132	6	0	titanite + anatase
H701	14	135	1	50	anatase
H702	14	135	2	18	78% titanite + 22% anatase
H703	14	135	3	8	98% titanite + 2% anatase
H649	20	136	0.6	67	anatase + rutile
H634	19	138	0.1	65	anatase + rutile
H665	40	139	1	43	anatase
H648	20	146	0.2	60	anatase
H752	40	220	6	2	titanite + rutile
H650	20	241	0.2	50	anatase + rutile
H1102	21	245	1	90	anatase + rutile
H1103	21	245	3	60	titanite + anatase
H1104	21	245	4	33	titanite + anatase
H1105	21	245	5.8	60	titanite + anatase
H753	38	246	1	38	anatase + rutile
H1194	32	247	1.2	*	anatase
H1196	23	247	1.5	*	anatase + rutile
H1197	23	247	1.7	*	anatase + rutile
H1136	22	247	2	14	titanite + anatase
H1141	22	247	3	6	titanite + anatase

Table 2. Cont.

H1137	22	247	4	9	titanite + anatase
H1138	22	247	5	42	titanite + anatase
H1139	22	247	6	33	titanite + anatase
H1140	22	247	6.5	18	titanite + anatase
H480	12	114	7**	0	No change
H492	30	139	7**	0	No change
H490	30	144	7	0	No change
H872	24	145	13	0	No change
H526	24	214	7	0	No change
H531	14	216	7**	0	No change
H569	63	217	7**	0	No change
H931	19	249	13	0	No change
H652	20	124	***	18	titanite + anatase
H635	19	140	***	68	titanite + anatase

HCl in distilled deionized solutions and NaOH + HCl buffer
solutions for pH 6 to 6.5
*   Not determined
**   NaCl solutions
*** Oxalic acid solutions

rays of needle-like crystals (Figures 1G and 1H). The acicular crystals are very similar to rutile crystals described by Morad (1986). X-ray diffraction of this sample indicates it is composed of both rutile and anatase; these needle-like crystals are either rutile or anatase.

Table 3 lists Ca, Si, and Ti concentrations in solutions from experiments at low-temperatures where the titanite seed crystals remained unaltered (i.e. no change detected by x-ray diffraction or SEM and EDAX). Up to 22 ppm Ca and 8 ppm Si occur in these solutions but no Ti was detected. This indicates that Ca and Si are released from the titanite even at very low temperatures.

DISCUSSION AND CONCLUSIONS

The inability to experimentally produce anatase pseudomorphs after titanite below 55° C in HCl solutions can be due to one of two causes. First, the pseudomorphs may only form at higher temperatures, or second, the reaction rate at temperatures below 55° C is so slow that 75 day long experiments are too short for the pseudomorphs to form. We favor the second cause. The widespread occurrence of anatase pseudomorphs after titanite in the soils of the Piedmont are the result of weathering over a long time period in a low-temperature environment. The release of some Ca and Si into solution at 44° C (Table 3) suggests that under natural conditions prolonged contact with acid solutions could form the pseudomorphs. Also, the negative value of Gibbs free energy for equation 2 suggests that under acid conditions anatase is the stable Ti-mineral at 25° C. However, equations 2 and 3 that are proposed for anatase pseudomorph formation apply to either low- or high-temperatures.

The formation of the synthetic and natural pseudomorphs involves the breakdown of one crystal structure, the removal of mobile reactants and the formation of a different structure from the non-mobile reactants. As this process occurs atoms migrate into and out of the crystal in such a precise manner that the original crystal outline is preserved. A chemical reaction accounting for the origin of synthetic TiO_2 pseudomorphs after titanite in HCl solutions is:
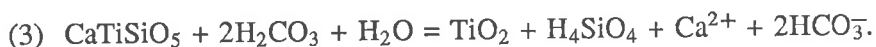
(2) $CaTiSiO_5 + 2H^+ + H_2O = TiO_2 + H_4SiO_4 + Ca^{2+}$.
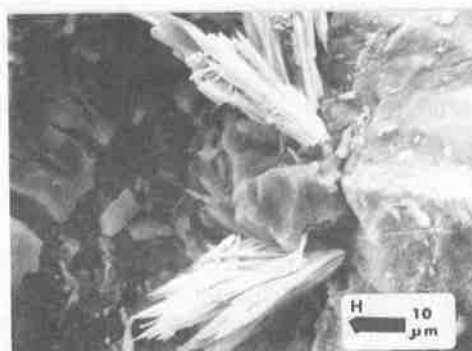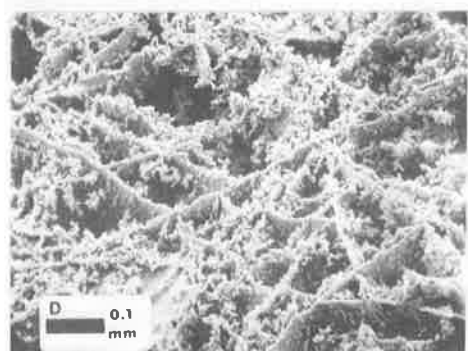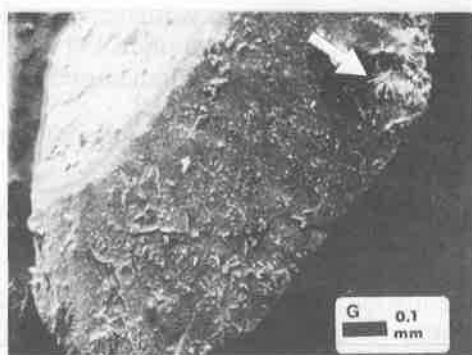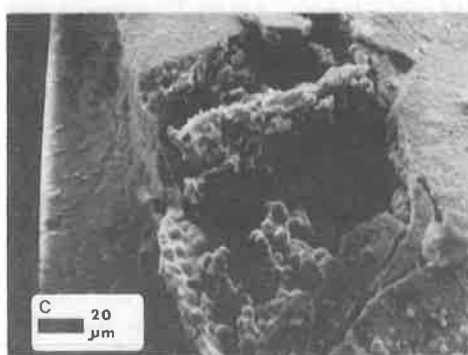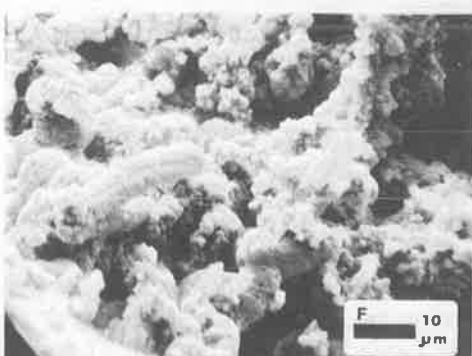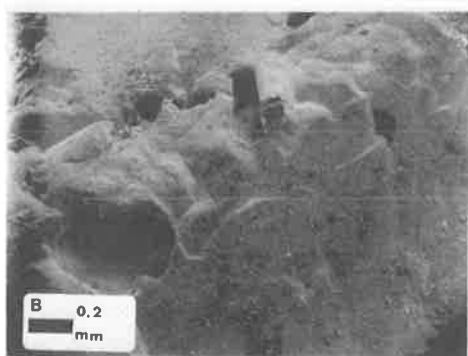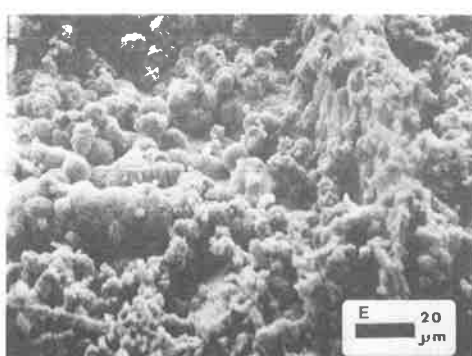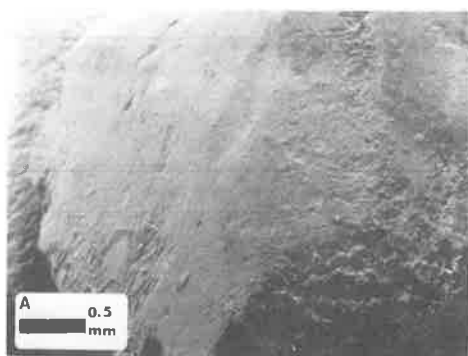
Anatase pseudomorphs formed by carbonic acid rich solutions can be formed by:

(3) $CaTiSiO_5 + 2H_2CO_3 + H_2O = TiO_2 + H_4SiO_4 + Ca^{2+} + 2HCO_3^-$.

Reactions (2) and/or (3) are the reactions by which the natural anatase pseudomorphs after titanite are formed. Thermodynamic calculations for reaction (2) using data from Robie and others. (1978) at 25° C and 1 bar yield a standard Gibbs free energy of reaction of -47847 J/mole. Several constraints exist on any chemical model proposed to explain the formation of natural anatase pseudomorphs after titanite. (1) The process is a constant volume process. Anatase pseudomorphs formed in our experiments have the same crystal form and volume as the titanite seed crystals. (2) The process starts at the crystal faces and migrates inward. Removal of elements (Si and Ca) and growth of anatase progresses as a "wave front". In weak acid solutions the cores of the seed crystals remain unaltered titanite with a rind of anatase formed around the core, and the boundary between anatase and titanite is sharp. (3) Both the anatase and the titanite are well crystallized. X-ray diffraction patterns for samples from 100% anatase to 1% anatase have sharp, narrow peaks. (4) The process occurs in HCl (or acid) solutions of pH between 2 and 6.5. In strong HCl solutions of pH = 1 solution pits are formed (Figure 1). The natural anatase pseudomorph has no solution pits (Figure 1). (5) Crystal structure bond strengths are less important than the ability of an element to form complexes and the solubility of the complex. Calculation of bond strengths for titanite (Hollabaugh, 1980), based on charge and bond length, show that Si-O bonds are stronger than Ti-O bonds. However, the Si goes into solution as H_4SiO_4 and the Ti remains as an immobile solid, TiO_2. This is in agreement with the interpretation of Ti (with Fe and Al) as a relatively immobile element during chemical weathering (Goldich, 1938; Loughnan, 1969). (6) H^+ ions play a key role in pseudomorph formation. In neutral water solutions the titanite remains unchanged and stronger and stronger acid solutions produce greater and greater changes. The F appears not to be of importance in pseudomorph formation (other than forming a more complex synthetic pseudomorph consisting of both CaF_2 and TiO_2 [Callaham, 1985]). Solutions of NaF produced no change in titanite seed crystals (Table 1).

Figure 1. Scanning electron micrographs showing natural and synthetic pseudomorphs and non-pseudomorphs: (A) Natural anatase pseudomorph after titanite from north of Palmetto, Fulton County, Georgia. Synthetic anatase pseudomorphs formed at pH = 2-6.5 are identical. (B) Synthetic anatase pseudomorph after titanite showing solution pits (lower left and center pits are outlines from euhedral crystals that were formerly attached to the seed), H701, 14 days at 135° C with initial pH of 1. (C) Solution pits lined with microspheres, H701. (D) Crystalline form distorted by solution pits, H649, 20 days at 136° C with initial pH of 0.6. (E) Anatase microspheres on surface of deeply etched crystal, H649. (F) Structure of microspheres showing discrete tetragonal crystals, H649. (G) Pseudomorph with scattered rutile crystals on the surface (arrow), H753, 38 days at 246° C with initial pH of 1. (H) Clusters of acicular rutile crystals, H753.
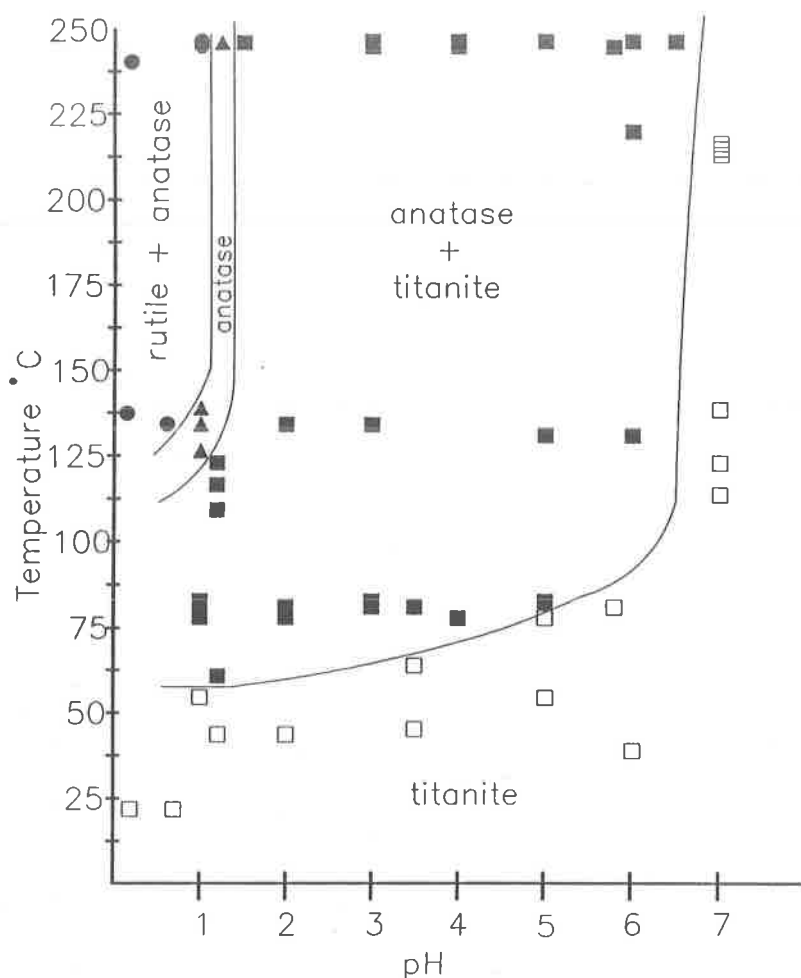
Figure 2. Graphical representation of the experimental results of the alteration of titanite seed crystals in distilled water and HCl solutions. Data from Table 2.

Table 3. Atomic absorption analysis of solutions from low temperature hydrothermal experiments on titanite seed crystals.

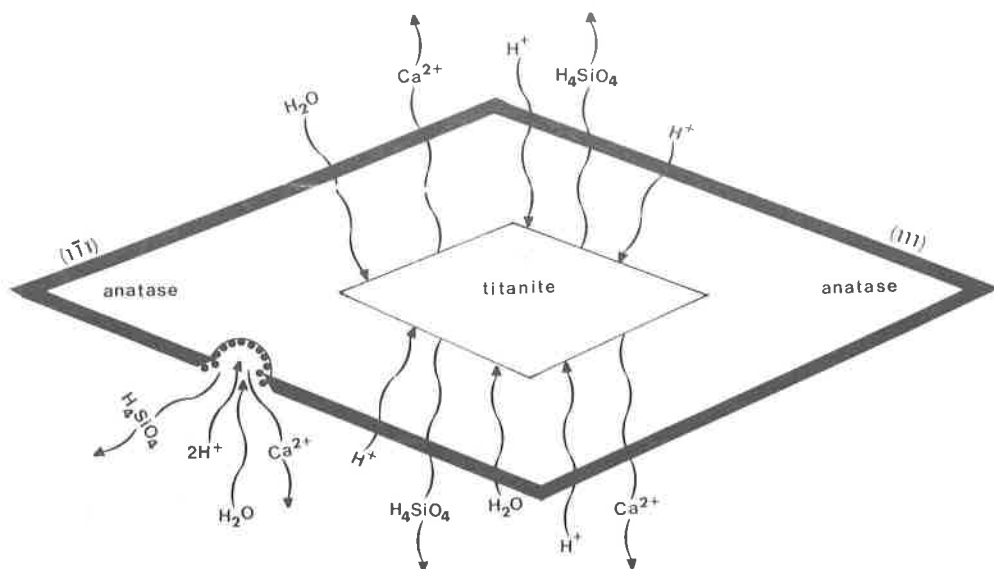| RUN NUMBER	TIME (days)	TEMP. (°C)	pH	Ca (ppm)	Si (ppm)	Ti (ppm)
H1065	60	81	3.5	21.0	2.2	---*
H1066	58	81	5.8	4.5	---	---
H1067	58	81	6.5	11.5	1.3	---
H1070	58	81	6.5	11.4	0.8	---
H1071	60	81	1.2	17.0	0.8	---
H1073	53	81	3.5	4.5	---	---
H1074	53	81	5.8	1.0	---	---
H1075	53	81	6.5	2.8	---	---
H1076	55	44	3.5	5.4	0.8	---
H1077	55	44	0.7	8.2	2.2	---

* None detected.

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Figure 3. Local reactions and movement of ions in the model for the formation of anatase pseudomorphs after titanite. Solution pits occur only if initial pH < 1. Unaltered core would remain at low temperatures and weak acid solutions. Boundary between unaltered core and altered material is sharp. Size of anatase microspheres in solution pits not to scale.

Additional considerations are the crystal structures of titanite, anatase and rutile. The titanite structure consists of chains of TiO_6 octahedra parallel to $\underline{a}$ that are linked by isolated SiO_4 tetrahedra and CaO_7 polyhedra. The substitution of Al^{3+} and OH^- for Ti^{4+} and O^{2-} produces a large and variable number of $P2_1/a$ domains related to one another by a half turn parallel to $\underline{b}$ (Speer and Gibbs, 1976). The crystal structure of an Al-rich titanite (2.41 weight percent Al_2O_3 compared to 2.16 weight percent Al_2O_3 in the seed crystals) indicates that Al has very little effect on the titanite structure (Hollabaugh and Foit, 1984). The minor Al substitution for Ti in the titanite seed crystals is not expected to affect titanite solubility because Al is immobile and insoluble like the Ti that it substitutes for. The structure of both rutile and anatase consist of TiO_6 octahedra. Two edges of the octahedra are shared in rutile and four edges are shared in anatase. The octahedra form chains in rutile but no distinct chains exist in anatase (Lindsley, 1976). The model proposed to describe the formation of anatase pseudomorphs after titanite is illustrated in Figures 3 and 4. On the surface of a crystal H^+ ions combine with O, local charge balance is disrupted causing the breaking of bonds and the destruction of the titanite crystal structure. Each cation polyhedron behaves differently to the breakup of the titanite structure. The strong Si-O bonds are preserved as the isolated SiO_4 tetrahedra are converted to H_4SiO_4. The silica goes into solution (i.e. no silica is detected in pseudomorphs by EDAX scans). The weaker Ca-O bonds are broken and Ca^{2+} ions are put into solution. The Ti remains relatively insoluble in HCl solutions (e.g. on going experiments with titanite and ilmenite in HCl indicate 0-5 ppm Ti in solution). The removal of Ca and Si from the structure leaves an open space between the TiO_6 octahedra. These chains are broken as Ti migrates across the space and reforms into the

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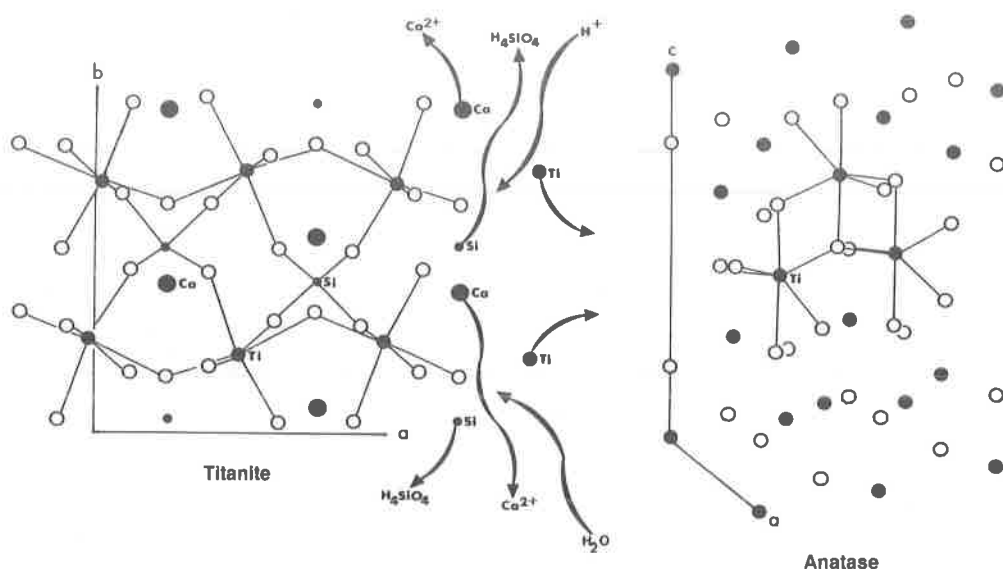
Figure 4. Crystal structures of titanite and anatase and movement of ions in the titanite structure during formation of anatase. Titanite structure from Hollabaugh and Foit (1984) and anatase structure from Lindsley (1976).

anatase structure. Velde (1988) experimentally created talc and serpentine pseudomorphs after diopside and shows that sharp boundaries in pseudomorphs are caused by metasomatic diffusion processes. This experimental research on pseudomorphism by Velde (1988) suggests that sharp anatase-titanite boundary forms because the titanite is relatively impermeable and that the transformation of titanite to anatase is surface controlled.

Recent low-temperature experimental titanite research has focused on determining the feasibility of using synthetic titanite as the ceramic in a glass-ceramic host for long-term storage of reprocessed nuclear fuel waste (Hayward, 1986; Speranzini and Hayward, 1986). The proposed Canadian waste storage system includes underground burial at 500 to 1000 meters in a granite of the Canadian Shield. This storage vault will contain one weight percent fission waste and reach a maximum average vault temperature of 100° C and a ceramic surface temperature of 150° C. Radiation damage from α recoil will cause structural damage of the titanite and a transformation into metamict titanite. The metamict titanite has an enhanced dissolution rate (up to 5 times greater) than undamaged titanite (Vance and others., 1986). Breaching of the storage vault by natural groundwaters are expected to occur during the 100,000 to 1,000,000 year time span that the nuclear waste should be isolated from the biosphere (Hayward and others., 1987). The groundwater will have a pH from 6.2 to 6.7 and contain high concentrations of Na^+, Ca^{2+}, and Cl^-. Figure 2 suggests leaching of titanite at a pH of 6.2 if elevated temperatures occur in the underground vault. We suggest that vault temperatures be kept low by placing less than 1% nuclear waste in the titanite ceramic-glass.

ACKNOWLEDGMENTS

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NOTE CONCERNING THE PETROGRAPHY AND K-Ar AGE OF Cr-SPINEL-BEARING OLIVINE THOLEIITE IN THE SUBSURFACE OF CHOCTAW COUNTY, NORTH-CENTRAL MISSISSIPPI

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ABSTRACT

Core samples taken at 9,306 and 9,309 ft (2,820 and 2,821 m) from the Pan American Petroleum Corporation (AMOCO), #1 USA-Tombigbee Forest well in Choctaw County, Mississippi have been investigated. The rock is a Cr-spinel-bearing olivine tholeiite. Cr-spinel most commonly is associated with altered idiomorphs of olivine phenocrysts in the basalt. The whole-rock K-Ar age of the tholeiite is 199 ± 10 Ma.

INTRODUCTION

A core from an oil well drilled in Choctaw County of north-central Mississippi (Figure 1) contains an interval of mafic hypabyssal rock emplaced within the Pottsville Fm. This note is a report on the petrology and isotope age of selected samples taken from the igneous-rock portion of that core (other samples were taken as sidewall cores during the drilling operation, but none of them contained igneous rock).

Pan American Petroleum Corporation (AMOCO) drilled the 14,886 ft

LEGEND

1. Buried Ouachita Tectonic Belt
2. Buried Appalachian Tectonic Belt
3. Mississippi Embayment Axis
4. Black Warrior Basin
5. Amerada, #1 Moore 190 Ma granite 3500-3650 ft deep (Denison and Muehlberger, 1963)
6. Vardaman sill, in 3 wells J-Tr tholeiitic diabase 3750-3900 ft deep (Mellen, 1979)
7. Pan American, #1 USA-Tombigbee Forest 199+10 Ma tholeiitic basalt; 9306 ft deep
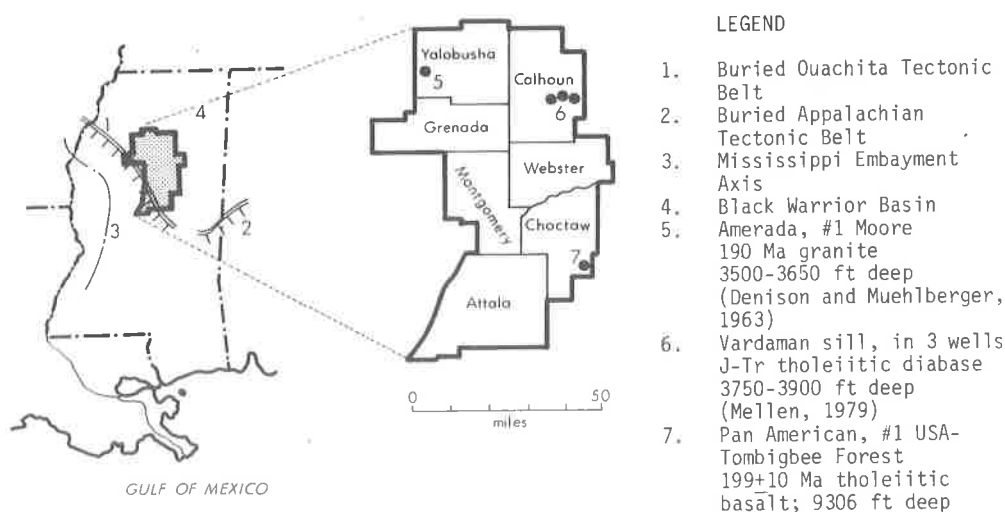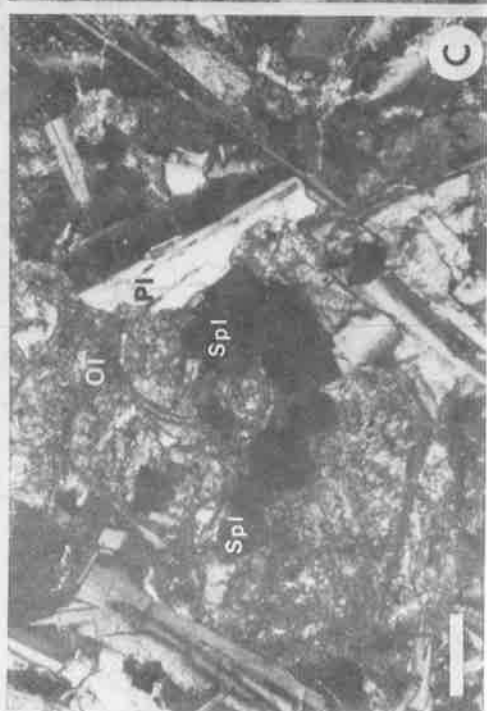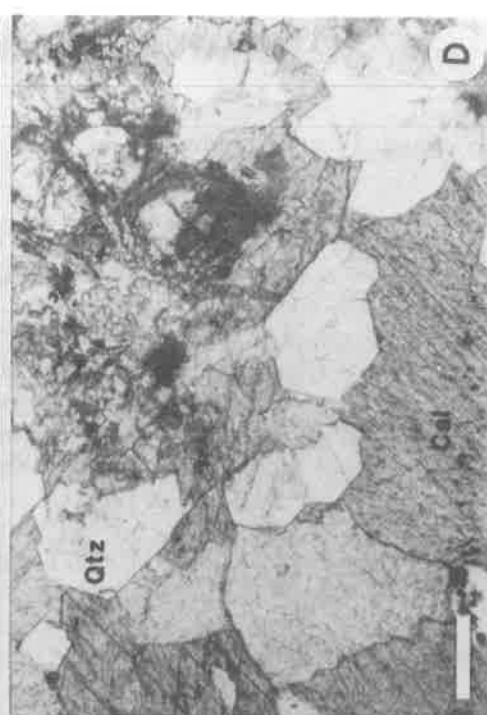
Figure 1. Location of well penetrating olivine tholeiite in Choctaw County, Mississippi. Stippled area includes other known subsurface occurrences of rocks of similar composition and/or age and their relationship to local structural features.

(4,511 m) #1 USA-Tombigbee Forest well in the south-eastern corner of Choctaw County, Mississippi in 1964 (Figure 1). The well is located in section 14, tier 16N, range 11E, and penetrated about 900 ft (273 m) of Tertiary sedimentary rocks, about 3,100 ft (940 m) of Cretaceous strata, and entered the Paleozoic section at a depth of about 4,070 ft (1,233 m). Drilling reports indicate that the well bottomed while still in Pennsylvanian age sedimentary rocks (Pottsville) at a depth of 14,886 ft (4,511 m). A 33-ft (10 m) interval was cored beginning at a depth of 9,300 ft (2,818 m). The upper 15 ft (5 m) of this cored interval contains mafic hypabyssal rocks and associated mineral products. This igneous-rock interval shows up on the electric log as a well-defined and anomalous resistivity spike.

The well is located on the southwestern edge of the Black Warrior Basin and is northeast of the southeastern limit of the buried Ouachita Tectonic Belt. The Mississippi Embayment axis lies about 40 miles (64 km) to the west, and the western end of the buried Appalachian Tectonic Belt is about the same distance to the southeast (Figure 1).

Other hypabyssal rocks have been reported in the general area of this study (Figure 1). In Yalobusha County, there is a 190 Ma old granite at 3,500-3,650 ft (1,061-1,106 m) (Denison and Muehlberger, 1963), and in Calhoun County a tholeiitic diabase found in three wells at depths of 3,700-3,750 ft (1,121-1,136 m) has been correlated by Mellen (1979) as a continuous sill of Jurassic-Triassic age.

PETROGRAPHY

The core contains olivine tholeiite and additional mineralization that is either synchronous with or emplaced later than the intrusive event. The rock sample is a fine-grained, massive to slightly porphyritic, dark greenish-gray olivine tholeiite which has been intruded by a thin, vuggy quartz-calcite vein. In thin section, the unaltered rock is holocrystalline, sub-ophitic with a massive to slightly trachytic texture (Figure 2-A).

The major minerals are plagioclase (labradorite) and augite. About half (48%) of the rock is plagioclase (An 68) which occurs as elongate euhedral laths (0.2-1.7 mm) that display common Carlsbad-albite twinning and a slight oscillatory zoning. About 23% of the rock is a slightly pinkish, light brown augite which occurs as subhedral to anhedral forms (0.1-0.9 mm), and is interstitial to plagioclase.

A minor mineral, olivine (7%) is totally altered. It appears as idiomorphic phenocrysts (0.5-2.0 mm) that give the rock its slightly porphyritic texture (Figure 2-B). The olivine phenocrysts have altered to calcite that is laced with ribbons of limonite and serpentine.

Figure 2. Photomicrographs of thin sections of olivine tholeiite and associated minerals and mineralization processes. All rocks and minerals are from cores taken at depths between 9,303-9,313 ft (2,819-2,822 m) below derrick floor at drillsite of Pan American Petroleum Corporation (AMOCO), #1 USA-Tombigbee Forest, in Choctaw County, Mississippi. Scale bars are 0.5 mm except 2-C (0.15 mm) and 2-G (1 cm). A. Flow texture exhibited by sub-parallel orientation of plagioclase laths in groundmass (crossed nicols). B. Altered olivine idiomorph in plagioclase matrix (crossed nicols). C. Cr-spinel euhedra in altered olivine (crossed nicols, bar is 0.15 mm). D. Quartz euhedra in calcite; both minerals are major components of a vuggy vein intruding the olivine tholeiite (plane polarized light).
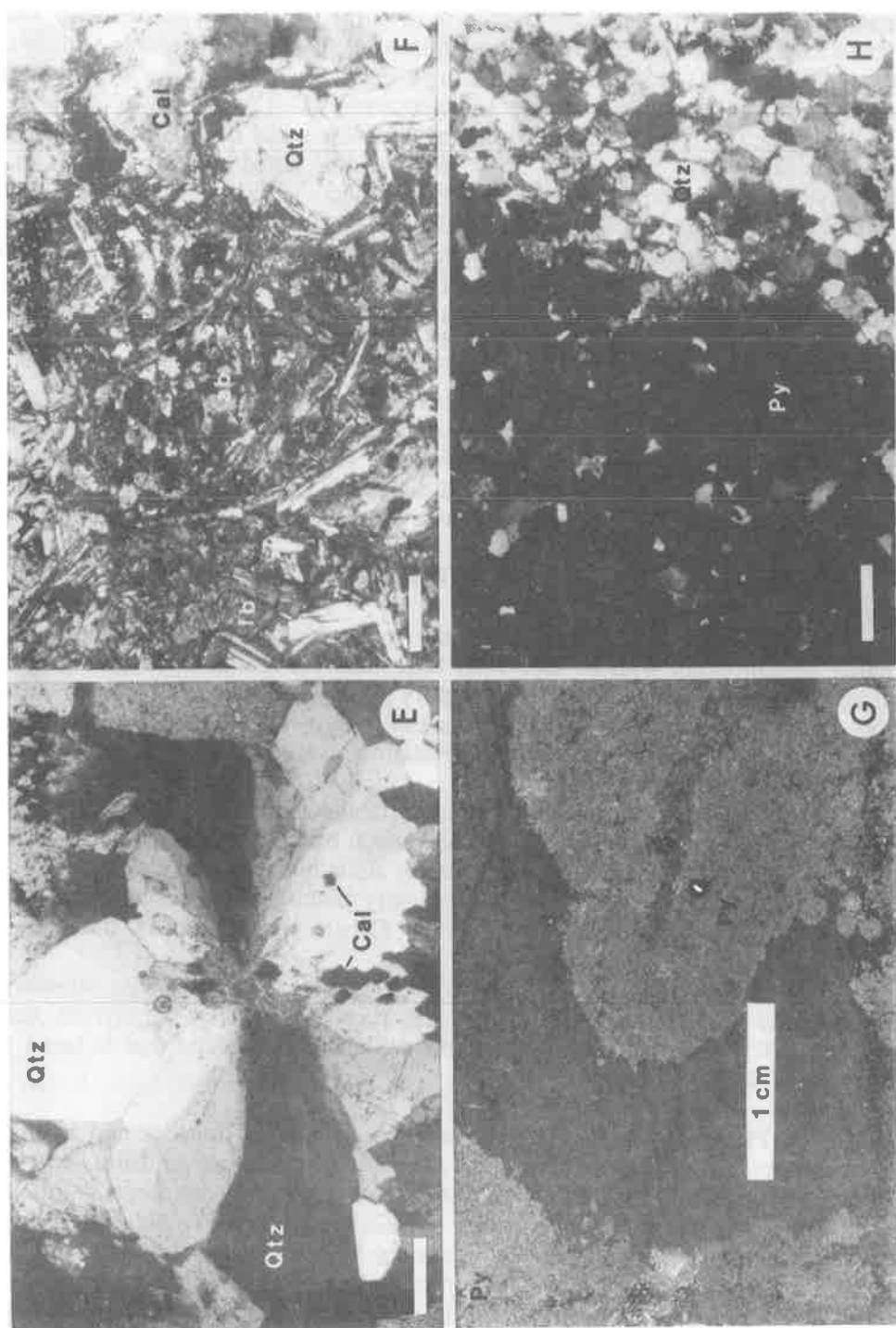
Table 1. Chemical analyses of selected chromian spinel crystals in an olivine tholeiite in Choctaw county, north-central Mississippi.

Element oxide	Sample 1 %	Sample 1 SD*	Sample 2 %	Sample 2 SD	Sample 3 %	Sample 3 SD
Cr_2O_3	23.35	(0.55)	22.95	(0.31)	23.51	(0.43)
Al_2O_3	38.32	(1.31)	39.98	(0.85)	39.66	(0.55)
FeO**	20.73	(0.35)	19.18	(0.73)	18.66	(0.63)
V_2O_3	0.13	(0.01)	0.13	(0.01)	0.13	(0.02)
TiO_2	0.40	(0.02)	0.35	(0.02)	0.33	(0.03)
MgO	6.16	(0.38)	16.68	(0.28)	16.97	(0.31)
MnO	0.16	(0.02)	0.15	(0.02)	0.14	(0.01)
ZnO	0.10	(0.01)	0.09	(0.02)	0.09	(0.01)
NiO	0.21	(0.02)	0.23	(0.02)	0.24	(0.02)
CaO	0.30	(0.06)	0.14	(0.04)	0.13	(0.01)
SiO_2	0.14	(0.07)	0.14	(0.03)	0.16	(0.01)
TOTAL	100.00		100.02		100.02	

* SD = standard deviation; % based on average of 10 points/sample
** Total (FeO + Fe_2O_3); Microprobe analyses by Todd Solberg, Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061.

Accessory minerals are Cr-spinel and pyrite which make up 4% and 3% of the rock respectively. Cr-spinel appears in thin section as dark reddish-brown cubic euhedra (0.01-0.1 mm) that occur in or with the altered olivine idiomorphs (Figure 2-C). Microprobe analyses of the spinel are given in Table 1. Microprobe mapping indicated no zoning of elements in the spinel.

Pyrite is fresh and usually fills small interstices between plagioclase laths. Very thin, calcite-filled fractures and small zones of fine-grained unknown minerals make up the rest of the rock.

A vuggy quartz-calcite vein cross-cuts the olivine tholeiite (Figure 3). The vein has well formed crystals of both quartz and calcite in the vugs. In thin section, examples of both quartz euhedra in calcite (Figure 2-D), and calcite rhomb inclusions in radiating quartz prisms (Figure 2-E) are present. At the vein-olivine tholeiite contact, the plagioclase and augite are altered to clay, chlorite and iron oxides (Figure 2-F). The thickness of the altered zone is about 1 mm in the samples studied to date.

Although pyrite is a minor accessory mineral in the olivine tholeiite, it is

Figure 2 (continued). E. Radiating prisms of quartz with inclusions of calcite rhombs in vein described above (crossed nicols). F. Altered basalt (ab) at contact of fresh basalt (fb) and quartz-calcite vein (Qtz-Cal) (crossed nicols). G. Polished core slab showing pyrite that permeated quartz sandstone host rock (bar is 1 cm). H. Photomicrograph of G displaying relict sandstone grains as "inclusions" in opaque pyrite (crossed nicols). Symbols for minerals are as follows (after Kretz, R., 1983): Aug-augite, Cal-calcite, Chl-chlorite, Ol-olivine, Spl-spinel, Pl-plagioclase, Py-pyrite, Qtz-quartz.
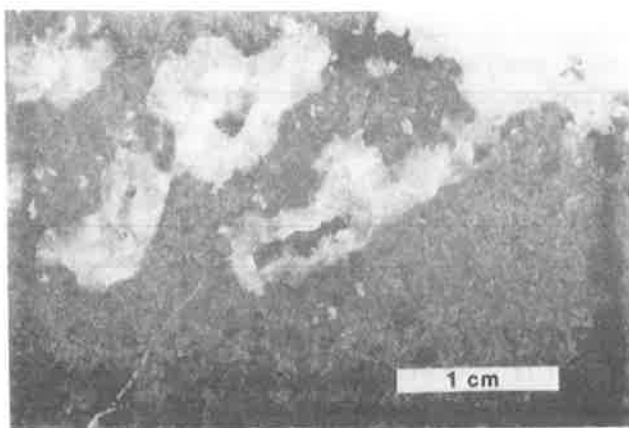
Figure 3. Photograph of polished slab of vuggy quartz-calcite vein in olivine tholeiite.

prominent in the cored sections of the sedimentary host rock. A fine-grained, slightly micaceous and feldspathic, quartz sandstone appears to have been replaced (?) by massive, microcrystalline pyrite (Figure 2-G). In thin section, small relicts of the host rock can be seen as inclusions in the pyrite (Figure 2-H). No similar occurrences of pyrite were observed in the cored sections olivine tholeiite.

K-Ar AGE

Two fresh appearing samples of the olivine tholeiite were submitted for whole rock K-Ar age determinations. Dates of 143 ± 8 Ma and 199 ± 10 Ma were reported (Table 2).

Although the dates came from two samples located within approximately 3 ft (1 m) of each other in the same core, came from the same lithology, and were from apparently fresh and unweathered rock, their values differ significantly. The older date is interpreted to represent the approximate time of intrusion. The 199 ± 10 Ma date falls in the range of K-Ar dates of very similar rocks in the southeastern and eastern region of North America (Deininger and others, 1975; Dooley and Wampler, 1983; Dye and others, 1985; McHone, 1978; Seidemann and others, 1984).

The 143 ± 8 Ma apparent age is not interpreted as a meaningful age. Fracturing and volatile intrusions associated with a Cretaceous (78 - 91 Ma) igneous event in the nearby Mississippi Embayment (Sundeen and Cook, 1977) may have been responsible for disturbing the K-Ar clock in the sample with the younger apparent age. The calcite vein seen in Figure 3 occurs approximately 10 to 30 cm from the sample submitted for dating (estimated by reconstructing the core from available samples). In addition, these types of rocks are difficult to date using standard K-Ar techniques as discussed by Dooley and Wampler (1983), and Seidemann and others (1984).

With information available from only a few feet of core, a possible mechanism for disrupting the original K-Ar composition may have been the intrusion of a very thin quartz-calcite vein (Figure 3). The sample could have been either chemically and/or thermally disturbed by the intrusion of this or similar veins. The vein in the basalt core is small (< 2 cm thick) and it would affect the

Table 2. K-Ar dates for a Cr-spinel-bearing olivine tholeiite in Choctaw county, north-central Mississippi.

Depth (ft)	(m)	K (%)	Avg K (%)	^{40}K (ppm)	$^{40*}Ar$ (ppm)	$^{40*}Ar$ total ^{40}Ar	Avg $^{40*}Ar$	Age (Ma)
9,306	(2,820)	0.197	0.199	0.237	0.002996	0.457	0.002904	199 ± 10
		0.201			0.002811	0.557		
9,309	(2,821)	0.191	0.195	0.232	0.001838	0.505	0.002001	143 ± 8
		0.198			0.002242	0.481		
					0.001924	0.408		

Note: Constants: ^{40}K, $\lambda_e + \lambda'_e = 0.581 \times 10^{-10}$/yr; $\lambda_\beta = 4.962 \times 10^{-10}$;

$^{40}K/K = 1.193 \times 10^{-4}$ g/g; $^{40*}Ar$ = radiogenic argon.
Analysts: Kreuger Enterprises, Inc., Geochron Laboratories Division.

stability of the K-Ar isotope distribution in only a limited volume of the intruded rock. Hence, only rock immediately adjacent to the vein would be disturbed to the extent that a K-Ar date would be anomalous.

DISCUSSION

Several approaches were used to classify the rock. Mineral composition by itself is inadequate for classifying basaltic rocks. Results from chemical analyses and normative mineral calculations (Table 3) plotted on the ($Na_2O + K_2O$) vs. SiO_2 diagram and the normative Ol-Ne-Q (Ab-Opx-Ol subset) ternary diagram of Irvine and Baragar (1971) indicate a tholeiitic rock classification for the cored rock sample. The consistent presence of olivine in the rock modifies the classification to olivine tholeiite. The normative mineral classification diagram using Di-Hy-Ol-Ne-Q as end points (Yoder and Tilley, 1962) also plotted the rock as an olivine tholeiite, although it plotted close to the alkali olivine basalt field. The CIPW normative minerals were calculated without the volatile components H_2O, SO_2, and CO_2 (Table 3).

Wiegand and Ragland (1970) provide a good regional summary of doleritic and diabasic dikes in eastern North America from Alabama to Nova Scotia. Rock ages ranging from 196-230 Ma are reported in that study. They subdivided the numerous samples into four groups based on composition. The quartz tholeiites were split into three groups based on iron and titanium compositions. The first group has a low $TiO_2\%$ (< 0.90), the second group has a high $TiO_2\%$ (>0.95), and the third group has a high $Fe_2O_3\%$ (total Fe), (MI>0.66) where
$$MI = Fe_2O_3(\text{total Fe})/(Fe_2O_3(\text{total Fe}) + MgO).$$
The fourth subdivision has normative-olivine tholeiite dikes.

When the location of the rock was plotted against the compositional subgroup, a trend was noted where quartz tholeiites were most common in the northern Appalachians, whereas olivine tholeiite was predominant in North and South Carolina. Georgia and eastern Alabama have both olivine tholeiite and low-$TiO_2\%$ quartz tholeiite. The olivine tholeiite in Choctaw County, with its low $TiO_2\%$ (0.80), appears to extend westward the geologic and geographic trends of

Table 3. Chemical, normative, and modal analyses of a Cr-spinel-bearing olivine tholeiite in Choctaw county, north-central Mississippi.

Oxides	Weight percent*	Normative minerals**	Normative mineral %	Modal minerals	Percent
SiO_2	44.72	Q	. .	- - - -	. .
TiO_2	0.80	Cd	. .	- - - -	. .
Al_2O_3	15.13	Or	1.1	- - - -	. .
Fe_2O_3	0.00	Ab	17.5	- - - -	. .
FeO	9.45	An	31.4	- - - -	. .
MnO	0.19	Ne	. .	- - - -	. .
MgO	7.34	Pl	(48.9)	Plagioclase	48
CaO	11.95	Di	23.1	- - - -	. .
Na_2O	2.07	Hy	2.5	Augite	26
K_2O	0.19	Ol	12.8	Olivine	7
P_2O_5	0.12	Mt	1.8	- - - -	. .
H_2O+	1.51	Il	1.5	Cr-spinel	4
H_2O-	0.38	Ap	0.3	- - - -	. .
CO_2	4.43	Cc	. .	Calcite	12
S	0.16	Pr	. .	Pyrite	3
-S=O	-0.08	Mg#	(0.62)	- - - -	. .
		An% Pl	(64)	An% Pl	(68)
Total	98.36%	Total	92.0%	Total	100%

* Chemical analysis done with XRF of fluxed fused glass by John and JoAnn Sinton, Department of Geology and Geophysics, University of Hawaii, Honolulu, HI 96822.

** Normative minerals calculated with Fe_2O_3/FeO (mol) = 0.15 and without use of volatiles H_2O, CO_2, S.

Weigand and Ragland (1970). The age of 199 ± 10 Ma is within the range of dates for the rocks in their study (196 ± 230 Ma).

CONCLUSIONS

The Choctaw County, Mississippi, deep cored section has interesting mineralogy in and around it, represents one of the deeper occurring samples to have been studied to date, and is reasonably well preserved. These conclusions seem indicated:

1. The rock is a Cr-spinel-bearing olivine tholeiite.
2. Its whole-rock K-Ar age is 199 ± 10 Ma.
3. The olivine tholeiite in this study (as well as the apparently related rocks in adjacent counties, Figure 1) appear in composition and age to demonstrate a westward extension of the igneous activity which produced the Early Mesozoic diabases located in the eastern North American province.

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ACKNOWLEDGMENTS

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