GEOCHEMICAL TRENDS ASSOCIATED WITH THE TIOGA ASH AND ORIGIN OF THE HUNTERSVILLE CHERT, EAST-CENTRAL WEST VIRGINIA

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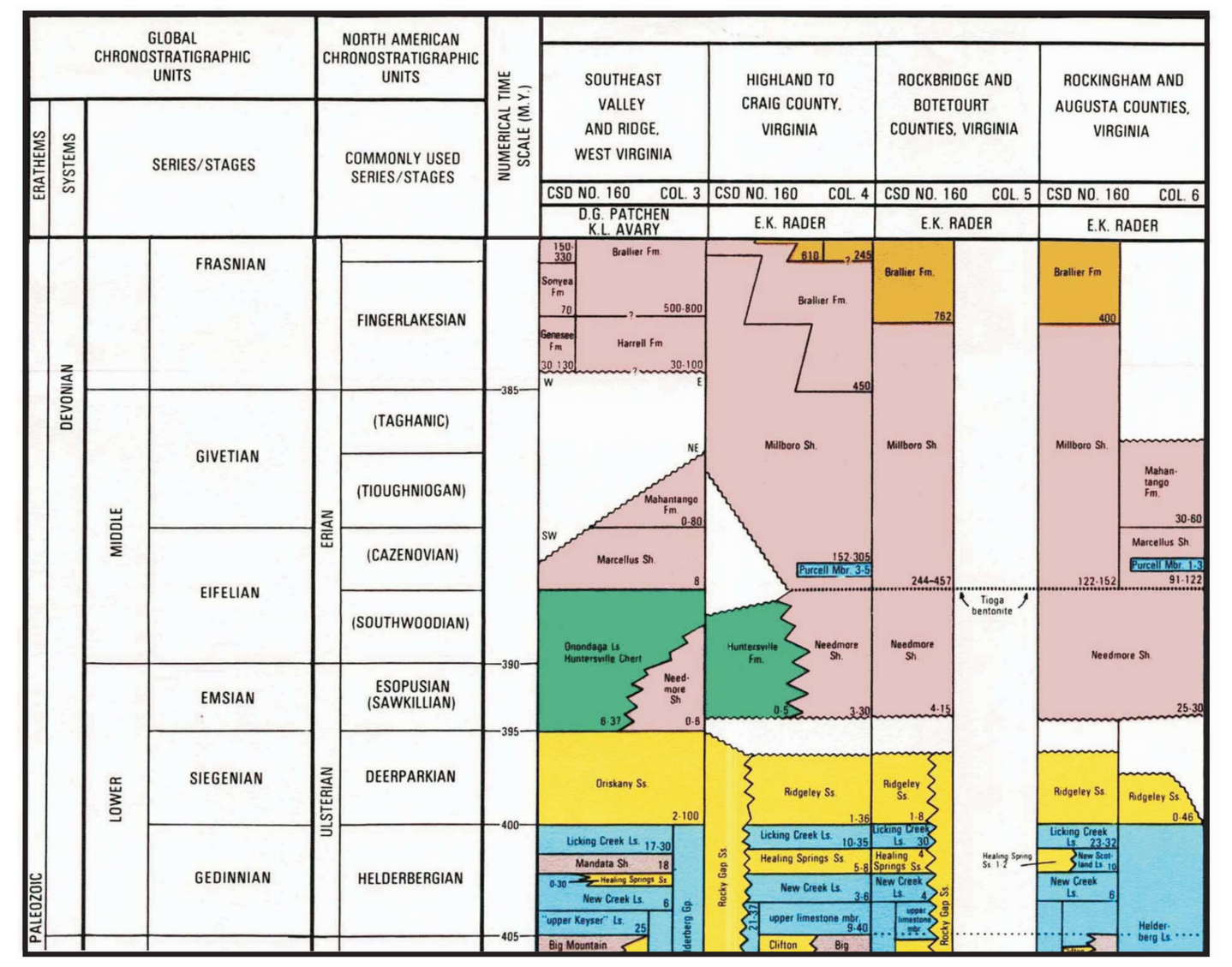
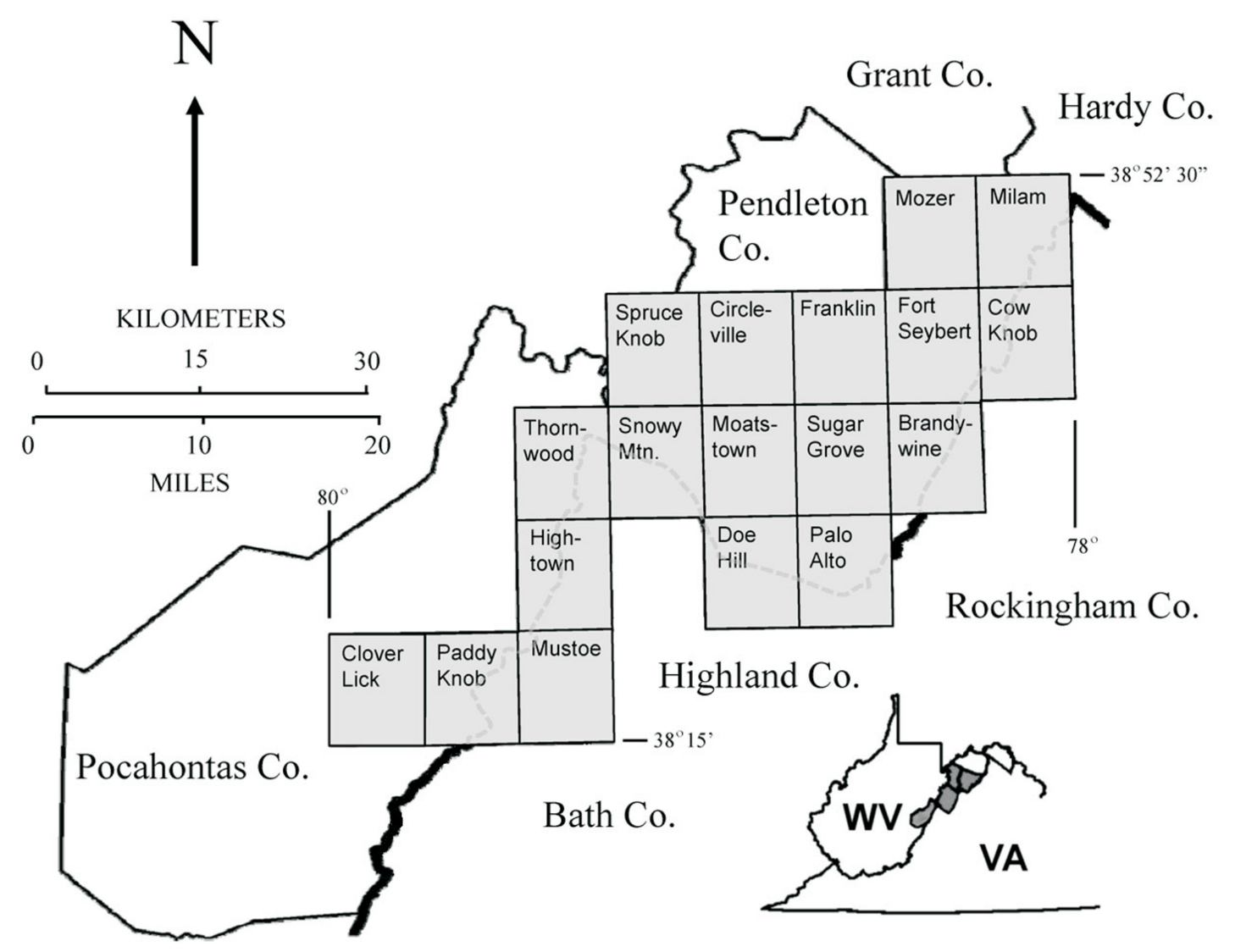
ABSTRACT

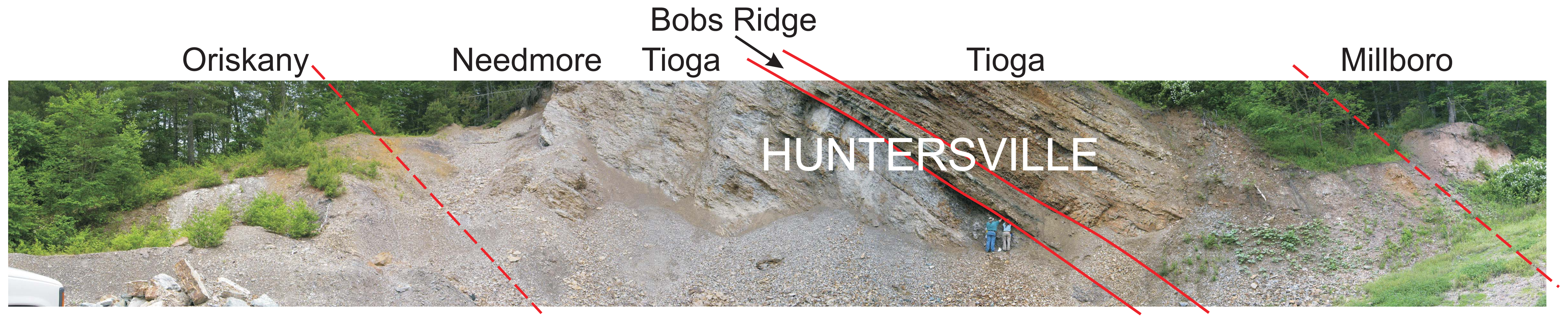
In east-central West Virginia and adjacent western Virginia, the Lower-Middle Devonian Needmore and Millboro shale sequence is separated by the Tioga Ash (Bentonite). To the south, the Needmore thins and is replaced by the Huntersville Chert and Bobs Ridge Formation, both interbedded with the Tioga. Geochemical analysis of samples recovered during STATEMAP field investigations has been an ongoing project since 1997. Examination of trace, rare-earth, and precious metals content of samples from this stratigraphic interval indicates that there is a notable enrichment of gold and rare earths in the two shales, the Tioga, and the Bobs Ridge. In contrast, analytical values for the Huntersville do not appear to reflect these trends. Because of the general immobility of these elements, the author postulates that their enrichment reflects sea water chemistry resulting from a long period of volcanic activity that began during Needmore deposition, peaked during the development of the Tioga, and may have continued into the deposition of the Millboro. The lack of enrichment in the Huntersville is curious, since this unit is generally considered to be a stratal equivalent of the Needmore. However, field observations by the author suggest that the Huntersville is not a simple facies equivalent but, rather, formed by silicification of pre-existing portions of the Needmore, Tioga, and Bobs Ridge. As a result, the Huntersville represents an unique chemostratigraphic unit younger than the other formations in this interval. This lack of contemporaneity may help explain why the Huntersville does not exhibit the same pattern of enhanced metal content.



Early-Middle Devonian stratigraphy for east-central West Virginia and western Virginia (Patchen and others, 1984).

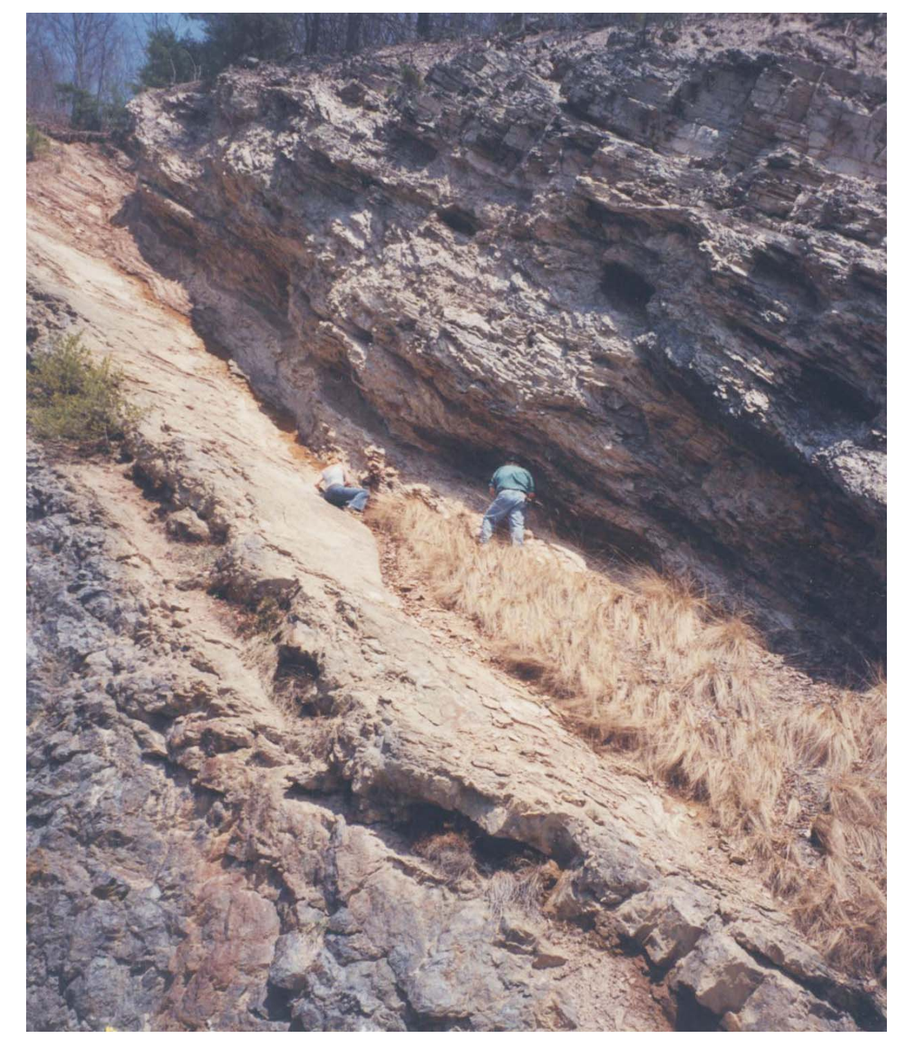


Mapping areas for the author's STATEMAP projects extending back to 1997. Each project included geochemical sampling and analyses (McDowell, 2001).



Panoramic view of the Huntersville interval exposed at the Cove Hill Quarry, Pocahontas Co., WV. View is to the north.

Poorly preserved trace fossil *Zoophycus? or Spirophyton?* in the Huntersville Chert (or silicified Needmore Shale) at the Frost Quarry, Pocahontas Co., WV. Coin is 3 cm in diameter.



Sampling one of several discrete Tioga Ash layers at Wytheville, VA.

Silicified Tioga Ash with tectonic fracturing and vertical burrows containing silicified detrital infillings or glauconitic sand (arrows), Michael Mtn. Quarry, Pocahontas Co., WV.

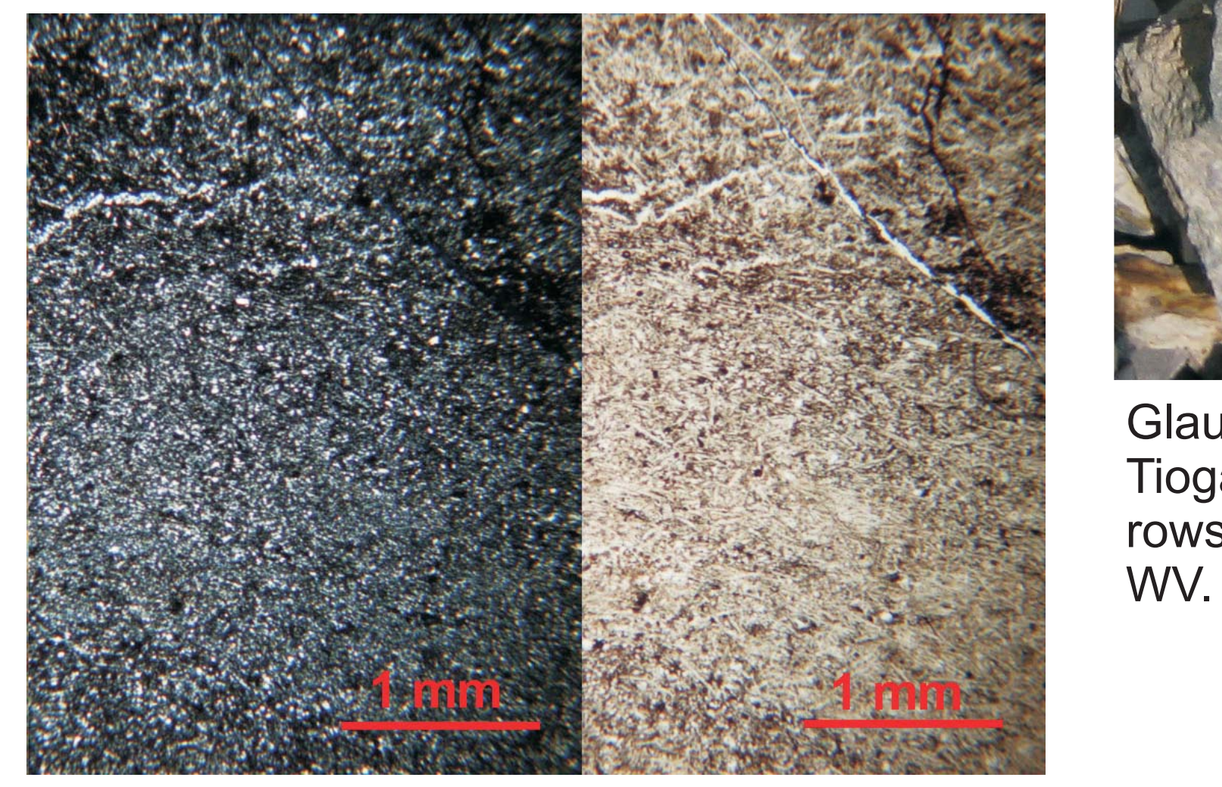
Tectonic fracturing in the Huntersville Chert, which makes it a popular aggregate material, Michael Mtn. Quarry, Pocahontas Co., WV.

Nodular chert within the Tioga Ash - interbed of Bobs Ridge glauconitic sandstone is present at the top of the specimen. Coin is 3 cm in diameter. Michael Mtn. Quarry, Pocahontas Co., WV.

Interbedded Bobs Ridge glauconitic sandstone and Tioga Ash from Pocahontas Co., WV. The unusual "zebra" appearance is due to the top-down view of the trace fossil *Spirophyton*? mixing sediment from the two units. Coin is 3 cm in diameter. Cove Hill Quarry, Pocahontas Co., WV.

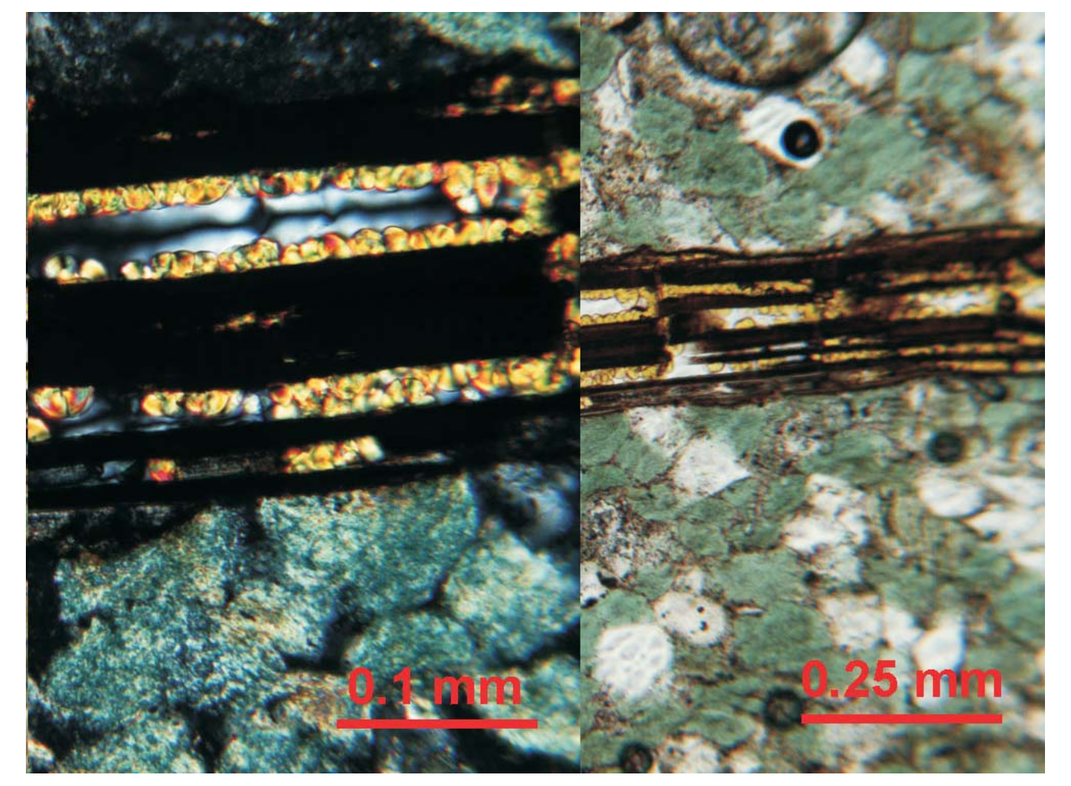
Interbedded Tioga Ash and Bobs Ridge glauconitic sandstone from Cove Hill Quarry, Pocahontas Co., WV crosscut by vertical burrows with silicified fillings and marked by a halo of iron mineralization.

Interference ripples and vertical burrows in silicified Tioga Ash from the Michael Mtn. Quarry, Pocahontas Co., WV.

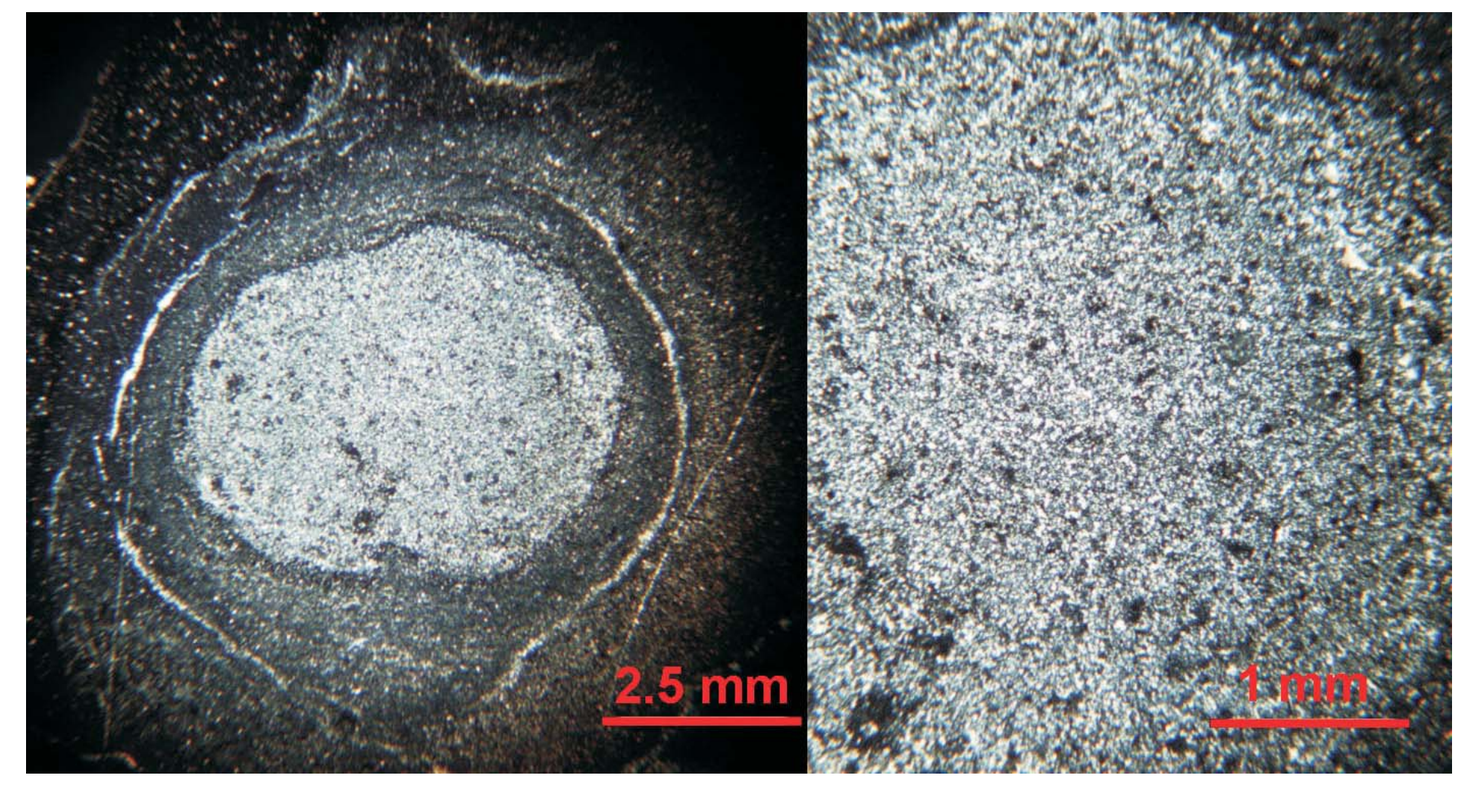


Plain light (right) view photomicrograph of Huntersville Chert reveals the presence of sponge spicules. Cross-polars (left) shows that the rock was formerly a silty shale, probably Needmore. CL-2-11, Frost Quarry, Pocahontas Co., WV.

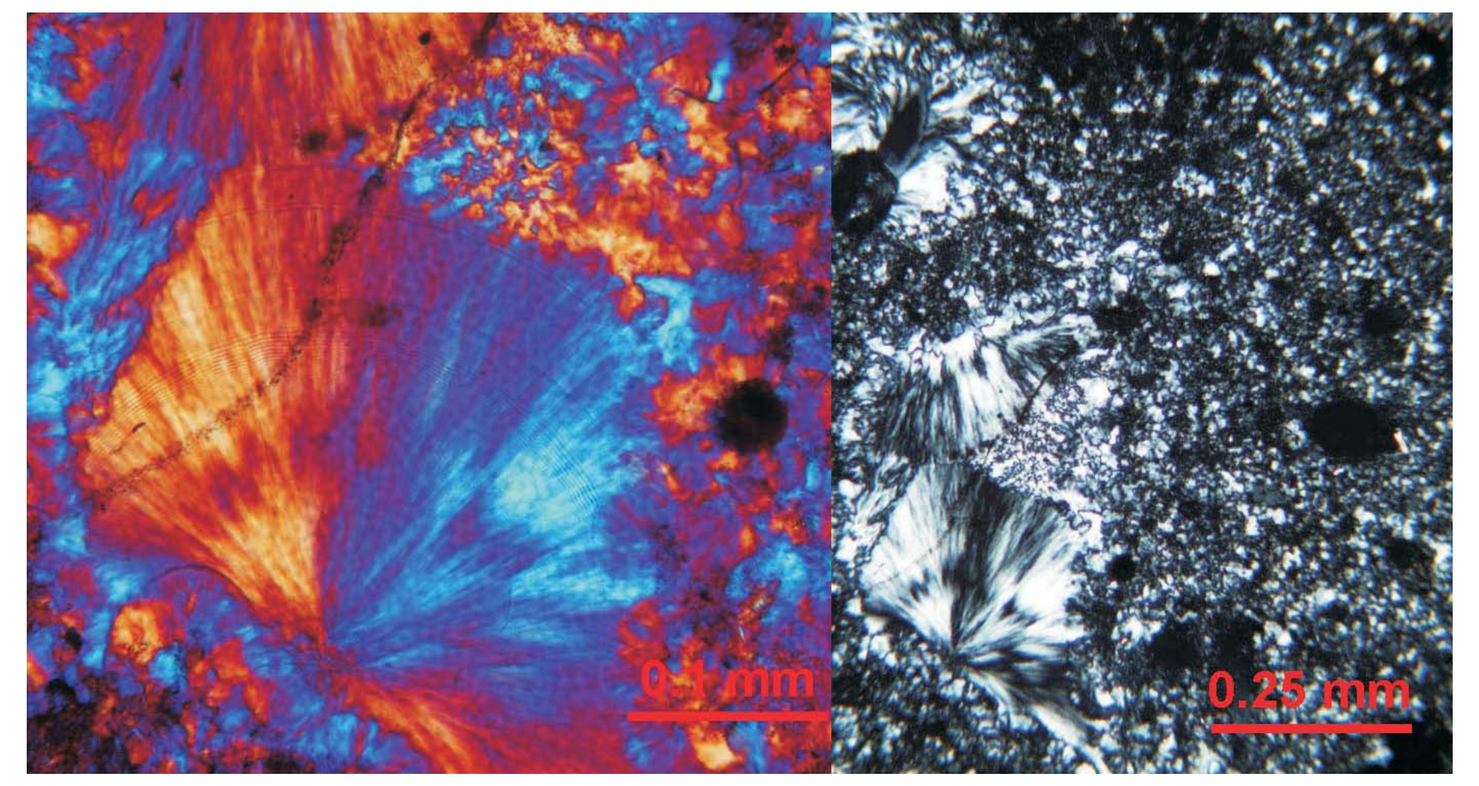
Glauconitic Bobs Ridge with silicified clasts of Tioga Ash, some intact and some skeletal (arrows), Michael Mtn. Quarry, Pocahontas Co., WV. Coin is 3 cm in diameter.



Photomicrographs of the peloidal glauconitic sand of the Bobs Ridge. Also visible is the partially altered shell of a phosphatic inarticulate brachiopod. CL-4a-11, Frost Quarry, Pocahontas Co., WV.

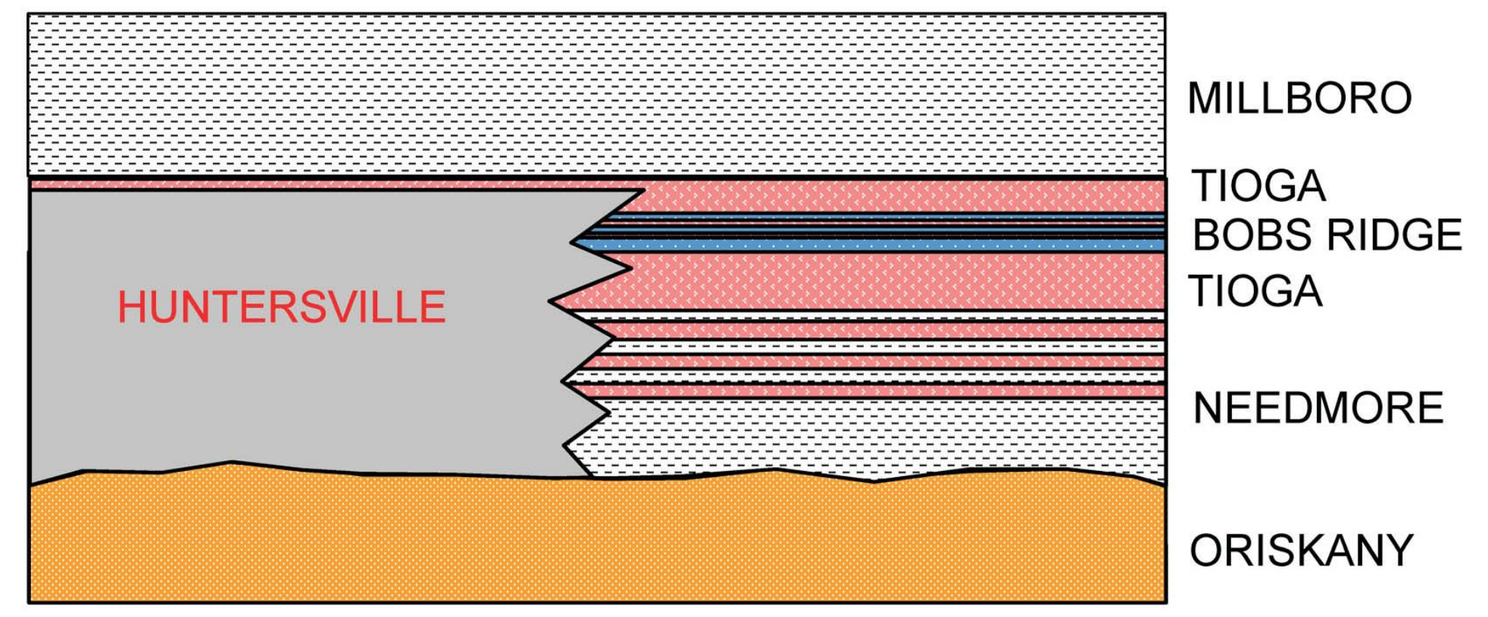


Photomicrographs of silicified silty filling in a vertical burrow. Chert sample from Cove Hill Quarry, Pocahontas Co., WV appears to have originally been a silty shale, probably Needmore. PK-19a-09, Cove Hill Quarry, Pocahontas Co., WV.

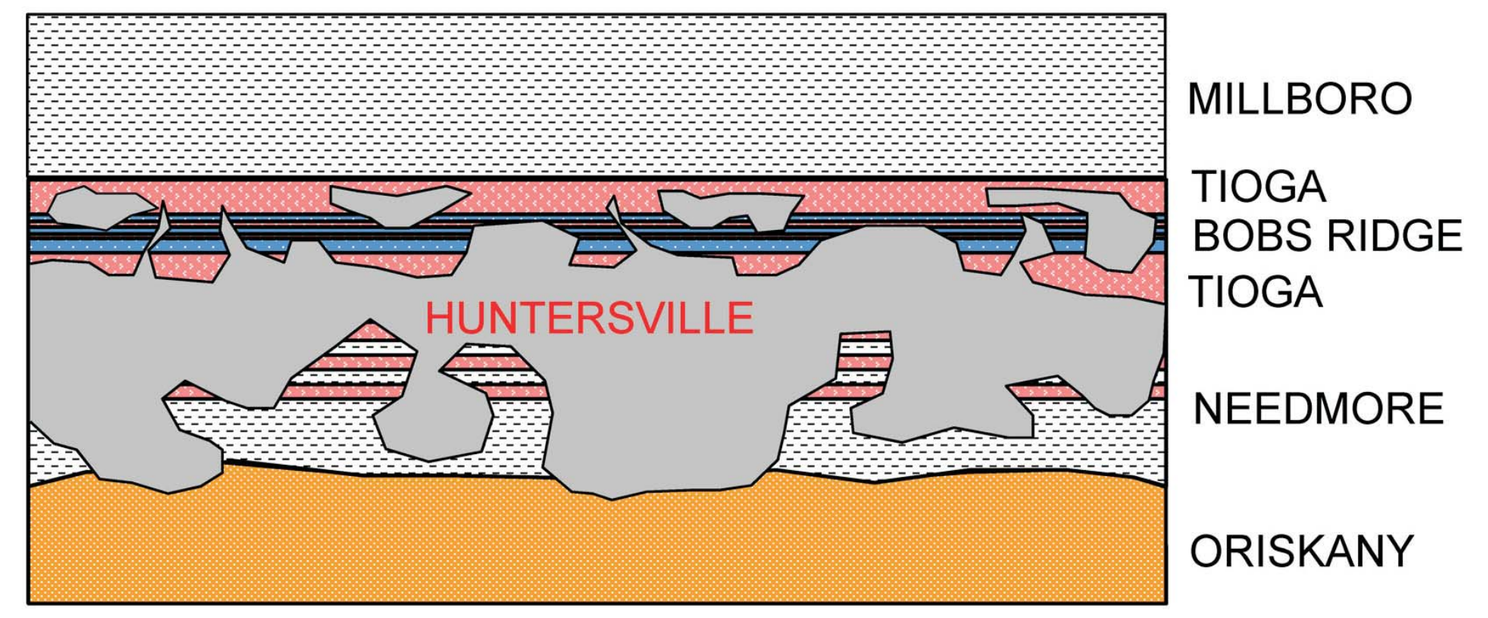


Photomicrographs of silicification within a sample of Huntersville Chert. Chalcedony and microquartz visible on the right; closer view on the left with 1/4-wave plate to show the length-fast nature of the chalcedony. CL-2-11, Frost Quarry, Pocahontas Co., WV.

The Huntersville "Interval" - Needmore to Millboro



The conventional view of the Huntersville Chert treats it as a "normal" stratigraphic unit equivalent to the uppermost Oriskany Sandstone (Price, 1929) or to the Needmore Shale (Dennison, 1960; Weed, 1982; Patchen and others, 1984).



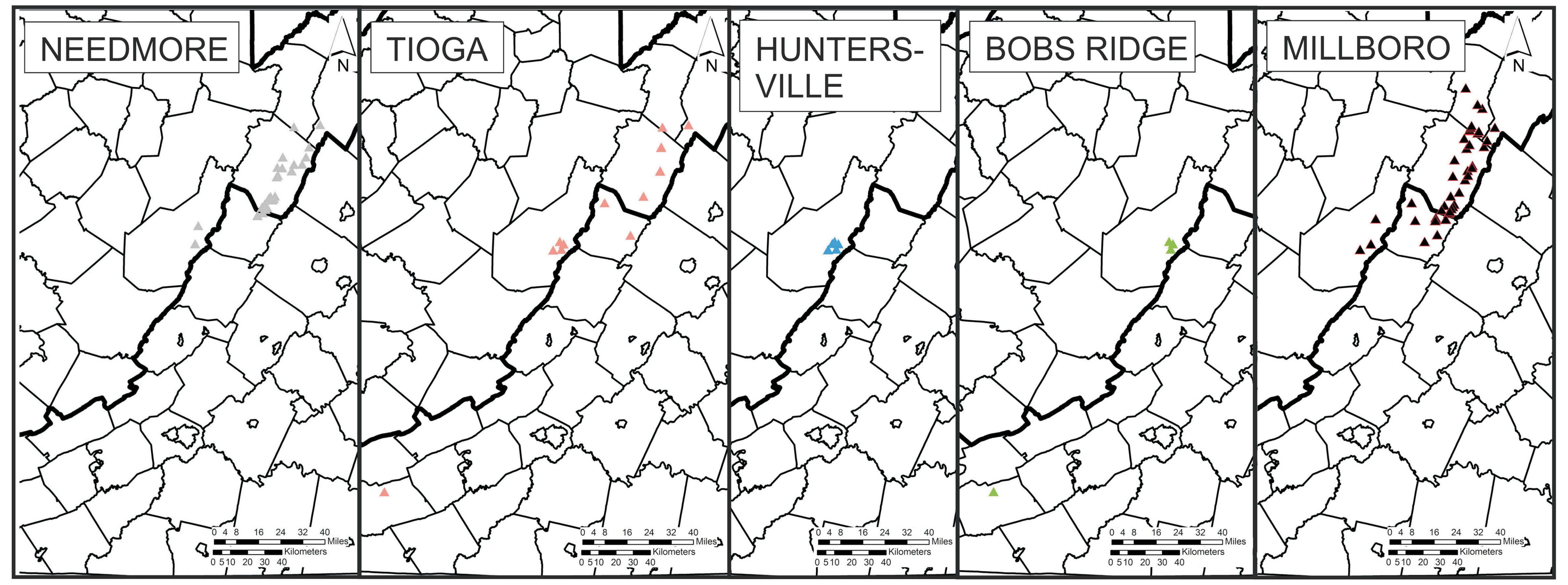
For the study area, the author follows the lead of Woodward (1943) and suggests that the Huntersville is an approximately *stratiform* chemostratigraphic unit that has been developed by the silicification of pre-existing sedimentary units.

DISCUSSION

Within the study area, the Tioga Ash changes character from being several discrete ash layers to a more diverse sedimentary unit with interbedded glauconitic sandstone of the Bobs Ridge. Mixing of these two units by bioturbation indicates that they are nearly contemporaneous in their deposition. In fact, geochemically, the trace element compositions of these units, together with the underlying Needmore Shale and overlying Millboro Shale, show a great deal of similarity.

The Huntersville Chert occurs within this same stratigraphic interval and, in the study area, is found intimately associated with the Needmore, Tioga, and Bobs Ridge. Macroscopic and microscopic sedimentary features seen in these latter three units have been observed in material attributable to the Huntersville. However, the Huntersville does not appear to form discrete layers of chert (or flint) but is more discontinuous in its outcrop expression. Geochemically, the Huntersville stands out from other contemporary units in its depletion in trace elements. Thirty-one of fifty elements analyzed for in the Huntersville are notably reduced or absent compared to samples from **all** the other units in this stratigraphic interval.

This suggests that the formation of the Huntersville was by a process chemically dissimilar to associated units. The fact that it contains sedimentary features similar to those units and is intimately associated with them, further suggests that the Huntersville is a chemostratigraphic unit formed by the silicification of pre-existing lithologies. The Huntersville probably represents a nearly *stratiform,* but diachronous diagenetic unit, formed by the selective silicification of earlier sedimentary material. The source of excess silica in pore fluids was, most likely, water-lain ash of the Tioga.



Locations of geochemical samples taken from the Needmore Shale, Tioga Ash, Huntersville Chert, Bobs Ridge Sandstone, and Millboro Shale in the study area.

ALL ANALYSES DONE BY INAA (INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS)

Needmore																																		
Element	AU	AS	BA	BR	CA	CO	CR	CS	FE	HF	HG	IR	MO	NA	NI	RB	SB	SC	SE	SN	SR	TA	TH	U	W	ZN	LA	CE	ND	SM	EU	TB	YB	LU
Units	PPB	PPM	PPM	PPM	%	PPM	PPM	PPM	%	PPM	PPM	PPB	PPM	%	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Background	5.00	13.50	990.00	3.1**	14.5**	3.00	98.00	7.00	4.50**	4.00	1.5**	na	2.00	0.07	120.00	150.00	1.6**	21.70	17.0**	na	na	1.10	12.00	3.80	1.00	142.0**	46.4**	86.00	33.0**	6.4**	1.5**	1.20	4.30	0.60
Tioga																																		
Element	AU	AS	BA	BR	CA	CO	CR	CS	FE	HF	HG	IR	MO	NA	NI	RB	SB	SC	SE	SN	SR	TA	TH	U	W	ZN	LA	CE	ND	SM	EU	TB	YB	LU
Units	PPB	PPM	PPM	PPM	%	PPM	PPM	PPM	%	PPM	PPM	PPB	PPM	%	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Background	4.00	17.90**	870.00**	7.20**	10.50**	2.00	89.00**	12.00	3.28**	4.00	na	na	23.00**	0.11	127.00**	140.00**	1.90**	15.80	24.00**	na	na	1.50**	13.30**	4.80	5.00	220.00	31.30	95.00	37.00**	8.40**	1.90**	1.50	4.41**	0.690**
Huntersville																																		
Element	AU	AS	BA	BR	CA	CO	CR	CS	FE	HF	HG	IR	MO	NA	NI	RB	SB	SC	SE	SN	SR	TA	TH	U	W	ZN	LA	CE	ND	SM	EU	TB	YB	LU
Units	PPB	PPM	PPM	PPM	%	PPM	PPM	PPM	%	PPM	PPM	PPB	PPM	%	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Background	na	6.10**	365.00**	2.80**	na	2.00	39.50**	2.00*	.95**	1.00	na	na	na	0.06	na	38.00**	0.20	6.00**	na	na	na	na	2.55**	1.90**	na	na	11.00**	37.00	14.00**	1.70	0.40	na	1.00	0.19
Bob's Ridge																																		
Element	AU	AS	BA	BR	CA	CO	CR	CS	FE	HF	HG	IR	MO	NA	NI	RB	SB	SC	SE	SN	SR	TA	TH	U	W	ZN	LA	CE	ND	SM	EU	TB	YB	LU
Units	PPB	PPM	PPM	PPM	%	PPM	PPM	PPM	%	PPM	PPM	PPB	PPM	%	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Background	3.50**	31.45**	1470.00**	na	5.00**	6.00	136.00**	2.00	3.27**	4.00**	na	na	na	0.10	76.00**	113.00**	1.30**	22.60**	na	na	na	na	11.30**	13.60**	na	4525.00**	78.00**	203.00**	93.00**	27.60**	7.60**	5.10**	32.90	1.190**
Millboro																																		
Element	AU	AS	BA	BR	CA	CO	CR	CS	FE	HF	HG	IR	MO	NA	NI	RB	SB	SC	SE	SN	SR	TA	TH	U	W	ZN	LA	CE	ND	SM	EU	TB	YB	LU
Units	PPB	PPM	PPM	PPM	%	PPM	PPM	PPM	%	PPM	PPM	PPB	PPM	%	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Background	8.00**	11.30**	710.00**	2.30**	20.00**	2.00	86.70**	9.00	3.35**	3.00	na	na	24.50**	0.09	50.00	160.00	0.90	17.00	9.00**	na	na	1.20**	9.10**	4.56**	3.00	91.00	39.00	62.70**	24.00	5.30**	1.30**	1.00	3.20**	0.490**
WV Rocks																																		
Element	AU	AS	BA	BR	CA	CO	CR	CS	FE	HF	HG	IR	MO	NA	NI	RB	SB	SC	SE	SN	SR	TA	TH	U	W	ZN	LA	CE	ND	SM	EU	TB	YB	LU
Units	PPB	PPM	PPM	PPM	%	PPM	PPM	PPM	%	PPM	PPM	PPB	PPM	%	PPM	PPM	PPM	PPM	PPM	%	%	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM
Background	3.00	2.80	110.00	1.50	2.00	2.00	20.00	2.00	0.63	4.00	2.0**	na	2.00	0.03	50.00	71.00**	0.20	0.60	7.50**	0.04	0.05	1.50**	6.10**	1.00	2.00	99.00**	25.92**	9.00	9.00	4.00	1.32**	0.60	2.00	0.40

ALL ANALYSES DONE BY SELECTIVE EXTRACTION AND ICP (IGNITION COUPLED PLASMA) ANALYSIS

Needmore																					
Element	MO	CU	PB	ZN	AG	NI	MN	SR	CD	BI	V	CA	P	MG	TI	AL	K	Y	BE	S	LI
Units	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	%	%	%	%	%	PPM	PPM	%	PPM
Background	134.00	45.47**	28.0**	63.95**	1.075**	34.00	30.00	70.0**	0.50	7.74**	223.0**	0.04	0.037**	0.53	0.48	3.85	2.91**	30.81**	2.00	0.110**	na
Tioga																					
Element	MO	CU	PB	ZN	AG	NI	MN	SR	CD	BI	V	CA	P	MG	TI	AL	K	Y	BE	S	LI
Units	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	%	%	%	%	%	PPM	PPM	%	PPM
Background	15.492**	91.035**	25.00	84.397**	0.60	51.019**	44.423**	74.000**	2.63**	4.497**	193.00**	0.02	0.0460**	0.67	0.430**	5.947**	3.182**	34.496**	3.000**	0.0400**	55.00**
Huntersville																					
Element	MO	CU	PB	ZN	AG	NI	MN	SR	CD	BI	V	CA	P	MG	TI	AL	K	Y	BE	S	LI
Units	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	%	%	%	%	%	PPM	PPM	%	PPM
Background	3.500**	25.000**	16.000**	7.00	na	7.00	41.000**	40.00	na	na	64.000**	0.08	0.023	0.08	0.115**	1.390**	0.465**	12.000**	1.00	0.020	29.00**
Bob's Ridge																					
Element	MO	CU	PB	ZN	AG	NI	MN	SR	CD	BI	V	CA	P	MG	TI	AL	K	Y	BE	S	LI
Units	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	%	%	%	%	%	PPM	PPM	%	PPM
Background	4.747**	51.000**	86.000**	252.000**	1.248**	39.658**	130.000**	178.000**	0.50	na	273.000**	1.120**	0.7740**	0.880**	0.090**	3.950**	2.470**	115.000**	17.000**	0.2688**	159.00**
Millboro																					
Element	MO	CU	PB	ZN	AG	NI	MN	SR	CD	BI	V	CA	P	MG	TI	AL	K	Y	BE	S	LI
Units	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	%	%	%	%	%	PPM	PPM	%	PPM
Background	2.00	43.698**	8.00	50.000**	0.70	26.142**	220.000**	96.026**	0.90	4.369**	31.00	0.05	0.0380**	1.21	0.350**	4.550**	3.20	25.00	2.00	0.120	46.00**
WV Rocks																					
Element	MO	CU	PB	ZN	AG	NI	MN	SR	CD	BI	V	CA	P	MG	TI	AL	K	Y	BE	S	LI
Units	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	PPM	%	%	%	%	%	%	PPM	PPM	%	PPM
Background	2.00	2.00	6.00	2.00	0.40	2.00	220.00**	30.00	0.50	4.51**	2.00	0.02	0.007	0.01	0.03	0.14	0.08	18.00	2.00	0.010	29.00

Elemental background levels for various stratigraphic units sampled in West Virginia and Virginia. Unless marked with **, values listed represent the mode calculated for all analyses; marked values are multimodal and the median is given instead. Values in red are depleted compared to other stratigraphic units in the database (McDowell, 2001) which currently contains analyses for rock samples ranging from Precambrian to Eocene in age. Entries of "na" indicate that an insufficient number of samples are present to calculate either a mode or median value. The Huntersville Chert is depleted in 31 of 50 elements compared to the other Devonian units associated with it and to all other sampled stratigraphic units in the database.

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