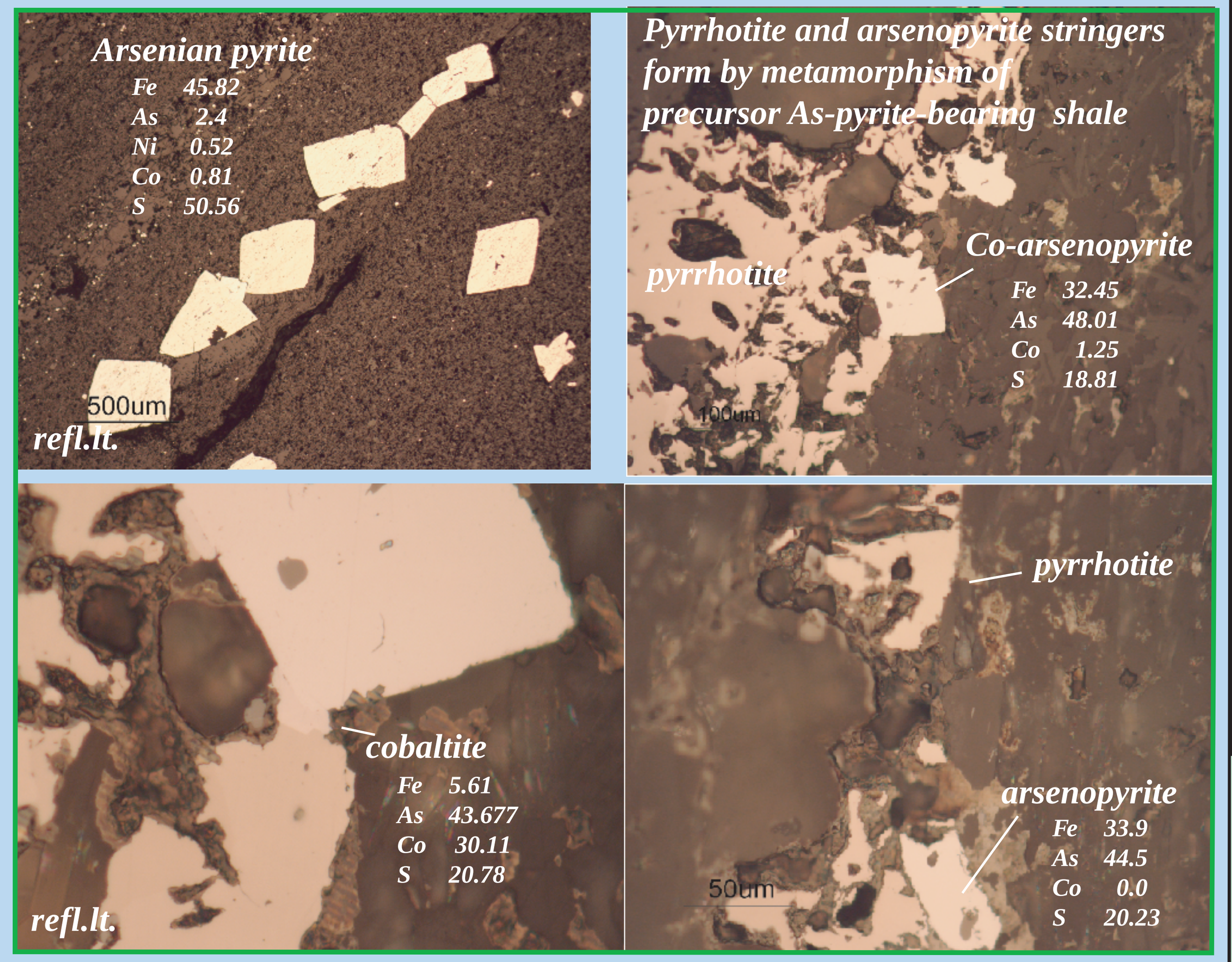
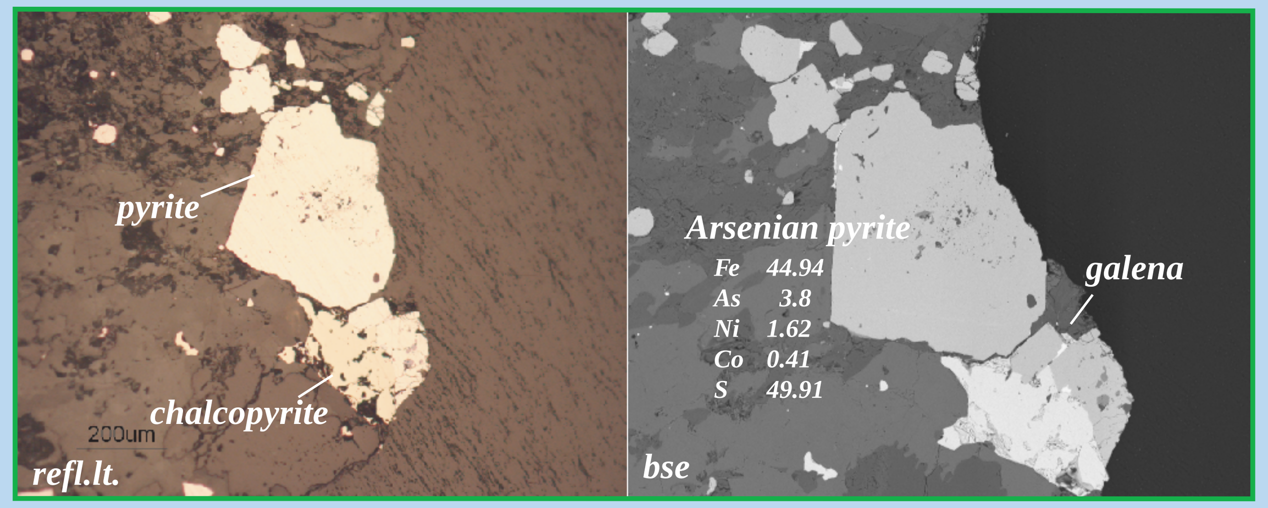
Mineralogical Pathways for Arsenic in Weathering Meta-Shales: Regional and Site Studies in the Northern Appalachians

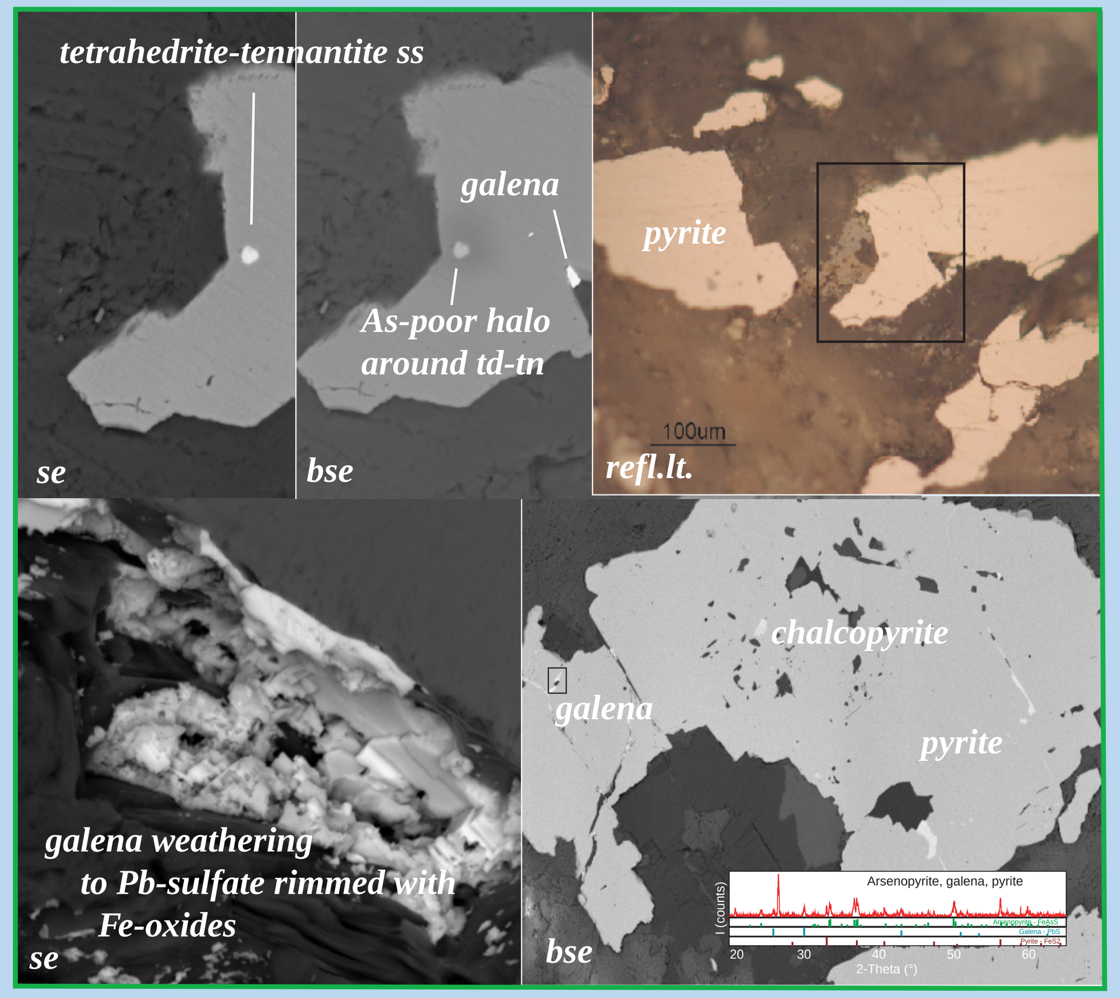
By Nora K. Foley1, Robert A. Ayuso1, Nicole West1, Jeremy Dillingham1, Joseph D. Ayotte2, Robert G. Marvinney3, Andrew S. Reeve4, Gilpin R. Robinson, Jr1
U.S. Geol. Survey, Reston, VA;U.S. Geol. Survey, Pembroke, NH; Maine Geol. Survey, Augusta ME; Dept. of Geol. Sciences, Univ. of Maine, Orono, ME

INTRODUCTION

Concerns about arsenic-bearing groundwaters in New England, coupled with inconsistencies in published literature identifying potential arsenic hosts, convinced us to undertake a careful examination of possible mineralogical sources of significant arsenic in local bedrock. Detailed petrographic, x-ray diffraction, scanning electron microscope, and electron microprobe analyses of iron-sulfides and rock samples collected from over 70 bedrock localities of coastal New Hampshire and Maine, including 22 in the regionally extensive and sulfide-mineral-rich Penobscot Formation and 10 associated with mineral deposits from coastal New Hampshire and Maine, coupled with data from drill core collected at several sites including areas where well waters contain anomalous arsenic abundances (e.g., Northport, ME), were used to establish a diversity of primary and secondary mineralogical hosts for arsenic in bedrock of these areas of New England.







LOCATION

Over 70 localities (white circles) were examined for this study. Mine locations are shown by white squares (black mine symbol). Drill-core locations in Maine and New Hampshire are shown with black stars. See Map of Maine (see Ayuso and others, poster, this on-line open file

ACKNOWLEDGEMENTS

We thank the residents of Central and Coastal Maine who generously provided access to private property sites for sampling. We thank Ann Lyon, Eric Binnie, and John Burns for sampling and laboratory support.

ANALYTICAL PROCEDURES:

Samples were examined using a JEOL 840 scanning electron microscope and a JEOL JXA-8900R elctron probe microanalyser. X-ray diffraction patterns were obtained using a Scintag X1 Advanced Diffraction system and the ICDD database (2000) and JADE 5.0 software program.

MINERALOGY

Primary arsenic-bearing minerals identified include pyrite (<4 wt.% As in FeS2), pyrrhotite (max. 0.5 wt.% As in Fe1-xS), löllingite, realgar (?), cobaltite, arsenopyrite, cobaltian arsenopyrite (max. 8.4 wt.% Co), and tennantite. Supergene minerals that constitute intermediate mineralogical sources include orpiment and arsenolite-like minerals, Co-Ni-arsenates (?), Ca-arsenates (rauenthalite, phaunouxite?), scorodite (FeAsO4.2H2O) and secondary arsenopyrite, pyrite, and marcasite.

Regional Meta-Shales: Arsenic-bearing meta-shales are prevalent throughout the Northern Appalachians (e.g., Silurian Smalls Falls Formation: Guidotti and Van Baalen, 1999; Ordovician Penobscot Formation: Stewart, 1998; Robinson and others, 2000; Ayuso and others, 2001). Sulfide-bearing portions of the Penobscot Formation, a graphitic schist thought to have formed in a deep-sea, anoxic depositional environment (Stewart, 1998), contain trace to minor amounts of base-metal sulfide minerals primarily in the form of anisotropic pyrite, arsenian-pyrite, and pyrrhotite with accessory arsenopyrite, and trace to minor amounts of chalcopyrite, sphalerite, löllingite, cobaltite, and galena, and other Pb-, As-, Ni-, and Co-bearing sulfide minerals (Horesh, 2001; Foley and others, 2002). In meta-shales, coexisting pyrrhotite, cobaltite, and arsenopyrite constitute a probable source for high As contents (e.g., Penobscot Fm.).

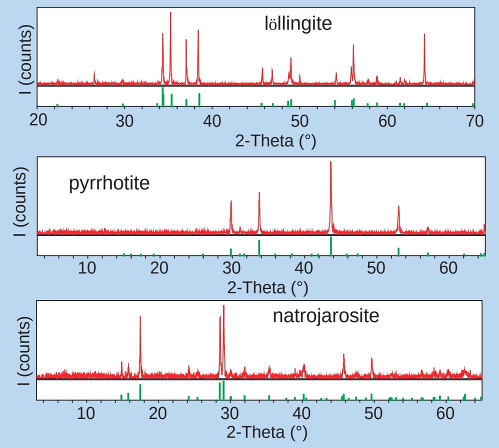
Mineral Occurrences and Mines: More highly mineralized parts of the meta-shales contain subeconomic metallic sulfide mineralization including pyrite, galena, chalcopyrite, stibnite, pyrrhotite, löllingite, sphalerite and arsenopyrite. Pyrite, the most abundant iron-sulfide mineral in many of the rocks, is a primary host for As in low-grade mineral deposits (e.g., volcanic-associated massive sulfides, metamorphic-Au, and Carlin-Au deposit types). Arsenopyrite and löllingite are also important sources for As at many mines. Deposits and occurrences at mines likely act as highly enriched point-sources for arsenic in groundwater.

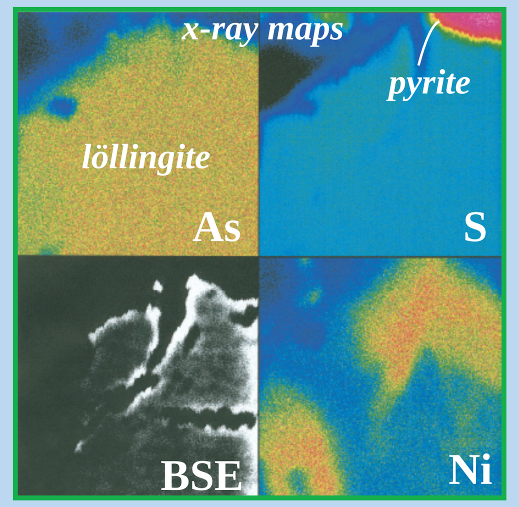
Drill Core Sites: Additional samples were selected for comparison from drill core obtained from three sites: one drilled at Northport, Maine (Reeve and others, this study), and two well sites drilled in the Great Bay National Wildlife Refuge (AP-Adam's Point Well 1 and NR-National Refuge Well).

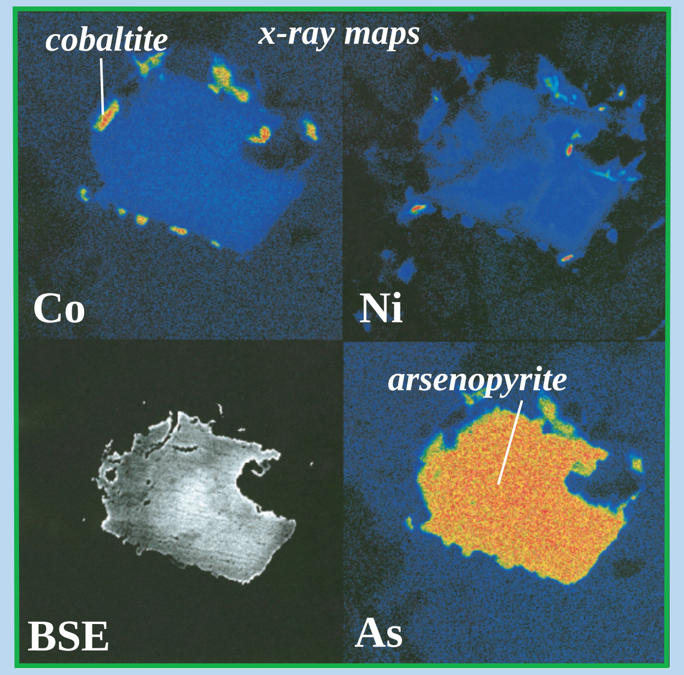
REFERENCES

Kim and others, 2000, Environmental Science and Technology, 34, 3094-3100.
Ayuso and others, 2001)
Foley and others, 2002).
Guidotti and Van Baalen, 1999
Horesh, 2001;
Robinson and others, 2000;
Stewart, 1998;

MINERAL	FORMULA	ALTERATION PRODUCTS
Pyrite	FeS2 (As content varies from ~0 to 4 % by weight)	Goethite (FeOOH) (50-5000 ppm As) Lepidocrocite (FeOOH), Ferrihydrite (Fe2O3.0.5H2O) Rozenite (FeSO4.4H2O) Melanterite (FeSO4.7H2O) Secondary arsenopyrite (FeAsS) Hematite (Fe2O3) Jarosite (KFe3(SO4)2(OH)6)
Pyrrhotite	Fe1-xS	Pyrite (FeS2) Marcasite (FeS2) Jarosite (KFe3(SO4)2(OH)6) Ferrihydrite (Fe2O3.0.5H2O) Rozenite (FeSO4.4H2O) Melanterite (FeSO4.7H2O)
Löllingite Realgar	FeAs2 AsS	Orpiment (As2S3) Arsenolite (As2O3), Scorodite (FeAsO4.2H2O)
Cobaltite Arsenopyrite Cobaltian-arsenopyrite Ni-As sulfides	CoAsS FeAsS (Co content ranges up to 8.4 % by weight) (Ni,Co)AsS	Co-Ni-arsenates (?) Goethite (FeOOH), (50-5000 ppm As) Orpiment (As2S3) Arsenolite (As2O3) Jarosite (KFe3(SO4)2(OH)6), with up to ~40 ppm As) Scorodite (FeAsO4.2H2O) Co-Ni-arsenates (?)
Galena Stibnite	PbS Sb2S3	Pb-sulphate (PbSO4)
Chalcopyrite Tetrahedrite-tennantite	CuFeS2 (Fe)12(As,Sb)4S13	Goethite (FeOOH) Secondary arsenopyrite (FeAsS) Fe-oxyhydroxides(?)
Calc-silicate minerals	Ca, Si, Al, Fe, C	Ca-arsenates, (e.g., rauenthalite, phaunouxite?)

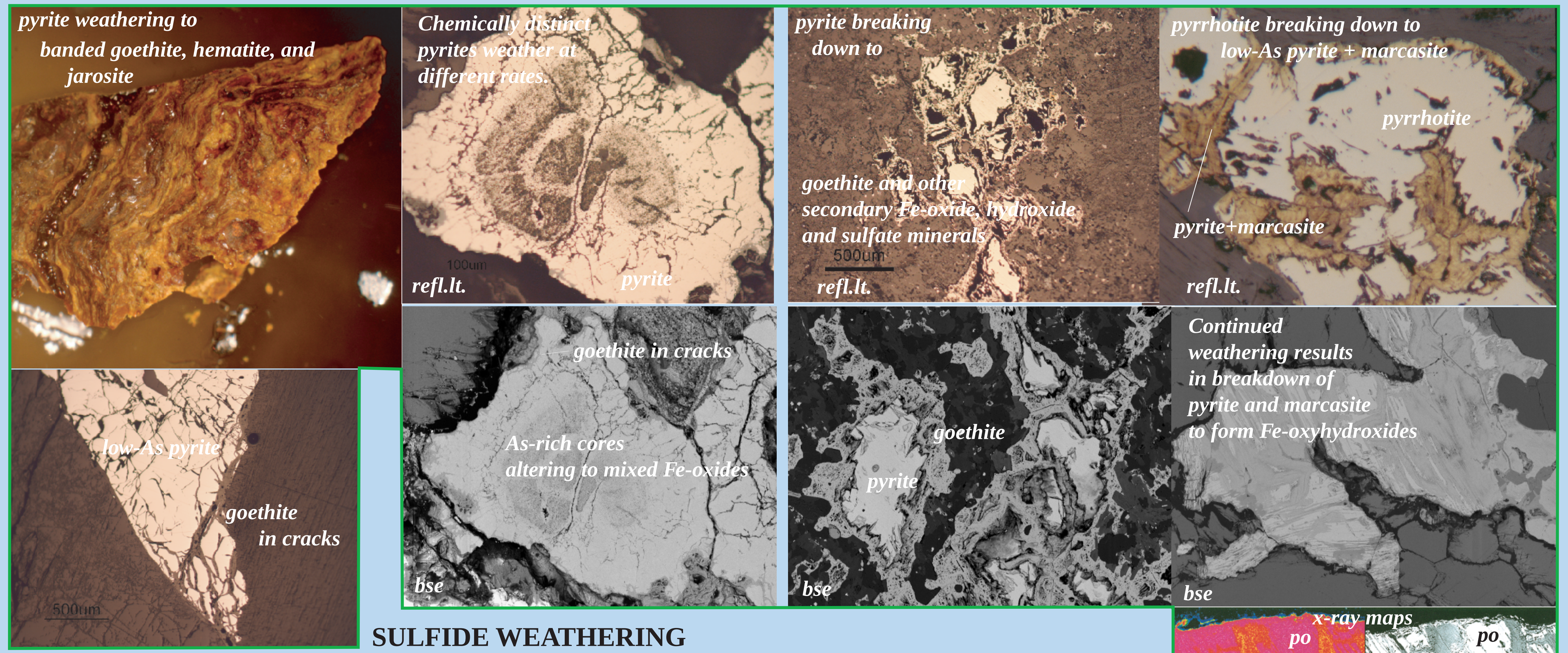


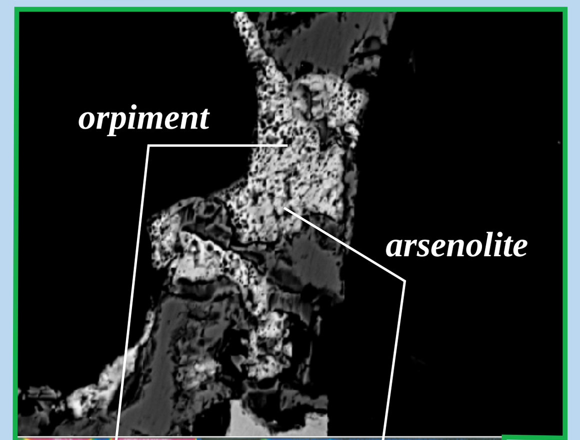


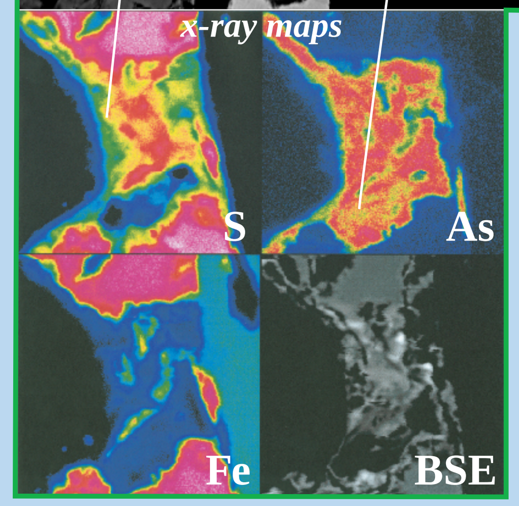


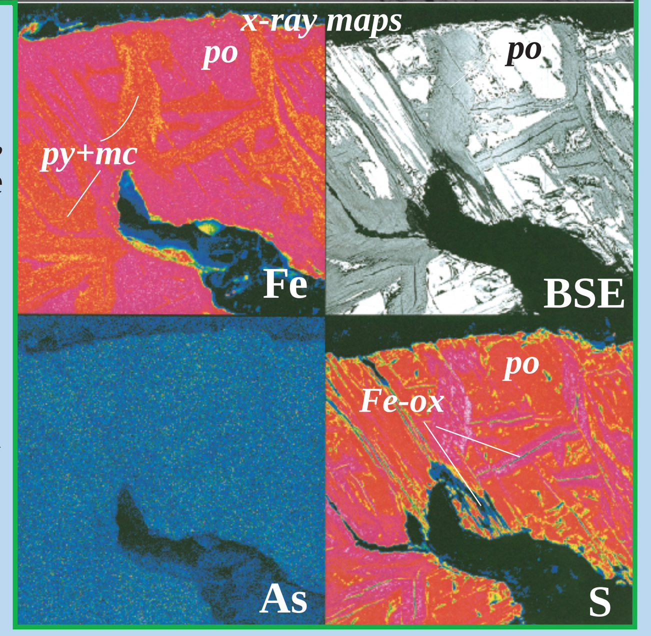
MINERAL CHEMISTRY

Multiple types and generations of Fe, Fe-As, and As sulfide minerals can occur in shales and their metamorphosed equivalents. Each type and generation can have a characteristic trace element composition. Differential weathering will result in the release of trace metals in proportions that do not reflect the bulk composition of the host mineral nor that of the host rock. For example, pyrrhotite typically alters first to a fine grained mix of pyrite and marcasite, primarily along exposed surfaces such as cracks in crystals and at grain boundaries. Further weathering results in Fe-oxyhydroxide minerals. Cobaltite appears to oxidize less readily than coexisting pyrrhotite or arsenopyrite, however, more cobalt-rich varieties of arsenopyrite are less resistant to weathering than cobalt-poor arsenopyrite. Löllingite weathers readily, especially varieties containing small amounts of Ni.









SULFIDE WEATHERING

Weathering of pyrrhotite and pyrite in the Penobscot Fm. results in (1) complex mixtures of pyrite + marcasite, and (2) iron oxy-hydroxides and secondary salts, such as ferrihydrite, rozenite and melanterite. Löllingite occurring at mineralized localities oxidizes to scorodite or iron oxy-hydroxides products and other arsenic minerals. Orpiment and arsenolite are intermediate oxidation products in this environment. Ca-arsenates are thought to form at some sites by the reaction of acidic, As-bearing waters with calc-silicate substrates.

Oxidation processes: Weathering of pyrite, pyrrhotite, löllingite, realgar (?), and arsenopyrite, tetrahedrite, and other sulfide minerals in these settings causes the production of acid and release of trace metals, including As, Co, Ni, Pb, etc., which can sorb on and off iron oxy-hydroxide substrates. Oxidation of arsenopyrite or other As-bearing minerals to produce iron oxides and release sulfur and arsenic, which under specific conditions may produce arsenolite or orpiment. Subsequent breakdown of the goethite + arsenolite or orpiment assemblages will release As into the groundwater system.

Carbonation processes: As may be liberated from bedrock by interaction between anaerobic HCO3- groundwaters and As-minerals and subsequently re-precipitated at low pH. When solubility is controlled by Ca-arsenate, Ca in solution suppresses the solubility of arsenic, however, the long-term ability of these minerals to sequester As is untested.

SUMMARY

The mineralogy of meta-shales in the Northern Appalachian is more complex than previously thought. Bedrock mineralogy is critical to contributing arsenic to groundwater and suggests a number of possible mineralogical bounds on pathways for arsenic that help define weathering processes. There is substantial evidence for acid drainage and metals being generated from the regionally extensive meta-shales by the breakdown of pyrrhotite, pyrite, arsenopyrite, cobaltite and other minerals, and from metal-sufide-rich mines by the breakdown of high-arsenic minerals such as löllingite, realgar, arsenian pyrite and arsenopyrite. Intermediate alteration and weathering minerals--including orpiment, arsenolite-compounds, scorodite, and secondary arsenopyrite--are likely to act as important intermediate controls on the release arsenic to groundwater. Examining the mineral chemistries of these intermediate phases may better account for groundwater chemistry. Mineralogical modeling studies are now being employed to apply weathering rates to understand how the geochemical processes affect acid generation and metal release from sulfide-bearing portions of the meta-shales in New England, and for meta-shales in general. Mineralogical factors that contribute to natural acid rock drainage can be useful in predicting background metal compositions and levels. Models that employ accurate mineralogical data will better predict the environmental impacts of acid drainage.