Pb Isotopes, Arsenic Sources, and Enrichment Pathways: Linking Sulfides from Mines and Unmineralized Rocks to Secondary Iron Oxy-hydroxides, Coastal New England

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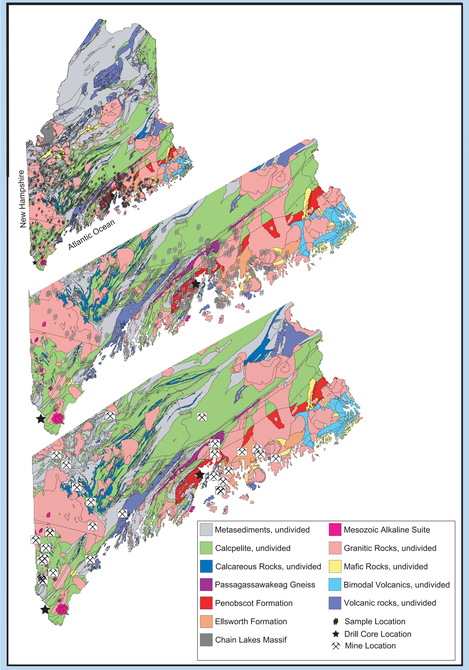
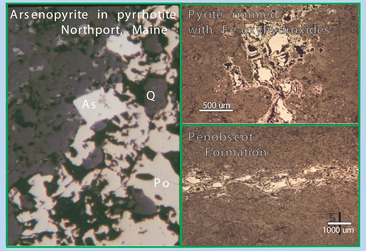
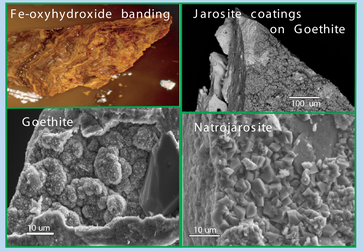
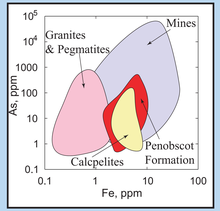
INTRODUCTION

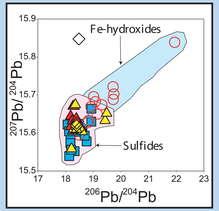
Sulfide and secondary iron oxy-hydroxides minerals (n = 56) collected from mines and sulfidic meta-shales were analyzed for their Pb isotopic compositions and for trace elements in an effort to test the link between arsenic-rich sulfide minerals and secondary oxy-hydroxides presently forming along rock surfaces, joints, crevices, fractures, etc. This study is part of a detailed mineralogical and geochemical analysis of iron-sulfide minerals in bedrock (e.g., the sulfide-rich Cambrian-Ordovician Penobscot Formation) and drill cores in coastal Maine and New Hampshire (Ayuso et al, in press; Foley et al., this volume; Reeve et al, this volume). Weathering of pyrite, pyrrhotite, and other sulfide minerals generates acid and releases metals (e.g., Pb, Cu, As, Co, Ni) that are then sequestered in secondary minerals (e.g., ferrihydrite, goethite, scorodite, jarosite, natrojarosite, rosenite, and melanterite). The iron oxy-hydroxide minerals constitute the ideal substrates for sorption reactions involving As, Pb, and other metals in solution. Our study shows that Pb isotopic compositions of the sulfides and iron oxy-hydroxides overlap and establish a genetic link between the sulfides and secondary minerals. Pb isotopic ratios of the iron oxy-hydroxides also establish the isotopic compositions of the fluids in which the iron oxy-hydroxides crystallized.

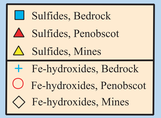






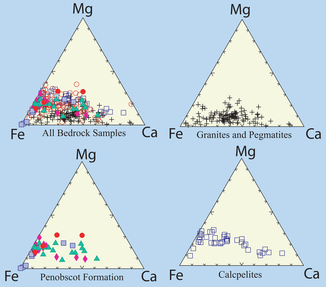






ANALYTICAL PROCEDURES:

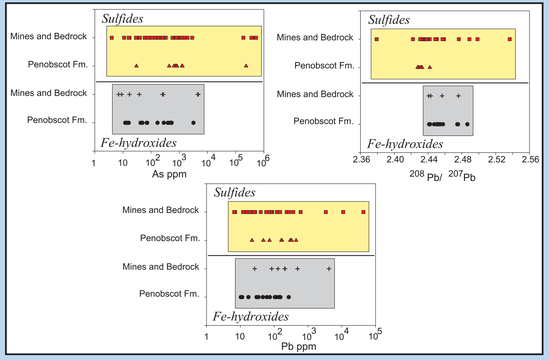
Minerals were examined using a JEOL 840 SEM, a Scintag X1 Advanced Diffraction system and the ICDD minerals database (2000) and JADE 5.0 software program. Geochemical analyses of rocks and minerals were done by WD-XRF (major elements), ICP (trace elements), and long-range INAA (rare earth elements). Pb isotopic compositions were determined by thermal ionization mass spectrometry (TIMS) at the U.S. Geological Survey, Reston, VA 20192.



MINERAL	FORMULA	ALTERATION PRODUCTS
Pyrite	FeS2 (As 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 (Fe2S3) Jarosite (KFe3(SO4)2(OH)6
Pyrrhotite	FeS1-x	Pyrite (FeS2) Marcasite (FeS2) Jarosite (KFe3(SO4)2(OH)6
Löllingite	FeAs2	Orpiment (As2S3) Arsenolite (As2O3) Scorodite (FeAsO4.2H2O
Cobaltite	CoAsS	Co-Ni-arsenates (?)
Arsenopyrite	FeAsS (Co content up to 8.4 % by weight)	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	PbS	Pb-sulphate (PbSO4)
Stibnite	Sb2S3	
Chalcopyrite	CuFeS2	
Tetrahedrite -tennantite	(Fe)12(As,Sb)4S13	Goethite (FeOOH) Secondary arsenopyrite (FeAsS)

As AND Pb CONTENTS OF ROCKS SECONDARY MINERALS

As and Pb contents in the sulfides vary widely. For example, in the Penobscot Formation, pyrites range from ~20 ppm to ~2000 ppm As and ~10 ppm to >400 ppm Pb, but pyrites from the mine areas are substantially higher in As and Pb and range to thousands of ppm. Bedrock occurrences represented by bulk rock samples also have a wide range in As and Pb contents. For example, in the Northport area, Maine, where As in groundwater is elevated (Reeve et al., this volume), As contents as high as 730 ppm have been found in rocks of the Penobscot Formation. As and Pb contents of the secondary minerals are also highly variable but characteristically closely match the ranges found in the sulfides and bulk rock samples.



Pb ISOTOPIC COMPOSITIONS

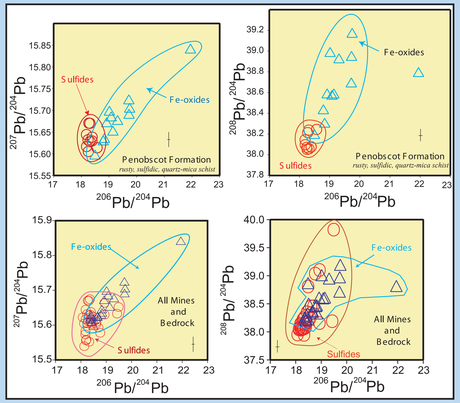
Pb isotopic compositions were determined by thermal ionization mass spectrometry using bulk samples and acid-leached samples of galena, arsenian-pyrite, pyrrhotite, löllingite, cobaltite, and arsenopyrite. Pb isotopic compositions range as follows: 206Pb/204Pb = 18.073-19.489; 207Pb/204Pb = 15.539-15.675; 208Pb/204Pb = 37.947-39.102 and plot as nearly vertical fields on standard uranogenic and thorogenic Pb diagrams. Pb isotopic compositions of secondary minerals, including goethite, jarosite, and natrojarosite had the following ranges: 206Pb/204Pb = 18.356-21.945; 207Pb/204Pb = 15.595-15.839; 208Pb/204Pb = 38.169-39.162. The isotopic compositions plot on uranogenic and thorogenic Pb diagrams as broad and steep fields that extensively overlap the field of the sulfides but extend to more radiogenic compositions. The similarity of isotopic compositions provides evidence that fluid-mineral reactions leading to the decomposition of the sulfides released metals and As and imprinted the Pb isotopic signatures of the sulfides on the secondary minerals. Pb isotopic values of the iron oxy-hydroxides match the compositions of coexisting fluids.

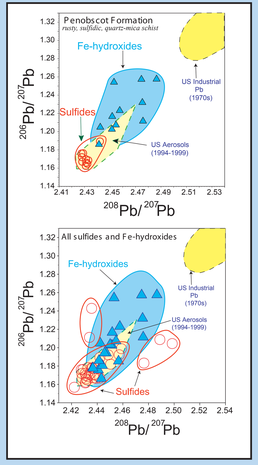
Table. Selected trace elements in sulfides

		As ppm	Bi ppm	Cu ppm	Zn ppm	Pb ppm	Hg ppb
Sulfide Mines							
Pyrite	Acton	1440	19	555	55	87	5
Galena	Blackhawk	30	677	138	564	43500	
Chalcopyrite	Deer Isle silver	576	57	228000	3100	1300	126
Pyrrhotite	Porter	696	29	26	238	5	
Granites and pegmatites							
Pyrite	Mt Glines pegmatite mine	4	9	100	79		
Loellingite	Mica Mt. pegmatite mine	524000	920	15			
Arsenopyrite	Bessie quarry pegmatite	366000	89	14	234	12	
Calcareous schists and limestones							
Pyrite	Waterville Fm.	328	6	438	287	366	104
Pyrrhotite	Calcpelites	29	34	899	105	70	5
Bedrock, undivided							
Pyrite	Schist	1240	26	108	38	40	
Chalcopyrite	Mafic schist	269	0	278000	6880	3370	46
Pyrrhotite	Biotite schist	784	20	116	64	16	8
Penobscot Formation							
Pyrite		644	9	20	470	163	
Pyrite		1250	8	105	313	298	
Pyrrhotite		30	18	1020	55	22	8

Table. Selected trace elements in Fe-hydroxides

		As ppm	Bi ppm	Cu ppm	Zn ppm	Pb ppm	Hg ppb
Sulfide Mines							
Goethite (and minor carbonate)	Eggmoggin	4720	0	50500	4190	209	
Goethite	Antimonial Silver	4490	0	143	216	492	294
Goethite (and minor jarosite)	Swett Silver	270	3	39	496	210	75
Granites and pegmatites							
Goethite	Black Mtn. pegmatite	255	0	75	485	36	
Bedrock, undivided							
Goethite (and minor jarosite)		9	4	175	265	206	7
Goethite (and minor jarosite)		38	0	76	74	85	47
Goethite		7	0	209	96	129	18
Penobscot Formation							
Goethite		282	1	323	156	137	36
Goethite (and minor arsenolite)		475	3	380	360	270	54
Goethite (and minor arsenolite)		68	0	196	196	113	12
Goethite		72	1	20	160	46	30
Goethite (and minor arsenolite)		3180	1	330	364	61	14
Jarosite (and minor natrojarosite)		14	0	25	60	10	7
Natrojarosite		42	0	66	90	17	6





CONCLUSIONS

Although the isotopic compositions of the sulfides can account for most of the variations in the secondary minerals as a result of weathering, a more radiogenic Pb component could also be present. This establishes the initial pathway for As and Pb originating in the sulfides, into the fluids and resulting in the As-rich secondary minerals.

Possible Pb contributions from anthropogenic sources cannot be disregarded. Additional sources in soils may include remnants of older industrial Pb and Pb-rich pesticides.

REFERENCES

Ayuso et al., USGS OF Report, in press
Foley et al., this volume;
Reeve et al., this volume
Stewart, 1998, USGS Map I-2551

ACKNOWLEDGEMENTS

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