Prospecting Through TEM Analyis of Metallic Nanoparticles in Groundwater

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The Power of AND

Abstract

With the search for new deposits of metallic resources pushing prospecting into increasingly poorly exposed areas, this project aims to test an experimental prospecting technique developed in China to discover potential zones of mineralization in areas where host units may have little to no outcrop. Potential detection of metallic ore bodies is achieved through TEM analysis of nanoparticles within groundwater samples collected in an area of interest, with their characteristics providing evidence for the existence of an ore body located at depth. To verify this method, groundwater samples have been collected from two areas with known metallic deposits, the eagle mine in the Upper Peninsula of Michigan and the Kingston Mining district in New Mexico. Initial results have shown a positive correlation of metals in nano-particle chemistry from areas of mineralization. In samples from the eagle mine, metallic components of nanoparticles include Cr up to 10,000ppm, Zn up to 22,000ppm and Co up to 620ppm while analyses of nanoparticles within Kingston groundwater reveal a large component of Zn from 5-13%. If this method continues to show promise, it could be used in a future project to provide evidence for or against existence of an ore body in a targeted location, possibly in combination with other prospecting methods such as hydrogeochemistry.

Statement of Project

- Metallic mineral exploration can be difficult and expensive for deposits with extensive overburden.
- Nanoparticles (NP) produced by oxidation and faulting of unexposed ore bodies can function as potentially more sensitive indicators of their composition than bulk water chemistry.
- This project was designed to evaluate the feasability of a prospecting technique developed in China that analyzed NP in groundwater in and around a polymetallic ore district.

Methods

Water was collected from 2 mineralized areas into clean polyethylene bottles. Copper (300 mesh size) TEM grids were prepared by immersing in chloroform to partially dissolve a plastic formvar layer, creating a microscopic carbon only substrate mesh. Water samples were agitated, then sampled with a disposable pipette which was used to place a drop on the surface of the TEM grid. The drop was allowed to evaporate, after which the grid was placed within a 200kV TEM with an energy dispersive x-ray spectrometer. Nano-particles that were once suspended in the water could then be viewed and analyzed for elemental composition. Crystal structure was also evaluated through electron diffraction patterns.



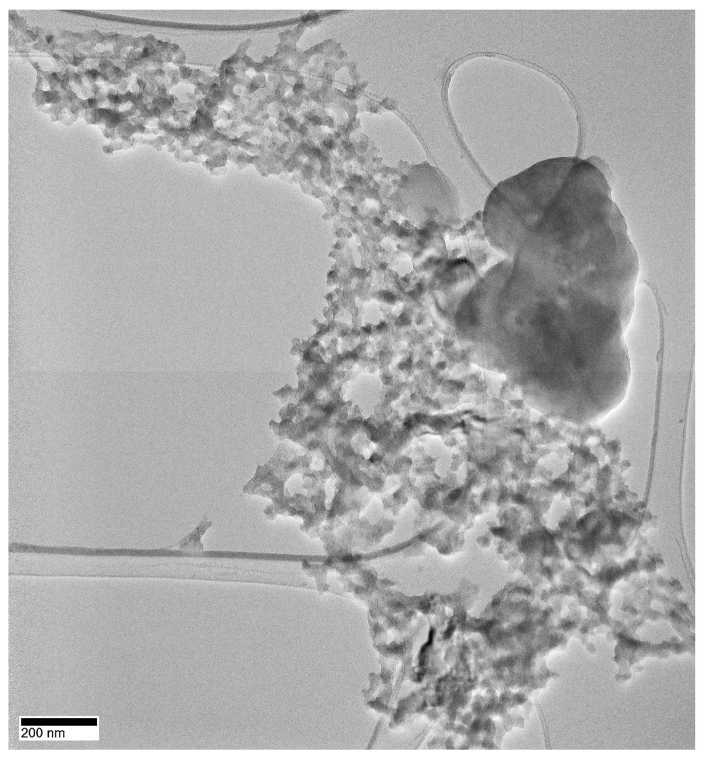
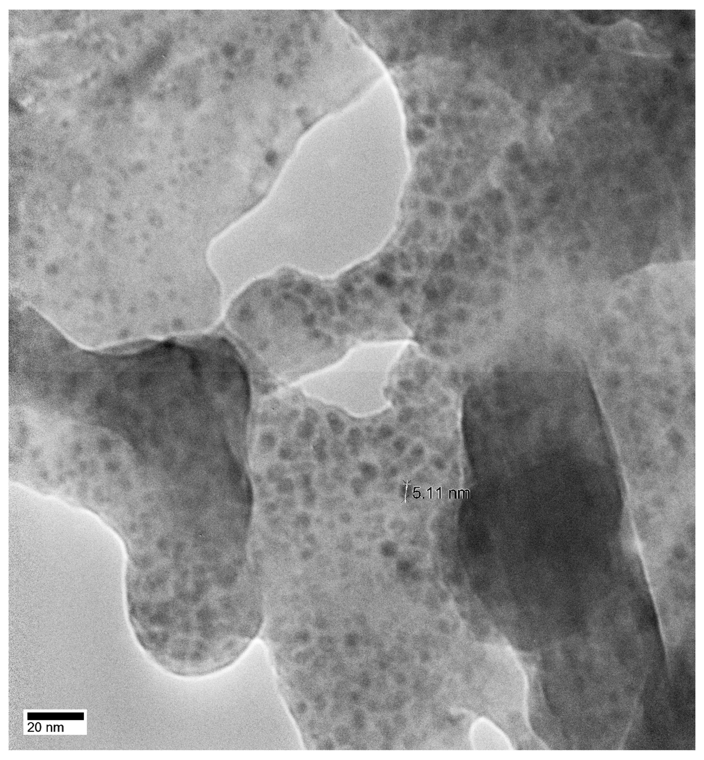
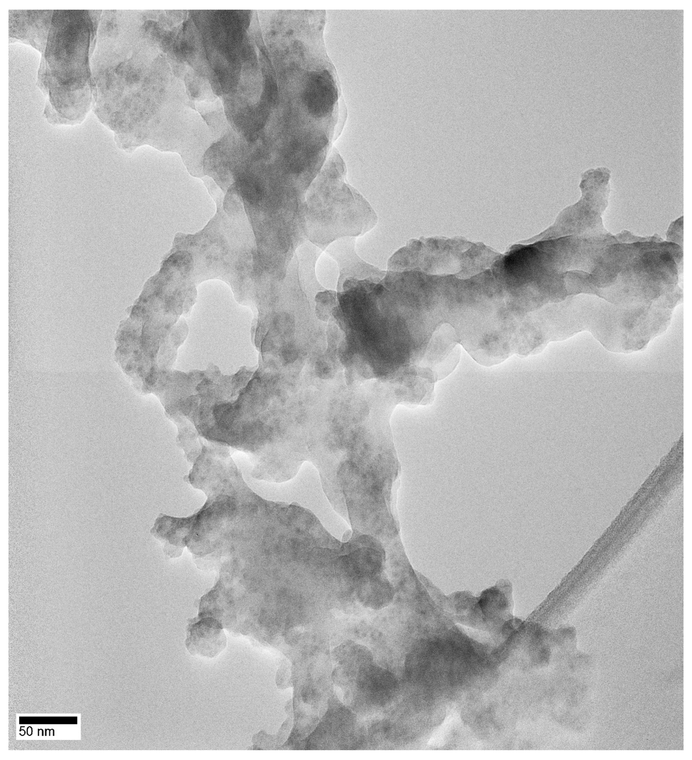
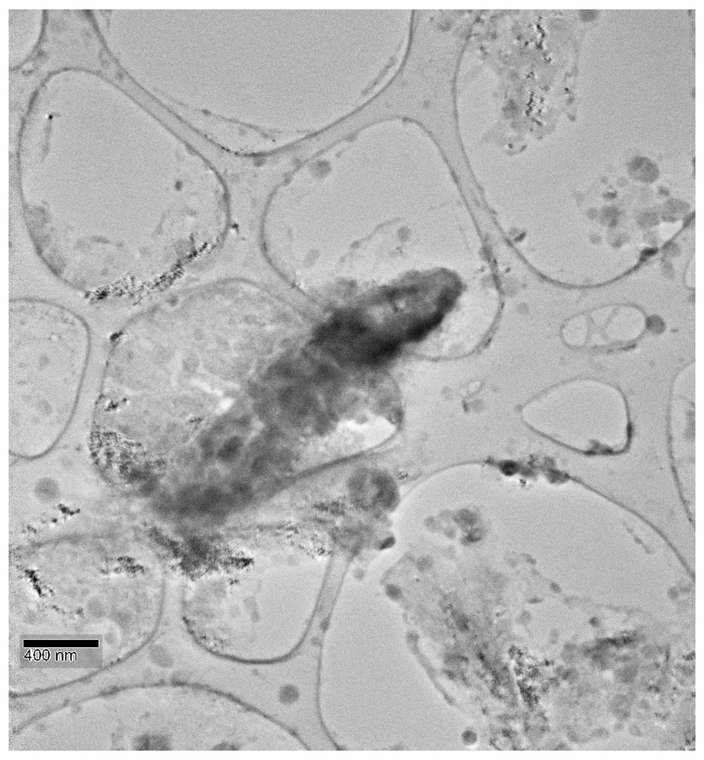
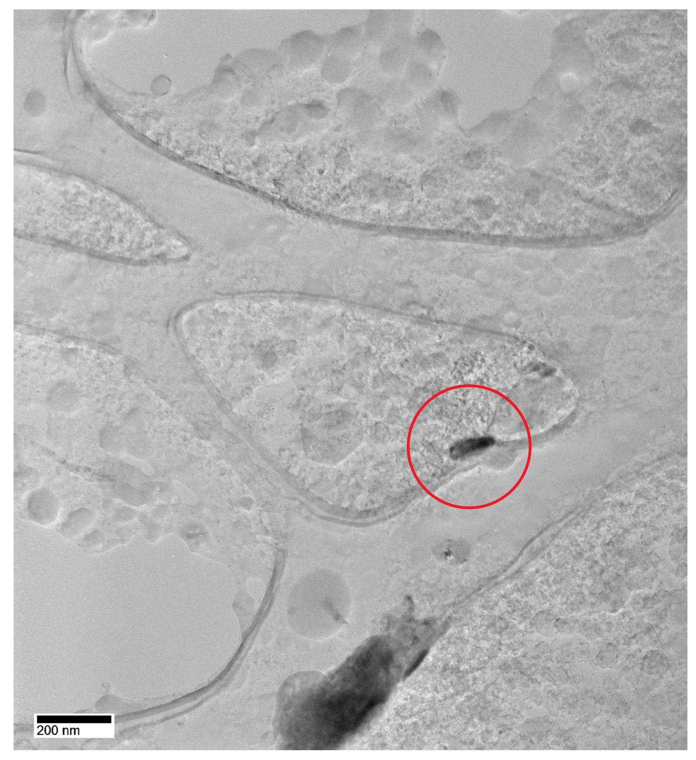
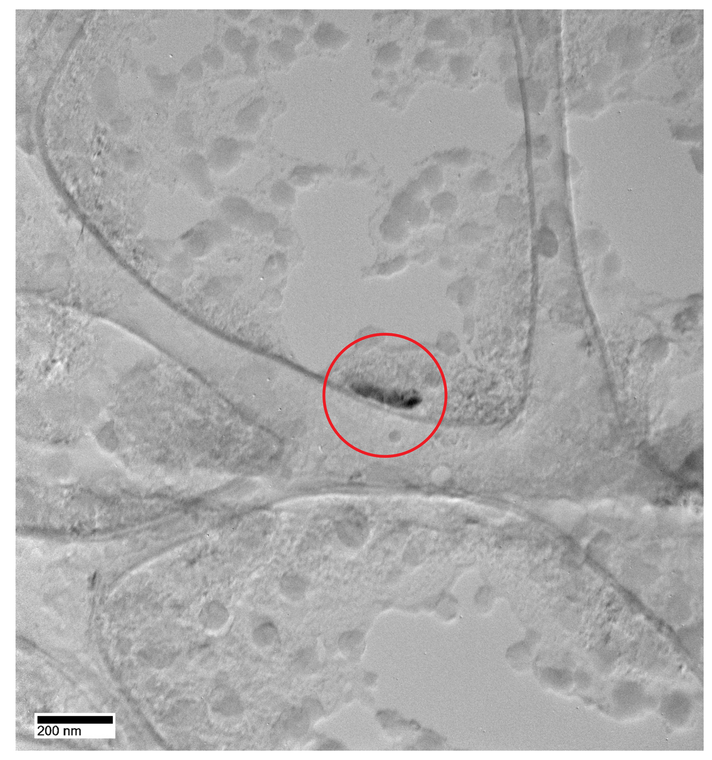
3 sampling sites from the Kingston mining district, NM. All collection points were where water was clearly seeping from a groundwater source.

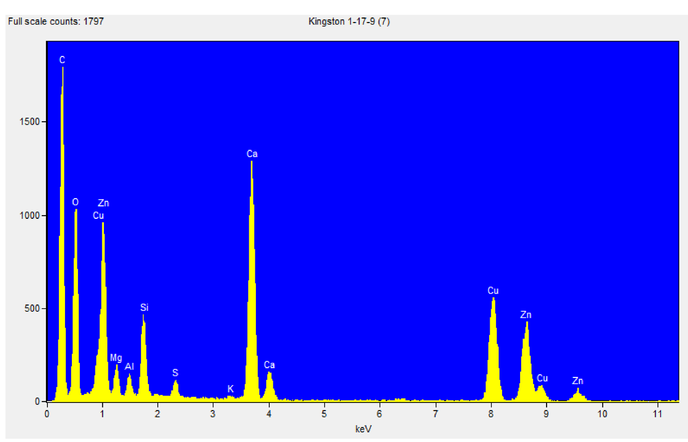
Kingston Mining District

- Cu-Pb-Zn-Ag mineralized area home to a silver mining rush during the 1880's.
- Deposits emplaced by hyrothermal fluids associated with rhyolitic intrusives of a post-resurgent phase of the nearby Emory Caldera complex.
- Intruded into lower Paleozoic sedimentary rocks in the area including limestones, dolomite, and shale.

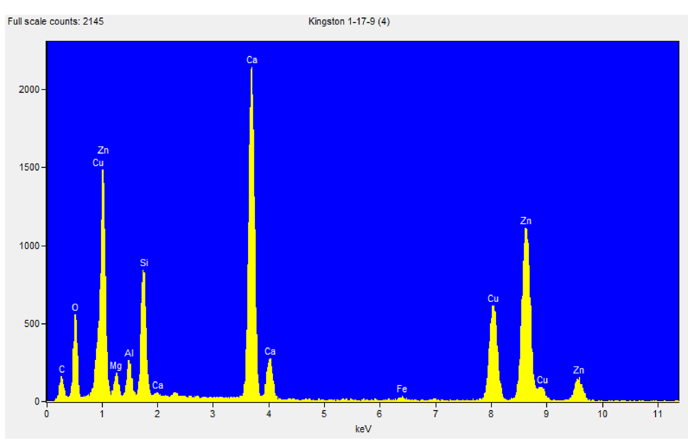
Eagle Deposit

- Magmatic sulfide deposit estimated at 4.05 million tonnes.
- Nickel, copper as main ores with lesser amounts of cobalt, gold, platinum and palladium.
- Hosted by peridotites related to tholeiitic volcanism in the mid-continent rift.
- Emplaced within Proterozoic siltstones of the Marquette supergroup.

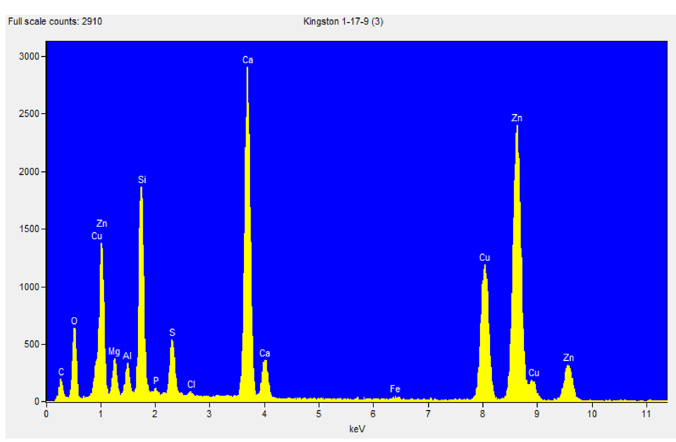









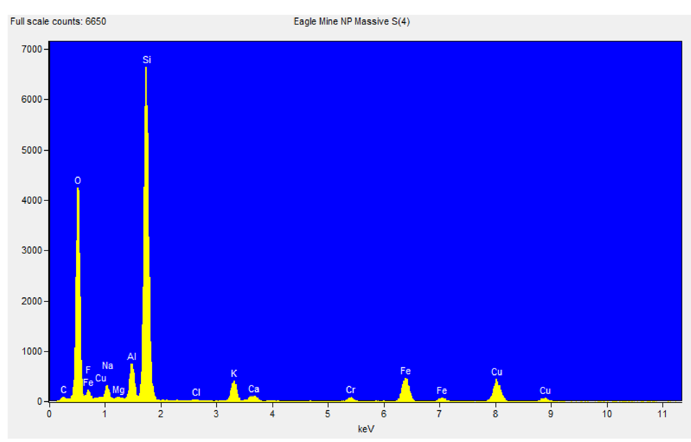
Element Line	Net Counts	Net Counts Error	Oxide Formula	Norm. Compd. %	2σ Error
Na K	1819	± 322	Na2O	4.00	0.71
Mg K	745	± 82	MgO	1.65	0.18
Al K	1538	± 102	Al2O3	3.15	0.21
Si K	7476	± 202	SiO2	15.82	0.43
P K*	B.D.				
S K	229	± 58	SO3	0.55	0.14
Cl K	B.D.				
K K	B.D.				
Ca K	28231	± 376	CaO	38.29	0.51
Fe K	239	± 48	Fe2O3	0.41	0.08
Co K	68	± 36	CoO	0.11	0.06
Ni K	B.D.				
Zn K	21154	± 306	ZnO	35.42	0.51
Sr K*	B.D.				
Ag L*	B.D.				
Total				100	
Below Detection: B.D.					



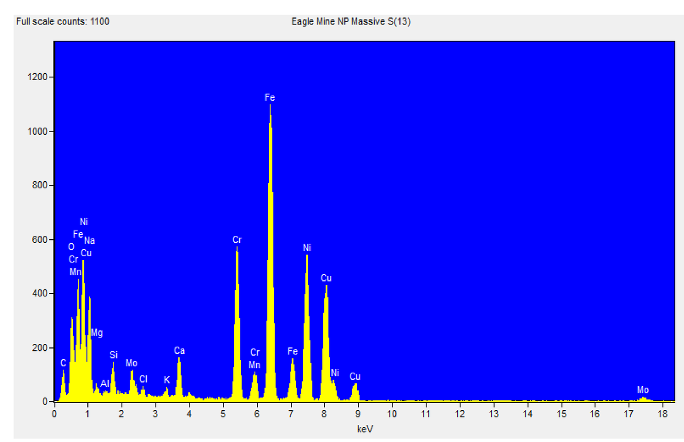
Element Line	Net Counts	Net Counts Error (2σ)	Oxide Formula	Norm. Compd. %	2σ Error
Na K	2398	± 280	Na2O	2.30	0.27
Mg K	2803	± 140	MgO	2.71	0.14
Al K	164	± 90	Al2O3	0.15	0.08
Si K	3458	± 164	SiO2	3.19	0.15
P K*	298	± 82	P2O5	0.30	0.08
S K	2448	± 128	SO3	2.58	0.14
Cl K	648	± 88	Cl	0.27	0.04
K K	652	± 86	K2O	0.32	0.04
Ca K	140416	± 1070	CaO	83.00	0.63
Fe K	115	± 54	Fe2O3	0.09	0.04
Co K	112	± 52	CoO	0.08	0.04
Ni K	152	± 52	NiO	0.11	0.04
Zn K	5875	± 166	ZnO	4.29	0.12
Sr K*	135	± 42	SrO	0.17	0.05
Ag L*	466	± 100	Ag2O	0.37	0.08
Total				100	
Below Detection: B.D.					



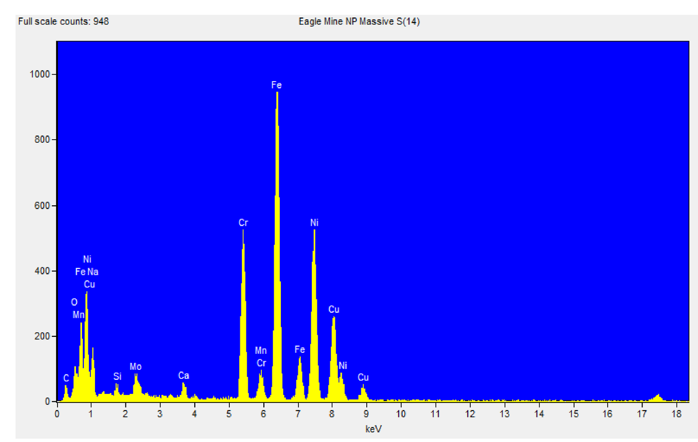
ĜÕÑÖ ÑŌPI ÕÕÑ	Net Counts	Net Counts Error (2σ)	Oxide Formula	Norm. Compd. %	2σ Error
Na K	B.D.				
Mg K	B.D.				
Al K	B.D.				
Si K	9921	± 290	SiO2	14.45	0.42
P K*	B.D.				
S K	1617	± 162	SO3	2.69	0.27
Cl K	B.D.				
K K	B.D.				
Ca K	33735	± 434	CaO	31.49	0.41
Fe K	B.D.				
Co K	B.D.				
Ni K	B.D.				
Zn K	44374	± 458	ZnO	51.14	0.53
Sr K*	81	± 36	SrO	0.16	0.07
Ag L*	B.D.				
Total				100	
Below Detection: B.D.					



Element Line	Net Counts	Net Counts Error (2σ)	Oxide Formula	Norm. Compd. %	2σ Error
Na K	1964	± 188	Na2O	2.458	0.24
Mg K	138	± 64	MgO	0.174	0.08
Al K	6642	± 182	Al2O3	7.727	0.21
Si K	63187	± 648	SiO2	76.074	0.78
S K	20	± 48	SO3	0.028	0.07
Cl K	139	± 54	Cl	0.075	0.03
K K	5244	± 160	K2O	3.342	0.10
Ca K	1169	± 90	CaO	0.902	0.07
Cr K	1051	± 80	Cr2O3	1.046	0.08
Mn K	93	± 48	MnO	0.085	0.04
Fe K	7897	± 190	Fe2O3	7.625	0.18
Co K	65	± 44	CoO	0.062	0.04
Ni K	61	± 36	NiO	0.059	0.03
Zn K	62	± 32	ZnO	0.059	0.03
Mo K*	B.D.				
Total				100	
Below Detection: B.D.					



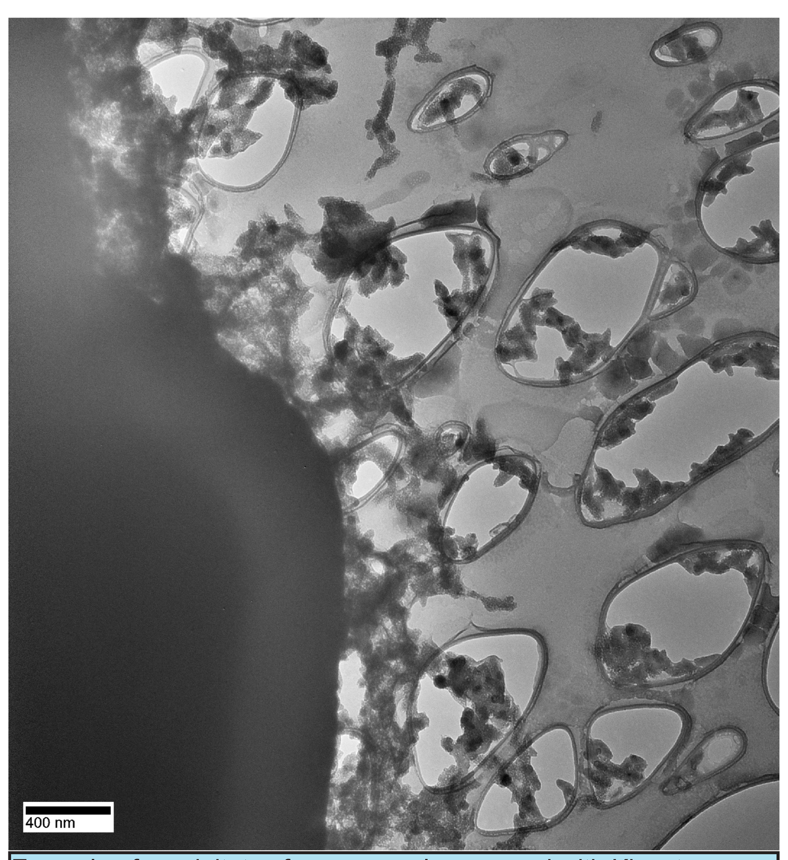
ĜÕÑÖ ÑŌPI ÕÕÑ	Net Counts	Net Counts Error (2σ)	Oxide Formula	Norm. Compd. %	2σ Error
Na K	2752	± 204	Na2O	8.06	0.60
Mg K	B.D.				
Al K	B.D.				
Si K	809	± 74	SiO2	2.28	0.21
S K	B.D.				
Cl K	238	± 52	Cl	0.30	0.07
K K	345	± 54	K2O	0.51	0.08
Ca K	1775	± 96	CaO	3.20	0.17
Cr K	8480	± 202	Cr2O3	19.74	0.47
Mn K	649	± 90	MnO	1.39	0.19
Fe K	18402	± 290	Fe2O3	41.56	0.65
Co K	153	± 52	CoO	0.34	0.12
Ni K	9112	± 200	NiO	20.60	0.45
Zn K	65	± 30	ZnO	0.15	0.07
Mo K*	341	± 44	MoO3	1.57	0.20
Total				100	
Below Detection: B.D.					



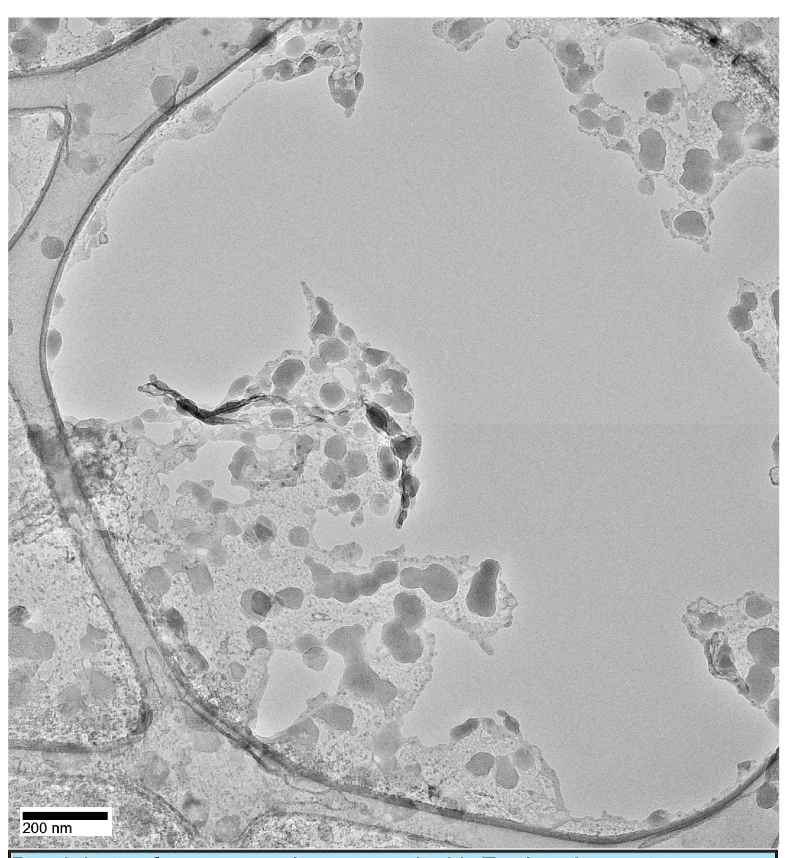
Element Line	Net Counts	Net Counts Error (2σ)	Oxide Formula	Norm. Compd. %	2σ Error
Na K	720	± 120	Na2O	2.65	0.44
Mg K	B.D.				
Al K	B.D.				
Si K	81	± 46	SiO2	0.29	0.16
S K	B.D.				
Cl K	B.D.				
K K	B.D.				
Ca K	576	± 60	CaO	1.30	0.14
Cr K	7681	± 190	Cr2O3	22.44	0.55
Mn K	451	± 82	MnO	1.21	0.22
Fe K	15706	± 266	Fe2O3	44.50	0.75
Co K	121	± 48	CoO	0.34	0.13
Ni K	8877	± 196	NiO	25.19	0.56
Zn K	B.D.				
Mo K*	324	± 42	MoO3	1.87	0.24
Total				100	
Below Detection: B.D.					

Problems With the Method: Evaporite Network (TDS)

- Water from both sampling districts contained large amounts of dissolved minerals which precipitated out on the grid during sample preparation.
- A dense evaporite network was created which hindered the study by obscuring potential metallic nanoparticles
- Plan to address problem by centerfuging water above a dense organic solvent which would allow particles to travel across the liquid interface while keeping dissolved ions in the water layer.



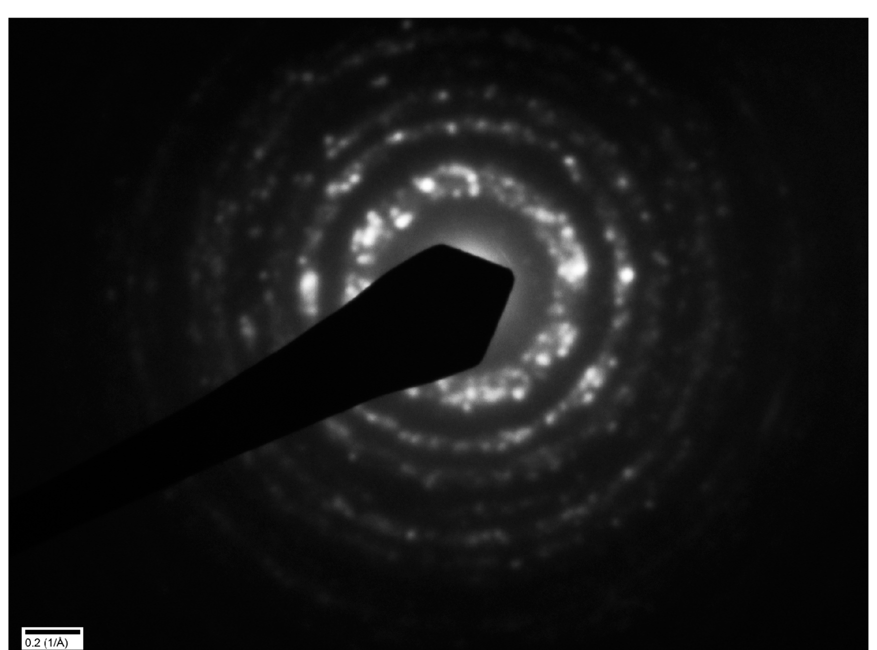
Example of precipitates from a sample prepared with Kingston mining district water. Dark area on left side of picture is a small calcite grain that was suspended in the water.



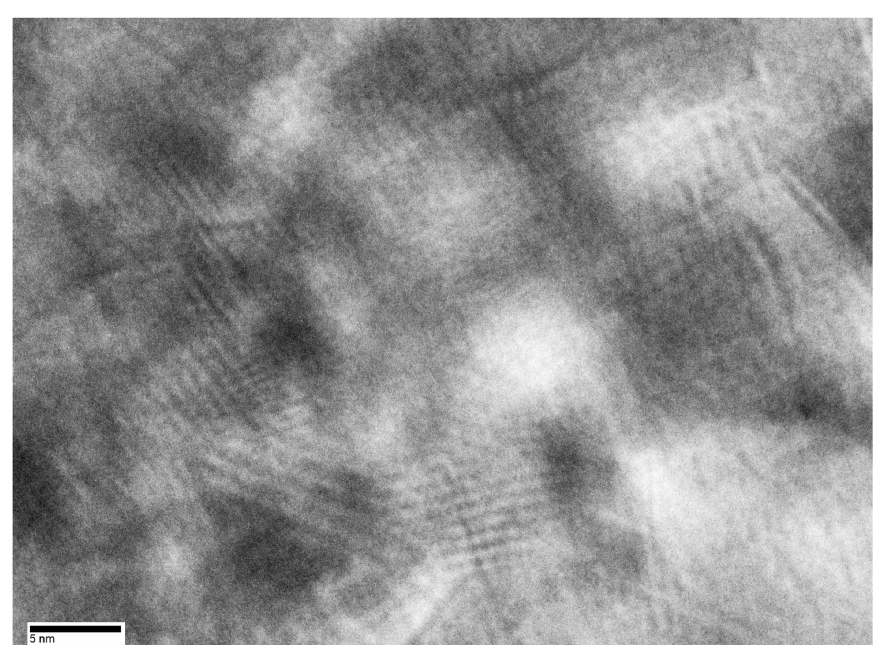
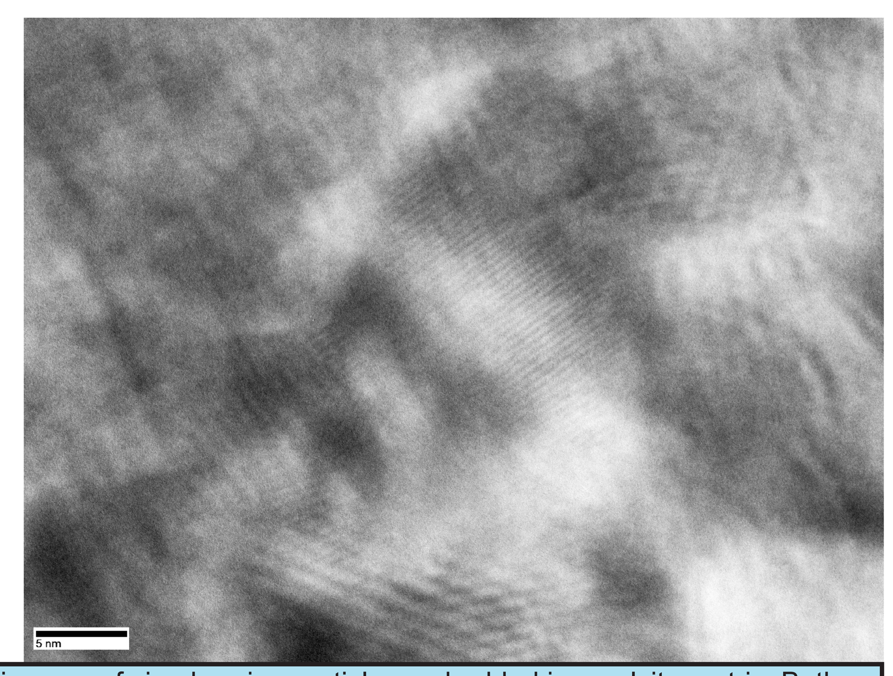
Precipitates from a sample prepared with Eagle mine water. Medium-gray pseudo-hexagonal particles are small calcite crystals.

Multi-Phase Zinc Bearing Particles from the Kingston Mining District

- Particles with significant amounts of zinc from samples prepared with Kingston mining district water appear to be made up of 2 distinct phases.
- Majority made up of a calcite matrix that encloses small (~5nm) particles that likily contain most of the zinc.
- Identification of these particles as a distinct phase supported by large numbers of dots on diffraction patterns and a change in lattice orientation when viewed at very high magnification (4,000,000x).
- Composition of particles most likely a zinc-silicate as the two elements show a positive correlation.



Selected area electron diffraction pattern for a multi-component metallic/carbonate composite grain. Density of diffraction pattern implies at least 3 phases are present.

High-Resolution (HR) TEM photomicrographs showing NP lattice images of zinc-bearing particles embedded in a calcite matrix. Both images are from a single multi-phase particle.

What's Next

- Test new sample preparation method that avoids evaporite precipitation by isolating nanoparticles suspended in water from dissolved minerals.
- Combine method with hydrogeologic modeling to pinpoint source regions for nanoparticles in groundwater samples.
- Collect and evaluate samples from an area suspected to have unexposed mineralization.
- Obtain gold TEM grids so copper can be analyzed in future studies.

Results

- Nanoparticles from groundwater in mineralized areas show a casual correlation with characteristics of the larger ore bodies.
- Not all water samples from mineralized zones contain particles with a significant metal component.
- NP with metallic signatures from the Kingston area occur as multi-phase aggregates with a carbonate network surrounding very small zinc-rich phases.
- Collecting groundwater from carbonate aquifers like in the Kingston area created a significant challenge by obscuring metallic NP with evaporites precipitated during sample preparation.

Citations

Li, Y., et al., 2016, The discovery of the metallic particles of groundwater from the Dongshengmiao polymetallic deposit, Inner Mongolia, and their prospecting significance: Journal of Geochemical Exploration, v. 161, p. 49-61.

Rossell, D., and Coombes, S., 2005, The Geology of the Eagle Nickel-Copper Deposit Michigan, USA: Kennecott Exploration Report.

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