Individual Grain Analysis of the Rare Dioctahedral Mica Celadonite Using Analytical Transmission Electron Microscopy

Todd R. Lau

Department of Geology, University of Wisconsin-Eau Claire

Faculty Mentor: Robert L. Hooper

Department of Geology, University of Wisconsin-Eau Claire

Abstract

This project explores the occurrence of a rare dioctahedral micafound along the Cambrian –Precambrian boundary at Big Falls county park in Eau Claire county, Wisconsin. Bulk chemical analysis has been done on the altered amphibolites that appear to contain the blue green aluminoceladonite $KAl(Mg,Fe)(Fe,Al)[Si_4O_{10}](OH)_2$. Celadonite forms a solid solution with iron and magnesium rich illite/smectite (I/S 90% I). The celadonite crystals are near stoichiometric with a maximum celadonite composition of $\{K_{0.82}Al_{1.18}(Mg_{1.40}Fe_{0.40})[Si_{3.71}Al_{0.29}O_{10}](OH)_2\}$. Our goal is to do individual grain quantitative chemical analysis, using a Jeol Jem-2010 high resolution Analytical Transmission Electron Microscope (ATEM), by Energy Dispersive X-ray Spectroscopy (EDX) (Thermo Electron Corporation). This allows us to quantitatively measure the composition of individual grains on the nanoscale, without the contamination of non-celadonite grains, which bulk chemical analysis, cannot provide. We used the following microbeam standards provided by the Smithstonian Institution for calibration of the TEM: Natural Bridge Diopside; Johnstown Meteorite Hypersthene; Kanaui Hornblende, Yellowstone National Park Rhyolitic Glass. We expect to report individual grain chemical analysis, as well as continue to study the relationship between the celadonite mica and the clay mineral illite, for the altered rock found in Big Falls county park, Wisconsin.

Method

Samples used in the calibration of the EDX detector were obtained from the Smithstonian Institution then ground in a agate mortar and pestle using analytical grade ethanol as a solvent. The mixture was then transferred to a vial to allow settle for further size separation. A single drop of the mixture was then placed on a lacey carbon sample grid, with the formvar removed from it, the ethanol was then allowed to evaporate depositing the sample on the sample grid. Samples were then placed in the TEM for analysis. A large number (20-30) of analyses were taken using the EDX system for each standard to assure representative sampling. TEM sample composition was then compared to the accepted values for each standard to determine the correct K-factors for the JEOL 2010 TEM.

Ion milled samples are standard thin sections removed from the glass slide and milled to electron transparency (~100nm) with a 4kV Argon ion beam.

Table 1. Major Element Geochemistry of Altered and Unaltered Rocks from Big Falls County Park

Description (Depth M)	Sample Number	Na2O	MgO	Al2O3	SiO2	K2O	CaO	TiO2	MnO	Fe2O3	P2O5	Totals
Unaltered Amphibolite												
surface	BB95-1	3.11	5.97	15.50	51.10	0.29	9.07	1.34	0.19	13.73	0.23	100.54
surface	BB95-2	3.56	6.57	13.25	52.66	1.46	8.05	1.71	0.20	12.12	0.17	99.76
Altered Amphibolites												
surface	BF-101	0.32	2.70	17.36	61.93	7.10	0.63	0.94	0.02	4.98	0.19	96.18
0.25m	BF-102	0.20	3.05	17.18	62.79	7.22	0.65	0.99	0.04	6.10	0.19	98.41
0.5m	BF-103	0.21	3.02	17.04	61.48	6.97	0.64	0.84	0.02	5.04	0.18	95.44
0.65m	BF-103.5	0.23	2.68	16.26	62.62	7.15	0.64	0.88	0.04	5.42	0.18	96.09
0.75m	BF-104	0.07	2.89	16.84	60.07	7.45	0.64	0.95	0.04	5.60	0.21	94.75
1.0m	BF-105	0.08	3.24	16.31	58.69	7.18	0.66	0.87	0.07	7.30	0.19	94.60
Unaltered Banded Amphibolites												
surface	BF2-R1	2.21	0.72	30.43	47.10	0.20	15.18	0.17	0.03	2.14	0.05	98.23
surface	BF2-R2	2.97	1.38	30.56	48.43	0.25	14.65	0.21	0.04	3.35	0.04	101.87
surface	BF2-R4	2.85	0.88	30.24	46.63	0.18	14.51	0.23	0.03	2.47	0.03	98.04
Altered Banded Amphibolites												
surface	BF2-T	0.11	5.21	16.66	52.06	9.28	0.88	0.44	0.04	6.72	0.03	91.42
0.5m	BF2-TM	0.05	6.18	15.28	50.26	9.14	0.63	0.74	0.05	11.65	0.28	94.25
1.0m	BF2-BM	0.05	5.17	17.36	52.55	9.04	1.06	0.34	0.03	7.28	0.03	92.92
1.5m	BF2-B	0.09	4.91	18.23	52.92	9.37	0.80	0.32	0.02	5.79	0.03	92.49

Table 1. Major Element Geochemistry of Altered and Unaltered Rocks from Big Falls County park (in compound %). This table illustrates the dioctahedral substitution occurring as the rock loses aluminum and increases in Potassium, which is oppositethe normal weathering trend. (Hooper, 1998)

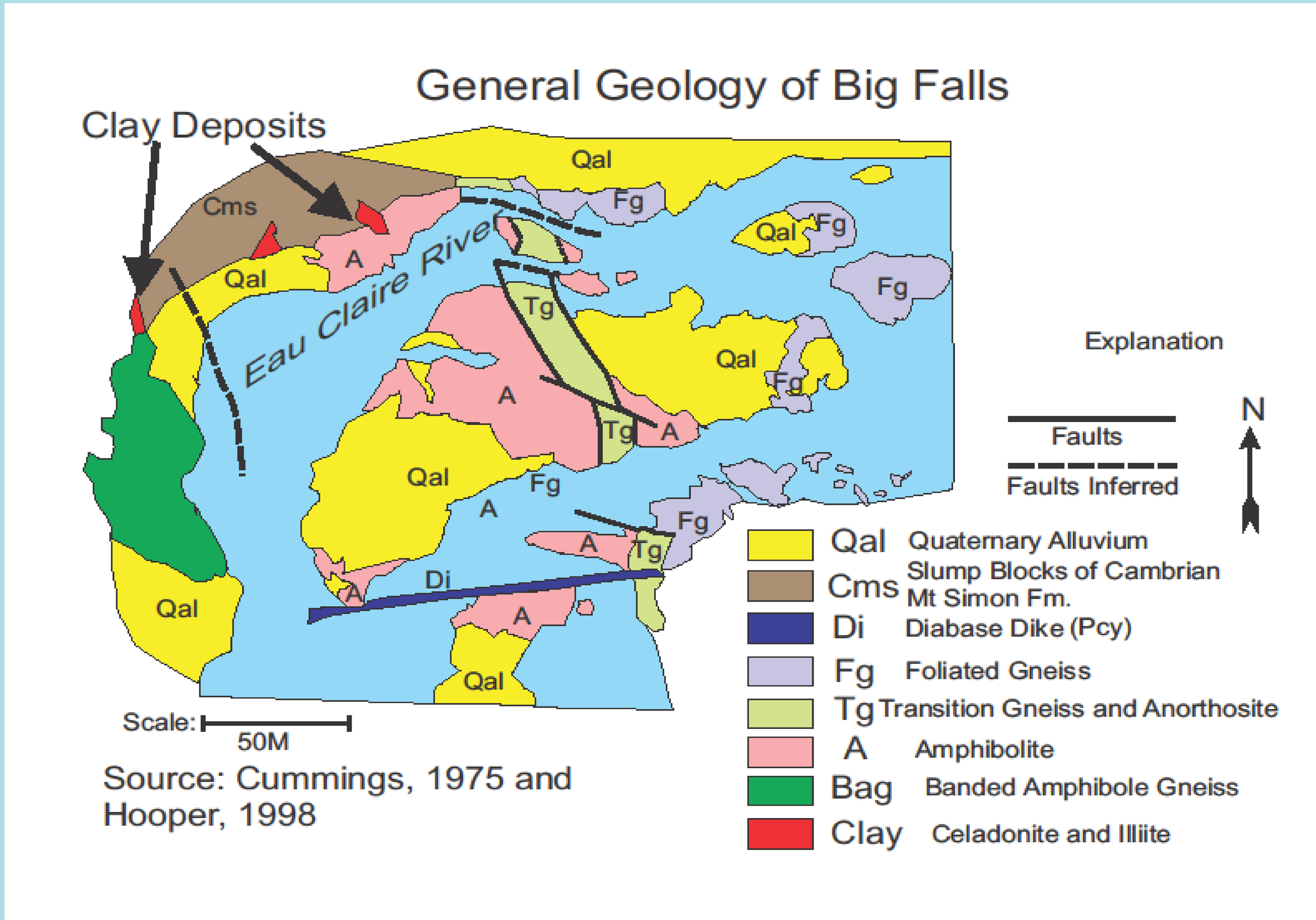
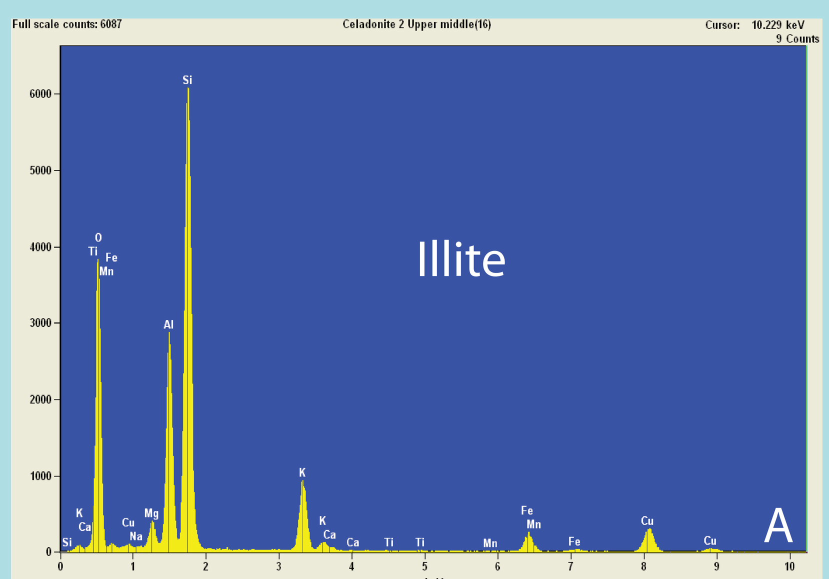
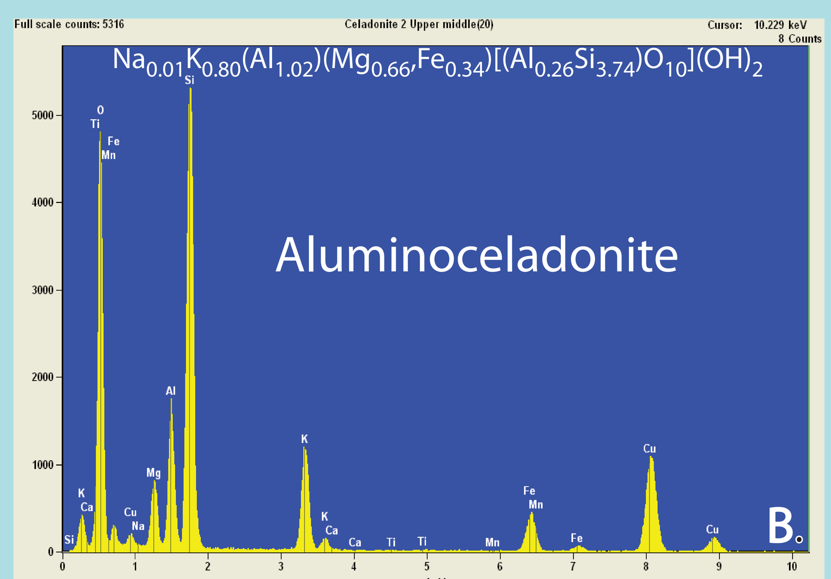


Figure 6. The Geology of Big Falls County Park. Samples for our study we taken in the northern section of this map area, where the mafic amphibolite is covered by the Cms Cambrian Mt. Simon Formation. This contact represents the Great Unconformity where there is a layer of blueish green illitic clay. (Cummings, 1984)

Geologic Background

The Geology of Big Falls County Park, in Eau Claire Wisconsin consists of three main areas of geologic distinction; A Precambrian Meta Layered Gabbro, The Cambrian Mt. Simon Formation, and a section which divides the two formations which consists of a blue illitic clay layer marked by numerous springs, known as the Great Unconformity.(Figure 5, 6.) The Precambrian meta layered gabbro at Big Falls County Park can be further classified as a banded amphibole gneiss which is characterized by alternating hornblende and plagioclase rich layers, which range in size from less than 1cm to 20cm thick. The bulk analysis of the banded amphibolites are shown in Table 1. The banded amphibolites closer to the Great Unconformity show signs of alteration and are enriched in Potassium (from 0.25wt% to 9.0%) and depleated in Aluminum (from ~30 wt% to ~17wt%) during the hydrothermal alteration. As a result of the alteration the amphibolites have been altered primarily to illite, K-feldspar. The illitization of amphibolites require that the rocks are subjected to a potassium-rich brine at elevated temperatures. Understanding how the gabbro was altered to its present composition (illite, celadonite, K-feldspar) will put geochemical constraints on the hydrothermal alteration along the great unconformity.





Quantitative Results for: Celadonite 2 Upper middle(16)

Element	Net Counts		Net Counts Error	K-Factor	Weight %	Norm. Compnd%	# Cations
O	0		0	---	47.799S	---	---
Na	136	+/-	28	1.5100	0.094	0.126	0.0150
Mg	3357	+/-	66	1.1980	1.835	3.042	0.2779
Al	27581	+/-	191	1.1200	14.093	26.627	1.9231
Si	61083	+/-	314	1.0000	27.866	59.615	3.6532
K	12119	+/-	119	1.0400	5.750	6.926	0.5415
Ca	579	+/-	37	1.0500	0.277	0.388	0.0255
Ti	88	+/-	20	1.1000	0.044	0.074	0.0034
Mn	69	+/-	19	1.2600	0.040	0.051	0.0027
Fe	3628	+/-	65	1.3310	2.203	3.150	0.1452
Total					100.000	100.000	6.5875

Quantitative Results for: Celadonite 2 Upper middle(20)

Element	Net Counts		Net Counts Error	K-Factor	Weight %	Norm. Compnd%	# Cations
O	0		0	---	45.983S	---	---
Na	44	+/-	32	1.5100	0.034	0.046	0.0057
Mg	6816	+/-	93	1.1980	4.209	6.980	0.6629
Al	15660	+/-	140	1.1200	9.042	17.084	1.2826
Si	53276	+/-	287	1.0000	27.465	58.755	3.7427
K	15249	+/-	135	1.0400	8.176	9.848	0.8003
Ca	20	+/-	30	1.0500	0.011	0.015	0.0010
Ti	68	+/-	22	1.1000	0.039	0.064	0.0031
Mn	23	+/-	19	1.2600	0.015	0.019	0.0010
Fe	7326	+/-	91	1.3310	5.027	7.187	0.3445
Total					100.000	100.000	6.8437

Figure 4. EDX analysis of a Illite (A) and an Aluminoceladonite (B). The Solid solution of Illite and Aluminoceladonite is easily pictured here. Aluminum compound % drops as it is replaced by Potassium causing the compound percentage of Magnesium and Iron to increase.

What is Celadonite?

Celadonite is an extremely rare dioctahedral mica and is usually found only in hydrothermaly altered volcanic rocks on the seafloor. A iron and magnesium rich dioctahedral mica has 2 of its 3 octahedral cation positions filled. It has the chemical formula $KAl(Mg,Fe)[Si_4O_{10}](OH)_2$. Celadonite forms a solid solution with the clay mineral Illite, which has a formula $K_{0.8}Al_2[Al_{0.8}Si_{3.2}O_{10}](OH)_2$. Figures 1,2,3,4.

Why Do We Care?

Hydrothermal alteration along the Great Unconformity has been recognized across the midwest. Big Falls is the only exposed area where the unconformity overlies meta gabbroic rocks. Understanding how mafic rocks can be altered to generate K rich clays and micas will result in a better understanding of the nature of the hydrothermal fluids. Table 1, illustrates the dramatic chemical changes of mafic rocks altered by this hydrothermal event.

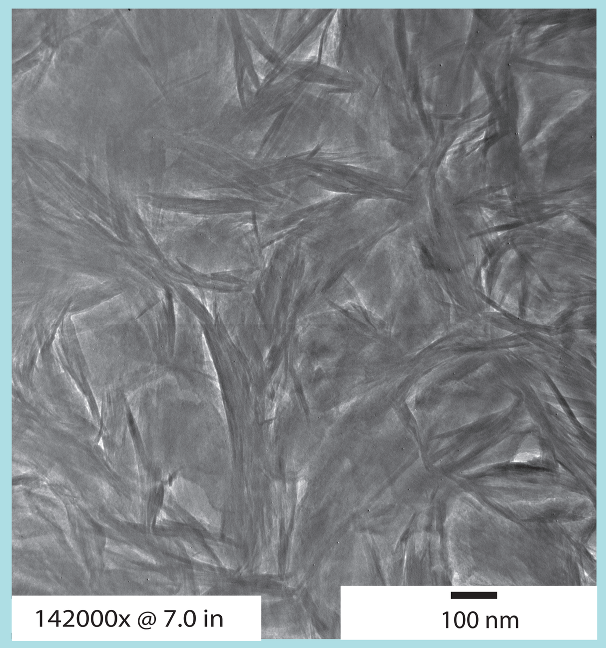


Figure 2. Illite laths in an ion milled sample.

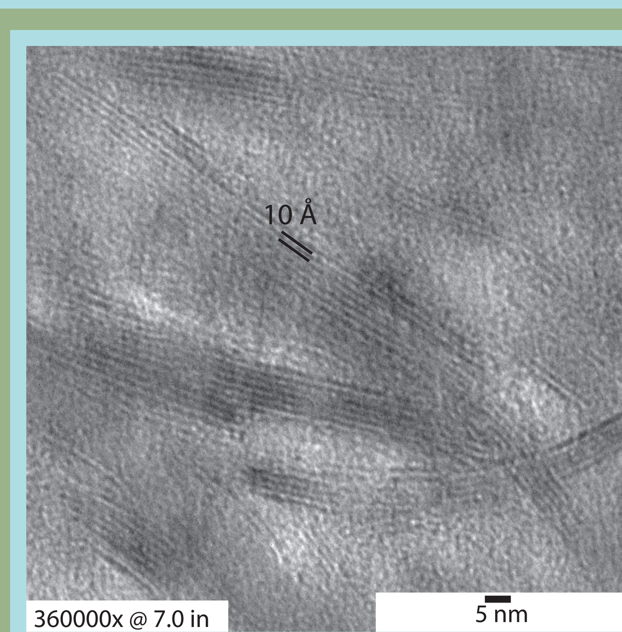


Figure . Illite atomic lattice which is 10 angstroms apart

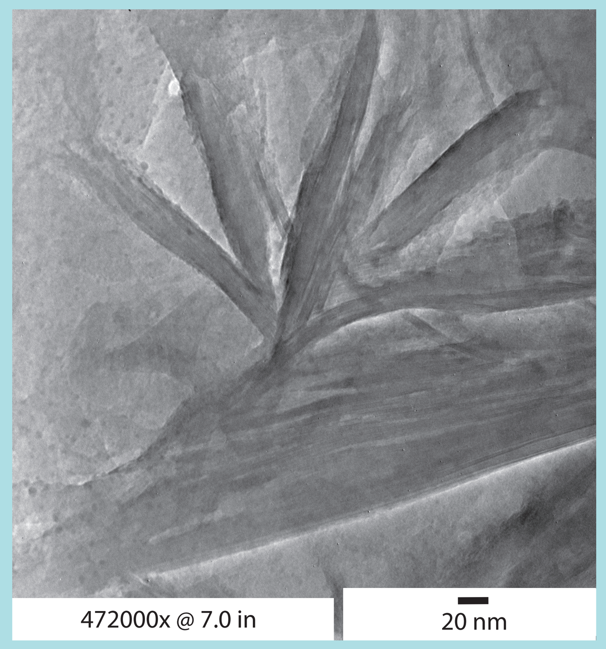


Figure 3. Illite glomerocryst (muliple crystals nucleating from a single point)

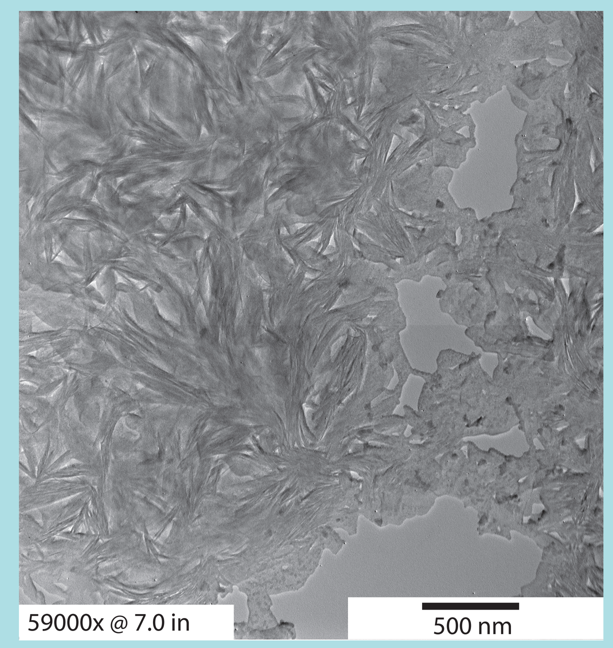


Figure 1. Ion milled sample from Big Falls showing typical intergrown illite.

Results and Future Research

We have confirmed that both illite and aluminoceladonite occur in the clay at Big Falls County Park, in Wisconsin. The fact that celadonite is an extremely rare mineral and usually only found in altered volcanic rocks on the ocean floor, makes this an exciting discovery! To determine the spatial relationship between the clay illite and the mica phase aluminoceladonite requires examining samples without disaggragation. We will collect fresh samples for thin sectioning and ion milling. Our goal is to understand the relationship between the illite and celadonite. This will help to define the conditions of hydrothermal alteration at the Cambrian/Precambrian unconformity in the upper midwest.

References: Cummings, M. L., 1984, The Eau Claire River Complex: A metamorphosed Precambrian mafic intrusion in western Wisconsin: Geological Society of America Bulletini, v. 95, no. January, p. 75-86.

Hooper, R. L., 1998, Big Falls County Park - Precambrian Amphibolites and Contact Zone with the Cambrian Mt. Simon Formation, Tri-State/University of Wisconsin system Geological Field Conference, p. 39-45.