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Collaborative Research: Chemical Equilibria Involving Iron and Hydrogen in Metapelites From Western Maine

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Final Report for Period: 08/1999 - 07/2001**Submitted on:** 10/10/2001**Principal Investigator:** Guidotti, Charles V.**Award ID:** 9902857**Organization:** University of Maine**Title:**

Collaborative Research: Chemical Equilibria Involving Iron and Hydrogen in Metapelites From Western Maine

Project Participants**Senior Personnel****Name:** Guidotti, Charles**Worked for more than 160 Hours:** Yes**Contribution to Project:**

Charles V. Guidotti; University of Maine

Collaborative Research: Chemical Equilibria Involving Iron and Hydrogen in Metapelites From Western Maine

Post-doc**Graduate Student****Undergraduate Student****Research Experience for Undergraduates****Organizational Partners****Mount Holyoke College**

This project was formally funded by NSF as a collaborative research project between this P.I. at the University of Maine and M. M. Dyar at Mount Holyoke College and Jeremy S. Delaney at Rutgers University.

Rutgers University New Brunswick

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Other Collaborators or Contacts**Activities and Findings****Research and Education Activities:** (See PDF version submitted by PI at the end of the report)**Findings:** (See PDF version submitted by PI at the end of the report)**Training and Development:**

This funding greatly impacted the undergraduate students at Mount Holyoke College (See the Ann. Rept. of my CO-PI, M.D. Dyar. Here at Maine which received only a small fraction of the total funding of the Grant was the involvement of one student (Ian Sollitt) in the processing of some of the data obtained by the Microprobe analyses required for the project.

Outreach Activities:**Journal Publications**

Dyar, M.D., Grew, E.S., Guidotti, C.V., Hughes, J.M., Bloodaxe, E., Tagg, S. L., Cho, H., Shearer, C.K., Robertson, J.D., Paul, R.L., and Yates, M.G. (1999), "The search for tetrahedral boron in tourmaline: an analytical challenge.", 2nd European Workshop on Tourmaline and Borosilicates. Paris., p. , vol. , (1999). Accepted

Dyar, M.D., Lowe, E. W., Delaney, J.S., and Guidotti, C. V., "Ferric and ferrous iron partitioning among silicates in metapelites: a synchrotron micro-XANES (Smx) study. (invited).", Geological Soc. Amer., Reno, NV, A-53., p. A-53, vol. , (2000). Published

Dyar, M.D., Wiedenbeck, M., Cross, L., Delaney, J.S., Francis, C.A., Grew, E.S., Guidotti, C.V., Hervig, R.L., Hughes, J.M., Leeman, W., McGuire, A.V., Paul, R.L., Robertson, J.D., and Yates, M., "Mineral standards for microanalysis of light elements (invited)", Geoanalysis 2000, Pont Ó Mousson, Lorraine France, in press., p. , vol. , (). Submitted

Guidotti, C.V., Grew, E.S., Yates, M.G., Dyar, M.D., Francis, C.A., Fowler, G., Husler, J., Shearer, C.K., and Wiedenbeck, M., "Lithium in coexisting micas and tourmaline from western Maine.", Geological Soc. Amer., Reno, NV, (invited), A-53, p. A-53, vol. , (2000). Published

Guidotti, C. V., and Sassi, F. P., "Petrologic and mineralogic studies involving metamorphic K-Na natural micas: state of the art and suggestions for future research. (invited) 40 P. Ms)", Micas 2000 Conference, Italian National Academy, Rome, 2000. , p. , vol. , (). Submitted

Hughes, J.M., Ertl, A., Dyar, M.D., Grew, E.S., Shearer, C.K., Yates, M.G., and Guidotti, C.V., "Boron in the tourmaline tetrahedral site: Chemistry and structure of a boron-rich olenite.", Can. Mineral. , p. 861, vol. 38, (2000). Published

Johnson, K.E., Dyar, M.D., Brady, J.B., Holcombe, B., Velasquez, M., Carmichael, S., Acosta, R., Core, D., Wearn, K., Francis, C.A., Wise, M.A., and Guidotti, C.V., "Stable isotope geochemistry of tourmaline from the Oxford Pegmatite Field, southwestern Maine.", Geochim. Cosmochim. Acta., p. , vol. , (). Submitted

Bloodaxe, E.S., Hughes, J.M. Dyar, M.D., Grew, E.S. and Guidotti, C.V., "Linking structure and chemistry in the schorl-dravite series", Amer. Mineral., p. 922-928, vol. 84, (1999). Published

Dyar, M.D., Lowe, E. W., Guidotti, C.V., and Delaney, J.S., "Fe³⁺ and Fe²⁺ partitioning among silicates in metapelites: A synchrotron micro-XANES study.", Amer. Mineral., p. , vol. , (2001). Accepted

Books or Other One-time Publications

Web/Internet Site

URL(s):

Description:

Other Specific Products

Contributions

Contributions within Discipline:

Although our data base to date is limited and preliminary, it still can serve very useful purposes within the fields of mineralogy and metamorphic petrology. Specifically, petrologists working with metapelites will now have a much clearer picture as to (1) how Fe³⁺ fractionates among the key minerals, (2) how much to adjust the Mg/(Mg + Fe²⁺) ratio in the phases when making various thermodynamic calculations such as geothermometry, and (3) how to formulate more accurate and realistic activity models for these phases.

Contributions to Other Disciplines:

The primary contribution in this area is a clear demonstration as to how still more of the highly sophisticated analytical techniques being

developed by chemists and physicists can be applied with good results to less exact sciences like the geological sciences, thereby aiding them in the attempts to make them more quantitative.

Contributions to Human Resource Development:

The vast bulk of the contribution here has taken place at Mount Holyoke College (See report of CO-PI, M. D. Dyar). Here at Maine it has involved only providing one student (Ian Sollitt) with an opportunity to gain experience in data tabulation and some manipulation of the data. Moreover, C. V. Guidotti also participated as an unofficial advisor to Emily Lowe ('00) of Mount Holyoke College, reading her theseis and making suggestions for changes.

Contributions to Resources for Research and Education:

The vast bulk of the contribution here has taken place at Mount Holyoke College (See report of CO-PI, M. D. Dyar). Here at Maine it has involved only providing one student (Ian Sollitt) with an opportunity to gain experience in data tabulation and some manipulation of the data. Moreover, C. V. Guidotti also participated as an unofficial advisor to Emily Lowe ('00) of Mount Holyoke College, reading her theseis and making suggestions for changes.

Contributions Beyond Science and Engineering:

Categories for which nothing is reported:

Activities and Findings: Any Outreach Activities

Any Book

Any Product

Contributions: To Any Beyond Science and Engineering

The goals of this one year exploratory research program were two-fold: 1) to quickly and effectively demonstrate the potential importance of synchrotron micro-XANES (X-ray absorption near-edge spectroscopy) as a petrologic tool, and 2) to evaluate the chemical equilibria involving ferrous and ferric iron and hydrogen in metapelitic rocks from western Maine using the new technique of synchrotron micro-XANES. This work formed the basis of a Mount Holyoke College B.A. thesis by Emily Lowe ('00), and also provided support for Sarah Hale '01 to work in Dyar's lab and assist with both Mössbauer and synchrotron measurements.

For this project, we selected samples covering a range of temperatures from lower garnet grade to Kfs + Sil grade and a range of mineral assemblages representing f_{O_2} from graphite/ilmenite to magnetite and hematite-bearing rocks (Table 1). The $Fe^{3+}/\Sigma Fe$ measurements were made on standard 1" round petrographic thin sections using beam sizes of less than 10 x 15 μm and the relatively rapid, non-destructive technique of synchrotron microXANES spectroscopy (SmX) for $Fe^{3+}/\Sigma Fe$ and the electron microprobe (EPMA) for other major elements.

Table 1. Assemblage Data for Samples Studied[†]

Location	Grade		Silicate Phases	Opaques
Ra-d75-66	Rangeley	1	Grt-Bt-Chl-(Ap, Tur, Mnz)	Ilm-Gr
Ra-c91-66	Rangeley	2	Bt-Chl-(Ap, Tur, Mnz)	Ilm-Mag(?)
Ra-a48-66	Rangeley	4	St-Grt-Bt-Chl-(Ap, Tur, Mnz)	Ilm-Gr-Po
Ra-c1-66	Rangeley	4	St-Grt-Bt-Chl-(Ap, Tur, Mnz)	Ilm-Gr
Ra-c69-66	Rangeley	5	(And) [‡] -St-Grt-Bt-Chl-(Ap, Tur, Mnz)	Ilm-Gr
Ra-b42-66	Rangeley	6	Sil-St-Grt-Bt-(Ap, Tur, Mnz)	Ilm-Gr(?)
Ra-b4-66	Rangeley	7	(And) [‡] -Sil-St-Grt-Bt-(Ap, Tur, Mnz)	Ilm-Gr-Po
O-J-65	Oquossoc	7 [*]	Sil-St-Grt-Bt-(Tur, Mnz)	Ilm-Gr-Po
O-C-17	Oquossoc	8	Sil-Grt-Bt-(Ap, Tur, Mnz)	Ilm-Gr(?) -Po
O-H-49 [*]	Oquossoc	8	Sil-Bt-(Ap, Tur, Mnz)	Ilm-Mag-Po
O-H-56	Oquossoc	8	Sil-Grt-Bt-(Ap, Mnz)	Ilm-Mag-Po(??)
71-62B	Black Mt. NH	≈5/6	Ky-St-Cld-Chl ^(S) -(Ap)	Ilm-Mag-Hem
71-60R	Black Mt. NH	≈5/6	St-Cld-Grt-Chl ^(S) -(Ap, Tur)	Ilm
CVG-A16 ^(Pg)	Black Mt. NH	≈5/6	Ky-St-Cld-(Tur, Aln(?))	Ilm-Hem(?) ^(R)
CVG-A17	Black Mt. NH	≈5/6	Ky-St-Cld-Chl ^(S) -(Tur, Mnz)	Ilm-Mag(?) -Po(?)

[†]All samples except those from Black Mountain have Ms, Qtz and Pl; Black Mt. Samples have no Pl.

^{*}Metastable remnant from M2 metamorphic event.

^(S)Chl probably secondary.

^(R)This is the same as Rumble's sample 68-44. Rumble (1971) listed Ilm-Rt-Hem(tr.), but Rumble (1978) lists only Ilm.

^(Pg)Contains paragonite; therefore Black Mt rocks are probably Zone 5, but at somewhat higher T than Zone 5 of the Rangeley area.

The results of this project were summarized in Lowe (2000) and in Dyar et al. (2000b and 2002). To accomplish this task, we first needed to do a large amount of technique development work on many of the individual phases to be studied (see “Publications supported by EAR 9909587”, below). Armed with a better understanding of the XANES pre-edge method, we used more than twelve three-day sessions at the National Synchrotron Light Source to make our measurements on all the Fe-bearing phases in the metapelites, including biotite, muscovite, chlorite, staurolite, tourmaline, aluminosilicates, feldspar, and quartz. Roughly 20 analyses were made on each thin section. We have now calculated Fe^{2+}/Mg , Fe^{3+}/Al , and Fe^{3+}/Fe^{2+} among all these phases, as shown below. These tables show data for graphite/ilmenite-bearing rocks only; we are still collecting results on the magnetite- and hematite-bearing rocks.

Table 1. Fe^{2+}/Mg at Different Grades, XANES Data Only

Grade	Bt	Ms	Chl	St	Grt	Tur
Lower Garnet, Rangeley Fm.	1.29		1.43		12.27	
Lower Staurolite, Rangeley Fm.	1.19	0.36	1.07	7.05	9.10	
Upper Staurolite, Rangeley Fm.	1.14	0.28	1.03	4.85	8.58	
Transition Zone, Rangeley Fm.	0.99	0.39		4.58	7.26	0.63
Lower Sillimanite, Rangeley Fm.	1.16	0.45		5.69	8.45	
Lower Sillimanite, Oquossoc Fm.	1.48	0.31		6.75	11.27	
Upper Sillimanite, Oquossoc Fm.	1.67	0.90			9.97	0.60

Because of its significance in geothermometry (c.f. Ferry and Spear, 1978 and numerous improvements thereon published subsequently), partitioning of Fe^{2+}/Mg (Table 1) has been studied intensely, albeit in the absence of $Fe^{3+}/\Sigma Fe$ data. Our new data on Fe^{2+}/Mg distribution among metapelitic phases constitutes an improvement in the details, albeit not for the main, previously known trends, in such rocks. In garnet grade rocks, Fe^{2+}/Mg preference is $Grt \gg Chl \approx Bt > Ms$; when St enters the assemblage at higher grades its preference for Fe^{2+}/Mg is almost as strong as that of Grt. Fe^{2+}/Mg in Tur falls between Bt and Ms. At sillimanite-bearing grades, the preference for Fe^{2+}/Mg is $Grt > St \gg Bt > Tur > Ms$. In summary, the main conclusion is that Fe^{2+} partitions strongly into Grt and St in metapelites at all temperatures where those phases are stable, followed by $Bt \approx Chl$, Tur (if B is present), and Ms. The fact that the Bt – Chl relations differ a little from the previous views based on use of $Mg/(Mg + Fe_T)$ ratio may reflect in part the fact that Bt contains significant Ti whereas Chl does not.

Table 2. Partition Coefficients for Fe^{3+}/Al at Different Grades, XANES Data Only

Grade	Bt	Ms	Chl	St	Tur
Lower Garnet, Rangeley Fm.	0.77	0.02	0.11		
Lower Staurolite, Rangeley Fm.	0.09	0.02	0.17	0.03	
Upper Staurolite, Rangeley Fm.	0.05	0.02	0.05	0.02	
Transition Zone, Rangeley Fm.	0.23	0.01		0.02	0.04
Lower Sillimanite, Rangeley Fm.	0.13	0.01		0.01	
Lower Sillimanite, Oquossoc Fm.	0.10	0.02		0.01	
Upper Sillimanite, Oquossoc Fm.	0.17	0.01			0.03

Relative preference of Fe³⁺ over Al in octahedral sites of metapelite minerals has not previously been addressed due to lack of Fe³⁺ data. This ratio is complicated to interpret for several reasons. 1) Due to the presence of significant Ti in many of these minerals (especially Bt), the substitution of Fe³⁺ may not be purely a function of Al content (just as Fe²⁺/Mg is affected by Mn, Zn, and other constituents). 2) Chl has two different types of octahedral sites, which probably have different site preferences. 3) Because these are Al-saturated rocks, the Al contents are intrinsically high in most of the minerals, such that the Fe³⁺/Al ratios can be very small. However, our data (Table 2) do show some systematics worthy of mention.

In nearly all the graphite/ilmenite-bearing rocks, the partitioning preference for Fe³⁺/^[VI]Al is Bt > Chl > Ms > Grt (which has no Fe³⁺); only in lower staurolite-grade rocks does Fe³⁺ prefer Chl over Bt. At highest grades, there is very little Fe³⁺ relative to Al in any of the phases. These data suggest that the Fe³⁺/^[VI]Al ratio is primarily affected by the amount of ^[VI]Al rather than any energetic preference for one cation or the other in that site. For example, Ms has 3-4 atoms p.f.u. ^[VI]Al relative to the tiny amount of Fe³⁺ (>0.1 Fe³⁺ a.p.f.u.). However, Bt and Chl have relatively little (<1.0 cation p.f.u.) ^[VI]Al, so their Fe³⁺/^[VI]Al ratio is high.

Table 3. Partition Coefficients for Fe³⁺/Fe²⁺ at Different Grades, XANES Data Only

Grade	Bt	Ms	Chl	St	Grt	Tur
Lower Garnet, Rangeley Fm.	0.26	2.57	0.06		0.06	
Lower Staurolite, Rangeley Fm.	0.05	2.21	0.12	0.22	0.09	
Upper Staurolite, Rangeley Fm.	0.02	4.38	0.03	0.09	0.11	
Transition Zone, Rangeley Fm.	0.15	1.17		0.15	0.15	0.25
Lower Sillimanite, Rangeley Fm.	0.05	0.56		0.03	0.00	
Lower Sillimanite, Oquossoc Fm.	0.05	2.45		0.07	0.00	
Upper Sillimanite, Oquossoc Fm.	0.05	0.94		0.28	0.02	

The interpretation of the Fe³⁺/Fe²⁺ ratios (Table 3) is different from the ratios just discussed because it does not involve a simple substitution; instead, it must reflect coupled substitutions that occur to accommodate the prevailing oxygen fugacity at the time of re-equilibration. The order of partitioning at all grades is Ms >> Bt ≈ St > Tur > Chl > Grt. This ratio really reflects the crystal chemical constraints (e.g. cation size and charge, and presence of other high-valence cations) imposed on substituting a trivalent cation into the crystal structure of each species. Of the minerals present, the structure best suited to accommodating Fe³⁺ is dioctahedral Ms, which shows the largest “preference” for Fe³⁺ (relative to Fe²⁺).

In summary, our new SmX results regarding Fe³⁺ in metapelite generally compares quite favorably with previous Mössbauer data. It emphasizes several features relevant for work on metapelite parageneses. These include:

(1) Local variation in the Fe³⁺-contents of a given mineral may have to be considered in response to localized, either prograde or retrograde reactions.

(2) Fe³⁺-contents can impact the Mg/Fe²⁺ ratio in some minerals, especially Ms and Bt and the effect is clearly reflected by the oxidation conditions implied by the opaque minerals present.

(3) Although needing considerable additional refinement, our results to date can be used for adjusting the Mg/Fe²⁺ ratios obtained by EMPA for several key minerals in metapelites.

Finally, Synchrotron microXANES (SmX) initiates a third generation of microanalysis techniques that allows us to explore the chemical state of elements in situ in addition to the now routine abundance and isotopic results that are characteristic of the first and second generations (electron, proton and ion probes) during the last 45-50 years of microbeam analysis. Progress in the development of compact, tunable x-ray sources proceeds rapidly and allows us to realistically imagine a time when these third generation probes will no longer be trapped at huge 'national' facilities but will be as common on university and industrial campuses as electron microprobes are today.