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Boron in Antarctic granulite-facies rocks: under what conditions is boron retained in the middle crust?

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Final Report for Period: 06/2009 - 11/2009

Principal Investigator: Grew, Edward S.

Organization: University of Maine

Submitted By:

Grew, Edward - Principal Investigator

Title:

Boron in Antarctic granulite-facies rocks: under what conditions is boron retained in the middle crust?

Project Participants

Senior Personnel

Name: Grew, Edward Worked for more than 160 Hours: Yes Contribution to Project:

Name: Yates, Martin

Worked for more than 160 Hours: Yes

Contribution to Project:

Yates operates the electron microprobe at U Maine and has collected all the microprobe data obtained to date on minerals collected in the Larsemann Hills; these data include element scans, element maps, back-scattered electron images and quantitative analyses. He has developed special protocols for quantitative analysis of borosilicates and phosphates because both types of compounds require special experimental set-ups and operating conditions. The grant is providing funds both for the U Maine electron microprobe laboratory and for Yates's summer salary in 2004 and 2005

Post-doc

Graduate Student

Name: Wadoski, Eva

Worked for more than 160 Hours: Yes

Contribution to Project:

Eva Wadoski is working on a Master of Science thesis entitled 'Microstructural and Chemical Study of Borosilicate Minerals in Pegmatites from the Larsemann Hills, Prydz Bay, East Antarctica', which is an integral part of the project. Her research consists of detailed microstructural study and analysis with the electron microprobe of the borosilicate minerals with an emphasis on the tourmaline group, dumortierite and prismatine in order to identify the succession of borosilicate mineral assemblages and infer changes in the pressure-temperature-fluid activity conditions responsible for the changes in mineral chemistry and assemblage in Larsemann Hills pegmatites.

Most of Eva's support comes from the University of Maine and miscellaneous sources. Eva has used the department's Cameca SX100 electron minroprobe, which has received support from this award. She has been awarded a travel grant from NSF OPP to attend the conference 'Granulites & Granulites 2009' in the Czech Republic in July, 2009.

Undergraduate Student

Name: Harris, John

Worked for more than 160 Hours: No

Contribution to Project:

John Harris has begun a project analyzing and dating monazite and xenotime from the Larsemann Hills. He is being supported by an REU supplement.

Technician, **Programmer**

Submitted on: 12/16/2009 Award ID: 0228842

Other Participant

Name: Carson, Christopher

Worked for more than 160 Hours: Yes

Contribution to Project:

Carson assumed responsibility for arranging the fieldwork in the Larsemann Hills with the Australian National Antarctic Research Expedition. During the two-month season in the Larsemanns (November 24, 2003-January 23, 2004) he provided valuable support in camp. Having worked several seasons in the Larsemanns, including mapping for his Ph.D. dissertation, Carson was familiar with the geology and was able to guide the PI to localities for borosilicate minerals as well as discover new localities. He has developed a structural evolution based on field relationships obtained over several seasons of fieldwork. Over the past year or so, Carson compiled his field data and prepared a new geologic map of the Larsemanns, which is now being finalized by the Australian Antarctic Division and Geoscience Australia.

Name: Christy, Andrew

Worked for more than 160 Hours: No

Contribution to Project:

Andrew Christy is overseeing the whole-rock geochemical analyses of samples from the Larsemann Hills at the Australian National University.

Name: Armbruster, Thomas

Worked for more than 160 Hours: No

Contribution to Project:

Contributed crystal structure refinements of the three new minerals and determined polytype of wagnerite.

Name: Medenbach, Olaf

Worked for more than 160 Hours: No

Contribution to Project:

Contributed optical properties and X-ray powder patterns of the three new minerals after extracting grains of the minerals from thin sections.

Name: Kawakami, Tetsuo

Worked for more than 160 Hours: No

Contribution to Project:

Tetsuo Kawakami, a professor at Kyoto University, invited me to collaborate with him on a study of kornerupine from Akarui Point near Syowa Station, Antarctica.

Name: Shearer, Charles

Worked for more than 160 Hours: No

Contribution to Project:

Charles Shearer and Paul Burger are carrying out ion microprobe analyses of kornerupine and other minerals for Li, Be and B at the University of New Mexico.

Name: Burger, Paul

Worked for more than 160 Hours: No

Contribution to Project:

Charles Shearer and Paul Burger are carrying out ion microprobe analyses of kornerupine and other minerals for Li, Be and B at the University of New Mexico.

Name: Graetsch, Heribert

Worked for more than 160 Hours: No

Contribution to Project:

Co-author on a paper on boralsilite and 'boron-mullite'

Name: Buick, Ian

Worked for more than 160 Hours: No

Contribution to Project:

Co-author on projects on boralsilite and 'boron-mullite', including discovery of a new mineral

Name: Maas, Roland Worked for more than 160 Hours: No **Contribution to Project:** Contributed Sm-Nd analyses of 6 samples from the Larsemann Hills Name: Gerbi, Christopher Worked for more than 160 Hours: No **Contribution to Project:** Gerbi is co-author on the manuscript reporting chopinite in meteorite Graves Nunatak 959209 Name: Beane, Rachel Worked for more than 160 Hours: No **Contribution to Project:** Beane is co-author on the manuscript reporting chopinite in meteorite Graves Nunatak 959209 Name: Floss, Christine Worked for more than 160 Hours: No **Contribution to Project:** Floss is co-author on the manuscript reporting chopinite in meteorite Graves Nunatak 959209 Name: Wilson, Christopher Worked for more than 160 Hours: No **Contribution to Project:** Co-authored a paper on monazite and feldspar from the Napier Complex, Antarctica

Research Experience for Undergraduates

Organizational Partners

Australian Antarctic Division

The Australian Antarctic Division, which is based in Hobart, provided all the logistics support for the 2003-2004 fieldwork in the Larsemann Hills, Prydz Bay, about 100 km southwest of Australia's Davis Station, viz. transportation by ship from Hobart to Davis, transportation by helicopter from Davis to the field campsite, camping supplies and provisions, and containers for returning rock samples to Hobart.

In addition, Henk Brolsma of the Australian Antarctic Division and Gayle Young of Geosciences Australia (KSO3) collaborated with C. J. Carson in preparing a revised digital geological map of the Larsemann Hills.

Geosciences Australia

Gayle Young of Geosciences Australia (KSO3) collaborated with C. J. Carson in preparing a revised digital geological map of the Larsemann Hills.

Other Collaborators or Contacts

Henk Brolsma Gayle Young Fabrice Brunet Christian Chopin Yoichi Motoyoshi

Activities and Findings

Fieldwork was carried out in the Larsemann Hills, Prydz Bay, Antarctica, about 100 km southwest of Australia's Davis Station. Deployment was 24th Nov 2003, and retrieval 23rd Jan 04 by helicopter from Davis. Base camp was set up on Stornes Peninsula at 69degrees 24.207'S, 76degrees 06.155'E for the duration of the summer. All transport during the field season was via foot, the majority of work being conducted on Stornes Peninsula, but several other locations were visited specifically to collect borosilicate minerals: Seal Cove (near the former Law Base on Broknes Peninsula), Fisher Island, Brattnevet, an unnamed island between Breadloaf and Solomon Islands, McLeod Island, Sandercock Island, and McCarthy Point south of Stornes. These additional sites were visited early in the season when sea ice was favourable for passage.

About 550 kg of clean rock samples were collected for the laboratory phase of the project and the bedrock geology of Stornes Peninsula was remapped. The mapping component has resulted in a new geological map of the Larsemann Hills that was published in 2007 by Geoscience Australia.

Over 370 thin sections of the rock specimens have been prepared. Most have been studied optically and electron microprobe chemical analysis has been carried on over 20 selected sections from the Larsemann Hills. Martin Yates has developed several protocols for measuring boron with U Maine's new Cameca SX 100 electron microprobe. One protocol was successfully applied to analyzing the borosilicates boralsilite, grandidierite, werdingite and dumortierite collected in the Larsemann Hills, and synthetic and natural 'boron-mullite', the latter a new mineral, boromullite, from Mount Stafford, Australia. He developed a second protocol for the iron analogue of werdingite from the Rogaland area, SW Norway. He has also developed protocols for analyzing phosphates and can now obtain satisfactory analyses not only of apatite, wagnerite, monazite and xenotime, four important accessory minerals in Larsemann Hills. Chopinite was subsequently discovered in a meteorite, GRA92509, one of the stones collected in Antarctica. Six papers reporting the new minerals, new data on boralsilite and the electron microprobe methodology have been published or are in press.

One of the Ph.D. students I am advising, Jeffrey Marsh, discovered a new yttrium-rich garnet in his thesis area in Parry Sound, Ontario, Canada. I assisted Jeff in characterizing the new garnet, which was approved by the Commission on New Minerals, Nomenclature and Classification, as menzerite-(Y). Marty Yates developed a protocol for analyzing this garnet, which contains a challenging combination of heavy rare-earth elements and usual elements found in ferromagnesian aluminosilicates.

Fifty-one paragneiss and orthogneiss samples have been analyzed at the Australian National University under the direction of A.G. Christy. Christy has obtained 9 major elements and 56 trace elements, including Li, Be, B and the rare earths. A preliminary report was presented at Goldschmidt 2006 in Melbourne, Australia.

Crystal structures have been refined for five new minerals, stornesite-(Y), tassieite, chopinite, boromullite and menzerite-(Y) by Thomas Armbruster. Olaf Medenbach obtained optical properties and X-ray powder patterns on the first four; Hans-Juergen Bernhardt measured the refractive index for menzerite-(Y).

Chris Carson obtained SHRIMP U-Pb and LA-ICPMS Hf isotope data on zircons from three samples and Roland Maas obtained Sm-Nd isotope data on six samples from the Larsemann Hills. An extended abstract reporting a portion of the dataset was published in the Proceedings of the 10th International Symposium on Antarctic Earth Sciences and a second abstract reporting the full dataset was presented at the 33rd International Geological Congress, Oslo, Norway. A manuscript is in preparation

Undergraduate student John Harris carried out his project supported by a REU supplement. His research addressed three questions concerning the metamorphic evolution of a gneissic complex in the Larsemann Hills, Prydz Bay, East Antarctica: (1) dating monazite in quartzite associated with the boron-enriched metasediments and in basement gneisses from which zircons have been separated for analysis with the SHRIMP; (2) the relative ages of granulite-facies metamorphism, phosphate segregations interpreted to be restitic and anatectic pegmatites that contain a diverse suite of borosilicate minerals; and (3) temperature of monazite crystallization. Yttrium content of monazite coexisting with xenotime is being used as a thermometer to estimate temperature. The results give estimates on how temperature varied with time. Harris presented the results in a poster at the Northeast Meeting of the Geological Society of America in March, 2008. In preparation for the project, John did an independent study course during the spring semester, 2007. He read several papers for background and studied thin sections containing the monazite and xenotime.

Eva Wadoski successfully defended her MSc thesis 'Microstructural and Chemical Study of Borosilicate Minerals in Pegmatites from the Larsemann Hills, Prydz Bay, East Antarctica'. Her research consists of detailed microstructural study and analysis with the electron microprobe of the borosilicate minerals with an emphasis on the tourmaline group, dumortierite and prismatine in order to identify the succession of borosilicate mineral assemblages and infer changes in the pressure-temperature-fluid activity conditions responsible for the changes in mineral chemistry and assemblage. Her results to date show a wide range in composition in both tourmaline-group minerals and dumortierite, that is, tourmaline-group minerals are highly zoned and at least two generations of tourmaline and dumortierite are present, whereas prismatine is

much less abundant. Tourmaline-group minerals are solid solutions between schorl, dravite and foitite. Second generation dumortierite contains distinctly more arsenic and niobium than first-generation dumortierite and fills fractures cutting the latter. The results of her thesis provide information on crystallization history of borosilicate-bearing pegmatites in the Larsemann Hills. Initial crystallization could have been relatively rapid due to chemical quenching, which was followed by more protracted episodes of complex replacement and secondary growth of minerals. The crystallization of the pegmatites occurred along a retrograde decompression P-T path similar to that of the host rocks.

Eva wrote abstracts and prepared posters for presentation of her research at the annual meeting of the Northeast Section of Geological Society of America in March, 2009 (Portland, Maine), the Joint Assembly AGU-MAC-GAC in May, 2009 (Toronto, Ontario) and the 'Granulites & Granulites 2009' conference in July, 2009 (Hrub? Sk?la Chateau, Czech Republic).

Findings:

1) BOROSILICATE MINERALS: The abstracts of my two published papers and of Eva Wadoski's Master's thesis:

Title: Boralsilite, Al16B6Si2O37, and 'boron-mullite': compositional variations and associated phases in experiment and nature

Authors: Edward S. Grew, Heribert A. Graetsch, Birgit P?ter, Martin G. Yates, Ian Buick, Heinz-J?rgen Bernhardt, Werner Schreyer, G?nter Werding, Christopher J. Carson, Geoffrey L. Clarke

Journal: American Mineralogist, 93, 283-299 (2008)

Abstract: Boralsilite, the only natural anhydrous ternary B2O3-Al2O3-SiO2 (BAS) phase, has been synthesized from BASH gels with Al/Si ratios of 8:1 and 4:1 but variable B2O3 and H2O contents at 700-800?C, 1-4 kbar, close to the conditions estimated for natural boralsilite $(600-700 \ ?C, 3-4 \ kbar)$. Rietveld refinement gives monoclinic symmetry, C2/m, a = 14.797(1), b = 5.5800(3), c = 15.095(2)?, β 91.750(4)?, V = 1245.8(2)?3; B replaces 14% of the Si at the Si site and Si or Al replaces ca. 12% of the B at the tetrahedral B2 site. A relatively well ordered boralsilite was also synthesized at 450?C, 10 kbar with dumortierite and the OH analog of jeremejevite. An orthorhombic phase ('boron-mullite') synthesized at 750 ?C, 2 kbar has mullite-like cell parameters a = 7.505(1), b = 7.640(2), c = 2.8330(4) ?, V = 162.44(6) ?3; 'boron-mullite' also accompanied disordered boralsilite at 750-800?C, 1-2 kbar. A possible natural analog of 'boron-mullite' is replacing the Fe-dominant analog of werdingite in B-rich metapelites at Mount Stafford, central Australia; its composition extends from close to stoichiometric Al2SiO5 to Al2.06B0.26Si0.76O5, i.e., almost halfway to Al5BO9. Boralsilite is a minor constituent of pegmatites cutting granulite-facies rocks in the Larsemann Hills, Prydz Bay, East Antarctica, and at Almgotheii, Rogaland, Norway. Electron microprobe analyses (including B) gave two distinct types: (1) a limited solid solution in which Si varies inversely with B over a narrow range, and (2) a more extensive solid solution containing up to 30% (Mg,Fe)2Al14B4Si4O37 (werdingite). Boralsilite in the Larsemann Hills is commonly associated with graphic tourmaline-quartz intergrowths, which could be the products of rapid growth due to oversaturation, leaving a residual melt thoroughly depleted in Fe and Mg, but not in Al and B. The combination of a B-rich source and relatively low water content, together with limited fractionation, resulted in an unusual buildup of B, but not of Li, Be and other elements normally concentrated in pegmatites. The resulting conditions are favorable in the late stages of pegmatite crystallization for precipitation of boralsilite, werdingite and grandidierite instead of elbaite and B minerals characteristic of the later stages in more fractionated pegmatites.

Title: Boromullite, Al9BSi2O19, a new mineral from granulite-facies metapelites, Mount Stafford, central Australia: a natural analogue of a synthetic 'boron-mullite'

Authors: Ian S. Buick, Edward S. Grew, Thomas Armbruster, Olaf Medenbach, Martin G. Yates, Gray E. Bebout and Geoffrey L. Clarke

Journal: European Journal of Mineralogy, 20, 935-950 (2008)

Abstract: Boromullite is a new mineral corresponding to a 1:1 polysome composed of Al5BO9 and Al2SiO5 modules. Electron-microprobe analysis of the holotype prism is SiO2 19.01(1.12), TiO2 0.01(0.02), B2O3 6.52(0.75), Al2O3 74.10(0.95), MgO 0.07(0.03), CaO 0.00(0.02), MnO 0.01(0.04), FeO 0.40(0.08), Sum 100.12 wt.%, which gives Mg0.01Fe0.03Al8.88Si1.93B1.14O18.94 (normalised to 12 cations), ideally Al9BSi2O19. Overall, in the type specimen, it ranges in composition from Mg0.01Fe0.03Al8.72Si2.44B0.80O19.20 to Mg0.01Fe0.03Al9.22Si1.38B1.35O18.67. Single-crystal X-ray diffraction gives orthorhombic symmetry, Cmc21, a 5.7168(19) ?, b 15.023(5) ?, c 7.675(3) ?, V 659.2(7) ?3, calculated density 3.081 g/cm3, Z = 2. The refined structure model indicates two superimposed modules present in equal proportions in the holotype prism. Module 1 has the topology and stoichiometry of sillimanite and carries all the Si, whereas module 2 is a type of mullite defect structure in which Si is replaced by B in triangular coordination and by Al in tetrahedral coordination, i.e., Al5BO9. The strongest lines in the powder pattern [d in ?, (Imeas.), (hkl)] are 5.37(50) (021), 3.38(100) (022, 041), 2.67 (60) (042), 2.51(60) (221, 023), 2.19(80) (222), 2.11(50) (043), 1.512(80) (263). Boromullite is colourless and transparent, biaxial (+), nx 1.627(1), ny 1.634(1), nz 1.649(1) (589 nm). 2Vz (meas) = 57(2)◦, 2Vz (calc) = 69(12)◦. In the type specimen boromullite tends to form prisms or bundles of

prisms up to 0.4 mm long, typically as fringes or overgrowths on aggregates of sillimanite or as narrow overgrowths around embayed werdingite prisms. In other samples boromullite and sillimanite are intergrown on a fine scale (from < 1 μm to > 10 μm). Sekaninaite-cordierite, potassium feldspar, biotite, werdingite and its Fe-dominant analogue, hercynite, and ilmenite are other commonly associated minerals, whereas ominelite-grandidierite, plagioclase, andalusite, and tourmaline are much subordinate. The most widespread accessories are monazite-(Ce), an apatite-group mineral and zircon. Boromullite formed during anatexis of B-rich pelitic rocks under granulite facies conditions (810 ◦C ≈ T ≥ 775−785 ◦C, P = 3.3?4 kbar), possibly due to a shift in bulk composition to lower SiO2 and B2O3 contents associated with melt extraction. The assemblage boromullite + cordierite + sillimanite lies at lower SiO2 and B2O3 leads to the replacement of werdingite by boromullite, consistent with textural relations.

Title: Microstructural and Chemical Study of Borosilicate Minerals in Pegmatites from the Larsemann Hills, Prydz Bay, East Antarctica

Author Eva Wadoski

Source: Master's Thesis, University of Maine (2009)

Abstract: Pegmatites are present in many metamorphic complexes. Their distinctive mineral assemblages, especially when rich in boron, provide a distinct perspective into the pressure-temperature-chemical environment. Granulite-facies metasedimentary gneisses and associated anatectic pegmatites in Larsemann Hills, Antarctica are unusually enriched in B, and thus, provide a unique opportunity for the petrologic application of boron minerals. The seven pegmatites on which the thesis is based contain the borosilicate minerals prismatine, werdingite, boralsilite, grandidierite, dumortierite and tourmaline-group minerals. Six belong to the folded and discordant D2 and D3 generations and one belongs to the discordant and planar D4 generation. Research for the thesis included microstructural observations and chemical analyses with the electron microprobe analyses with an emphasis on tourmaline-group minerals. The first minerals to form in the D2 and D3 pegmatites were tourmaline in a graphic intergrowth with quartz, prismatine, plagioclase, K-feldspar and sillimanite. Werdingite, grandidierite and boralsilite soon followed. After a deformation event that fractured and allowed fluid infiltration secondary mineral growth occurred. This included tourmaline prisms, dumortierite, and andalusite. Tourmaline compositions evolve as crystallization proceeded in both the D2 and D3 and the D4 pegmatites resulting in an increase in X-site vacancy, a decrease in Ti content and a decrease in F at the W-site, changes consistent with decreasing temperatures. The D2-D3 pegmatites were emplaced at close to peak conditions, that is, the early-formed minerals could have crystallized at temperatures as high as 750-800 ?C, P ~ 5 kbar, whereas the D4 pegmatite could have been emplaced relatively soon after. The D2-D3 and D4 pegmatites experienced the same evolution after initial crystallization, and crystallization continued until temperatures were below 600 ?C, P ~ 3 kbar. The Larsemann Hills pegmatites show evidence that initial crystallization could have been relatively rapid due to chemical quenching, which was followed by more protracted episodes of complex replacement and secondary growth of minerals. The crystallization of the pegmatites occurred along a retrograde decompression P-T path similar to that of the host rocks.

Nine phosphate minerals have been found in the Larsemann Hills. The most widespread are fluorapatite, monazite-(Ce), xenotime-(Y) and wagnerite (two polytypes have been found: 5b and 7b). The other 5 phosphates are rare constituents of apatite and wagnerite segregations. Two are known species: isokite, CaMgPO4F, and melonjosephite (Ca(Mg,Fe2+)Fe3+(PO4)2(OH). Three are new species: (1) stornesite-(Y), (Y, Ca)Na6(Ca,Na)8(Mg,Fe)43(PO4)36; (2) tassieite, NaCa2(Mg2)(Fe3+Mg)sum2(Fe2+)2(PO4)6 .2H2O; and (3) chopinite (Mg,Fe)3(PO4)2. In collaboration with Olaf Medenbach (Ruhr-Universitaet Bochum) and Thomas Armbruster (University of Bern), I have characterized the 3 new minerals, which have been approved by the Commission on New Minerals and Mineral Names, International Mineralogical Association (IMA). In addition, chopinite has been found in a meteorite. Descriptions of all three minerals have been published, including the meteoritic chopinite.

Title: Stornesite-(Y), (Y, Ca)vac2Na6(Ca,Na)8(Mg,Fe)43(PO4)36, the first terrestrial Mg-dominant member of the fillowite group, from granulite-facies paragneiss in the Larsemann Hills, Prydz Bay, East Antarctica

Authors: E. S. Grew, T. Armbruster, O. Medenbach, M.G. Yates, and C. J. Carson

Journal: American Mineralogist, 91, 1412-1424 (2006)

Stornesite-(Y), end-member formula Yvac2Na6(Ca5Na3)Mg43(PO4)36, is a new Y-dominant analogue of the meteoritic mineral chladniite. A representative electron microprobe analysis is SiO2 0.02, P2O5 48.11, SO3 0.05, MgO 23.16, MnO 0.24, FeO 15.55, Na2O 5.04, CaO 5.66, SrO 0.02, Y2O3 1.43, Yb2O3 0.24, UO2 0.01, Sum 99.53 wt%, which gives

Y0.68Yb0.06Na8.69Ca5.40Sr0.01Mg30.71Fe11.56Mn0.18Si0.02S0.04P36.22O144. Overall, Y + rare earth elements range from 0.542 to 0.985, and atomic Mg/(Mg + Fe) ratio, from 0.684 to 0.749. Single-crystal X-ray diffraction gives trigonal symmetry, R-3, a 14.9628(27) ?, c 42.756(11) ?, V 8290(4) ?3, calculated density 3.196 g/cm3, Z = 3. The mineral is isostructural with synthetic chladniite, but the (0, 0, 0) site is

dominantly occupied by Y instead of Ca. Bond lengths are considerably shorter than for Ca sites; Y and Yb are fully ordered at this site, which is our rationale for recognizing stornesite-(Y) as a distinct species. The strongest lines in the powder pattern [d in ?, (I), (hkl)] are 3.67 (40) (0 3 6, 3 0 6), 3.52 (40) (0 0 12, 3 1 2, 1 3 -2), 2.94 (60) (0 1 14, 3 2 ?2, 2 3 2), 2.73 (100) (2 0 14, 0 3 12, 3 0 12), 1.84 (40) (1 5 14, 5 1 ?14, 0 6 12, 6 0 12). The mineral is optically uniaxial +, ω 1.6215(10), ε 1.6250(10) at 589 nm. Its color is pale yellow in standard thin sections. Stornesite-(Y) is found as inclusions in fluorapatite nodules in two paragneiss specimens from Johnston Fjord, Stornes Peninsula (whence the name) and in a third from Brattnevet, Larsemann Hills. Associated minerals are wagnerite, xenotime-(Y), monazite-(Ce), P-bearing K-feldspar, biotite, sillimanite, quartz and pyrite; it is commonly altered to rusty material and secondary phosphates. Grains are anhedral, subhedral or locally euhedral with hexagonal or rhombic outlines; maximum dimensions are 1 ? 0.25 mm. It is inferred to have formed at 800 ? 860 ?C, 6 ? 7 kbar by reaction of biotite with an anatectic melt locally enriched in P by interaction with fluorapatite.

Title: Tassieite, (Na,vac)Ca2(Mg,Fe2+,Fe3+)2(Fe3+,Mg)2(Fe2+,Mg)2(PO4)6.2H2O, a new hydrothermal wicksite-group mineral in fluorapatite nodules from granulite-facies paragneiss in the Larsemann Hills, Prydz Bay, East Antarctica.

Authors: E. S. Grew, T. Armbruster, O. Medenbach, M.G. Yates, and C. J. Carson

Journal: The Canadian Mineralogist, 45, 293-305 (2007)

Abstract: Tassieite (IMA 2005-051), with an end-member formula NaCa2(Mg2)(Fe3+Mg)Σ2(Fe2+)2(PO4)6.2H2O, is a new Mg-dominant phosphate of the wicksite group. A representative composition derived with an electron microprobe is SiO2 0.01, P2O5 44.54, SO3 0.06, MgO 10.95, MnO 0.38, FeO 25.40 (measured), FeO 14.93 (calculated), Fe2O3 11.63 (calculated); Na2O 1.96, CaO 11.56, SrO 0.02, Y2O3 0.26, Ce2O3 0.08, Yb2O3 0.13, UO2 0.04, F 0.04, H2O 3.78 (calculated), Sum 100.34 wt% (excluding F), which gives Na0.60Ca1.96Mg2.59Mn0.05Fe2+1.98Fe3+1.39Y0.02Yb0.01S0.01P5.98O24.2H2O for 14 cations excluding Na and 24 O; the Fe2+:Fe3+ ratio calculated from stoichiometry and H2O from ideal content. Overall, analyses of all grains gave Na in the range 0.46? 0.97 atoms per formula unit, and atomic XMg = Mg/(Mg + Fe2+) ratio in the range 0.45 ? 0.77 (for tassieite: XMg > 0.5). Single-crystal X-ray diffraction gives orthorhombic symmetry, Pbca, a 12.4595(7) ?, b 11.5955(16) ?, c 12.7504(7) ?, V 1842.1(3) ?3, calculated density 3.45 g/cm3, Z = 4. The mineral is isostructural with wicksite, but with the M1 site dominated by Mg. Mg is the dominant divalent octahedral cation in the structure, which is our rationale for recognizing tassieite as a distinct species. Indexed lines in the powder pattern [d in ?, (I), (hkl)] are 6.40 (5) (0 0 2), 3.497 (40) (3 0 2), 3.000 (80) (1 1 4), 2.895 (80) (0 4 0), 2.735 (100) (4 2 0) (4 1 2), 2.545 (10) (2 2 4) and 2.091 (30) (1 0 6). The mineral is optically biaxial +, α 1.712(2), β 1.713(2), γ 1.722(2) (589 nm). 2V (meas.) = 46(1)˚, 2V (calc.) = 37˚. Pleochroism: X dark blue, Y blue, Z light brown; absorption ? X > Y >> Z. Tassieite occurs in bands of secondary fluorapatite or in pseudomorphs of stornesite-(Y) within a fluorapatite nodule in a paragneiss specimen from between Johnston Fjord and Tassie Tarn (whence the name), Stornes Peninsula, Larsemann Hills. Associated minerals are stornesite-(Y), wagnerite, xenotime-(Y), monazite-(Ce), pyrite, m?lonjosephite and several, unidentified Ca ? Na ? Mg ? Fe phosphates. Larger tassieite grains (0.5 ? 1 mm) show crystal faces and cleavage traces, but most grains (up to 0.3 mm) are platy and anhedral or irregular in outline. It is inferred to have formed hydrothermally from the alteration of stornesite-(Y) and wagnerite.

Title: Chopinite, [(Mg,Fe)3vac](PO4)2, a new mineral isostructural with sarcopside, from a fluorapatite segregation in granulite-facies paragneiss, Larsemann Hills, Prydz Bay, East Antarctica

Authors: E. S. Grew, T. Armbruster, O. Medenbach, M.G. Yates, and C. J. Carson

Journal: European Journal of Mineralogy, 19, 229-245 (2007)

Abstract: Chopinite, the Mg-dominant analogue of sarcopside, is a new mineral corresponding to synthetic Mg3(PO4)2-II, a high-pressure polymorph of the meteoritic mineral farringtonite. A representative electron-microprobe analysis is SiO2 0.32, P2O5 47.32, Al2O3 0.05, MgO 30.35, MnO 0.15, FeO 20.99, CaO 0.35, F 0.02, Cl 0.01, Sum 99.54 wt%, which gives Ca0.02Mg2.20Fe0.86Mn0.01Si0.02P1.95O8. Single-crystal X-ray diffraction gives monoclinic symmetry, P21/c, a = 5.9305(7)?, b = 4.7583(6)?, c = 10.2566(10)?, b = 90.663(9)?, V 289.41(6) ?3, calculated density 3.34 g/cm3, Z = 2. Chopinite is of the olivine structure type, but with ordered vacancies and strongly distorted octahedra due to the valence 5+ for P, which results in marked ordering of Mg at M2, whereas Fe2+ concentrates at M1, most likely because of its axial symmetry. The strongest lines in the powder pattern [d in ?, (Icalc), (hkl)] are 5.92 (42) (100), 3.84(100) (102), 3.48(52) (11-1, 012, 111), 2.51(72) (11-3, 113), 2.44 (73) (21-1, 211). Chopinite is colorless and transparent, biaxial (?), α 1.595(2), β 1.648(2), γ 1.656(2) (589 nm). 2Vx (meas.) = 40(2) ˚, 2Vx (calc.) = 41 ˚; X // b, Z ^ a ~ 55 ˚. Chopinite is found as four inclusions isolated in a fluorapatite segregation in a quartz mass in a paragneiss from Brattnevet, Larsemann Hills, East Antarctica. Grains are mostly anhedral and range from 0.1 ? 0.3 mm to 0.2 ? 0.6 mm in size. Minerals present in the chopinite-bearing specimen include wagnerite-Ma5bc, xenotime-(Y), stornesite-(Y), P-bearing K-feldspar and plagioclase, Ti-rich biotite, sillimanite, orthopyroxene, sapphirine, hercynite, and corundum. It is inferred to have formed as a result of high melt P concentrations by reaction of biotite with an anatectic melt in which P/Ca ratio exceeded that buffered by apatite saturation due to the very slow diffusion of P relative to Ca in anatectic melt.

Title: Chopinite-sarcopside solid solution, [(Mg,Fe)3vac](PO4)2, in GRA95209, a transitional acapulcoite: Implications for phosphate genesis in meteorites.

Authors: E. S. Grew, M. G. Yates, R. J. Beane, C. Floss and C. Gerbi

Journal: American Mineralogist, 95, in press (2010)

Abstract: Orthophosphate, (Mg,Fe,Mn)3(PO4)2 with XMg = Mg/(Mg+Fe) = 0.089 and Mn/Fe = 0.05-0.3 and chladniite-johnsomervilleite, MnNa8(Ca4Na4)(Mg,Fe,Mn)43(PO4)36 with XMg = 0.44?0.81 and Mn/Fe = 0.3-0.8, are minor constituents of meteorite Graves Nunataks (GRA) 95209, a transitional acapulcoite consisting mostly of forsterite (Fa7), and enstatite (Wo3Fs7-8) with subordinate clinopyroxene (Wo41-45Fs4-6) and plagioclase (Or1-2An10-19), and cut by Fe,Ni metal veins. Electron backscatter diffraction patterns and maps, together with chemical analyses and Fe-Mg-Mn distribution among phosphates, confirm identification of the orthophosphate as sarcopside, chopinite and farringtonite; no graftonite was found. Phosphates are found as (1) narrow rims between metal and forsterite or orthopyroxene, (2) aggregates having the same outline as metal and (3) inclusions and stringers in metal, including a ring around a graphite rosette. Electron microprobe analyses of sarcopside/chopinite?johnsomervilleite/chladniite pairs give a regular Fe-Mg distribution with KD = (Mg/Fe)Src/Chp/(Mg/Fe)Jhn/Cld = 0.584 consistent with terrestrial sarcopside-johnsomervilleite pairs, whereas analyses of farringtonite?chladniite pairs give KD = 1.51, but the Mg-Fe distribution is less regular. Textural relations suggest that Fe-Mn sarcopside originally formed by oxidation of P in metal and replacement of the metal and, through interaction with silicates, was converted to magnesian sarcopside-chopinite and farringtonite, i.e., the silicate matrix acted as a reservoir of Mg that could be exchanged with Fe and Mn in the sarcopside. Using the farringtonite-chopinite univariant curve determined in hydrothermal experiments by F. Brunet and others, isopleths calculated for the most magnesian chopinite in GRA 95209, XMg = 0.65, give 4?7 kbar at 500?1100?C, pressures far too high for the acapulcoite-lodranite parent body. Two scenarios could explain the discrepancy: (1) chopinite and magnesian sarcopside persisted metastably into the farringtonite stability field as Mg-Fe exchange progressed and the source volume for GRA95209 cooled; (2) a very mild shock event was intense enough to convert Fe-rich farringtonite (XFe = 0.4-0.6) to magnesian sarcopside and chopinite, but not enough to deform olivine in the source volume. Whether metastability could have played a role in chopinite formation would best be answered by experiments on the Mg3(PO4)2 - Fe3(PO4)2 system under anhydrous conditions. If the transformation were found to be as kinetically fast as in the hydrothermal experiments, then shock would become the more plausible explanation for the presence of chopinite in this meteorite

(3) GEOCHEMISTRY

The 51 analyzed rocks include 3 tourmaline-quartz granulites ('meta-tourmalinites'), 6 borosilicate-rich sillimanite gneisses, 13 biotite gneisses that host prismatine-bearing segregations, 7 metapelites with little or no borosilicate, 3 calcic granulites, 3 rocks enriched in Fe oxides (Fe 40-60 wt% as Fe2O3), 5 quartzofeldspathic gneisses, and 11 miscellaneous rocks that include quartz-rich granulites, prismatine-feldspar granulites, and rocks having pelitic affinities. The biotite gneisses are aluminous (Al/(K+Na+2Ca) > 1), but with one exception K/(K+Na) < 0.5; metapelites have K/(K+Na) > 0.5. Most of the rocks are enriched in light rare earths with negative Eu anomalies, but numerous exceptions suggest a complex origin for these rocks. My presentation for origin of these rocks was presented at the Goldschmidt Conference in Melbourne, Australia, last August. The text (figure not included) of the abstract is:

Title: A Boron-Enriched Province in Granulite-facies rocks, Larsemann Hills, Prydz Bay, Antarctica

Authors: E.S. Grew, A.G. Christy and C.J. Carson

Proceedings volume: Geochimica et Cosmochimica Acta, 70, Issue 18 Supplement, A217 (2006)

Paragneisses containing borosilicates are found over a 15 km stretch in the Larsemann Hills. B contents reach 11000 ppm, well above the 0.2-16 ppm B in associated metapelites containing Crd, Grt, Sil and/or Hc and the 5 ppm B characteristic of the granulite-facies [1]. Richest in B are massive tourmaline quartzites and well-lineated borosilicate-sillimanite gneisses, which are locally blue-green in colour from abundant, aligned grandidierite prisms. The most widespread B-rich rocks are biotite-plagioclase gneisses containing segregations of cm-sized prismatine and granular tourmaline in cordierite or feldspar. A few B-rich rocks are enriched in P, but most P-enriched rocks, e.g., apatitic quartz granulites (0.6-1.4 wt% P2O5) are not enriched in B. Prismatine-plagioclase gneiss, calcic rocks and magnetite rich layers occur locally. Paragneiss Li contents commonly exceed the 30 ppm maximum found in most granulites. Tourmaline quartzites, most biotite gneisses and metapelites are LREE enriched and show marked negative Eu anomalies, whereas prismatine-plagioclase gneisses and borosilicate-sillimanite gneisses show positive Eu anomalies or no anomaly (see Figure). Possible precursors are clastic and volcanogenic rocks altered by submarine hydrothermal processes analogous to those proposed for tourmalinite formation at Broken Hill [2]. Alternatively, epigenetic B metasomatism related to a Fe oxide-Cu-Au hydrothermal system could have played a major role.

Reference

[1] Leeman, W.P., Sisson, V.B. (1996) Rev. Mineral., 33, 645-708. [2] Slack, J.F., Palmer, M.R., Stevens, B.P.J., Barnes, R.G. (1993). Econ. Geol., 88, 505-541

Dr. Tetsuo Kawakami of Kyoto University invited me to collaborate with him, Yoichi Motoyoshi and others on a study of kornerupine and associated minerals from Akarui Point near Syowa Station, Antarctica. We obtained electron and ion microprobe data on these minerals, as well as information geologic and petrologic context. Kawakami has presented two papers at meetings and the paper reporting the occurrence has been published. The study adds perspective to my own work on borosilicate parageneses from the Larsemann Hills.

Title: Kornerupine sensu stricto associated with mafic and ultramafic rocks in the L?tzow-Holm Complex at Akarui Point, East Antarctica: what is the source of boron?

Authors: T. Kawakami, E. S. Grew, Y. Motoyoshi, C. K. Shearer, T. Ikeda, P. V. Burger and I. Kusachi

Proceedings volume: M. Satish-Kumar, Y. Motoyoshi, Y. Osanai, Y. Hiroi and K. Shiraishi (eds) 'Geodynamic evolution of East Antarctica: A key to the East-West Gondwana connection', Geological Society of London Special Publication, 308, 351-375 (2008)

Abstract: Kornerupine, (vac, Mg, Fe)(Al, Mg, Fe)9(Si, Al, B)5O21(OH, F), is known from only five mafic or ultramafic settings worldwide (of the >70 localities overall). We report a sixth occurrence from Akarui Point in the Lutzow-Holm Complex, East Antarctica, where two ruby corundum (0.22?0.34 wt% Cr2O3)?plagioclase lenses are found at the same structural level as boudinaged ultrabasic rocks in hornblende gneiss and amphibolite. Ion microprobe analyses of kornerupine give 13?59 ppm Be, 181?302 ppm Li, and 5466?6812 ppm B, corresponding to 0.38?0.47 B per 21.5 O; associated sapphirine also contains B (588?889 ppm). Peak metamorphic conditions are estimated to be 770?790 oC and 7.7?9.8 kbar. Kornerupine encloses tourmaline and plagioclase, which suggests the prograde reaction tourmaline (1) + plagioclase (>An34) + sapphirine +/- spinel => kornerupine + corundum (ruby) + plagioclase (<An82)+(fluid or melt). Alternatively, kornerupine and tourmaline could have formed sequentially under nearly constant P?T conditions during the infiltration of fluid that was originally B-bearing, but then progressively lost Na (or gained Ca) and B through reaction with mafic rocks. Kornerupine later reacted with H2O?CO2 fluid in cracks at P?T conditions in the andalusite stability field: kornerupine + plagioclase + (Na, K, +/-Si in fluid) => tourmaline + biotite + corundum (sapphire)+/magnesite +/- and alusite + (Ca in fluid). Secondary tournaline differs from the included tournaline in containing less Ti and having a higher Na/(Na + Ca + K) ratio. There are two possible scenarios for introducing B into the lenses: (1) infiltration of boron-bearing aqueous fluids released by prograde breakdown of muscovite in associated metasedimentary rocks; (2) hydrothermal alteration of mafic and ultramafic rocks by seawater prior to peak metamorphism. The latter scenario is consistent with an earlier suggestion that Akarui Point could be part of an ophiolite complex developed between the Yamato?Belgica and Rayner complexes.

Title: Age of boron- and phosphorus-rich paragneisses and associated orthogneisses, Larsemann Hills: New constraints from SHRIMP U-Pb zircon geochronology.

Authors: C. J. Carson, E. S. Grew, S. D. Boger, C. M. Fanning and A.G. Christy

Source: Antarctica; a keystone in a changing world; online proceedings for the Tenth International Symposium on Antarctic Earth Sciences. Open-File Report - U. S. Geological Survey, Report: OF 2007-1047, Extended Abstract 003, 2007

Summary: SHRIMP U-Pb detrital zircon geochronology of a phosphate-rich metaquartzite from the Larsemann Hills, southern Prydz Bay, suggests that the maximum constraint on deposition was latest Neoproterozoic, possibly as young as ca. 550 Ma. The metaquartzite, together with metapelite, metapsammite and boron-rich units, collectively the 'Brattstrand Paragneiss', were deposited on composite ca. 1125 Ma and ca. 940-990 Ma felsic orthogneiss basement, which was subsequently interleaved with the metasediments during ca. 515-530 Ma regional high-grade tectonism. The presence of ca. 550-870 Ma rims indicates detrital contribution from sources characteristic of the East African orogen and adjacent regions. The unusual boron and phosphate enrichment in the Neoproterozoic Brattstrand Paragneiss of the Larsemann Hills could have resulted from subseafloor alteration of clastic sediments related to an exhalative-synsedimentary hydrothermal system that mobilised boron from underlying non-marine evaporite borate, suggesting deposition of the Brattstrand Paragneiss in a deepening continental back-arc rift or basin.

Title: Granulite-facies rocks, Larsemann Hills, Prydz Bay, East Antarctica: new interpretations based on zircon U-Pb-Hf and whole rock Sm-Nd isotopes

Authors: C. J. Carson, E. S. Grew, R. Maas, C. M. Fanning, and G. Yaxley

Source: Proceedings, 33rd International Geological Congress 2008 Oslo, August 6-14, Abstract AAN01801L http://www.cprm.gov.br/33IGC/1319843.html.

Gneisses of the Larsemann Hills have been customarily divided into a basement igneous complex (S?strene Orthogneiss) and overlying metasediments (Brattstrand Paragneiss), with mappable units containing boron and phosphate minerals. To better constrain the depositional age and provenance of the Brattstrand Paragneiss, we obtained SHRIMP U-Pb and LA-ICPMS Hf zircon and whole-rock Sm-Nd data on (1) the Tassie Tarn Metaquartzite (TTM), a unit in the Brattstrand Paragneiss; (2) the S?strene Orthogneiss and (3) the Blundell Orthogneiss, a composite unit that may also represent basement, but we cannot exclude an intrusive origin into the Brattstrand Paragneiss on field relationships alone. The S?strene and Blundell Orthogneiss samples yield zircon emplacement ages of 1120? 10 Ma and 967? 17 Ma, respectively. Detrital igneous zircon cores from the TTM sample are dominantly 1100-1150 Ma, with scattered younger ages to ca. 956 Ma. Low Th/U metamorphic rims on the TTM zircons define a broad discordia array between ca. 530 Ma and ca. 900 Ma. Zircon Hf isotope signatures in the S?strene Blundell Orthogneiss samples, and in the ca. 1100-1150 Ma detrital zircon population within the TTM sample, are all similar (HfTDM 1.4 to 1.6 Ga, εHfi -5 to +5). A second detrital zircon population in the TTM sample with U-Pb ages between 1100-1800 Ma are characterised by significantly older HfTDM model ages (2.0-2.2 Ga). Whole rock Nd model ages (NdTDM) for 2 samples of TTM are near 2.0 Ga, with εNd956 near -6, whereas two samples of S?strene Orthogneiss have somewhat younger NdTDM model ages (ca. 1.7 Ga) with less evolved εNd1120 of ca. -0.5. Two samples of Blundell Orthogneiss have NdTDM model ages of 1.8-2.0 Ga (εNd967 = -3.0 and -5.9). Based on the new zircon data, the maximum constraint on deposition of the TTM, and by inference the Brattstrand Paragneiss sequence, is best represented by the youngest detrital igneous zircon cores at ca. 956 Ma. This maximum deposition age, given analytical uncertainties, does not preclude the possibility that the Brattstrand Paragneiss is older than the Blundell Orthogneiss. Sediments were metamorphosed at ca. 900 Ma and again at ca. 530 Ma, the regionally recognised granulite-facies event in southern Prydz Bay. Similarities between the dominant detrital zircon age population within the TTM and the igneous protolith age in S?strene Orthogneiss, and similar zircon-Hf isotopic signatures, suggest a major role of S?strene-type basement as a source of clastic detritus in the TTM. However, whole rock εNd values for TTM are lower than in the S?strene Orthogneiss, implying additional sedimentary contributions from low-εNd sources. Such sources may be represented in our TTM sample by the zircon subpopulation with older HfTDM model ages. The Blundell Orthogneiss apparently preserves Hf zircon and Nd whole rock isotopic signatures indicating derivation from partial melting or assimilation of both S?strene Orthogneiss and Brattstrand Paragneiss.

Title: Aureoles of Pb(II)-enriched feldspar around monazite in paragneiss and anatectic pods of the Napier Complex, Enderby Land, East Antarctica

Authors: Grew, E.S., Yates, M.G. and Wilson, C.J.L.

Journal: Contributions to Mineralogy and Petrology, 155, 363-378 (2008)

Abstract: Extraordinarily high Pb content in K-feldspar and plagioclase has been found contiguous to monazite in two occurrences in the ultrahigh-temperature Napier Complex of Antarctica. Monazite shows a variety of textures and compositions. In a garnet-sillimanite-orthopyroxene paragneiss at Mount Pardoe (Amundsen Bay), grains range 80-150 ?m across and are anhedral; two grains are Th- and Si-dominant. In pods that crystallized from anatectic melts at 2500 Ma at Zircon Point, Casey Bay, monazite grains range 0.05 mm ? 1 cm in length and are highly variable in texture. The coarsest grains (>0.7 cm) are skeletal and euhedral, whereas the smallest grains are anhedral and associated with fine- to medium-grained quartz, K-feldspar, plagioclase, garnet, sillimanite and rutile in aggregates that form interstitial veinlets interpreted to a second generation of anatexis during an event at 1100 Ma. The huttonite component (ThSiO4) reaches 30 mole% in the cores of the coarsest skeletal grains, whereas other grains, particularly smaller ones, show complex and irregular zoning in Th and U. The latter zoning is attributed to dissolution-reprecipitation, which also resulted in complete Pb loss during the 1100 Ma event.

In the paragneiss at Mount Pardoe, K-feldspar and myrmekitic plagioclase (An16) are found a 70-80 ?m band between monazite and orthopyroxene and contain up to 12.7 wt% and 2.7 wt% PbO, respectively, corresponding to 18.5 % and 3.4 % PbAl2Si2O8 component, respectively. Cathodoluminescence of both feldspars increases with distance from a nearby monazite grain and is not correlated with Pb content. Incorporation of Pb in K-feldspar and plagioclase could be a result of diffusion, even though the monazite adjacent to feldspar apparently lost little Pb, viz. Pb could have been transported by fluid from the Th-rich grains, which did lose Pb.

In contrast to the paragneiss, cathodoluminescence correlates with Pb content of K-feldspar in aureoles surrounding skeletal monazite grains 0.7-1 cm across in anatectic pods at Zircon Point. Pb content of K-feldspar decreases monotonically to near detection limits within several

millimetres of monazite grains; the greatest PbO concentration is attained in K-feldspar inliers and embayments in monazite, 8.8 wt%, corresponding to 11.7 % PbAl2Si2O8 component. Fine-grained quartz in the K-feldspar suggest that the mechanism for Pb incorporation involved breakdown of feldspar: Pb2+ + 2(K,Na)AlSi3O8 => PbAl2Si2O8 + 4SiO2 + 2(K,Na)+. The smooth decrease of Pb in the aureoles is not characteristic of dissolution-reprecipitation, which is characterized by abrupt changes of composition, and it seems more likely that Pb was incorporated in K-feldspar by diffusion at 1100 Ma.

We suggest a model whereby fluid introduced during the 1100 Ma flowed along grain boundaries and penetrated mineral grains. Temperatures were sufficiently high, i.e., 700 ?C, assuming burial in the mid-crust, for the fluid to induce localized melting of quartzofeldspathic matrix of the anatectic pods. Loss of radiogenic Pb was complete. Some penetration of K-feldspar by aqueous fluid is suggested by the presence of scattered galena specks and by rays of turbidity emanating from monazite. Aqueous fluid or water-rich granitic melt may have mediated the diffusion of Pb in feldspar, but it did not cause dissolution-reprecipitation. Although Pb was mobilized by aqueous fluid or water-rich granitic melt, it was not entirely flushed from the immediate vicinity of the monazite, but nearly half was incorporated in adjacent feldspar.

Fluid activity that could cause Pb loss in monazite does not always leave an obvious trace, i.e., hydrous minerals, such as sericite, are very sparse, and biotite is absent in the anatectic pods at Zircon Point. Nonetheless, electron microprobe dating of monazite from the pods could not detect the 2500 Ma age of original crystallization determined by isotopic dating.

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(6) A NEW YTTRIUM GARNET
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Title: Menzerite-(Y), a new garnet species, {(Y, REE)(Ca, Fe2+)2}[(Mg,Fe2+)(Fe3+,Al)](Si3)O12, end-member, {Y2Ca}[Mg2](Si3)O12, from a pyroxene granulite, Parry Sound, Ontario: A new carrier of yttrium and heavy rare-earth elements in metamorphic and igneous rocks

Authors: Grew, E. S., Marsh, J.H., Yates, M.G., Lazic, B., Armbruster, T., Locock, A., Bernhardt, H.-J. and Medenbach, O.

Source: Submitted to The Canadian Mineralogist.

Abstract: Menzerite-(Y) forms reddish-brown cores (n = 1.844) up to 75 ?m across rimmed, successively by euhedral almandine containing up to 1.8 wt% Y2O3 and moats of K-feldspar in a pyroxene-plagioclase granulite on Bonnet Island in the interior Parry Sound domain, Central Gneiss Belt, Grenville Orogenic Province, Canada. It is named after Georg Menzer (1897-1989), the German crystallographer who first solved the crystal structure of garnet. The mineral and mineral name have been approved by the Commission on New Minerals, Nomenclature and Classification, IMA (2009-050). Single crystal X-ray diffraction results yielded space group Ia-3d, a 11.9947(6) ? and showed that Mg occupies the octahedral site. Electron microprobe analysis of the grain richest in Y2O3 (16.93 wt%) gave the following formula normalized to 8 cations and 12 oxygen atoms:

{Y0.83Gd0.01Dy0.05Ho0.02Er0.07Tm0.01Yb0.06Lu0.02Ca1.37Fe2+0.49Mn0.07}[Mg0.55Fe2+0.42Fe3+0.58Al0.35V0.01Sc0.01Ti0.08](Si2.82A or $\{(Y, REE)(Ca, Fe2+)2\}[(Mg,Fe2+)(Fe3+,Al)](Si3)O12$. The dominance of divalent cations with Mg > Fe2+ at the octahedral site (in square brackets) is the primary criterion for distinguishing menzerite-(Y) from other garnet species; the menzerite-(Y) end-member is {Y2Ca}[Mg2](Si3)O12. The contacts of menzerite-(Y) with almandine are generally sharp and, in places, cuspate. Electron microprobe traverses and compositional maps of menzerite-(Y) grains show that, in going from cores to rims contiguous to almandine and K-feldspar, Y, Er, Mg and Ti increase, Al and Ca decrease, and Yb is constant. The Y content of the enclosing almandine increases from its outer rim inward toward the contact with menzerite-(Y) except for a small decrease right at the contact. Menzerite-(Y) is also in contact with allanite-(Ce), ilmenite and apatite-(CaF). It is interpreted to have equilibrated with ferrosilite (Fs56-61En38-43Wo1-3 plus ~1%MnSiO3), clinopyroxene (Fs27-29En29-30Wo41-43), quartz, oligoclase (An25-28), magnetite, and ilmenite in the absence of almandine on the prograde path, and subsequently dissolved incongruently in an anatectic melt to form almandine. Microtexturial relationships and thermodynamic modeling constrain menzerite-(Y) to have formed on the prograde path outside the stability field of almandine and melt, that is, most likely, at 7-8.5 kbar and T ~700-800 ?C, with subsequent break down during melting at P ~ 8.5-9.5 kbar and T ~800-850 ?C. The chemical compositions of euhedral almandine associated with menzerite-(Y), and of spessartine, from the Xihuashan granite in SE China, suggest that Y and HREE are incorporated as the components {Y2Ca}[Mg2](Si3)O12 (menzerite end-member) and {Y2Ca}[Fe2+2](Si3)O12 (Fe2+ analogue of menzerite) rather than as 'yttrogarnet' (YAG), {Y3}[Al2](Al3)O12. Pressure, mineral association, and bulk composition, all play a role in determining whether the menzerite-type or yttrogarnet-type substitution is favored. The critical factors controlling the prevalence of menzerite-type substitutions appear to have been the presence of clinopyroxene in the Bonnet Island granulite, and conditions of low pressure in the Xihuashan granite.

Training and Development:

I helped undergraduate student John Harris develop his proficiency at optical identification of minerals with the petrographic microscope. Martin Yates instructed Harris in the operation of the electron microprobe analyzer.

As chair of Eva Wadoski's thesis committee, I worked closely with her on her master's thesis research, e.g., helping her improve her proficiency at optical identification of minerals with the petrographic microscope, calculating formulae from chemical analyses of minerals and in plotting up her chemical data. Martin Yates instructed Wadoski in the operation of the electron microprobe analyzer, and she was able to operate this instrument independently. I was responsible for the approval of her oral defense and written thesis, listening to her rehearse her presentation and commenting on several drafts.

As a member of Meredith Petrie's thesis committee, I commented on one draft of her master's thesis.

As a member of Jeff Marsh's thesis committee, I have worked closely with Jeff on several aspects of his Ph.D. thesis research, including a review of one of his manuscripts, and collaboration on the description of the new garnet species, menzerite-(Y). I have been supervising his contribution to the collaboration. I spent several days in his field area in Parry Sound, Ontario, in order to collect more samples of the new mineral at the type locality and to gain insight on the petrologic context for its paragenesis.

Outreach Activities:

Two photomicrographs of borosilicates from my Larsemann Hills samples are featured in the exhibit 'Experience Antarctica: A century of Earth Science discoveries' permanently hosted at the LSU Museum of Natural Science, 119 Foster Hall, BR, LA 70808: see http://appl027.lsu.edu/MNSEducation/exp_antarctica/11_rocks.html.

Three photomicrographs of borosilicates and one of tassieite from my Larsemann Hills samples were submitted for posting in the NSF Multimedia Gallery.

On the occasion of my discovering three new minerals in the Larsemann Hills, I was interviewed by two U Maine student reporters and a staffer from the university. These interviews resulted in articles on my discoveries in the student newspaper The Maine Campus (10/29/2007) and in UMaine Today (January-February 2008 issue). An interview with Channel 7 evening news was aired in Bangor on October 24, 2007.

Journal Publications

Grew, E.S, Armbruster, T., Medenbach, O., Yates, M.G., Carson, C.J., "Stornesite-(Y), (Y, Ca)vac2Na6(Ca,Na)8(Mg,Fe)43(PO4)36, the first terrestrial Mg-dominant member of the fillowite group, from granulite-facies paragneiss in the Larsemann Hills, Prydz Bay, East Antarctica", American Mineralogist, p. 1412, vol. 91, (2006). Published,

Grew, E.S, Armbruster, T., Medenbach, O., Yates, M.G., Carson, C.J., "Tassieite, (Na,vac)Ca2(Mg,Fe2+,Fe3+)2(Fe3+,Mg)2(Fe2+,Mg)2(PO4)6(H2O)2, a hydrothermal wicksite-group mineral in fluorapatite nodules from granulite-facies paragneiss in the Larsemann Hills, Prydz Bay, East Antarctica", Canadian Mineralogist, p. 293, vol. 45, (2007). Published,

Grew, E.S., Yates, M.G. and Wilson, C.J.L., "Aureoles of Pb(II)-enriched feldspar around monazite in paragneiss and anatectic pods of the Napier Complex, Enderby Land, East Antarctica: The roles of dissolution-reprecipitation and diffusion", Contributions to Mineralogy and Petrology, p. 363, vol. 155, (2008). Published, DOI 10.1007/s00410-007-0247-z

Grew, E.S, Armbruster, T., Medenbach, O., Yates, M.G., Carson, C.J, "Chopinite, [(Mg,Fe)3vac](PO4)2, a new mineral isostructural with sarcopside, from a fluorapatite segregation in granulite-facies paragneiss, Larsemann Hills, Prydz Bay, East Antarctica.", European Journal of Mineralogy, p. 229, vol. 19, (2007). Published,

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Grew, E.S., Yates, M.G., Beane, R.J., Floss, C. and Gerbi, C., "Chopinite-sarcopside solid solution, [(Mg,Fe)3vacancy](PO4)2, in GRA95209, a transitional acapulcoite: Implications for phosphate genesis in meteorites", American Mineralogist, p., vol. 95, (2010). Accepted,

Belkin, H.E., MacDonald, R., Grew, E.S., "Chevkinite-group minerals from granulite-facies metamorphic rocks and associated pegmatites of East Antarctica and South India.", Mineralogical Magazine, p. 149, vol. 73, (2009). Published, 10.1180/minmag.2009.073.1.149

Books or Other One-time Publications

Kawakami, T., Grew, E.S., Motoyoshi, Y., Shearer, C. K., Ikeda, T., Burger, P.V. and Kusachi, I., "Kornerupine sensu stricto associated with mafic and ultramafic rocks in the L?tzow-Holm Complex at Akarui Point, East Antarctica: What is the source of boron?", (2008). Book, Published Editor(s): SATISH-KUMAR, M., MOTOYOSHI, Y., OSANAI, Y., HIROI, Y. & SHIRAISHI, K. Collection: Geodynamic evolution of East Antarctica: A key to the East-West Gondwana connection

Bibliography: Geological Society of London Special Publications 308

Wadoski, E.R., "Microstructural and Chemical Study of Borosilicate Minerals in Pegmatites from the Larsemann Hills, Prydz Bay, East Antarctica", (2009). Thesis, Accepted by the University as a Master's thesis Bibliography: A Thesis submitted in partial fulfillment of the requirements for the Degree of Master of Science (in Earth Sciences)

Web/Internet Site

URL(s):

http://gcmd.nasa.gov/getdif.htm?NSF-ANT02-28842

Description:

This is the metadata description (DIF) to the Antarctic Master Directory (AMD) describing my data and its location as required for the annual report.

Other Specific Products

Product Type:

map

Product Description:

Carson, C.J. and Grew, E.S. (2007) Geology of the Larsemann Hills Region, Antarctica. First Edition (1:25 000 scale map) Geoscience Australia, Canberra. This is compilation based on the 2003-2004 field season together with 3 earlier field seasons.

Sharing Information:

The map is being distributed by Geoscience Australia

Contributions

Contributions within Discipline:

A geologic map of the Larsemann Hills compiled by Chris Carson based on several seasons of fieldwork, including 2003-2004 supported by this project, was published jointly by Geoscience Australia and the Australian Antarctic Division, both of which funded preparation of the map.

Contributions to Other Disciplines:

My discovery of the phosphate chopinite, (Mg, Fe)3(PO4)2, in the Larsemann Hills led to my finding it in meteorite Graves Nunatak 95209, a transitional acapulcoite collected in Antarctica. Since chopinite requires several kilobars of pressure to be stabilized, its occurrence in a primitive achondrite poses a dilemma requiring a rethink on the origin of this particlar meteorite and on the relationships between silicates and phosphates in it. A manuscript reporting the occurrence has been accepted for publication in early 2010.

My work on boron and beryllium minerals, including research supported by this grant, led to my being invited by Robert Hazen to collaborate with him on his evolution of minerals project, which he launched with his 2008 paper 'Mineral Evolution' in American Mineralogist (v. 93, p. 1693-1720). This project is transforming mineralogical science by adding a new dimension to the study of minerals. I presented a poster with

Hazen 'Evolution of the minerals of beryllium, a quintessential crustal element' at the 2009 Annual Meeting of the Geological Society of America (Abstracts with Programs, 41(7), 99-100), which I plan to write up as a full-length paper for publication. I have also begun work on the evolution of boron minerals.

My work on boron minerals, including research supported by this grant, led to my being invited by Milan Nov?k to co-convene a session on boron at the 20th general meeting of the International Mineralogical Association in Budapest, Hungary, in August, 2010. The session I proposed was approved for inclusion in the program by the organizing committee: GM74 entitled 'Boron minerals, geochemistry and isotopes: What do they tell us about geologic processes?'

Contributions to Human Resource Development:

In addition to chairing Eva Wadoski's thesis committee, I served on the thesis committees of three students in the Department of Earth Sciences, University of Maine: Ph.D. candidates Jeff Marsh and Felice Naus-Thijssen and MSc candidate Meredith Petrie. In addition, I regularly attend weekly get-togethers of students and faculty in the crustal studies group within the department. Students make informal presentations on their thesis research, and I offer suggestions or help them address problems encountered in their research. I also evaluate student presentations at the department's sack lunch seminar, a more formal venue for presentations.

After receiving their Master's degrees, Eva Wadoski and Meredith Petrie have gone on to Ph.D. programs at the University of Bern and University of Iowa, respectively.

Contributions to Resources for Research and Education:

Contributions Beyond Science and Engineering:

The discovery of three new minerals in the Larsemann Hills has contributed to conservation of this area. My discoveries have factored into the decision by Australia and other countries to make the Larsemann Hills an Antarctic Specially Managed Area, which will protect the Larsemann Hills environment. This was reported in the December issue (#13 - December, 2007, p. 18-19) of Antarctic Magazine, which is published by the Australian Antarctic Division (AAD).

At present, the AAD is considering whether an Antarctic Specially Protected Area is required for Stornes Peninsula, which constitutes a part of the Larsemann Hills, following the successful adoption of the Larsemann Hills Antarctic Specially Managed Area. The Division is seeking information regarding the latest geological findings to address this question. I supplied copies of my publications and other information for this purpose.

Conference Proceedings

Categories for which nothing is reported:

Contributions: To Any Resources for Research and Education Any Conference