DR2015305

SUPPLEMENTARY MATERIAL

Appendix A: Detailed description of methods used for geochemical modeling and list of supplementary references.

DR1: Whole-rock analyses of biotite and calcic A-type granites, with estimated magmatic parameters and degree of partial melting.

DR2: Partition coefficients for selected trace elements used for geochemical modeling.

DR3: Petrographic description of Neoproterozoic intermediate rocks of the Cobequid Highlands.

DR4: Whole-rock analyses of intermediate and mafic rocks from the Cobequid Highlands used as sources for geochemical models.

APPENDIX A

Methodology for geochemical models

Fractionation of mafic sources

The fractionation models used in this work include a two-step process. First the changes in major elements through fractionation were modeled by the use of PELE software for Windows (Boudreau, 1999). Whole-rock analyses of selected mafic sources were used as input. PELE uses a list of mineral phases that can crystallize during the fractionation sequence. From the given list certain minerals were excluded such as leucite, nepheline, mellilite, garnet, kalsilite, whitlockite, corundum, perovskite, muscovite, troilite, pyrrhotite, pyrite, sulphide liquid, graphite, calcite, dolomite, anhydrite and immiscible liquid. Although pyrite is reported as an accessory phase in the Wentworth gabbros, the exclusion of this mineral is not considered to significantly compromise the model, since there no S was determined in whole-rock for these rocks, and therefore there was no input for that element. Other parameters involve temperature, pressure, oxygen fugacity, entropy, enthalpy and volume. In the absence of constraints for entropy, enthalpy and volume, an isobaric fractionation was assumed and was tested for a range of pressures from 2 to 0.6 GPa. An initial 0.5 wt.% H_2O was assumed although not measured. An anhydrous composition for the Fountain Lake basalts is assumed from their mineralogy which includes olivine, plagioclase, pyroxene and Fe-oxides. Fractionation models were performed under different oxygen fugacities ranging from NNO to +3 QFM. For different oxygen fugacities the program will adjust the amounts of FeO and Fe_2O_3 in the whole-rock input. The range of temperature for all runs was from the liquidus, as determined by the program for a given pressure

and oxygen fugacity, to 800 °C, which is an average zircon-saturation temperature for the studied granites.

After the parameters were set, PELE performed a fractionation simulation until the lowest temperature was achieved. During the simulation, the program predicted mineralogical assemblages that would be in equilibrium with the remaining melt for a given temperature. For each equilibrium stage (or "step" as reported by the program) the following are predicted: mass of liquid, mass of solids, fractionating mineral phases (chemistry and mass for each phase), whole-rock chemistry of the remaining melt, viscosity, volume, enthalpy, entropy and oxygen fugacity. Any invalid parameters or unrealistic set of parameters would crash the program.

The most realistic output for the fractionation models was considered to be from the run at 0.6 GPa, under an oxygen fugacity of -2 QFM. The fractionated minerals predicted were olivine, plagioclase, pyroxene, apatite, and Fe-Ti oxides. The minerals predicted to remain in the melt at the latest stages were alkali feldspar, quartz, titanite, ilmenite, and aenigmatite. Since all the predicted fractionating minerals reflect the mineralogy of the mafic rocks, the output was considered reliable. The predicted viscosity was comparable with the viscosity estimates for the sodic granites, using the method of Giordano et al. (2008). The felsic melt under these conditions was produced in ten steps.

As a second procedure the trace elements were modeled using Rayleigh fractionation (Rayleigh, 1896) as applied by Neuman et al. (1954) which is described by the equation

$$C_L = C_O F^{(D-1)} \qquad (1)$$

Where C_L : concentration of element in remaining liquid, C_O : concentration of element in the parent melt, F: fraction of remaining melt defined as M_L/M_O (M_L: mass of original melt, M_O:

mass of remaining melt), D: the bulk partition coefficient for element calculated as $\Sigma X_A D_i$ (X_A: weight fraction of mineral A in the rock, D_i: partition coefficient of element i in mineral A).

Trace elements were therefore modeled for each step produced by PELE, where D was estimated by the modal amounts of the predicted fractionating minerals and the chemistry of the remaining melt, and F was calculated by the estimated masses of the original and remaining melts. Since the produced melts varied from mafic to felsic, the partition coefficients used, varied accordingly. For produced melts with SiO_2 up to 52 wt.% the partition coefficients used were for basaltic melts. For melts from 52 to 54 wt.% the partition coefficients used were those for basaltic andesite. For melts with 54 to 62 wt.% SiO_2 partition coefficients for andesite were used. For melts with SiO_2 ranging from 62 to 69 wt.% partition coefficients for dacites were used. Melts more silicic than 69 wt.% were considered rhyolitic and the appropriate partition coefficients were used (Table DR2).

Partial melting models

Batch partial melting was modeled by the equation

$$C_L/C_O=1/(D(1-F)+F) \qquad (2)$$

Where C_L: the concentration of element in extracted melt, C_O: concentration of element at the source, D: bulk partition coefficient as defined above, F: fraction of extracted melt. For highly incompatible elements such as Rb, Nb, and Th, the above equation may be simplified as:

$$C_L/C_O=1/F \qquad (3)$$

which if rearranged will be:

$$F= C_O/C_L \qquad (4)$$

Using the above simplified equation for selected highly incompatible elements, and their average concentrations in Neoproterozoic intermediate rocks, the degrees of partial melting were estimated. The rest of the trace elements were modeled with the original equation for the range of F values determined by the highly incompatible elements.

REFERENCES CITED IN SUPPLEMENTARY MATERIAL

Aignertorres, M., Blundy, J., Ulmer, P., and Pettke, T., 2007, Laser Ablation ICPMS study of trace element partitioning between plagioclase and basaltic melts: an experimental approach: Contributions to Mineralogy and Petrology, v. 153, p. 647-667.

Bacon, C.R., and Druitt, T.H., 1988, Compositional Evolution of the Zoned Calcalkaline Magma Chamber of Mount Mazama, Crater Lake, Oregon: Contributions to Mineralogy and Petrology, v. 98, no. 2, p. 224-256.

Beattie, P., 1993, The effect of partial melting of spinel peridotite on uranium series disequilibria: constraints from partitioning studies: Earth and Planetary Science Letters, v. 177, p. 379-391.

Beattie, P., 1994, Systematics and energetics of trace-element partitioning between olivine and silicate melts: Implications for the nature of mineral/melt partitioning: Chemical Geology, v. 117, p. 57-71.

Bindeman, I., and Davis, A., 2000, Trace element partitioning between plagioclase and melt: Investigation of dopant influence on partition behavior: Geochimica et Cosmochimica Acta, v. 64, p. 2863-2878.

Bindeman, I.N., Davis, A.M., and Drake, M.J., 1998, Ion microprobe study of plagioclase-basalt partition experiments at natural concentration levels of trace elements: Geochimica et Cosmochimica Acta, v. 62, p. 1175-1193.

Boudreau, A.E., 1999, PELE– a version of the MELTS software program for the PC platform: Computers and Geosciences, v. 25, p. 201-203.

Bougault, H., and Hekinian, R., 1974, Rift valley in the Atlantic Ocean near 36 degrees 50'N; petrology and geochemistry of basalt rocks: Earth and Planetary Science Letters, v. 24, p. 249-261.

Drake, M.J., and Weill, D.F., 1975, Partition of Sr, Ba, Ca, Y, Eu2+, Eu3+, and Other REE between Plagioclase Feldspar and Magmatic Liquid - Experimental Study: Geochimica et Cosmochimica Acta, v. 39, p. 689-712.

Dostal, J., Dupuy, C., Carron, J.P., Dekerneizon, M.L., and Maury, R.C., 1983, Partition-Coefficients of Trace-Elements - Application to Volcanic Rocks of St Vincent, West Indies: Geochimica et Cosmochimica Acta, v. 47, p. 525-533.

Dudas, M.J., Schmitt, R.A, and Harward, M.E., 1971, Trace element partitioning between volcanic plagioclase and dacitic pyroclastic matrix: Earth and Planetary Science Letters, v. 11, p. 440-446.

Duke, J.M., 1976, Distribution of the period four transition elements among olivine, calcic clinopyroxene and mafic silicate liquid; experimental results: Journal of Petrology, v. 17, p. 499-521.

Dunn, T., and Sen, C., 1994, Mineral/Matrix Partition-Coefficients for Ortho-Pyroxene, Plagioclase, and Olivine in Basaltic to Andesitic Systems - a Combined Analytical and Experimental Study: Geochimica et Cosmochimica Acta, v. 58, p. 717-733.

Esperança, S., Carlson, R.W., Shirey, S.B., and Smith, D., 1997, Dating crust-mantle separation: Re-Os isotopic study of mafic xenoliths from central Arizona: Geology, v. 25, p. 651-654.

Ewart, A., and Griffin, W.L., 1994, Application of Proton-Microprobe Data to Trace-Element Partitioning in Volcanic-Rocks: Chemical Geology, v. 117, p. 251-284.

Ewart, A., Bryan, W.B., and Gill, J.B., 1973, Mineralogy and Geochemistry of the Younger Volcanic Islands of Tonga, S. W. Pacific: Journal of Petrology, v. 14, p. 429-465.

Frey, F.A., 1969, Rare earth abundances in a high-temperature peridotite intrusion: Geochimica et Cosmochimica Acta, v. 33, p. 1429-1447.

Fujimaki, H., Tatsumoto, M., and Aoki, K.-I., 1984, Partition coefficients of Hf, Zr, and REE between phenocrysts and groundmasses: Journal of Geophysical Research, v. 89, p. 662-672.

Gaetani, G.A., and Grove, T.L., 1997, Partitioning of moderately siderophile elements among olivine, silicate melt, and sulfide melt: Constraints on core formation in the Earth and Mars: Geochimica et Cosmochimica Acta, v. 61, p. 1829-1846.

Gallahan, W.E., and Nielsen, R.L., 1992, The Partitioning of Sc, Y, and the Rare-Earth Elements between High-Ca Pyroxene and Natural Mafic to Intermediate Lavas at 1-Atmosphere: Geochimica et Cosmochimica Acta, v. 56, p. 2387-2404.

Giordano, D., Russell, J. K., and Dingwell, D. B., 2008, Viscosity of magmatic liquids: A model: Earth and Planetary Science Letters, v. 271, p. 123-134.

Hart, S.R., and Brooks, C., 1974, Clinopyroxene-matrix partitioning of K, Rb, Cs, Sr and Ba: Geochimica et Cosmochimica Acta, v. 38, p. 1799-1806.

Hart, S.R., and Dunn, T.,1993, Experimental cpx/melt partitioning of 24 trace elements: Contributions to Mineralogy and Petrology, v. 113, p. 1-8.

Hauri, E.H., Wagner, T.P., and Grove, T.L., 1994, Experimental and natural partitioning of Th, U, Pb and other trace elements between garnet, clinopyroxene and basaltic melts: Chemical Geology, v. 117, p. 149-166.

Huang, F., Lundstrom, C., and Mcdonough, W., 2006, Effect of melt structure on trace-element partitioning between clinopyroxene and silicic, alkaline, aluminous melts: American Mineralogist, v. 91, p. 1385-1400.

Jenner, G.A., Foley, S.F., Jackson, S.E., Green, T.H., Fryer, B.J., and Longerich, H.P., 1994, Determination of partition coefficients for trace elements in high pressure-temperature experimental run products by laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS): Geochimica et Cosmochimica Acta, v. 57, p. 5099-5103.

Johnson, K.T.M., 1994, Experimental cpx/ and garnet/melt partitioning of REE and other trace elements at high pressures; petrogenetic implications: Mineralogical Magazine, v. 58, p. 454-455.

Johnson, K.T.M., 1998, Experimental determination of partition coefficients for rare earth and high-field-strength elements between clinopyroxene, garnet, and basaltic melt at high pressures: Contributions to Mineralogy and Petrology, v. 133, p. 60-68.

Kloeck, W., and Palme, H., 1988, Partitioning of siderophile and chalcophile elements between sulfide, olivine, and glass in a naturally reduced basalt from Disko Island, Greenland, *in* Proceedings of the Lunar and Planetary Science Conference, Ryder, G. (Editors), Pergamon, New York, v. 18, p. 471-483.

Larsen, L.M., 1979, Distribution of REE and Other Trace-Elements between Phenocrysts and Peralkaline Undersaturated Magmas, Exemplified by Rocks from the Gardar Igneous Province, South Greenland: Lithos, v. 12, p. 303-315.

Latourrette, T.Z., and Burnett, D.S., 1992, Experimental-Determination of U-Partitioning and Th-Partitioning between Clinopyroxene and Natural and Synthetic Basaltic Liquid: Earth and Planetary Science Letters, v. 110, p. 227-244.

Latourrette, T.Z., Burnett, D.S., and Bacon, C.R., 1991, Uranium and Minor-Element Partitioning in Fe-Ti Oxides and Zircon from Partially Melted Granodiorite, Crater Lake, Oregon: Geochimica et Cosmochimica Acta, v. 55, p. 457-469.

Leeman, W.P., 1979, Partitioning of Pb between volcanic glass and coexisting sanidine and plagioclase feldspars: Geochimica et Cosmochimica Acta, v. 43, p. 171-175.

Lemarchand, F., Benoit, V., and Calais, G., 1987, Trace element distribution coefficients in alkaline series: Geochimica et Cosmochimica Acta, v. 51, p. 1071-1081.

Long, P.E., 1978, Experimental determination of partition coefficients for Rb, Sr and Ba between alkali feldspar and silicate liquid: Geochimica et Cosmochimica Acta, v. 42, p. 833-846.

Luhr, J.F., and Carmichael, I.S.E., 1980, The Colima volcanic complex, Mexico. I: post-caldera andesites from Volcan Colima: Contributions to Mineralogy and Petrology, v. 71, p. 343-372.

Luhr, J.F., Carmichael, I.S.E., and Varekamp, J.C., 1984, The 1982 eruptions of El Chichon volcano, Chiapas, Mexico: mineralogy and petrology of the anhydrite-bearing pumices: Journal of Volcanology and Geothermal Research, v. 23, p. 69-108.

Mahood, G.A., and Hildreth, E.W., 1983, Large partition coefficients for trace elements in high-silica rhyolites: Geochimica et Cosmochimica Acta, v. 47, p. 11-30.

Mahood, G.A., and Stimac, J.A., 1990, Trace-element partitioning in pantellerites and trachytes: Geochimica et Cosmochimica Acta, v. 54, p. 2257-2276.

Marks, M., Halama, R., Wenzel, T., and Markl, G., 2004, Trace element variations in clinopyroxene and amphibole from alkaline to peralkaline syenites and granites: implications for mineral-melt trace-element partitioning: Chemical Geology, v. 211, p. 185-215.

McKay, G.A., and Weill, D.F., 1977, KREEP petrogenesis revisited *in* Proceedings, Lunar Science Conference, 8th, Houston, Volume 2: Pergamon Press Inc., p. 2339-2355.

McKenzie, D., and O'Nions, R.K., 1991, Partial melt distributions from inversion of rare Earth element concentrations: Journal of Petrology, v. 32, p. 1021-1091.

Michael, P.J., 1988, Partition coefficients for rare earth elements in mafic minerals of high silica rhyolites: The importance of accessory mineral inclusions: Geochimica et Cosmochimica Acta, v. 52, p. 275-282.

Mysen, B., 1976, Partitioning of samarium and nickel between olivine, orthopyroxene, and liquid: preliminary data at 20 kbar and 1025 °C: Earth and Planetary Science Letters, v. 31, p. 1-7.

Mysen, B., 1978, Experimental determination of nickel partition coefficients between liquid, pargasite and garnet peridotite minerals and concentration limits of behavior according to Henry's Law at high pressure and temperature: American Journal of Science, v. 278, p. 217-243.

Mysen, B.O., and Virgo, D., 1980, Trace element partitioning and melt structure: an experimental study at 1 atm pressure: Geochimica et Cosmochimica Acta, v. 44, p. 1917-1930.

Nabelek, P.I., 1980, Nickel partitioning between olivine and liquid in natural basalts: Henry's Law behavior: Earth and Planetary Science Letters, v. 48, p. 293-302.

Nagasawa, H., 1973, Rare-Earth distribution in alkali rocks from Oki-Dogo Island, Japan: Contributions to Mineralogy and Petrology, v. 39, p. 301-308.

Nagasawa, H., and Schnetzler, C.C., 1971, Partitioning of rare Earth, alkali, and alkaline Earth elements between phenocrysts and acidic igneous magmas: Geochimica et Cosmochimica Acta, v. 35, p. 953-968.

Nagasawa, H., Wakita, H., Higuchi, H., and Onuma, N., 1969, Rare Earths in peridotite nodules: an explanation of the genetic relationship between basalt and peridotite nodules: Earth and Planetary Science Letters, v. 5, p. 377-381.

Nash, W.P., and Crecraft, H.R., 1985, Partition coefficients for trace elements in silicic magmas. Geochimica et Cosmochimica Acta, v. 49, p. 2309-2322.

Neuman, H., Mead, J., and Vitaliano, C.J., 1954, Trace element variations during fractional crystallization as calculated from the distribution law: Geochimica et Cosmochimica Acta, v. 6, p. 90-101.

Nicholls, I.A., and Harris, K.L., 1980, Experimental rare Earth element partition coefficients for garnet, clinopyroxene and amphibole coexisting with andesitic and basaltic liquids: Geochimica et Cosmochimica Acta, v. 44, p. 287-308.

Nielsen, R.L., 1988, A model for the simulation of combined major and trace element liquid lines of descent: Geochimica et Cosmochimica Acta, v. 52, p. 27-38.

Nielsen, R.L., 1992, BIGD: a FORTRAN program to calculate trace-element partition coefficients for natural mafic and intermediate composition magmas: Computers and Geosciences, v. 18, p. 773-788.

Nielsen, R.L., Gallahan, W.E., and Newberger, F., 1992, Experimentally determined mineral-melt partition coefficients for Sc, Y and REE for olivine, orthopyroxene, pigeonite, magnetite and ilmenite: Contributions to Mineralogy and Petrology, v. 110, p. 488-499.

Okamoto, K., 1979, Geochemical study on magmatic differentiation of Asama Volcano, central Japan: Journal of the Geological Society of Japan, v. 85, p. 525-535.

Pe-Piper, G., 1991, Granite and associated mafic phases, North River pluton, Cobequid Highlands, Nova Scotia: Atlantic Geology, v. 27, p. 15-28.

Pe-Piper, G., 1995, The Carboniferous plutons and associated igneous rocks of the western Cobequid Highlands, Nova Scotia: Geological Survey of Canada, Open file report No. 3252.

Pe-Piper, G., 1998, The Devonian- Carboniferous Wentworth plutonic complex (Folly Lake and Hart Lake-Byers Lake plutons) of the central Cobequid Highlands, Nova Scotia: Geological Survey of Canada, Open file report 3373.

Pe-Piper, G., and Turner, D., 1988, The Jeffers Group, western Cobequid Hills, Nova Scotia, Geological Survey of Canada, Open File Report No. 1782.

Pe-Piper, G., and Piper, D.J.W., 1998, Geochemical and structural evolution of the Pleasant Hills pluton, Cobequid Highlands, Nova Scotia, Canada: Geological Survey of Canada, Open File Report No. 3372.

Pe-Piper, G., Piper, D.J.W., and Hilton, E., 2002, Neoproterozoic plutonic rocks of the western Cobequid Highlands, N.S., Canada: Geological Survey of Canada, Open File Report No. 4189, p. 46.

Pedersen, A.K., 1979, Basaltic Glass with High-Temperature Equilibrated Immiscible Sulfide Bodies with Native Iron from Disko, Central West Greenland: Contributions to Mineralogy and Petrology, v. 69, p. 397-407.

Philpotts, J.A., and Schnetzler, C.C., 1970, Phenocryst-matrix partition coefficients for K, Rb, Sr and Ba, with applications to anorthosite and basalt genesis: Geochimica et Cosmochimica Acta, v. 34, p. 307-322.

Reid, F., 1983, Origin of the Rhyolitic Rocks of the Taupo Volcanic Zone, New-Zealand: Journal of Volcanology and Geothermal Research, v. 15, p. 315-338.

Ronov, A.B., and Yaroshevskiy, A.A., 1976, A new model for the chemical structure of the Earth's crust: Geochemistry International, v. 13, p. 89-121.

Schnetzler, C.C., and Philpotts, J.A., 1970, Partition coefficients of rare-earth elements between igneous matrix material and rock-forming mineral phenocrysts: II: Geochimica et Cosmochimica Acta, v. 34, p. 331-340.

Sisson, T.W., 1991, Pyroxene-High Silica Rhyolite Trace-Element Partition-Coefficients Measured by Ion Microprobe: Geochimica et Cosmochimica Acta, v. 55, p. 1575-1585.

Sisson, T.W., 1994, Hornblende-Melt Trace-Element Partitioning Measured by Ion Microprobe: Chemical Geology, v. 117, p. 331-344.

Skulski, T., Minarik, W., and Watson, E.B.,1994, High-Pressure Experimental Trace-Element Partitioning between Clinopyroxene and Basaltic Melts: Chemical Geology, v. 117, p. 127-147

Stix, J., and Gorton, M.P., 1990, Variations in Trace-Element Partition-Coefficients in Sanidine in the Cerro Toledo Rhyolite, Jemez Mountains, New-Mexico - Effects of Composition, Temperature, and Volatiles: Geochimica et Cosmochimica Acta, v. 54, p. 2697-2708.

Streck, M.J., and Grunder, A.L., 1997, Compositional gradients and gaps in high-silica rhyolites of the Rattlesnake Tuff, Oregon: Journal of Petrology, v. 38, p. 133-163.