Yttrium-rich garnet: a source of HREE?

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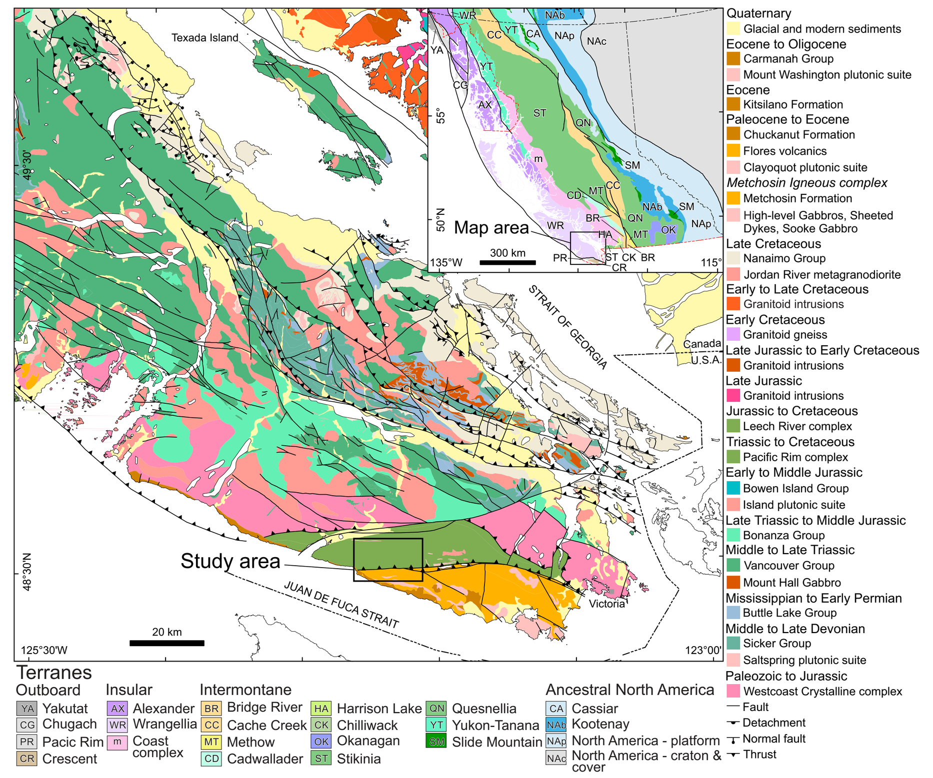
1. Introduction

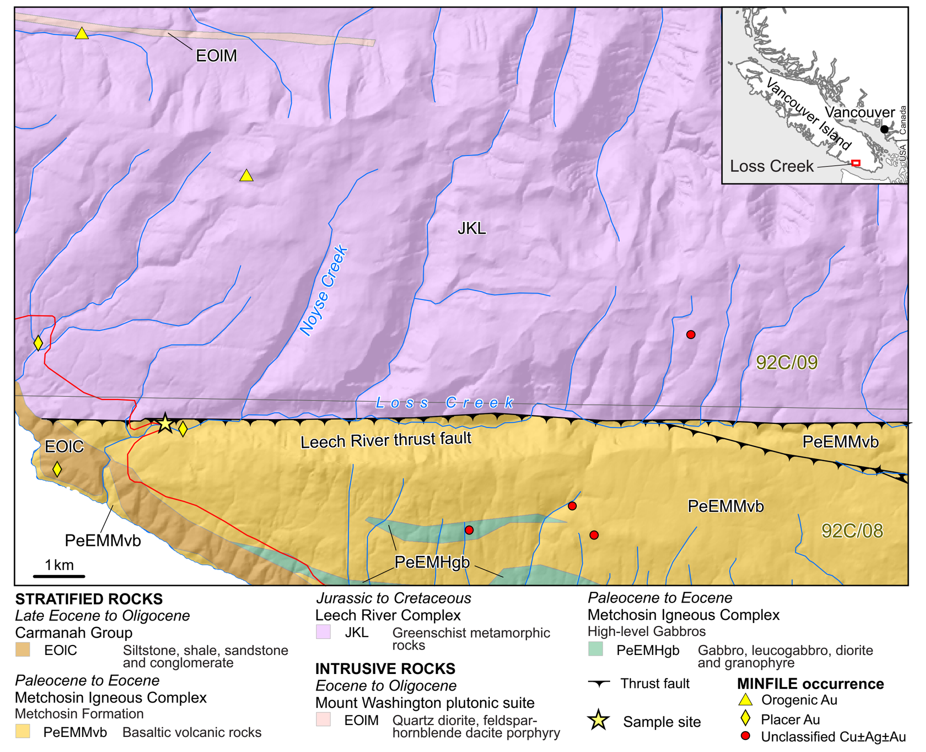
Rare earth elements (REE), including Sc, Y, and lanthanides (La to Lu), are increasingly important in high-technology industries and are considered 'critical' materials. Rukhlov et al. (2020) reported anomalous concentrations of heavy REE (HREE, i.e. Sc, Y, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu) in heavy-mineral concentrate (HMC) samples at Loss Creek on southern Vancouver Island. Deposits of HREE are rare when compared with those of light REE (LREE, i.e. La to Eu), with most HREE produced from ion adsorption clays (up to 0.5 wt% REE) in southern China. Some HREE also recovered from placer and peralkaline intrusion-hosted deposits. Gadolinite ($Y_2FeBe_2Si_2O_{10}$), xenotime (YPO_4), and REE-bearing Ta-Nb oxides are the main HREE minerals. Heavy REE also occur in Zr-minerals such as zircon and eudialyte, and in some Mn-rich garnets (up to 2.64 wt% Y_2O_3; Jaffe, 1951). Based on the HMC mineralogy and garnet chemistry, this study finds that Mn-rich almandine with up to 0.563 wt% REE is the main host of HREE associated with placer Au at Loss Creek and thus could be a potentially viable source of HREE and other 'critical' metals.

2. Geological setting



Vancouver Island is mainly underlain by Late Paleozoic to Early Mesozoic rocks of Wrangell terrane, with slivers of Pacific Rim and Crescent terranes along the west coast and southern tip of the Island. Lithologic units at Loss Creek consist of greenschist rocks of the Leech River complex (Jurassic to Cretaceous), juxtaposed against basalts and gabbro of the Metchosin Igneous complex (Paleocene to Eocene) along the Leech River fault. Along the coast, these older rocks are overlain by a narrow fringe of siliciclastic rocks of the Carmanah Group (Late Eocene to Oligocene). Intermediate intrusions of the Mount Washington plutonic suite (Eocene to Oligocene) intrude the metamorphic rocks of the Leech River complex (Muller, 1977, 1980, 1982). Placer gold occurs in Loss Creek and adjacent drainages.

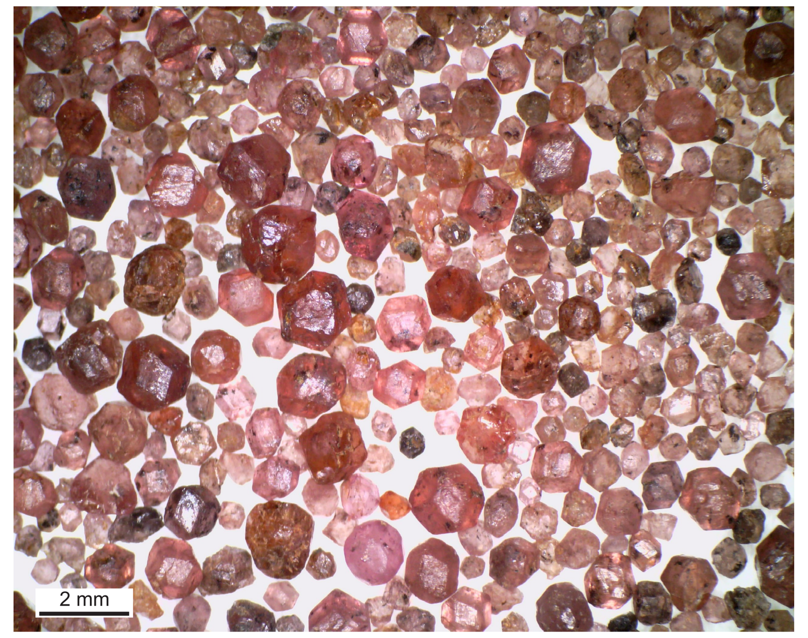
Location of sample site and geology of the Loss Creek watershed



3. Samples and methods

HMC samples were recovered from <2 mm fraction of alluvium (13 kg) by panning, shaking table, and sluice box as described in Rukhlov et al. (2020). Representative splits (2 g) of sieved, 0.5-1.0 mm and <0.18 mm fractions were analyzed for modal mineralogy by an FEI QEMSCAN 650F field emission gun-scanning electron microscope (FEG-SEM) at Actlabs (Ancaster, Ontario). Agate-pulverized, 3.1 to 3.7 g splits of hand-picked, pure garnet fraction (0.25-2.0 mm) were fused with lithium borate and analyzed in solution for 56 analytes by a combination of inductively coupled plasma optical emission and mass spectrometry (ICP-OES/MS) in the same laboratory. Six garnet crystals were mounted in epoxy, polished, and analyzed by a CAMECA SX50 electron probe microanalyzer (EPMA) in wavelength dispersion mode for Mg, Al, Si, Ca, Ti, Cr, Mn, Fe, and Y at the Department of Earth, Ocean and Atmospheric Sciences, University of British Columbia. Elemental X-ray maps of the garnets were produced by a Philips XL-30 scanning electron microscope (SEM) with Bruker Quantax 200 energy-dispersion X-ray microanalysis system (EDS) in the same laboratory. Thirty-seven elements (Z=12 to 92) were analyzed by a Thermo X-Series II (X7) ICP-MS with an LSX213 laser ablation (LA) system at the School of Earth and Ocean Sciences, University of Victoria. Precision is better than 10% for most elements.

Manganese-rich almandine from Loss Creek



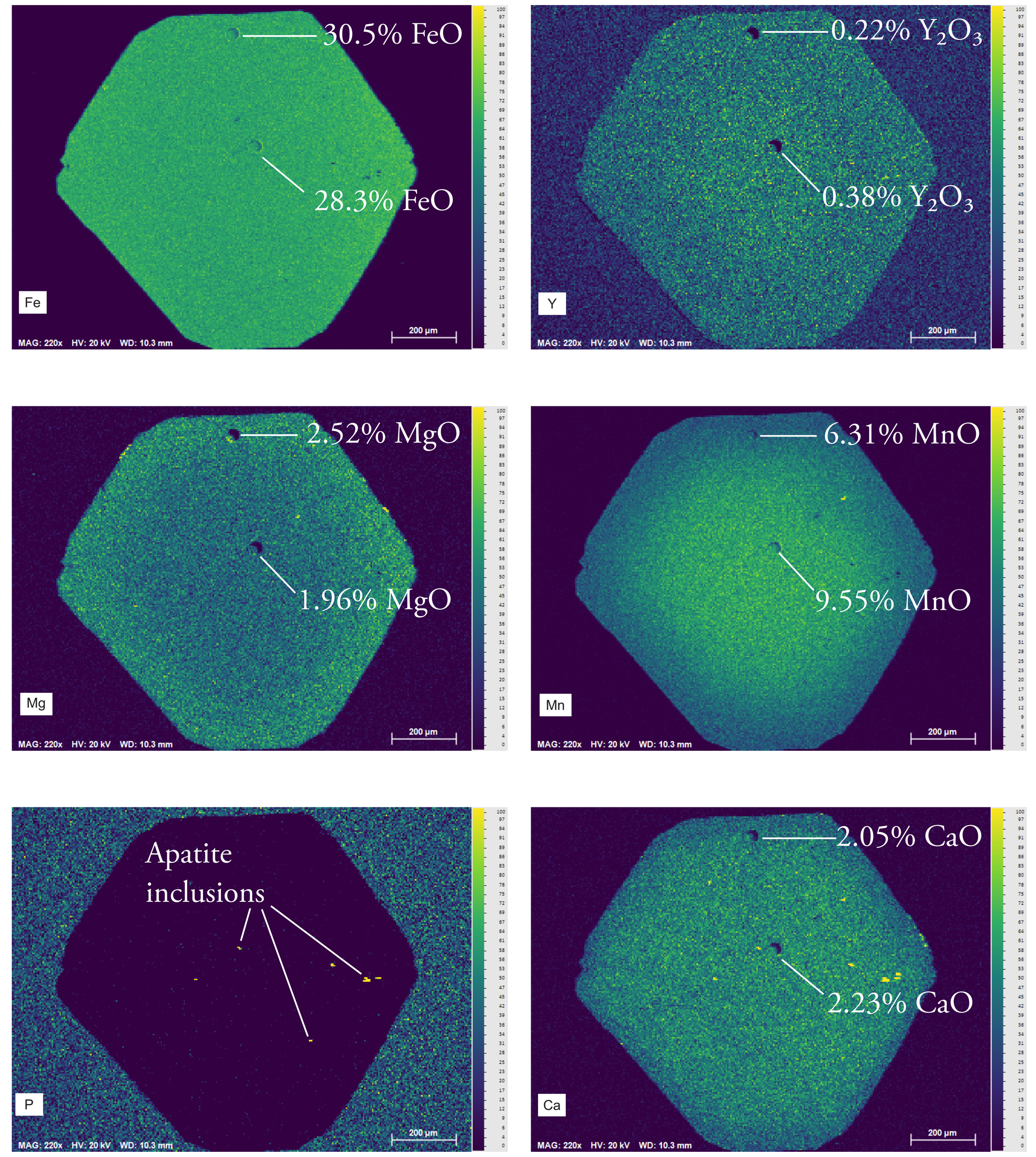
4. HMC mineralogy by QEMSCAN

Mineral	Formulae	Heavy mineral concentrate type / Sieved size-fraction	Panned <0.18 mm	Sluice box 0.5-1.0 mm
Arsenopyrite (wt%)	$FeAsS$		<0.01	n.d.
Pyrite	FeS_2		0.02	0.01
Tungstite	$WO_3 \cdot H_2O$		0.04	n.d.
Cr-spinel	$Mg(Al, Cr)_2O_4$		0.01	n.d.
Magnetite	$Fe^{2+}Fe^{3+}{}_2O_4$		22.86	0.01
Chromite	$FeCr_2O_4$		0.24	n.d.
Hematite[1]	Fe_2O_3		3.48	0.28
Goethite	$FeO(OH)$		n.d.	3.83
Ilmenite	$FeTiO_3$		24.84	0.58
Pseudobrookite	Fe_2TiO_5		2.77	n.d.
Leucoxene	mostly TiO_2		2.55	n.d.
Rutile	TiO_2		0.59	0.03
Titanite	$CaTi(SiO_4)O$		0.53	0.42
Zircon	$Zr(SiO_4)$		0.80	n.d.
Quartz	SiO_2		0.60	20.33
K-Feldspar	$K(AlSi_3O_8)$		0.06	1.84
Plagioclase	$(Na, Ca)(Al_{1-2}Si_{2-3}O_8)$		0.55	16.40
Biotite	$K(Mg, Fe)_3(AlSi_3O_{10})(OH, F)_2$		0.31	2.38
Muscovite	$KAl_2(AlSi_3O_{10})(OH)_2$		0.15	4.12
Garnet	$(Fe^{2+}, Mn^{2+}, Ca)_3(Al, Fe^{3+})_2(SiO_4)_3$		28.01	25.45
Orthopyroxene	$(Mg, Fe)_2(Si_2O_6)$		0.33	n.d.
Clinopyroxene	$(Ca, Mg, Fe)_2(Si_2O_6)$		2.55[2]	0.54
Amphibole[3]	$(\square, Na)(Ca, Na, Mg, Fe^{2+})_2(Mg, Fe^{2+})_{3-5}(Al, Fe^{3+}, Ti)_{0-2}[(Al_{0-2}Si_{6-8})O_{22}](OH, O)_2$		0.26	10.81
Epidote	$Ca_2(Al_2Fe^{2+})(Si_2O_7)(SiO_4)O(OH)$		1.21	2.36
Low-Fe sillimanite	Al_2SiO_5		5.85	n.d.
Staurolite	$Fe^{2+}{}_2Al_9Si_4O_{23}(OH)$		n.d.	4.22
Chamosite	$(Fe^{2+}, Mg, Al, Fe^{3+})_6[(Si, Al)_4O_{10}](OH,O)_8$		0.34	2.66
Illite	$\square K_{0.65}(Al, Mg, Fe)_2(Si_{3.35}Al_{0.65}O_{10})[OH, (H_2O)]_2$		0.07	0.82
Si-Al-clays[4]	$Al_2Si_2O_5(OH)_4 \cdot nH_2O$		0.07	2.23
Allanite	$(Ca, Ce, Y, La, Th)_2(Al_2Fe^{2+})(Si_2O_7)(SiO_4)O(OH)$		0.29	n.d.
Monazite	$(Ce, La, Nd, Th)PO_4$		0.02	n.d.
Xenotime	YPO_4		0.001	n.d.
Apatite	$Ca_5(PO_4)_3(F, Cl, OH)$		0.11	0.14
Siderite	$FeCO_3$		n.d.	0.03
Calcite	$CaCO_3$		0.01	n.d.
Others			0.49	0.52

In addition, a total of 14 gold grains were picked. [1] Includes low-Ti and specular varieties. [2] Includes 0.01 wt% of aegirine-augite. [3] Includes augite. [4] Si-Al clays occur as alteration products of silicate minerals and fine-grained, intergrown minerals. **n.d.** - not detected.

Manganese-rich almandine garnet comprises 25 to 28 wt% in the HMC samples from Loss Creek. Other abundant heavy minerals include ilmenite, magnetite, hematite, pseudobrookite, leucoxene, pyroxene, staurolite, sillimanite, and epidote. Note that REE-bearing minerals such as allanite, xenotime, monazite, apatite, and zircon occur only as very rare accessory minerals, some as single grains in the HMC samples.

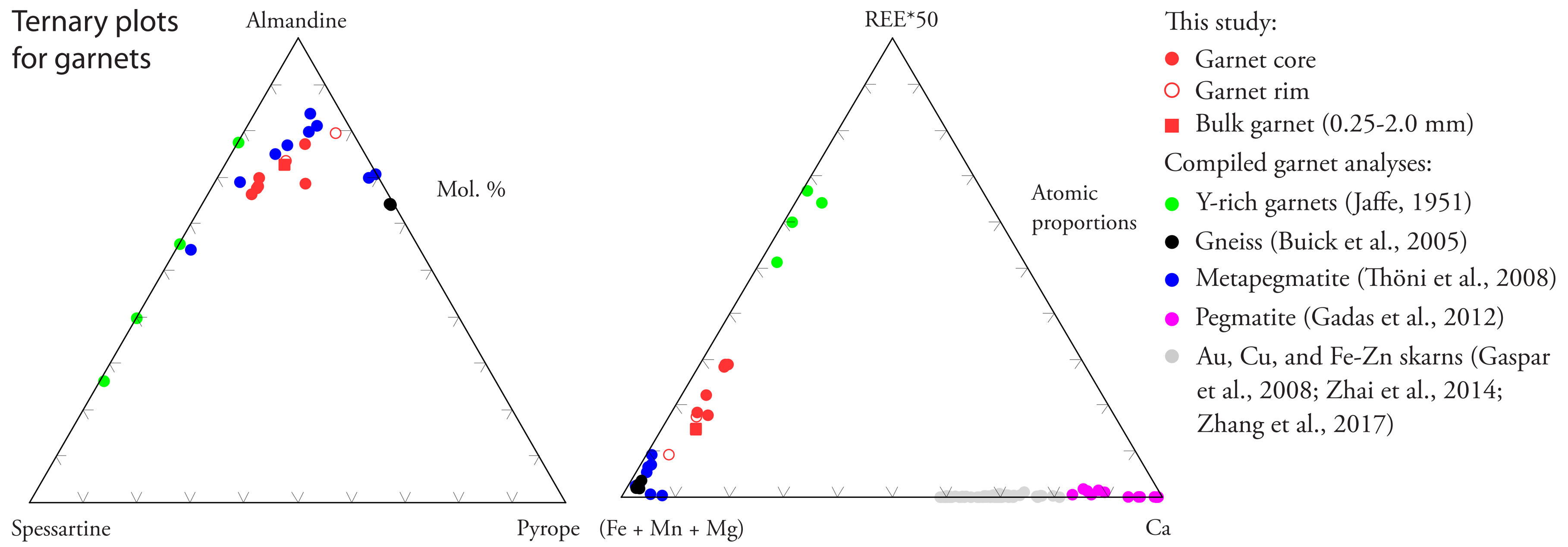
5. Elemental X-ray maps of garnet

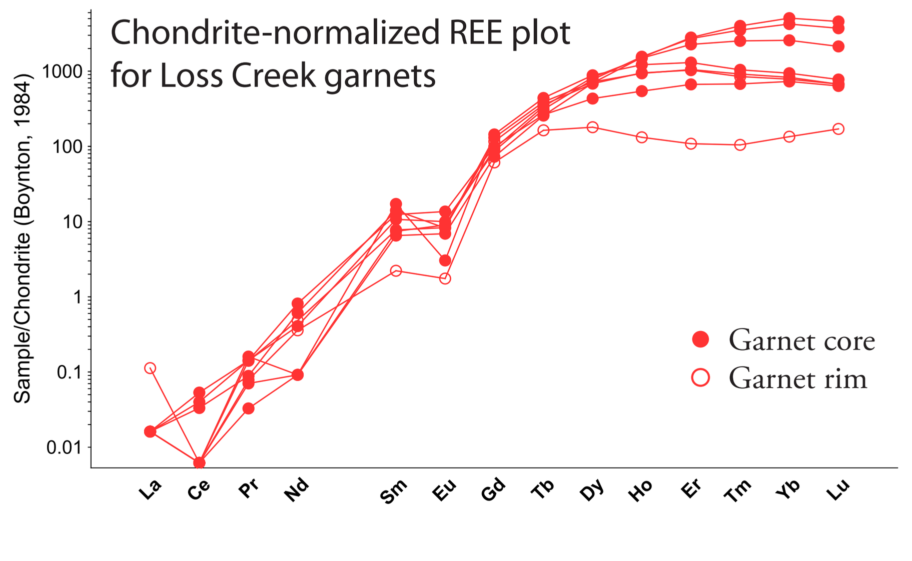


All analyzed garnets (Mn-rich almandine) display zoning, with Mn-Y-rich cores and Mn-Y-poor rims. Magnesium and iron contents increase and calcium and yttrium contents decrease from core to rim. Rare microinclusions of apatite, quartz, ilmenite, and Fe-Mg-Al silicates (up to 1%) occur in these garnets, but no xenotime or other REE-bearing mineral inclusions were found. The observed distribution of Y and other elements in the Loss Creek garnets suggests that Y might substitute into the Mn-rich garnet as an $Y_3Al_2Al_3O_{12}$ molecule according to the scheme (Jaffe, 1951):

$$Y^{3+} + Al^{3+} \rightleftarrows Mn^{2+} + Si^{4+}.$$

6. Chemical composition of garnets from Loss Creek

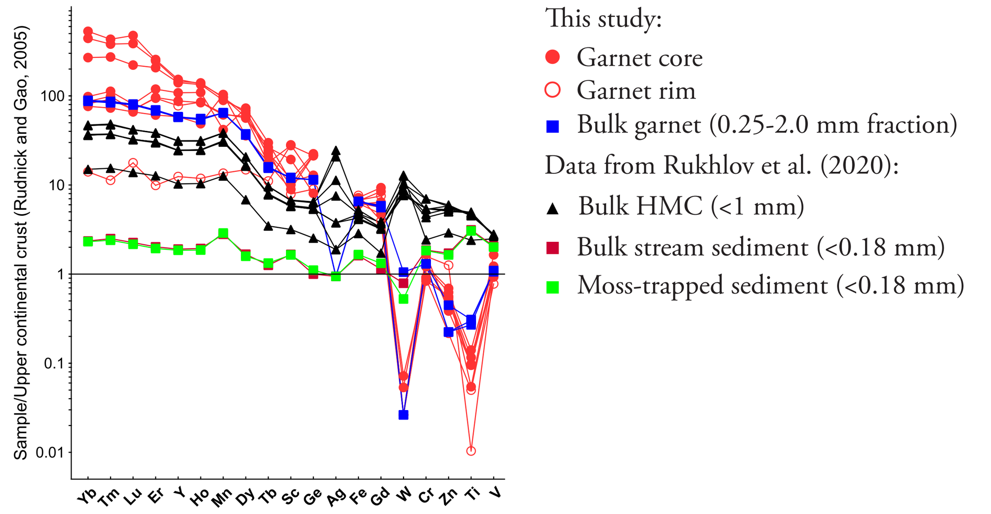




Manganese-rich garnets at Loss Creek have up to 0.563 wt% REE (3000x chondritic), with HREE comprising >99.8% of the total REE. Yttrium is up to 153x the average abundance of the Earth's crust (21 ppm Y; Rudnick and Gao, 2005). This is in contrast to most garnets that have much lower REE levels (<0.06 wt%). Jaffe (1951) reported spessartines with up to 2.64 wt% Y_2O_3 in some pegmatites, and synthetic yttrian spessartines containing >8.89 wt% Y_2O_3. The REE grade of the Loss Creek garnet is comparable with that of the world's producing ion-adsorption clay (0.05-0.5% REE) and alkaline intrusion-hosted REE deposits such as Bokan-Dotson Ridge in Alaska with indicated resource of 4.79 Mt @ 0.602% REE_2O_3.

7. Summary: garnet is the main host of HREE at Loss Creek

Leaders of ranked element contrast relative to the average Earth crust for garnets, HMC, and bulk stream- and moss-trapped sediment samples at Loss Creek, southern Vancouver Island



Anomalous HREE (up to 600x average Yb concentration in the upper continental crust) associated with placer Au at Loss Creek are hosted by Mn-Y-rich almandine garnet derived from the greenschist metamorphic country rocks of the Leech River complex. HMC samples contain >25% garnet that has HREE contents comparable with those of the world's largest HREE producers such as the ion-adsorption clay deposits (0.05-0.5% REE) in southern China and peralkaline-intrusion hosted REE deposits (e.g, Bokan-Dotson Ridge, Alaska; eudialyte-bearing Ilímaussaq massif in southern Greenland). The significant prognostic resources of HREE, Mn, and Ge in the Loss Creek catchment basin (Rukhlov et al., 2020) suggest that the Mn-Y-rich garnet concentrate recovered in the placer operations could be a potentially viable source for the recovery of the 'critical' green-energy metals.

Selected cited reference:
Rukhlov, A.S., Fortin, G., Kaplenkov, G.N., Lett, R.E., Lai, V. W.-M., and Weis, D., 2020. Multi-media geochemical and Pb isotopic evaluation of modern drainages on Vancouver Island. In: Geological Fieldwork 2019, British Columbia Ministry of Energy, Mines and Petroleum Resources, British Columbia Geological Survey Paper 2020-01, pp. 133-167.

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