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Critical metal enrichment in crustal melts: the role of metamorphic mica

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APPENDIX 1. Sample descriptions

Sikkim
SK-10-12 is an arkosic metasediment containing ~1–2 mm clasts of quartz and plagioclase wrapped by a fine-grained matrix comprising chlorite (5%) and muscovite (40%).
SK-10-15 is a fine-grained (~100 μm) phyllite with a strong planar fabric, containing an assemblage of chlorite (25%) muscovite (45%) and quartz with accessory zircon, xenotime, allanite and ilmenite.

SK-10-16 is a fine-grained crenulated schist containing quartz, muscovite (50%), biotite (10%), garnet, staurolite, chlorite (5%) and plagioclase with accessory ilmenite and apatite. Pressure shadows around garnet are filled with quartz, and staurolites lie parallel to the foliation.

SK-10-17 is a medium-grained schist containing quartz, muscovite (25%), biotite (15%), chlorite (5%), K-feldspar, garnet and plagioclase with accessory ilmenite, apatite, rutile and tourmaline. The phyllosilicate grains are mostly aligned with the fabric although subordinate clusters of muscovite and biotite lie oblique.

SK-10-19 is a coarse schist containing quartz, muscovite (25%), biotite (25%), chlorite (2%) and garnet with accessory ilmenite, rutile, apatite and tourmaline. ~0.5 mm muscovite grains cross-cut the main foliation formed of smaller grains of muscovite and biotite.

SK-10-20 is a coarse schist containing quartz, muscovite (20%), biotite (20%), chlorite (5%), plagioclase, K-feldspar and garnet with accessory ilmenite, apatite and rutile.

SK-10-21 is a coarse schist containing quartz, muscovite (25%), biotite(10%), garnet and quartz with few accessory phases.

SK-10-22 is a course-grained schist that contains quartz, plagioclase, muscovite (20%), biotite (10%), garnet (with mica inclusions), kyanite, sillimanite and staurolite with accessory tourmaline, ilmenite, rutile, and apatite.

Overall, Si ions per formula unit (pfu) in muscovite range from 6.2- 6.42 and Ti ranges from 0.03-0. Na/(Na+K) ranges from 0.02-0.2. Si pfu in biotite ranges from 5.52-6.25 and Ti ranges from 0.37-0.5. The full datasets are presented in Mottram et al., (2014a,b).

Langtang
N13 is a muscovite garnet schist that contains muscovite (25%), garnet, quartz, plagioclase and minor biotite (1-2%).

N2 is a muscovite biotite garnet schist that contains muscovite (25%), biotite (25%), garnet, quartz and plagioclase.

N5 and N11 are biotite sillimanite migmatitic gneisses containing biotite, garnet, sillimanite, quartz and K-feldspar. N5 contains more biotite and sillimanite (25% each) than N11 (15% biotite and sillimanite only in the leucosome).

Si ions per formula unit (pfu) in muscovite in these samples range from 5.8-6.1 and Ti from 0.08-0.17. Na/(Na+K) ranges from 0.06-0.12. Si pfu in biotite ranges from 5.1-5.9 and Ti ranges from 0.15-0.46. Average compositions of muscovite and biotite per sample are presented in Table S2.

Ivrea Zone

IZ 410 is a folded augen gneiss containing quartz, plagioclase, biotite (40%), muscovite (7%) and sillimanite with accessory apatite, zircon and monazite.

IZ 418 is a foliated gneiss containing quartz, plagioclase, biotite (30%) and sillimanite with minor muscovite (<5%) and accessory zircon, monazite, apatite, hematite and pyrite.

IZ 419 is biotite gneiss containing quartz, plagioclase, biotite (40%), sillimanite, muscovite (<5%) and minor tourmaline and accessory monazite, xenotime, apatite, ilmenite, graphite, zircon hematite and pyrite.

IZ 420 is a biotite gneiss containing plagioclase + quartz + garnet + biotite (35%) + sillimanite, muscovite (<2%) and minor tourmaline and accessory monazite, xenotime, apatite, ilmenite, graphite, zircon and pyrite.

IZ 421 is a biotite-muscovite gneiss containing plagioclase + quartz + garnet + biotite (30%) + sillimanite, with muscovite (<5%) and accessory zircon, monazite, xenotime, apatite, ilmenite, graphite, and hematite and pyrite.

IZ 422 is a coarse-grained gneiss containing plagioclase + quartz + garnet + biotite (40%) + K-feldspar + sillimanite with minor remnant muscovite and graphite and accessory zircon, apatite, monazite, hematite and pyrite.

IZ 409 is a banded gneiss with coarser and finer-grained layers. It contains quartz + plagioclase + garnet + biotite (25%) + K-feldspar + sillimanite and accessory zircon, apatite, monazite, ilmenite, hematite and pyrite.

IZ 407 is a highly strained, fine-grained gneiss containing quartz + plagioclase + garnet + biotite (20%) + K-feldspar + sillimanite and accessory zircon, apatite, monazite, graphite, rutile, hematite and pyrite.

IZ 406A is a restitic garnet-sillimanite gneiss containing plagioclase + garnet + sillimanite + K-feldspar + quartz with minor biotite (5%) and accessory zircon, rutile, and monazite.

IZ 405 is a restitic gneiss containing mainly quartz + plagioclase + garnet + K-feldspar + sillimanite with minor biotite (5%) and accessory zircon, rutile, graphite, monazite, ilmenite and pyrite.

Si ions per formula unit (pfu) in muscovite range from 6.1- 6.3 and Ti ranges from 0.06-0.12. Na/(Na+K) ranges from 0.11-0.2. Si pfu in biotite ranges from 5.2-5.9 and Ti ranges from 0.17-0.74. The full dataset is presented in Table S2.

APPENDIX 2. Mineral assemblages

	Qtz	Kfs	Pl	Mu	Bt	Grt	Sil	Tur	St	Chl	Accesory	Opaque	peak T estimate (°C)	Coordiantes (WGS84)	
Sikkim Himalaya														Lat.	Lon.
SK-10-12	x		x	x						x	Aln, Ap, Mnz, Xtm, Zrn	Ilm	400*	27.0135	88.422817
SK-10-15	x			x						x	Aln, Xtm, Zrn		440*	27.012133	88.4036
SK-10-16	x			x	x	x				x	(Aln), Ap, Mnz, Xtm, Zrn		573*	27.012767	88.3809
SK-10-17	x	x	x	x	x	x		x		x	Aln, Ap, Mnz, Xtm, Zrn	Ilm	559*	27.015817	88.373383
SK-10-19	x			x	x	x		x		x	Aln, Mnz, Zrn	Ilm	674*	27.021917	88.359267
SK-10-20	x	x	x	x	x	x				x	Aln, Mnz, Zrn	Ilm	697*	27.031767	88.353117
SK-10-21	x			x	x	x					Aln, Ap, Mnz, Xtm, Zrn		688*	27.037533	88.350683
SK-10-22	x		x	x	x	x	x	x	x		Ap, Mnz, Xtm, Zrn, Rt	Ilm, Fe-oxides	668*	27.0333	88.342
Langtang Himalaya															
N2	x	x	x	x	x	x		(x)			Ap, Zrn, Mnz,	Gr	680*	28.0934	85.2531
N13	x	x	x	x	x	x					Mnz, Zrn, Ttn, (Ap)	Ilm	591*	28.0923	85.2524
N5	x	x		x	x	x	x				Zrn, Mnz, Ap		797*	28.1102	85.2629
N11	x	x	x	x	x	x	x				Mnz, Zrn	Ilm	726*	28.1141	85.2655
Ivrea Zone, Italy															
IZ 410	x		x	x	x		x				Ap, Zrn, Mnz		690**	45.897391	8.383102
IZ 418	x		x	x	x		x				Ap, Zrn, Mnz	Hem, Py	710**	45.903955	8.37376
IZ 419	x		x	x	x		x	x			Mnz, Xtm, Ap, (Zrn)	Py, Hem, Ilm, Gr	720**	45.904829	8.35601
IZ 420	x		x	x	x	x	x	x			Mnz, Ap, Xtm, (Zrn)	Gr, Ilm, Py	730**	45.908179	8.348429
IZ 421	x		x	x	x	x	x				Zrn, Mnz, Ap, Xtm	Gr, Ilm, Hem	740**	45.906435	8.32853
IZ 422	x	x	x	(x)	x	x	x				Ap, Zrn, Mnz	Hem, Gr, Py	750**	45.911661	8.31293
IZ 409	x	x	x		x	x	x				Ap, Zrn, Mnz, Rt?	Ilm, Py, Hem, Gr	780**	45.919968	8.296591
IZ 407	x	x	x		x	x	x				Ap, Zrn, Mnz	Ilm, Py, Gr	850**	45.932201	8.290993
IZ 406A	x	x	x		(x)	x	x				Rt, Zrn, Mnz		910**	45.934553	8.264404
IZ 405	x	x	x		x	x	x				Zrn, Mnz, Rt	Ilm, Py, Gr	940**	45.932372	8.24738

x = present
(x) = rare

* Ti-in-Bt (callibration from Wu et al., 2015)
**Thermocalc (Taken from Kunz & White, 2019)

APPENDIX 3. Detailed method description for LA-ICP-MS analysis

Major element analysis

Major element concentrations in Sikkim (SK) sample micas were taken from Mottram et al. (2014). Those for the Ivrea Zone (IZ) and Langtang (N) sample micas were analysed on a Cameca SX100 5-spectrometer wavelength dispersive electron microprobe at the Open University, UK. The spectrometers were calibrated using a selection of synthetic and natural standards. The analyses were collected under operating conditions of a 20 nA beam, 20 kV accelerating current and a 10 µm beam size. Data are reported in Table S4.

Temperatures for the SK and N samples were calculated using the Ti-in-biotite thermometer calibration of Wu & Chen (2015) using the mean Ti concentrations measured by EMPA. Temperatures for the IZ samples are taken from Kunz & White (2019), and were calculated from *P–T* pseudosection modelling in THERMOCALC and Zr-in-rutile thermometry (Luvizotto & Zack, 2009).

Trace element analysis

Concentrations of 45 trace (and nine major) elements were measured *in*-situ in muscovite and biotite in thick polished sections by LA-ICP-MS using a Photon Machines Analyte G2 193 nm excimer laser system, equipped with a HelEx II 2-volume cell, coupled to an Agilent 8800 ICP-QQQ-MS at the Open University, UK. Analyses were carried out with a 10 Hz repetition rate, 3.6 J/cm^2 fluence and a 50 µm spot size. Ablated material was transported in 0.9 l/min He carrier gas mixed with ~0.77 l/min Ar in a down-flow mixing bulk.

Each measurement included 30 s of background measurement prior to ablation, 30s of sample analysis during ablation, and a 40 s washout after ablation ended. Sample analyses were bracketed by analyses of standard reference SRM-NIST 612 (primary for traces, secondary for majors) and BCR-2G (secondary for traces, primary for majors) every 10-12 analyses. Major element concentrations were compared to those measured on the EMPA for further consistency checks. BCR-2G analyses are within 3–10% of preferred values (Jenner and O'Neill, 2012) and long-term lab averages (see Table S4).

The data were reduced using the Iolite software v3.71. Mica analyses were standardised to ^{29}Si concentrations measured in the same or nearby grains in the same polished sections by EMPA. Due to the low concentration of major elements in NIST glasses, Mg, Na, Al, Fe, Ti, Mn, Ca, K concentrations were standardised to BCR-2G; all other trace elements were standardised to NIST612. Raw signals were screened for mis-identification of mica variety (muscovite, chlorite, biotite and sillimanite) or for 3D effects causing mixing during drilling using the Mg, Fe and Al concentrations.

Laboratory & Sample Preparation	
Laboratory name	School of Environment, Earth and Ecosystem Sciences, Open University, UK
Sample type/mineral	muscovite & biotite
Sample preparation	60µm polished thick sections
Laser ablation system	
Make, Model & type	Photon Machines Analyte G2 193 nm excimer laser
Ablation cell & volume	HelEx II 2-volume cell
Laser wavelength (nm)	193 nm
Pulse width (ns)	4 ns
Fluence (J.cm^{-2})	3.63 J.cm^{-2}

Repetition rate (Hz)	10 Hz
Ablation duration (s)	30 s
Spot diameter (mm) nominal/actual	50 mm
Sampling mode / pattern	Static spot ablation
Carrier gas	100% He in the cell, Ar make-up gas combined in a mixing bulb down stream
Cell carrier gas flow (l/min)	0.9 l/min He
ICP-MS Instrument	
Make, Model & type	Agilent 8800 ICP-QQQ-MS
Sample introduction	Ablation aerosol in He & Ar gas mix
RF power (W)	1250 W
Ar carrier gas flow (l/min)	0.77 l/min
Detection system	Dual-mode discrete dynode electron multiplier
Masses measured; Integration time per peak/dwell times (ms)	^{7}Li 0.005, ^{9}Be 0.005, ^{23}Na 0.002, ^{24}Mg 0.005, ^{27}Al 0.002, ^{29}Si 0.002, ^{31}P 0.01, ^{39}K 0.005, ^{43}Ca 0.005, ^{45}Sc 0.005, ^{49}Ti 0.005, ^{51}V 0.005, ^{53}Cr 0.005, ^{55}Mn 0.005, ^{56}Fe 0.005, ^{59}Co 0.005, ^{60}Ni 0.005, ^{65}Cu 0.005, ^{66}Zn 0.005, ^{71}Ga 0.005, ^{74}Ge 0.005, ^{85}Rb 0.005, ^{88}Sr 0.005, ^{89}Y 0.005, ^{90}Zr 0.005, ^{93}Nb 0.01, ^{95}Mo 0.01, ^{111}Cd 0.01, ^{115}In 0.01, ^{118}Sn 0.01, ^{121}Sb 0.02, ^{133}Cs 0.02, ^{137}Ba 0.01, ^{139}La 0.01, ^{140}Ce 0.01, ^{141}Pr 0.01, ^{146}Nd 0.01, ^{147}Sm 0.01, ^{153}Eu 0.01, ^{157}Gd 0.01, ^{159}Tb 0.01, ^{163}Dy 0.01, ^{165}Ho 0.01, ^{166}Er 0.01, ^{169}Tm 0.01, ^{172}Yb 0.01, ^{175}Lu 0.01, ^{177}Hf 0.01, ^{181}Ta 0.01, ^{182}W 0.02, ^{205}Tl 0.02, ^{208}Pb 0.02, ^{209}Bi 0.02, ^{232}Th 0.01, ^{238}U 0.01
Total integration time (s)	0.6566
Data Processing	
Gas blank	30 seconds
Washout	40 seconds
Calibration strategy	SRM-NIST 612 (primary for traces, secondary for majors), BCR-2G (secondary for traces, primary for majors) every 10-12 analyses
Reference Material info	SRM-NIST 612 (Jenner and O'Neill, 2012) BCR-2G (Jenner and O'Neill, 2012 & in house long-term averages)
Data processing package used	Iolite v3.71; DRS: X_Trace_Elements_IS; internal standard ^{29}Si
Uncertainty level & Quality control / Validation	BCR-2G within 3-10% of the preferred value depending on element concentration and homogeneity of secondary standard. Major element concentrations obtained by LA-ICP-MS were compared to those measured by EMPA for consistency checks and data defines on a 1:1 line

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