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Version: Accepted Manuscript

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

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ABSTRACT

Metals such as Li, Be, V, Co, Nb, In, Cs, Sn, Ta, and W are considered resources that are critical for modern economies. They can be significantly enriched in granites and pegmatites, but the mechanisms of enrichment remain poorly understood. Many metal-enriched granitic magmas form through mica dehydration reactions during high-grade metamorphism. The preferential incorporation of these metals into micas provides a mechanism for concentration and mobilisation during crustal melting. Comprehensive datasets of these elements and their partitioning in metamorphic micas across different metamorphic grades are currently lacking. We present the first extensive in-situ LA-ICP-MS element dataset collected from metasediment-hosted muscovite and biotite from three different metamorphic cross-sections traversing sub-greenschist (~400°C) to granulite-facies conditions (>900°C). Within the same sample, Li, V, Co, Cs, and Ta concentrations are higher in biotite, whereas Be, In, Sn, and W concentrations are higher in muscovite. Sub-solidus micas record only non-systematic compositional variations between samples. Supra-solidus biotites show systematic depletion in Li, Be, Sn and Cs and enrichment in V and Co with increasing temperature in the highest-grade (muscovite-absent) samples. Indium and W reach peak concentrations in biotite at 750°C and 850°C respectively. Muscovites record systematic enrichment in In and W and
depletion in Be, Sn and Cs with increasing metamorphic grade. These distinctive trends appear independent of tectonic setting (i.e. continental collision and crustal thinning). Our dataset highlights the importance of higher-temperature melting (>750°C), in particular, biotite breakdown reactions, for the release of Li, Be, Sn, Cs and W into crustal melts.

**INTRODUCTION**

Most trace metal-enriched granites and pegmatites (e.g. Li-Cs-Ta) are highly peraluminous, suggesting they formed via mica-melting reactions from metasedimentary protoliths (e.g., Patiño Douce and Harris, 1998; Cerny et al., 2012). During these reactions, trace elements that are hosted in micas may be released into the melt (Dahl et al., 1993). Along with enriched protolith compositions (Clemens et al., 2009; Romer and Kroner 2016; Wolf et al., 2018), melting reactions may play an important role in generating crustal magmas that are sufficiently enriched to eventually fuel formation of critical metal deposits at shallower levels in the crust (e.g., Linnen et al., 2012; London, 2018). Both fluid-present and fluid-absent reactions involving micas will generate melt, with muscovite melting at lower temperatures and biotite melting at higher temperatures (e.g., Weinberg and Hasalová, 2016).

The concentrations of different elements in these micas, and their behaviour during melting reactions, will influence the composition of the melt produced at different temperatures (Wolf et al., 2018). For example, residuum (melanosomes) in migmatites that formed by muscovite-melting reactions at ~750°C in the Iberian Massif (Spain) are enriched in metals such as Li, Cs, Sn and W compared to the crystallised partial melt (leucosome). However both leucosomes and melanosomes in slightly higher temperature (800°C) migmatites generated by biotite-melting reactions record similar concentrations of these elements (Wolf et al., 2018). These data suggested that higher temperature melting reactions release critical metals (previously stored in restitic mineral phases) into the melt.
It is unclear if these trends and observations can be applied more generally to crustal melting over a larger range of temperatures, different tectonic settings and different protolith compositions. Additionally, direct comparisons between the compositions of leucosomes and melanosomes are compromised by magmatic dilution, crystallisation, segregation or transport (Wolf et al., 2018). The role of sub- and supra-solidus metamorphic reactions in concentrating and releasing critical elements is also poorly constrained. These shortcomings make it difficult to assess why granites that are generated by crustal melting have such variable critical element concentrations. Here we present a new approach for placing constraints on the partitioning of critical elements with increasing temperatures during crustal melting. By measuring the concentrations of 57 elements in-situ in muscovite and biotite from metapelites at different metamorphic grades, we have found systematic changes in the concentrations of different critical metals as temperatures rise and dehydration reactions initiate. This provides a new opportunity to constrain the input of different critical metals into crustal melts at different stages of the metamorphic-melting cycle.

**METHODS and SAMPLE MATERIAL**

We analysed trace element concentrations by LA-ICP-MS in muscovite and biotite in 22 samples from three different metamorphic cross-sections covering sub-greenschist to granulite-facies conditions. Supplementary material S1–4 contains sample descriptions, mineral assemblages, analytical methods and photomicrographs showing laser spot locations. The full dataset of major and trace elements, secondary standards and all element plots are presented in Table S5.

We selected samples from two different tectonic settings. The samples from the Himalayas were metamorphosed during continent-continent collision, whereas the samples
from the Ivrea Zone received their metamorphic imprint during post-orogenic collapse and extension.

The eight samples labelled SK-10-XX were collected from a cross-section through the 5–10 km-thick Main Central Thrust in the Sikkim Himalaya, India. An inverted prograde metamorphic sequence is well-developed across this ductile structure, from low-greenschist (chlorite and biotite grades) at the lowest levels through to upper-amphibolite (kyanite and sillimanite grade) at the highest levels. The sampling localities, sample descriptions and pressure-temperature results are documented in detail in Mottram et al. (2014). This sample set covers the onset of muscovite melting.

The four samples labelled N-XX were collected from the hanging wall of the Main Central Thrust in the Langtang Himalaya, Nepal, from higher structural levels and similar metamorphic grades to the highest-grade Sikkim samples. These samples were metamorphosed at kyanite to sillimanite grade, with coarser leucocratic streaks and patches interpreted as leucosome in samples N5 and N11, across the muscovite-out isograd.

The ten IZ-4XX samples were collected from the Val Strona di Omega, in the Ivrea Zone of the European Alps, Italy. They were metamorphosed at upper amphibolite to granulite facies conditions, and show both muscovite and biotite melting reactions. Sampling localities, sample descriptions and pressure-temperature results are documented in detail in Kunz et al. (2018) and Kunz and White (2019).

RESULTS

The within-sample average concentrations of 26 elements in biotite and muscovite shown in Fig. 1 are normalised to Bulk Silicate Earth concentrations (Palme and O’Neill, 2013) and plotted in order of increasing bulk partitioning behaviour (Jenner, 2017). Both biotite and muscovite record concentration variability within and between samples, and
record enrichments and depletions in the concentrations of some critical elements (e.g., Sn, In, Cs) compared to the composition of the bulk continental crust. We have not observed any systematic patterns in element concentrations with petrographic location. The lowest-temperature samples SK12 and SK15 were too fine grained to acquire “clean” analyses of individual micas and the data are not presented.

Elemental concentrations in biotite vary more systematically than in muscovite particularly in the high-temperature samples from the Ivrea Zone compared to the samples from the lower grade Sikkim section (Figs. 2 and 3; Tab. S1). Specifically, there are systematic changes of up to two orders-of-magnitude in the concentrations of Li, Be, F, V, Co, Nb, In, Sn, Cs, Ta, and W with increasing metamorphic grade that are all greater than analytical uncertainty; we have therefore focussed attention on these eleven elements. Additionally, there are clear differences in concentration between the different field areas that are most likely related to different bulk rock abundances of these elements.

Typically, biotite contains higher concentrations of Li, F, V, Co, Nb, Cs and Ta than muscovite, whereas muscovite systematically hosts higher concentrations of Be, In, Sn and W (Figs. 2 and 3). Concentrations of most elements in muscovite generally show little to no systematic change with increasing metamorphic temperature except in the Langtang samples which show increases in In and W concentrations and decreases in Li, Be and Cs concentrations at supra-solidus temperatures.

Sub-solidus biotites in the Sikkim samples show no systematic changes in trace element concentration. Above solidus temperatures, biotite in the Langtang and Ivrea Zone samples show a gradual decrease in Li, Cs, Be and Sn concentrations and an increase in V and Co concentrations with increasing temperature (Fig. 2). Concentrations of In and W increase in biotite as temperatures increase to ~850 and 750°C respectively; concentrations then decrease with increasing metamorphic grade (Fig. 2). Ta and Nb concentrations remain
fairly constant in biotite with increasing metamorphic temperature, except in the two highest-grade samples that have abundant rutile (Fig. 3).

DISCUSSION

Controls on trace element concentrations in sub-and supra-solidus phases

Our data show that Li, Cs, and Ta (commonly enriched together in LCT-pegmatites) are predominantly hosted in biotite, while Be, Sn, and W are predominantly hosted in muscovite (c.f. Dutrow et al., 1986; Dahl et al., 1993; Bea et al., 1994; Yang and Rivers, 2000; Tischendorf et al., 2001; Neiva et al., 2002; Van Lichtervelde et al., 2008; Simons et al., 2017). In the sub-solidus samples, concentrations of most critical metals measured in both micas are variable and show no systematic changes. For example, in the Sikkim samples SK19–SK22 (which equilibrated at similar temperatures within uncertainty of 650–700°C) we observe an order-of-magnitude difference in Li and Ta concentrations in both micas. We therefore interpret this as either reflecting (i) differences in bulk composition and therefore different initial trace element abundance (Romer and Kroner, 2016), or (ii) differences in the continuity of this metamorphic sequence due to ductile deformation.

Partitioning of metals between biotite and muscovite can be explained by differences in site and interlayer site preferences of these elements (Dahl et al., 1993). The apparent increase in concentration of V, Co, and In in biotite with increasing metamorphic grade could be an effect of decreasing modal abundance of biotite. However, the concentration increase starts at the onset of muscovite melting when the modal abundance of biotite is still increasing. Therefore we interpret the observed trends for these elements as resulting from differential partitioning in the presence of a melt phase. Conversely, the increase of W in muscovite coincides with the decrease in modal abundance of muscovite, suggesting that this might be a modal abundance effect.
The partitioning of critical metals between micas and other metamorphic minerals may also be important at sub- and supra-solidus conditions. For example Li is hosted in tourmaline and staurolite (e.g., Dutrow et al., 1986; London, 2011), Be in cordierite (Evensen and London, 2002) and Sn and W in rutile, ilmenite and titanite (e.g., Zack et al., 2002; Klemme et al., 2006). However, there are currently only sparse datasets for many critical metals for solid/solid partitioning at high-temperature metamorphic conditions (e.g., Icenhower and London, 1995; Dutrow et al., 1986) making a quantification of partitioning difficult to assess.

Implications for the formation of enriched granites and pegmatites

Our dataset demonstrates the importance of melting reactions involving biotite for the concentration (in the melanosome) and release (into the leucosome) of a number of critical metals, specifically Li, Be, Sn, Cs and W. Biotite is widely present in a variety of bulk-rock compositions and is a known host of critical metals (e.g. Dahl et al., 1993; Evensen and London, 2002). Our data show that concentrations of these elements in metapelitic biotite remains approximately constant until the onset of biotite dehydration melting reactions, when these elements are released into the melt. Our findings are in agreement with bulk rock data from the Ivrea Zone (Bea and Montero, 1999) that show a similar depletion in bulk rock for Li, Be, Cs and an increase in V with metamorphic grade.

This scenario of high-temperature biotite melting as the key for the enrichment of Li-Cs-Ta in the melt is in conflict with previous hypothesis of LCT-enriched pegmatites being generated by minimum-temperature melting of muscovite (e.g. Cerny, 1991; Romer and Kroner, 2015, 2016). Instead, our data suggest that enrichment of LCT-enriched granitic magmas most likely occurs during low-volume biotite melting of a mostly muscovite-absent assemblage, a scenario that has also been argued for granitic Sn enrichment (Wolf et al.,
Biotite provides the source of these elements as well as a mechanism for allowing more effective melt and metal transport. Crustal melts are viscous (Rutter and Neumann, 1995) and therefore difficult to mobilise without additional help, e.g. from pervasive ductile deformation or the addition of fluxing elements such as F, which lower melt viscosity (Dingwell et al., 1996). Additionally, F allows metals to be transported in the melt more readily through complexing (London, 1987). High-temperature biotite can host F at weight-% levels (Finch and Tomkins, 2016); in our samples the Sikkim and Ivrea Zone biotites contain higher F concentrations than muscovite (0.13–1.6 wt% F compared to 0.04–0.16 wt% F respectively; Fig 2).

Sn and W enrichments in granites have been linked to high-temperature melting of a biotite-rich source (Romer and Kroner, 2016; Wolf et al., 2018). Our data show that, in general, concentrations of Sn and W are higher in muscovite than in co-hosted biotite. Concentrations of W in muscovite increase slightly with metamorphic grade; we do not observe systematic changes of Sn concentrations in muscovite with metamorphic grade. In contrast, biotite from the Ivrea Zone and Langtang samples show clear decreases in Sn and W concentrations with increasing metamorphic grade. This observation supports the theory of higher-temperature melting being critical for melt enrichment (Wolf et al., 2018; Michaud et al., 2021). However we do not observe sequestering of Sn into biotite across the muscovite-melting temperature interval, as previously suggested (Wolf et al., 2018).

Further investigation into different biotite melting reactions, including those which are fluid-absent or fluid-present, are needed to understand the conditions/reactions under which critical metal release is optimised and therefore provides the highest potential for melt enrichment. Biotite is also a key constituent in non-pelitic metasediments (e.g. meta-
graywackes) that may also be source rocks for enriched granites and pegmatites. Focus on biotite-melting reactions across a range of metasedimentary bulk compositions is therefore key to constraining how and under which conditions critical metal enriched granites and pegmatites form.

CONCLUSIONS

Micas are the main reactant during dehydration melting of metasediments. As micas host significant concentrations of many critical metals and H$_2$O, their breakdown facilitates the transfer of these metals from metamorphosed country rocks into melts. Our data show that prograde sub-solidus metamorphic reactions do not lead to systematic changes in the concentrations of different critical metals in micas. Upon crossing the muscovite dehydration solidus, both muscovite and biotite concentration for Cs and Be start to decrease, while W concentration increase. Once conditions for biotite dehydration melting are reached, concentrations of Li, Be, Sn, Cs, and W in biotite decrease markedly as they are released into the melt.

ACKNOWLEDGMENTS

We’d like to thank G. Degli-Alessandrini for help with EMPA work at the OU. K. Goodenough and R. Shaw (BGS) for fruitful discussions and C. Mottram for providing thin sections from the Sikkim section. We thank three anonymous reviewers for their constructive comments and Gerald Dickens for editorial handling.

FIGURE CAPTIONS

**Fig. 1** Average trace element concentration per sample of (a) muscovite (b) biotite. Normalised to Bulk Silicate Earth (Palme and O’Neill, 2013); black line is the composition of
the bulk continental crust (Rudnick and Gao, 2003); element ordering is based on bulk partitioning during differentiation of mid-ocean ridge basalts (Jenner, 2017).

**Fig. 2** Concentrations of Li, F, Cs, Be, Sn, W, V, Co and In vs. peak metamorphic temperature. Grey shaded areas represent muscovite- (light grey) and biotite-melting (dark grey) ranges. Trends in: biotite (solid arrow), muscovite (dashed arrow) data.

**Fig. 3** Concentration of Nb and Ta vs. peak metamorphic temperature. Grey shaded areas represent muscovite- (light grey) and biotite-melting (dark grey) ranges. Trends in: biotite (solid arrow), muscovite (dashed arrow) data.

**SUPPLEMENTARY MATERIAL**

**APPENDIX 1.** Sample description

**APPENDIX 2.** Table with mineral assemblages

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

**APPENDIX 4.** LA-ICP-MS spot location

**APPENDIX 5.** Major and trace element data table for samples and secondary standard

**REFERENCES CITED**


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Figure 1

Kunz et al., Fig. 1
Figure 3