# How much metal can you get? Quantified mass balancing of base metal release during epidosite zone alteration in ophiolite-hosted VMS systems

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**Abstract.** Understanding source-deposit relationships in VMS systems is important for mineral exploration and to increase knowledge of seafloor hydrothermal processes and ocean–crust fluxes. Although it is known that metals are stripped from oceanic crust by hydrothermal fluids and are partly redeposited in orebodies, some aspects are poorly understood. It has been proposed that metal-depleted epidosites (epidote–quartz–chlorite–Fe-oxide–titanite units within sheeted dyke complexes) were the source rocks for ophiolite-hosted VMS deposits. To test this hypothesis, the Spilia-Kannavia epidosite zone in the Troodos ophiolite, Cyprus, was investigated. This zone ($\geq 1.9$ km$^3$), at the base of the Sheeted Dyke Complex, extends ~5 km parallel to and ~2 km across dyke strike and vertically $\geq 400$ m. During alteration, this zone released ~0.4 Mt Zn, ~0.06 Mt Ni, ~5.2 Mt MnO, and 0.14 Mt Cu. This exceeds the Zn within any ophiolite-hosted VMS deposit, and provides enough Cu for a medium-large deposit. In comparison, published data suggest a similar volume of background diabase could mobilise less Zn, Cu and Ni and no Co or Mn. It is concluded that epidosite zone formation releases significant amounts of base metals into ophiolite-hosted VMS systems.

**Keywords:** VMS, source rock, epidosite, ophiolite

## 1 Introduction

Understanding the mobilisation and removal of base metals during alteration of igneous rocks within ophiolite-hosted Volcanogenic Massive Sulphide (VMS) systems is important for both mineral exploration and our knowledge of processes occurring in modern-day VMS systems. In particular, it has been proposed that metal-depleted epidosites within the Sheeted Dyke Complex of ophiolites are the source of metals for ophiolite-hosted VMS deposits (e.g. Richardson et al. 1987). However, the mobilisation and removal of base metals from epidosite zones during hydrothermal alteration has yet to be quantified. Indeed, quantification is important as without it, it is impossible to know whether these zones could provide enough base metals, and in the right ratios, to form VMS deposits. An alternative source of base metals is the incipient alteration found within the majority of the Sheeted Dyke Complex outside of epidosite zones. However, whether this alteration (here termed *background diabase*) could have provided appropriate amounts of base metals to form VMS deposits is, again, unknown. In addition, the

movement of Co and Ni, metals which are concentrated in VMS deposits (Constantinou 1980) and are generally immobile during sub-seafloor alteration (Pearce 1996) has also not been satisfactorily addressed.

To investigate the processes that mobilise metals in VMS systems, this study focuses on the Spilia-Kannavia epidosite zone at the base of the Sheeted Dyke Complex in the Troodos ophiolite, Cyprus. This is a site where intense water-rock interaction occurred (e.g. Richardson et al. 1987). It comprises a mixture of epidosite (an alteration assemblage of epidote-quartz-chlorite-Fe-oxide-titanite) and epidosite zone diabase (amphibole–albite–chlorite–epidote–quartz–Fe-oxide–titanite) units and is located in an elongate zone parallel to dyke strike.

## 2 Mass Balance Calculations

### 2.1 Prerequisites

To undertake mass balance calculations and determine the amount of base metal mobilised during Spilia-Kannavia epidosite zone formation a number of variables need to be quantified:
a) The volume of the epidosite zone;
b) The variability of alteration in the epidosite zone;
c) The change in composition during alteration.
Quantification of these parameters is discussed below.

### 2.2 Volume of the Spilia-Kannavia epidosite zone

The Spilia-Kannavia epidosite zone represents the largest known epidosite zone on Cyprus. Previously, it was described as two separate epidosite zones (Richardson et al. 1987), however, new mapping shows it to be continuous. It has an areal extent of 5 km by up to 2 km across dyke strike, with a minimum thickness of ~400 m. Based on this mapping its minimum volume is estimated to be $\geq 1.9$ km$^3$.

### 2.3 Variability of alteration

Altered samples were assigned to one of four differing facies according to mineralogy. The first is an actinolite and plagioclase rich rock that retains an igneous texture and is similar to the background diabase found outside of epidosite zones. This is termed *epidosite zone*

*diabase*. Increasing abundance of chlorite and loss of an igneous texture defines a second *transitional diabase-epidosite facies*. Decreasing modal chlorite and increasing epidote and quartz, characterises the transition to *intermediate epidosite facies*. Rocks consisting entirely of epidote and quartz define an *end-member epidosite facies* (Fig. 1). These four facies may represent a continuum of alteration and can be closely spatially related even within a single dyke. These distinctions allow the epidosite zone to be characterised in terms of individual units, each with their own distinctive base metal budgets. The relative abundances of these differing facies were determined by detailed lithological logging over small (e.g. cm scale over 4 m) and medium (e.g. every 10s of metres over 0.8-1 km) scale. These data indicate that the epidosite zone is composed of around 5% end-member epidosite, 30% intermediate epidosite, 41% transitional diabase-epidosite and 24% epidosite zone diabase facies.
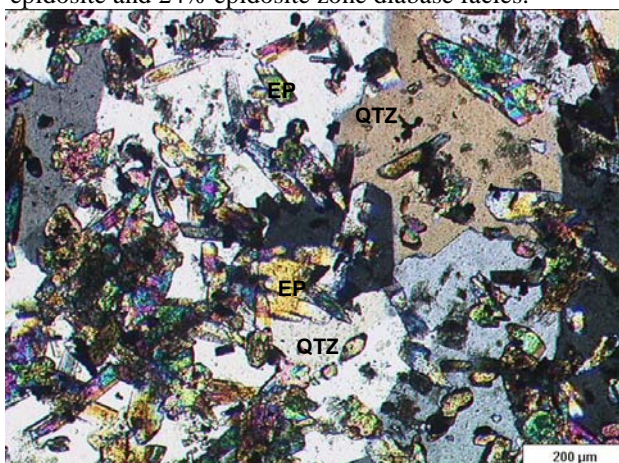


**Figure 1**. Photomicrograph (crossed polars) showing typical end-member epidosite mineralogy dominated by epidote (EP) and quartz (QTZ), with no remnant igneous texture.

## 2.4  Background diabase alteration

A database of the compositions of background diabase outside of epidosite zones was compiled (Baragar et al. (1989), Tarney and Marsh (1987) and Adamides (1984)). These data were used because the sampling in these studies was generally distant from any known epidosite zones, decreasing the likelihood of samples being affected by the same processes that formed these zones. This means a clear distinction can be drawn between epidosite zone diabase and background diabase alteration. As a result, a direct comparison can be made between base metal mobility during both epidosite and non-epidosite alteration within the Sheeted Dyke Complex of the Troodos ophiolite.

## 2.5  Release of Base Metals

Whilst no unaltered units exist in the Sheeted Dyke Complex to provide direct analogues to the altered Spilia-Kannavia epidosite zone, fresher units occur in the overlying lava sequences. The only material within the Troodos ophiolite that retains melt compositions is volcanic glass found within these lavas. As all lavas must have been fed through a dyke, lava compositions

must be reflected in the Sheeted Dyke Complex. It is plausible that there are dyke compositions for which there are no eruptive equivalents; however, using the volcanics to define differentiation trends allows any intermediate, unerupted, compositions to be constrained.

The release of base metals was determined by comparison between protolith compositions and altered samples. Protolith compositions were determined by electron probe microanalysis (EPMA; MnO, at the University of Leicester) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS; Co, Ni, Cu and Zn, at the British Geological Survey) of fresh volcanic glass from the Troodos ophiolite. Volcanic glass samples were used as they may not have been modified by post-formation processes. Furthermore, alteration or devitrification of the glass could be identified during optical and SEM examination and excluded from LA-ICP-MS analysis.

Before comparison to altered samples the glass data were filtered using immobile elements to enable the selection of a subset that represented protoliths for the Spilia-Kannavia epidosite zone. These glass data were used to generate equations relating the protolith base metal concentration to that of an immobile trace element (Zr and Y). This allows changes in protolith base metal concentrations generated by magmatic differentiation to be 'seen through' and base metal release to be calculated (e.g. Fig. 2).
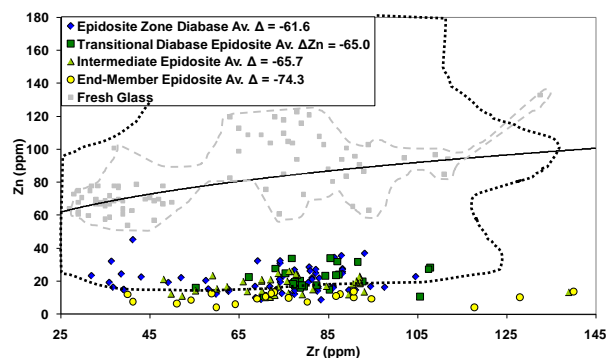


**Figure 2**. Example of a bivariate variation diagram used to calculate base metal mobility in this study. Zn and Zr data are shown for fresh glass data (grey squares and the dashed grey field), altered epidosite zone samples (coloured symbols) and the background diabase data (dotted black line, extending to concentrations >180 ppm Zn) in this example. A fractionation equation is used to construct a best fit line for base metal concentrations in the fresh glass, shown in black; any movement along the y-axis away from this line that is greater than the standard deviation of the glass data (±13.1 ppm Zn) can be ascribed to loss or gain during alteration.

# 3  Mass Balance Calculations

## 3.1  Methodology

The total amount of metal removed or added during hydrothermal alteration must be determined to enable comparison of the amounts of base metals released from the Spilia-Kannavia epidosite zone with the amounts in Cyprus-type VMS deposits. The metal budget for an individual alteration facies can be calculated using:

$$Metal = (V \times \rho) * (\Delta Zn / 1000000)$$

where *Metal* (t) equals the total amount of metal lost or gained, $V$ (m$^3$) is the volume of altered rock, $\rho$ (t m$^{-3}$) is rock density and $\Delta Zn$ (ppm) is the average change in elemental abundance during alteration. To give an overall value for base metal change the result for each facies was multiplied by its abundance within the Spilia-Kannavia epidosite zone. Mass balance calculations for background diabase of equal volume to the Spilia-Kannavia epidosite zone were also undertaken.

## 4 Epidosite Zones versus VMS Deposits

The formation of the Spilia-Kannavia epidosite zone released ~0.4 Mt of Zn, ~0.06 Mt of Ni, ~5.2 Mt of MnO and ~0.14 Mt of Cu (Fig. 3). The Zn released during the formation of the Spilia-Kannavia epidosite zone exceeds that contained within any single Troodos VMS deposit, whilst the amount of Cu released could form a medium to large size orebody. This is in contrast to background diabase alteration, which can only release around a third of the Zn for an identical volume of rock. This is enough to form most ophiolite-hosted VMS deposits, although an order of magnitude less Cu is released. In addition to Cu and Zn, Co is a common minor constituent in VMS deposits. However, in the Spilia-Kannavia epidosite zone, only the end-member epidosite alteration facies is capable of mobilising significant Co (3200 t). Thus epidositisation is the only effective method of mobilising Co. Furthermore, the large amount of Mn released during epidosite formation indicates that this alteration may be directly associated with the formation of umbers in VMS systems (e.g. Boyle 1990). This contrasts with background diabase alteration which has no apparent depletion in Mn.
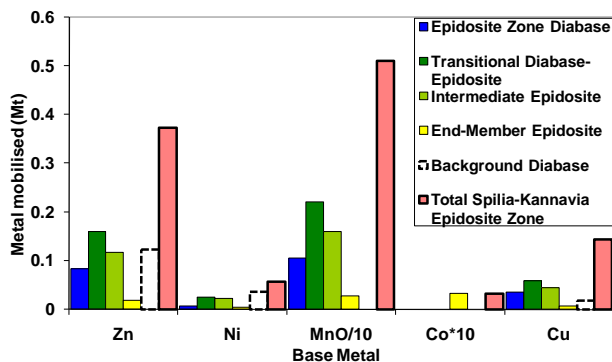


**Figure 3.** Base metals removed from individual alteration facies and the entire Spilia-Kannavia epidosite zone (with bold outline) compared to background diabase (with dashed outline). Note that MnO is presented as MnO/10 and Co as Co*10 for scaling purposes.

In addition, ratios of base metal removal during epidosite formation also correlate with ratios of base metal concentrations in ophiolite-hosted VMS deposits, unlike background diabase alteration. Though processes such as zone refining and differential precipitation efficiency may modify Cu:Zn ratios these modifications would have to be extreme for fluids derived from altering background diabase to produce VMS-like ratios.

## 5 Conclusions

Mass balance calculations show that epidosite zone-type alteration is not a prerequisite to form ophiolite-hosted VMS deposits as background diabase alteration outside of epidosite zones can supply a significant amount of Zn and a minor amount of Cu to active VMS systems. However, negligible Mn or Co is released by this alteration, and the amount of Cu released during background diabase alteration is far smaller than that released during epidosite zone formation. Indeed, ratios of base metal release during the formation of the Spilia-Kannavia epidosite zone are closer to the ratios of Troodos VMS deposits than those associated with background diabase alteration. This strongly suggests that epidosite facies alteration plays an important role in the formation of base-metal rich ophiolite-hosted VMS deposits and that epidosites are linked to larger, more Ni-Co rich deposits.

## Acknowledgements

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