Vanadium Deportment in the Middle Ore Layer (MOL) of the Mustavaara Fe–Ti–V Deposit, Northern Finland: Implications for Beneficiation

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1. Introduction

The Mustavaara Fe–Ti–V deposit in northern Finland hosts a significant vanadium-bearing titanomagnetite (VTM) resource within the ~2.44 Ga Koillismaa layered intrusion (Juopperi, 1977; Karinen et al., 2022), and is part of a globally significant class of vanadium resource associated with mafic–ultramafic layered intrusions (Cawthorn et al., 2005; Charlier et al., 2015; Simandl and Paradis, 2022). Currently, there is no primary vanadium production in Europe. The European Commission included vanadium on the EU Critical Raw Materials list in 2017, and low-grade European VTM deposits such as Mustavaara are being re-evaluated in an effort to establish decarbonised critical-metal supply chains. This work forms part of the Horizon Europe AVANTiS project (Grant Agreement No. 101137552), targeting sustainable co-extraction of vanadium and titanium from Europe's low-grade VTM resources. Mustavaara was mined from 1976 to 1985 as an open-pit operation by Rautaruukki company, and together with the orthomagmatic Otanmäki mine, it was a significant historical source of vanadium (Karinen et al., 2015).

Conventional processing models for VTM ores assume that vanadium is hosted predominantly in titanomagnetite and therefore recovered through magnetic separation followed by pyrometallurgical extraction. This study shows that pervasive post-magmatic hydrothermal alteration at Mustavaara has redistributed a meaningful proportion of the vanadium budget into secondary silicate phases, with direct consequences for beneficiation strategy.

2. Geological setting

The Mustavaara magnetite gabbro forms a coherent, layered body within the upper stratigraphic part of the Porttivaara Block of the Koillismaa intrusion (Juopperi, 1977), located at the western part of the 2.4 Ga Koillismaa-Näränkävaara igneous complex. The stratigraphy of the oxide-bearing units in the sheet-like intrusion, up to 3 km thick and 100 km in strike length, is subdivided into four ore layers (Disseminated, Upper, Middle, and Lower), each differing in modal oxide abundance and associated Ti–V anomalies. Fe–Ti oxides occur as ilmenomagnetite (magnetite hosting fine cloth-type and coarser trellis-type ilmenite exsolution lamellae; van Gerve et al., 2026), which is a defining textural feature of VTM mineralisation,

rather than discrete magnetite and ilmenite grains. Regionally, titanomagnetite V_2O_3 content across the intrusion is relatively consistent, containing 1.0–1.5 wt% (≈1.21–1.82 wt% V_2O_5) (Karinen et al., 2022).

3. Materials and methods

Six polished thin sections were prepared from two previously studied drill cores, MV-63 and MV-64 (Karinen et al., 2015, 2022), sampling the Middle Ore Layer (MOL) at depths of 133–186 m and spanning a range of hydrothermal alteration intensity. Mineral textures were characterised by transmitted- and reflected-light petrography and field-emission scanning electron microscopy (FE-SEM: JEOL JSM 7100F, 20 kV, 1 nA). Phase-specific compositions, including vanadium, were determined by electron microprobe analysis (EPMA: JEOL JXA-iHP200F, WDS mode, 20 kV, 20 nA, 1-20 µm defocused beam). All elements were measured on Kα lines except vanadium, measured on Kβ to avoid the Ti Kβ–V Kα overlap (Cr Kα, the nearest potential interference on V Kβ, was negligible, Cr_2O_3 < 0.03 wt%). Matrix correction was via the XPP algorithm (Pouchou and Pichoir, 1991), and background was determined by mean-atomic-number correction (Donovan and Tingle, 1996). Per-analysis detection limits for V were 0.06–0.07 wt% V_2O_5 (≈320–390 ppm V), depending on the matrix. Analyses below the detection limit were retained in the phase means. Some sections were additionally mapped by micro-XRF (Bruker M4 Tornado Plus, 50 kV, 600 µA, 20 µm spot), and chemical analyses (ALS methods ME-XRF21n for main elements, and ME-MS61L for trace elements) were obtained from for the sample suite. A mineral-scale vanadium mass balance was constructed by combining EPMA vanadium concentrations with modal mineral proportions from automated mineralogy image analysis, converted to mass% using standard mineral densities and normalised to 100%, to estimate the proportion of the total vanadium budget hosted in magnetically recoverable oxide phases (magnetite, ilmenite) in concentrate versus silicate and reaction-product phases in tailings. The mass-balance-derived bulk vanadium content was cross-checked against measured bulk-rock geochemistry (Section 4.3) as an independent validation.

4. Results

4.1. Petrography and modal mineralogy

The MOL is a small- to medium-grained plagioclase–clinopyroxene–ilmenomagnetite cumulate (Figure 1), dominated by plagioclase (30–42 vol%, 25–37 wt%) and clinopyroxene (18–25 vol%, 18–27 wt%), with combined magnetite + ilmenite contents of 7–11 vol%, rising to 12–18 wt% owing to the higher density of the oxide phases; the same density contrast explains why plagioclase and clinopyroxene show correspondingly higher vol% than wt%. Alteration minerals (amphibole, epidote, chlorite, titanite, minor biotite) collectively represent a substantial secondary mineral population, reflecting extensive post-magmatic hydrothermal overprinting.

Drill core MV-63 shows pronounced alteration with depth: primary clinopyroxene is largely replaced by uralitic amphibole, a fine-grained amphibole that pseudomorphously replaces pyroxene during hydrothermal alteration (uralitisation; Leake et al., 1997), rimmed by chlorite, and plagioclase is altered to epidote and sericite along transecting fractures (Figure 1). Combined alteration-mineral content increases from 18.9 vol% at 153 m to 28.0 vol% at 185 m depth in MV-63, with amphibole reaching 13.9 vol% and chlorite 4.2 vol% in the deepest section. MV-64 is petrographically similar but more texturally uniform with depth. At equivalent depths, MV-63 consistently shows more advanced alteration than MV-64, with amphibole

content (13.9 vol%) nearly doubling the equivalent MV-64 section (7.1 vol%) at the expense of primary clinopyroxene.

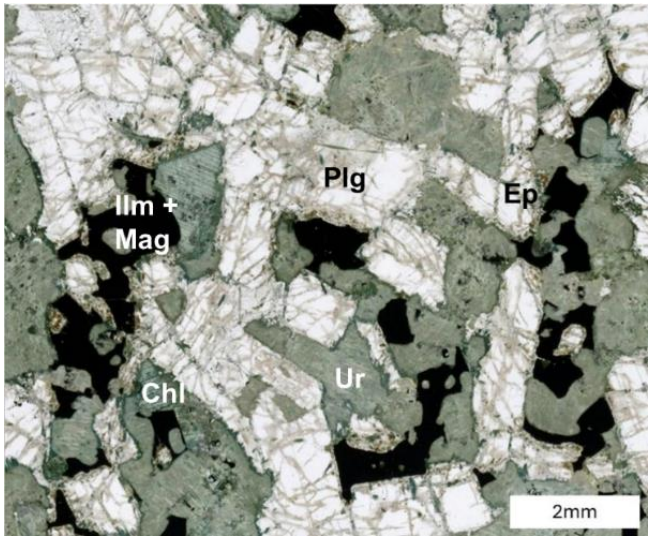


Figure 1. Uralites (Ur) after pyroxene alteration (green), with oriented exsolution lamellae (striped minerals) and blueish chlorite (Chl) rims. Plagioclase (Plg, white) is altered to epidote (Ep) and sericite along traverse fractures. Ilmenomagnetites (Ilm+Mag) are opaque (black) minerals, filling interstitial cavities between silicates.

4.2. Mineral chemistry and vanadium deportment

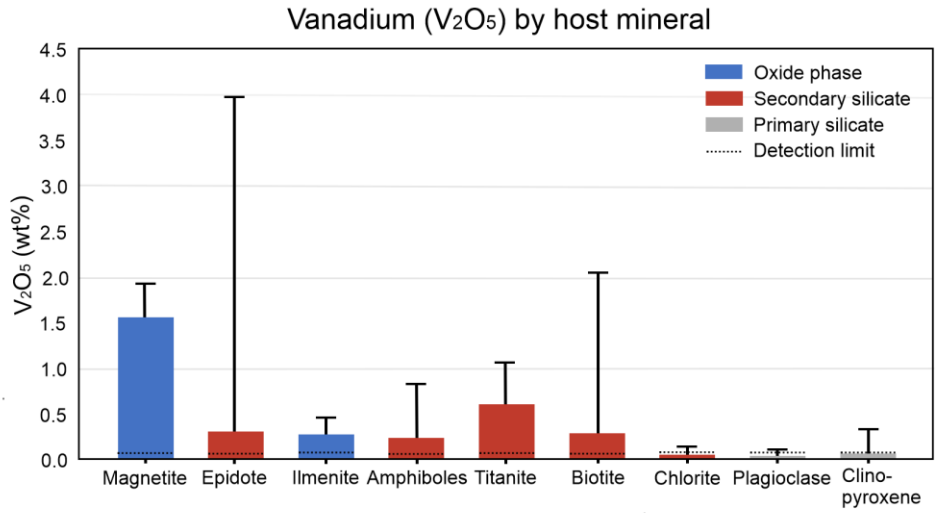
EPMA analyses confirm magnetite (n = 106) as the principal vanadium host (FeOt average 89.6 wt%; V_2O_5 0.97–1.91 wt%, average 1.56 wt%; TiO_2 averaging 0.82 wt%, up to 5.87 wt% owing to sub-microscopic ilmenite lamellae). Ilmenite (n = 103) carries only minor vanadium (V_2O_5 up to 0.42 wt%, average 0.26 wt%) alongside 44.0–51.2 wt% TiO_2 and notable Mn (1.65–2.72 wt% MnO). Titanite (n = 16), which forms at magnetite–ilmenite interfaces as a fluid-mediated reaction product, contains V_2O_5 averaging 0.61 wt% (0.07–1.04 wt%), a minor but distinct additional vanadium host.

The primary silicates plagioclase (n = 45) and clinopyroxene (n = 160) contain very little vanadium (0.01 and 0.06 wt% V_2O_5 respectively, below and at the detection limit), indicating that silicate-hosted vanadium is predominantly alteration-driven rather than a primary magmatic signature. Vanadium partitions significantly into secondary silicates (Figure 2). Epidote (n = 102) is the principal secondary carrier, averaging 0.29 wt% V_2O_5 (median 0.20) and reaching up to 3.98 wt% in localised, fracture-associated domains in sample 253, comparable in magnitude to magnetite itself. This epidote is Fe-rich (11.2 wt% FeO), within the compositional field of epidote sensu stricto (Armbruster et al., 2006), which may itself favour vanadium uptake alongside crystal-chemical compatibility (Franz and Liebscher, 2004). Amphibole (n = 189) is the second-most significant silicate host (0.22 wt% V_2O_5, up to 0.81 wt%), additionally carrying notable Cl (average 0.41 wt%, up to 1.15 wt%), consistent with crystallisation from saline hydrothermal fluids. Biotite (n = 6) contains approximately 0.28 wt%, up to 0.38 wt% V_2O_5, whereas chlorite (n = 10), despite forming part of the same alteration assemblage, carries no significant vanadium (average 0.03 wt%, below the detection limit), indicating that vanadium uptake is mineral-specific rather than a general property of alteration, with implications for using bulk alteration indices as a proxy for vanadium loss. Detection rates for vanadium close to the analytical detection limit. Substitution of V^{3+} for Al^{3+} and Fe^{3+} in the octahedral sites of epidote and amphibole provides a plausible crystal-chemical mechanism,

consistent with direct structural evidence that V occupies the same octahedral M-sites in epidote-supergroup minerals (Bačík et al., 2023). Exclusion of chlorite in vanadium despitentrated along fractures, indicates vanadium was mobilised from primary oxides and locally reprecipitated during fluid–rock interaction.

4.3. Bulk geochemistry

Whole-rock geochemistry supports the silicate-dominated bulk composition of the MOL: SiO_2 ranges from 37.3 to 43.5 wt%, FeOt from 19.9 to 23.8 wt%, Al_2O_3 from 13.2 to 14.0 wt%, MgO from 4.5 to 5.2 wt%, CaO from 9.0 to 10.0 wt%, and TiO_2 from 2.5 to 3.9 wt%, with the highest TiO_2 values coinciding with the lowest SiO_2, consistent with local oxide enrichment. Vanadium ranges from 1470 to 2180 ppm (average 1767 ppm) and correlates positively with TiO_2, consistent with its dominant association with Ti–V oxide phases. Minor Cu (583–711 ppm), Ni (121–147 ppm), and Co (81–100 ppm) represent potential by-products.



	Magnetite	Epidote	Ilmenite	Amphiboles	Titanite	Biotite	Chlorite	Plagioclase	Clino-pyroxene
n	106	102	103	189	16	6	10	45	160
Modal (wt%)	11.7%	9.2%	3.5%	9.6%	0.7%	0.9%	2.5%	30.2%	22.8%
% above DL	100%	81%	99%	72%	100%	100%	30%	4%	44%

Figure 2. Vanadium (as V2O5, wt%) by host mineral in the Mustavaara MOL, including oxides, secondary silicates, and primary silicates. Bars show mean values, with below-detection analyses retained. Whiskers show maximum. Dashed grey lines mark the mineral-specific

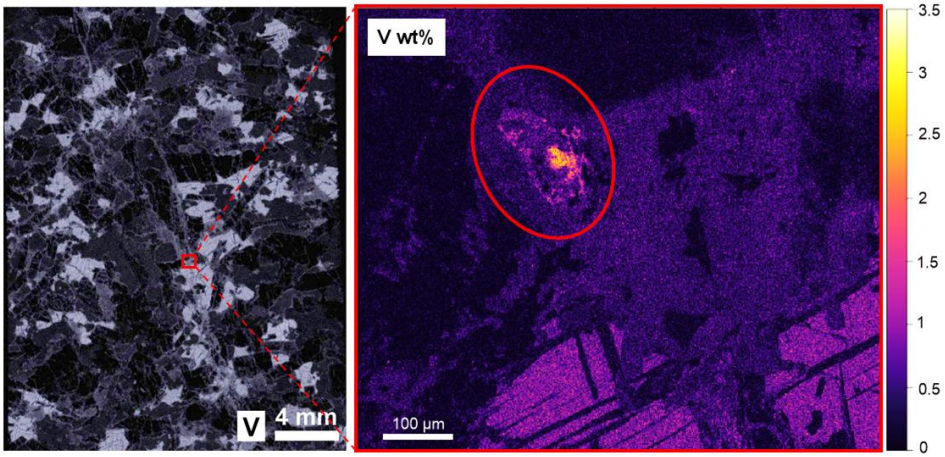


Figure 3. Vanadium distribution in sample 202400253 (drill core MV-63). The left panel shows a micro-XRF vanadium intensity map, where bright grains are V-rich magnetite and the bright, thread-like network follows fracture-hosted epidote. The right panel shows a q

5. Discussion

5.1. Implications for vanadium recovery

Hydrothermal alteration has redistributed a portion of the vanadium from primary oxide phases into secondary silicate minerals, potentially reducing its recovery by conventional processing methods. A mineral-scale mass balance (Table 1) combining EPMA vanadium concentrations with modal mineralogy indicates that magnetite and ilmenite together host, on average, 74% of the estimated vanadium budget with the remaining 26% hosted mostly in secondary alteration phases (about three quarters) and, to a lesser extent, in primary clinopyroxene and plagioclase, where vanadium is at or near the detection limit. Treating sub-detection-limit values as zero lowers this share by only ~1 percentage point. This non-recoverable fraction ranges from 19% to 39%, rising to its highest values in the most fracture-altered samples, including sample 253, the section hosting the V-rich epidote domain described above. This mass balance is broadly consistent with measured bulk-rock geochemistry (see section 4.3): the calculated mean bulk vanadium content (V 1628 ppm) is within 8% of the measured mean (V 1767 ppm), with individual samples showing greater scatter, reflecting simplifying assumptions in the mass-balance approach (e.g. literature-derived density, unidentified minerals with assumed densities, and grouped mineral classes in modal mineralogy analysis) and the altered character of Mustavaara MOL.

Table 1. Vanadium mass balance by thin section, combining EPMA mineral V_2O_5 concentrations with modal mineralogy. Oxide-hosted = magnetite + ilmenite (magnetically recoverable), non-recoverable = all remaining minerals (epidote, amphibole, titanite, biotite, chlorite, clinopyroxene, plagioclase). Of the non-recoverable fraction, approximately three-quarters is hosted in secondary alteration minerals (epidote, amphibole, titanite, biotite), with the remainder in primary clinopyroxene and plagioclase, where vanadium lies at or near the detection limit.

Sample	Drill core	Oxide-hosted V (%)	Non-recoverable V (%)
202400251	MV-63	74.8	25.2
202400252	MV-63	78.9	21.1
202400253	MV-63	61.1	38.9
202400254	MV-64	71.3	28.7
202400255	MV-64	76.6	23.4
202400256	MV-64	81.1	18.9
Mean (n = 6)		**74.0**	**26.0**

This redistribution has direct implications for VTM processing. Conventional flowsheets rely typically on magnetic separation to recover an oxide concentrate, followed by pyrometallurgical roasting or smelting to extract vanadium into a form amenable to subsequent recovery: pentoxide (V_2O_5) or ferrovanadium (Xu et al., 2025). Vanadium hosted in silicate phases is not amenable to magnetic concentration and will preferentially report to non-magnetic tailings, a loss mechanism that scales with local alteration; because V-enriched epidote locates along irregular, fracture-controlled pathways rather than a texturally predictable population, conventional physical separation cannot selectively target it. Vanadium extraction technologies are optimized for oxide mineral phases, whereas vanadium structurally incorporated into silicate minerals is generally less amenable to conventional extraction. Recovery of silicate phase bound vanadium requires intensive thermal and/or chemical treatment to disrupt the silicate structure and liberate vanadium, potentially resulting in higher energy and/or reagent requirements. A closely analogous substitution mechanism, V^{3+} replacing Al^{3+} in mica lattices, underlines the well-documented difficulty of recovering

vanadium from Chinese stone coal, the dominant published analogue for silicate-hosted vanadium extraction generally (Zhang et al., 2011; Wang et al., 2024).

5.2. Processing considerations

Vanadium-bearing oxide phases are recoverable by low-intensity magnetic separation. Flotation is relevant for the recovery of exsolved ilmenite lamellae. However, the presence of altered silicates, including clinopyroxene, amphibole, and chlorite, introduces mineral-scale surface and textural heterogeneity that affect the flotation response. These effects should be evaluated through dedicated bench-scale flotation testing, which is beyond the scope of the present study. Comminution is also affected by textural complexity of Mustavaara MOL: the fine-scale (<2 μm) cloth-type ilmenite exsolution lamellae in magnetite are effectively below the practical limits of conventional comminution, while coarser (2–50 μm) trellis-type lamellae are more amenable to liberation by conventional grinding, consistent with texture-controlled liberation behaviour documented for cloth- versus trellis-textured Bushveld magnetite (van Gerve et al., 2026). Given this complexity, a staged processing approach is recommended. Complete physical separation of magnetite and ilmenite is unlikely to be achievable. Therefore, the production of a bulk oxide concentrate through magnetic separation represents a more realistic first-stage target than separate magnetite and ilmenite concentrates. As MV-63 and MV-64 differ systematically in alteration intensity and oxide content, domain-based ore characterisation and blending are recommended before flowsheet design.

6. Conclusions

Vanadium deportment in the Mustavaara MOL is controlled by the interplay between primary magmatic crystallisation and secondary hydrothermal alteration. While ilmenomagnetite remains the dominant vanadium host (V_2O_5 average 1.56 wt%), a substantial and spatially heterogeneous proportion of the vanadium budget, locally occurring at concentrations comparable to those measured in the oxide phase, resides in secondary epidote (up to 3.98 wt% V_2O_5) and, to a lesser extent, amphibole, biotite, and titanite. Together, these silicate minerals, with a minor contribution from primary clinopyroxene and plagioclase (near the detection limit), account for an average of 26% of the total vanadium budget (Table 1), increasing to 39% in the most altered sections.

Chlorite, despite forming part of the same alteration assemblage, contains negligible vanadium, confirming that uptake is mineral-specific rather than a general property of alteration intensity. This silicate-hosted vanadium is not recoverable by conventional magnetic separation and represents a loss mechanism that scales with alteration intensity, which itself varies systematically between and within drill cores. These findings support a geometallurgical, domain-aware approach to Mustavaara flowsheet design, with physical beneficiation of oxide phases via magnetic separation as the primary recovery route and mineral-specific characterisation of ore domains as important component of flowsheet development. Recovering silicate-hosted vanadium through a complementary hydrometallurgical or smelting route remains technically conceivable but is not yet proven at an economic scale for this style of mineralisation.

7. Acknowledgements

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