

**Preliminary experiments on prospects of vanadium recovery
from graphite shales (Norråker, Sweden).**

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Part I.

Microprobe analysis of black shale from Norråker, Sweden

The analysis was carried on thin section cut from the sample (drill core): KRODD 07052 L3 11-13m. The purpose of the analysis was to determine whether the presence of V in the rock can be attributed to any of the mineral components.

Limitations: This rock consists of mineral skeleton mixed with “graphitic” carbonaceous matrix. In general, a microprobe analysis can reliably determine the presence of V in mineral grains (larger than ca. 1 μm). Potential presence of V bound to organic carbon is less likely to be determined with this method.

Summary of the results:

Rutile TiO_2 has been identified as one of vanadium carriers in the shale (within capabilities and the detection limit of microprobe analysis). The quantitative analysis indicates up to 0.5 wt% of V_2O_3 in selected agglomerates of rutile grains.

There are two generations of rutile in the rock which differ in morphology and structure:

Rutile Type A: isometric grains 10 – 20 μm in size, no cracks, usually single crystals;

Rutile Type B: aggregates of very small grains (below 1 μm), the size of aggregates ca. 10 – 20 μm .

Rutile Type A does not contain V (or contains very little, below 0.05 wt% of V_2O_3).

Rutile Type B contains up to 0.57 wt% of V_2O_3 .

Discussion:

The content of V-bearing rutile Type B in the rock is probably below 0.5wt% (to be determined quantitatively). This rutile contains up to 0.57 wt% V_2O_3 (equivalent of 0.19 wt% V). This means that this rutile is responsible for no more than 0.0029 wt% of V_2O_3 in the rock (an equivalent of 0.001 wt% of V, or 10 ppm of V in the whole rock). Previously done chemical analysis indicate that the rock contains up to several hundreds of ppm of V (nearly 900 ppm of total V). This means, that only less than 10 ppm of V is bound to rutile, the rest of V is in the other form. So far no other mineral component analyzed with the electron microprobe indicated V content above the detection limit (equal to 0.01 wt% V_2O_3).

This may suggest that significant amount of V is bound to carbonaceous matter present in this rock. Similar is observed in certain types of hard coal. The examples come from China where the attempts have been made to recover V from hard coal.

Part II.

Preliminary tests on acid and base extraction of V from black shale from Norråker, Sweden

The experiments were carried on pulverized fragment of a sample (drill core): KRODD 07052 L3 11-13m.

The objective of the experiments was to determine the presence of vanadium in the forms extractable with strong acid or strong base (forms other than simple oxides or metallo-organic compounds).

The procedure:

Two types of leaching solutions have been used:

- I. 5M NaOH in 0.1M Na₂EDTA
- II. H₂SO₄ 1:1 in 0.1M Na₂EDTA

Na₂EDTA (also called: complexon III) is a salt of organic acid (disodium salt of ethylenediaminetetraacetic acid). It is a relatively strong chelating agent that sequesters cations from minerals or rocks into aqueous solution through formation of water-soluble complexes with metals.

Two types of solids have been tested:

- A. Pulverized rock.
- B. Pulverized rock oven roasted at 550 °C for 3 hours.

The objective of oven roasting was mineralization of all the organic compounds, removal of carbonaceous and carbonate compounds and conversion into oxides.

Vanadium content in resulting solutions was determined using atomic absorption spectrometry AAS with a nitrous oxide – acetylene flame (detection limit = 5 mg V/L). The standards were

prepared in solution matrix similar to experimental solutions. Due to a very high concentrations of matrix in analyzed solutions (strong acids and bases, high content of Na) the results are considered as semi-quantitative.

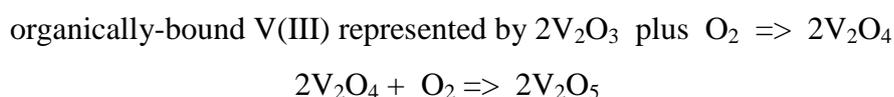
Summary of the results:

ID	Experimental setup	Concentration of V in final solution (semi-quantitative)
1. A.I.	2g of rock + 10mL 5M NaOH + 10mL 0.2M Na ₂ EDTA	below detection
2. A.Ia.	3g of rock + 50mL 5M NaOH	below detection
3. A.II.	2g of rock + 10mL H ₂ SO ₄ 1:1 + 10mL 0.2M Na ₂ EDTA	3.5 ±1.6 mg V/L
4. B.I.	1g of roasted rock + 10mL 5M NaOH + 10mL 0.2M Na ₂ EDTA	below detection
5. B.II.	1g of roasted rock + 10mL H ₂ SO ₄ 1:1 + 10mL 0.2M Na ₂ EDTA	2.0 ±0.8 mg V/L

Discussion:

Strong base does not mobilize vanadium from this rock.

Sulfuric acid in the presence of complexing agent is the solvent capable of leaching some vanadium from both, raw material and roasted rock. The effect of oven-heating of this rock at 550 °C for 3 hours is conversion of organically-bound vanadium at various oxidation stages into vanadium(V) oxides, for example:



Recalculation of the results indicate, that sulfuric acid leaching may potentially allow for recovery of ca. 35 mg V/kg of raw rock (35gV/t) or ca. 40 mg V/kg of roasted rock (40gV/t). These numbers are preliminary and carry at least 50% uncertainty.

The results of leaching experiments may indicate, that:

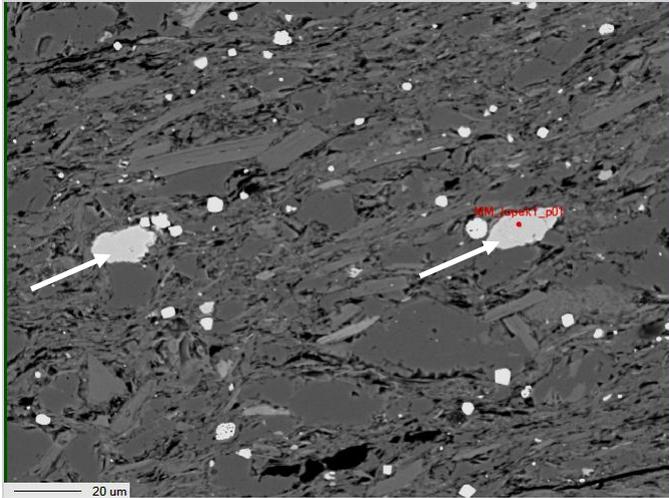
- Acid leaching is partly effective in recovery of V
- The amount of V mobilized from raw and from roasted rock is similar: roasting does not improve the effectiveness
- This procedure allows for recovery of ca. 40 ppm of V. The rock contains ca. 700 ppm V. This means that vast majority of V has not been mobilized using this procedure.

Recommendations:

It is recommended to follow this preliminary analyses with the attempts to chemically extract V from this shale. Vanadium bound to TiO_2 in small quantities. Also, vanadium bound to rutile may be very difficult to recover. Strong acid in the presence of complexing agent allows for recovery of only small portion of V potentially present in this rock. This may indicate, that the remaining V is bound to carbonaceous matter through organo-metal compounds. This is indirect conclusion which is not supported with direct results yet. The research reported herein targeted mineral components only. All the vanadium potentially bound to carbonaceous matter may be more available via extraction with solutions containing organic solvents.

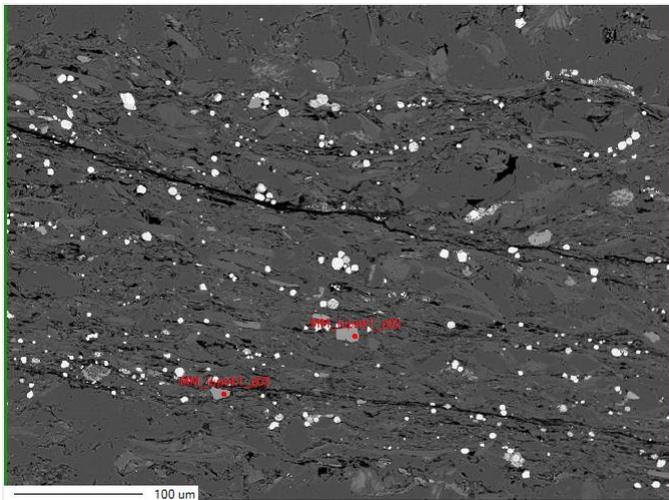
Appendix.

Examples of the structures and content of V in rutile analyzed with the use of electron microprobe.



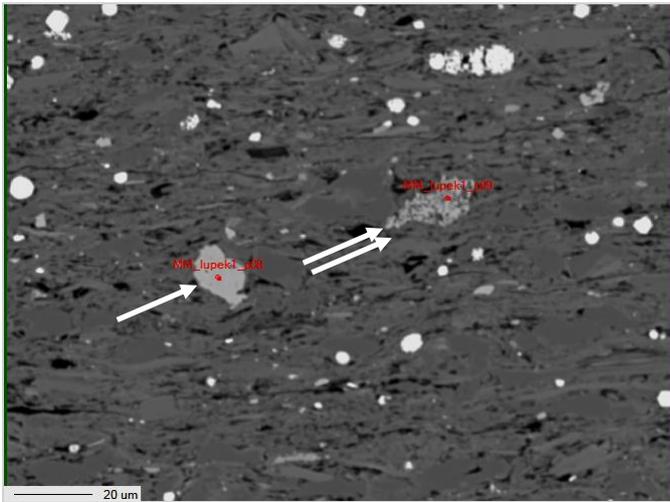
Rutile Type A (arrows).

marker on the photo	TiO ₂	V ₂ O ₃	SiO ₂	Al ₂ O ₃	ZrO ₂	Total
MM_lupek1_p01 [wt%]	97.76	0.00	0.22	0.11	0.08	98.4



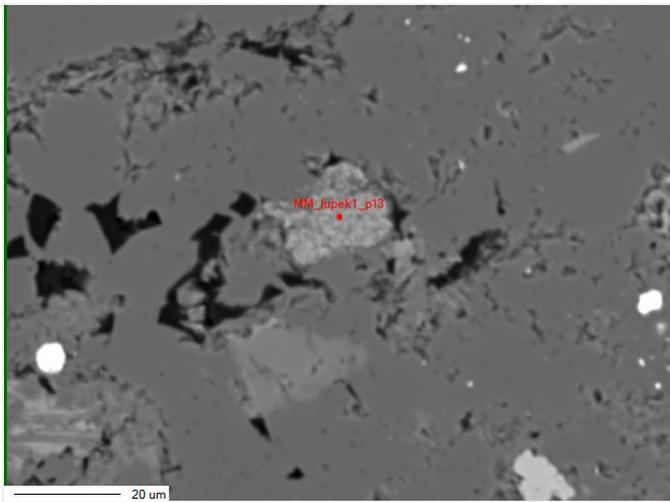
Rutile Type A

marker on the photo	TiO ₂	V ₂ O ₃	SiO ₂	Al ₂ O ₃	ZrO ₂	Total
MM_lupek1_p02 [wt%]	98.24	0.00	0.20	0.11	0.13	98.8
MM_lupek1_p03 [wt%]	98.67	0.00	0.09	0.07	0.04	99.0



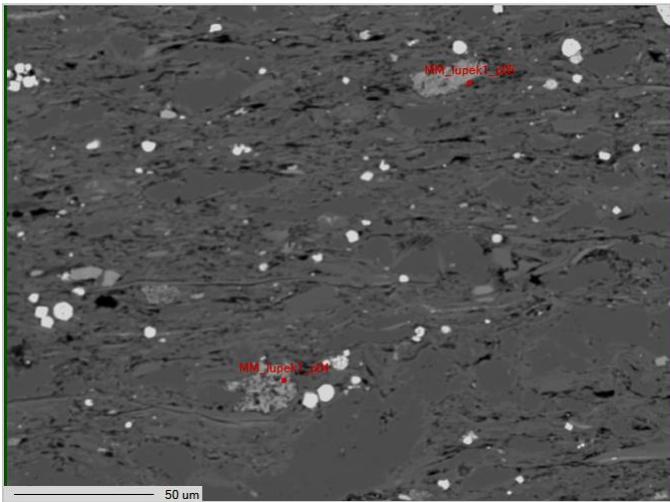
Rutile Type A (arrow) and Type B (double arrows).

marker on the photo	TiO2	V2O3	SiO2	Al2O3	ZrO2	Total
MM_lupek1_p08 Rutile Type A [wt%]	95.72	0.01	0.21	0.23	0.62	97.1
MM_lupek1_p09 Rutile Type B [wt%]	71.24	0.39	12.96	7.72	0.03	93.3



Rutile Type B.

marker on the photo	TiO2	V2O3	SiO2	Al2O3	ZrO2	Total
MM_lupek1_p13 [wt%]	73.20	0.57	0.72	0.23	0.00	75.0



Rutile Type B.

marker on the photo	TiO2	V2O3	SiO2	Al2O3	ZrO2	Total
MM_lupek1_p04 [wt%]	78.77	0.17	0.94	0.48	0.06	80.6
MM_lupek1_p05 [wt%]	88.20	0.18	0.38	0.14	0.05	89.1