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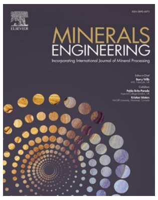

The process mineralogy of leaching sandstone-hosted uranium-vanadium ores

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ABSTRACT

In the United States, sandstone-hosted ore deposits of the Paradox Basin (Colorado Plateau) are major resources of uranium and vanadium, two metals important to green energy among other applications. Despite historic and current mining interest, and their significance as major domestic resources of critical elements, the geometallurgy of these deposits has received little study. This article documents the geometallurgy and process mineralogy of the U-V ores and identifies the principal barriers to optimal recovery by acid leaching.

Most of the metals occur as pitchblende (mixed uranium oxide-silicate), V-hydroxides, V-bearing phyllosilicates, and diverse vanadates of U, Pb, Cu, and other metals. Commercial extraction is by two-stage heated tank leaching with H_2SO_4 and $NaClO_3$, yielding high U but lower V recovery (70–75% in the industrial operation). Laboratory leaching experiments coupled with comparisons of head and residue mineralogy indicate that the unrecovered U consists of micron-scale pitchblende grains locked within quartz and other insoluble minerals. The principal cause of suboptimal V recovery is the V-phyllosilicates, which show variable but generally poor solubility at room temperatures. An ancillary cause is locking of a small amount of fine-grained V-hydroxide and pitchblende by authigenic quartz and V-phyllosilicates. Comparison with other global V resources suggests that variable solubility of V-phyllosilicate ore minerals may also diminish recovery from more common ore deposit types, such as V hosted in black shales or stone coal, particularly in heap leaching of low-grade ores at coarse grain sizes.

1. Introduction

1.1. Importance of uranium and vanadium

Uranium, an actinide, and vanadium, a first-row transition metal, are both major mineral resources in the green energy transition. Both are considered strategic or critical elements in the US: U for its nuclear potential and V as an ingredient in superalloy steels (Kelley et al., 2017; Fortier et al., 2018). More recently, V has also garnered research interest for developing novel batteries capable of storing the huge amounts of energy required for grid-scale implementation of renewable energy.

Supply is a pressing problem for both metals. Recently the USA has imported most of its U from Kazakhstan, Russia, and Canada, and most of its V from China and South Africa (US Geological Survey, 2021). Rising demand for green energy and concerns over strategic metal supply security are turning attention to available domestic resources. Some V can be produced from spent oil-refining catalysts, power plant waste products, and steelmaking slags (US Geological Survey, 2021). These yield no U and are not sufficient to meet the demand for V, necessitating primary production.

The principal known resources of U and V in the USA are found in the Paradox Basin, a roughly circular, uplifted basin on the Colorado Plateau (Fig. 1). Among the best-known and largest historical producers were the mines in the Uravan Mineral Belt, which stretches across eastern Utah and western Colorado. The only recent to current producers are mines in the La Sal Creek district in Uravan, which produced 29 million pounds of V_2O_5 and an uncertain but large amount of U_3O_8 between the early 1900 s and 1980 (Kovschak and Nylund, 1981). Intermittent production since 2006 has totaled $>$ 8 M lbs V_2O_5, and the district still contains 21.5 million lbs of measured and indicated reserves and resources (Peters Geosciences, 2014).

1.2. Geological background

The deposits in the La Sal district are mainly tabular orebodies occurring in quartz-dominated sandstones of the Jurassic Salt Wash (lower Morrison) formation. Detailed geology of the district is reviewed by Fischer (1942) and Carter and Gualtieri (1965), and the ores are closely analogous to those of the Slick Rock district to the southeast, described in detail by Shawe (2011). A more recent study by Barton et al. (2018b) summarizes the petrography of other Uravan deposits, as well as the historical research into their metallogenesis.

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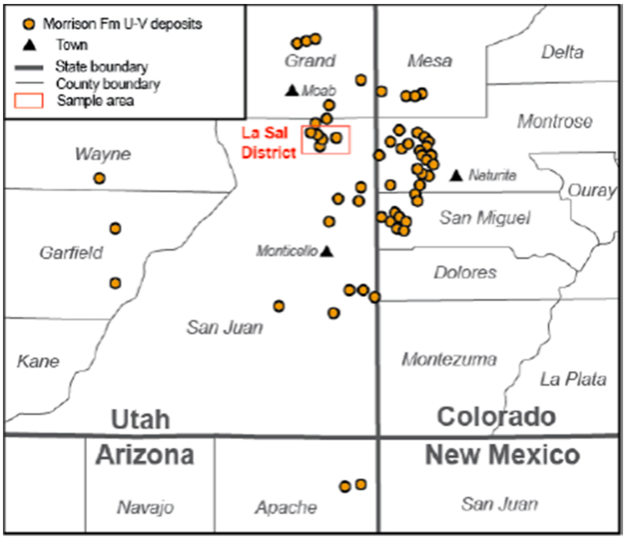

Fig. 1. Map of the Paradox Basin region, modified after Fischer (1942), showing the Salt Wash-hosted U-V deposits and the La Sal district.

Ores in the Salt Wash belong mainly to the tabular subtype of sandstone hosted uranium-vanadium deposits, although roll-front processes overprint and redistribute metals in some areas (Burrows, 2010). Vanadium, and its common associate uranium, are most soluble in their oxidized V(V) and U(VI) forms and precipitate mainly by reduction. The most likely reductant in the Salt Wash deposits is H_2S, which occurs at high concentrations in Paradox Basin petroleum plays and is one of the few geologically common species with enough reducing power to precipitate montroseite ($(V,Fe)OOH$) (Wanty and Goldhaber, 1992). Montroseite is one of the principal ore minerals, having precipitated along with pitchblende (a mix of uraninite [UO_2] and coffinite [$USiO_3{\cdot}nH_2O$]) early in the sequence of ore deposition (Barton et al., 2018a,b). During or after the ore stage, some V was dissolved from montroseite and/or V in solution reacted with authigenic quartz to form vanadian phyllosilicates such as roscoelite ($K(V,Al,Mg)_2AlSi_3O_{10}(OH)_2$), V-illite ($K_{0.65}(V,Al)_2(Al,Si)_4O_{10}(OH)_2$), and V-smectite or V-chlorite ($(V,Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$), which occur as intergranular cements and fringes around quartz grains. The last stage in the ore mineral paragenesis was supergene redistribution of metals to form vanadates and other high-valent V(V) minerals (Barton et al., 2018b). In detail, the sequence of events and resulting mineralogy and mineral textures vary considerably within deposits and individual orebodies. Table 1 gives the common minerals in the La Sal district U-V ores. Accompanying gangue is mainly quartz (SiO_2), but includes potassic feldspar ($KAlSi_3O_8$), calcite ($CaCO_3$), pyrite (FeS_2), and assorted minor metallic phases such as hematite (Fe_2O_3), anatase (TiO_2), ferroselite ($FeSe_2$), clausthalite ($PbSe$), chalcopyrite ($CuFeS_2$), galena (PbS), and jarosite ($KAl_3(SO_4)_2(OH)_6$).

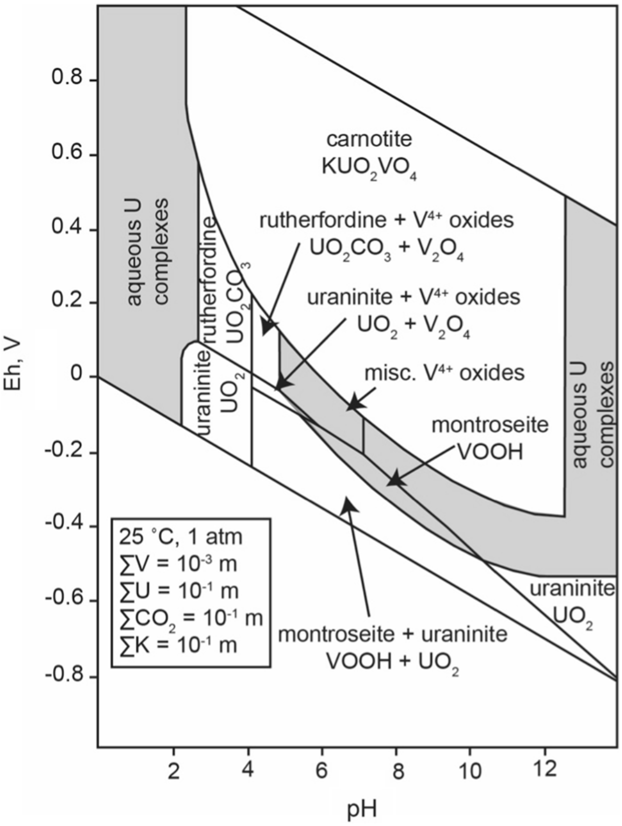

Fig. 2. Simplified Eh-pH diagram for the K-U-V—C—O system at 25 °C, from Barton et al. (2018) and modified from Evans and Garrels (1958) and Garrels (1960).

Except for a few uranyl vanadates, virtually all of the U at La Sal occurs in pitchblende. In terms of volume, the phyllosilicate minerals roscoelite, illite and chlorite are the most common V-bearing phases, with the (hydr)oxides corvusite, montroseite, duttonite, and hewettite also occurring at multiple localities and hosting most of the recoverable V overall (Weeks and Thompson, 1954; Weeks et al., 1959; Carter and Gualtieri, 1965). Most of these minerals deviate significantly from the ideal compositions in Table 1. The uraninite and coffinite that nominally comprise pitchblende in reality contain up to 15 mol % U(VI) rather than pure U(IV) (Finch and Murakami, 1999). Similarly, Wanty et al. (1990) found that the oxidation state of both V and Fe in natural hydroxides such as montroseite is commonly mixed and highly variable with the average V(III)/V_{total} being 0.66 and the average Fe(III)/Fe_{total} being 0.62. Mixtures of V(III) and V(IV) in hydroxides may represent direct hydrolysis and precipitation of dissolved V(IV) in groundwater (Wanty

Table 1
Principal ore mineralogy of the La Sal U-V deposits.

Oxides and Hydroxides	Silicates	Vanadates
Corvusite	***Roscoelite***	***Carnotite***
$(Na,Ca,K)\ (V,Fe)_8O_{20}{\cdot}4H_2O$	$K(V,Al,Mg)_2AlSi_3O_{10}(OH)_2$	$K_2(UO_2)_2(V_2O_8)\ {\bullet}1\text{-}3H_2O$
Duttonite	***V-chlorite***	***Tangeite***
$(V,Fe)O(OH)_2$	$(V,Fe,Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$	$CaCu(VO_4)(OH)$
Hewettite	***V-illite***	***Tyuyamunite***
$CaV_6O_{16}{\cdot}9H_2O$	$K_{0.65}(V,Al)_2(Al,Si)_4O_{10}(OH)_2$	$Ca(UO_2)_2(V_2O_8)\ {\bullet}5\text{-}8H_2O$
Montroseite	***Coffinite***	***Uvanite***
$(V,Fe)OOH$	$USiO_3{\cdot}nH_2O$	$U_2V_6O_{21}{\cdot}15H_2O$
Paramontroseite		***Vesigneite***
VO_2		$BaCu_3(VO_4)_2(OH)_2$
Uraninite		
UO_2		

et al., 1990), solid state oxidation and dehydration of montroseite to form paramontroseite (VO_2) (Evans and Mrose, 1955; Forbes and Dubessy, 1988), and/or in-situ oxidation and hydration of montroseite to form duttonite ($(V,Fe)O(OH)_2$) (Thompson et al., 1957). A simplified Eh-pH diagram for U-V systems is shown in Fig. 2.

1.3. Metallurgical background

Virtually anything oxidizing will dissolve U from uraninite and coffinite, and the presence of a carbonate, sulfate, organic, or other ligand stabilizes U in solution (Lunt et al., 2007; Bowell et al., 2011). Thus, hydrometallurgical methods have long been the preferred approach for U extraction. They have been recently reviewed by Schnell (2014) and Bhargava et al. (2015), and the electrochemical and kinetic details are provided by Nicol et al. (1975) among others. Briefly, leaching systems for U are always oxidizing, typically with $NaClO_3$, Fe^{3+} ion, or MnO_2 (Lunt et al., 2007). Acidic systems such as H_2SO_4 are the most common, but alkaline $(NH_4)_2CO_3$ is preferred for in-situ recovery or for leaching U in carbonate-rich deposits. A reaction for uraninite leaching in sulfuric acid with sodium chlorate is:

$$3UO_2 + 3H_2SO_4 + NaClO_3 \leftrightarrow 3(UO_2)SO_4 + NaCl + 3H_2O. \tag{1}$$

Recoveries by acid leaching are high even when the ore is pitchblende rather than pure uraninite. The major geometallurgical issues identified for U leaching in sandstone-hosted ores are slower dissolution rates due to cationic impurities in uraninite (Ram et al., 2013); preg-robbing by smectite, other clays, phosphates, and organic carbon (Lunt et al., 2007; Youlton and Kinnaird, 2003; Pownceby and Johnson, 2014); and acid consumption by carbonates, which raises pH and decreases dissolution rates (Eligwe et al., 1982; Youlton and Kinnaird, 2003).

By comparison, V is much more difficult to leach effectively and the reasons for its leaching behavior are virtually unknown. Prior to the 1950s, most U-V ores were treated by salt roasting rather than leaching in order to extract maximum V. In salt roasting, V ores are heated in an oxidizing atmosphere to 750-840 °C in the presence of NaCl (Burwell, 1961). This converts V into soluble sodium vanadates (e.g., sodium orthovanadate, Na_3VO_4) and separates it from accompanying metals (Burwell, 1961). The roasted ores are then leached in water or acid, yielding typical recoveries of 83–90 % (Burwell, 1961). By the late 1950 s salt roasting of U-V ores had fallen out of favor, since recovery of U was prioritized over V during the Cold War and leaching was cheaper for that purpose (Gupta and Krishnamurthy, 1992). Today the majority of sandstone-hosted U-V ores are crushed and directly leached in an agitated, heated H_2SO_4 – $NaClO_3$ tank (Gupta and Krishnamurthy, 1992). The mixed pregnant leach solution is sent for U solvent extraction first, and the raffinate from this step goes to V solvent extraction before being recycled through the leaching system. An overall reaction for direct leaching of an idealized montroseite under those conditions is:

$$NaClO_3 + 6VOOH + 12H^+ \leftrightarrow NaCl + 6VO^{2+} + 9H_2O. \tag{2}$$

No reaction has yet been proposed for V leaching from phyllosilicates, but a plausible reaction for an ideal roscoelite is:

$$6KVAl[AlSi_3]O_{10}(OH)_2 + NaClO_3 + 18H^+ + 0.5O_2 = 3Al_4Si_4O_{10}(OH)_2 + 6VO^{2+} + 6K^+ + 12H_2O + NaCl + 6SiO_2. \tag{3}$$

This is hypothetical but would be consistent with the incongruent degeneration of micas toward kaolinite compositions as observed in the oxidized acid leaching of copper (Baum, 1999). A study by Tavakoli et al. (2014) examined the kinetics of synthetic vanadium oxide (V_2O_5) leaching in sulfuric acid and found that VO_2 dissolves quickly but that its solubility is relatively low. This leads to lower recovery at high solid–liquid ratios, exacerbated by decreases in solubility with increasing pH and increasing temperature.

Geometallurgical issues in V leaching are not well understood, because most V is extracted as a byproduct of steelmaking by non-hydrometallurgical methods. However, it is clear from unpublished historical and present research that V leaching yields far lower recoveries than U leaching in sediment-hosted ore types. Hazen Research performed metallurgical tests on low-grade U- and V-bearing tailings from Naturita, Colorado (Hazen Research Inc., 1976). The head grade of the test samples was 0.32 % V_2O_5, with the dominant ore minerals consisting of tyuyamunite and roscoelite (Hazen Research Inc., 1976). Recoveries of V were < 40 % from agitated sulfuric acid leaching and sodium carbonate/carbonic acid leaching. The most successful method was agglomeration of the tailings with sulfuric acid, followed by an overnight cure, and then percolation of dilute sulfuric acid through the agglomerate at a rate of 0.01–0.02 gpm/ft^2 (Hazen Research Inc., 1976). The reasons for the poor recoveries were not documented. Recoveries at the White Mesa Mill, operating since 1980 on La Sal ores, are higher, at around 70–75 %, but still considerably lower than the U recovery (96 %) despite V grades generally being much higher than U grades (Peters Geosciences, 2014). The mill has operated since 1980, crushing and grinding ores to −600 µm followed by two-stage tank leaching in heated sulfuric acid with a sodium chlorate oxidant (Baker and Sparling, 1981).

More recent published studies on V leaching are generally lacking due to the unique nature of the deposits and the relative scarcity of active mining. The Colorado Plateau is one of very few provinces worldwide in which sandstone U deposits contain significant V, so most research on tabular U deposit geometallurgy omits discussion of V. Both U and V were produced in large volumes from the Colorado Plateau during most of the 20th century, but mining in the region has virtually shut down since the early 1980s. Research dwindled along with production, so studies on the geometallurgy of V mainly shifted to slags, titanomagnetite deposits, stone coal, and other feedstocks (e.g. Zheng et al., 2019a,b; Gilligan and Nikoloski, 2020). Since such ores are refractory to leaching, extraction is by salt roasting, which has thus become the main focus of geometallurgical research on V in recent years (Peng, 2019). Thus, most references to the geometallurgy of V in leaching date from the middle to late 20th century. A renewal of interest in the Colorado Plateau U-V deposits, however, is underway, and may trigger additional commercial and research activity (Mills and Jordan, 2021).

1.4. Objective of this study

This study aims to examine the geometallurgy of sandstone-hosted U-V ores in acid leaching systems. A particular objective is to identify the causes of suboptimal V recovery during leaching, through leaching experiments coupled with comparisons of head and tail mineralogy. The implications are twofold. Firstly, this study will add an important new direction to the literature on the process mineralogy of sandstone-hosted U ores. This has been a topic of significant research, but almost all of it concerns V-poor deposits and the behavior of V minerals in these leaching systems is thus almost completely unknown (Youlton and Kinnaird, 2003; Youlton, 2014). Secondly, this study will shed light on geometallurgical problems in the hydrometallurgy of V, a subject of increasing interest in settings including black shale or stone coal. These low-grade but large V resources, like La Sal, host a considerable fraction of their V as phyllosilicates. This study can therefore help elucidate the likely geometallurgical problems in this type of unconventional V resource (Li et al., 2009, 2010).

2. Materials and methods

2.1. Samples and sample preparation

Six coherent rocks on the order of 1 cubic foot each were sampled from the Energy Fuels ore stockpiles located on the Pandora Mine property. Each block was broken up by hammer and individually bagged. The six samples were crushed and split at Freeport-McMoRan's

Tucson Technology Center. The material was stage-crushed to −850 μm and split using a rotary splitter. For each sample, three 3-g splits of −850 μm material were mounted in epoxy and polished for mineralogical analysis. A split of 120 g of material from each sample was further ground to −106 μm from which eight 10-gram splits were set aside for leach tests and others pulverized, dissolved with 3-acid (nitric, hydrochloric, fluoboric) microwave digestion, and finally analyzed with ICP-OES. Carbon was assayed by Leco furnace.

2.2. *Mineralogical analysis and identifications*

Thin sections taken for geological fieldwork were examined in transmitted- and reflected-light petrography (Bos-Orent, 2021). Head sample mineralogical mounts were analyzed using reflected-light petrography and a Tescan TIMA3. The TIMA scans were performed at 25 kV accelerating voltage, with a working distance of 15.0 mm and a pixel size of 5 μm. Leached residues were mounted in epoxy, polished, and analyzed on a JEOL 6010LA benchtop scanning electron microscope (SEM). Ore mineral compositions for both head and residue samples were obtained using a Cameca SX100 electron probe microanalyzer (EPMA). For most EPMA analyses a 2 μm beam was used to minimize alkali migration and hydrous mineral damage, however a spot beam was used where grain size was especially small. Magnification of 10,000X was used during analysis. The beam conditions were 15 kV voltage and 20nA current. Standards for each element were analyzed for calibration and peak fitting before and after each analytical session. Standard compositions, detection limits, and other analytical conditions are given in the Supplementary Material.

The two major V-hydroxide minerals, montroseite and duttonite, are difficult to distinguish based on backscatter and chemical data despite being distinct in optical petrography. Table 2 compares their features. In this study, they were not distinguishable by TIMA or SEM and were grouped together as V-hydroxides. On EPMA, the only discernable chemical difference between montroseite and duttonite is the unanalyzable volatile (OH^{-}) content, which shows up as lower analytical totals, and the Na content (Thompson et al., 1957). The V/Fe ratio and Na content both increase dramatically in analyses with analytical totals < 80 %. This boundary is interpreted to indicate a structural (crystallographic) difference and is used as the cutoff to distinguish duttonite (analytical totals < 80 %, > 0.9 % Na, V/Fe > 10) from montroseite (analytical totals ≥ 80 %, low Na, V/Fe < 10) in this study. Oxygen percentages reported are calculated assuming all iron as Fe(II) and all vanadium as V(III) for purposes of consistency and comparison. In reality, V-hydroxides are known to contain Fe(II), Fe(III), V(III), and V(IV)

Table 2

Comparative features of montroseite and duttonite. (Analytical totals reported are for V_2O_3 and FeO, though most natural samples have mixed-valence V and Fe; see text for discussion.) Optical features are based on Weeks et al. (1953) and Thompson et al. (1957).

Physical Features	**Montroseite VOOH**		**Duttonite $VO(OH)_2$**	
Color (transmitted light)	*Opaque, black*		*Translucent, brown*	
Crystal Habit	*Acicular, blades, laths*		*Massive, platy or pseudomorphous*	
Cleavage	*Parallel to c-axis*		*Perpendicular to c-axis*	
Occurrence	*Embedded in quartz overgrowths or in radiating clusters*		*Pseudomorph of montroseite or massive and anhedral*	
Chemical Composition	**Ideal VOOH**	**Observed (n = 33)**	**Ideal VO $(OH)_2$**	**Observed (n = 31)**
Average V_2O_3*	89.3 %	64.3 %	74.2 %	58.7 %
Average FeO*	0	14.7 %	0	11.7 %
Average Al_2O_3	0	2.1 %	0	1.5 %
Average Na_2O	0	0.1 %	0	0.8 %
Average K_2O	0	0.2 %	0	0.7 %
Average analytical total	89.3 %	83.6 %	74.2 %	76.5 %

with a variety of single and coupled substitution mechanisms (Evans and Mrose, 1955; Thompson et al., 1957; Forbes and Dubessy, 1988; Wanty et al., 1990).

The distinctions among V-phyllosilicates are also somewhat ambiguous. This study uses the classification developed by Meunier (1994) based on the atomic proportion of octahedral V and the extent of K deficiency. A phyllosilicate with $V/(V + {}^{vi}Al + M^{2+}) > 0.5$ is defined as roscoelite, and one with $V/(V + {}^{vi}Al + M^{2+}) < 0.5$ is defined as V-muscovite. Either of these compositions combined with an overall interlayer cation atomic charge of < 0.80, i.e. K-deficient species, are designated V-illite. The few sheet silicates with (Mg + Fe) > Al are designated V-chlorite.

2.3. *Experimental procedures*

The 10-g leaching splits of all six ore samples, ground to −106 μm, were subjected to a three-hour agitated leach to evaluate the process mineralogy of leaching. A solution of 10 g/L H_2SO_4 and 1 g/L $NaClO_3$ in deionized water, representing the reagents used in industrial practice, was placed in a 500 mL beaker with a magnetic stirring rod. Each leaching test used a solid-to-liquid ratio of 5 % solids to avoid saturating the solution in the beaker.

All chemicals used were reagent-grade from Sigma-Aldrich. One approximately 10-g split for each ore sample was fully emptied into each beaker of solution. During the experiment the beaker was covered with a watch glass to minimize splashing and evaporation. All tests were performed at 25 °C. Sample volumes of 3–5 mL were obtained after 10, 20, 30, 60, 120 and 180 min of active leaching time using a syringe equipped with a filter tip with a 1 μm pore size. Filtered leach liquor samples were expelled into polypropylene test tubes and labeled with sample number and leaching time. One drop of concentrated nitric acid was added to each vial of leach liquor to stabilize elements in solution and prevent precipitation. After each 3-hour leach session, the solid residue was filtered, rinsed in deionized (DI) water and air-dried for epoxy mounting and mineralogical analysis.

For leachate analysis, each solution sample was diluted 250,000x using a 100 μL Eppendorf pipette in a diluent of 2 % HNO_3. Samples LS04, LS05 and LS11 were diluted one week after the leach experiments and samples LS01, LS02 and LS03 were diluted on the same day as the leach experiments. Despite the acidic conditions, the formation of an orange precipitate (presumably V_2O_5) was apparent in several samples from LS11, and these leach liquors (120 min, 180 min) were not submitted for dilution and analysis. The rest of the diluted leach liquors were analyzed for V, Ni, Zn, Pb, U, and Cu at the University of Arizona Economic Geology and Geometallurgy lab on an Element2 ICP-MS. One nitric and seven sulfuric acid blanks, four multi-element standards, and two U-V standards at concentrations from 0.2 to 10 ppb were made from certified standard reference materials in the lab. Standards were run before and after the analyses of the unknown samples; blanks were distributed at intervals through the analytical run and also analyzed before the final standard run. Analytical results were corrected to final concentrations using the standards and blanks.

3. Results

3.1. *Head sample compositions*

The six ore samples are quartz sandstones in which rounded quartz grains and minor feldspar, lithic clasts, heavy detrital minerals, and coalified plant material are the detrital constituents. Consistent with this lithology, whole-rock geochemical results from sandstone ores of the same deposit contain from 57 % to 81 % SiO_2 (Bos-Orent, 2021). Quartz is the most volumetrically abundant phase, comprising between 53 and 89 % (Table 3). The V-phyllosilicates comprise 9 to 31 %, and V-hydroxides comprise from 1 to 18 % of the sample volume. Uranium minerals make up < 1 % of the samples by volume, mainly as uranyl

Table 3
Modal mineralogy of samples in this study as determined by Tescan TIMA. Numbers show average and 1 standard deviation, based on three replicates analyzed for each sample. Dash indicates the phase occurs as<1% by volume. Phases detected at<1% in all samples are not listed. Vanadium deportments in the bottom row are approximate since V hydroxide and phyllosilicate compositions vary from sample to sample.

Phase	LS01	*σ*	LS02	*σ*	LS03	*σ*	LS04	*σ*	LS05	*σ*	LS11	*σ*
Quartz (%)	89.1	*0.56*	82.7	*0.70*	59.9	*0.40*	81.6	*0.46*	54.6	*0.89*	53.5	*2.0*
V-phyllosilicates (%)	8.9	*0.50*	12.6	*0.42*	27.9	*0.60*	14.8	*0.37*	23.0	*0.41*	30.9	*1.5*
V-hydroxide (%)	1.8	*0.04*	3.7	*0.24*	11.1	*0.26*	1.2	*0.08*	17.9	*0.42*	14.8	*0.53*
U minerals (%)	–	–	–	–	0.6	*0.11*	–	–	2.9	*0.18*	–	–
K-Feldspar (%)	–	–	–	–	–	–	1.1	*0.09*	–	–	–	–
All other phases (%)	0.19	*0.01*	1.02	*0.07*	0.48	*0.01*	1.23	*0.04*	1.58	*0.29*	0.84	*0.02*
% of total V in hydroxides	34.7		43.5		51.1		17.5		67.1		55.7	

vanadates with compositions corresponding to uvanite and carnotite-tyuyamunite mixtures. The only pitchblende present consists of inclusions under quartz overgrowths. K-feldspar and calcite are minor but consistently present in the samples (Table 3). In all cases, these results should be taken to include substantial uncertainty due to the sampling statistics associated with automated mineralogy work.

The diameter of quartz grains is 0.05 – 0.5 mm. Detrital grains are overgrown by euhedral quartz rims of 10–20 µm thickness. Partially or fully enclosed within the quartz rims are montroseite and pitchblende, some of which can also be found in the interstices between grains. Where the edges of quartz grains are ragged, suggesting dissolution, the grains are typically fringed by V-illite (proximal to quartz grain) and duttonite (distal to quartz grain) (Fig. 3). The V-illite also commonly contains anhedral quartz islands and necklace-like rings of tiny pitchblende grains that formerly marked the boundary between detrital quartz and quartz overgrowths. In addition to forming these rims around quartz grains, V-phyllosilicates also form the main cement to the rock. Fig. 3 shows representative photomicrographs of ore minerals and textures.

Assay results for the six ore samples ranged from 1.87 to 10.37 % V, 0.05 – 1.51 % U and V/U ratio range from 6.9 to 37.6. Carbon and sulfur contents are below 2.5 % and 1 % respectively for each sample. Table 4 shows the percentages of the analyzed elements in the samples.

Table 4
Select elemental assays of the six ore samples. b.d.l. = below detection limit. ACT = acid consumption.

Sample	LS01	LS02	LS03	LS04	LS05	LS11
Al (%)	0.65	1.17	2.39	1.97	2.07	2.62
C (%)	*b.d.l.*	0.06	0.03	*b.d.l.*	2.37	1.05
Ca (%)	0.06	0.47	0.18	0.09	0.17	0.16
Fe (%)	0.40	0.65	1.55	0.86	2.65	2.67
K (%)	0.31	0.56	1.06	0.34	0.97	1.30
Mg (%)	0.10	0.15	0.39	0.86	0.24	0.44
Na (%)	*b.d.l.*	*b.d.l.*	*b.d.l.*	0.08	*b.d.l.*	0.10
P (%)	0.01	0.02	0.03	0.01	0.03	0.02
S (%)	0.13	0.19	0.15	0.13	0.64	0.37
Ti (%)	0.02	0.06	0.07	0.15	0.04	0.07
U (%)	0.05	0.37	0.81	0.19	1.51	0.45
V (%)	1.95	2.98	7.23	1.87	10.4	10.1
Total ACT (lb/t)	114	158	251	87	306	285
V/U ratio	37.6	8.1	9.0	10.1	6.9	22.5

3.2. Vanadium mineral compositions

Textural and compositional features apparent during petrographic, SEM and electron microprobe analysis indicated that the samples contained two different V-hydroxide minerals, identified as duttonite and

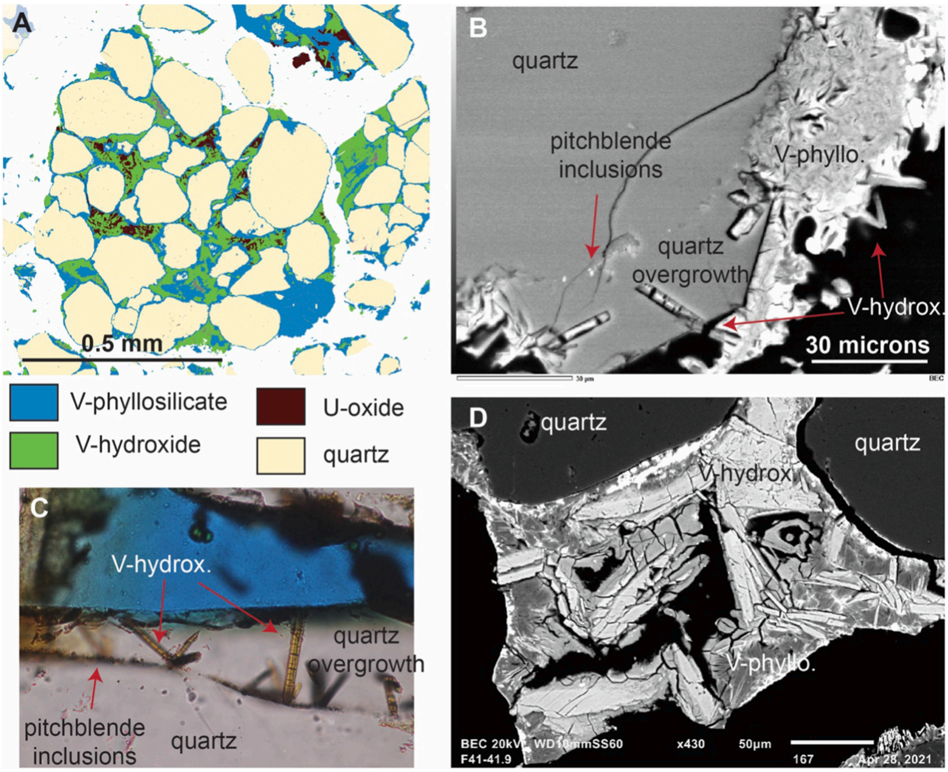

Fig. 3. Representative textures of the ores leached in this study (heads). A: TIMA image showing a sample ground to −20 mesh. B: Backscattered SEM image showing occurrence patterns of pitchblende as inclusions under quartz overgrowths; V-hydroxides enclosed within quartz overgrowths and fringing V-phyllosilicates; and V-phyllosilicates as coronas around corroded quartz overgrowths. C: Transmitted-light optical photomicrograph showing pitchblende and V-hydroxides, in this case duttonite, locked in the overgrowth of a single quartz grain. D: Backscattered SEM image showing V-hydroxides and phyllosilicates as interstitial species between quartz grains. Variations in backscatter coefficient are caused by variable U, V, and Fe contents of the V-hydroxides and variable V contents of the phyllosilicates.

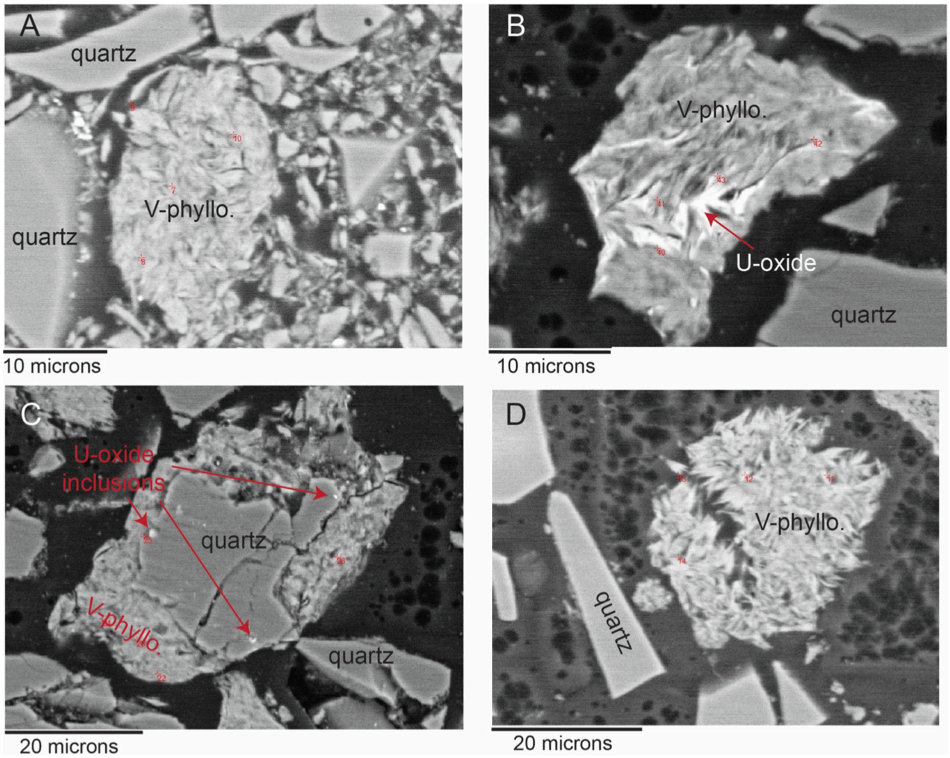

Fig. 4. Representative textures of ore minerals found in the leached residues. A: Clumped V-phyllosilicate loosely agglomerated with fine quartz grains. B: Fine U-oxide grains, probably pitchblende, locked inside V-phyllosilicates and not leached. C: Preserved corona of V-phyllosilicates around a quartz grain, also locking in U-oxide inclusions. D: Partially disaggregated but unleached clump of V-phyllosilicates.

montroseite in roughly equal proportions based on the cutoffs described above in Section 2.2. On average, duttonite contains about 40 % V, and montroseite contains about 44 % V, by weight (Table 2).

Three types of V-phyllosilicate were identified in this study using the criteria in Section 2.2: roscoelite, V-illite, and V-chlorite. The V-illite and V-chlorite are fine-grained (<5 μm) plates and mostly occur within 5–20 μm-thick reaction rims around detrital quartz or as an intergranular phase with quartz + V-hydroxide (Fig. 4e). The atomic proportion of V in the La Sal V-illite and V-chlorite samples from this study shows a negative linear correlation with Al, which is taken to indicate that V(III) is primarily incorporated into the octahedral site of the silicate structure (Foster, 1959; Meunier, 1994). In four of the six samples (LS01, LS03, LS05 and LS11) the only V-phyllosilicate identified is V-illite. Sample LS02 contained a mix of roscoelite and V-illite, and LS04 contained V-chlorite as the only phyllosilicate. Compositionally, the V-illite analyzed in this study are very similar to those described by Meunier (1994) from other Salt Wash localities. Representative compositions are given in Table 5.

A small amount of V also occurs in minor vanadate minerals making up < 1 % of the rock by volume. Uranyl vanadates occurred in most of the samples as a supergene alteration product. Most are < 10 μm in diameter and difficult to analyze, rendering identifications somewhat tentative. Of those analyzed, the most common mineral appears to have the composition of uvanite, followed by carnotite-tyuyamunite. Samples LS02 and LS04 also contain a few grains of a Ti-Fe-V (hydr)oxide with V contents averaging 4 %, but ranging as high as 20 %. Based on this composition, its occurrence, and common igneous exsolution textures, these grains appear to be a detrital heavy mineral such as vanadiferous titanomagnetite. Only a few grains were observed and their contribution to the overall V budget is negligible.

3.3. Leach test results

Uranium removal was quantitative in samples with high enough U grades for reliable measurement (LS05, see table 4) and no U minerals were observed in any of the residues except for pitchblende under quartz overgrowths and minor U-enriched zones in clays. For V, recoveries are variable but all below 35 % (Table 5). In the cases of LS05 and LS11, partially leached V-hydroxides were observed in the tails, suggesting that the low recoveries were due to the leach solution saturating in V. Recoveries in the industrial process are typically higher, most likely due to the use of multiple leaching stages (rather than single-stage beaker leaching) and the higher temperature.

3.4. Tails sample compositions

Fig. 4 shows the typical appearance of the leached tails. Analysis by SEM and EPMA shows that the leach residues consist primarily of angular quartz fragments up to 100 μm diameter and clumps of V-illite. Most of the V-illite clumps are ~ 10 μm in diameter with individual illite grains ~ 2 μm in length, however some clumps are as large as ~ 50 μm in diameter. This is somewhat larger than the typical occurrences in the heads and may reflect agglomeration during the leaching experiments. The only U phase observed in any of the tails was a minor U-enriched area in some of the clays, too fine to identify and volumetrically minor. Duttonite was identified in the tails from LS03 and LS05. The leached residues of other samples did not contain observed V-hydroxides. The duttonite in LS05 appeared to be partially leached, with a ragged appearance and an average of 14 % lower V than the duttonite in the corresponding head. An exception was duttonite observed in the residue of LS03, which consisted of a single clump of fine grains with no significant difference with the head in V content. Otherwise, the V-hydroxides in LS03 were completely dissolved by leaching, so locking was probably the reason for the residual duttonite.

Comparison of V-illite compositions in corresponding head and tail (residue) samples suggest that V leaching from V to illites is highly variable even within the same sample, with a maximum of roughly 36 % extraction in sample LS01 judging by the difference between heads and

Table 5
Representative compositions of V-bearing minerals in La Sal head samples by electron microprobe.

Reduced & intermediate minerals (oxygen calculated assuming all V as V^{3+}, Fe as Fe^{2+}, and U as U^{4+})								
Mineral sample	montr-oseite LS02	montr-oseite LS05	duttonite LS01	duttonite LS04	V-illite LS03	V-illite LS03	V-chlorite LS04	V-Ti-Fe oxide LS04
Analysis	2-17_20	5-4_1	12-2_15	2-17_57	12-7_17	5-4_54	2-17_49	2-17_41
Na	0.2	0.0	1.6	1.3	0.1	0.2	0.1	0.0
F	0.2	*n.a.*	0.1	0.0	0.1	*n.a*	0.0	0.0
Mg	0.1	0.1	0.0	0.1	1.5	1.0	3.9	0.0
Al	0.9	1.1	0.5	0.3	8.3	7.4	8.6	0.1
Si	0.1	0.1	0.1	0.1	21.0	19.0	11.9	0.4
K	0.1	0.1	1.2	1.5	5.0	5.9	0.8	0.0
Ti	0.2	0.6	0.1	0.2	0.1	0.0	0.2	42.8
Ca	0.3	0.0	0.1	0.0	0.1	0.1	0.2	0.0
V^{3+}	43.0	45.3	37.7	39.2	9.8	16.0	16.0	4.0
Fe^{2+}	13.5	10.4	9.9	10.8	3.5	2.1	8.5	10.2
Mn	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Cl	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0
Ba	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.9
U^{4+}	0.1	0.0	2.5	0.0	1.2	0.6	1.9	0.0
O (calc)	25.4	25.8	22.4	22.9	39.3	38.4	34.4	34.1
Total	**84.1**	**83.4**	**76.4**	**76.4**	**90.1**	**90.6**	**86.5**	**92.7**
Oxidized minerals (oxygen calculated assuming all V as V^{5+}, Fe as Fe^{3+}, and U as U^{6+})								
Mineral, sample		Uvanite, LS01			Carnotite, LS03			
Analysis		12-7_34			12-7_21			
Na		0.4			0.1			
F		0.0			0.0			
Mg		0.1			0.0			
Al		1.0			0.1			
Si		0.1			0.1			
K		0.5			5.5			
Ti		0.0			0.0			
Ca		0.4			0.7			
V^{5+}		24.7			14.4			
Fe^{3+}		1.3			0.4			
Mn		0.0			0.0			
Cl		0.1			0.0			
Ba		0.0			0.0			
U^{6+}		34.6			48.1			
O (calc)		28.5			22.9			
Total		**91.7**			**92.5**			

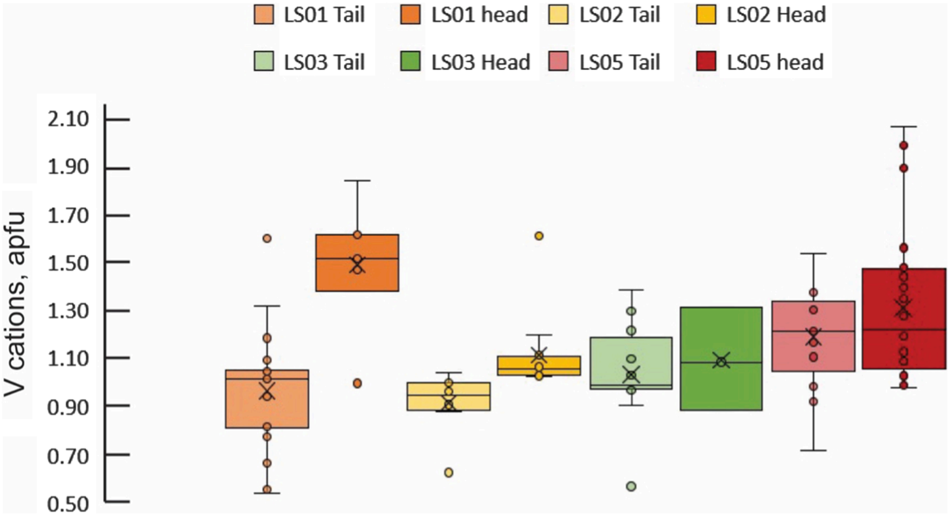

Fig. 5. Box-and-whisker plot comparing V atoms per formula unit (apfu) V-phyllosilicate in heads and tails.

tails (Fig. 5). Extraction of around 10 % was achieved from the V-illites in LS02, and in no other sample was there a statistically significant difference in the V content of the phyllosilicates in heads and tails.

4. Discussion

4.1. Sources of decreased recovery

This study identified two principal barriers to optimal recovery in the La Sal ores: locking of highly soluble V-hydroxides and pitchblende in insoluble minerals, and the large proportion of V hosted by low-solubility minerals, mainly V-illite and V-chlorite.

Locking is either by quartz overgrowths (pitchblende), or by clumps of V-illite (pitchblende, V-hydroxides. It is apparent from SEM images of the −850 μm head mounts and the −106 μm tail mounts that V-illite clumps are not fully disaggregated by grinding or by the agitated leach process. High-resolution microscopy reveals that these clumps of V-phyllosilicate lock fine grains of V-hydroxide and pitchblende (Fig. 4b, c). For U, physical locking appears to be the principal cause of low recovery. However, for V it is less important than the low solubility of V phyllosilicates.

Whereas the V-hydroxides leach readily when exposed, and are absent or nearly absent from the tailings samples, V-phyllosilicates dominate much of the tails and retain most of their V. In the SEM images of tail samples, V-illite is abundant and texturally intact, showing little evidence of dissolution. Comparing EPMA analyses of V-illites in heads and tails showed reductions in V content of only 3 – 36 % (Fig. 5). The reasons for the variability in recovery from V to illite are a subject for future investigation, but may relate to the varied siting and bonding structure of V in phyllosilicates. The minor Ti-Fe-V oxide mineral also appears insoluble: grains of it were identified in the tails containing up to 20 % V, roughly the same concentration as in the heads.

4.2. Effect of V-phyllosilicate type

A mineralogical difference between the two lowest-grade samples – LS01 (1.95 % V) and LS04 (1.87 % V) is likely to be one cause for their very different V recoveries. As discussed above, in sample LS01 all available vanadium was leached from the V-hydroxide along with approximately 1/3 of the vanadium contained in V-illite, yielding an overall recovery of 34.2 %. In contrast, sample LS04 yielded only 18.6 % recovery despite identical leach conditions and similar grade (Table 6). Vanadium in LS04 is hosted by V-chlorite (82.5 % of V) and duttonite (17.5 % of V). The recovery of 18.6 % is thus consistent, within error, with extracting more or less all of the V from duttonite and none of it from the V-chlorite. Therefore, the type of V-phyllosilicate in the deposit is likely to be important to leaching: V-chlorite appears to be very resistant to leaching while V-illite yields higher, though still relatively low, recovery at the same conditions.

4.3. Comparison with previous studies

The metallurgy of uranium ores in sandstone-hosted deposits is both well-understood and tractable (Youlton and Kinnaird, 2003; Pownceby and Johnson, 2014). The main process mineralogy issues identified are acid consumption by carbonate gangue and preg-robbing by phyllosilicates, organic carbon, and phosphates (Pownceby and Johnson, 2014; Youlton, 2014). Neither of those was noted as a problem in this study. Pownceby and Johnson (2014) identified locking by quartz as a problem for fine-grained pitchblende and suggested fine grinding to liberate it, but the extremely small grain size of the pitchblende (Figs. 3 and 4) renders this solution uneconomic for the La Sal ores.

By contrast, V in sandstone-hosted ores is rarer and is relatively poorly studied. The primary example of the U-V deposit type outside the Paradox Basin is the Bigrlyi deposit in Australia, whose ore and gangue mineralogy is virtually identical to La Sal's but whose metallurgy has not been studied (Schmid et al., 2020). The literature that does exist on the metallurgy of sandstone-hosted U ores, and of V in sediments, is mostly consistent with the results here for both U and V. Recovery of U from pitchblende, and of V from hydroxides, is generally high (Peters Geosciences, 2014; Tavakoli et al., 2014). In contrast, recovery of V from phyllosilicates is a well-known problem outside the Paradox Basin. The results presented here are consistent with those of Li et al. (2009, 2010), who recovered < 80 % of V from phyllosilicate hosts in a black shale ore even with pressure leaching 130 °C and > 9 atm P_{O2}. At ambient conditions, such as those in the present study, recoveries from V-phyllosilicates are generally far lower, usually < 50 %. Zheng et al. (2019a) suggested adding fluoride ion to the leaching solution as a way to improve recovery from phyllosilicates, as the hydrofluoric acid (HF) that it forms is one of the few acids capable of rapidly dissociating silicates. While their results did show improved recovery in the leaching system, the overall viability of fluoride addition as a process option is not clear given the environmental ramifications of HF formation.

Table 6
Results of leach tests from the samples in this study.

Sample	Assay %V	V recovery, %
LS01	1.95	34.2 ± 1.26
LS02	2.98	28.8 ± 0.94
LS03	7.23	27.7 ± 1.86
LS04	1.87	18.6 ± 0.76
LS05	10.4	33.2 ± 2.02
LS11	*10.1*	*25.6** ± 0.80

*Precipitates were observed after sampling.

The results of this study support previous investigations that have concluded that V recovery from phyllosilicates varies with phyllosilicate type; however, the details are unresolved. Based on density functional theory, Zheng et al. (2019b) suggested that V exists as V^{3+} in the octahedral site of micas, and that the main control on leachability is whether the mica is dioctahedral (muscovite) or trioctahedral (biotite). According to their calculations, V should be easiest to leach in dioctahedral micas. However, the accompanying experimental data they show do not clearly indicate the type of mica, and in at least one of the two analyses presented, the given composition corresponds to a chlorite or clay rather than a mica (Zheng et al., 2019b). In this study, the highest recoveries from the phyllosilicates were achieved from sample LS01, which contained V as V-illite, and were lower in the V-chlorite-dominated sample. This contrasts with Zheng et al.'s results, as V-illite is a K-deficient dioctahedral mica; V-chlorite is not a mica but is more analogous to trioctahedral (biotite) than to dioctahedral (muscovite) types. Chlorite has a *T*-O-*T*-O rather than a *T*-O-T structure, so its behavior may not be entirely analogous to that of either mica anyway. The other V-illite-dominated samples yielded much lower recovery, leaving open the possibility that the higher recovery from LS01 results from unrecognized complicating factors below the resolution of the analytical techniques employed in this study. At any rate, the significance of V-phyllosilicate type for V leachability is ambiguous given the current state of research.

4.4. Implications for leaching in industrial settings

This study has identified the principal sources of sub-ideal leaching recovery from sandstone-hosted U and V ores. Recommendations for addressing the problems are less simple. For uranium, the main loss to tailings is caused by physical locking. Some losses are inevitable given the extremely fine grain sizes of the lost grains in quartz (Fig. 4), which precludes the possibility of increasing recovery through fine grinding. For pitchblende grains locked in phyllosilicate clumps, increasing agitation speed or residence time in the tank leach may disaggregate the locking grains enough to enhance recovery. However, improvements are likely to be minor given the already high U recoveries and the small grain sizes of the locked ores.

For V recovery, the main hindrance is the insolubility of some of the ore minerals even when fully liberated. This could potentially be addressed by chemical additives that are better than H_2SO_4 at dissolving silicate minerals. Zheng et al. (2019a) has suggested fluoride for this purpose. Unfortunately, fluoride and other silicate-dissolving additives are probably uneconomic even apart from environmental considerations. A reagent capable of dissolving phyllosilicates would probably also attack quartz and feldspar, which make up the large majority of the ore-bearing rocks (Table 3). Without expensive pre-concentration of the ore minerals, a leaching system using fluoride or other additives would encounter prohibitive gangue reagent consumption. A more viable option may be to lengthen leaching times. The economics would depend on the relative impact of decreased throughput compared to increased V recovery, but costs would likely be far lower than those incurred by using a silicate-dissolving additive.

4.5. Implications for U and V extraction in other deposit types

The results of this study also carry implications for U and V geometallurgy beyond the relatively narrow field of sandstone-hosted U-V ores. The extraction of V from phyllosilicate ores is a concern for other types of ores, such as the low-grade but high-volume resources of black shale found principally in China (Li et al., 2009, 2010; Kelley et al., 2017). Salt roasting is most often recommended as the technique that yields maximum V recovery, but its expense makes it uneconomic for much of the low-grade V resource. Leaching is probably the cheapest way to process the ores (Zheng et al., 2019a,b). But the results given here, in conjunction with the existing literature, suggest that V recovery from phyllosilicates is a considerably more complex problem than is generally recognized. Further research will focus on disentangling the influences of phyllosilicate type, V siting and bonding, crystallinity, and other factors on V leaching.

5. Conclusions

Geometallurgical problems in sandstone-hosted U-V ores vary. For U, recoveries are generally high, limited only by the locking of a very small proportion of fine pitchblende grains under insoluble minerals, mainly quartz overgrowths and within clumps of V-phyllosilicates. When exposed, pitchblende grains are highly soluble and leach easily; however, exposing the extremely fine grains found in leach residues would require prohibitively fine grinding.

For V, the main problem is the insolubility of V-phyllosilicates. Grain size is typically larger than for U and liberation is accordingly better, but V recoveries are lower than U recoveries. The main reason for this is that a large fraction of the V resource is held in V-illite, roscoelite, and V-chlorite. Leach recovery from V to illite and roscoelite ranges up to nearly 1/3, but is near zero from the V-chlorites. The reason for the variation in V recovery from V to illite and roscoelite is the subject of ongoing investigation, but may relate to variations in V siting and bonding. The geometallurgy of V in these sandstone-hosted ores is expected to be similar to its behavior in leaching other phyllosilicate- and (hydr)oxide-dominated ore types worldwide, including V in stone coal or black shale deposits.

CRediT authorship contribution statement

Molly R. Radwany: Investigation, Formal analysis, Visualization, Writing – original draft. **Isabel F. Barton:** Conceptualization, Supervision, Resources, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mineng.2022.107811.

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