# Leaching Metals from Phyllosilicate Ores

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## ABSTRACT

Phyllosilicate minerals are important ores of V, Zn, Ni, and sometimes Cu. This paper uses phyllosilicate crystal chemistry, leaching experiments, and transmission electron microscopy to examine metals' three distinct modes of occurrence and leachability in these ores. (1) Adsorbed metals can be liberated via exchange with solution cations, depending on chemical conditions and phyllosilicate type. (2) Crystallographically contained metals are partially leachable, typically at elevated temperatures, if they are in octahedral or higher coordination. (3) V, Ni, Cu, and possibly other metals, form discrete nanometer-scale inclusions within phyllosilicates whose leachability is mostly controlled by their mineralogy, not the phyllosilicate host's.

## INTRODUCTION

### Background

The phyllosilicate or sheet silicate minerals are important ores of V, Zn, Ni, and sometimes other metals such as Cu, in laterites and some other low-temperature deposit types. Often these ores are as intractable as they are important. Most separation processes fail to work on phyllosilicates, which have similar density, magnetic, and flotation characteristics to most of the rest of the mined rock. Metal extraction from these ores thus relies largely on whole-ore operations, either pyrometallurgical (roasting, smelting), hydrometallurgical (leaching, pressure leaching), or combinations of these, after limited beneficiation (Dalvi et al., 2004). The expense of smelting, particularly on sulfide-poor ore types, increasingly renders leaching a more economically attractive option.

Yet the leaching behavior of phyllosilicates, as a mineral class, remains poorly understood. A few theoretical studies have applied crystal-chemical calculations to predict how they should dissolve (Terry, 1983a,b; Crundwell, 2014; Chetty, 2018). Since dissolving phyllosilicates is not the goal of most leaching operations, experimental studies are few. They also reach inconsistent results, recording full, partial, or no dissolution of target metals from what seem to be the same minerals (e.g. Radwany and Barton, 2022).

Much of the inconsistency is perhaps due to the under-recognized complexity of metal occurrence in phyllosilicates, which can include multiple valence states, coordination numbers, and (nano)mineral types. Characterizing these exceeds the scope and power of most analytical techniques applied in leaching research, so the actual speciation of a metal in a phyllosilicate sample is often assumed rather than established. As a consequence, complex leaching behavior seldom matches the predictions of simple crystal-chemical theory, or the results of other leaching studies. This paper and the accompanying presentation explore the various styles of occurrence of metals in phyllosilicates and their effects on leaching.

## Mineralogical and leaching overview

The phyllosilicates are a large family of minerals that includes micas, chlorites, kandites, serpentine, talc, and clays among others. Their common feature is a layered structure in which each layer is a sheet of cations in octahedral (vi) or tetrahedral (iv) coordination with oxygen anions, with an overall ratio of 4 tetrahedral cations (usually $Al^{3+}$ and $Si^{4+}$) per 10 $O^{2-}$ anions. The ratio and arrangement of octahedral and tetrahedral sheets varies, and some phyllosilicates contain additional layers of larger (usually alkali, x or xii-coordinated) cations, adsorbed cations, and/or water. Figure 1 shows a few of the more common phyllosilicate variants. In these structures, target metals (V, Ni, Zn, Cu) are typically assumed to exist in the octahedral sites, replacing Mg, Fe, and/or Al. As this paper will show, this assumption is probably correct for Zn but is a vast oversimplification for the other metals, which can occur in multiple different forms in phyllosilicates.

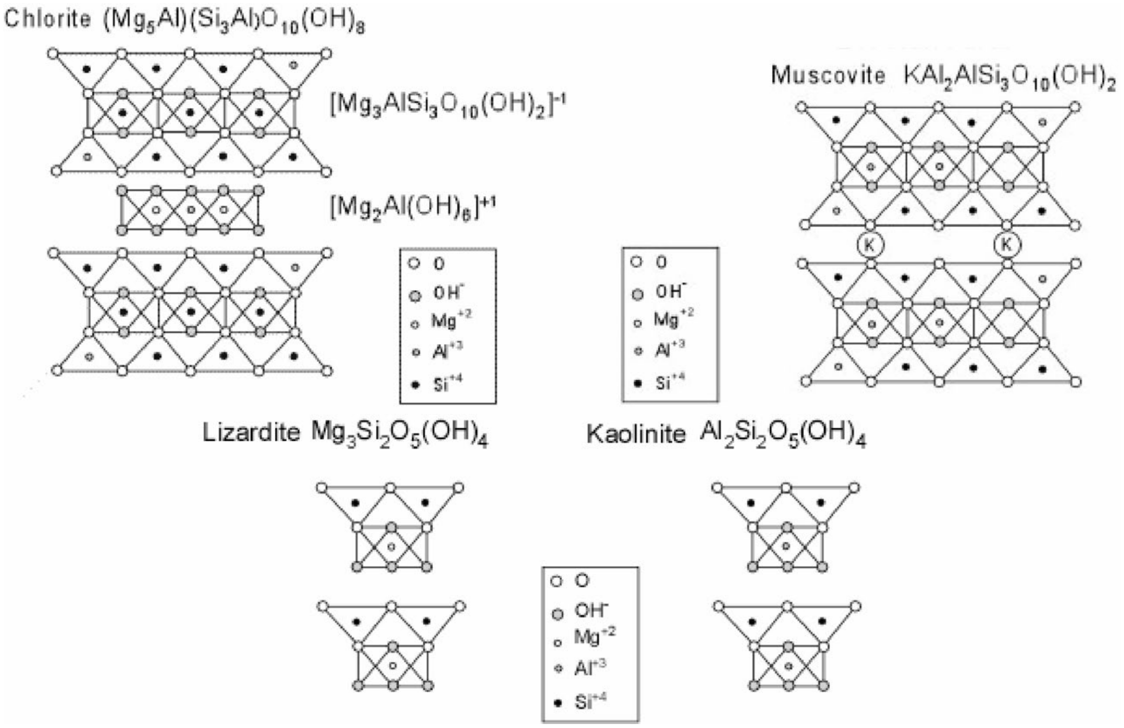

**Figure 1. Structures of selected phyllosilicate examples: clinochlore (chlorite), muscovite (mica), lizardite (serpentine), and kaolinite (clay), showing arrangement of octahedral and tetrahedral sites. Images from Tulane University mineralogy website**

The phyllosilicates are common rock-forming minerals and less common ore minerals. Virtually all contain metal, most often octahedrally coordinated Mg and Fe (biotites, chlorites, smectite clays) and octahedral and/or tetrahedral Al (nearly all). Strong crystal bonding makes these metals difficult to extract, so they are recovered from the more tractable and usually higher-grade oxide mineral types instead. The concentrations of other, rarer base metals are generally < 1%. The exceptions to this are the phyllosilicate ores of V, Ni, and Zn, shown in Table 1. Clays, micas, and chrysocolla may also contain Cu, making them a small but non-negligible ore host at some Cu mines, particularly porphyries. In phyllosilicates metals occur in one or more of three possible modes: as ions adsorbed to the mineral surface, as ions occupying sites in the phyllosilicate crystal lattice, and/or as nanoscale exsolutions or inclusions of metallic minerals within the phyllosilicate.

**Table 1. Common phyllosilicate ores of metal**

| *Metal* | *Deposit types with ore phyllosilicates* | *Principal minerals (phyllosilicate group)* | *Formulas* |
|---|---|---|---|
| Ni | Laterite; supergene zones of other deposit types | "Garnierite" | Mix of other Ni-phyllosilicates |
| | | Pimelite (clay) | $Ni_3Si_4O_{10}(OH)_2 \cdot 4H_2O$ |
| | | Lizardite (serpentine) | $Mg_3(Si_2O_5)(OH)_4$ |
| | | Nepouite (serpentine) | $(Ni,Mg)_3(Si_2O_5)(OH)_4$ |
| | | Ni-chlorite (chlorite) | $(Mg,Fe)_5Al(AlSi_3O_{10})(OH)_8$ |
| | | Willemseite (talc) | $Ni_3Si_4O_{10}(OH)_2$ |
| Zn | Supergene zones of multiple deposit types | Hendricksite (mica) | $KZn_3(Si_3Al)O_{10}(OH)_2$ |
| | | Zn-illite (mica) | $K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$ |
| | | Zn-smectite (clay) | $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ |
| | | Baileychlore (chlorite) | $(Zn,Fe^{2+},Al,Mg)_6(Si,Al)_4O_{10}(OH)_8$ |
| | | Greenalite (kaolinite) | $(Fe^{2+},Fe^{3+})_{2-3}Si_2O_5(OH)_4$ |
| V | Sandstone-hosted | Roscoelite (mica) | $K(V^{3+},Al)_2(AlSi_3O_{10})(OH)_2$ |
| | | V-illite (mica) | $K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$ |
| | | V-chlorite (chlorite) | $(Mg,Fe)_5Al(AlSi_3O_{10})(OH)_8$ |
| Cu | Supergene zones of multiple deposit types | Chrysocolla | $Cu_{2-x}Al_x(H_{2-x}Si_2O_5)(OH)_4 \cdot nH_2O$, $x < 1$ |
| | | Cu-biotite (mica) | $K(Mg,Fe)AlSi_3O_{10}(OH)_2$ |
| | | Cu-chlorite (chlorite) | $(Mg,Fe)_5Al(AlSi_3O_{10})(OH)_8$ |
| | | Cu-illite (mica) | $K_{0.65}Al_{2.0}[Al_{0.65}Si_{3.35}O_{10}](OH)_2$ |
| | | Cu-smectite (clay) | $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$ |

Responses to acid leaching vary, depending mostly on the type of phyllosilicate. Some, such as kaolinite, the kandites, and aluminosilicate clays, are stable in acid and tend to break down slowly if at all. Others, typically those with high Mg and Fe contents (chlorites, biotite, talc, serpentine, and the magnesian clays) are highly reactive to acid and break down on a timescale of days to months, consuming leaching acid in the process. In between are alkali-bearing aluminosilicate species such as muscovite, which rapidly exchanges its $K^+$ and some $Al^{3+}$ for $H^+$ but thereafter becomes largely unreactive to acid as the weakly bonded species have been removed (Chetty, 2018).

## ADSORBED METALS

The small grain size and platy shape of phyllosilicates make them a ready substrate for adsorption of dissolved cations in solution. Since the cleavage surfaces of plates tend to be only weakly charged, most adsorption actually takes place on the edges (rather than faces) of the plate-shaped grains. Many phyllosilicates, such as the smectite or swelling clay group, also have capacious charged interlayers that will absorb water molecules and anything in solution, including and especially cations. Copper and other metals notoriously adsorb into this interlayer as outer-sphere complexes with hydroxyl and as inner-sphere monomers and dimers, as well as adsorbing to the edges of smectite crystals where the adsorbed metals essentially extend the octahedral sheets (Fig. 1; Schlegel et al., 2001). The exact balance of edge and interlayer adsorption varies with the solution's alkali-metal concentration, but typically interlayer adsorption dominates at acid pH (Morton et al., 2001). While adsorption is entirely a charge-based phenomenon for some metals (Cu), adsorption of Ni, Zn, and some other divalent cations can produce a solid metallic precipitate adhering to the phyllosilicate surface (Strawn et al., 2004). Typically, this is an oxide or hydroxide, but Zn adsorption has been found to lead to the epitaxial growth of Zn phyllosilicates on smectites (Schlegel et al., 2001). The amount of metal that can be adsorbed depends on the metal ion and type of phyllosilicate involved, as well as the pH and other solution conditions, but in general loading capacities range from < 5 micromoles per gram of phyllosilicates to > 3000, though they tend to be somewhat lower than the maximum possible values at the acid conditions of leaching. In general the higher values are for smectite-group minerals such as bentonite, montmorillonite, and vermiculite (Graefe et al., 2017).

Adsorption may be reversible, but in most cases reversibility is partial. Species that chemisorb, or precipitate on the phyllosilicate surfaces, may or may not dissolve when pH changes depending on their solubility. Even for simply adsorbed (non-chemisorbed) metals, some 10-20% is adsorbed via a non-pH-dependent mechanism and will remain stuck to the phyllosilicate surfaces irrespective of changes in pH (Strawn et al., 2004).

Adsorption of metals can be a major problem in leaching, for example with preg-robbing from leaching solutions. However, among the ore phyllosilicates it is rare for the target metals to exist in adsorbed form, with a few exceptions. These exceptions include rollfront uranium deposits, where U adsorbs to clays and other species (Hall et al., 2017), and black shales where some V appears to be adsorbed on illite and clays (Peacor et al., 2000). The other two modes of occurrence are far more common and harder to deal with in leaching.

## CRYSTALLOGRAPHIC METALS

In theory most ore metals (except Si and some Al) occupy the octahedral site in phyllosilicates due to cation-anion radius ratio and charge constraints. The canonical view is that nickel is octahedral $Ni^{2+}$ in garnierite minerals, vanadium is octahedral $V^{3+}$ in roscoelite, and so forth. Based on the bond strength (charge divided by coordination number), theoretical crystal-chemical studies predict an order of dissolution:

$$M^{+,\,\mathrm{x\ or\ xii}} \rightarrow M^{+,\,\mathrm{vi}} \rightarrow M^{2+,\,\mathrm{x\ or\ xii}} \rightarrow M^{2+,\,\mathrm{vi}} \rightarrow M^{3+,\mathrm{vi}} \rightarrow M^{4+,\,\mathrm{vi}} \rightarrow M^{3+,\,\mathrm{iv}} \rightarrow M^{4+,\,\mathrm{iv}} \tag{1}$$

Toward the end of this sequence, dissolution requires the strong acids and high temperatures of a chemical digestion. Under most industrial leaching conditions, the practical limit for dissolution lies somewhere around the sixth step, where the octahedral layers of the phyllosilicate decompose. Tetrahedral bonding is typically too strong for conventional hydrometallurgy, though the remains of the phyllosilicate at that point often form a siliceous gel. Under the assumption that target metals in phyllosilicates are octahedral monovalent to trivalent cations, this should translate into a high overall recovery by leaching.

Natural mineralogical reality eats these elegant theories for breakfast. Where crystal and solution chemistry predict complete or near-complete dissolution of target metals, atmospheric leach recovery of Ni, Co, V, and Cu from phyllosilicate ores in practice falls well short of that mark (e.g. Dalvi et al., 2004; Gao, 2021; Radwany and Barton, 2022). Recent detailed analyses indicate that the valence states and siting of ore metals in phyllosilicates are far more varied than has generally been thought. For example, the theoretical compositions of roscoelite and vanadian illite assume that V exists as $V^{3+}$ in the octahedral site (Table 1). In contrast, detailed analysis by electron energy-loss spectroscopy shows that some 60 to 80% of it is actually $V^{4+}$ (Zanetta et al., 2023; Drexler et al., 2023). Results of TEM imaging were ambiguous, but combined with the high charge they suggested that at least some of the $V^{4+}$ occupies the tetrahedral site. Given that tetrahedral $V^{4+}$ is twice as strongly bonded as octahedral $V^{3+}$, this has an obvious and profound potential impact on the rate and extent of dissolution (Eq. 1). In practice, historical V recoveries of 70-75% in heated tank leaching for a mix of V-phyllosilicate and V-(hydr)oxide ores, plus SEM examination showing an absence of V oxides and presence of V-bearing phyllosilicate remains in tails, suggests that much of the phyllosilicate V is not leachable (Peters Geosciences, 2014; Gao, 2021). This would be unexpected if all V is octahedral, but is consistent with at least partial tetrahedral occupancy.

The other target metals common in phyllosilicate lattices (Ni, Zn) are easier to leach, mainly because none of them has a stable tetravalent ion. Nickel, which can speciate as $Ni^{2+}$ and/or $Ni^{3+}$ in phyllosilicates, occupies the octahedral site almost exclusively; tetrahedrally coordinated $Ni^{3+}$ is rare in phyllosilicates (Manceau and Calas, 1985, 1987). However, in leach-based processes Ni recovery decreases as the proportion of it hosted in smectites increases, and overall Ni recovery plateaus under 90% irrespective of the reagents or temperatures applied (Hirasawa and Horita, 1987; Dalvi, 2004; McDonald and Whittington, 2008). In the Caron process, typical Ni recoveries are 60-80% with most of the loss accruing during the leaching stage (Crundwell et al., 2011). This suggests that some 10% or more of Ni in phyllosilicates is fundamentally unleachable under standard conditions. This could be due either to tetrahedral siting and consequent strong bonding, or to some of the nickel existing as an undetected insoluble species within the phyllosilicate lattice, as described below.

Deviations from theory are probably minimal for phyllosilicates containing Zn, whose single stable cationic state is divalent and too large for tetrahedral coordination. This gives Zn in phyllosilicates a relatively low overall bond strength and makes it comparatively easy to leach. The fact that the first step in most Zn production is roasting also renders its primary leachability in phyllosilicates somewhat moot (Sinclair, 2005).

Copper in most phyllosilicates exists as exsolutions of native Cu, covered below. The major exception is chrysocolla, a phyllosilicate with $Cu^{2+}$ in the octahedral sheet. Acid leaching recoveries from chrysocolla are typically high (> 80%), as would be expected from Eq. 1. Similar substitution of $Cu^{2+}$ in octahedral coordination has been obtained from synthetic kaolinite, but has not been conclusively demonstrated in natural kaolinites (Petit et al., 1995). Selck (2017) speculated that smectite and slightly phengitic illite can host $Cu^{2+}$ substituting for $Mg^{2+}$, but TEM measurements have not verified or disproved this.

## EXSOLVED OR INCLUDED METALS

Metals that appear to be part of the phyllosilicate lattice in conventional electron microscopy frequently turn out, on closer examination, to be nothing of the sort (Fig. 2). Ilton and Veblen (1988) first reported that the Cu in an anomalously high-Cu biotite existed as inclusions of native metal, with no detectable Cu actually present in the phyllosilicate lattice. The same is true of illite, chlorite, and serpentine, which contain Cu and Ni as nanoscale domains of native metal (Ahn et al., 1997; Suarez et al., 2011). Nickel also occupies octahedral sites in the crystal lattice as $Ni^{2+}$ and $Ni^{3+}$ (Suarez et al., 2011). In at least one case domains of Ni-oxyhydroxide, rather than native Ni, have also been found (Putzolu et al., 2020).

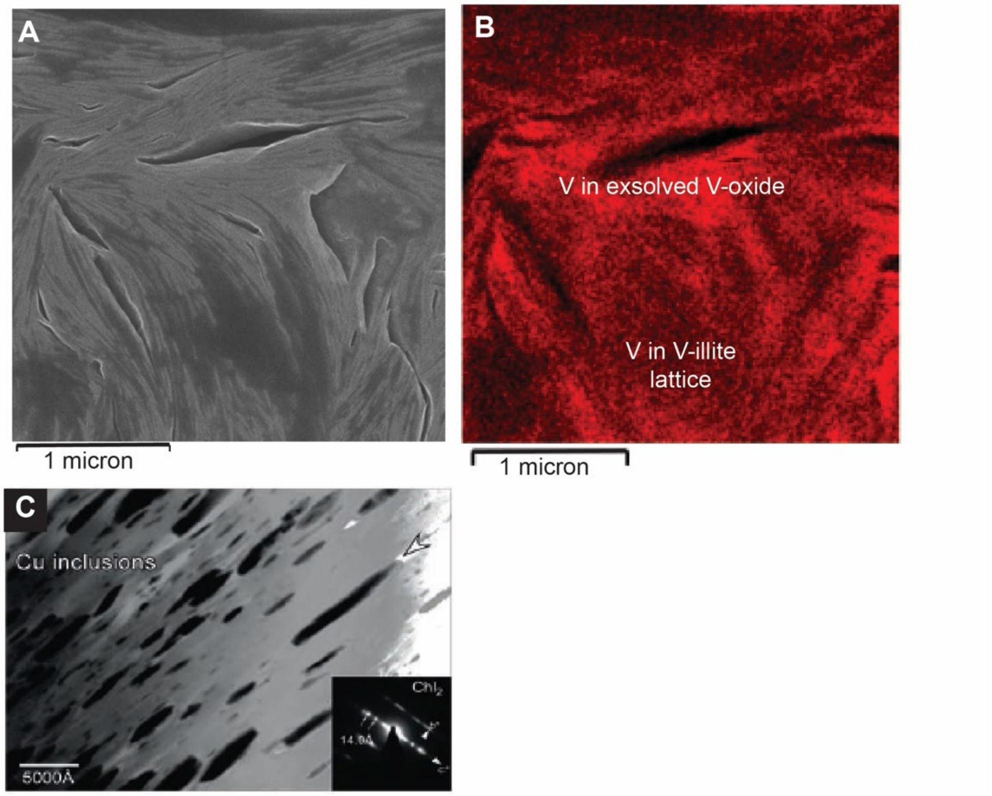

**Figure 2. Example transmission electron microscopy images of two styles of metal occurrence in phyllosilicates. A: Secondary electron image of a V-illite from the La Sal mine, Utah. B: Energy-dispersive spectroscopy map of A, showing the distribution of V between exsolved V oxides and the V-illite lattice proper. C: Image of nanoscale inclusions of copper (dark) in a chlorite from the Aguablanca deposit, Spain (Suarez et al., 2011). In this case Cu is virtually absent from the lattice of the phyllosilicate proper. A and B are from Drexler (2022)**

The proportions of metal in the phyllosilicate lattice proper and in exsolutions vary. Most Ni substitutes comfortably for $Mg^{2+}$ and $Fe^{2+}$ on phyllosilicate lattices and the proportion in exsolved native Ni or Ni-oxyhydroxides seems to be small. No cases of Zn exsolving separate oxide, hydroxide, or other domains are known; its mode of occurrence appears to be entirely octahedral $Zn^{2+}$. By contrast, Cu appears to exist mostly as nanoscale domains of native metal. Chrysocolla is the only phyllosilicate mineral reported with a non-negligible amount of Cu in the actual lattice. Vanadium is a middle case, with illites from sandstone-hosted deposits containing V both as lattice substitutions (described above) and as exsolved domains of V oxide with an approximate composition of $VO_2$ (Drexler, 2022; Drexler et al., 2023). The proportion of V occurring as exsolved nanophase oxides versus crystallographic substitutions is unclear. In all cases these metals or metal oxides exist at spatial scales on the order of a few nanometers, invisible to most electron microscopes and microprobes and requiring transmission electron microscopy to detect. This effectively precludes a rigorous study with sufficient samples for statistical representation.

For this type of phyllosilicate-hosted metal, leachability depends entirely on the solubility and location of the metal phases. In the case of V, the presence of these $VO_2$ domains correlates with higher V recovery, since $VO_2$ is readily acid-soluble and most of it is at or near the edges of the illite grains (Drexler, 2022; Drexler et al., 2023). No comparable study has been performed for Cu, but both its principal mode of occurrence as native Cu and its typical position deep inside the biotite crystals suggests recovery to acid leaching would be negligible. In this case the actual metal host is poorly soluble in acid, at least without added oxidant, and is locked by an even more insoluble silicate mineral for most of the leaching period.

## DISCUSSION

The variety of natural modes of occurrence of metals in phyllosilicates (summarized in Table 2) presents a complex problem for hydrometallurgy. Firstly, recoveries will vary. Leaching can dissolve most adsorbed metals with relative ease, but this mode of occurrence is rare in most ore deposits. Of the two more common modes of occurrence, acid leaching will usually recover metals in the octahedral layers of the phyllosilicates, though long times may be required. Recovery is poor from metals in tetrahedral sites due to their stronger bonding. The presence of nanoscale metals or metal oxide/hydroxide exsolutions in the phyllosilicate lattice can mean high recovery (if these phases are soluble and accessible to lixiviant) or practically zero (if they are insoluble and/or locked by the phyllosilicate). This leads to an overall sequence of leachability for phyllosilicate-hosted metals of:

$$\text{Zn} \sim \text{Ni} \sim \text{Cu (in chrysocolla)} > \text{V} > \text{Cu (in other phyllosilicates)} \qquad (2)$$

**Table 2. Summary of metal occurrence in phyllosilicates**

| *Metal* | *Occurrence in phyllosilicates* | *Species* | *Leachability* |
|---|---|---|---|
| Cu | Octahedral site of chrysocolla | $Cu^{2+}$ | High |
| | Nanoscale exsolutions | Native Cu | Very low |
| V | Octahedral site | $V^{3+}$, $V^{4+}$ | High |
| | Tetrahedral site | $V^{3+}$, $V^{4+}$ | Low |
| | Nanoscale exsolutions | $VO_2$ or similar oxide | High unless locked |
| Ni | Octahedral site | $Ni^{2+}$, $Ni^{3+}$ | High |
| | Nanoscale exsolutions | Native Ni; NiOOH species | Low; high unless locked |
| Zn | Octahedral site | $Zn^{2+}$ | High |

Recovery prediction in detail is difficult or impossible with most analytical techniques currently applied in geometallurgy. Electron microscopy-based analyses, including SEM, QEMSCAN, MLA, TIMA, and even electron microprobes, can detect the chemical presence of a metal in a phyllosilicate but not its mode of occurrence. For metals with more than one possibility, such as V and Ni, which mode of occurrence (crystallographic metal or exsolved phase) dominates may well be deposit- or rock-specific. Further questions such as the proportion of octahedral or tetrahedral site occupancy require even more detailed analysis.

Specialized testing, however, may help with some of these questions. Cation-exchange capacity and similar tests can measure the amount of metal reversibly adsorbed to phyllosilicates, and is already routine at many mines to assess preg-robbing capacity. Short-wave infrared spectroscopy, at high enough spectral resolution, can relate wavelength shifts to substitution at least in the octahedral sites of phyllosilicates, though quantification is difficult. Transmission electron microscopy is a difficult and preparation-intensive process, but helps distinguish included from crystallographic metals – if the distinction is important enough to merit the time and expense of the analysis.

The prospect of improving leach recovery from phyllosilicates may or may not justify operational adjustments. Leaching at higher temperatures or with stronger acids, roasting, or autoclaving are likely to help liberate more crystallographically bound metals, but since these tactics also enhance recovery in general, they are already in use at mines where they are needed. Finer grinding is expensive and using it to liberate metal oxide or hydroxide inclusions within the phyllosilicates would be prohibitive given their size (Fig. 2).

## CONCLUSIONS

Metal recovery from leaching phyllosilicate ores varies strongly. The probable cause is under-recognized complexity in how phyllosilicate minerals contain metals. Metals may occur in phyllosilicates as reversibly or irreversibly adsorbed species; as cations of varying charge in the octahedral or tetrahedral sheets of the phyllosilicate crystal lattice; as nanoscale inclusions or exsolutions of metal-rich nonsilicate phases; or multiple of these, ranging from easily leachable to completely unrecoverable under standard conditions. Most characterization techniques in geometallurgy lack the spatial resolution to identify these, although specialized tests such as cation exchange capacity, infrared spectroscopy, and transmission electron microscopy can help assess particular cases (adsorption, octahedral siting, inclusions).

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## REFERENCES

Ahn, J.H., Xu, H., and Buseck, P.R. 1997. Transmission electron microscopy of native copper inclusions in illite. *Clays and Clay Minerals* 45: 295-297.

Chetty, D. 2018. Acid-gangue interactions in heap leach operations: a review of the role of mineralogy for predicting ore behavior. *Minerals* 8: 47, 11 p.

Crundwell, F., Moats, M., Ramachandran, V., Robinson, T., and Davenport, W.G. 2011. *Extractive metallurgy of nickel, cobalt and platinum group metals.* Elsevier.

Crundwell, F.K. 2014. The mechanism of dissolution of minerals in acidic and alkaline solutions: Part II Application of a new theory to silicates, aluminosilicates and quartz. *Hydrometallurgy* 149: 265-275.

Dalvi, A.D., Bacon, W.G., and Osborne, R.C. 2004. The past and future of nickel laterites. In *Proceedings of PDAC 2004*, 27 p.

Drexler, M.S. 2022. Vanadium in phyllosilicates. Unpub. M.S. thesis, University of Arizona, 58 p.

Drexler, M.S., Barton, I.F., and Zanetta, P.M., 2023. Vanadium in phyllosilicate ores: occurrence, crystal chemistry, and leaching behavior. *Minerals Engineering* 201: 108205.

Gao, F., Olayiwola, A.U., Liu, B., Wang, S., Du, H., Li, J., Wang, X., Cheng, D., and Zhang, Y. 2021. Review of vanadium production. Part I: Primary resources. *Mineral Processing and Extractive Metallurgy Review* 43: 466-488.

Graefe, M., McFarlane, A., and Klauber, C., 2017, Clays and the minerals processing value chain (MPVC). In *Clays in the Minerals Processing Value Chain*. Edited by Graefe, M., et al. Cambridge University Press, Cambridge, UK: 1-80.

Hall, S.M., Mihalasky, M.J., Tureck, K.R., Hammarstrom, J.M., and Hannon, M.T. 2017. Genetic and grade and tonnage models for sandstone-hosted roll-type uranium deposits, Texas Coastal Plain, USA. *Ore Geology Reviews* 80: 716-753.

Hirasawa, R., and Horita, H. 1987. Dissolution of nickel and magnesium from garnierite ore in an acid solution. *International Journal of Mineral Processing* 19: 273-284.

Ilton, E.S., and Veblen, D.R. 1988. Copper inclusions in sheet silicates from porphyry Cu deposits. *Nature* 334(11): 516-518.

Manceau, A., and Calas, G. 1985. Heterogeneous distribution of nickel in hydrous silicates from New Caledonia ore deposits. *American Mineralogist* 70: 549-558.

Manceau, A., and Calas, G. 1987. Absence of evidence for Ni/Si substitution in phyllosilicates. *Clay Minerals* 22(3): 357-362.

McDonald, R.G., and Whittington, B.I. 2008. Atmospheric acid leaching of nickel laterites review Part I. Sulphuric acid technologies. *Hydrometallurgy* 91: 35-55.

Morton, J.D., Semrau, J.D., and Hayes, K.F. 2001. An X-ray absorption spectroscopy study of the structure and reversibility of copper adsorbed to montmorillonite clay. *Geochimica et Cosmochimica Acta* 65(16): 2709-2722.

Peacor, D.R., Coveney, R.M., and Zhao, G. 2000. Authigenic illite and organic matter: the principal hosts of vanadium in the Mecca Quarry Shale at Velpen, Indiana. *Clays and Clay Minerals* 48: 311-316.

Peters Geosciences 2014. Technical report on La Sal District Project. NI 43-101 report, 94 p.

Petit, S., Petit, S., Decarreau, A., Mosser, C., Ehret, G., and Grauby, O. 1995. Hydrothermal synthesis (250 ˚C) of copper-substituted kaolinites. *Clays and Clay Minerals* 43.4: 482-494.

Putzolu, F., Abad, I., Balassone, G., Boni, M., and Mondillo, N. 2020. Ni-bearing smectites in the Wingellina laterite deposit (Western Australia) at nanoscale: TEM-HRTEM evidences of the formation mechanisms. *Applied Clay Science* 196: 105753.

Radwany, M.R. and Barton, I.F. 2022. The process mineralogy of leaching sandstone-hosted uranium-vanadium ores. *Minerals Engineering* 187: 107811.

Schlegel, M.L., Manceau, A., Charlet, L., Chateigner, D., and Hazemann, J.L. 2001. Sorption of metal ions on clay minerals. III. Nucleation and epitaxial growth of Zn phyllosilicate on the edges of hectorite. *Geochimica et Cosmochimica Acta* 65(22): 4155-4170.

Selck, J.G. 2017. Copper mineralogy in the oxide zone of the Lone Star porphyry copper deposit, eastern Arizona. Unpublished M.S. thesis, Brigham Young University, 86 p.

Sinclair, R.J. 2005. *Extractive Metallurgy of zinc*. Australasian Institute of Mining & Metallurgy: Victoria.

Strawn, D.G., Palmer, N.E., Furnare, L.J., Goodell, C., Amonette, J.E., and Kukkadapu, R.K. 2004. Copper sorption mechanisms on smectites. *Clays and Clay Minerals* 52(3): 321-333.

Suarez, S., Nieto, F., Velasco, F., and Martin, F.J. 2011. Serpentine and chlorite as effective Ni-Cu sinks during wethering of the Aguablanca sulphide deposit (SW Spain). TEM evidence for metal-retention mechanisms in sheet silicates. *European Journal of Mineralogy* 23: 179-196.

Terry, B. 1983. The acid decomposition of silicate minerals Part I. Reactivities and modes of dissolution of silicates. *Hydrometallurgy* 10: 135-150.

Terry, B. 1983. The acid decomposition of silicate minerals Part II. Hydrometallurgical applications. *Hydrometallurgy* 10: 151-171.

Zanetta, P.M., Drexler, M., Barton, I., and Zega, T. 2023. Vanadium electronic configuration determination from $L_{2,3}$ transition in V-oxide compounds and roscoelite. *Microscopy & Microanalysis*, doi: https://doi.org/10.1093/micmic/ozac057.