

alone. None of the secondary tungstates represents an economically important source of tungsten.

See Also

Minerals: Definition and Classification; Chromates; Molybdates. **Rocks and Their Classification.**

Further Reading

- Anthony JA, Bideaux RA, Bladh KW, and Nichols MC (2003) *Handbook of Mineralogy. Volume 5. Borates, Carbonates, Sulfates, Chromates, Germanates, Iodates, Molybdates, Tungstates, etc., and Organic Materials*. Tucson, AZ: Mineral Data Publishing.
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Vanadates

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Naturally occurring vanadate(V) minerals are described here, together with the environments in which they are found. Attention is drawn to the existence of polyvanadates as well as to normal vanadates. In the latter, extensive solid solution involving arsenate and phosphate is evident. The chemistry of polymerisation of vanadate in acidic solution is well understood and is reflected in many examples in the mineral kingdom. Depending upon the prevailing redox potential in the solutions from which such species crystallise, highly coloured, mixed V(IV, V) species are formed, the so-called vanadium bronzes. Significant amounts of vanadium are recovered from secondary vanadate minerals, but much is derived from the treatment of vanadium-rich fly ash and the mining of primary oxide minerals that carry minor amounts of the element.

Vanadates are compounds containing negatively charged oxyvanadium ions and are extremely widespread in the natural environment in small amounts. A list of them is given in [Table 1](#). Nearly all of the

vanadates are found in the oxidised zones of base metal ore bodies or in other supergene environments, such as drainage channels and oxidised sedimentary rocks. A few, including wakefieldite-(Y), clinobisvanite, and pucherite occur as accessory minerals in granite pegmatites, while others such as leningradite, averierite, and stoiberite are volcanic sublimates. Many vanadate minerals contain the simple tetraoxovanadate(V) or vanadate ion, VO_4^{3-} . The arrangement of such minerals under the first heading in [Table 1](#), however, obscures the fact that in many cases complex solid solution phenomena attend naturally occurring examples. Some of the formulae indicate solid solution series where these are found to be significant for all known examples of particular phases. Nevertheless, all of the simple vanadates incorporate other ions in their lattices. With cations, this phenomenon is common and several series are known, including the descloizite-mottramite and mounanite-krettnichite pairs, for example. Solid solution involving anionic substitution is ubiquitous. Phosphate and arsenate frequently substitute for vanadate in these minerals, albeit to different extents. The vanadate ion, VO_4^{3-} , is somewhat larger than phosphate and arsenate ions, whose thermochemical radii are 230 and 237 picometres, respectively. Other

Table 1 Vanadate minerals*Normal vanadate, oxyvanadate and chlorovanadate(V) minerals*

Averievite	$\text{Cu}_5\text{O}_2(\text{VO}_4)_2 \cdot n(\text{Cu}, \text{Cs}, \text{K})\text{Cl}$ ($n \approx 1.2$)
Brackebuschite	$\text{Pb}_2(\text{Mn}, \text{Fe}, \text{Zn})(\text{VO}_4)_2(\text{OH}, \text{H}_2\text{O})$
Čechite	$\text{Pb}(\text{Fe}, \text{Mn})\text{VO}_4(\text{OH})$
Cheremnykhite	$\text{Pb}_3\text{Zn}_3\text{O}_2(\text{TeO}_4)(\text{VO}_4)_2$
Clinobisvanite	BiVO_4
Descloizite	$\text{Pb}(\text{Zn}, \text{Cu})\text{VO}_4(\text{OH})$
Dreyerite	BiVO_4
Duhamelite	$\text{Pb}_2\text{Cu}_4\text{Bi}(\text{VO}_4)_4(\text{OH})_3 \cdot 8\text{H}_2\text{O}$
Fingerite	$\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$
Gamagarite	$\text{Ba}_2(\text{Fe}, \text{Mn})(\text{VO}_4)_2(\text{OH})$
Hechtsbergite	$\text{Bi}_2(\text{VO}_4)(\text{OH})$
Heyite	$\text{Pb}_5\text{Fe}_2\text{O}_4(\text{VO}_4)_2$
Howardevansite	$\text{NaCu}(\text{Fe}, \text{Al}, \text{Mn})_2(\text{VO}_4)_3$
Kolovratite	$\text{Ni}_x\text{Zn}_y(\text{VO}_4)_z \cdot n\text{H}_2\text{O}$
Kombatite	$\text{Pb}_{14}\text{O}_9(\text{VO}_4)_2\text{Cl}_4$
Krettnichite	$\text{PbMn}_2(\text{VO}_4)_2(\text{OH})_2$
Leningradite	$\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$
Lyonsite	$\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6$
Mcbirneyite	$\text{Cu}_3(\text{VO}_4)_2$
Mottramite	$\text{Pb}(\text{Cu}, \text{Zn})\text{VO}_4(\text{OH})$
Mounanaite	$\text{PbFe}_2(\text{VO}_4)_2(\text{OH})_2$
Namibite	$\text{Cu}(\text{BiO})_2(\text{VO}_4)(\text{OH})$
Palenzonaite	$\text{NaCa}_2\text{Mn}_2[(\text{V}, \text{As}, \text{Si})\text{O}_4]_3$
Pottsite	$\text{HPbBi}(\text{VO}_4)_2 \cdot 2\text{H}_2\text{O}$
Pucherite	BiVO_4
Pyrobelonite	$\text{PbMnVO}_4(\text{OH})$
Reppiaite	$\text{Mn}_5(\text{VO}_4)_2(\text{OH})_4$
Rusakovite	$(\text{Fe}, \text{Al})_5[(\text{V}, \text{P})\text{O}_4]_2(\text{OH})_9 \cdot 3\text{H}_2\text{O}$
Santafeite	$(\text{Na}, \text{Ca}, \text{Sr})_3(\text{Mn}, \text{Fe})_2\text{Mn}_2(\text{VO}_4)_4(\text{OH}, \text{O})_5 \cdot 2\text{H}_2\text{O}$
Schumacherite	$\text{Bi}_3[(\text{V}, \text{As}, \text{P})\text{O}_4]_2(\text{OH})$
Stoiberite	$\text{Cu}_5\text{O}_2(\text{VO}_4)_2$
Tangeite	$\text{CaCuVO}_4(\text{OH})$
Turanite	$\text{Cu}_5(\text{VO}_4)_2(\text{OH})_4$
Vanadinite	$\text{Pb}_5(\text{VO}_4)_3\text{Cl}$
Vésignière	$\text{BaCu}_3(\text{VO}_4)_2(\text{OH})_2$
Wakefieldite-(Ce)	$(\text{Ce}, \text{La}, \text{Nd}, \text{Y}, \text{Pr}, \text{Sm})[(\text{V}, \text{As})\text{O}_4]$
Wakefieldite-(Y)	YVO_4
<i>Layered uranyl vanadate(V) minerals</i>	
Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 3\text{H}_2\text{O}$
Curienite	$\text{Pb}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$
Francevillite	$(\text{Ba}, \text{Pb})(\text{UO}_2)(\text{VO}_4)_2 \cdot 5\text{H}_2\text{O}$
Margaritasite	$(\text{Cs}, \text{K}, \text{H})_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot \text{H}_2\text{O}$
Metatyuyamunitite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 4\text{H}_2\text{O}$
Metavanuralite	$\text{Al}(\text{UO}_2)_2(\text{VO}_4)_2(\text{OH}) \cdot 8\text{H}_2\text{O}$
Sengierite	$\text{Cu}(\text{UO}_2)(\text{VO}_4)(\text{OH}) \cdot 3\text{H}_2\text{O}$
Strelkinite	$\text{Na}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 6\text{H}_2\text{O}$
Tyuyamunitite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 8\text{H}_2\text{O}$
Vanuralite	$\text{Al}(\text{UO}_2)_2(\text{VO}_4)_2(\text{OH}) \cdot 11\text{H}_2\text{O}$
Vanuranylite	$(\text{H}_3\text{O}, \text{Ba}, \text{Ca} \cdot \text{K})_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 4\text{H}_2\text{O}(?)$
<i>Pyrovanadate(V) minerals</i>	
Blossite	$\text{Cu}_2(\text{V}_2\text{O}_7)$
Chervetite	$\text{Pb}_2(\text{V}_2\text{O}_7)$
Fianelite	$\text{Mn}_2(\text{V}_2\text{O}_7) \cdot 2\text{H}_2\text{O}$
Volborthite	$\text{Cu}_3(\text{V}_2\text{O}_7)(\text{OH})_2 \cdot 2\text{H}_2\text{O}$
Ziesite	$\text{Cu}_2(\text{V}_2\text{O}_7)$
<i>Minerals containing the decavanadate(V) isopolyanion</i>	
Hummerite	$\text{K}_2\text{Mg}_2(\text{V}_{10}\text{O}_{28}) \cdot 16\text{H}_2\text{O}$
Huemulite	$\text{Na}_4\text{Mg}(\text{V}_{10}\text{O}_{28}) \cdot 24\text{H}_2\text{O}$
Pascoite	$\text{Ca}_3(\text{V}_{10}\text{O}_{28}) \cdot 17\text{H}_2\text{O}$
Rauvite	$\text{Ca}(\text{UO}_2)_2(\text{V}_{10}\text{O}_{28}) \cdot 16\text{H}_2\text{O}$

Metavanadate(V) minerals^a

Alvanite	$(\text{Zn}, \text{Ni})\text{Al}_4(\text{VO}_3)_2(\text{OH})_{12} \cdot 2\text{H}_2\text{O}$
Delrioite	$\text{CaSr}(\text{V}_2\text{O}_6)(\text{OH})_2 \cdot 3\text{H}_2\text{O}$
Metadelrioite	$\text{CaSrV}_2\text{O}_6(\text{OH})_2$
Metamunirite	NaVO_3
Metarossite	$\text{Ca}(\text{V}_2\text{O}_6) \cdot 2\text{H}_2\text{O}$
Munirite	$\text{NaVO}_3 \cdot (2-x)\text{H}_2\text{O}$, chains
Rossite	$\text{Ca}(\text{V}_2\text{O}_6) \cdot 4\text{H}_2\text{O}$

Layered $\text{V}_6\text{O}_{16}^{n-}$ vanadate(IV,V) minerals of the hewittite group^a

Barnesite	$(\text{Na}, \text{Ca})(\text{V}_6\text{O}_{16}) \cdot 3\text{H}_2\text{O}$
Grantsite	$(\text{Na}, \text{Ca})(\text{V}_6\text{O}_{16}) \cdot 4\text{H}_2\text{O}$
Hewittite	$\text{Ca}(\text{V}_6\text{O}_{16}) \cdot 9\text{H}_2\text{O}$
Hendersonite	$\text{Ca}_{1.3}(\text{V}_6\text{O}_{16}) \cdot 6\text{H}_2\text{O}$
Metaheewittite	$\text{Ca}(\text{V}_6\text{O}_{16}) \cdot 3\text{H}_2\text{O}$

Layered $\text{V}_8\text{O}_{20}^{n-}$ vanadate(IV,V) minerals of the straczekite group^a

Bariandite	$\text{Al}_{0.6}(\text{V}_8\text{O}_{20}) \cdot 18\text{H}_2\text{O}$
Bokite	$(\text{Al}, \text{Fe})_{1.4}[(\text{V}, \text{Fe})_8\text{O}_{20}] \cdot 7 \cdot 4\text{H}_2\text{O}$
Corvusite	$(\text{Na}, \text{KCa}, \text{Mg})_2(\text{V}_8\text{O}_{20}) \cdot 6-104\text{H}_2\text{O}$
Fernandinite	$\text{Ca}_{0.6}(\text{V}_8\text{O}_{20}) \cdot 10\text{H}_2\text{O}$
Straczekite	$(\text{Ca}, \text{K}, \text{Ba})_2(\text{V}_8\text{O}_{20}) \cdot 6\text{H}_2\text{O}$

Other vanadium bronze-type minerals^a

Bannermanite	$\text{Na}_{0.7}(\text{V}_6\text{O}_{15})$
Fervanite	$\text{Fe}_4(\text{V}_4\text{O}_{16}) \cdot 5\text{H}_2\text{O}$
Kazakhstanite ^b	$\text{Fe}_5(\text{V}_{15}\text{O}_{39})(\text{OH})_9 \cdot 9\text{H}_2\text{O}$
Melanovanadite	$\text{Ca}(\text{V}_4\text{O}_{10}) \cdot 5\text{H}_2\text{O}$
Schubnelite	$\text{Fe}_{2-x}(\text{V}_2\text{O}_4)(\text{OH})_8$ (x is small)

Miscellaneous vanadate minerals

Phosphovanadylite ^c	$(\text{Ba}, \text{Ca}, \text{K}, \text{Na})_x[(\text{V}, \text{Al})_4\text{P}_2(\text{O}, \text{OH})_{16}] \cdot 12\text{H}_2\text{O}$
Rankachite ^d	$\text{CaFeV}_4\text{W}_8\text{O}_{36} \cdot 12\text{H}_2\text{O}$
Satpaevite ^e	$\text{Al}_{12}\text{V}_8\text{O}_{37} \cdot 30\text{H}_2\text{O}$
Sherwoodite ^f	$\text{Ca}_9[\text{AlV}_{14}\text{O}_{40}]_2 \cdot 56\text{H}_2\text{O}$
Simplotite ^g	$\text{CaV}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$
Uvanite	$(\text{UO}_2)_2(\text{V}_6\text{O}_{17}) \cdot 15\text{H}_2\text{O}(?)$
Vanalite ^h	$\text{ca NaAl}_9(\text{V}_{12}\text{O}_{44})(\text{OH})_4 \cdot 33\text{H}_2\text{O}$

^aVanadium bronzes that contain variable amounts of V(IV); stoichiometries are indicative.

^bRelated to minerals of the straczekite group.

^cContains V(IV) in a V_4O_{16} cluster linked by phosphate groups.

^dA heteropolytungstate containing V(V) and W(VI).

^eA hydrated, mixed Al(III)-V(IV,V) oxide cluster species.

^fSherwoodite is the calcium salt of the 14-vanadoaluminate heteropolyanion $[\text{AlV}_{14}\text{O}_{40}]^{7-}$, in which a portion of the vanadium is in the V(IV) state.

^gContains a V(IV) oxyanion cluster.

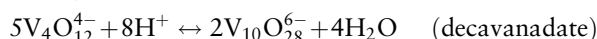
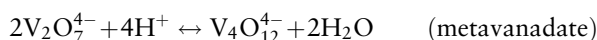
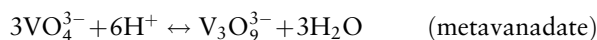
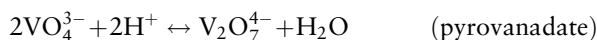
^hContains a mixed V(IV,V) isopoly- or heteropolyanion.

comparable ions, such as silicate, may also substitute with charge balance compensation. Thus, many of the formulae conceal more complex compositions for natural materials, although substitution for vanadate is more limited in many cases than is found for mutually soluble phosphate and arsenate analogues and related minerals.

Separate mention is made in Table 1 of the layered uranyl vanadates, which represent important ore minerals both of uranium and vanadium. Carnotite and tyuyamunitite are perhaps the most significant in this respect. All of these species are members of the group of minerals known as the uranium micas. Their structures are based on infinite sheets of linked uranyl

(UO_2^{2+}) and vanadate ions (phosphate and arsenate in the cases of the autunite, meta-autunite, and related groups), with other cations, hydroxide ions, and water molecules lying between the sheets. Limited substitution of phosphate and arsenate is reported for the vanadate minerals, which are extremely insoluble species.

In aqueous V(V) solutions at low concentrations, only mononuclear species are present, these comprising VO_2^+ , $\text{VO}(\text{OH})_3$, $\text{VO}_2(\text{OH})_2^-$, $\text{VO}_3\text{OH}^{2-}$, and VO_4^{3-} . In contrast to this, at higher total V(V) concentrations under acid conditions, extensive polymerisation of vanadate occurs according to the following equations:



Protonated analogues are also present in solution. The pyrovanadates, metavanadates, and decavanadates are all expressed in a number of mineral structures, as listed in Table 1. Metavanadates, in the solid state, consist of infinite chains of VO_3^- composition, $(\text{VO}_3^-)_n$.

Divanadate and tetravanadate chains are the basic structural units of many of the vanadium bronzes, also listed in Table 1. These minerals assume a variety of colours, owing to the fact that a variable though usually small proportion of the V(V) present is reduced to V(IV). Consequent variations of stoichiometry are noted as a result of charge compensation and this is an additional feature of other members of the mineral groups containing both metavanadate and decavanadate, and their protonated derivatives. Other vanadium bronzes are based on different structural motifs, but all share the above characteristics in terms of the presence of V(IV) and attendant compositional variation. The natural expression of the vanadium bronzes, exhaustively studied as artificial compounds, is dependent upon subtle fluctuations of redox potential in the solutions from which they form. They, and other vanadium species, are important constituents of sandstone vanadium deposits and their geochemical relationships have been thoroughly explored, based on pioneering studies dating back nearly five decades. The mineral phosphovanadylite contains V(IV) in a V_4O_{16} cluster linked by phosphate groups, but its chemistry of formation remains to be elucidated.

Like the tetraoxomolybdate(VI) and tetraoxotungstate(VI) ions, vanadate forms heteropolyanions in acid solutions. Rankachite and sherwoodite are two examples, the former carrying W(VI) in the cluster and the latter being a naturally occurring salt of the

well-known synthetic 14-vanadoaluminate heteropolyanion $[\text{AlV}_{14}\text{O}_{40}]^{n-}$. No doubt, other congeners exist in nature in line with observations concerning the geochemistry of molybdenum and tungsten.

As mentioned above, vanadate minerals are an important source of the element vanadium. In addition to species already singled out in this connection, vanadinite, mottramite, and descloizite have been exploited as vanadium ores. However, the bulk of present vanadium production comes from vanadium-bearing oxides (principally magnetite) and by-product refining.

See Also

Minerals: Arsenates. **Sedimentary Rocks:** Phosphates.

Further Reading

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