Caseyite, a new mineral containing a variant of the flat-Al\textsubscript{13} polyoxometalate cation

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**Abstract**

Caseyite, [(V\textsuperscript{5+}O\textsubscript{2})Al\textsubscript{10–}O\textsubscript{2}(OH)\textsubscript{20–}2(H\textsubscript{2}O)\textsubscript{18–}2][V\textsubscript{4+}V\textsubscript{9}O\textsubscript{2}8\textsuperscript{5–}, ideally [(V\textsuperscript{5+}O\textsubscript{2})Al\textsubscript{10–}O\textsubscript{2}(OH)\textsubscript{20–}2(H\textsubscript{2}O)\textsubscript{18–}2][H\textsubscript{2}V\textsuperscript{4+}V\textsubscript{9}O\textsubscript{2}8\textsuperscript{5–}]\textsuperscript{11+}, closely related to the technologically important decavanadate \([\text{V}_{10}\text{O}_{28}]^{6–}\) isopolyanion, and its protonated and mixed-valence \([\text{H}_2\text{V}^{4+}\text{V}^{9}\text{O}_{28}]^{5–}\) decavanadate isopolyanions, and a novel vanadoaluminate heteropolycation ("flat-Al\textsubscript{10–}V\textsubscript{2}D\textsubscript{2}“), ideally [(V\textsuperscript{5+}O\textsubscript{2})Al\textsubscript{10–}O\textsubscript{2}(OH)\textsubscript{20–}2(H\textsubscript{2}O)\textsubscript{18–}2]\textsuperscript{11+}, closely related to the technologically important flat-Al\textsubscript{13} polyoxocation.

**Keywords:** Caseyite, new mineral, polyoxometalate, flat-Al\textsubscript{13} polyoxocation, crystal structure, Packrat mine, Burro mine, West Sunday mine, Colorado

**Introduction**

Millions of synthetic compounds have been prepared in the laboratory, but only about 5500 minerals have been characterized to date. Nature is much more parsimonious owing to its more limited combinations of physical conditions and abundant chemical constituents than are available in a laboratory. However, natural environments sometimes surprise us by duplicating unusual synthetic phases or by creating entirely new phases unknown from laboratory synthesis.

Polyoxometalate anions and, more rarely, polyoxometalate cations have been the subject of numerous synthesis studies in recent years, largely because of their potential technological uses. Low-temperature, near-surface environments, particularly those containing highly charged metal cations, also have the potential to form polyoxometalate ions, some of which have been proposed to exist in solution as precursors of more extended structural components (chains, sheets, and frameworks) in mineral structures. Only rarely are polyoxometalate ions found as isolated units in minerals.

Deposits in the Uravan Mineral Belt of Colorado and Utah have been a rich source of uranium and vanadium ores for more than a century. They have also been a rich source of post-mining secondary vanadium minerals that typically form in mine tunnels. Among the numerous secondary minerals that have been discovered within the Uravan deposits are various phases containing polyoxometalate anions. The most common among these are minerals containing the decavanadate \([\text{V}_{10}\text{O}_{28}]^{6–}\) isopolyanion, and its protonated and mixed-valence variants (Kampf et al. 2018). Sherwoodite, from the Peanut mine in Montrose County, Colorado (Thompson et al. 1958), was the first mineral confirmed to contain a heteropolyanion, the (Al\textsubscript{IV}V\textsubscript{V}V\textsubscript{V}O\textsubscript{38})\textsuperscript{2–} vanadoaluminate anion (Evans and Konnert 1978), which is structurally similar to the decavanadate anion. In recent years, new minerals containing variants of the Keggin heteropolyanion (Kondinski and Parac-Vogt 2018) have also been discovered in mines in the Uravan Mineral Belt. These include kegginite, Pb\textsubscript{9}Ca\textsubscript{4}[As\textsubscript{2}\textsubscript{V}\textsubscript{3}\textsubscript{O}\textsubscript{18}(VO)\textsubscript{2}]2\textsubscript{–}2H\textsubscript{2}O, from the Packrat mine (Mesa County, Colorado) containing a mono-capped Keggin e-isomer (Kampf et al. 2017), and bicapite, K\textsubscript{5}Na\textsubscript{2}Mg\textsubscript{2}(H\textsubscript{2}PV\textsubscript{5+}O\textsubscript{40})\textsubscript{2}25H\textsubscript{2}O, from the Pickett Corral mine (Montrose County, Colorado) containing a bi-capped Keggin α-isomer (Kampf et al. 2019). The Packrat mine has also yielded several new minerals containing a novel \([\text{As}^{3+}\text{V}^{4+}\text{V}^{5+}\text{As}^{4+}\text{O}_{38}]^{5–}\) heteropolyanion (Kampf et al. 2016).

Caseyite, the new mineral species described here, is the most remarkable polyoxometalate mineral yet discovered. Besides containing both normal \([\text{V}_{10}\text{O}_{28}]^{6–}\) and doubly protonated mixed-valence \([\text{H}_2\text{V}^{4+}\text{V}^{9}\text{O}_{28}]^{5–}\) decavanadate isopolyanions, it contains a novel vanadoaluminate heteropolycation, ideally [(V\textsuperscript{5+}O\textsubscript{2})Al\textsubscript{10–}O\textsubscript{2}(OH)\textsubscript{20–}2(H\textsubscript{2}O)\textsubscript{18–}2]\textsuperscript{11+}. This new heteropolycation is a variant of...