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Polyoxometalate chemistry at volcanoes: discovery of a novel class of polyoxocuprate nanoclusters in fumarolic minerals

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Polyoxometalate (POM) chemistry is an important avenue of comprehensive chemical research, due to the broad chemical, topological and structural variations of multinuclear polyoxoanions that result in advanced functionality of their derivatives. The majority of compounds in the polyoxometalate kingdom are synthesized under laboratory conditions. However, Nature has its own labs with the conditions often unconceivable to the mankind. The striking example of such a unique environment is volcanic fumaroles – the natural factories of gas-transport synthesis. We herein report on the discovery of a novel class of complex polyoxocuprates grown in the hot active fumaroles of the Tolbachik volcano at the Kamchatka Peninsula, Russia. The cuboctahedral nanoclusters $\{[MCu_{12}O_8](AsO_4)_8\}$ are stabilized by the core Fe(III) or Ti(IV) cations residing in the unique cubic coordination. The nanoclusters are uniformly dispersed over the anion- and cation-deficient NaCl matrix. Our discovery might have promising implications for synthetic chemistry, indicating the possibility of preparation of complex polyoxocuprates by chemical vapor transport (CVT) techniques that emulate formation of minerals in high-temperature volcanic fumaroles.

Polyoxometalates (POMs) constitute a large group of materials with discrete metal-anion clusters of various shapes and sizes^{1–3}. Traditionally, POMs were associated with *d*-block metals in high oxidation states (V^{5+} , Nb^{5+} , Ta^{5+} , Mo^{6+} and W^{6+}), but recent studies extended the field to other elements such as actinides⁴ and noble metals⁵. In 1990, Achim Müller and co-workers⁶ introduced the term ‘polyoxocuprates’ (POCus) to identify clusters formed by polymerization of Cu coordination polyhedra, previously reported for synthetic inorganic compounds such as $Ba_{44}Cu_{45}O_{87}Cl_4$ and $Ba_{88}Cu_{88}O_{175}Br_2$ ⁷. The POCus have been intensively investigated recently as reviewed by Kondinski and Monakhov⁸, due to their potential applications in catalysis, molecular magnetism and superconductivity. Usually POCus are obtained by crystallization from aqueous solutions at pH values between 3.5 and 7 *via* polymerization of $Cu(OH)_4$ planar-square units.

Natural crystalline POMs have been under extensive investigation over the last ten years and are known for Mo^9 , $V^{10–12}$, and Nb^{13} . Besides, uranyl carbonate nanoscale clusters have been reported for U^{6+} carbonate minerals such as ewingite, $Ca_8Mg_8(UO_2)_{24}(CO_3)_{30}O_4(OH)_{12}(H_2O)_{138}$ ¹⁴, and paddlewheelite, $Ca_5MgCu_2(UO_2)_4(CO_3)_{12}(H_2O)_{33}$ ¹⁵. Other examples are two natural arsenates, bouazzerite¹⁶, $Bi_6(Mg,Co)_{11}Fe_{14}(AsO_4)_{18}O_{12}(OH)_4(H_2O)_{86}$, and whitecapsite¹⁷, $H_{16}Sb^{3+}_6Fe^{2+}_5Fe^{3+}_{14}(AsO_4)_{18}O_{16}(H_2O)_{120}$, which are based upon heptanuclear iron-oxide-arsenate nanoclusters. We note that discrete Cu-OH clusters have also been reported in minerals, *e.g.*, the $[Cu_{12}(OH)_{24}]$ clusters in zeolite tschörtnerite¹⁸, $Ca_4(Ca,Sr,K,Ba)_3Cu_3[Al_3Si_3O_{12}]_4(OH)_8 \cdot nH_2O$, the $[Cu_{24}(OH)_{48}]$ clusters in boleite¹⁹, $KPb_{26}Ag_9Cu_{24}(OH)_{48}Cl_{62}$, and pseudoboleite²⁰, $Pb_{31}Cu_{24}Cl_{62}(OH)_{48}$, and the $[Cu_{20}(OH)_{40}]$ clusters in cumengeite²¹, $Pb_{21}Cu_{20}Cl_{42}(OH)_{40} \cdot 6H_2O$. It is noteworthy that all the reported

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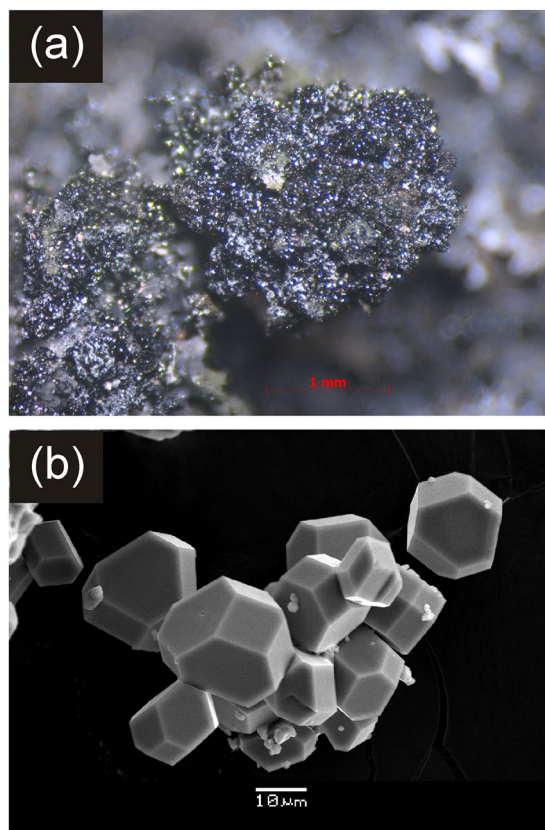


Figure 1. Crystalline crusts of greenish black arsmirandite (a) and scanning electron microscopy (SEM) image of clusters of arsmirandite crystals (b).

occurrences of POMs in nature have been restricted to low-temperature aquiferous systems, namely oxidation zones of ore deposits (<50–70 °C) or last-stage hydrothermal environments (<150–200 °C).

Volcanic fumaroles are unique in both physical and chemical (geochemical) aspects. In fumarolic systems minerals either directly precipitate from volcanic gases as sublimates or form as a result of their interactions with host rocks. Among fumarolic minerals, copper-based anhydrous mineral phases constitute one of the most rich and diverse groups. The explosion of recent discoveries of Cu^{2+} fumarolic minerals is related to the Tolbachik volcano at Kamchatka Peninsula, Russia. The Cu mineralization at Tolbachik was reviewed by Pekov *et al.*²², and the most recent descriptions of new mineral species can be found in refs.^{23–26}. The Cu minerals found in Tolbachik fumaroles are remarkable by their structural architecture, which frequently contain polymeric Cu-oxo units based upon oxocentered OCu_4 tetrahedra. These tetrahedra may polymerize to form structural units of different dimensionalities^{27,28}. Herein we report two novel halide-arsenate mineral species, arsmirandite and lehmannite, found at Tolbachik that represent the first example of natural POCus and provide a unique insight into the ability of Cu^{2+} cations to form discrete nanoclusters in anhydrous natural environments. Our discovery also provide some important clues for the synthesis and chemical tuning of cubic POCus for further studies of their physical and chemical properties.

Results

Two new mineral species, arsmirandite and lehmannite, have been found in the active Arsenatnaya fumarole^{29,30} located at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption 1975–1976, Tolbachik volcano, Kamchatka Peninsula, Far-Eastern Region, Russia (55°41'N 160°14'E, 1200 m asl). The mineral assemblages encasing these halide-arsenates were formed in the temperature range between 500 and 700 °C^{22,30} and were located inside the fumarole. The detailed mineralogical description of the minerals will be given elsewhere. Polyoxocuprates occur as aggregates of greyish-green well-shaped crystals resembling rhombic dodecahedra (Fig. 1) that could easily be separated from the surrounding matrix. The chemical composition of arsmirandite and lehmannite were determined using electron-microprobe analysis (Table S0). The empirical formula of arsmirandite, calculated on the basis of 45 anions (O + Cl) *pfu*, is: $\text{Na}_{17.06}\text{K}_{0.51}\text{Ca}_{0.06}\text{Pb}_{0.08}\text{Mg}_{0.11}\text{Mn}_{0.01}\text{Cu}_{11.73}\text{Zn}_{0.08}\text{Al}_{0.02}\text{Fe}^{3+}_{0.92}\text{Ti}_{0.10}(\text{As}_{7.91}\text{S}_{0.08}\text{P}_{0.03}\text{Si}_{0.02}\text{V}_{0.01})_{\Sigma 8.05}\text{O}_{40.23}\text{Cl}_{4.77}$. The empirical formula of lehmannite, calculated on the basis of the sum of tetrahedrally coordinated components (As + P + S + Si) = 8 *apfu*, is: $\text{Na}_{17.92}\text{K}_{0.18}\text{Ca}_{0.24}\text{Cu}_{11.59}\text{Fe}^{3+}_{0.21}\text{Ti}_{0.85}\text{Sn}_{0.11}(\text{As}_{7.74}\text{S}_{0.14}\text{P}_{0.09}\text{Si}_{0.03})_{\Sigma 8}\text{O}_{40.10}\text{F}_{0.75}\text{Cl}_{5.42}$. The idealized chemical formulae for arsmirandite and lehmannite were determined as $\text{Na}_{18}\text{Cu}_{12}^{2+}\text{Fe}^{3+}\text{O}_8(\text{AsO}_4)_8\text{Cl}_5$ and $\text{Na}_{18}\text{Cu}_{12}^{2+}\text{Ti}^{4+}\text{O}_8(\text{AsO}_4)_8\text{FCl}_5$, respectively.

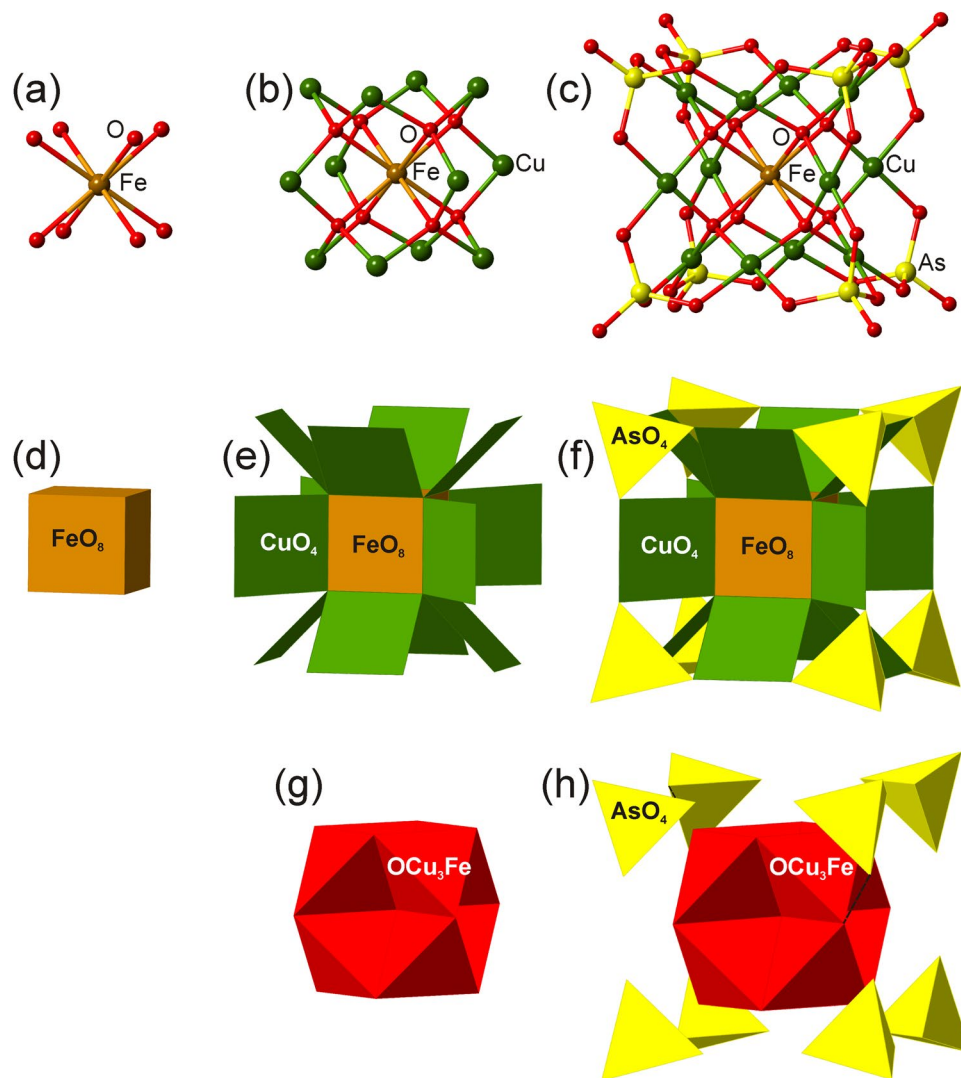


Figure 2. The structure of the polyoxocuprate nanoclusters in arsmirandite and lehmannite shown in ball-and-stick (a–c) and polyhedral (cation-centered (d–f) and combined anion- and cation-centered (g,h)) representations (exemplified by arsmirandite).

The crystal structures of arsmirandite and lehmannite (Tables S1–S7) are very similar, yet not identical. From the structural point of view, they are quite unusual and unique. The basic structural unit in both structures is a novel nanoscale (~ 1.5 nm across) polyoxocuprate cluster with the composition $\{[MCu_{12}O_8](AsO_4)_8\}$ ($M = Fe^{3+}$ and Ti^{4+} , for arsmirandite and lehmannite, respectively) shown in Fig. 2. The most peculiar feature of the nanocluster is the presence of Fe^{3+} (arsmirandite) or Ti^{4+} (lehmannite; the tetravalent state of Ti confirmed by XANES spectroscopy (Fig. S3)) in a cubic coordination (Fig. 2a): the central unit of the nanocluster represents the slightly distorted (MO_8) cube (Fig. 2a,d). The cubic coordination of Fe(III) and Ti(IV) has not been encountered so far in natural minerals, though several examples are known for synthetic compounds^{31–34}. Each O atom of the (MO_8) configuration is further coordinated by three Cu^{2+} cations (Fig. 2b) that have square-planar geometry by O atoms of the (AsO_4) groups (Fig. 2c,e,f). The metal-oxide core of the nanocluster can also be represented in terms of oxocentered (OCu_3M) tetrahedra^{27,28} that form an eightfold unit (Fig. 2g), which can be considered as a fragment of the crystal structure of fluorite, if the latter is described as a framework of (FCa_4) tetrahedra. The $[O_8MCu_{12}]$ core formed by eight oxocentered tetrahedra is surrounded by eight AsO_4 tetrahedra that are in the face-to-face orientation relative to the (OCu_3M) tetrahedra³⁵ (Fig. 2h). The cubic nanoclusters are negatively charged and are surrounded by an array of Na^+ cations and X^- anions ($X = F, Cl$) (Fig. 3), which requires further remark. The analysis of the Na array in arsmirandite and lehmannite (Figs. S1 and S2) shows that it is in fact a highly deficient face-centered cubic (*fcc*) lattice as observed, e.g. in the crystal structure of halite, NaCl³⁶. The halite-like cubic pseudo-subcell can be obtained from the true unit cell using the matrix $\begin{pmatrix} 1/2 & 0 & 0 \\ 0 & 1/4 & 1/4 \\ 0 & 1/4 & 1/2 \end{pmatrix}$, i.e. the structures of arsmirandite and lehmannite can be considered as the $2 \times 4 \times 4$ supercell relative to the halite cell. The parameters of the halite-like cubic subcell, e.g., in lehmannite, are: $a_{hal} = 5.418$, $b_{hal} = 5.273$, $c_{hal} = 5.279$ Å, which shows that, relative to halite, the deficient Na *fcc* array is compressed and tetragonally distorted.

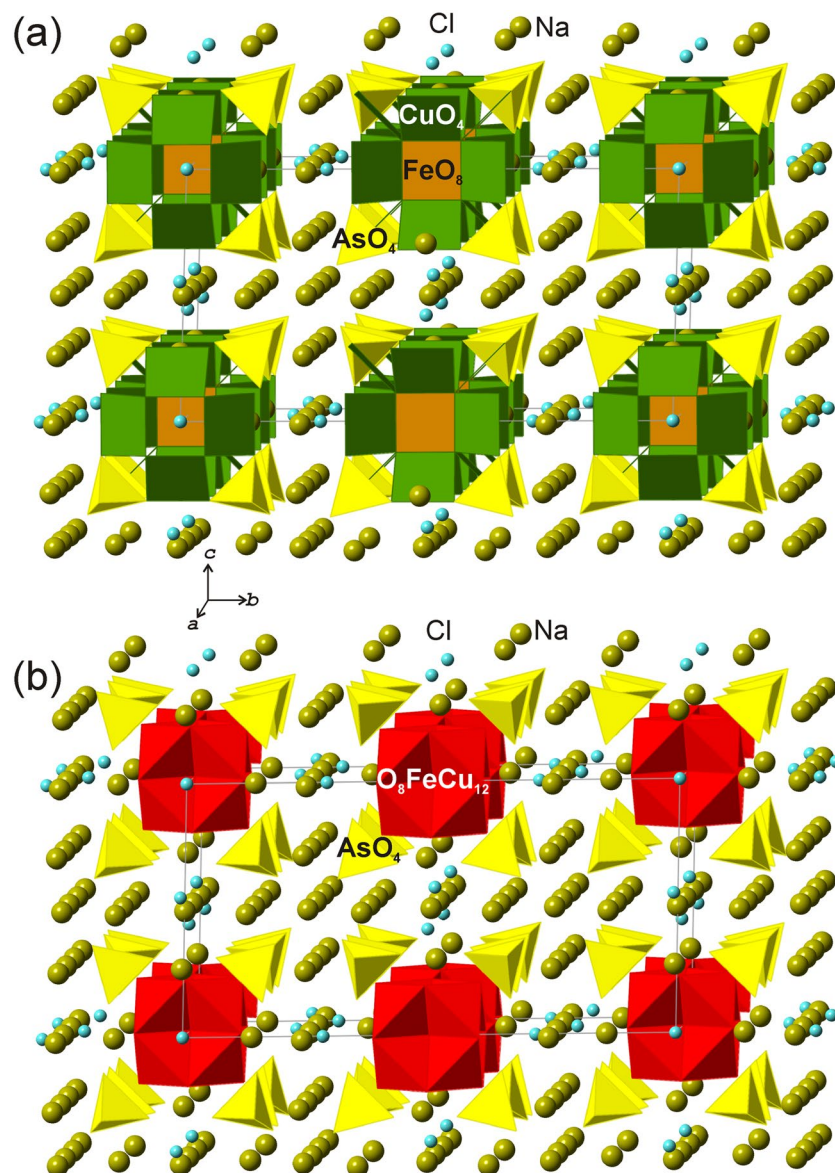
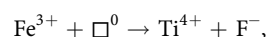


Figure 3. The crystal structure of arsmirandite with nanoclusters shown in cation-centered (a) and combined anion- and cation-centered (b) representations.

Discussion

The difference between arsmirandite and lehmannite is in the nature of the *M* cation, which triggers the re-arrangement of the halogen substructure. Since Fe^{3+} and Ti^{4+} possess different charges, the Fe^{3+} -for- Ti^{4+} substitution requires the mechanism of charge compensation, which is achieved *via* the incorporation of the additional anionic site, F, in lehmannite (Ti^{4+} species) relative to arsmirandite (mineral with Fe^{3+}). The charge compensation, therefore, is governed by the following substitution scheme:

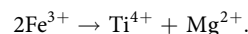


where the ' \square ' sign stays for vacancy.

In lehmannite, the substitution is realized through the following crystal chemical mechanism. The Cl1 site with the $2/m$ site symmetry with the coordinates (1/2, 1/2, 0) in arsmirandite is shifted along the *a* axis to the Cl1 site with the *m* site symmetry (approximate coordinates: 0.53, 1/2, 0) in lehmannite, resulting in the splitting of the Cl1 site into two mutually exclusive sites. The F site with the same *m* site symmetry is incorporated (approximate coordinates: 0.65, 1/2, 0) into the structure so that the Cl1 \cdots F distance is equal to *ca.* 1.3 Å. The short distance precludes the simultaneous occupancy of the Cl1 and F sites with the maximum total occupancy $\text{F}_{0.50}\text{Cl}_{0.50}$. Note that the Cl1 \cdots Cl1 distance in disordered configuration is very short (~ 0.6 Å in lehmannite), prohibiting more-than-50% occupancy of the Cl1 site, whereas the F \cdots F distance (~ 3.1 Å) allows for the full occupancy of the two F sites assuming that the Cl1 site is empty.

In lehmannite, the disordered configuration has the total occupancy $F_{0.52}Cl_{0.34\Box 0.16}$ or $F_{1.04}Cl_{0.68\Box 0.32}$ per formula unit (*pfu*) with the -1.72 total negative charge. The corresponding occupancy of the *M* site is calculated as $Ti^{4+}_{0.69}Fe^{3+}_{0.28}Sn^{4+}_{0.03}$ with the total positive charge $+3.72$, which provides the formula electroneutrality. The full substitution of Fe^{3+} by Ti^{4+} in lehmannite would correspond to the total occupancy of the anionic sites $F_{0.50}Cl_{0.50}$ or $F_{1.00}Cl_{1.00}$ *pfu* with the -2 total negative charge.

The crystal chemical formula of arsmirandite determined on the basis of chemical analysis and crystal-structure refinement can be written as $(Na_{17.54}K_{0.46})_{\Sigma 18.00}(Fe^{3+}_{0.78}Mg_{0.11}Ti_{0.11})_{\Sigma 1.00}Cu^{2+}_{12}(AsO_4)_8O_8Cl_5$. Note that the incorporation of Ti^{4+} into the *M* site is compensated by the coupled substitution of Fe^{3+} by Mg^{2+} :



The crystal chemical formula of lehmannite can be written as $(Na_{17.62}K_{0.38})_{\Sigma 18.00}(Ti^{4+}_{0.69}Fe^{3+}_{0.28}Sn^{4+}_{0.03})_{\Sigma 1.00}Cu^{2+}_{12}(AsO_4)_8O_8Cl_{4.68}F_{1.04}$.

Taking into account the discussion given above, the general formula of the hypothetical arsmirandite-lehmannite series can be written as $Na_{18}(Ti^{4+}_{1-x}Fe^{3+}_x)Cu_{12}(AsO_4)_8O_8Cl_{6-x-y}F_y$. The ideal formula of arsmirandite corresponds to $x = 1$ and $y = 0$, whereas that of lehmannite requires $x = 0$ and $y = 1$. Note that $0 \leq x \leq 1$, whereas $0 \leq y \leq 2$. The experimental case of lehmannite corresponds to $x = 0.28$ and $y = 1.04$. The case $y = 2$ corresponds to the full occupancy of the F site and the complete emptiness of the Cl1 site and results in the 'theoretical' formula $Na_{18}(Ti^{4+}_{1-x}Fe^{3+}_x)Cu_{12}(AsO_4)_8O_8Cl_{4-x}F_2$. For this formula, $x = 1$ results in the formula $Na_{18}Fe^{3+}Cu_{12}(AsO_4)_8O_8Cl_3F_2$ (hypothetical F-rich analogue of arsmirandite), whereas $x = 0$ corresponds to $Na_{18}Ti^{4+}Cu_{12}(AsO_4)_8O_8Cl_4F_2$ (hypothetical F-rich analogue of lehmannite). These two potentially possible species may occur in F-enriched fumarolic environments.

The metal-oxide $[O_8Me_{13}]$ nanoclusters (*Me* = metal) consisting of eight (OMe_4) tetrahedra sharing central *Me* atom are well-known in synthetic inorganic chemistry. It seems that the first detailed structural report was done for *Me* = Pb^{2+} found in the crystal structure of $Pb_{13}O_8(OH)_6(NO_3)_4$ ³⁷. In this compound, the central 8-coordinated cation in the nanocluster is Pb^{2+} , which has a stereochemically inactive lone-electron pair, in contrast to twelve peripheral Pb^{2+} that possess strongly asymmetrical coordination environments. Later Kolitsch and Tillmanns³⁸ reported $Pb_{13}O_8(OH)_6(NO_3)_4$ as an anthropogenic compound formed in old mine dumps due to the use of nitrate explosives. The phase $Pb_{13}O_8(OH)_6(NO_3)_4$ forms in the $Pb(NO_3)_2$ -NaOH system at pH = 9-10³⁹.

In 2008, Chubarova *et al.*⁴⁰ reported on the synthesis and structure of $Na_8\{[Pd_{13}O_8](AsO_3(OH))_6(AsO_4)_2\} \cdot 42H_2O$, the compound, which opened up the whole new field of polyoxopalladate chemistry⁵. The crystal structure of this compound is based upon $\{[Pd_{13}O_8](AsO_3(OH))_6(AsO_4)_2\}^{8-}$ nanoclusters structurally identical to those found in arsmirandite and lehmannite (which are also arsenates). Later it was found that arsenate groups can be replaced by phosphate⁴¹ or selenite groups⁴²⁻⁴⁴. The central Pd^{2+} cation in the Pd-based 13-nuclear nanoclusters (Fe^{3+} and Ti^{4+} in arsmirandite and lehmannite, respectively, play the same role as Pd^{2+} in this compound) can be replaced by Na^+ ⁴⁵, REE^{3+} (REE = rare-earth element^{42,46}), divalent or trivalent metal cations M^{2+} (M = Sc^{3+} , Mn^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , or Zn^{2+}), and tetravalent Sn^{4+} and Pb^{4+} cations⁴⁷. Very recently, Bhattacharya *et al.*⁴⁸ reported on the use of the 13-nuclear Pd-based nanoclusters, $[Pd_{13}O_8(AsO_4)_8H_6]^{8-}$, incrustated by Ba^{2+} cations for the construction of novel types of porous metal-organic frameworks. It is remarkable that, in arsmirandite and lehmannite, the role of Pd^{2+} cations in peripheral metal positions is played by Cu^{2+} cations, whereas the central cation in the metal-oxide core is either Fe^{3+} or Ti^{4+} , respectively. The observed stereochemical similarity is due to the similar square planar coordination by O^{2-} anions specific for both Pd^{2+} and Cu^{2+} . Our findings indicate the chemical possibility of the family of novel polyoxocuprate clusters with interesting functional properties. Yang and Kortz⁵ indicate that the Pd nanoclusters are stable in the solid state, solutions (both aqueous and organic) and gases, which allows for their applications in catalysis, nanotechnology, molecular spin qubits and in biology as aqueous-phase macromolecular models.

Kondinski and Monakhov⁸ identified targeted synthesis of the hypothetical $[Cu \subset Cu_{12}O_8L_8]^{q-}$ polyoxoanion (*L* = inorganic or organic ligand, e.g. arsenate, phosphate, selenite, *etc.*) with two different coordination modes of central and peripheral Cu^{2+} ions as an interesting challenge for synthetic chemistry of POCus. The discovery of the $[M \subset Cu_{12}O_8(AsO_4)_8]^{q-}$ clusters (M = Fe^{3+} , Ti^{4+}) in arsmirandite and lehmannite found in Tolbachik fumaroles provides a useful clue for the targeted synthesis of their analogues under laboratory conditions. As it has been demonstrated previously⁴⁹⁻⁵¹, fumarolic minerals with oxocentered cores can be conveniently synthesized using chemical vapor transport techniques. The occurrence of the $[M \subset Cu_{12}O_8(AsO_4)_8]^{q-}$ nanoclusters in Tolbachik fumaroles testifies that they are stable under high temperatures (500–700 °C) at least in the gaseous and crystalline phases and may as well possess interesting physical and chemical properties. They could also play the role of metal transport forms in fumarolic gases, in agreement with the previous proposal⁵² about the similar geochemical role of tetranuclear (OCu_4) clusters.

The geometrical similarity of the Na array in arsmirandite and lehmannite to that observed in halite, NaCl, allows to describe both minerals as consisting of cubic-shape nanoclusters periodically integrated into deficient NaCl matrix, a feature that is quite uncommon for inorganic materials. There has been a recent interest in salt-inclusion compounds (SICs), which possess hierarchical structures consisting of porous metal-oxide frameworks with voids filled with simple ionic salts⁵³. The examples of natural SICs are averievite, $Cu_5O_2(VO_4) \cdot nMCl_x$ (M = Cu, Cs, Rb, K)⁵⁴⁻⁵⁷, and aleutite, $Cu_5O_2(AsO_4)(VO_4) \cdot (Cu_{0.5\Box 0.5})Cl^{25}$. In the case of arsmirandite and lehmannite, we have the opposite situation, *i.e.*, the incorporation of metal-oxide clusters into the salt matrix, which, as to our knowledge, had never been observed at least in minerals and mineral phases.

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Author contributions

I.V.P., A.G.T. and E.G.S. collected the samples and performed detailed mineralogical study; chemical characterization was carried out by V.O.Y. and N.N.K.; S.N.B. collected X-ray diffraction data and solved the crystal structures; S.V.K. refined the crystal structure models and proposed their interpretation; J.G. measured and interpreted XANES spectra; S.N.B., S.V.K. and I.V.P. together wrote the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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