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The mineral deposits of strategic metals are vulnerable to political and economic changes, and their availability is essential for high-technology, green energy, and other applications. The most of them are related to the deep-seated alkaline magmas. This book offers a collection of papers presented at the 36th International Conference on “Magmatism of the Earth and Related Strategic Metal Deposits” held from May 23th to 26th 2019 in Saint Petersburg State University, Saint Petersburg, Russia. The conference articles are focused on the understanding of the geological processes that produce high concentrations of critical metals in geological systems such as the metal transport in the mantle and crust and enrichment processes, hydrothermal and metasomatic processes leading to the formation of such significant deposits. Papers in this book give a representative overview including mineralogy, geochemistry and origin of strategic metals deposits.

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The cover pictures – View down the Neva to the river between the Winter house of its Imperial Majesty and Academy of Sciences. G.A. Kachalov's engraving according to M.I. Makhayev's drawing (approx. 1750-1752).

MINERAL CRYSTAL CHEMISTRY OF TITANIUM: NEW DATA

**Pekov I.V.^{1,2}, Chukanov N.V.³, Zubkova N.V.¹, Agakhanov A.A.⁴, Sandalov F.D.¹, Britvin S.N.⁵,
Siidra O.I.⁵, Yapaskurt V.O.¹, Varlamov D.A.⁶, Turchkova A.G.¹**

¹Moscow State University, Moscow, Russia, igorpekov@mail.ru

²Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences,
Moscow, Russia

³Institute of Problems of Chemical Physics of Russian Academy of Sciences, Chernogolovka,
Russia

⁴Fersman Mineralogical Museum of Russian Academy of Sciences, Moscow, Russia

⁵Saint-Petersburg State University, Saint-Petersburg, Russia

⁶Institute of Experimental Mineralogy of Russian Academy of Sciences, Chernogolovka, Russia

Titanium belongs to the most geochemically and petrologically significant elements. It is a species-defining or important admixed component of many accessory and some rock-forming minerals in different magmatic, metamorphic and metasomatic rocks. The mineralogy of titanium is diverse: three hundred valid minerals with species-defining Ti^{4+} are now known. They demonstrate strongly uneven distribution between chemical classes: the overwhelming majority belongs to silicates (*ca.* 190 mineral species) and oxides and hydroxides (*ca.* 90). The crystal chemistry of titanium has been mainly developed for these minerals while only fragmentary data are reported for natural representatives of other chemical classes.

For last several years, we have obtained not too few new data on the mineralogy and mineral crystal chemistry of titanium. The studied minerals belong not only to "traditional" for this chemical element classes of silicates and oxides but also to arsenates and sulfates. In the present paper we give an overview of these data with focus on uncommon crystal chemical features of titanium in these minerals, including such aspects as isomorphous substitutions and cation ordering with participation of this element, character of coordination polyhedra or polyhedral motifs of Ti^{4+} , and the dependence of these characteristics on physical and chemical conditions of formation, in the frame of the elaboration on the genetic aspect of crystal chemistry of titanium.

Alkaline rocks demonstrate the widest diversity of Ti minerals among all geological formations. The family of titanosilicate minerals mainly occurring in agpaitic rocks, their derivatives and related metasomatic rocks is especially interesting in this aspect.

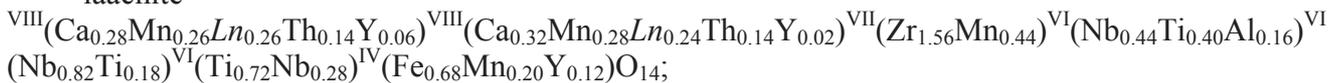
A new zeolite-like titanosilicate kamenevite $K_2TiSi_3O_9 \cdot H_2O$ isostructural with the zirconosilicate umbite $K_2ZrSi_3O_9 \cdot H_2O$ was found in two peralkaline pegmatites in the Khibiny alkaline complex, Kola peninsula, Russia. Kamenevite demonstrates a structural feature quite rare for minerals: it is a titanosilicate with a heteropolyhedral Ti-Si-O framework containing isolated from each other octahedra TiO_6 . This structural feature is very common for ZrO_6 octahedra in microporous zirconosilicates with heteropolyhedral Zr-Si-O frameworks, unlike titano- or niobosilicates in which TiO_6 or NbO_6 octahedra usually form condensed motifs, typically chains with shared oxygen vertices, *i.e.*, Ti/Nb–O–Ti/Nb bridges (Pyatenko et al., 1999). This explains, *e.g.*, the rarity of titanium minerals belonging to the eudialyte, lovozerite, benitoite and hilaire groups in comparison with zirconium members of these groups, in spite of significant prevailing of Ti over Zr in alkaline rocks and in Earth's crust in general. The pair umbite – kamenevite is in a good agreement with this empirical regularity: umbite is a common late-stage mineral in Khibiny whereas kamenevite has been found only in minor amount. Umbite and kamenevite are associated with one another and no solid-solution series between these minerals was found: the highest content of TiO_2 in umbite is 4.9 wt.% that corresponds to 0.24 *apfu* Ti whereas kamenevite contains up to 2.2 wt.% ZrO_2 = 0.07 *apfu* Zr (Pekov et al., 2019b).

A large mica group contains only two minerals with species-defining titanium. They were found in specific peralkaline, silica-oversaturated and lithium enriched rocks of the Darai-Pioz alkaline complex in Tadjikistan. Both these micas, orlovite $KLi_2Ti[Si_4O_{10}]OF$ and gorbunovite $CsLi_2(Ti,Fe)[Si_4O_{10}](F,OH,O)_2$ (Agakhanov et al., 2011, 2017), are trioctahedral and contain in the octahedral layer two univalent cations Li^+ per formula unit that makes possible the incorporation of a highly-valent cation Ti^{4+} in the third octahedron.

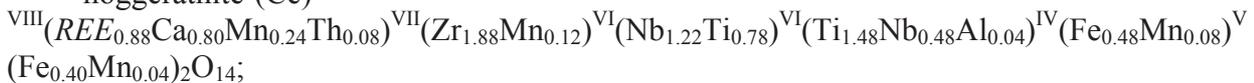
An unusual alkali pyroxene strongly enriched by titanium (7.0–7.5 wt.% TiO₂) has been identified by us in cavities within a xenolith of a Si-rich rock embedded in alkaline basalt of the Bellerberg paleovolcano, Eifel region, Germany. Initially it was probably polymictic sandstone which was thermally and chemically metamorphosed by host basalt to the rock mainly consisting of sanidine and tridymite. Average composition of the Ti-rich pyroxene corresponds to the empirical formula Na_{1.03}(Fe³⁺_{0.41}Mg_{0.22}Ti_{0.21}Mn_{0.06}Al_{0.06})_{Σ0.96}Si_{2.04}O₆. Thus, this is a variety of aegirine containing the Na(Mg_{0.5}Ti⁴⁺_{0.5})Si₂O₆ component in the amount of *ca.* 42 mol.%.

The series of zirconolite-family minerals was studied by us on samples from alkaline volcanic rocks of the Laacher See paleovolcano in the same Eifel region. Due to very young (Pleistocene) geological age of Eifel volcanic rocks, we have a unique chance to study crystal structures of these minerals which are metamict in the majority of other known localities. The problem of isomorphism and ordering of crystallochemically close Ti, Zr, Nb and Fe in complex oxides of this family was studied for three new mineral species, laachite (Ca,Mn)₂Zr₂Nb₂TiFeO₁₄, nöggerathite-(Ce) (Ce,Ca)₂Zr₂(Nb,Ti)(Ti,Nb)₂Fe²⁺O₁₄, and stefanweissite (Ca,REE)₂Zr₂(Nb,Ti)(Ti,Nb)₂Fe²⁺O₁₄ (Chukanov et al., 2014, 2018b, 2019) and zirconolite-3*T* (Zubkova et al., 2018). Zirconolite-family minerals are characterized by close packing of cation-centred polyhedra. The cationic isomorphism and cation ordering in the studied minerals, even in sites with mixed occupancies, strongly depend on volume and configuration of a polyhedron. Moreover, there are no isomorphous substitutions between Zr and Ti. The crystal chemical formulae (coordination numbers of cations are indicated with Roman numerals) of the new minerals are:

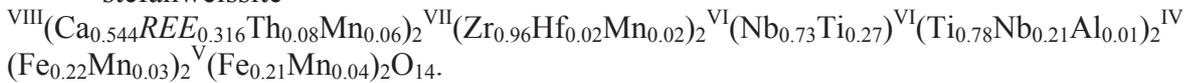
laachite –



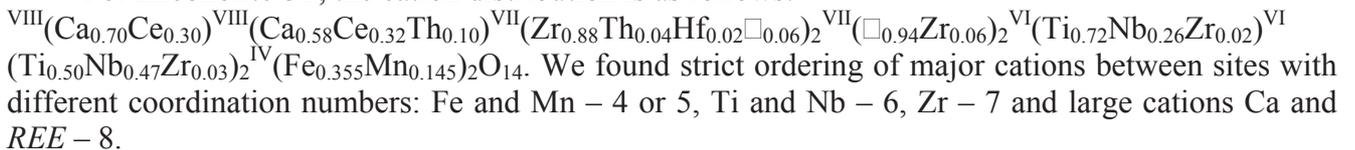
nöggerathite-(Ce) –



stefanweissite –



For zirconolite-3*T*, the cation distribution is as follows:



New data on minerals containing titanium together with chalcophile elements were obtained. Firstly, there are data concerning oxides in which Ti⁴⁺ and Sb⁵⁺ are in isomorphous relationship. They can be formed in different geological environments with the only common feature, high oxygen fugacity and, thus, strong deficiency of S²⁻.

The specific "ore" metamorphic/metasomatic rocks within the Pelagonian massif near Nežilovo in Republic of Northern Macedonia contain unusually wide diversity of Sb⁵⁺-bearing complex oxides with species-defining Ti⁴⁺. They belong to the högbomite, crichtonite, and magnetoplumbite groups and the pyrochlore supergroup. Representatives of the pyrochlore structure type demonstrate here the widest variation of the Ti:Sb-ratio and form a continuous solid-solution series including both Ti⁴⁺- and Sb⁵⁺-dominant minerals (Chukanov et al., 2015, 2018a; Varlamov et al., 2018).

In the rocks of the Pelagonian massif, intermediate members of the rutile – tripuhyite Fe³⁺Sb⁵⁺O₄ isomorphous series were also found (Varlamov et al., 2018). The same series extending from almost end-member rutile to tripuhyite with the composition (Fe_{0.741}Sb_{0.714}Ti_{0.460}Sn_{0.064}Al_{0.017}Cr_{0.004})_{Σ2.000}O_{3.976} was reported from exhalations of active fumaroles of the Tolbachik volcano (Kamchatka, Russia). Besides Sb and Fe, Tolbachik sublimate rutile formed at the temperature above 400°C and atmospheric pressure contains some other chalcophile elements, namely copper, zinc and tin: up to 1.9 wt.% CuO, up to 0.4 wt.% ZnO and up to 11.8 wt.% SnO₂. The major substitution scheme in this solid-solution system is Sb⁵⁺ + Fe³⁺ → 2Ti⁴⁺ while other schemes

involving chalcophile elements are $\text{Sn}^{4+} \rightarrow \text{Ti}^{4+}$ and $2\text{Sb}^{5+} + \text{M}^{2+} \rightarrow 3\text{Ti}^{4+}$ ($\text{M}^{2+} = \text{Cu}$ and Zn) (Sandalov et al., 2018). Sublimate cassiterite from the same fumarole contains up to 6.0 wt.% TiO_2 .

However, the main "titanium surprise" became a discovery in Tolbachik fumaroles of a series of high-temperature H-free arsenates with Ti^{4+} including three new minerals in which it is a species-defining component. Such minerals were unknown in nature before. Katiarsite $\text{KTiO}(\text{AsO}_4)$ (Pekov et al., 2016) is the only natural representative of the KTP [$\text{KTiO}(\text{PO}_4)$] structure type well-known for numerous synthetic oxysalts including very important materials with non-linear optical properties. Arsenatotitanite, ideally $\text{NaTiO}(\text{AsO}_4)$, having the same type of formula as katiarsite, is quite different in terms of crystal structure being belonging to the titanite structure type (Pekov et al., 2019a). Arsenatotitanite forms a solid-solution series with durangite $\text{NaAlF}(\text{AsO}_4)$, which contains up to 12 wt.% TiO_2 (Pekov et al., 2018a). In a complicated fluoro-chloro-arsenate lehmannite $\text{Na}_{18}\text{Cu}_{12}\text{TiO}_8(\text{AsO}_4)_8\text{FCl}_5$ from the same fumarole assemblage Ti^{4+} occurs in eight-fold coordination, in the centre of almost regular cube TiO_8 . It is first case of such coordination polyhedron of titanium in minerals (Pekov et al., 2018c). Arsenates are one of two, together with oxides, major forms of titanium concentration in the oxidizing-type Tolbachik fumaroles.

In deposits of active fumaroles at the Mutnovsky volcano at Southern Kamchatka Ti is mainly concentrated in sulfate form, substituting Al in godovikovite $(\text{NH}_4)\text{Al}(\text{SO}_4)_2$ which typically contains here 3–4 wt.% TiO_2 .

Supergene mineralogy of titanium is very scarce and is mainly represented by different "leucoxenes", the fine-grained aggregates of Ti oxides (typically anatase or rutile) formed as products of weathering of primary, endogenous Ti minerals and occurring as pseudomorphs after them. Supergene oxysalts of titanium are known from the only locality, Alcaparrosa mine in El Loa province, Northern Chile. There are two sulfates, namely alcaparrosaite $\text{K}_3(\text{Ti}^{4+}_{0.5}\text{Fe}^{3+}_{0.5})_2(\text{SO}_4)_4\text{O}\cdot 2\text{H}_2\text{O}$, in which Ti^{4+} and Fe^{3+} in nearly equal amounts are disordered in an octahedrally coordinated site (Kampf et al., 2012), and calamaite $\text{Na}_2\text{TiO}(\text{SO}_4)_2\cdot 2\text{H}_2\text{O}$ (Pekov et al., 2018b). They were formed in the oxidation zone of pyrite-quartz veins under conditions of abnormally arid climate of the Atacama desert. Mafic silicates of andesitic and dacitic host rocks destroyed by abundant sulfuric acid formed as a result of pyrite oxidation were the most probable source of Ti for these minerals. The appearance of titanium sulfates seems a very bright sign of extremely high activity of natural sulfuric acid during the oxidation of pyrite ores at Alcaparrosa where titanium, which is in nature usually almost immobile under low-temperature conditions, shows sufficient activity to form sulfates. Calamaite, demonstrating novel structure type, is the first natural sulfate with a tetravalent cation octahedrally coordinated by O^{2-} but not OH^- anions.

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