Crystal chemistry and miscibility of chernovite-(Y), xenotime-(Y), gasparite-(Ce) and monazite-(Ce) from Mt. Cervandone (Western Alps, Italy)

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Abstract

The crystal chemistry and crystal structure of the (REE)-bearing phosphates, monazite-(Ce), Ce(PO₄), and xenotime-(Y), Y(PO₄), as well as arsenates, gasparite-(Ce), Ce(AsO₄), and chernovite-(Y), Y(AsO₄), from the hydrothermal quartz-bearing fissures, related to pegmatites overprinted by amphibolite facies, outcropping at Mt. Cervandone (Western Alps, Piedmont, Italy), have been investigated by means of electron microprobe analysis in wavelength dispersion mode and single-crystal X-ray diffraction. The chemical data reveal the occurrence of a full solid solution among the isostructural chernovite-(Y) and xenotime-(Y) with tetragonal symmetry, whereas a wide
miscibility gap is observed for the isostructural gasparite-(Ce) and monazite-(Ce) of Mt. Cervandone, with monoclinic symmetry. A significant chemical heterogeneity has been observed for several investigated samples, especially related to the Th content, which is locally enriched in ThSiO$_4$ grains. The analysis of the refined structural models points out a significant control played by the composition of the tetrahedrally-coordinated (As,P)-bearing sites on the bulk unit-cell volume and on the size and shape of the (REE)-coordination polyhedra.

**Keywords**

Monazite, xenotime, chernovite, gasparite, rare earth elements, crystal chemistry, crystal structure, solid solution, X-ray diffraction.
1. Introduction

According to the IUPAC definition (Connelly et al. 2005), the Rare Earth Elements (REE) consist in a group of 17 elements, comprising the lanthanides (La-Lu or Ln series), Y and Sc, characterized by a similar geochemical behavior. REE are conventionally divided into Light REE (LREE) and Heavy REE (HREE) based on their atomic number, with the drawback that several authors provided a different threshold to separate the two groups (Zepf 2013). An elegant classification system has been provided by U.S. Geological Survey (2011), based on the electronic configuration of the 4f electron shell: LREE (Ce-Gd) are characterized by unpaired 4f electrons, whereas HREE (Tb-Lu) show paired electrons in the 4f shell; in addition, Y was included as one of the HREE (U.S. Geological Survey 2011), being its atomic radius intermediate between those of Ho and Er. REE are used in several applications, including permanent magnets, phosphors, catalytic converters, or as glass and metal alloys additives. Their mining exploitation is largely concentrated in China (U.S. Geological Survey, 2021) and their commodities export policy changed significantly in the last decade, introducing export quotas and taxes (Mancheri, 2015). For their elevated supply risk, all the REE have been classified as “critical raw materials” by the European Commission (Blengini et al. 2020). Major REE resources are hosted by carbonatites and other alkaline igneous rocks, pegmatites, iron oxide copper-gold deposits, skarn deposits and placers (Balaram, 2019). Hydrothermal alteration of granites and the related pegmatites, as well as the connected mobilization and concentration of REE minerals, is a phenomenon for which the importance has been reported by several authors (e.g., Andersson, 2019; Cheng et al. 2018; Migdisov et al. 2019). Along with the carbonate bastnäsite (Ce(CO$_3$)F) and common phosphates, i.e. monazite-(Ce) and xenotime-(Y), which are important REE ore minerals (Voncken, 2016), the isostructural arsenates gasparite-(Ce) and chernovite-(Y), respectively, have gained a raising attention (e.g., Cabella et al. 1999; Mancini, 2000; Anthony et al. 2000; Kolitsch and Holtsam 2004a; Ondrejka et al. 2007; Breiter et al. 2009; Mills et al. 2010; Förster et al. 2011; Kerbey, 2013; Papoutsa and Pe-Piper,
The aforementioned phosphates and arsenates belong to the large family of \( \text{ATO}_4 \) minerals, where \( A \) stands for REE, Ca, U and Th, whereas \( T \) stands for tetrahedrally-coordinated cations (As, P and minor Si). The crystal structure of these minerals has been object of a large number of studies and reviews (e.g., Mooney, 1948; Boatner, 2002; Ni et al. 1995; Kolitsch and Holtsam, 2004b; Clavier et al. 2011). These \( \text{ATO}_4 \) compounds show two possible structural arrangements (Fig. 1): a monoclinic monazite-type structure (Fig. 1a) and a tetragonal zircon-type (also known as “xenotime-type”) structure (Fig. 1b). Chernovite-(Y), the zircon-type structured HREE-bearing arsenate, is a rare mineral; its crystal structure has first been solved from the synthetic counterpart \( \text{YAsO}_4 \) (Strada and Schwendimann, 1934). The mineral chernovite-(Y) was first described from the Nyarta-Sya-Yu River, Urals (Goldin et al. 1967), and later found at the Mt. Cervandone mineral deposit, as a solid solution among chernovite-(Y) and xenotime-(Y) (Graeser et al. 1973). Chernovite-(Y) has been recovered as an accessory mineral in hydrothermal environments, commonly found as an alteration product of minerals within \( A \)-type granites and gneisses (Breiter et al. 2009, Förster et al. 2011, Papoutsas and Pe-Piper, 2014, Li et al. 2019) and within reduction spots in slates by Kerbey (2013). Microcrystalline \( \text{YAsO}_4 \), along with \( \text{LaAsO}_4 \) (i.e. gasparite-(La)), were also detected within the Fe–Mn deposits of the Corsaglia Valley, Maritime Alps, Italy (Cabella et al. 1999). Also Mills et al. (2010), along with arsenoflorencite-(La), reported the presence of chernovite-(Y) in Mn-rich nodules from the Grubependiticy Lake cirque, Komi Republic, Urals.

The monoclinic arsenate has been first described on the basis of the synthetic counterpart by Beall et al. (1981), as the As-bearing analogue of monazite. Only after Graeser and Schwander (1987) it was described for the mineral gasparite-(Ce), and for the recently discovered gasparite-(La) (Vereshchagin et al. 2019). A solid solution between monazite-(Ce) and gasparite-(Ce) has been found to occur at the Kesebol Mn-Fe-Cu deposit, Västra Götaland, Sweden (Kolitsch and Holtsman 2004a) and within the Tisovec-Rejkovo rhyolite, Slovakia (Ondrejka et al. 2007), whereas all the
studies conducted so far on the samples from Mt. Cervandone, Italy, showed the presence of a miscibility gap between the arsenate and phosphate end-members. Monazite and xenotime are two of the most widespread REE-bearing minerals and are, along with the carbonate bastnäsite (Ce(CO$_3$)F), the major ores exploited for REE. Monazite-(Ce) represents the most common form of monazite, whereas the natural La-, Nd- and Sm-dominant forms are fairly rare (Fleischer and Altschuler, 1969; Rosenblum and Fleischer, 1995; Long et al. 2012). Monazite-(Ce) is a rather common accessory mineral in different geological settings, including granites, aluminous metamorphic rocks (e.g., amphibolites or medium to high-grade pelitic rocks), carbonatites, pegmatites and hydrothermal veins (Cesborn, 1989). Moreover, monazite-(Ce) is also a common detrital mineral in sedimentary placers and a newly formed phase during diagenesis (Sengupta and Van Gosen, 2016; Čopjaková et al. 2011). Xenotime-(Y) is an accessory component in several metasedimentary or igneous rocks, hydrothermal systems and early diagenesis environments (Spear and Pyle, 2002; Richter et al. 2018).

In this work, focused on the case study of the Alpine quartz fissures (related to pegmatites overprinted by amphibolite facies) of Mt. Cervandone, the crystal chemistry and structure of chernovite-(Y), gasparite-(Ce), xenotime-(Y) and monazite-(Ce) will be reinvestigated on the basis of electron probe microanalysis in wavelength dispersion mode (EPMA-WDS) and single-crystal X-ray diffraction. Moreover, a comparative analysis of the crystal chemistry of chernovite-(Y), on the basis of literature data (Breiter et al. 2009; Förster et al. 2011; Kerbey, 2013, Papoutsa and Pe-Piper, 2014; Li et al. 2019) will be performed. This study is part of a broader project aimed at improving the knowledge on the hydrothermal mineral deposit of Mt. Cervandone and the role of REE on the minerals phase stability and structure-related properties (Gatta et al. 2019; 2021).

1.2 Crystal structure of chernovite-(Y), gasparite-(Ce), xenotime-(Y) and monazite-(Ce)

The aforementioned $\text{ATO}_4$ minerals crystallize in a monoclinic monazite-type or in a tetragonal xenotime-type structure. The two structural models share a similar topology, characterized by the
presence of chains, running along the [001] direction, made by the alternation of (REE)-polyhedra and tetrahedral units, the latter mainly occupied by As and P (Fig. 1c and Fig. 1d). In the monazite-type structure, space group $P2_1/n$, the REE cation is ninefold-coordinated in a distorted polyhedron (Clavier et al. 2011). REEO$_9$-polyhedra and (As,P)-tetrahedra are edge-sharing connected to form infinite chains running along the $c$ axis (Fig. 1c). The tetragonal zircon-type structure, space group $I4_1/amd$, shows the alternation of 8-coordinated (REE) polyhedra and tetrahedra, giving rise to infinite chains along [001] (Fig. 1d). Within the REE-bearing phosphates, the larger and lighter REE ranging from La to Eu are preferentially hosted by the monazite-type structure, whereas the smaller and heavier REE, from Tb to Lu, as well as Y and Sc, best fit into the zircon-type structure (Mooney, 1948; Boatner, 2002; Ni et al. 1995; Kolitsch and Holstam, 2004b; Clavier et al. 2011).

For synthetic Gd, Tb and Dy phosphates, the possible presence of two coexisting polymorphs is observed: they may crystallize in both monazite- and zircon-type structures. A similar behavior has been reported for the REEAsO$_4$ series: the monoclinic structure preferentially hosts the larger REE (from La to Nd), whereas the smaller REE (from Sm to Lu, as well as Y and Sc) are preferentially hosted by the tetragonal crystal structure (Ushakov et al. 2001; Boatner et al. 2002).

2. Geological background

The Mt. Cervandone mineral deposit is renowned for the findings of several REE-bearing minerals. These minerals are hosted within Alpine fissures in quartz veins (e.g., Graeser and Albertini, 1995), closely related to pegmatitic dykes (Guastoni et al. 2006). These dykes, tens of cm thick, intrude fine-grained two-mica leucocratic gneisses, metamorphosed under amphibolite-facies conditions (Dal Piaz, 1975), and extend for hundreds of meters within the ‘Mount Leone-Arbola’ nappe being concordant with the gneiss schistosity. The dykes show a pegmatitic texture and a strong NYF (niobium-yttrium-fluorine) chemical signature (Černý, 1991a,b; Ercit et al. 2005; Černý and Ercit, 2005), which reflects into the formation of Be-As-Nb-REE minerals, among which allanite-(Ce) and REE-bearing carbonates, arsenates, phosphates and oxides. Locally, the pegmatitic dykes are
interrupted by discordant, subvertical quartz veins, mainly composed by vitreous and smoky quartz and muscovite. These quartz veins commonly contain open Alpine-type fissures, which host several REE-bearing accessory minerals, including cafarsite, synchysite-(Ce), chernovite-(Y), gasparite-(Ce), xenotime-(Y), monazite-(Ce). Rutile, magnetite, hematite, titanite and tourmaline represent other common accessory minerals within these fissures. During the Alpine orogenic event, the circulation of hydrothermal fluids within the pegmatitic dykes, strongly enriched in arsenic, led to the mobilization of Y, Nb, Ta, REE, Th and U. Subsequently, the circulating hydrothermal fluids led to the formation of the aforementioned quartz veins with the concomitant precipitation of As-, P- and REE-enriched minerals (Guastoni et al. 2006; Gatta et al. 2018).

Unfortunately, no data on the temperatures of the hydrothermal fluids of this area are available. The discussion of the experimental data, carried out in the section 4, is somewhat hindered by the complexity of the geological evolution of the area, characterized by several steps and fluids of different nature within the vein system.

3. Materials and methods

Fourteen rock specimens, from different Alpine quartz fissures, cropping out at Mt. Cervandone, containing REE-bearing arsenates and phosphates, have been selected for this study. They were first observed under a stereomicroscope, with the aim to identify their mineralogical assemblage, which was later confirmed by single-crystal X-ray diffraction. In Table 1 is reported the mineral association within each rock sample, coupled with a specific label for the REE-bearing minerals. Fifteen REE-bearing phosphate and arsenate crystals have been selected and extracted from the fourteen rock specimens under study (see Table 1), and then characterized by means of electron probe microanalysis in wavelength dispersion mode (EPMA-WDS) and single-crystal X-ray diffraction.
3.1 Samples description

Chernovite-(Y) occurs as idiomorphic bipyramidal or prismatic crystals, as well as micrometric aggregates (Fig. 2). Bipyramidal crystals represent the most common form: they were identified within the samples Ch6, Ch7, Ch8, Ch9, Ch10 (Fig. 2a), Ch12 (Fig. 2c) and Ch13. Xenotime-(Y), has a bipyramidal habit as well (Fig. 2f). Chernovite-(Y) forms idiomorphic crystals as Ch11 (Fig. 2b) and Ch12 (Fig. 2c) or Ch13 and Ch16, ranging from 40 µm to 2 mm in size (Fig. 2d,e). Among the chernovites-(Y), only the Ch11 sample (Fig. 2b) shows a prismatic habit. The three monazite-(Ce) samples are euhedral and vitreous orangish aggregates (or millimetric crystals) (Fig. 3a), coupled with anhedral aggregates in Mon2 and Mon14. The samples of gasparite-(Ce) are characterized by brownish to green crystals (3 to 20 µm in diameter, Fig. 3b) clustered in aggregates. Both the samples of gasparite-(Ce) under investigation were formed by replacement of barrel shape crystals of synchysite-(Ce).

3.2 EPMA-WDS analysis

The chemical composition of the investigated REE-bearing phosphates and arsenates was determined using a JEOL JXA-8200 electron microprobe at the Earth Sciences Dept. of the University of Milano (ESD-MI), operating in wavelength dispersive mode (WDS) with a focused beam (~5 µm in diameter), an acceleration voltage of 20 kV, and a beam current of 20 nA. The counting time was set to 30 s for peaks and 10 s for the background, respectively. Correction for matrix effects was applied using the PhiRhoZ method, as implemented in the JEOL suite of programs. The following natural and synthetic standards (with spectral lines) were used: grossular (CaKα, SiKα), nickeline (AsKα), synthetic YPO₄ (YLa, PKa), synthetic Ln(PO₄) set (LaLa, CeLa, PrLa, NdLa, SmLa, EuLa, GdLa, TbLa, DyLa, HoLa, ErLa, TmLa, YbLa, LuLa), synthetic UO₂ (UMβ), synthetic ThO₂ (ThMa) and galena (PbMa). Backscattered (BSE) images were acquired (Fig. 4), as well as EDS compositional maps for the Ch11 sample, concerning the concentration of As, Ce, Sm and Th (Fig. 5). The average chemical composition for all the samples
(excluding the more heterogeneous Ch13 and Ch16 specimens) is reported in Table 2. The chemical composition, expressed as oxide wt% and atoms per formula unit (apfu), pertaining to all the points of analysis, is reported as supplementary material Tables (Tables S1-S15).

3.3 Single crystal X-ray diffraction and structure refinement protocol

The single-crystal X-ray diffraction experiments were performed at the ESD-MI using a Rigaku XtaLAB Synergy-S diffractometer, equipped with a HyPix-6000HE HPC area detector and a PhotonJet-S Mo-Kα (λ=0.71073 Å) microsource, operating at 50 kV and 1 mA. Each data collection was performed using a sample-to-detector distance of 62 mm and a step-scan width of 0.5°. The crystal size of all the samples investigated and the exposure times are reported in Table S16. For all the collected datasets, indexing of the diffraction peaks, unit-cell refinement and intensity data reduction were performed using the CrysAlisPro software (Rigaku Oxford Diffraction, 2019). The unit-cell parameters for all the samples under investigation are reported in Table 3.

The structure refinements were performed using the Jana2006 software (Petřiček et al. 2014), starting from the models reported by Strada and Schwendimann (1934) for chernovite-(Y), Ni et al. (1995) for xenotime-(Y), Kolitsch and Holtsman (2004a) for gasparite-(Ce) and Ni et al. (1995) for monazite-(Ce). The site occupancy factors of the $A$ (REE-bearing) and tetrahedral sites were fixed according to the average chemical composition obtained from EPMA-WDS analysis for each crystal sample (Table 2), leaving out the elements with a low concentration and assuming a full occupancy for both the sites. For the Ch11 and Ch13 samples, characterized by a significant chemical variability (Figs 4, 5; Tables S10, S12), the same strategy has been followed, but the relative occupancies of the different chemical species have been varied (keeping the consistency with the measured chemical data) in order to obtain the best figures of merit of the structure refinements. Each structure refinement was performed adopting anisotropic displacement parameters (ADP). All the refinements converged with no significant correlations among the refined variables. The refined structure models are deposited as Supplementary material (CIF files).
Some relevant structural features, including the interatomic bond distances and the volumes of the coordination polyhedra, are reported in Table 4.

4. Results and discussion

4.1 Chemical composition and REE pattern of the studied samples

In Table 2 is reported the average chemical composition of the samples Mon1, Mon2, Gasp3, Gasp4, Ch6, Ch7, Ch8, Ch9, Ch10, Ch11, Ch12, Xen14 and Mon14, while in Table S12 and Table S15 are reported the results from each point analysis of the chemically heterogeneous samples, Ch13 and Ch16. For the sample Ch11, the average chemical compositions of four domains, identified from EPMA compositional maps (Fig. 5), are reported in Table 2, labeled as Ch11a, Ch11b, Ch11c and Ch11d. Thorium is the most variable element within all the points analysis for both zircon- and monazite-type minerals. The enrichment of Th within the REETO₄ compounds is controlled by two potential substitution mechanisms:

\[(\text{Th},\text{U})^{4+} + \text{Ca}^{2+} = 2\text{REE}^{3+} \quad (\text{equation 1})\]

\[(\text{Th},\text{U})^{4+} + \text{Si}^{4+} = \text{REE}^{3+} + (\text{P},\text{As})^{5+} \quad (\text{equation 2})\]

respectively known as cheralite (equation 1) and thorite substitution mechanisms (equation 2). In Fig. 6a, all the data are reported in a P/(P+As+Si) vs. Y diagram, which clearly allows to distinguish between the four minerals under investigation, arranged in four distinct domains. The Y-poor side of the diagram contains the chemical data from the monazite-(Ce) and gasparite-(Ce) crystals, respectively enriched in P and As. Data from chernovite-(Y) and xenotime-(Y) lie on the Y-enriched side of the diagram, and are characterized by a highly variable P and As fraction, resulting in an almost complete solid solution along the join chernovite-(Y)–xenotime-(Y) (as also shown by the chemical compositions of samples Ch11 and Ch16, having equal fractions of As and P). On the contrary, the composition of gasparite-(Ce) and monazite-(Ce) crystals is closer to the ideal end-members, and only a partial solution is observed. Monazite-(Ce) and gasparite-(Ce) are
characterized by a poor Y content, coupled with an enrichment in LREE elements, with Ce (on average, 0.46(2) apfu) as the most common cation, followed by La (0.20(2) apfu) and Nd (0.17(2) apfu).

The A-site of the chernovite-(Y)–xenotime-(Y) series is characterized by a relatively constant composition, where Y is always the dominant cation (ranging from a maximum of 0.78 apfu to a minimum of 0.46 apfu), followed, on average, by Dy, Er, Gd, Yb and Ho. The fraction of LREE in chernovite-(Y) and xenotime-(Y) is generally low (see the section 4.1.3 for further details), reaching its maximal values in a few data points of analysis of Ch11. The REE pattern for all the samples under investigation is reported in Fig. 7, normalized to the REE concentration of the Carbonaceous Chondrite C1, after Wasson and Kallemejn (1988). For all the points, the abundance of Eu is always lower than the detection limit. As mentioned above, the tetragonal structure of chernovite-(Y) and xenotime-(Y) has a strong preference for Y and, in general, the smaller HREE: this pattern is reflected by the positive slope reported in Fig. 7b. Conversely, in the gasparite-(Ce)–monazite-(Ce) series, the LREE enrichment is responsible for the negative slope in Fig. 7a. It is worthwhile to point out that the relatively high Gd content, shown by the three monazites under investigation, has been already described in alpine-fissures minerals related to the circulation of hydrothermal fluids, as in the case of Mt. Cervandone (Demartin et al. 1991; Della Ventura et al. 1996). Due to their low content (<0.002 apfu), Er-Lu elements are not reported in Fig. 7a. In addition, the Carbonaceous Chondrite C1 REE-normalized diagram reported in Fig. 7b shows that there is a positive anomaly in the Ho and Lu concentrations in chernovite-(Y) and xenotime-(Y) from Mt. Cervandone. Literature data (Ondrejka et al. 2007; Förster et al. 2011; Papoutsas and Pe-Piper, 2014), reporting the Ho and Lu contents in chernovites-(Y) and xenotimes-(Y), reveal that the maximum Ho₂O₃ content detected in chernovite-(Y) is 2.44 wt % (Papoutsas and Pe-Piper, 2014), slightly lower than the highest average content of the samples of this study (Table 2),
whereas Förster et al. (2011) reported the maximum content in Lu₂O₃ (1.29 wt %) very close to that of the samples of this study (Table 2). Although a correction protocol for REE interferences has been applied to the experimental chemical data of this study, we cannot unambiguously exclude that the observed anomalies may be slightly affected to the adopted experimental strategy. However, the previous findings reported in the literature (e.g., Ondrejka et al. 2007; Förster et al. 2011; Papoutsa and Pe-Piper, 2014) corroborate the results of this study.

4.1.1 Chemical composition of the chernovite-(Y)–xenotime-(Y) series

Although the trivalent cations are always dominant within the A-site of the tetragonal series, some data points from the samples Ch6, Ch10, Ch11, Ch13 and Ch16 show a relatively large amount of Th. The thorite substitution mechanism (equation 2) likely occurs in the chernovite-(Y)–xenotime-(Y) series under investigation, as suggested by the strong positive linear correlation between Si and the Th+U fraction (Fig. 6b). For a better representation of the crystal-chemistry of the mineral samples of this study, the (tetragonal) 2-component system chernovite-(Y)–xenotime-(Y) could be replaced by a 3-component solid solution between the end-members chernovite-(Y), xenotime-(Y) and ThSiO₄ (Fig. 8). From Fig. 8, as well as in the P/(P+As+Si) vs. Y diagram (Fig. 6a), even in the more P-depleted samples (i.e., Ch6, Ch7, Ch8, Ch9, Ch10, Ch12), the concentration of this element is relatively high, with an average of 20(3) mol % of xenotime-(Y) component, coupled with a very small ThSiO₄ fraction (on average 3(1) mol %). Conversely, the xenotime-(Y) sample Xen14 shows a chemical composition (Table 2) much closer to the ideal end-member, being As usually low, corresponding to an average chernovite-(Y) component between 7.0 mol % and 12.9 mol %. Between the chernovite-(Y)–xenotime-(Y) edge and the ThSiO₄ corner, the samples investigated show that a wide miscibility gap occurs (Fig. 8).

The most Th-enriched analyses on the chernovite-(Y)-xenotime-(Y) edge belong to Ch13 and Ch16 (Fig. 8), which are also characterized by a highly altered texture (Fig. 4f) and variable composition. In these cases, the major chemical variations concern a strong Th-enrichment, reflected by a ThSiO₄
component ranging from 4.7 mol % to 15.3 mol % for Ch13, and between 1.3 mol % and 12.3 % for Ch16. The relatively large fraction of the ThSiO$_4$ component may be responsible for the greenish color observed only in these samples (Fig. 2d,e). Moreover, these samples are also characterized by a larger fraction of CaO (up to 1.93 wt %, in Ch16, vs. an average 0.1(3) wt % for the other chernovite-(Y) samples), suggesting the occurrence also of the cheralite substitution mechanism (equation 1). In addition, Ch16 reveals the presence of P-enriched domains, with a maximum xenotime-(Y) component of 45.10 mol % (Fig. 8). The P- and the As-enriched domains, respectively, are linked by an irregular lobate interface, as shown in Fig. 4f.

As mentioned above, the Ch11 sample (Fig. 4d and Fig. 5) shows a clear core-to-rim zonation, which is characterized by a P-enriched core and an As- and LREE-enriched rim (Fig. 7). EPMA X-ray compositional maps for the Ch11 sample (Fig. 5), showing the fraction of As (Fig. 5a), Ce (Fig. 5b), Sm (Fig. 5c) and Th (Fig. 5d), allow a subdivision into five domains: 1) a quasi-homogeneous core (Ch11$_a$; the blue-colored area of the insert of Fig. 4d), characterized by an intermediate composition between chernovite-(Y) and xenotime-(Y), with a slight predominance of the latter (up to 60.86 mol % of xenotime-(Y) component) as reported in Table 2; 2) a segment enriched in ThSiO$_4$ (thorite or huttonite) inclusions in form of grains (~1-5 µm in size), clearly visible in Fig. 4d (black area within the insert) and Fig. 5d; 3) an interface zone (Ch11$_b$; green area in the insert of Fig. 4d), characterized by an almost equal amount of P and As (xenotime-(Y) molar abundance reaches 52.68 mol %, slightly lower than the inner, darker core), as well as an enrichment in Th; 4) a chernovite-(Y) domain (Ch11$_c$; red area in the insert of Fig. 4d), with high HREE and Th; 5) a relatively Th-poor outer domain (Ch11$_d$; the yellow area in the insert of Fig. 4d), characterized by an enrichment in LREE, as shown by the increase in Ce and Sm fraction towards the rim (Fig. 5b and Fig. 5c), coupled with the highest As content (Fig. 5a). The contact between Ch11$_b$ and Ch11$_c$, as well as between Ch11$_c$ and Ch11$_d$, is marked by a discontinuous flame-like interface. The most As-enriched points of the EPMA-WDS analysis (up to 98.82 mol % of (REE)AsO$_4$ component)
refers to the Ch11d domain and show also the highest LREE and lowest Th concentration within the cernovite-(Y)–xenotime-(Y)–ThSiO₄ solid solution: Y is still the most abundant A cation (0.487 apfu), but depleted with respect to the inner portions and the other cernovite-(Y) samples (ca. 0.6-0.8 apfu; Table 2), whereas Nd is the second most abundant A cation, and significant fractions of Sm, Ce and Pr are also shown, up to 10.80 wt % for Nd₂O₃ (0.167 apfu vs. less than 0.01 apfu in the other cernovites), 5.18 wt % for Sm₂O₃ (0.077 apfu vs. < 0.015 apfu), 3.87 wt % for Ce₂O₃ (0.061 apfu vs. < 0.003 apfu) and 1.23 wt % for Pr₂O₃ (0.019 apfu vs. substantially absent in other cernovites). Overall, a comparative analysis of the A-site composition of the investigated cernovite-(Y) and xenotime-(Y) crystals does not reveal a preferential partitioning of Y and the other HREE among the investigated zircon-type tetragonal arsenates and phosphates (Fig. 7a and Tables S1-15). However, the chemical heterogeneity and altered texture of some selected investigated samples (e.g., Ch11, Ch13, Ch16) suggests a complex interplay with chemically variable hydrothermal fluids, which may have led to local chemical dissolutions of P-enriched cernovites-(Y) and precipitation of ThSiO₄ crystals. The identification of these crystals as thorite (isostructural with zircon) or huttonite (isostructural with monazite) is not straightforward. The phase stability relationships between the two ThSiO₄ polymorphs have been widely discussed by several authors (Harlov et al. 2007; Mazeina et al. 2005; Seydoux and Montel, 1997), reporting that huttonite is stable at higher T and P with respect to thorite. However, the presence of REE at the A-site, according to Speer (1982), may enlarge the stability field of huttonite to lower temperatures. Harlov et al. (2007) found out that the crystallization of metastable huttonite at the expenses of monazite-(Ce) crystals can take place at 400°C (and 500 MPa), in the thorite field, as also reported by Guastoni et al. (2016) for pegmatitic monazites of the Central Alps. In this light, given the difficulty to tell apart thorite and huttonite by means of EPMA analyses (Harlov et al. 2002; Harlov and Föster, 2002) and the lack of information on the (P,T) conditions of the hydrothermal fluids of Mt. Cervandone, it is impossible to unambiguously identify which polymorph of ThSiO₄ is associated to the zircon-type and monazite-type REETO₄ minerals of this study.
The sample Ch11 shows the presence of a reaction contact. In this case, a Th-rich layer, *i.e.* Ch11, (see Figs 4, 5), represents the reactional crown around the more chemically homogeneous Ch11a. The few ThSiO₄ grain inclusions show a chemical composition closely related to the surrounding. ThSiO₄ shows an As-enrichment over P, when in contact with the chernovite-(Y)–xenotime-(Y) s.s. (Ch11) and an evident P-enrichment when included in the Xen14 grains (Table S13). The three points of analysis falling into the ThSiO₄ field (Fig. 8) are characterized by a REE-pattern (Fig. S1) in which, considering only the lanthanides, the HREE slightly prevail over the LREE. This pattern likely reflects the chemical composition of the hydrothermal fluids, which may be affected and, in turn, modified in response of several processes. These may include, but are not limited to, the destabilization of REE-enriched minerals as, for example, allanite and gadolinite, as well as a different partitioning of the different REE’s as trace elements in nominally REE-free minerals. The paramount role of water in stabilizing the actinides and Ln orthosilicates has been suggested by several authors (e.g., Johan and Johan, 2005; Strzelecki et al. 2021) and the hydroxilized nature of the ThSiO₄ grain inclusions could explain the poor closure of their EPMA point analyses. Moreover, Mesbah et al. (2016) identified a complete solid solution between the zircon-type ErPO₄ and thorite, synthesized under hydrothermal conditions (250°C). However, in the natural samples here investigated a very sharp contact (Fig. 4c,d) has been observed between the ThSiO₄ grains and the surrounding phosphates and arsenates.

### 4.1.2 Chemical features of the gasparite-(Ce)–monazite-(Ce) series

All the gasparite-(Ce) and monazite-(Ce) samples show a rather similar composition of the ninefold-coordinated A site and the main differences concern in particular the abundance of Y and Ca. A relatively high amount of Y (Y₂O₃ on average, 0.7(2) wt %) is shown by the three monazite-(Ce) samples investigated, especially by the Mon1 sample (Y₂O₃ up to 1.12 wt %), whereas this element is almost absent in the two gasparite-(Ce) samples (Y₂O₃<0.13 wt %). Unlike monazite-(Ce), gasparite-(Ce) shows a higher content and more uniform distribution of Ca (CaO 1.8(2) wt %,
vs 1.1(4) wt % for monazite-(Ce). Also in the gasparite-(Ce)–monazite-(Ce) series, Th has been found as the most variable element and, in addition, gasparite-(Ce) incorporates the highest fraction of Si among the investigated REE minerals (see Table 2). In this case, a further charge-compensating mechanism should be involved, to fully explain the anomalous amount of Ca and Si, not compensated by Th+U, in gasparite-(Ce). The presence of monovalent anions, such as OH\(^-\), F\(^-\) or Cl\(^-\), in place of O\(^2-\), may compensate the presence of Si and Ca, according to the following equation:

\[
2(\text{OH,F,Cl})^- + \text{Ca}^{2+} + \text{Si}^{4+} = 2\text{O}^{2-} + \text{REE}^{3+} + (\text{P,As})^{5+} \quad (equation \ 3)
\]

According to equation 3, if just OH\(^-\) is taken into account, the corresponding amount of H\(_2\)O necessary to compensate the charge defect is, on average, \(\sim 0.45\) wt % for both Gasp3 and Gasp4. Instead, for all the samples of monazite-(Ce), the combination of equation 1 and equation 2 fully satisfy the pattern shown in Fig. 6b. The P and As contents in the arsenate and phosphate samples, respectively, are always low, as reflected by an average of 1.2(6) mol % of the phosphate component in gasparite-(Ce) and a maximum 6.60 mol % of the arsenate component in monazite-(Ce).

4.1.3 Comparison with chemical data reported in the literature

A comparison with the composition of chernovite-(Y) from Mt. Cervandone and that from the Binn Valley, reported by Graeser et al. (1973), shows a P and As content very close to that reported in Table 2 for our investigated samples, resulting in a \(\text{As}/(\text{As+P}) = 0.76\) and 0.84, respectively. A comparison with published chemical analyses of chernovite-(Y) and xenotime-(Y) occurring in different localities (Ondrejka et al. 2007; Förster et al. 2011; Breiter et al. 2009; Li et al. 2019; Alekseev and Marin, 2013; Kerbey, 2013; Mills et al. 2010; Papoutsa and Pe-Piper, 2014) shows that the zircon-type phosphates and arsenates here investigated selectively host HREE, with a very low LREE content. In Fig. 9, the HREE vs. LREE content of several xenotimes-(Y) and chernovites-(Y) from different geological environments is reported, including crystals from
hydrothermally-altered A-type granites, rhyolites, pegmatites (Ondrejka et al. 2007; Breiter et al. 2009; Li et al. 2019; Papoutsa and Pe-Piper, 2014; Förster et al. 2011) and Mn nodules contained in metasedimentary rocks (Mills et al. 2010). From Fig. 9, the majority of the chernovite-(Y)–xenotime-(Y) samples from Mt. Cervandone are mostly enriched in HREE, and only in the outer domains of Ch11 (Ch11_e and Ch11_d) the fraction of LREE is high (reaching a maximum of ~0.39 apfu in Ch11_d), where the LREE-enrichment is also shown by the compositional maps (Fig. 5c,d; Table 2). Therefore, a few points of analysis from this study, and those reported by Ondrejka et al. (2007) and Förster et al. (2011), confirm that, within the A-site of the series chernovite-(Y)–xenotime-(Y), a relatively large fraction of LREE (up to 0.48 apfu) may be hosted, despite being a fairly rare occurrence. As reported in Figure 8b, evidences of a complex solid solution between the end-members chernovite-(Y), xenotime-(Y) and ThSiO₄, according to the equation 2, were already reported by several authors (Ondrejka and Uher 2008; Breiter et al. 2009; Förster et al. 2011; Förster, 2006; Alekseev and Marin, 2013). Chemical data reported by Ondrejka et al. (2007) and Förster et al. (2011), in particular, show a 7-site range composition very close to that reported in the present study. In addition, the heavily altered crystals of Ch13 and Ch16 share similar features with the hydrated chernovites-(Y) and xenotimes-(Y) crystals described by Förster (2006) and Förster et al. (2011), including a similar Th-content (up to 18.4 wt % of ThO₂), as well as the variable composition, ranging between 9-84 mol % of chernovite-(Y) and 0-70 mol % of xenotime-(Y) component.

The barrel shaped morphology of gasparite-(Ce), pseudomorph after synchysite-(Ce), has been underlined by Graeser and Schwander (1987), and can be observed also for the sample Gasp4 (Fig. 3b). As an alteration product of synchysite-(Ce), gasparite-(Ce) shows rather different chemical features with respect to the three other investigated species crystallized from the hydrothermal fluids. In particular, a comparison with the isostructural monazite-(Ce) points out a Ca-enrichment and a depletion in Y, likely inherited from the parental REE-carbonate. This study, as the previous
one conducted at Mt. Cervandone by Graeser and Schwander (1987), reports rather straight compositions, very close to the ideal ones, resulting in a very limited solid solution along the join gasparite-(Ce)–monazite-(Ce). Since solid solutions among gasparite-(Ce) and monazite-(Ce) have been described by Ondrejka et al. (2007) and Kolitsch and Holtsman (2004a), respectively with $\text{As}/(\text{As}+\text{P}) = 0.57-0.64$ and $0.89-0.93$, the wide miscibility gap observed in this study within the monazite-type series is a local feature of the Mt. Cervandone deposit, possibly related to the formation of gasparite-(Ce) after synchysite-(Ce). Conversely, the gasparite-(La), which occurs in the close Binn Valley (Vereshchagin et al. 2019), the Swiss flank of Mt. Cervandone, is characterized by a more phosphatian composition with $\text{As}/(\text{As}+\text{P}+\text{Si}+\text{S})=0.80$.

4.2 Crystal structure of the investigated REE phosphates and arsenates

As previously discussed, the tetragonal minerals chernovite-(Y), xenotime-(Y) and thorite are isostructural. Considering the chernovite-(Y)–xenotime-(Y) side of the triangular compositional diagram, the unit-cell volume of the investigated minerals gradually decreases from chernovite-(Y) to xenotime-(Y), as shown by Fig. 10a, which reports the evolution of unit-cell $V$ vs. the As fraction. Similarly, Fig. 10b shows the evolution as a function of As of the tetrahedron volume, as calculated using the tools implemented in the software Vesta 3 (Momma and Izumi, 2011). Concerning the sample Ch11, the unit-cell and structural data, when compared to those of the other chernovite-(Y) samples (see Table S16), suggest that the investigated single-crystal (20×20×15 μm$^3$) belongs to the P-enriched core portion (Ch11a). This assignment is also corroborated by the BSE map shown in Fig. 4d, which suggests that the core portion is the only able to provide a sufficiently large single crystal. For these reasons, data pertaining to the sample Ch11 have been plotted in Fig. 10 assuming the average composition of the core portion reported in Table 2. Excluding the most Th-enriched samples, all the investigated chernovites-(Y) and xenotimes-(Y) share an almost identical composition of the REE-bearing $A$-polyhedral site (Tables S1-S15), dominated by HREE, which cannot be responsible for the observed variations in the unit-cell and $A$-
polyhedron volumes (Fig. 10a; Table 5). Conversely, the cationic population of the \( T \)-site affects the volumes of the tetrahedra, with larger values almost linearly correlated with an increase in As and a decrease in P (Fig. 10b). Fig. 10c and Fig. 10d show that a strong correlation exists between the tetrahedron volume, on one side, and the unit-cell and \( A \)-polyhedron volumes, on the other side, suggesting that the unit-cell volume within this series is significantly controlled by the tetrahedrally-coordinated cations. This is not surprising if we consider the bonding topology of the zircon-type structure, in which any (REE)-polyhedron is surrounded by 6 tetrahedra and, in turn, each tetrahedron share two edges with two adjacent (REE)-polyhedra. As a result, the volumes of the two building units (i.e., polyhedron and tetrahedron) are mutually interconnected. Thus, when the \( T \)-site is mostly occupied by the smaller phosphorous, the (REE)-bearing polyhedron adapts with a smaller volume which, in turn, affects also the unit-cell volume; conversely, the opposite trend is observed with an enrichment in arsenic.

A clear deviation from the previously described trends is represented by the Ch13 and Ch16 samples, which show appreciably larger unit-cell volumes, respectively of 312.89(3) Å\(^3\) and 313.75(9) Å\(^3\) (Fig. 10a). This misalignment is likely related to the enrichment in Th and Ca at the \( A \)-site, being these elements characterized by larger ionic radii with respect to the HREE (Shannon, 1976), which induce an expansion of the \( A \)-polyhedron and, in turn, of the unit-cell volume. A similar behavior to that described above for the (tetragonal) chernovite-(Y)-xenotime-(Y) series is also shown by the (monoclinic) gasparite-(Ce) and monazite-(Ce). However, in this case, the distribution of the chemical compositions in two clusters close to the ideal end-members prevents a robust extrapolation along the whole series (Fig. 10d).

A correlation among the volumes of (P,As)-tetrahedra and the \( A \)-site polyhedra is also shown by the synthetic REE\( T \)O\(_4\) compounds, of which structural models are reported in the International Crystal Structure Database. A comparative analysis of the structural parameters of synthetic REE-bearing phosphates (YPO\(_4\), LaPO\(_4\), CePO\(_4\), NdPO\(_4\), TbPO\(_4\), HoPO\(_4\), DyPO\(_4\), YbPO\(_4\) and LuPO\(_4\) (Ni et al.
and their As-dominant endmembers (Y\textsubscript{As}O\textsubscript{4} (Ledderboge et al. 2018), La\textsubscript{As}O\textsubscript{4} (Kang and Schleid, 2005), Ce\textsubscript{As}O\textsubscript{4} (Brahim et al. 2002), Nd\textsubscript{As}O\textsubscript{4} (Schmidt et al. 2005), Tb\textsubscript{As}O\textsubscript{4} (Long and Stager, 1977), Ho\textsubscript{As}O\textsubscript{4} (Schmidt et al. 2005), Dy\textsubscript{As}O\textsubscript{4} (Long and Stager, 1977), Yb\textsubscript{As}O\textsubscript{4} (Kang et al. 2005) and Lu\textsubscript{As}O\textsubscript{4} (Lohmüller et al. 1973)) has been carried out. Given the same elemental composition of the REE-bearing A site, the volume of its coordination polyhedron is different in phosphates and arsenates, being always lower in phosphates, pointing out the dominant role played by the TO\textsubscript{4} structural units ($V_{TO4}$~2.4 Å\textsuperscript{3} for As\textsubscript{O4} and ~1.8 Å\textsuperscript{3} for PO\textsubscript{4}) in controlling most of the structural features of the REE\textsubscript{T}O\textsubscript{4} compounds. Selected structural parameters of synthetic REE\textsubscript{T}O\textsubscript{4} compounds are reported in Table S17.

In addition, based on all the structure refinements, the A-polyhedron distortion index (Baur, 1974) has been calculated using the tools implemented in Vesta 3 (Momma and Izumi, 2011). The A-polyhedron distortion index ($DI$), following Baur (1974), is based on the measured A-O distances, i.e. $DI(A-O) = \frac{1}{n} \sum |AO_i - AO_{av}| / AO_{av}$ (equation 4) for the tetragonal series and $DI(A-O) = \frac{1}{n} \sum |AO_i - AO_{av}| / AO_{av}$ (equation 5) for the monoclinic series, reported in Table 4 (where $AO_{av}$ is the average A-O interatomic distance). The analysis of the calculated distortion index values (Table 4) shows that the increase in As (and decrease in P) leads to an increase in the distortion of the (REE)-site coordination polyhedra in both the tetragonal and monoclinic series.

5. Concluding remarks

The chemical composition and crystal structure of fifteen REE-bearing phosphates and arsenates from the Mt. Cervandone mineral deposit (Western Alps, Italy) have been investigated, using a multi-methodological approach. The REE-pattern of all the samples analyzed, shows, as expected, an enrichment in LREE for gasparite-(Ce) and monazite-(Ce), whereas chernovite-(Y) and xenotime-(Y) are characterized by HREE enrichment. Furthermore, a relative enrichment in Ho...
(when normalized to the CN-1 chondrite composition) has been observed for chernovite-(Y), xenotime-(Y) and monazite-(Ce). Conversely, the two samples of gasparite-(Ce) do not share the same REE-pattern, presumably for the genesis of gasparite-(Ce) as alteration product of the carbonate synchysite-(Ce) (Graeser and Schwander, 1987). An almost complete solid solution has been found along the chernovite-(Y) and xenotime-(Y) join, whereas a wide miscibility gap occurs among the investigated end-members of gasparite-(Ce) and monazite-(Ce) series from Mt. Cervandone, likely ascribable to the aforementioned different formation conditions of gasparite-(Ce). On average, chernovite-(Y) and xenotime-(Y) from Mt. Cervandone are characterized by a very selective composition, resulting in a rather low LREE concentration, if compared to chemical data available in the literature. Consequently, a limited solid solution occurs between the LREE-bearing monazite-(Ce) and gasparite-(Ce) and the HREE-bearing xenotime-(Y) and chernovite-(Y). However, the Ch11 sample, showing evidence of reaction, is characterized by a significant enrichment in LREE in its outer rim, suggesting a complex interplay with the circulating hydrothermal fluids. Furthermore, the analysis of the refined structural models reveals the principal role played by the tetrahedrally-coordinated cations in controlling the unit-cell volume and even the REE-polyhedral volume and distortion.

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7. Competing interests

The authors declare no competing interests.

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Fig. 1. The monazite-type (a) and the zircon-type crystal structures (b); (REE)-polyhedra and (P,As)-tetrahedra making the chains parallel to [001] in the monazite-type (c) and zircon-type structures (d).
Fig. 2. Photographs of selected samples from the Alpine quartz fissures of Mt. Cervandone bearing REE-phosphates and -arsenates: (a) yellow Ch10 chernovite-(Y) sample with magnetite and muscovite on quartz; (b) prismatic Ch11 chernovite-(Y) sample with magnetite grains on quartz; (c) yellow Ch12 chernovite-(Y) sample on quartz; (d) greenish microcrystals of Ch16 chernovite-(Y) sample, with plagioclase and magnetite, on quartz; (e) M-C13 orthogneiss lined with several Ch13 chernovite-(Y) microcrystals and few grains of clinochlore; (f) bipyramidal crystal of Xen14 xenotime-(Y) on quartz (see also Table 1). [Chv-Y: chernovite-(Y); Mag: magnetite; Ms: muscovite; Pl: plagioclase; Chl: clinochlore, Warr, 2021].
Fig. 3. Photographs of two samples of the gasparite-(Ce)–monazite-(Ce) series: (a) Mon2 monazite-(Ce) sample, with rutile (red); (b) greenish, barrel-shape Gasp4 gasparite-(Ce) sample, pseudomorph after synchysite-(Ce), with clinochlore grains, on quartz. [Rt: rutile; Mnz-Ce: monazite-(Ce); Gsp-Ce: gasparite-(Ce); Chl: clinochlore; Warr, 2021].
Fig. 4. BSE images of selected samples under investigation: (a) quasi-homogeneous crystal of Ch10, containing a brighter $\text{ThSiO}_4$-enriched level; (b) crystal of Mon2 monazite-(Ce) sample, showing brighter domains characterized by a higher Th-content; (c) chemically-homogeneous and fractured Xen14 xenotime-(Y) sample, containing $\text{ThSiO}_4$ grains (indicated by the yellow arrow); (d) highly zoned Ch11 sample, showing five main domains highlighted with different colours in the insert (see Fig. 5 and text), with $\text{ThSiO}_4$ grains indicated by the yellow arrow; (e) Gasp3 gasparite-(Ce) sample, made by several microcrystals (~10 µm size); (f) highly-zoned Ch16 chernovite-(Y) sample, containing P-enriched darker patchy domains and brighter As-enriched domains, separated by lobate interface.
**Fig. 5.** Compositional maps for the Ch11 chernovite-(Y) sample, showing the fraction of As (a), Ce (b), Sm (c) and Th (d) (see section 4.1.1).
Fig. 6. (a) $P/(P+As+Si)$ vs. $Y$ diagram and (b) $Si$ vs. $Th+U$ (in $\text{apfu}$) for all the samples under investigation.
Fig. 7. Average composition of REE (normalized to the CN-1 chondrite, after Wasson and Kallemeyn (1988)) of all the samples of the gasparite-(Ce)–monazite-(Ce) series (a) and of the chernovite-(Y)–xenotime-(Y) series (b). The grey belt in Fig. 7b represents the range of the lanthanides composition for all the points of analysis of the chernovite-(Y)-xenotime-(Y) series. For the sample Ch11 in Fig. 7b are reported four distinct chemical compositions referring to the core (Ch11a), the interface (Ch11b), the Th-rich rim zone (Ch11c) and the LREE-enriched outer rim zone (Ch11d) (see section 4.1.1, Table 2, Table S10 and Figs. 4-5 for further details). (Element with concentration < 0.002 apfu are not shown).
Fig. 8. (a) Triangular chernovite-(Y)–xenotime-(Y)–ThSiO₄ compositional diagram, based on the As–P–Si relative abundance, containing all the points of chemical analysis performed on the zircon-type tetragonal minerals. The three points closer to the ThSiO₄ corner represent the ThSiO₄ grains found within the Ch11 and Xen14 samples (see also Fig. 4). (b) The same diagram showing the chemical data from this and previously published studies on minerals of the chernovite-(Y)-xenotime-(Y) series.
Fig. 9. **LREE vs. HREE** diagram for all the chernovite-(Y)–xenotime-(Y) samples of this study, and for chernovites-(Y) (filled symbols), xenotime-(Y) and their solid solutions (void symbols) based on the data from Breiter et al. (2009), Ondrejka et al. (2007), Mills et al. (2010), Förster et al. (2011) and Kerbey (2013).
Fig. 10. Unit-cell volume vs. As fraction (in apfu) (a), volume of the TO₄ tetrahedron vs. As fraction (in apfu) (b) and volume of the TO₄ tetrahedron vs. volume of the (REE)-bearing A-polyhedron (c) for the samples pertaining to the chernovite-(Y)–xenotime-(Y) series. Volume of the TO₄ tetrahedron vs. unit-cell volume (d) for all the samples investigated.
Table 1. Mineralogical assemblage of each sample from the quartz Alpine-fissures of Mt. Cervandone (quartz is ubiquitous and not reported in the Table), identified by single-crystal X-ray diffraction, except for the ThSiO$_4$ grains.

| Quartz-fissure sample | REE-minerals     | REE-bearing sample name | Associated accessory minerals                  |
|-----------------------|------------------|-------------------------|------------------------------------------------|
| M-C1                  | monazite-(Ce)    | Mon1                    | muscovite, magnetite, rutile, hematite         |
| M-C2                  | monazite-(Ce)    | Mon2                    | muscovite, magnetite, rutile, hematite, clinohlore |
| M-C3                  | gasparite-(Ce)   | Gasp3                   | muscovite, magnetite, clinohlore               |
| M-C4                  | gasparite-(Ce)   | Gasp4                   | muscovite, magnetite, clinohlore               |
| M-C6                  | chernovite-(Y)   | Ch6                     | muscovite, magnetite                           |
| M-C7                  | chernovite-(Y)   | Ch7                     | titanite, muscovite, magnetite                 |
| M-C8                  | chernovite-(Y)   | Ch8                     | muscovite, magnetite, rutile, tourmaline       |
| M-C9                  | chernovite-(Y)   | Ch9                     | muscovite                                     |
| M-C10                 | chernovite-(Y)   | Ch10                    | muscovite, magnetite                           |
| M-C11  | chernovite-(Y)–xenotime(Y) s.s. | Ch11  | muscovite, magnetite, rutile, hematite, ThSiO$_4$ (thorite or huttonite) |
|--------|--------------------------------|-------|---------------------------------------------------------------------|
| M-C12  | chernovite-(Y)                  | Ch12  | muscovite                                                            |
| M-C13  | chernovite-(Y)                  | Ch13  | muscovite, clinochlore                                               |
| M-C14  | xenotime-(Y), monazite-(Ce)     | Xen14, Mon14 | muscovite, magnetite, rutile, hematite, ThSiO$_4$ (thorite or huttonite) |
| M-C16  | chernovite-(Y)                  | Ch16  | magnetite, plagioclase                                               |
Table 2. Average chemical composition (expressed in oxide wt % and in atoms per formula unit (apfu) calculated on the basis of 4 oxygen atoms) of all the samples under investigation (except for the heterogeneous Ch13 and Ch16 specimens, the compositions of which are reported in Table S12 and Table S15, respectively). For the sample Ch11, the average composition of four distinct domains is reported as Ch11a (P-enriched core), Ch11b (P- and Th-enriched intermediate zone), Ch11c (P-depleted and Th-enriched intermediate zone) and Ch11d (P-depleted and LREE-enriched outer rim) [see section 4.1.1 and Figs 4, 5 for further details].

|        | Mon1          | Mon2          | Gasp3         | Gasp4         | Ch6          | Ch7          |
|--------|---------------|---------------|---------------|---------------|--------------|--------------|
| As₂O₅  | 0.15          | (0.09-0.23)   | 2.26          | (1.40-3.14)   | 38.61        | (36.38-41.39)| 41.39        | (38.45-42.97)| 33.41        | (30.14-35.61)| 37.10        | (32.82-44.44)|
| P₂O₅   | 28.64         | (28.33-29.00) | 27.77         | (26.69-28.38) | 0.83         | (0.25-3.01)  | 0.13         | (0-0.61)     | 7.81         | (2.17-10.1)  | 5.29         | (4.01-8.87)  |
| SiO₂   | 0.21          | (0.05-0.37)   | 0.24          | (0.09-0.59)   | 1.72         | (1.21-2.39)  | 1.48         | (0.58-3.11)  | 0.65         | (0.39-3.17)  | 0.76         | (0.29-1.08)  |
| V₂O₅   | b.d.l.        | b.d.l.        | b.d.l.        | b.d.l.        | 0.01         | (0-0.07)     | 0.02         | (0-0.10)     | 0.02         | (0-0.03)     | 0.01         | (0-0.03)     |
| CaO    | 1.40          | (0.88-1.65)   | 0.68          | (0.20-1.22)   | 1.46         | (1.22-1.79)  | 1.92         | (1.64-2.26)  | 0.02         | (0-0.06)     | 0.01         | (0-0.03)     |
| Y₂O₃   | 0.90          | (0.65-1.12)   | 0.52          | (0.43-0.67)   | 0.01         | (0-0.07)     | 0.05         | (0-0.19)     | 33.97        | (25.38-35.05)| 35.87        | (35.11-43.39)|
| La₂O₃  | 13.24         | (12.12-14.76) | 13.08         | (12.39-13.34) | 11.38        | (10.74-12.20)| 12.86        | (10.89-14.43)| 0.04         | (0-0.22)     | 0.05         | (0-0.16)     |
| Ce₂O₃  | 29.88         | (28.77-31.23) | 31.31         | (29.13-33.35) | 28.3         | (27.08-32.20)| 26.86        | (24.56-27.95)| 0.13         | (0.01-0.37)  | 0.12         | (0.02-0.32)  |
| Pr₂O₃  | 3.28          | (2.79-3.45)   | 3.70          | (3.10-4.03)   | 2.98         | (2.68-3.38)  | 2.56         | (1.92-2.82)  | 0.04         | (0-0.17)     | b.d.l.       |              |
| Nd₂O₃  | 12.93         | (12.15-14.36) | 13.70         | (12.72-13.73) | 11.63        | (10.26-11.98)| 9.40         | (8.03-10.2)  | 0.58         | (0.38-2.20)  | 0.25         | (0.07-0.35)  |
| Sm₂O₃  | 2.51          | (2.07-2.31)   | 2.51          | (2.28-2.81)   | 1.43         | (0.90-1.84)  | 1.22         | (0.91-1.48)  | 0.96         | (0.73-2.36)  | 0.43         | (0.22-0.61)  |
| Eu₂O₃  | b.d.l.        | b.d.l.        | b.d.l.        | b.d.l.        | b.d.l.       | b.d.l.       | b.d.l.       | b.d.l.       |              |              |              |
| Gd₂O₃  | 1.88          | (1.33-2.33)   | 1.48          | (1.17-1.93)   | 0.38         | (0.04-0.62)  | 0.62         | (0.31-0.97)  | 2.58         | (2.10-4.52)  | 1.58         | (1.38-1.85)  |
| Tb₂O₃  | b.d.l.        | b.d.l.        | b.d.l.        | b.d.l.        | b.d.l.       | b.d.l.       | b.d.l.       | b.d.l.       | 0.59         | (0.31-0.77)  | 0.46         | (0.29-0.62)  |
| Dy₂O₃  | 0.39          | (0.18-0.70)   | 0.30          | (0.11-0.49)   | 0.03         | (0-0.13)     | 0.04         | (0-0.22)     | 4.86         | (4.45-5.36)  | 4.07         | (3.68-4.41)  |
| Ho₂O₃  | 0.45          | (0.21-0.75)   | 0.32          | (0.01-0.54)   | 0.03         | (0-0.16)     | 2.39         | (2.11-3.05)  | 1.87         | (1.57-2.28)  |              |
| Er₂O₃  | 0.02          | (0-0.10)      | b.d.l.        | 0.03          | (0-0.13)     | 0.03         | (0-0.23)     | 3.38         | (2.23-3.85)  | 3.36         | (3.20-3.72)  |
| Tm₂O₃  | 0.08          | (0-0.30)      | 0.04          | (0-0.32)      | 0.03         | (0-0.15)     | 0.01         | (0-0.13)     | 0.42         | (0.11-0.62)  | 0.36         | (0.18-0.53)  |
| Yb₂O₃  | 0.01          | (0-0.08)      | 0.01          | (0-0.06)      | 0.04         | (0-0.16)     | 0.04         | (0-0.22)     | 2.91         | (1.73-3.20)  | 2.94         | (2.56-3.25)  |
| Element | Value     | Range       | Value     | Range       | Value     | Range       | Value     | Range       | Value     | Range       |
|---------|-----------|-------------|-----------|-------------|-----------|-------------|-----------|-------------|-----------|-------------|
| Lu₂O₃   | 0.15      | (0.02-0.46) | 0.10      | (0-0.34)    | 0.04      | (0-0.14)    | 0.05      | (0-0.16)    | 1.21      | (0.82-1.54) |
| PbO     | 0.02      | (0-0.12)    | 0.01      | (0-0.05)    | 0.02      | (0-0.09)    | 0.05      | (0-0.21)    | 0.19      | (0-0.37)    |
| ThO₂    | 3.10      | (1.47-4.52) | 2.32      | (0.90-5.30) | 0.90      | (0.13-2.23) | 1.96      | (0-9.13)    | 2.51      | (1.72-10.8) |
| UO₂     | 0.05      | (0-0.20)    | 0.13      | (0.00-0.23) | b.d.l.    |             | 0.06      | (0-0.26)    | 0.91      | (0.60-1.96) |
| Tot.    | 99.39     |             | 100.6     |             | 99.91     |             | 100.8     |             | 99.76     |             |
| As      | 0.003     |             | 0.047     |             | 0.913     |             | 0.964     |             | 0.698     |             |
| P       | 0.968     |             | 0.933     |             | 0.031     |             | 0.005     |             | 0.264     |             |
| Si      | 0.008     |             | 0.009     |             | 0.078     |             | 0.066     |             | 0.026     |             |
| V       | /         |             | /         |             | /         |             | /         |             | /         |             |
| Ca      | 0.060     |             | 0.029     |             | 0.071     |             | 0.092     |             | 0.001     |             |
| Y       | 0.019     |             | 0.011     |             | /         |             | 0.001     |             | 0.723     |             |
| La      | 0.195     |             | 0.191     |             | 0.189     |             | 0.211     |             | /         |             |
| Ce      | 0.436     |             | 0.455     |             | 0.468     |             | 0.438     |             | 0.002     |             |
| Pr      | 0.047     |             | 0.053     |             | 0.049     |             | 0.041     |             | 0         |             |
| Nd      | 0.184     |             | 0.194     |             | 0.188     |             | 0.149     |             | 0.008     |             |
| Sm      | 0.034     |             | 0.034     |             | 0.022     |             | 0.019     |             | 0.013     |             |
| Eu      | /         |             | /         |             | /         |             | /         |             | /         |             |
| Gd      | 0.024     |             | 0.019     |             | 0.005     |             | 0.009     |             | 0.042     |             |
| Tb      | /         |             | /         |             | /         |             | /         |             | 0.007     |             |
| Dy      | 0.005     |             | 0.003     |             | /         |             | 0.001     |             | 0.062     |             |
| Ho      | 0.005     |             | 0.004     |             | /         |             | /         |             | 0.030     |             |
| Er      | /         |             | /         |             | /         |             | /         |             | 0.022     |             |
| Tm      | 0.001     |             | /         |             | /         |             | /         |             | 0.005     |             |
| Yb      | /         |             | /         |             | 0.001     |             | 0.001     |             | 0.035     |             |
| Lu      | 0.002     |             | 0.001     |             | 0.001     |             | 0.001     |             | 0.014     |             |
| Pb      | /         |             | /         |             | /         |             | /         |             | 0.002     |             |
| Th      | 0.028     |             | 0.021     |             | 0.009     |             | 0.019     |             | 0.022     |             |
| U       | .698      |             | 0.001     |             | /         |             | /         |             | 0.008     |             |
|      | Ch8          | Ch9          | Ch10         | Ch11<sub>a</sub> | Ch11 | Ch11<sub>c</sub> |
|------|-------------|-------------|-------------|------------------|------|------------------|
| As<sub>2</sub>O<sub>5</sub> | 36.12 (34.22-37.14) | 36.26 (34.38-) | 36.11 (34.77-) | 21.53 (19.55-22.21) | 23.27 | 38.7 (36.5-41.6) |
| P<sub>2</sub>O<sub>5</sub> | 5.41 (4.63-7.14) | 5.64 (3.94-7.27) | 5.41 (3.93-6.86) | 18.73 (17.24-19.10) | 15.81 | 2.79 (1.17-4.45) |
| SiO<sub>2</sub> | 0.67 (0.43-0.76) | 0.62 (0.16-0.81) | 0.82 (0.45-1.59) | 0.11 (0.04-0.17) | 0.87 | (0.83-0.86) |
| V<sub>2</sub>O<sub>5</sub> | 0.01 (0-0.04) | 0.01 (0-0.03) | 0.01 (0-0.05) | 0.02 (0.00-0.04) | b.d.l. | b.d.l. |
| CaO | b.d.l. | 0.01 (0-0.05) | 0.01 (0-0.03) | 0.02 (0-0.04) | 0.01 (0.00-0.02) | 0.06 (0.02-0.12) |
| Y<sub>2</sub>O<sub>3</sub> | 34.30 (33.67-35.22) | 34.31 (33.70-) | 33.10 (29.91-) | 39.24 (38.03-38.10) | 36.94 | (35.59-36.07) |
| La<sub>2</sub>O<sub>3</sub> | 0.03 (0-0.10) | 0.06 (0-0.14) | 0.01 (0-0.05) | 0.01 (0-0.02) | b.d.l. | 0.12 (0.04-0.24) |
| Ce<sub>2</sub>O<sub>3</sub> | 0.09 (0-0.19) | 0.14 (0-0.28) | 0.13 (0.01-0.25) | 0.03 (0-0.07) | 0.10 | (0.10-0.10) |
| Pr<sub>2</sub>O<sub>3</sub> | 0.02 (0-0.12) | 0.05 (0-0.14) | 0.04 (0-0.09) | 0.03 (0-0.06) | 0.03 | (0-0.06) |
| Nd<sub>2</sub>O<sub>3</sub> | 0.37 (0.09-0.54) | 0.37 (0.19-0.53) | 0.37 (0.03-0.65) | 0.36 (0.30-0.39) | 0.40 | (0.35-0.42) |
| Sm<sub>2</sub>O<sub>3</sub> | 0.86 (0.65-0.97) | 0.72 (0.34-0.93) | 0.73 (0.55-1.06) | 0.74 (0.68-0.75) | 0.56 | (0.41-0.68) |
| Eu<sub>2</sub>O<sub>3</sub> | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. | b.d.l. |
| Gd<sub>2</sub>O<sub>3</sub> | 2.98 (2.64-3.35) | 2.92 (1.82-3.45) | 2.30 (1.73-3.07) | 2.11 (1.99-2.11) | 1.98 | (1.89-1.94) |
| Tb<sub>2</sub>O<sub>3</sub> | 0.58 (0.49-0.68) | 0.66 (0.52-0.85) | 0.55 (0.39-0.60) | 0.50 (0.35-0.62) | 0.47 | (0.38-0.52) |
| Dy<sub>2</sub>O<sub>3</sub> | 5.27 (4.79-5.59) | 4.96 (4.23-5.27) | 5.10 (4.39-5.58) | 5.18 (4.92-5.13) | 5.31 | (5.11-5.19) |
| Ho<sub>2</sub>O<sub>3</sub> | 2.68 (2.55-2.91) | 2.64 (2.24-2.77) | 2.39 (2.09-2.78) | 2.33 (2.09-2.43) | 2.31 | (2.19-2.29) |
| Er<sub>2</sub>O<sub>3</sub> | 3.04 (2.72-3.19) | 3.11 (2.89-3.42) | 3.51 (2.98-4.24) | 4.22 (4.01-4.18) | 3.83 | (3.69-3.75) |
| Tm<sub>2</sub>O<sub>3</sub> | 0.46 (0.24-0.72) | 0.44 (0.38-0.61) | 0.48 (0.27-0.83) | 0.67 (0.52-0.78) | 0.33 | (0.30-0.34) |
| Yb<sub>2</sub>O<sub>3</sub> | 2.37 (1.69-2.22) | 2.40 (1.76-3.31) | 3.38 (1.87-5.07) | 4.34 (4.16-4.26) | 3.79 | (3.48-3.87) |
| Lu<sub>2</sub>O<sub>3</sub> | 1.26 (1.05-1.50) | 1.14 (0.87-1.39) | 1.29 (1.01-1.73) | 1.42 (1.36-1.38) | 1.43 | (1.28-1.49) |
| PbO | 0.24 (0.18-0.31) | 0.22 (0.06-0.47) | 0.26 (0.19-0.31) | 0.27 (0.25-0.28) | 0.28 | (0.24-0.29) |
| ThO<sub>2</sub> | 3.12 (2.07-3.39) | 2.72 (0.88-4.23) | 2.40 (0.78-4.94) | 0.68 (0.53-0.79) | 2.80 | (2.58-2.85) |
| UO<sub>2</sub> | 0.37 (0.28-0.58) | 0.76 (0.11-3.79) | 1.90 (1.26-2.32) | 0.02 (0.00-0.04) | 1.24 | (0.95-1.45) |
| Tot. | 100.39 | 100.3 | 100.41 | 99.58 | 98.87 | 100.01 |

|      | Ch11<sub>b</sub> | Ch11<sub>c</sub> |
|------|------------------|------------------|
| As   | 0.764            | 0.764            |
| P    | 0.185            | 0.192            |
| Si   | 0.027            | 0.025            |
| V    | /                | /                |

|      | Ch11<sub>b</sub> | Ch11<sub>c</sub> |
|------|------------------|------------------|
| As   | 0.764            | 0.764            |
| P    | 0.185            | 0.192            |
| Si   | 0.027            | 0.025            |
| V    | /                | /                |

|      | Ch11<sub>b</sub> | Ch11<sub>c</sub> |
|------|------------------|------------------|
| As   | 0.764            | 0.764            |
| P    | 0.185            | 0.192            |
| Si   | 0.027            | 0.025            |
| V    | /                | /                |

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|         | Ch11<sub>d</sub> | Ch12  | Xen14  | Mon1     |
|---------|-----------------|-------|--------|----------|
| Ca      | /               | /     | /      | 0.003    |
| Y       | 0.739           | 0.736 | 0.714  | 0.757    | 0.735    | 0.638    |
| La      | /               | /     | /      | /        | 0.002    |
| Ce      | 0.001           | 0.002 | 0.001  | /        | 0.001    | 0.019    |
| Pr      | /               | /     | /      | /        | 0.004    |
| Nd      | 0.005           | 0.005 | 0.005  | 0.004    | 0.005    | 0.042    |
| Sm      | 0.012           | 0.010 | 0.010  | 0.009    | 0.007    | 0.026    |
| Eu      | /               | /     | /      | /        | 0.000    |
| Gd      | 0.038           | 0.039 | 0.044  | 0.025    | 0.024    | 0.045    |
| Tb      | 0.007           | 0.008 | 0.007  | 0.006    | 0.005    | 0.007    |
| Dy      | 0.068           | 0.064 | 0.066  | 0.060    | 0.064    | 0.060    |
| Ho      | 0.034           | 0.033 | 0.030  | 0.026    | 0.027    | 0.035    |
| Er      | 0.028           | 0.039 | 0.022  | 0.048    | 0.045    | 0.038    |
| Tm      | 0.005           | 0.005 | 0.006  | 0.007    | 0.003    | 0.007    |
| Yb      | 0.029           | 0.029 | 0.042  | 0.048    | 0.043    | 0.035    |
| Lu      | 0.015           | 0.013 | 0.015  | 0.015    | 0.016    | 0.012    |
| Pb      | 0.002           | 0.002 | 0.002  | 0.002    | 0.002    | 0.002    |
| Th      | 0.028           | 0.024 | 0.022  | 0.005    | 0.023    | 0.026    |
| U       | 0.003           | 0.006 | 0.017  | /        | 0.010    | 0.015    |

|         | Ch11<sub>d</sub> | Ch12  | Xen14  | Mon1     |
|---------|-----------------|-------|--------|----------|
| As<sub>2</sub>O<sub>5</sub> | 44.23           | (43.35-43.35) | 38.71 | (37.68-38.71) | 5.49 | (3.45-6.81) | 1.95 | (1.36-2.84) |
| P<sub>2</sub>O<sub>5</sub>  | 0.27            | (0.26-0.27) | 4.73  | (3.55-5.49) | 28.7 | (25.99-28.71) | 27.71 | (26.60-28.55) |
| SiO<sub>2</sub>   | 0.03            | (0.02-0.05) | 0.11  | (0.02-0.16) | 0.34 | (0-0.81)     | 0.24 | (0.02-0.69) |
| V<sub>2</sub>O<sub>5</sub> | b.d.l.          |       | b.d.l. | b.d.l.    |       |       |       |       |
| CaO      | 0.11            | (0.10-0.12) | 0.01  | (0-0.04)   | 0.01 | (0-0.06)    | 1.19 | (0.54-1.59) |
| Y<sub>2</sub>O<sub>3</sub> | 21.44           | (20.05-22.83) | 34.84 | (34.23-34.86) | 39.44 | (37.11-39.44) | 0.54 | (0.39-0.62) |
| La<sub>2</sub>O<sub>3</sub> | 0.62            | (0.52-0.73) | 0.05  | (0-0.13)   | 0.03 | (0-0.12)    | 14.18 | (12.31-15.82) |
| Ce<sub>2</sub>O<sub>3</sub> | 3.67            | (3.47-3.87) | 0.11  | (0.01-0.21) | 0.07 | (0-0.20)    | 30.84 | (28.41-32.95) |
| Pr<sub>2</sub>O<sub>3</sub> | 1.04            | (0.84-1.24) | 0.02  | (0-0.09)   | 0.03 | (0-0.18)    | 3.46 | (3.09-3.93) |

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| Compound | Value       | Lower Limit | Upper Limit | Lower Limit | Upper Limit |
|----------|-------------|-------------|-------------|-------------|-------------|
| Nd₂O₃    | 9.91        | (8.99-10.82)| 0.51        | (0.26-0.78)| 0.26        | (0.08-0.48)| 12.88      | (12.21-14.64) |
| Sm₂O    | 5.01        | (4.85-5.18)| 0.79        | (0.52-1.23)| 0.73        | (0.43-1.04)| 2.20       | (1.86-2.45)   |
| Eu₂O₃   | b.d.l.      | b.d.l.      | b.d.l.      | b.d.l.      |            |            |            |               |
| Gd₂O₃   | 5.36        | (5.09-5.64)| 2.92        | (2.52-3.31)| 3.84        | (2.95-5.03)| 1.41       | (1.04-2.06)   |
| Tb₂O₃   | 0.58        | (0.57-0.60)| 0.78        | (0.65-0.97)| 0.87        | (0.68-1.07)| b.d.l.     |               |
| Dy₂O₃   | 3.05        | (2.96-3.14)| 5.62        | (5.10-6.18)| 6.23        | (5.36-6.70)| 0.27       | (0.13-0.43)   |
| Ho₂O₃   | 2.75        | (2.70-2.81)| 2.70        | (2.25-2.95)| 3.27        | (2.65-4.14)| 0.25       | (0.10-0.44)   |
| Er₂O₃   | 0.97        | (0.82-1.12)| 2.97        | (2.58-3.38)| 3.55        | (3.13-4.13)| 0.03       | (0-0.22)      |
| Tm₂O₃   | 0.47        | (0.44-0.51)| 0.34        | (0.27-0.54)| 0.46        | (0-0.68)   | 0.07       | (0-0.21)      |
| Yb₂O₃   | 0.87        | (0.83-0.91)| 2.11        | (1.74-2.43)| 3.08        | (2.34-3.71)| 0.04       | (0-0.39)      |
| Lu₂O₃   | 0.51        | (0.49-0.53)| 1.23        | (0.99-1.54)| 1.56        | (1.07-1.95)| 0.07       | (0-0.24)      |
| PbO      | 0.00        | (0-0)       | 0.23        | (0.18-0.29)| 0.25        | (0.04-0.47)| 0.03       | (0-0.20)      |
| ThO₂     | 0.03        | (0-0.06)    | 0.38        | (0.21-0.66)| 1.89        | (0.31-3.87)| 2.55       | (0.57-5.70)   |
| UO₂     | 0.04        | (0-0.08)    | 0.78        | (0.60-0.99)| 0.40        | (0.01-0.74)| 0.05       | (0-0.17)      |
| Tot.     | 100.97      | 100.0       | 100.62      | 100.0       |            |            |            |               |

| Element | Value       | Lower Limit | Upper Limit | Lower Limit | Upper Limit |
|---------|-------------|-------------|-------------|-------------|-------------|
| As      | 0.988       | 0.817       | 1.02        | 0.040       |
| P       | 0.010       | 0.161       | 0.861       | 0.934       |
| Si      | 0.001       | 0.004       | 0.012       | 0.009       |
| V       | /           | /           | /           | /           |
| Ca      | 0.005       | /           | /           | 0.051       |
| Y       | 0.487       | 0.748       | 0.744       | 0.011       |
| La      | 0.010       | /           | /           | 0.208       |
| Ce      | 0.058       | 0.001       | /           | 0.449       |
| Pr      | 0.016       | /           | /           | 0.050       |
| Nd      | 0.151       | 0.007       | 0.003       | 0.183       |
| Sm      | 0.074       | 0.011       | 0.008       | 0.030       |
| Eu      | /           | /           | /           | /           |
| Gd      | 0.076       | 0.037       | 0.039       | 0.018       |
| Tb      | 0.008       | 0.01        | 0.010       | /           |
| Element | b.d.l. | 1 | 2 | 3 |
|---------|--------|---|---|---|
| Dy      | 0.042  | 0.073 | 0.071 | 0.003 |
| Ho      | 0.037  | 0.034 | 0.036 | 0.003 |
| Er      | 0.013  | 0.003 | 0.015 | /    |
| Tm      | 0.006  | 0.004 | 0.005 | /    |
| Yb      | 0.011  | 0.026 | 0.033 | /    |
| Lu      | 0.007  | 0.015 | 0.016 | /    |
| Pb      | /      | 0.002 | 0.002 | /    |
| Th      | /      | 0.003 | 0.015 | 0.023 |
| U       | /      | 0.007 | 0.003 | /    |

b.d.l.: below the detection limit
Table 3. Unit-cell parameters of all the samples under investigation.

| Sample | mineral             | a (Å)      | b (Å)      | c (Å)      | β (°)  | V (Å³)  |
|--------|---------------------|------------|------------|------------|-------|---------|
| Ch6    | chernovite-(Y)      | 7.0030(2)  | 7.0030(2)  | 6.2117(3)  |       | 304.63(2) |
| Ch7    | chernovite-(Y)      | 7.0056(3)  | 7.0056(3)  | 6.2307(6)  |       | 305.79(3) |
| Ch8    | chernovite-(Y)      | 7.0216(3)  | 7.0216(3)  | 6.2455(3)  |       | 307.92(3) |
| Ch9    | chernovite-(Y)      | 7.0176(3)  | 7.0176(3)  | 6.2343(4)  |       | 307.02(3) |
| Ch10   | chernovite-(Y)      | 7.0321(2)  | 7.0321(2)  | 6.2552(2)  |       | 309.32(2) |
| Ch11   | xenotime-(Y) s.s.   | 6.9591(4)  | 6.9591(4)  | 6.1386(7)  |       | 297.29(4) |
| Ch12   | chernovite-(Y)      | 7.0351(2)  | 7.0351(2)  | 6.2630(3)  |       | 309.97(2) |
| Ch13   | chernovite-(Y)      | 7.0540(3)  | 7.0540(3)  | 6.2882(4)  |       | 312.89(3) |
| Ch16   | chernovite-(Y)      | 7.0648(10) | 7.0648(10) | 6.2860(12) |       | 313.75(9) |
| Xen14  | xenotime-(Y)        | 6.9008(3)  | 6.9008(3)  | 6.0447(4)  |       | 287.86(3) |
| Gasp4  | gasparite-(Ce)      | 6.9259(3)  | 7.1201(3)  | 6.7137(3)  | 104.752(5) | 320.16(2) |
|        | Mineral       | Stock Concentration 1 | Stock Concentration 2 | Stock Concentration 3 | Stock Concentration 4 |
|--------|---------------|-----------------------|-----------------------|-----------------------|-----------------------|
| Gasp3  | gasparite-(Ce)| 6.9274(3)             | 7.1273(3)             | 6.7118(3)             | 104.668(3)            |
| Mon1   | monazite-(Ce) | 6.77986(11)           | 7.00460(12)           | 6.4587(1)             | 103.526(2)            |
| Mon2   | monazite-(Ce) | 6.7924(2)             | 7.0173(2)             | 6.4735(2)             | 103.519(3)            |
| Mon14  | monazite-(Ce) | 6.78910(14)           | 7.01221(12)           | 6.47346(13)           | 103.595(2)            |
**Table 4.** A-O and T-O bond distances (in Å), volumes of A- and T-coordination polyhedra (in Å³) and distortion index (calculated using the routine implemented in the software Vesta 3, Momma and Izumi, 2011), based on the structure refinements conducted on all the samples.

| Sample | A-O1 | A-O1' | A-O2 | A-O2' | A-O2* | A-O3 | A-O3' | A-O4 | A-O4' | T-O1 | T-O2 | T-O3 | T-O4 | V(AO₈,₉) | V(TO₄) | DI(A) | DI(T) |
|--------|------|-------|------|-------|-------|------|-------|------|-------|------|------|------|------|-----------|---------|-------|-------|
| Mon1   | 2.525(4) | 2.452(4) | 2.783(4) | 2.557(3) | 2.642(4) | 2.577(3) | 2.464(3) | 2.519(3) | 2.441(3) | 1.525(3) | 1.546(4) | 1.534(3) | 1.536(4) | 32.29(3) | 1.844(10) | 0.031 | 0.004 |
| Mon2   | 2.510(3) | 2.465(3) | 2.789(3) | 2.559(3) | 2.643(2) | 2.583(2) | 2.469(3) | 2.521(2) | 2.460(2) | 1.536(3) | 1.556(3) | 1.546(2) | 1.523(3) | 32.44(2) | 1.859(5)  | 0.031 | 0.007 |
| Mon14  | 2.519(3) | 2.456(3) | 2.791(3) | 2.556(3) | 2.639(3) | 2.581(3) | 2.461(3) | 2.516(3) | 2.449(3) | 1.535(2) | 1.557(3) | 1.549(3) | 1.536(4) | 32.31(2) | 1.875(7)  | 0.031 | 0.005 |
| Gasp3  | 2.550(5) | 2.463(5) | 2.931(5) | 2.532(5) | 2.603(5) | 2.605(6) | 2.435(5) | 2.550(5) | 2.463(5) | 1.668(5) | 1.676(5) | 1.675(5) | 1.660(6) | 32.75(6) | 2.350(14) | 0.037 | 0.003 |
| Gasp4  | 2.553(8) | 2.449(8) | 2.924(7) | 2.527(7) | 2.618(9) | 2.618(9) | 2.440(8) | 2.460(7) | 1.678(7) | 1.660(7) | 1.674(7) | 1.668(8) | 32.80(9) | 2.351(5)  | 0.038 | 0.004 |
| Ch6    | 2.4089(13) | 2.3019(12) | 1.6363(13) | | | | | | | | | | | | | |
| Ch7    | 2.414(3) | 2.298(3) | 1.644(3) | | | | | | | | | | | | | |
| Ch8    | 2.419(4) | 2.297(4) | 1.655(4) | | | | | | | | | | | | | |
| Ch9    | 2.410(4) | 2.302(3) | 1.650(3) | | | | | | | | | | | | | |
| Ch10   | 2.419(4) | 2.306(3) | 1.653(3) | | | | | | | | | | | | | |
| Ch11   | 2.401(5) | 2.298(5) | 1.603(5) | | | | | | | | | | | | | |
| Ch12   | 2.416(2) | 2.301(3) | 1.663(3) | | | | | | | | | | | | | |
| Ch13   | 2.424(4) | 2.305(5) | 1.673(2) | | | | | | | | | | | | | |
| Ch16   | 2.422(8) | 2.308(9) | 1.675(9) | | | | | | | | | | | | | |
| Xen14  | 2.389(3) | 2.308(3) | 1.545(3) | | | | | | | | | | | | | |