Abstract

Australasian Muong Nong-type tektites from the locality centered at 16.46150° N, 106.48917° E in Laos contain sporadic spherical heterogeneous sulfide inclusions less than 10 µm in diameter, which have been identified by electron probe microanalyzer and electron back scatter diffraction to represent a mixture of rare mineral shenzhuangite with a pyrrhotite polytype (possibly troilite). Contrary to type shenzhuangite found in the shocked L6 chondrite Suizhou the mineral embedded in the tektite glass is nearly free of copper providing the composition close to its expected end-member not yet found in the nature; the empirical formula closest to ideal end-member composition based on 4 atoms per formula unit is Ni_{1.007}Fe_{0.998}Cu_{0.016}Co_{0.058}S_{1.922}. The described occurrence also represents the first find of shenzhuangite in terrestrial material.
Presented is the Raman spectrum for shenzhuangite with tentative assignment of spectral bands based on the analogy with synthetic chalcopyrite-structured phases. The chemical composition of shenzhuangite close to NiFeS$_2$ is not consistent with any stable phase in the Fe–Ni–S system up to melting temperature. Available data so far on phase relations in this system do not allow unambiguous interpretation of conditions under which sulfide association within inclusions had formed.

**Keywords**: shenzhuangite; tektites, Australasian strewn field; electron back scatter diffraction; electron probe microanalysis; Raman spectroscopy; meteoritic component

**INTRODUCTION**

Tektites are generally claimed to represent highly siliceous glassy products of hypervelocity impacts of extraterrestrial bodies on the Earth derived from the uppermost crustal unconsolidated rocks. They are commonly considered as distal ejecta of these high-energy events and occur in geographically well-defined areas called strewn fields (Koeberl 2014). The youngest and largest of these strewn fields is the Australasian field covering about 15% of the earth surface (Goderis et al. 2017; Folco et al. 2018). Among tektites, three major morphological types are recognized – splash-forms and Muong Nong-type tektites, and ablated forms. Small splash-forms sized below 1 mm are called microtektites.

The Muong Nong-type tektites are commonly blocky, layered, and chemically more variable than splash-forms and enriched in volatile species (e.g., H$_2$O, F, Cl, Bi, Sb; Koeberl 1992, 2014). They are also known to contain mineral inclusions, which may be relict phases that did not transform during the impact, or they can represent decomposition products or even newly formed...
phases. Vast majority of these minerals, present as inclusions in tektite glass, are oxygen-bearing compounds (oxides, phosphates, silicates) and comprehensive data on them may be found in e.g., Glass and Barlow (1979) and Cavosie et al. (2018). In addition to these inclusions, the so-called “metallic spherules” were reported from several Australasian tektites. The first note on metallic spherules comes from Chao et al. (1962). They found spherules consisting of dominant kamacite and minor troilite and phosphide in tektites from Isabela on Luzon, Philippine Islands. In the further paper, Chao et al. (1964) report on finds of metallic inclusions in Australasian tektites from Ortigas site on Luzon (The Philippines) and Dalat in Vietnam. Beside kamacite and troilite (up to 5 vol%), they unambiguously identified schreibersite ((Fe,Ni)₃P attaining the content of up to 35 vol%). The inclusions were either spherical or elliptical and range from a few micrometers to 800 µm across, with most of them being sized > 100 µm. Similar, yet smaller inclusions have been reported from impact glasses of several impact craters worldwide (e.g., Aouelloul, Barringer, Bosumtwi, Wabar; see Chao et al., 1966; El Goresy, 1966; Brett, 1967 and references therein). Mineral composition of the inclusions consisting of kamacite ± troilite ± schreibersite was by most considered to be a proof of their meteoritic origin. However, Ganapathy and Larimer (1983) and O’Keefe (1984) claimed that the meteoritic origin of inclusions is not supported by the results of chemical analyses. In the course of study of Muong Nong-type Australasian tektites from Laos, we found small (less than 10 µm in diameter) purely sulfide spherules, which display chemical composition close to NiFeS₂. Such composition resembles that of the end-member of the recently described chalcopyrite-structured mineral shenzhuangite (empirical formula [⁴Ni²⁺₀.₆₉Cu⁺₀.₃₁][⁴Fe²⁺₀.₆₉Fe³⁺₀.₃₁]S₂₀₀) found in the shocked L6 chondrite Suizhou (Bindi and Xie 2018).
The purpose of this paper is to characterize the NiFeS$_2$ phase assemblage found in Laotian tektites to test its identity with previously described mineral shenzhuangite and discuss the origin of the Fe–Ni sulfide spherules in tektite glass.

SAMPLES AND EXPERIMENTAL TECHNIQUES

Forty-seven polished thin sections were prepared from 31 samples of Muong Nong-type tektites collected during our fieldwork at different locations in Laos. One to three polished thin sections (~400 µm thick) were prepared from each specimen. Rare sulfide inclusions containing NiFeS$_2$ phase were identified only in samples found at the single locality east of a local main road about 10 km north of the village Muong Nong (GPS coordinates 16.46150° N, 106.48917° E; see Žák et al. 2019). Sixteen thin sections were prepared from 12 samples of Muong Nong-type tektites from this locality and studied in detail. The inclusions of shenzhuangite were found only in four samples (MN 7, MN 12, MN 13 and MN 16). The macroscopic appearance and the photographs of the thin section of the samples MN 12, MN 13, and MN 16 are shown in Fig 1. The sample MN 7 is imaged in Žák et al. (2019). Overall, only 6 inclusions exceeding the diameter of ~5 µm allowing their unambiguous identification as shenzhuangite were observed in five thin section.

Optical polarization microscope Olympus BX 51 was used for preliminary characterization of the spherules and their mutual relationships with hosting glass. Scanning electron microscope Tescan VEGA3XMU (Department of Analytical Methods, Institute of Geology of the Czech Academy of Sciences, Prague) was used to screen tektites with back-scattered electron imaging as well as to obtain semiquantitative analyses with an energy-dispersive spectrometer Bruker X’Flash 5010.
Electron microprobe analyses of sulfide inclusions were carried out using a CAMECA SX-100 electron microprobe equipped with four wavelength-dispersive X-ray spectrometers (WDS) at the Institute of Geology of the Czech Academy of Sciences in Prague. The operating conditions to analyze sulfide inclusions were 15 kV accelerating voltage, 10 nA beam current, focused electron beam and counting times 20 s for peak and 10 s for background. The following elements were analyzed using their Kα spectrum lines (standard, spectrometer crystal, and detection limit, respectively, are given in parentheses): Fe (hematite, LLIF, 1400 ppm), Mn (rhodonite, LLIF, 1700 ppm), Co (cobalt, LLIF, 1700 ppm), Ni (nickel, LLIF, 1400 ppm), Cr (chromium, LLIF, 1000 ppm), Cu (copper, LLIF, 2000 ppm). The X-phi (Merlet, 1992) correction procedure was used to process the measured data. The accuracy of analyses is 5 rel% or better for each element.

Major element compositions of tektite glass surrounding the inclusions were also obtained by electron microprobe (EPMA) CAMECA SX-100. A loss of volatile elements has been prevented by using defocused electron beam (diameter 2 µm) and a sample current of 4 nA the accelerating voltage was 15 kV. Analyses followed the protocol given in Jonášová et al. (2016) and Skála et al. (2016).

Identification of the crystal structure type for individual inclusions and/or their parts was performed through electron backscatter diffraction (EBSD). Before the EBSD examination, surfaces of the thin section were polished using a colloidal silica suspension (OP-U, Struers). The electron backscatter patterns (EBSP) were obtained using a Tescan MIRA 3GMU scanning electron microscope equipped with NordlysNano (Oxford Instruments) detector housed at the Czech Geological Survey, Prague. For EBSP collection, the FEG-SEM was operated at an accelerating voltage of 20 kV, with the thin section tilted at an angle of 70° to the beam, and at a working distance of 20 mm. The obtained EBSPs were processed and indexed using AZtec.
acquisition software. For the phase identification, the collected EBSPs were matched with simulated diffraction patterns determined from candidate phases based on crystal structure data for shenzhuangite (Bindi and Xie 2018), troilite (Keller-Besrest and Collin 1990), pyrrhotite 1C (ICSD code 29301; Bergerhoff and Brown 1987), cubanite (ICSD code 53263; Bergerhoff and Brown 1987) and pentlandite (Rajamani and Prewitt 1975).

To supplement structural information on Fe-Ni sulfide spherules, a Raman microspectrometer S&I MonoVista CRS+ was used (Institute of Geology of the Czech Academy of Sciences in Prague). The system is based on Princeton Instruments SP2750i spectrometer with a focal length of 750 mm and a CCD detector Andor iDus 416. Laser beam was focused on a sample with a 100× magnifying objective (providing ~1 µm lateral resolution) attached to an Olympus BX 51WI microscope. The spectra were obtained in back-scattered geometry. The accuracy of the wavenumber axis was calibrated with an Intellical Hg-Ne/Ar lamp (Princeton Instruments). The system was calibrated with a silicon standard. Raman spectra were excited with a laser of nominal 532 nm wavelength and power at the sample surface was about 2.5 mW to prevent sample deterioration that is known to occur in Raman experiments involving natural sulfides, see discussion by Weber et al. (2017). Spectra were acquired with a grating of 1200 gr/mm density. Band positions and other profile parameters have been fitted with Fityk software (Wojdyr 2010).

RESULTS

Two-phase sulfide inclusions of spherical shape less than 10 µm in diameter occur in the Muong Nong-type tektites recovered from a large tektite body close to Muong Nong village. They were found in portions of tektite glass, which is substantially vesiculated. The bubbles are usually spherically shaped and their diameter varies in broad range from less than 10 µm to as much as 400 µm. The glass is finely layered in the transmitted light in optical microscope. The lighter
Schlieren and patches are of yellowish color whereas darker ones are brownish-colored.

Lechatelierite (pure silica glass) filaments have also been noticed in the glass (Fig. 2). In BSE images, the glass highlighting its finely layered structure immediately surrounding the spherules is light gray usually irregularly crosscut by vermiform darker features of thickness less than 5 µm and tens to hundreds of µm in length. Chemical composition of tektite glass of five thin sections hosting the inclusions immediately in the inclusion surroundings is relatively uniform varying between following limits (in wt%): SiO$_2$ 73.0–75.5, TiO$_2$ 0.70–0.76, Al$_2$O$_3$ 11.9–12.7, FeO 4.14–4.66, MgO 1.71–2.07, CaO 1.31–2.33, Na$_2$O 1.54–1.84, and K$_2$O 2.41–2.58.

All the inclusions display sharp contacts with the host tektite glass. In some cases, a few fine protrusions radiate to a surrounding glass from the surface of inclusions; the length of protrusions is well below 10 rel% of inclusion diameter, however, in most cases this proportion is less than 5 rel% (Fig. 3). All discovered Fe–Ni–S inclusions are chemically heterogeneous consisting essentially of two well spatially separated phases, which differ in Ni content. Mutual proportions of Fe–Ni–S and Ni-bearing Fe–S phases are variable from one inclusion to the other. The distribution of the phases within spherules has either patchy or segmented appearance. The former type of inclusion is illustrated in the BSE image in Fig. 3b while the latter is shown in Fig. 3c.

Crystal structure type of both minerals forming the inclusions has been identified from 8 Kikuchi bands in EBSP taken from parts seemingly homogeneous in BSE. The lowest values of the mean angular deviation (MAD) representing the misfit value of the indexing of a measured EBSP from the pattern calculated for given match unit were 0.42° for Ni-richer phase and 0.46° for Ni-poorer phase, respectively. Since the values MAD <1° are considered as indicators of good fit, the Ni-richer phase may be unambiguously identified as shenzhuangite (Fig. 4) while the Ni-
poorer phase correspond to troilite. It should be noted, however, that other ordered pyrrhotite polytypes with low number of stacking layers (e.g. 1C) used as match units provided similar MAD values making the identification of the Ni-poorer phase less reliable.

The chemical composition of Fe–Ni–S inclusions vary considerably, nevertheless, two mineral phases are clearly defined. Mineral structurally corresponding to shenzhuangite contains typically more than 23 at% Ni. Nickel contents in troilite/pyrrhotite phase vary in the range from 0.2 to 8.9 at% possibly representing an analytical artefact due to intimate intergrowths of Ni-free troilite/pyrrhotite with shenzhuangite. Shenzhuangite contains also up to 1.5 at% Co. All shenzhuangite analyses are slightly sulfur-deficient, the mineral contains between 46.8 to 49.7 at% S. Complete results of EPMA analyses of shenzhuangite are summarized in Table 1 and shown in Fe–Ni–S plot (Fig. 5). Totals of almost all analyses are below 98 wt% due to small size of the spherules, which also means that their thickness is low so the electron beam penetrates the complete volume of the inclusion and hits the glass below; this feature was explained for complex metallic-sulfide spherule inclusions described from the glass of the Bosumtwi crater by El Goresy (1966). Consequently, we decided to neglect other elements otherwise present solely in glass, which were observed only at very low contents, and to normalize the analytical data in Table 1 to 100 wt%.

The Raman spectrum of shenzhuangite (Fig. 6) displays the prominent bands at 288, 370, and 390 cm$^{-1}$. In addition to them, there are several weaker further unresolved bands and shoulders to the main bands. Results of the fitting of the Raman spectrum are summarized in Table 2. It should be also noted that despite the relatively long overall counting time the signal-to-noise ratio for shenzhuangite Raman spectrum is worse than that for the isostructural chalcopyrite
taken under the same spectrum acquisition conditions. The Raman spectra of chalcopyrite and pentlandite are shown in Fig. 6 for comparison with spectrum of shenzhuangite.

**DISCUSSION**

The inclusions found in vesiculated glass of tektite samples found close to Muong Nong village in Laos are, contrary to so far known spherules from Australasian tektites, completely devoid of pure metal, which was a substantial portion of the so-called “metallic spherules” described by Chao et al. (1962, 1964) from philippinites and indochinites. The inclusions described by Chao et al. (1962, 1964) contain next to kamacite also troilite and/or schreibersite; the latter mineral was not found in the studied inclusions in Laotian Muong Nong-type tektites. Clearly, the inclusions in studied Muong Nong-type Australasian tektites represent a new chemical type of inclusions in the tektite glass consisting solely of sulfides. In addition, they are much smaller (less than 10 µm across) than the metallic spherules from splash-form tektites that typically exceed 100 µm in diameter. Obviously, both types of inclusions formed under different conditions and reflect different character of both tektite types.

Refinement of the crystal structure of shenzhuangite carried out by Bindi and Xie (2018) showed that chalcopyrite and shenzhuangite are isostructural. Chalcopyrite-structured phases crystallize in the space group $I42d$. In the end-member chalcopyrite, $\text{Cu}^+$ is located in the tetrahedrally coordinated site $4a$ while $\text{Fe}^{3+}$ is in tetrahedrally coordinated $4b$ site and $\text{S}^{2-}$ in the $8d$ site (Hall and Stewart 1973). Distribution of valences for Cu and Fe in chalcopyrite was confirmed by several experimental and theoretical studies (e.g., Boekema et al., 2004; Goh et al., 2006; Klekovkina et al., 2014). Taking into account the chemical composition of shenzhuangite from the Suizhou chondrite, Bindi and Xie (2018) suggested a mixed ($\text{Cu}^+\text{+Ni}^{2+}$) occupancy in site $4a$. 
To keep the mineral electroneutral, introduction of ferrous iron to structure is required, hence the site 4b shows a mixed occupancy of (Fe$^{2+}$+Fe$^{3+}$) type. They, however, admitted also the possibility of atom partitioning over the structure sites following the formula

$$(\text{Ni}^{2+}_{0.69}\text{Fe}^{2+}_{0.31})(\text{Fe}^{2+}_{0.38}\text{Fe}^{3+}_{0.31}\text{Cu}^{+}_{0.31})\text{S}_2,$$

which would better fit the trend in the distribution of cations over the two structure sites based on their ionic radii. Since chalcopyrite structure may be derived from the sphalerite-based archetype structure, we applied the Vegard rule otherwise most appropriated for cubic lattices to estimate the crystal structure of the end-member shenzhuangite found in our Muong Nong-type Australasian tektites. The model with Ni occupying 4a site and Fe completely located in 4b site was adopted. An extrapolation of the data for end-member chalcopyrite (Hall and Stewart, 1973) and published shenzhuangite structure (Bindi and Xie 2018) provides following unit-cell dimensions $a = 5.3225$ Å, $c = 10.502$ Å, $V = 297.48$ Å$^3$ and distances Ni-S of 2.260 Å and Fe-S of 2.328 Å, respectively. Then, the distances has been used to estimate the fractional coordinate of sulfur atom in 8d site using the quantity of tetragonal distortion defined in, e.g., Camassel et al. (1990) or Mintairov et al. (1999), as $x_S = 0.2390$.

To provide an independent insight to the crystal structure of shenzhuangite, we applied the Raman microspectroscopy. Since chalcopyrite-structured phases of $\text{A}^{VI}_{1}\text{B}^{III}_{1}\text{C}^{V}_{1}$ and $\text{A}^{IV}_{1}\text{B}^{IV}_{1}\text{C}^{V}_{1}$ types often display semiconducting properties and/or they are used as photovoltaic or nonlinear-optical materials (Mintairov et al. 1999), there is a wealth of dedicated Raman and lattice dynamics studies of these phases (e.g., van der Ziel et al. 1974; Artus et al. 1990; Camassel et al. 1990; Ohrendorf and Haeuseler 1999a, 1999b and references therein). Unfortunately, only few studies have been focused at least in part on the chalcopyrite sensu stricto (e.g., Koschel et al. 1975; Ohrendorf and Haeuseler 1999a; Łażewski et al. 2004). That makes the interpretation of the spectra of shenzhuangite rather ambiguous. In addition, as far as we know there are no
Raman data available for chalcopyrite-structured phase of general formula $A^{II}B^{II}C^{VI}_2$ which further markedly complicates the assignment of the Raman bands.

In general, the total number of Raman-active optic modes that can be observed in the Raman spectra of chalcopyrite-structured phases is seventeen: $1A_1(\Gamma_1)+3B_1(\Gamma_3)+2B_2(\Gamma_4)(TO)+2B_2(\Gamma_4)(LO)+2E(\Gamma_5)(LO)+4E(\Gamma_5)(LO+TO)$, where $(LO+TO)$ indicates an unsplit polar mode; atop of the optic modes there are 2 acoustic modes ($1B_2+2E$) (Kaminow et al. 1970; Mintairov et al. 1999; Huang et al. 2016). To test the possibility to assign Raman bands in the spectrum of shenzhuangite, we compared it to the Raman spectrum of natural chalcopyrite taken from the RRUFF database (R050222; Lafuente et al., 2015) that we processed in the same way as we did for shenzuangite. The most prominent band in the Raman spectrum of chalcopyrite is an asymmetric feature consisting of two overlapping peaks centered at 286 and 291 cm$^{-1}$ with half-widths of 10 and 5 cm$^{-1}$, respectively (Fig. 6). The position of higher and narrower peak at 286 cm$^{-1}$ is consistent with $A_1$ mode (e.g., Łażewski et al., 2004), which is the most intensive band in many chalcopyrite-structured synthetic materials. In shenzhuangite Raman spectrum, however, the most intensive band occurs at 370 cm$^{-1}$ which value coincides with the peak corresponding to $E(LO)$ and $B_2(LO)$ modes of chalcopyrite spectrum with only ca 6 % relative intensity. Pentlandite spectrum (RRUFF database entry R060144) is incompatible with both shenzhuangite and chalcopyrite spectra precluding its presence in the inclusions.

Since studies of synthetic chalcopyrite-structured phases showed sphalerite structure as useful archetype to interpret Raman spectra of the former materials, we inspected published data investigating the role of impurities on sphalerite Raman spectra. Influence of transitional metals, in most cases iron, contents in sphalerite on the position of Raman bands and their intensities has
been assessed by Zigone et al. (1981), Jiménez-Sandoval et al. (2003), Kharbish (2007), Osadchii and Gorbaty (2010) and Buzatu et al. (2013). They observed shift of Raman band positions, emergence of new peaks as well as changes in mutual intensity ratios between individual peaks. Zigone et al. (1981) noticed systematic shift of $A_1$ mode from 303 to 293 cm$^{-1}$ for $\sim$1 % admixture of transient metals from Ni to Cr; obviously, an introduction of lighter element to sphalerite structure results to shift of the Raman band to lower wavenumbers. Generalizing these observations to chalcopyrite-type structures allowed consideration of the role of the change of atomic masses, force constants and structural distortions on the Raman band positions, intensities and percentages of atomic contribution to individual Raman-active modes (Artus et al. 1990; Pascual et al. 1991). Developed concept of alternating anion-cation bond strength (Pascual et al. 1991) allows explanation of the differences between chalcopyrite and shenzhuangite in terms of $\sim$8 rel. % change in atomic mass at the structure site 4$a$, lengthening cation-anion distance within the tetrahedron occupied by Fe while the distances involving Ni and S shorten in comparison with those for equivalent structure sites in chalcopyrite. In addition, local force variation may be also expected due to change in 3$d$-electron configuration (Ni$^{2+}$ $3d^8$ and Fe$^{2+}$ $3d^6$ in shenzhuangite vs. Cu$^+$ $3d^{10}$ and Fe$^{3+}$ $3d^5$ in chalcopyrite). As a consequence, modes involving Ni–S vibrations will harden and shifts up while those reflecting Fe–S displacements will soften and shifts down. The tentative assignment of the Raman band mode symmetries based on crude estimate of analogies with natural chalcopyrite and synthetic chalcopyrite-structured phases of similar atomic mass ratios is provided in Table 2. The mode $A_1$ reflects solely vibrations of anionic part of the structure while other modes are due combined displacements of cations and anions, which mutually influence each other making

Worse quality in terms of signal-to-noise ratio of the shenzhuangite Raman spectrum than that of isostructural chalcopyrite is most probably due to defects of the crystal structure. Possible reasons why these defects were introduced to the structure may involve undercooling resulting in slight positional disorder or lattice strain developed along interfaces with pyrrhotite/troilite domains.

Bindi and Xie (2018) described shenzhuangite from Suizhou L6 meteorite. It occurs in immediate association with taenite. In the Fe–Ni–Cu–S system under terrestrial conditions, no stable phase of the composition they measured for shenzhuangite is known. Consequently, they hypothesized that the mineral formed as a product of sulfurization of taenite under specific $pS_2/pO_2$ ratio. Since no sulfur has been reported in any study of chemical composition of Australasian tektites (see Glass and Barlow 1979; Koeberl 1992, 2014 and references therein), the process of sulfurization as suggested by Bindi and Xie (2018) cannot be adopted to explain the origin of shenzhuangite in Muong Nong-type Australasian tektites.

Chemical composition of shenzhuangite found in inclusions in a tektite glass plot in the Fe–Ni–S system (Fig. 5) near a region of monosulfide solid solution + liquid, monosulfide solid solution + high-form pentlandite + liquid or monosulfide solid solution + high-form pentlandite fields in isothermal sections at 875, 850, and 800 °C, respectively (Kitakaze and Sugaki 2004; Kitakaze et al. 2011, 2016). Previous study on phase relations in a system Fe–Ni–Co–S by Kitakaze and Sugaki (2004) quotes the melting temperature for Fe$_{4.5}$Ni$_{4.5}$S$_8$ as 982 °C. Although the bulk chemical composition of the spherules is hard to ascertain due to variable proportions of shenzhuangite and troilite/pyrrhotite, that temperature still provides a reasonable constraint on
the potential cooling history of the inclusions. Obviously, they have to be quenched in a narrow
range between ca 1000 °C and 900 °C. Origin and time of crystallization of pyrrhotite/troilite
phase is questionable, it can crystallize simultaneously with shenzhuangite directly from an
initial sulfide melt, which was enriched in Fe compared to the composition of shenzhuangite, or
it may exsolve later in subsolidus. Tektite glass immediately surrounding the shenzhuangite-
troilite inclusions lacks radial fractures and the spherules occasionally display the cusp
protrusions intruding to the glass. This feature seems to be compatible with concomitant
solidification of tektite glass and crystallization of sulfide inclusions. The diameters of observed
inclusions do not exceed 10 µm and this size is small enough to keep them spherical since the
surface tension predominates over body forces under such conditions (Barnes et al. 2017).

The origin of sulfur and nickel to form described sulfide inclusions is uncertain, yet principally
only two sources represent a viable explanation. Either the parentage is purely terrestrial and
sulfides with unstable chemical composition formed due to thermodynamically unequilibrated
conditions at high temperatures and pressures associated with highly reducing conditions ruling
during the impact of the extraterrestrial body or the inclusions may represent an extraterrestrial
matter derived from a projectile that were in some way incorporated to the tektite glass. In both
cases, the inclusions likely formed from impact melt of original troilite-pentlandite-like phases.
Nevertheless, further studies will be required to provide unambiguous explanation of the origin
of these enigmatic inclusions.

**IMPLICATIONS**

Recent finds of Fe–Ni sulfide inclusions embedded in Muong Nong-type tektites from the
locality close to the Muong Nong village in Laos represent an important observation constraining
not only the origin of Australasian tektites but also a general behavior of Fe–Ni–S system under
extreme conditions. In addition, applied methodologies showed their importance and limitations in identifying such small objects like these inclusions.

- This is the first reported occurrence of this mineral close to ideal end-member composition and the first ever occurrence in terrestrial materials.
- Electron back scatter diffraction proved its indispensability in identification of small volumes of material; the structural identity of the Fe–Ni sulfide occurring as segments or patches within the spherical inclusions has been confirmed by unambiguous matching of the EBSP to the structure of shenzhuangite determined by Bindi and Xie (2018). Nevertheless, the structures displaying subtle variance among their crystal structures may pose significant limitation on the use of the technique. In particular, EBSD study could not unambiguously resolve whether iron monosulfide associated with shenzhuangite is a higher-order polytype of pyrrhotite or troilite (2H polytype).

- Raman spectrum of shenzhuangite display considerable differences in relative intensities in comparison to isostructural natural chalcopyrite as well synthetic chalcopyrite-based phases. Next to variance in intensities, also some shifts of the band positions were observed. Particularly, intensity of the band, which is tentatively ascribed to the Raman modes of $B_2$ and $E$ symmetries and involves Ni displacements, increases substantially. On the other hand, the intensity of band expected to represent the $A_1$ Raman mode decreases markedly. These features are obviously related to the coupled substitution of monovalent copper by divalent nickel and ferric by ferrous iron and expectable changes in electronic configurations around the individual ions. Thus, the Raman spectroscopy provides a useful tool to uncover such effects though they cannot be quantitatively constrained solely from the Raman data.
• Pyrrhotite nickel enrichment observed in the analyses reaches up to ~10 at% and is not corroborated by the results of published experimental phase relations studies within the Fe–Ni–S system. Consequently, the elevated nickel content represent an analytical artefact and must be attributed to either contamination from coexisting shenzhuangite or extremely fine inclusions of not yet identified Ni-rich phase intergrown with Ni-free pyrrhotite/troilite.

• Of general importance is the chemical composition of the phase in inclusions, which is close to ideal NiFeS$_2$ stoichiometry. Such a composition is not consistent with any stable phase in the Fe–Ni–S system up to melting temperature. Consequently, this indicates specific conditions under which this mineral formed. Available data, however, do not provide unambiguous clue to determine whether the phase association consisting of shenzhuangite and pyrrhotite/troilite formed from sort of a superheated melt generated during and shortly after an impact from tektite parent sediments or if it may be considered an indicator of meteoritic component trapped in tektite glass. Further study aiming to find and characterize additional inclusions is required to shed light on this issue.

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**Figure captions**

**Figure 1.** Macroscopic appearance of the Australasian tektites hosting the inclusions of shenzhuangite (a,c,e) and images illustrating textures of individual samples as seen in transmitted light in thick (~400 µm) polished sections (b,d,f). Note prominent layering and vesiculation in the samples MN 12 and MN 16.

**Figure 2.** Optical micrographs of Muong Nong-type tektite hosting sulfide inclusions illustrating bubbles, and lechatelierite filaments emphasizing fluidal structure on micrometer scale (a) and marked macroscopic layering (b). Plane polarized transmitted light.
Figure 3. Back-scattered electron images of the shenzhuangite-bearing inclusions in the Muong
Nong-type tektite from Laos. Next to shenzhuangite (sh), inclusions contain also troilite (tr). The
inclusions show sharp border towards hosting tektite glass yet in some cases fine protrusions
(prts) radiate to a surrounding glass. Distribution of low-Ni phase within shenzhuangite is
either of patchy (b) or segmented (c) appearance.

Figure 4. Electron back-scatter diffraction patterns of shenzhuangite (a,c) and corresponding
indexing of Kikuchi bands (b,d).

Figure 5. The triangular diagram (a) shows the extent of the plot (b) in the Fe-Ni-S system. The
plot (b) illustrates the chemical composition (in at%) of shenzhuangite in spherules enclosed in
Muong Nong-type tektites from Laos (triangles) and the extent of monosulfide solid solution
(mss; gray field); at 1000 °C after Vaughan and Craig (1997). Note that most analyses of
shenzhuangite overlap; the only outlier corresponds to the analysis MN 16 i4b.

Figure 6. Comparison of Raman spectra of shenzhuangite from the inclusion MN 7 i7,
chalcopyrite and pentlandite. Mutual differences in band intensities between shenzhuangite and
chalcopyrite are due to different occupation of structure sites in them. Pentlandite spectrum is
incompatible with both shenzhuangite and chalcopyrite spectra. The spectrum of shenzhuangite
is shown in pale blue. Below it, individual deconvoluted bands are displayed. Overlaid over the
shenzhuangite measured spectrum is the model summed from individual deconvoluted bands
(dark blue line). Below the spectrum, shown in gold, is the difference curve illustrating the match
between modelled and measured data. Spectra of chalcopyrite and pentlandite were taken from
the RRUFF database. Raman scattering intensity is given in arbitrary units (a.u.).
Table 1 Chemical composition (in at%, normalized wt% and apfu) of shenzhuangite domains found in inclusions embedded in Laotian Muong Nong-type tektites determined by EPMA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Inclusion</th>
<th>Ni at%</th>
<th>Fe at%</th>
<th>Cu at%</th>
<th>Co at%</th>
<th>S at%</th>
<th>Ni wt%</th>
<th>Fe wt%</th>
<th>Cu wt%</th>
<th>Co wt%</th>
<th>S wt%</th>
<th>Total wt%</th>
<th>Ni apfu</th>
<th>Fe apfu</th>
<th>Cu apfu</th>
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* a-c single point analyses in particular inclusion
* b.d.l. below detection limit
* low total is due to uneven surface of the inclusion
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<th>ω, cm⁻¹</th>
<th>FWHM, cm⁻¹</th>
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<th>Area, a.u.</th>
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Notes: ext = external modes; comb = combination bands / overtones
ω = band position
FWHM = band full width in half maximum
Height = band height
Area = band intensity
Tentative assignment = assignment of bands to vibrational modes