Implications of the unusually high degrees of Pb and Se substitutions in bismuth tellurides from the Stall Lake VMS deposit, Canada

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Abstract

Five discrete bismuth telluride compositions, characterized by high and variable degrees of Pb and Se substitutions, were observed at the Stall Lake VMS deposit in the Snow Lake area, Canada. The major cation substitutions are Pb (3.0 to 11.0 wt%), Fe (0.2 to 1.4 wt%), Cu (up to 0.9 wt%), and Ag (up to 3.2 wt%). The main anion substitution is Se (0.3 to 7.9 wt%); S never exceeds 0.3 wt%. These results were compared to a literature data compilation of all publicly available data for the pure bismuth tellurides tsumoite and tellurobismuthite, and the Pb-bearing rucklidgeite and kochkarite. Based on the new data and the literature compilation, a few generalizations about the substitutions in bismuth tellurides can be made. The major of these is that bismuth tellurides always contain at least some substitution cations (Pb, Ag, Fe, Cu, Sb, and Au), typically combining to about 2 wt% if Pb is excluded, and anions (mostly Se and some S, typically less than 1 wt% combined).

Another conclusion is that bismuth tellurides have highly variable chemical compositions, sometimes fairly far from their theoretical ones, to the point of defining specific mineral varieties such as high-Pb tsumoite, low-Pb kochkarite, and high-Se rucklidgeite. Finally, two high-Se bismuth telluride compositions were observed at Stall Lake (average Se ~4.9 and ~7.2 wt%), which had never been documented before. This observation, in conjunction with the bismuth tellurides literature data, emphasises the high potential for both cation and anion substitutions in these minerals.

Keywords

Bismuth tellurides, kochkarite, rucklidgeite, tsumoite, tellurobismuthite, poubaite, element substitutions, bismuth, tellurium, lead, selenium.

1. Introduction

Pure bismuth tellurides are a group of five minerals (ehrigite, hedleyite, pilsenite, tsumoite, and tellurobismuthite) with varying characteristics, including their chemical compositions and crystallinity (Anthony et al 1990). One of the ways to differentiate them from each other is the Bi/Te ratio of their structural formulas (e.g., Cook et al 2007; Gu et al 2001), which varies from 0.667 for tellurobismuthite (Bi_2Te_3) to 2.667 for the newly discovered ehrigite (Bi_8Te_3; Ciobanu et al 2024). Most of bismuth tellurides belong to the trigonal/hexagonal crystal system and have a layered structure (Anthony et al 1990). Their diversity is conditioned by different factors, specifically the order of layer alternation, the tolerance of their crystalline structure to incorporating substitution elements, and the possibility of an ordered distribution of substitution elements in their structure (Belogub et al 2011; Cook et al 2007).

In terms of the chemical composition of these minerals, Bi is commonly substituted by Pb, while Te is substituted by S and less frequently by Se, leading to the existence of several minerals – many of which are rather rare – with varying complexity, including a few solid solutions (e.g., Anthony et al 1990; Cook et al 2007; Gu et al 2001; Alexandre et al 2019). However, when only Pb and Se substitutions in bismuth tellurides are considered (Fig. 1), it becomes apparent that it is much more common for one or the other of these substitutions to exist to the point of defining a distinct mineral, but it is rather uncommon for both Pb and Se substitutions to define a specific discrete mineral, with poubaite

($PbBi_2Te_2Se_2$) being the unique example (Fig. 1). Other cations, such as Fe, Cu, Sb, Sn, and Ag, can also substitute for Bi in pure bismuth tellurides to varying degrees, from very low to sufficiently high to form distinct minerals (Anthony et al 1990). In general terms, the chemical compositions of bismuth tellurides and its substitutions are relatively well studied, even though some knowledge gaps remain; the most notable of these involve the chemical variability of these minerals and the extent of the cation and anion substitutions.

As a part of a large-scale project on the comparative ore mineralogy of several volcanogenic massive sulfide deposits in the Flin Flon - Snow Lake Mineral Belt (Manitoba, Canada; Fig. 2), a bismuth telluride mineral – or rather a range of compositions – with significant and highly variable degrees of both Pb and Se substitutions was observed at the Stall Lake VMS deposit. It was soon appreciated that its degree of Pb substitution was comparable to that of other Pb-rich bismuth tellurides such as rucklidgeite ($(Bi,Pb)_3Te_4$) and kochkarite ($PbBi_4Te_7$). However, the degree of Se substitution in this phase was significantly higher than that of any of these minerals, without reaching the levels of kawazulite (Bi_2Te_2Se), skippenite (Bi_2TeSe_2), or telluronevskite (Bi_3TeSe_2).

It was the unusually high degrees of Pb and Se substitutions in this phase that prompted a comprehensive comparison with the all literature data available on similar minerals, specifically the more or less pure bismuth tellurides tsumoite and tellurobismuthite, and the Pb-rich bismuth tellurides rucklidgeite and kochkarite. Tsumoite and tellurobismuthite were preferred for this comparison ahead of other pure bismuth tellurides, as their Bi/Te ratios were very similar to those of the Stall Lake phase; rucklidgeite and kochkarite were selected because their Pb contents is very similar to that of the Stall Lake phase. The findings of this comparison are presented in this paper, together with a few observations about Pb and Se substitutions in bismuth tellurides.

2. Geological background of the Stall Lake deposit

The mined-out Stall Lake deposit is one of the 12 volcanogenic massive sulfide (VMS) deposits from the Snow Lake arc assemblage in Manitoba, Canada, itself the easternmost part of the Flin Flon-Snow Lake Mineral Belt (Fig. 2). The Snow Lake assemblage was produced at ca. 1.87–1.85 Ga as a result of intraoceanic accretion (Lewry and Collerson 1990; Lucas et al 1996).

The Stall Lake deposit was the third largest in the Snow Lake area, with ~6.4 million tonnes total ore containing 4.41 wt% Cu, 0.5 wt% Zn, 0.01 wt% Pb, 12.34 g/t Ag, and 1.41 g/t Au (Pehrsson et al 2016). It was discovered in 1956 by ground electromagnetics followed by drilling and mined between 1964 and 1982. The host lithology is dominated by gneisses (quartz-eye gneiss, staurolite-garnet gneiss, and sillimanite gneiss) and schists (chlorite-garnet schist, chlorite schist), with minor andesitic tuffs and amphibolite sills (Studer, 1982).

The ore at the Stall Lake deposit was contained in 7 sulphide lenses, each dipping between approximately 30 and 60^{o} to the SW, with a maximum length between approximately 50 and 300 m, and thickness varying between roughly 10 and 50 meters (Studer, 1982). These lenses were zoned and heterogeneous, dominated by massive coarse-grained pyrrhotite with lesser pyrite, chalcopyrite, and sphalerite, minor galena, magnetite, and gahnite, and traces of hessite (Ag_2Te) and the Bi-Te phase subject of this paper (Studer, 1982; our observations; Fig. 3). The main ore mineral, chalcopyrite, is fairly typical, with minor Pb (0.36 wt%) and Bi (0.09 wt%); sphalerite contains 6.38 wt% Fe, 0.37 wt% Cu, and 0.35 wt% Pb (EMPA, our unpublished data).

3. Sampling and analytical methodology

Approximately 50 representative drill core samples from the Stall Lake deposit main ore bodies were collected from the Manitoba Geological Survey's Centennial core storage facility at Baker Lake, approximately 20 km south of Flin Flon (Manitoba, Canada), as a part of a larger study of the Flin Flon – Snow Lake Mineral Belt VMS deposits ore mineralogy. Of these, 20 high-grade ore samples, composed mostly of sulfide minerals, were selected for further analyses. Polished thin sections were prepared from these samples and were used for microscope observations and electron microprobe analyses.

Optical microscopy (reflected light) and scanning electron microscopy (SEM) were used to identify the ore minerals present at Stall Lake. The SEM instrument used was Jeol JSM-6390 at Brandon University, Canada.

Chemical compositions of the Bi-Te phase were obtained via wavelength dispersive spectroscopy (WDS) using the University of Manitoba's Cameca SX100 electron microprobe. The elements analysed were: Se (X-ray line used Lα, analytical crystal used TAP); Pb (Mα, LPET); S (Kα, LPET); Sb (Lα, PET); Ag (Lα, PET); Bi (Mβ, PET); Cu (Kα, LLIF); Ni (Kα, LLIF); Co (Kα, LLIF); Fe (Kα, LLIF); and Te (Lα, LLIF). The analytical conditions were: 15 keV, 20 nA, 1 μm beam; peak counting times were 20 s (except for Te, Se, and S: 30 s), with the background counted for half of that time, once on each side of the peak. The ZAF corrections followed the PAP procedure (Pouchou and Pichoir 1984; Pouchou and Pichoir 1985). Reference materials are natural and synthetic CdSe (for Se), PbTe (for Pb and Te), pyrite (for S and Fe), stibnite (for Sb), silver (for Ag), bismuthinite (for Bi), chalcopyrite (for Cu), pentlandite (for Ni) and cobalt (for Co).

It was impossible to collect any structural data for the Bi-Te phase from the Stall Lake deposit, due to its small grain size (Fig. 3) and very low amounts. If X-ray diffraction analysis had been performed on a bulk sample, the signal emanating from the small Bi-Te phase grains would be too low to be distinguished from the background noise. Further, micro-Raman is impossible to apply, because the method is not applicable to telluride minerals, which oxidise under the laser beam and thus do not produce a recognisable spectrum or signature (Alexandre and Aisida 2023). In the absence of structural data, this work relies only on the chemical composition of the Bi-Te phase observed at the Stall Lake deposit.

A significant component of this work is the literature data compilation of the chemical composition of Bi-Te minerals comparable to the Stall Lake phase, used to situate the new data within a relevant compositional context. To that end, all publicly available literature on tsumoite, tellurobismuthite, rucklidgeite, and kochkarite were collected and summarized here. These minerals were selected as they are comparable to the Stall Lake phase, based on the Bi/Te (or total cation/total anion) ratio of its structural formula (0.73 to 1.05) and its Pb contents. The results of this compilation are provided, alongside the Stall Lake phase data, in Table 1 and will be discussed in the Results section; the references used are Rucklidge 1969; Zavyalov and Begizov 1977; Haranczyk 1978; Spiridonov et al 1989; McQueen 1990; McQueen and Solberg 1990; Kase et al 1993; Gu et al 2001; Cepedal et al 2006; Cook et al 2007; Ivashchenko et al 2008; Sejkora et al 2009; Belogub et al 2011; Voloshin et al 2012; Maslennikov et al 2013; Jian et al 2014; Sabau et al 2014; Xue and Campbell 2014; Stenco et al 2014; Roberts 2017; Haing 2019; Kondratieva et al 2021; Kasatkin et al 2022; Alfonso et al 2023; Kasprowicz 2023; Ma et al 2024.

4. Analytical results and literature data compilation findings

In this section, the Stall Lake Bi-Te phase will be described (Fig. 3) and its chemical compositions, obtained as part of this project, will be presented, followed by the results of the compilation of all available literature data on the chemical composition of tsumoite, tellurobismuthite, kochkarite, and rucklidgeite. The summary data for all minerals, using the minimum, maximum, and mean values (both in terms of wt% and apfu), are provided in Table 1; all data are also represented in Figures 4 and 5.

4.1 Mineral description

Based on optical microscope (reflected light; Fig. 3 A and B) and SEM observations (Fig. 3 C-F), the Stall Lake Bi-Te phase studied here has the following characteristics. Its colour is pale yellow to white (Fig. 3 A, B). Due to the small grain size, anisotropy was difficult to estimate, but appears to be very low. Its reflectivity is very high – not as high as galena – estimated at approximately 80 % (Fig. 3 A, B). In size this phase varies from a few microns to approximately 30 microns across (Fig. 3). Its shape varies between mostly isomorphic (Fig. 3 E, F) to moderately elongated (Fig. 3D); it is mostly anhedral and occasionally subhedral (Fig. 3 C, F).

The Stall Lake Bi-Te phase is associated with the major minerals present at this deposit, mostly with pyrite and pyrrhotite, but also chalcopyrite and magnetite (Fig. 3); it is also sometimes closely associated with hessite (Ag_2Te; Fig. 3 C, E). Based on its textural relationships with other minerals, it likely formed later than the main stage (coarse-grained) minerals and together with other (minor and rather small-grained) sulfides, possibly during the lower to middle almandine–amphibolite facies metamorphism that affected the deposit area (maximum conditions 5 kb and 535 ^{o}C; Froese & Moore 1980), in imitation of other deposits in the near vicinity (Alexandre et al 2019; Alexandre and Aisida 2023).

4.2 The composition of the Stall Lake deposit Bi-Te phase

At a first glance, this phase is dominated by Bi and Te, with concentrations anywhere between approximately 41 and 56 wt% for the former and between approximately 35 and 41 wt% for the latter, when all analyses are considered. The major cation substitutions are Pb, varying between 3.0 and 11.0 wt%, Fe (0.2 to 1.4 wt%), Cu (up to 0.9 wt%), Ag (up to 3.2 wt%), and traces of Sb and Au (Table 1). Co, Ni, Zn, Mn, As, Sn, and Hg were also analyzed, but were always just about or below the quantification limit. The main anion substitution is Se, varying overall from 0.3 to 7.9 wt%; S never exceeds approximately 0.3 wt% (Table 1).

When the data are considered from the point of view of the two main substitutions, Pb for Bi and Se for Te (Fig. 4), five clearly discrete compositional groups can be empirically defined (Fig. 5), as described below.

Compositional groups 1 and 2 are fairly similar to each other and are defined by the two lowest amounts of Pb substitutions (~3.3 wt% and 5.1 wt% on average) and the lowest Se substitution (~0.3 wt% for both groups, on average; Figs. 4 and 5). Fe and Cu are present in both groups (~1.2 wt% for Fe, ~0.7 and ~0.6 wt% for Cu); Au, Ag, and Sb are present in trace amounts (Table 1). Their average structural formulas, on the basis of two atoms in imitation of tsumoite, can be written as $(Bi_{0.841}Fe_{0.068}Pb_{0.051}Cu_{0.034})_{\Sigma=0.996}(Te_{0.981}Se_{0.012}S_{0.011})_{\Sigma=1.004}$ for group 1 and $(Bi_{0.841}Pb_{0.080}Fe_{0.069}Cu_{0.031})_{\Sigma=1.024}(Te_{0.952}Se_{0.012}S_{0.012})_{\Sigma=0.976}$ for group 2.

Compositional group 3 is notable by increased Pb and Se substitutions, with average Pb of ~7.2 wt% and average Se of ~0.75 wt% (Table 1). There is less Fe (~0.9 wt%), Ag (~0.3 wt%), and Cu (~0.1 wt%); Sb and Au are present at trace level (Table 1). S is relatively low, at ~0.1 wt%. The average structural formula for this compositional group can be written, based on 12 atoms as in kochkarite, as $(Bi_{4.034}Pb_{0.654}Fe_{0.307}Cu_{0.039})_{\Sigma=5.089}(Te_{6.674}Se_{0.179}S_{0.056})_{\Sigma=6.909}$.

Compositional groups 4 and 5 contain higher Pb (~10.9 wt% on average) than group 3, but are remarkable by the largest degree of Se substitutions, with, on average, ~4.9 wt% for group 4 and ~7.2 for group 5 (Table 1; Fig. 4). While Se in these two groups is indeed high, it does not reach the levels of poubaite (approximately 13.6 wt%; Anthony et al 1990; Johan et al 1987; Kalinin 2021). There is less Fe (~0.4 wt%) and Cu (~0.2 and ~0.3 wt%) than the other groups, but more Ag (~0.6 and ~0.7 wt%, on average; Table 1); Sb and Au are present at trace level. S is also the lowest among all Stall Lake analyses, at about 0.1 wt%; Table 1). The average structural formula for these two compositional groups can be written, also based on 12 atoms, as $(Bi_{3.819}Pb_{0.973}Fe_{0.140}Cu_{0.045})_{\Sigma=5.089}(Te_{5.722}Se_{1.154}S_{0.034})_{\Sigma=6.911}$ for group 4 and $(Bi_{3.775}Pb_{0.958}Fe_{0.138}Cu_{0.076})_{\Sigma=5.064}(Te_{5.217}Se_{1.655}S_{0.064})_{\Sigma=6.936}$ for group 5.

The main point of these observations is the continuous increase in both Pb and Se substitution from group 1 to group 5, without Se reaching poubaite levels (Fig. 5). Fe and Cu are always present in measurable amounts but tend to decrease with increasing degree of Pb and Se substitution; Ag is the highest in groups 4 and 5, whereas Au and Sb are always present at trace amounts (Table 1). It should also be mentioned here that the average Bi/Te (or total cations/total anions) ratio for groups 1 and 2 is close to 1, whereas in the other three groups this ratio is closer to 0.74 (Table 1), justifying using the tsumoite and kochkarite structural formula patterns (2 and 12 atoms, respectively), as indicated above.

4.3 Literature data compilation

Tsumoite literature data fall into two compositional groups. The first one corresponds to a fairly typical tsumoite with 62.3 wt% Bi and 36.4 wt% Te, and relatively low degree of cation and anion substitutions (~1.6 wt% and ~0.33 wt% in total, respectively; Table 1). The main substitution cations are Pb, Fe, Sb, and Ag, all at about 0.4 wt%; Au is also present (~0.1 wt%). Its structural formula can be written as $(Bi_{0.984}Fe_{0.027}Sb_{0.010}Sb_{0.009})_{\Sigma=1.038}(Te_{0.943}S_{0.010}Se_{0.009})_{\Sigma=0.962}$.

The second compositional group for tsumoite, observed in two deposits (from the Ural mountains and from the Karelian Peninsula in Russia; Belogub et al 2011; Ivashchenko et al 2006), is characterized by the presence of Pb substitution (~4.6 wt% of Pb on average, ranging from 3.2 to 5.9 wt%) and was labelled Pb-rich tsumoite. No other substitution cations or anions were observed (Table 1); its structural formula can be written as $(Bi_{0.927}Pb_{0.075})_{\Sigma=1.002}Te_{0.998}$.

Kochkarite literature data also define two discrete two compositional groups, distinguished from each other by their Pb concentrations (Figs. 4 and 5, Table 1). The major group corresponds to typical kochkarite, with, on average, about 43.7 wt% Bi, 11.8 wt% Pb, 1.3 wt% Ag, and 1.0 wt% Fe; Sb and Cu are also present (Table 1). The anions are dominated by Te (~45.0 wt%); the amount of Se is relatively low (0.2 wt%; Table 1). Significantly, the data show a high degree of variation of all elements present, with Pb, for instance, varying from ~9.5 to ~16.0 wt% (Table 1). The average structural formula for this group is $(Bi_{3.645}Pb_{1.055}Fe_{0.346}Ag_{0.231})_{\Sigma=5.365}(Te_{6.539}S_{0.049}Se_{0.047})_{\Sigma=6.635}$.

The second kochkarite group, observed at the Deer Horn intrusion-related polymetallic deposit in British Columbia, Canada (Roberts 2017), contains more Bi (about 43.7 wt% on average), less Pb (~7.0 wt% on average), some Ag (~1.0 wt%), Sb (~0.5 wt%) and traces of Fe, Au, and Cu (Table 1); its anion substitutions are very low (Se ~0.03 wt% on average, no S). This compositional group was labeled low-Pb kochkarite and its average structural formula is $(Bi_{4.031}Pb_{0.648}Ag_{0.170}Sb_{0.086})_{\Sigma=4.962}(Te_{7.029}Se_{0.007})_{\Sigma=7.038}$.

Rucklidgeite is another mineral for which two distinct sub-populations were observed in the compilation dataset; it is also the one with the highest variation in the concentrations of most elements (Fig. 4B; Table 1). Most analyses form a group of more or less typical rucklidgeite, with approximately 40.0 wt% Bi on average, about 16.1 wt% Pb (varying from ~10.8 to ~20.9 wt%), ~1.6 wt% Ag (~0.4 to ~4.7 wt%), and some Fe and Sb (~0.5 wt% for both; Table 1). This group contains about 44.4 wt% Te on average, and limited Se (~0.3 wt% on average, ranging from below detection to ~1.1 wt%); S is minimal. Its average structural formula is $(Bi_{2.098}Pb_{0.709}Ag_{0.159}Fe_{0.104})_{\Sigma=3.124}(Te_{3.820}Se_{0.037}S_{0.007})_{\Sigma=3.876}$.

A minor subpopulation of rucklidgeite, from a VMS deposit in Quebec, Canada (Kasprowicz 2023), is characterized by high Se (~3.1 wt% on average: Table 1) and was labeled Se-rich rucklidgeite. The concentrations of all other elements in this group are similar to those in the main rucklidgeite population (Table 1). Its average structural formula is $(Bi_{1.997}Pb_{0.829}Ag_{0.140}Fe_{0.097})_{\Sigma=3.114}(Te_{3.444}Se_{0.414}S_{0.027})_{\Sigma=3.886}$.

Tellurobismuthite also shows some chemical variation, in particular in its Se concentrations, which vary from below detection to about 2.7 wt% (~0.45 on average; Table 1). The average Bi concentrations are approximately 51.9 wt%; Te is present at about 47.1 wt% on average (Table 1). Tellurobismuthite has the lowest Pb concentrations of all the minerals considered (~0.3 wt% on average); Fe, Sb, Cu, and Ag are also present (~1.0 wt%, ~0.4, wt%, ~0.4 wt%, and ~0.2 wt%, on average, respectively). The average structural formula of tellurobismuthite, based on this compilation, is $(Bi_{1.899}Fe_{0.130}Cu_{0.046}Ag_{0.011})_{\Sigma=2.120}(Te_{2.822}Se_{0.043}S_{0.015})_{\Sigma=2.880}$.

5. Discussion

The literature compilation of all publicly available compositions data for tsumoite, tellurobismuthite, kochkarite, and rucklidgeite (based on the references at the end of Section 3), provide some interesting insights and some general comments can be made about their chemical purity and their chemical composition variability; these questions have never been addressed. The chemical composition of the Stall Lake deposit phases will also be discussed, in the context of the other bismuth tellurides (e.g., Cook et al 2007; Gu at al 2001).

5.1 Extent of substitutions in bismuth tellurides

All minerals considered and documented by both the literature compilation and the new data from Stall Lake contain at least some amount of Pb, Fe, Cu, Sb, Ag and Au (Table 1). Ag is most abundant in rucklidgeite (~1.6 wt%) and kochkarite (~1.4 wt%); Fe is most abundant in kochkarite and tellurobismuthite (~1.0 wt% on average). Tellurobismuthite also has the most Sb and Cu, both at about 0.4 wt% on average. The average concentrations of Pb vary from about 0.3 wt% in tellurobismuthite to about 16.1 wt% in Se-rich rucklidgeite. Overall, the cations observed in these minerals, other than Bi and Pb, typically combine to about 2 wt%.

All minerals considered show some degree of Se substitution, with Se varying from below detection limit to approximately 3.6 wt% for Se-rich rucklidgeite (VMS deposit in Quebec; Kasprowicz 2023). The amounts of Se are low for tsumoite and kochkarite (both at about ~ 0.2 wt% on average), higher and tellurobismuthite (~0.5 wt% on average, up to 2.7 wt%; Cook et al 2007), and highest for Se-rich rucklidgeite (~3.1 wt% on average; Kasprowicz 2023; Table 1). Overall, Se and S typically combine to just under 1 wt% in these minerals.

From this point of view, it could be argued that there is no such thing as pure bismuth telluride (in clear contradiction of the first three words of this paper): all and any of them will always contain a certain amount of both cation and anion substitutions, as demonstrated by the literature data compilation and the new data obtained at Stall Lake. The cation substitutions are mostly Pb, but also, in decreasing amount, Ag, Fe, Sb, Cu, and Au; the anion substitutions are predominantly Se and much less S

(Table 1). As a practical corollary, these are the bare minimum of elements that should always be analyzed in any bismuth telluride.

5.2 Chemical variability of bismuth tellurides

Another important observation originating from the literature data compilation is the significant chemical variability observed for all the minerals concerned, to the point of defining distinct sub-groups (high-Pb tsumoite, low-Pb kochkarite, high-Se rucklidgeite; Fig. 5). That variability, in particular for the Pb concentrations, is the highest for kochkarite and rucklidgeite: in fact, their Pb concentrations overlap to a very high extent (Fig. 5). This observation incites questions about the chemical definition of these two minerals (but also about labeling them in any particular study, as discussed below; see also Cook et al 2007 and Gu at al 2001). For instance, it should be possible to chemically distinguish kochkarite and rucklidgeite from each other by the Bi/Pb ratio in their structural formulas: it is ideally 0.750 for rucklidgeite ($(Bi, Pb)_3Te_4$) and 0.714 for kochkarite ($PbBi_4Te_7$) (Anthony et al 1990). However, the average total cation/total anion ratios resulting from this compilation are on the order of 0.80 for kochkarite, rucklidgeite, and high-Se rucklidgeite, and about 0.71 for low-Pb kochkarite (Table 1): these are significantly different from the theoretical values.

5.3 Labeling, or naming, of bismuth tellurides

A direct and practical consequence of the above comments is that sometimes it may be problematic, in the absence of structural information, to know which bismuth telluride is observed when new data are collected. The present study is a pertinent example of this difficulty.

The Stall Lake deposit bismuth tellurides fall into 5 empirically defined compositional groups, as described above (section 4.1; Table 1; Fig. 5), and the question that emerged immediately was to what minerals these compositions correspond (again, in the absence of structural data). This question is most easily answered for compositional groups 1 and 2, which seem to closely resemble the high-Pb tsumoite visible in the literature data compilation (Fig. 5; Table 1). Specifically, (1) the cation/anion ratios in their structural formulas are very similar, at about 1 (no other bismuth tellurides have the same ratio; telluronevskite is not an option because of its high Se; Anthony et al 1990); and (2) the amounts of Pb in the Stall Lake groups 1 and 2 (~3.3 and ~5.1 wt%) are fairly comparable to those of literature data high-

Pb tsumoite (~4.6 wt%; Table 1; VMS deposits in the Ural, Russia: Belogub et al 2011). It seems that these two compositional groups can be safely labelled as high-Pb tsumoite (e.g., Cook et al 2007).

The other three compositional groups from Stall Lake are more difficult to label. The total cation/total anion ratio of their average structural formulas are about 0.74, which is the closest to theoretical rucklidgeite (0.75; Anthony et al 1990). However, the literature compilation (Table 1; references at the end of Section 3) reveals that kochkarite and rucklidgeite have cation/anion ratios between 0.71 (low-Pb kochkarite) and 0.81 (kochkarite, rucklidgeite), indicating that it may be indeed challenging to decide what the Stall Lake compositions are.

Based on its amount of Pb, the Stall Lake deposit compositional group 3 (Pb ~ 7.2 wt%) is closest to low-Pb kochkarite (compilation group 8: Pb ~ 7.0 wt%; Roberts 2017; Table 1); the amount of Pb is significantly lower than that of rucklidgeite (ranging from ~10.8 to ~20.9 wt%; references at the end of Section 3). Hence, this bismuth telluride compositional group can be likely named low-Pb kochkarite.

The greatest difficulty is deciding what the Stall Lake compositional groups 4 and 5 are, the high-Se bismuth tellurides. The average cation/anion ratio of their structural formulas (about 0.73) are not sufficiently close to either literature data kochkarite or rucklidgeite (about 0.8) to be of any help. Based uniquely on the Pb contents of these two groups (at about 10.9 wt%; Table 1), kochkarite was preferred, as its Pb contents is about 11.8 wt% on average (Table 1; references at the end of Section 3). This is not ideal and serves to illustrate the difficulties in naming unknown bismuth tellurides.

5.4 The high-Se bismuth telluride phases from Stall Lake

The difficulty described above is compounded by the very high degree of Se substitution observed in the Stall Lake deposit compositional groups 4 and 5 (average Se ~4.9 and ~7.2 wt%, respectively; Figs. 4 and 5), which had never been observed in either kochkarite or rucklidgeite (references at the end of Section 3). These concentrations are lower than in poubaite (Se ~13.6 wt% on average; Anthony et al 2009; Kalinin 2021; Johan et al 1987); poubaite also has more Pb (~20.1 wt% on average). The high amounts of Se in the Stall Lake compositional groups 4 and 5 clearly demonstrate the potential for anion substitutions in bismuth tellurides, as noted above, but also raise the question of what mineral(s) these two groups correspond to.

The two most likely hypotheses are (1) the existence of new minerals or (2) the existence of a high-Se kochkarite or rucklidgeite. New minerals with these compositions would have the ideal structural formulas of Bi_4PbTe_6Se (group 4) and $Bi_4PbTe_5Se_2$ (group 5). However, such a hypothesis cannot be addressed here because of the absence of structural data, highlighting in the process the absolute necessity to collect, when at all possible, crystallinity information for any mineral studied. The second hypothesis seems more likely and, based on the Pb contents of these compositional groups (both are, on average, at about 10.9 wt%; Table 1) the moniker of *high-Se kochkarite* was preferred for them. This labeling is far from satisfactory or conclusive and should be taken with a pinch of scepticism.

One corollary of the high Se observed in the Stall Lake bismuth tellurides is the *speculation* about a possible solid solution between kochkarite and poubaite or between rucklidgeite and poubaite (e.g., Kase et al 1993). The former possibility can be dismissed immediately, as kochkarite is cubic (point group 4/m 3 2/m), whereas poubaite is hexagonal (point group 3 2/m; Anthony et al 1990). The latter possibility remains theoretically possible, as both poubaite and rucklidgeite are hexagonal, with the same point group (3 2/m); they also have comparable amounts of Pb (~20.1 for poubaite and ~16.1 for high-Se rucklidgeite; Table 1) and the same cation/anion ratio of 0.75 (Anthony et al 1990). In such a scenario, the high-Se phases from Stall Lake (compositional groups 4 and 5) could be considered as belonging to this hypothetical solid solution if they are in fact (low-Pb) rucklidgeite; the high-Se literature data rucklidgeite (compositional group 11; Kasprowicz 2023) would also belong to such a solid solution (Fig. 6). However, the lower amount of Pb in Stall Lake compositional groups 4 and 5 compared to poubaite, and the far from consistent or continuous Te-Se anti-correlation (Fig. 6) are arguments against such a possibility. In can be concluded that while a poubaite – rucklidgeite solid solution may be theoretically possible, the present work, specifically the existence of a high-Se bismuth telluride compositions at Stall Lake, is not a sufficient proof of that.

6. Summary of findings

A few interesting generalizations can be made in the light of the literature data compilation of four bismuth tellurides and the new data obtained at the Stall Lake VMS deposit, the very first of which is that these minerals have a highly variable chemical composition (Fig. 4, Table 1). They all contain at least a modest degree of cation and anion substitutions, with (in decreasing concentrations) Pb, Ag, Fe, Cu, Sb, and Au substituting Bi, and Se and S substituting Te; all these elements should be therefore routinely analysed in bismuth tellurides. The amount of substitution cations other than Bi and Pb is in the vicinity of 2 wt%, Se and S combine to under 1 wt%.

Bismuth tellurides are not only more chemically complex than previously appreciated, but demonstrate fairly high chemical variability, to the point of defining specific mineral varieties such as high-Pb tsumoite, low-Pb kochkarite, and high-Se rucklidgeite (Fig. 5). Their empirical chemical compositions are often different from what their ideal structural formulas would indicate (Fig. 5). The highest variability is observed in the amount of Pb in kochkarite and rucklidgeite, with the former varying between ~9.5 and ~16.0 wt%, and the latter between ~10.8 and ~20.9 wt% (Table 1). These two minerals' compositions overlap to such an extent that distinguishing them from each other conclusively may, in some cases, only be possible using crystallinity information. In practical terms, this chemical variability can sometimes represent a difficulty with the classification of an unknown bismuth telluride, as this study demonstrates.

Two new high-Se bismuth telluride chemical compositions were discovered at the Stall Lake VMS deposit, containing, on average, approximately 43.4 wt% Bi, 10.9 wt% Pb, 39.6 and 36.8 wt% Te, and 4.9 and 7.2 wt% Se (Table 1; Fig. 5).These two compositional groups were tentatively labeled high-Se kochkarite. Such high extent of Se substitution had never been observed for kochkarite or rucklidgeite and opens a few exciting possibilities, one of which is the existence of two new minerals (with the ideal structural formulas of Bi_4PbTe_6Se and $Bi_4PbTe_5Se_2$). It can even be *speculated* that the Stall Lake high-Se bismuth telluride belongs to a hypothetical rucklidgeite-poubaite solid solution (Fig. 6), even though the available data, from literature or newly obtained, do not conclusively support such a possibility.

As defining a new mineral or a solid solution would strongly rely on crystallinity data, which were not available for the Stall Lake phases, these *speculations* cannot be fully addressed at present. However, the new data – showing high and variable Pb and Se substitutions – emphasise the high chemical variability and the high extent of both cation and anion substitutions in bismuth tellurides, which is the main significance of this contribution.

7. Acknowledgements

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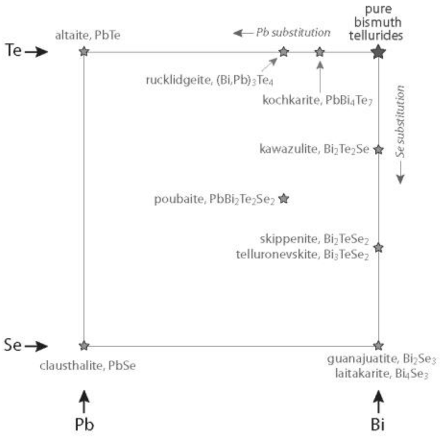
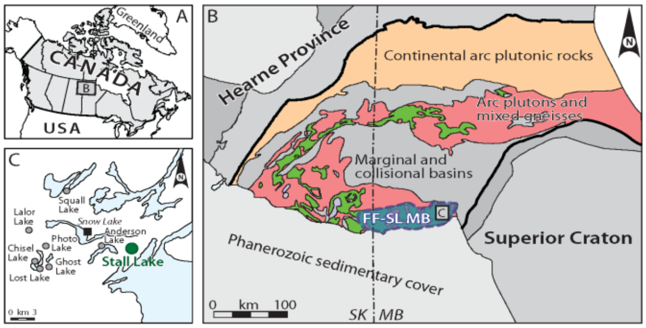
Figure captions

Figure 1. Theoretical positions of minerals in the Bi-Pb-Te-Se space. The pure bismuth tellurides tsumoite and tellurobismuthite and the Pb-bearing kochkarite and rucklidgeite were subject of a literature data compilation.



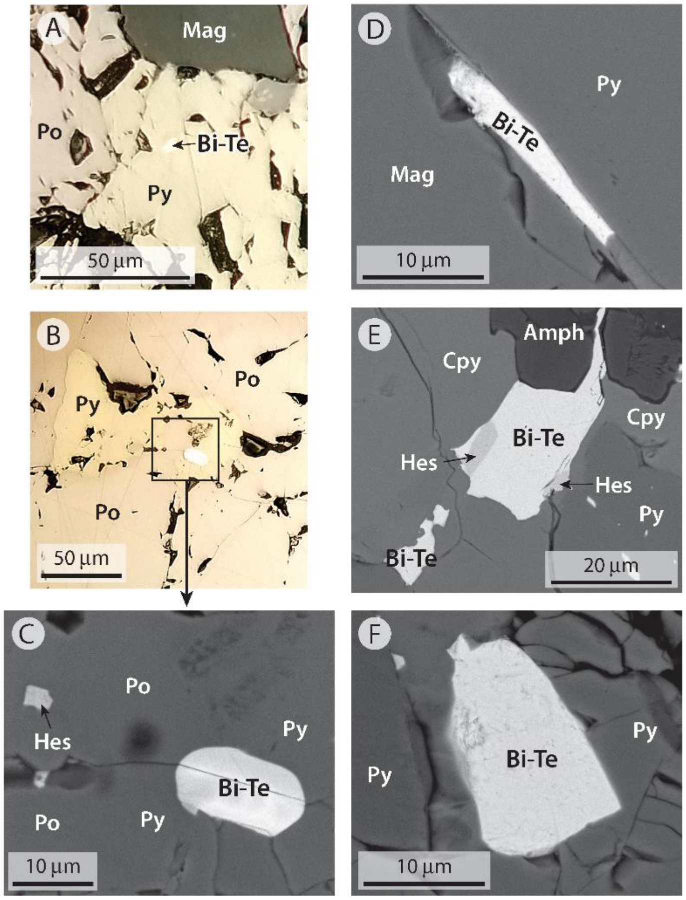
Alexandre, Figure 1

Figure 2. Simplified geological context of the Stall Lake and other VMS deposits within North America (A), the Trans-Hudson Orogen of Canada (B), and the Snow Lake area (C). The approximate extent of the Flin Flon-Snow Lake Mineral Belt (FF-SL MB) is indicated in B. SK=Saskatchewan, MB=Manitoba.



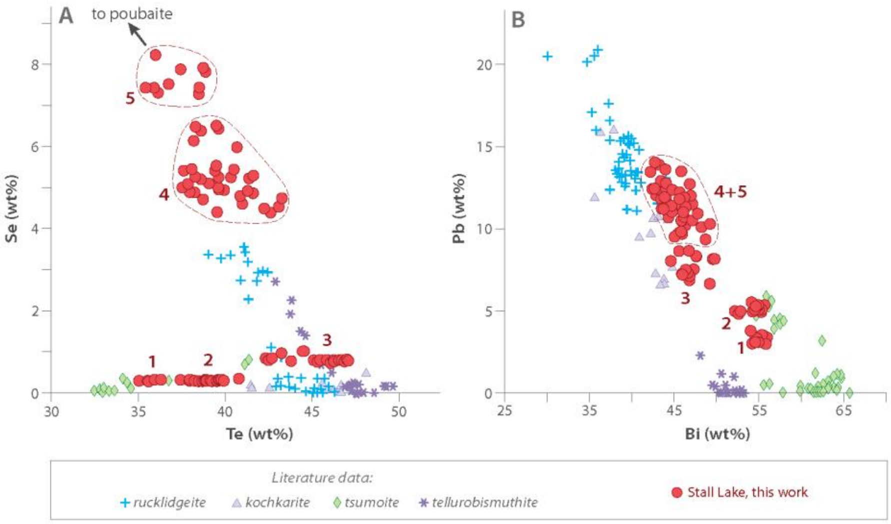
Alexandre, Figure 2

Figure 3. Examples of the Stall Lake VMS deposit bismuth tellurides (Bi-Te) in reflected light (A and B) and in backscattered electron images (C through F), together with other minerals present (Po: pyrrhotite; Py, pyrite; Cpy, chalcopyrite; Mag, magnetite; Hes, hessite, and Amph, amphibole).



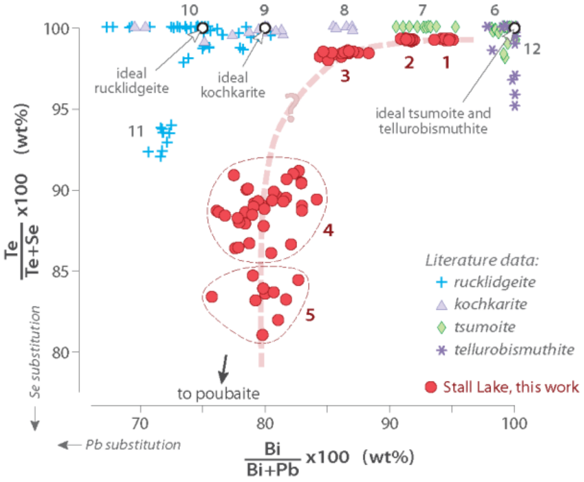
Alexandre, Figure 3

Figure 4. Se and Pb substitutions in the Stall Lake bismuth tellurides (A and B, respectively), compared to those of the pure bismuth tellurides tsumoite and tellurobismuthite and the Pb-bearing kochkarite and rucklidgeite, based on the references given in the text (Section 3). The empirically defined Stall Lake compositional groups are numbered 1 to 5. Please note that weight percent (wt%) were used rather than atoms per formula unit (apfu), as minerals with different numbers of atoms in their structural formula (2, 5, 7, and 12) are being compared.



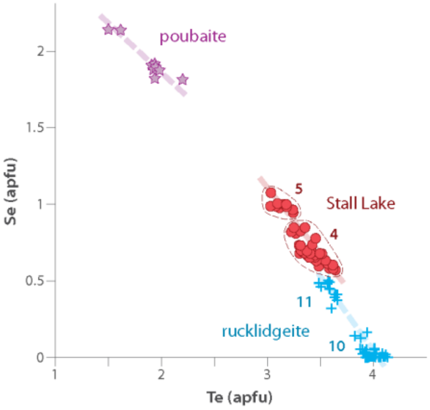
Alexandre, Figure 4

Figure 5. The empirically defined Stall Lake bismuth tellurides compositional groups (numbered 1 to 5), compared to the literature data for tsumoite, tellurobismuthite, kochkarite, and rucklidgeite (numbered 6 to 12), in a Pb substitution vs. Se substitution diagram, based on the references given in the text (Section 3). The extent of substitution was based on the weight percents (wt%), even though fairly similar results would have been obtained if atoms per formula unit (apfu) were used, given that the substitutions are expressed as ratios.



Alexandre, Figure 5

Figure 6. A *speculative* rucklidgeite-poubaite solid solution, visualized by the Se substitution of Te in rucklidgeite, high-Se rucklidgeite, the two high-Se Stall Lake compositional groups, and poubaite. The atoms per formula unit (apfu) were calculated based on 7 atoms, for a generic formula $(Bi,Pb)_3(Te,Se)_4$, which describes both rucklidgeite and poubaite. The Se-Te anti-correlation is far from perfect in terms of consistency and connectivity, which, combined with the low Pb concentrations in the Stall Lake bismuth telluride and the lack of crystallinity data for it, renders the existence of such a solid solution currently unsubstantiated.



Alexandre, Figure 6

Table 1. Summary (min, mean, max) of the analytical results for the Stall Lake bismuth telluride compositional groups seen in Figures 4 and 5 (1 to 5) and the literature data compilation for tsumoite, tellurobismuthite, rucklidgeite, and kochkarite (6 to 12 in Fig. 5; based on the references provided in the text, Section 3). Co, Ni, Zn, Mn, As, Sn, and Hg were also analyzed in the Stall Lake phase, but were always just about or below the quantification limit; Zn, As, and Hg were occasionally reported in the litterature data, but the values were always very near the quanitication limit for the respective method (predominantly electron microprobe), and are not reported here.

	STALL LAKE Bi-Te MINERALS															LITERATURE DATA Bi-Te MINERALS																				
	High-Pb tsumoite						Low-Pb kochkarite			High-Se kochkarite						Tsumoite			High-Pb tsumoite			Low-Pb kochkarite			Kochkarite			Rucklidgeite			High-Se rucklidgeite			Tellurobismuthite		
	1			2			3			4			5			6			7			8			9			10			11			12		
wt%	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max	min	**mean**	max
Bi	54.35	**55.25**	56.19	52.56	**54.67**	55.91	43.61	**45.03**	47.60	40.99	**43.24**	46.30	42.04	**43.55**	45.04	55.55	**62.31**	65.71	54.65	**57.21**	62.46	42.79	**43.74**	44.81	35.66	**41.06**	44.29	30.05	**39.98**	44.34	34.73	**39.03**	44.03	48.12	**51.88**	53.84
Pb	2.97	**3.31**	3.78	4.80	**5.13**	5.52	6.18	**7.24**	8.39	8.79	**10.92**	13.35	9.33	**10.96**	13.55	*bdl*	**0.39**	1.20	3.16	**4.60**	5.91	6.54	**6.98**	7.62	9.46	**11.78**	15.98	10.77	**13.39**	20.91	13.11	**16.07**	20.52	*bdl*	**0.26**	2.27
Fe	1.08	**1.20**	1.33	1.03	**1.20**	1.38	0.74	**0.92**	1.25	0.22	**0.42**	0.79	0.33	**0.42**	0.55	0.42	**0.45**	0.48		*bdl*		*bdl*	**0.06**	0.20	0.17	**1.04**	1.76	*bdl*	**0.53**	1.36	0.06	**0.51**	0.99	0.02	**0.95**	2.24

Sb		*bdl*		*bdl*	**0.06**	0.17	*bdl*	**0.02**	0.18	*bdl*	**0.02**	0.16	*bdl*	**0.02**	0.13	0.14	**0.35**	0.67		*bdl*		0.43	**0.54**	0.63	0.05	**0.35**	0.70	0.06	**0.47**	1.15	0.18	**0.27**	0.44	0.28	**0.39**	0.72
Cu	0.51	**0.68**	0.93	0.40	**0.62**	1.11	0.03	**0.13**	0.30	0.07	**0.16**	0.27	0.13	**0.27**	0.45		*bdl*			*bdl*		*bdl*	**0.01**	0.01	*bdl*	**0.12**	0.45	*bdl*	**0.06**	0.45	*bdl*	**0.17**	0.59	*bdl*	**0.38**	1.47
Ag	*bdl*	**0.03**	0.11	*bdl*	**0.02**	0.14	0.18	**0.30**	0.47	0.34	**0.63**	0.87	0.28	**0.66**	3.23	0.01	**0.34**	2.25		*bdl*		0.82	**0.95**	1.10	*bdl*	**1.34**	3.70	0.37	**1.56**	4.69	1.15	**1.41**	1.99	*bdl*	**0.15**	0.36
Au	*bdl*	**0.01**	0.06	*bdl*	**0.01**	0.07	*bdl*	**0.02**	0.06	*bdl*	**0.01**	0.07	*bdl*	**0.02**	0.06	0.01	**0.09**	0.19		*bdl*		*bdl*	**0.03**	0.13		*bdl*		*bdl*	**0.01**	0.07				*bdl*	**0.01**	0.03
Te	38.48	**39.33**	40.79	35.06	**37.77**	39.77	42.56	**45.49**	47.17	37.44	**39.56**	42.34	35.39	**36.75**	38.33	32.48	**36.43**	41.36	34.36	**37.59**	39.34	45.89	**46.57**	47.51	41.46	**44.98**	48.11	42.55	**44.44**	46.29	39.05	**41.10**	42.38	42.90	**47.07**	49.65
Se	0.28	**0.30**	0.34	0.27	**0.30**	0.32	0.68	**0.75**	0.94	4.12	**4.94**	6.18	6.90	**7.21**	7.85	0.02	**0.22**	0.80		*bdl*		*bdl*	**0.03**	0.07	0.10	**0.20**	0.46	*bdl*	**0.27**	1.11	2.27	**3.06**	3.56	*bdl*	**0.45**	2.71
S	0.07	**0.11**	0.19	0.07	**0.12**	0.21	0.05	**0.10**	0.27	*bdl*	**0.06**	0.11	0.00	**0.11**	0.16	*bdl*	**0.09**	0.80		*bdl*		*bdl*	**0.00**	0.01	*bdl*	**0.08**	0.30	*bdl*	**0.06**	0.14	0.04	**0.08**	0.19	*bdl*	**0.06**	0.28
Total		**100.24**			**99.94**			**100.02**			**99.97**			**99.99**			**99.32**	1.61		**99.39**			**98.92**			**100.41**			**100.83**			**101.72**			**99.90**	
APFU		*2 atoms*			*2 atoms*			*12 atoms*			*12 atoms*			*12 atoms*			*2 atoms*			*2 atoms*			*12 atoms*			*12 atoms*			*7 atoms*			*7 atoms*			*5 atoms*	
Bi		0.841			0.841			4.034			3.819			3.775			0.984			0.927			4.031			3.645			2.098			1.997			1.899	

Pb	0.051	0.080	0.654	0.973	0.958	0.006	0.075	0.648	1.055	0.709	0.829	0.009
Fe	0.068	0.069	0.307	0.140	0.138	0.027		0.021	0.346	0.104	0.097	0.130
Sb		0.002	0.003	0.004	0.004	0.009		0.086	0.054	0.043	0.024	0.025
Cu	0.034	0.031	0.039	0.045	0.076			0.002	0.036	0.011	0.028	0.046
Ag	0.001	0.001	0.053	0.108	0.112	0.010		0.170	0.231	0.159	0.140	0.011
Au				0.001	0.002	0.001		0.003		0.001		
Σ_{CAT}	***0.996***	***1.024***	***5.089***	***5.089***	***5.064***	***1.038***	***1.002***	***4.962***	***5.365***	***3.124***	***3.114***	***2.120***
Te	0.981	0.952	6.674	5.722	5.217	0.943	0.998	7.029	6.539	3.820	3.444	2.822
Se	0.012	0.012	0.179	1.154	1.655	0.009		0.007	0.047	0.037	0.414	0.043
S	0.011	0.012	0.056	0.034	0.064	0.010		0.002	0.049	0.019	0.027	0.015
Σ_A	***1.***	***0.***	***6.***	***6.***	***6.***	***0.***	***0.***	***7.***	***6.***	***3.***	***3.***	***2.***

N	*004*	*976*	*909*	*911*	*936*	*962*	*998*	*038*	*635*	*876*	*886*	*880*
Cat/ An	***0.99***	***1.05***	***0.74***	***0.74***	***0.73***	***1.08***	***1.00***	***0.71***	***0.81***	***0.81***	***0.80***	***0.74***