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^{197}Au MÖSSBAUER STUDY OF THE GOLD–SILVER DITELLURIDES SYLVANITE, KRENNERITE AND CALAVERITE

FRIEDRICH E. WAGNER
Physik-Department E15, Technische Universität München, D-8046 Garching, Germany

JERZY A. SAWICKI
AECL Research, Chalk River Laboratories, Chalk River, Ontario KOJ 1JO

JOSEF FRIEDL
Physik-Department E15, Technische Universität München, D-8046 Garching, Germany

JOSEPH A. MANDARINO
Department of Mineralogy, Royal Ontario Museum, Toronto, Ontario M5S 2C6

DONALD C. HARRIS
Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A OE8

LOUIS J. CABRI
Canada Centre for Mineral and Energy Technology, 555 Booth Street, Ottawa, Ontario K1A 0G1

ABSTRACT

Mössbauer spectroscopy of the 77.3 keV γ-rays of ^{197}Au was used to investigate the gold ditellurides sylvanite $AuAgTe_4$, krennerite $Au_{1-x}Ag_xTe_2$ ($x \approx 0.2$) and calaverite $AuTe_2$. The gold ditellurides have been found to exhibit distinctive Mössbauer spectra that can be explained by different amounts of gold on the (4+2) and (2+2+2) type of sites, with the former occupied only by gold, and the latter by gold as well as silver. The Lamb–Mössbauer factors of the (2+2+2) sites were found to be 75% or less of those for the (4+2) sites. The overall Lamb–Mössbauer factors for sylvanite, krennerite and calaverite are only about 60% of the Lamb–Mössbauer factor for metallic gold.

Keywords: Au–Ag ditellurides, sylvanite, krennerite, calaverite, ^{197}Au Mössbauer spectroscopy, isomer shift, electric quadrupole interaction, Lamb–Mössbauer factors.

SOMMAIRE

Nous avons utilisé la spectroscopie de Mössbauer des raies γ émises à 77.3 keV par les noyaux ^{197}Au pour étudier les bitellurures de l'or sylvanite, $AuAgTe_4$, krennerite $Au_{1-x}Ag_xTe_2$ ($x \approx 2$) et calavérite $AuTe_2$. Ces bitellurures possèdent des spectres de Mössbauer distinctifs qui seraient dus à des proportions variables des atomes Au dans les sites (4 + 2) et (2 + 2 + 2) des structures; le premier de ces sites contient uniquement des atomes Au, tandis que dans le second, Au et Ag seraient présents. Les facteurs de Lamb – Mössbauer des sites (2 + 2 + 2) ne sont que 75% ou moins de ceux des sites (4 + 2). Les facteurs globaux de Lamb – Mössbauer pour sylvanite, krennerite et calavérite ne sont que 60% du facteur pour l'or métallique.

(Traduit par la Rédaction)

Mots-clés: bitellurures de Au–Ag, sylvanite, krennerite, calavérite, spectroscopie de Mössbauer ^{197}Au, déplacement isomère, interaction électrique quadrupolaire, facteurs de Lamb – Mössbauer.

INTRODUCTION

As has been demonstrated recently, Mössbauer spectroscopy of the 77.3 keV γ rays of ^{197}Au can provide new information about gold minerals, gold-bearing ores and gold-recovery processes (Marion *et al.* 1986, Marion 1988, Wagner *et al.* 1986, 1988, 1992, Friedl *et al.* 1991, Sawicki *et al.* 1992). For this method to be used as a routine tool of assaying gold ores and assessing extractive processes, fundamental data on individual gold-bearing phases are required to identify unambiguously the various constituents of a mixture of minerals.

The structural and bonding information on gold compounds provided by Mössbauer spectroscopy is mainly derived from the isomer shift and electric quadrupole splitting of the Mössbauer line. The former is proportional to the electron density at the nuclei of gold, which increases with the oxidation state of the gold and the covalency of the bonds (Faltens & Shirley 1970, Bartunik *et al.* 1970, Bartunik & Kaindl 1978, Parish 1982). The latter depends on the tensor describing the electric field gradient at the gold nuclei, which reflects both the covalency and the symmetry of the bonds. For the fourfold-coordinated planar Au^{3+} and the twofold coordinated linear Au^+ compounds, different correlations between the isomer shift and the quadrupole splitting have been established (Bartunik *et al.* 1970, Bartunik & Kaindl 1978, Parish 1982). These correlations, for instance, permit one to distinguish between Au^+ and Au^{3+}, even though the electric quadrupole splitting of the Mössbauer line yields only the magnitude, and not the sign of the electric field gradient, which is expected to be negative for the Au^+ compounds and positive for the Au^{3+} compounds (Prosser *et al.* 1975, Parish 1982).

A further quantity that can be obtained from the Mössbauer spectra is the Lamb–Mössbauer *f*-factor, *i.e.*, the probability of elastic absorption of a γ ray by a resonant nucleus. The *f*-factor determines the intensity of the Mössbauer pattern and reflects the stiffness of the structure in which the Mössbauer nuclei are bound. Since the *f*-factors may be different for crystallographically different sites in the same compound, the relative intensities in the Mössbauer pattern of even a single compound are not directly proportional to the abundance of the Mössbauer nuclei on the different sites. Owing to the relatively high γ-ray energy of the 77.3 keV resonance in ^{197}Au, the *f*-factors of different sites in the same compound may differ substantially (Schmidbaur *et al.* 1987), as do the *f*-factors of different compounds and alloys of gold (Friedl *et al.* 1991). Lamb–Mössbauer factors, therefore, are not only an interesting feature reflecting stiffness of the structure and bond strength, but knowledge of these factors is also a prerequisite for the quantitative interpretation of Mössbauer spectra of mixtures of minerals, as well as single-phase compounds with crystallographically different sites.

Gold occurs in nature chiefly as native gold, as gold chemically bound in iron sulfides, and as gold tellurides, which may constitute a substantial component of gold-bearing ores. Ores rich in gold ditellurides are found, for instance, in Colorado, Ontario and Western Australia. The most common gold telluride minerals are calaverite (ideally $AuTe_2$) and sylvanite (ideally $AuAgTe_4$). Krennerite ($Au_{1-x}Ag_xTe_2$; $x \approx 0.2$), petzite (Ag_3AuTe_2) and kostovite (ideally $AuCuTe_4$) are found more rarely. More complex gold–tellurium minerals, such as nagyagite, bessmertnovite, bilibinskite, bogdanovite, montbrayite and criddleite, are considerably less common (Wilson 1982, Harris 1990). Tellurides forming a fraction of the gold in some gold ores may reduce the efficiency of gold-recovery processes (Cabri 1987, Chryssoulis & Cabri 1990, Harris 1990).

In the present work, we have investigated the Mössbauer spectra of a number of natural specimens of the gold ditellurides sylvanite, krennerite and calaverite, as well as synthetic krennerite and calaverite. All three gold ditellurides have similar physical and chemical properties, with the silver-to-gold ratio increasing from calaverite (0–2.8 wt.%) through krennerite (3.3–6.2 wt.%) to sylvanite (~9–13.4 wt.%) for minerals free of substituting elements (*cf.* Cabri & Rucklidge 1968). The crystal structure and chemical bonding in gold ditellurides were first studied by Tunell & Ksanda (1935, 1936, 1937), Tunell (1941), Tunell & Murata (1950), and Tunell & Pauling (1952). More recently, Pertlik (1984a, b, c) performed a detailed crystallographic study of these minerals, and van Tendeloo *et al.* (1983a,b, 1984) have studied synthetic Au–Ag ditellurides by electron diffraction. The crystal structures of these minerals are basically similar to that of cadmium iodide, although they have three different space-group symmetries (Table 1). The structures of all three minerals can be described as involving small distortions of a simple cubic arrangement of gold, silver and tellurium atoms. Each atom in the crystal structures is surrounded by six ligands. For the gold and silver atoms, the ligands are six tellurium atoms lying at the vertices of distorted octahedra. Each tellurium atom has three gold or silver atoms and three tellurium atoms as nearest neighbors.

Phase relations in the system Au–Ag–Te and their mineralogical significance have been investigated by

TABLE 1. CRYSTALLOGRAPHIC DATA FOR SPECIMENS OF SYLVANITE, CALAVERITE AND KRENNERITE SELECTED FOR STUDY*

SPECIMEN	SPACE GROUP	a(Å)	b(Å)	c(Å)	β(o)	REFERENCE
Sylvanite	$P2/c$-C^4_{2h} monoclinic	8.95(1)	4.478(5)	14.62(2)	145.35(5)	Pertlik (1984a)
M39285		8.860(4)	4.446(2)	14.640(3)	145.56(1)	this work
Krennerite	$Pma2$-C^4_{2v} orthorhombic	16.58(1)	8.849(5)	4.464(3)	-	Pertlik (1984b)
M23798		16.50(3)	8.80(2)	4.452(7)	-	this work
Calaverite	Pc monoclinic	8.76(1)	4.410(5)	10.15(1)	125.2(2)	Pertlik (1984c)
E2569		8.760(3)	4.415(1)	10.095(5)	124.84(4)	this work

* Literature data are given for comparison.

many authors (*e.g.*, Pellini 1915, Markham 1960, Luo & Klement 1962, Cabri 1965, Cabri & Rucklidge 1968, Legendre *et al.* 1980), with considerable disagreement in several important aspects, notably the status of krennerite and sylvanite and the relationship of these minerals to calaverite. There is a remarkable divergence of opinion regarding the phase relations in the vicinity of the Au_2Te_4–$AuAgTe_4$ join. On one hand, Legendre *et al.* (1980) proposed that krennerite and sylvanite are not stable phases in the system Au–Ag–Te. Their opinions have been adopted by Prince (1988) on the grounds that it "is a modern study of the whole ternary system", although Legendre *et al.* took little care to arrive at equilibrium at low temperatures. On the other hand, Cabri (1965) and other authors (*e.g.*, Markham 1960, Kelly & Goddard 1969, Afifi *et al.* 1988) have either synthesized krennerite and sylvanite or considered them to occur as stable minerals in the natural environment. The problem of the stability of krennerite and sylvanite will be addressed in more detail in the Discussion.

TABLE 2. RESULTS OF ELECTRON-MICROPROBE ANALYSES OF NATURAL DITELLURIDE SAMPLES*

MINERAL	Au (range)	Ag (range)	Te (range)	TOTAL	n
Sylvanite					
M39363	25.2(24.7-25.5)	12.6(12.4-12.8)	62.3(62.0-62.7)	100.1	4
NAGYAG	30.0(28.7-30.8)	9.0(8.8-9.3)	61.0(60.7-61.6)	100.0	10
M39285	27.4(27.1-27.6)	10.5(10.3-10.7)	61.8(61.5-62.1)	99.7	6
M19515	26.6(26.3-27.1)	11.2(11.1-11.4)	61.6(61.4-61.8)	99.4	4
Krennerite					
M15783	35.5(34.4-36.2)	5.4(5.3-5.4)	59.3(59.3-59.4)	100.2	3
M23798	35.8(35.3-36.4)	4.7(4.6-4.8)	59.1(58.7-59.5)	99.6	5
Calaverite					
E1924	41.7(41.0-42.3)	1.2(0.9-1.3)	57.6(57.1-58.0)	100.5	5
M13812	39.9(38.8-40.5)	1.9(1.8-2.1)	58.1(57.8-58.4)	99.9	4
M41543	41.3(41.0-41.8)	0.6(0.6-0.7)	57.5(57.3-57.8)	99.4	4
E2569	37.4(36.8-37.8)	3.6(3.2-4.0)	58.5(58.0-58.9)	100.0	10

* n: number of grains analyzed. Numbers in parentheses represent standard deviations. Compositions are given in wt.%.

ROM M39363. Sylvanite from Offenbánya (now Baia de Aries, Romania). Accessory phase, tennantite: Cu 39.7, Fe 1.5, Zn 6.9, Sb 6.5, As 15.2, S 27.7.

NAGYAG: Sylvanite from Nagyág (now Sacarimb, Romania), from the collections of the Institute for Mineralogy and Crystallography, University of Vienna, kindly supplied by Dr. F. Pertlik. Accessory phase, bournonite: Cu 13.0, Sb 23.2, As 1.2, Pb 41.6, S 19.4.

ROM M39285. Sylvanite from Kalgoorlie, Western Australia.

ROM M19515. Sylvanite from Nagyág.

ROM M15783. Krennerite from Nagyág. Accessory phases: altaite PbTe and seligmannite, Cu 13.2, Sb 6.9, As 12.2, Pb 45.2, S 21.0.

ROM M23798. Krennerite from Kalgoorlie, Western Australia. For part of this specimen Cabri & Rucklidge (1968) obtained the composition: Au 35.4, Ag 4.7, Te 58.3, total 98.4 wt.%.

ROM E1924. Calaverite from Cripple Creek, Colorado, USA.

ROM M13812. Calaverite from Kalgoorlie, Western Australia.

ROM M41543. Calaverite from Lamaque Mine, Bourlamaque, Quebec, Canada.

ROM E2569. Calaverite from Kalgoorlie, Western Australia. For part of this specimen Cabri & Rucklidge (1968) obtained the composition: Au 37.9, Ag 3.5, Te 57.5, Cu 0.3, Sb 0.77, total 99.97 wt.%.

EXPERIMENTAL

Most of the specimens studied are from the collection of the Royal Ontario Museum (ROM), Toronto, and will be referred to by ROM numbers. The samples usually were available as small crystals in quantities between a few milligrams and several hundred milligrams. The crystals were crushed to fine powders and filled into lucite absorber holders, to make absorbers of between 1 and 20 mm diameter, depending on the amount of material available. The absorbers usually contained between 30 and 100 mg/cm^2 of material. In addition to natural specimens, synthetic calaverite and krennerite were studied. The absorbers of the synthetic specimens were fine powders distributed uniformly over an area of 2 cm^2, the absorber thickness also being between 30 and 100 mg/cm^2.

The analysis of Debye–Scherrer X-ray diffraction photographs of sylvanite (ROM M39285, monoclinic), krennerite (ROM M23798, orthorhombic) and calaverite (ROM E2569, monoclinic) show these samples to be single-phase, with the possible exception of the sylvanite, which gave rise to an unidentified extra line. Unit-cell parameters were obtained by least-squares refinement of the powder data. The crystallographic data of representative specimens are given in Table 1.

The chemical compositions and degree of homogeneity of the samples were studied by electron-microprobe analysis (EPMA). This was especially important for samples with high contents of Ag, since the stoichiometry of the compound has a direct bearing on the interpretation of the Mössbauer spectra. The compositions were determined with a Cameca SX–50 microprobe operated at 20 kV, 20 nA, using the Au*M*α, Ag*L*α and Te*L*α X-ray lines, and native Au, Ag, as well as synthetic Bi_2Te_3 as standards. The results of the microprobe analyses are compiled in Table 2.

The ^{197}Pt sources (18-h half-life) for the ^{197}Au Mössbauer measurements were prepared by irradiating about 200 mg of enriched ^{196}Pt metal in a neutron flux of 2×10^{13} n cm^{-2}s^{-1} in the Munich Research Reactor for one or two days. The Mössbauer γ-rays were detected with a planar intrinsic Ge detector, which yielded count rates of up to 2×10^5 s^{-1} in the window of the single-channel analyzer set on the 77.3 keV line. All measurements were performed with both the source and absorber cooled to 4.2 K in a liquid He bath cryostat. The spectra were least-squares-fitted with superpositions of Lorentzian lines. All line positions and isomer shifts are given with respect to the source, *i.e.*, to ^{197}Au in Pt metal. To convert them to shifts relative to metallic gold, 1.23 mm/s must be added to the given values.

RESULTS

Typical Mössbauer spectra of the minerals studied are shown in Figure 1. The Mössbauer results for all samples are summarized in Tables 3–5. The least-squares analysis of the spectra with Lorentzian-shaped absorption lines shows that they can all be fitted with a superposition of two symmetrical quadrupole doublets, whereas only a single quadrupole doublet is inadequate. This analysis shows that in all cases two or more different sites of gold exist in the structures. The intensity ratio of the two doublets reflects the occupancy of these sites by the gold atoms and the relative values of the Lamb–Mössbauer *f*-factors for the two sites. A detailed discussion of the spectra is given below, together with additional information about the structural properties of each type of mineral studied.

Sylvanite

Sylvanite, a natural ditelluride of gold and silver with the ideal formula $AuAgTe_4$, usually deviates from stoichiometry in having a deficiency in silver. For stoichiometric sylvanite, one calculates a silver content of 13.23 wt.%. The specimens available in the present study have a silver content ranging from 9 to 12.6 wt.% (Table 2).

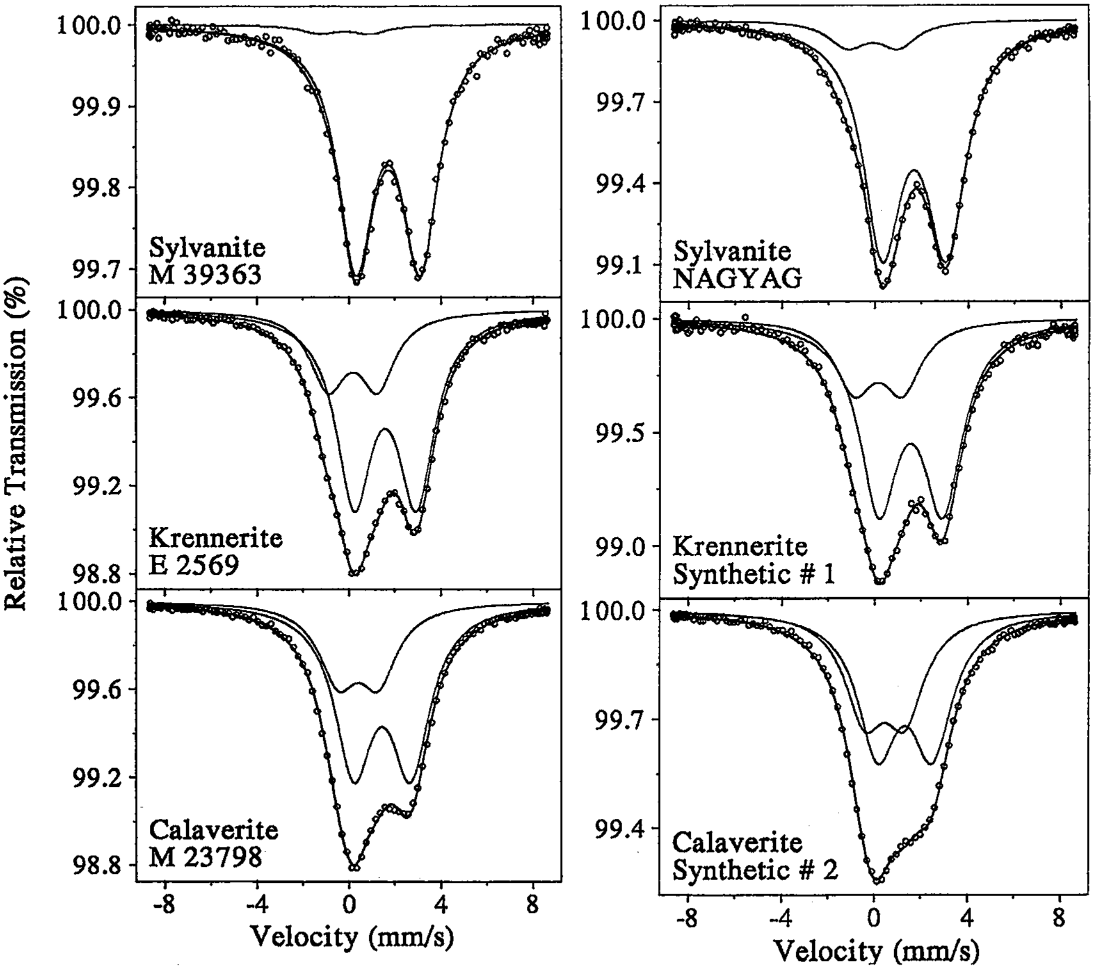

FIG. 1. ^{197}Au Mössbauer spectra of some natural and synthetic samples of sylvanite, krennerite and calaverite taken at 4.2 K. Solid curves represent the results of least-squares fits of the envelopes as well as the individual fitted quadrupole doublets.

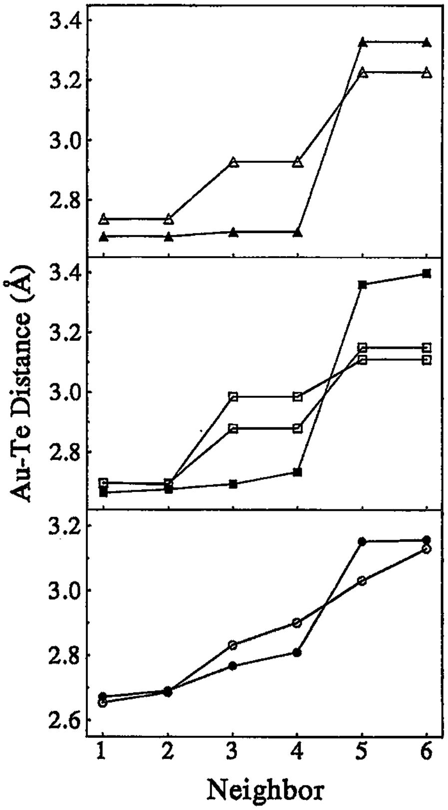

FIG. 2. Metal–tellurium distances for sylvanite, krennerite and calaverite, as given by Pertlik (1984a, b, c). Filled symbols represent (4+2) sites that are occupied by gold only, open symbols, the (2+2+2) sites occupied by silver in stoichiometric sylvanite, and by both silver and gold in the nonstoichiometric compounds, including krennerite. The metal–tellurium distances for the (2+2+2) sites are averages over the Au–Te and Ag–Te bond lengths.

TABLE 3. MÖSSBAUER PARAMETERS OF SYLVANITE*

SPECIMEN	mg/cm^2	IS(mm/s)	QS(mm/s)	W(mm/s)	RI(%)	LATICE SITE
NAGYAG	**	1.67(1)	2.75(2)	1.97(3)	89(1)	(4+2)
		-0.08(7)	2.38(10)	"	11(1)	(2+2+2)
M39363	20	1.70(1)	2.83(2)	1.87(3)	96(1)	(4+2)
		0.10***	2.19***	"	4(1)	(2+2+2)
M39285	51	1.69(1)	2.76(2)	1.90(4)	92(1)	(4+2)
		-0.12(15)	2.15(23)	"	8(1)	(2+2+2)
M19515	25	1.67(1)	2.76(2)	1.85(4)	92(2)	(4+2)
		0.10(15)	2.04(23)	"	8(2)	(2+2+2)

* IS is the isomer shift relative to the source of Au in Pt metal, QS the electric quadrupole splitting, W the full linewidth at half maximum and RI the relative intensity of the individual quadrupole doublets in the Mössbauer spectra. Numbers in parentheses give uncertainty in the last digit(s) reported.

** small crystals were used, thickness not known.
*** fixed during least squares fit.

In the monoclinic *P2/c* C^4_{2h} structure of sylvanite, the gold atoms occupy sites with a distorted octahedral symmetry and (4+2)-coordination, *i.e.*, with four tellurium neighbors at short distances of about 2.7 Å and two at rather long ones of 3.33 Å. The four close neighbors lie in a plane at the corners of a parallelogram that is nearly a square (Pertlik 1984a). Such coordination is typical for the Au^{3+} oxidation state (Haendler *et al.* 1974, Fenner & Mootz 1978). The silver atoms in sylvanite are in positions with a (2+2+2) coordination in the centers of distorted octahedra of Te atoms, which is characteristic of the Ag^+ oxidation state (Frueh 1959). The $AuTe_6$ and the $AgTe_6$ octahedra are linked by common edges and form layers parallel to the (100) plane. The unit-cell parameters of sylvanite are given in Table 1, and the bond lengths for the (4+2) and (2+2+2) sites are plotted in Figure 2.

Since sylvanite melts incongruently at a low temperature (354 ± 5°C) and because of slow equilibration below that temperature (Cabri 1965), it could not be synthesized. Only natural samples were studied. The Mössbauer spectra of sylvanite have been measured for four specimens from different locations (Fig. 1, Table 3). With the possible exception of sylvanite M39363, the spectra cannot be described by a single quadrupole doublet, even if one allows for unequal intensities of the two components, which could arise from the texture of the absorbers or an anisotropic Lamb–Mössbauer factor, although these effects are expected to cause only minor asymmetries of the quadrupole doublets for the ^{197}Au Mössbauer resonance (Prosser *et al.* 1975). An explanation of the asymmetry of the spectra due to presence of some of the gold in the form of an Au–Ag alloy also does not appear viable, since the X-ray diffractograms of the powdered samples revealed no metallic Au–Ag phase with the expected *fcc* structure. Depending on the composition, such alloys yield a single Mössbauer line with an isomer shift between –1.23 mm/s for pure metallic gold and +0.68 mm/s for dilute alloys of Au in Ag (Huray *et al.* 1971).

The spectra can best be described as superpositions of symmetrical strong and weak quadrupole doublets. The presence of two doublets requires that in addition to the gold on the (4+2) sites, some of the gold occupies the (2+2+2) sites, which normally accommodate the silver atoms. The parameters of the Mössbauer spectra obtained under this assumption are given in Table 3. The average Mössbauer parameters for the main doublet are an isomer shift IS of 1.68 ± 0.02 mm/s and a quadrupole splitting QS of 2.78 ± 0.04 mm/s, which can be attributed to Au^{3+} in the regular (4+2) sites of gold in sylvanite. The trivalent

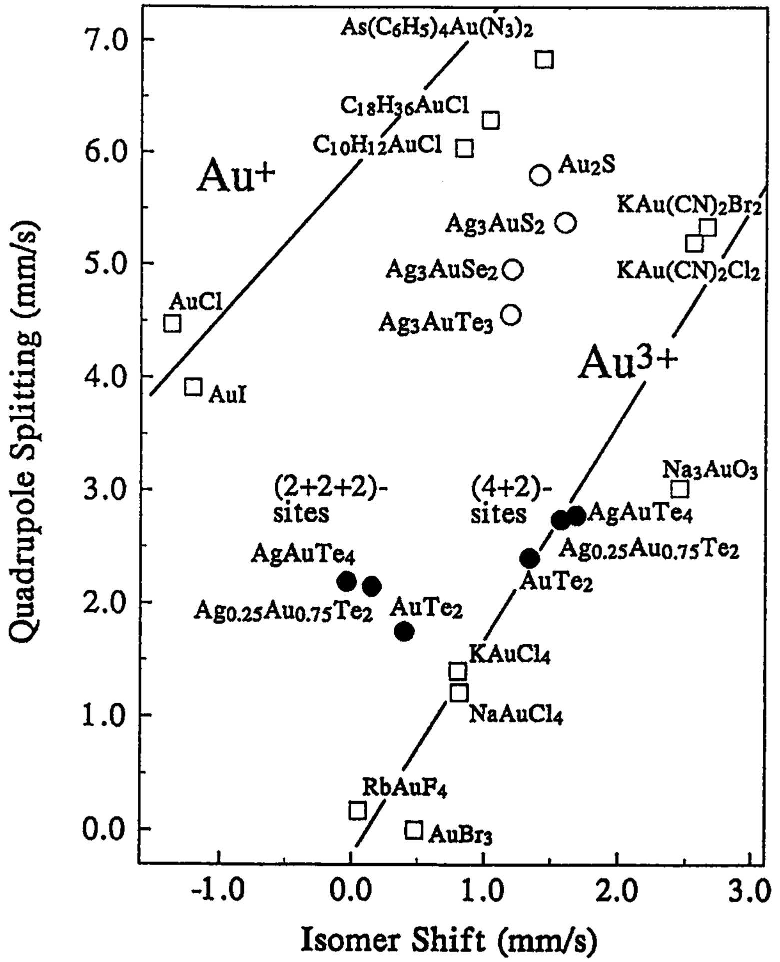

FIG. 3. Plot of the magnitude of the electric quadrupole splitting *versus* the isomer shift (relative to gold in a platinum matrix) for some Au^+ and Au^{3+} compounds, for the gold tellurides studied in this work, and for the minerals petzite (Ag_3AuTe_2), fischesserite (Ag_3AuSe_2) and uytenbogaardtite (Ag_3AuS_2).

state of gold on these sites is confirmed in Figure 3, which shows the correlations between the quadrupole splitting and isomer shift for linear Au^+ and planar Au^{3+} compounds. The weak doublet with the average parameters IS of −0.04 ± 0.11 mm/s and QS of 2.19 ± 0.17 mm/s must be associated with the gold in silver sites. The occupancy of silver sites by gold may be due to a gold content above that indicated by stoichiometry, or to a certain degree of disorder of Au and Ag between the (4+2) and (2+2+2) sites. The dominant cause can be determined by comparing the relative intensity of the weak doublet in the individual samples with the deviations of the Au/Ag ratio, as determined by microprobe analysis, from the value expected assuming stoichiometry. Such a comparison will be presented in the Discussion.

Krennerite

Whereas krennerite, $Au_{1-x}Ag_xTe_2$ (with $x \approx 0.2$), was considered a product of transformation of calaverite by Markham (1960), it was proposed as a unique species not derived by polymorphism by Cabri (1965). It contains from 3.3 to 6.2 wt.% Ag and crystallizes in the orthorhombic system, space group *Pma*2 C^4_{2v}. In krennerite, the atoms of gold can occupy three crystallographically different positions (Pertlik 1984b). One of these has a (4+2) environment of four close and two more distant Te neighbors, and is occupied by gold atoms only. The two other, fairly similar (2+2+2) sites can be occupied by either Au or Ag atoms, present in a ratio between 3:1 and 1:1 (Tunell & Ksanda 1936, Tunell & Murata 1950, Pertlik 1984b). The unit-cell parameters of krennerite are given in Table 1. The metal–tellurium distances are shown in Figure 2.

Two natural specimens and a synthetic specimen have been investigated. The Mössbauer spectra obtained can be described as a superposition of two symmetrical quadrupole doublets (Fig. 1, Table 4). As in the case of sylvanite, the doublet with the larger quadrupole splitting is ascribed to the Au(4+2) sites, and the doublet with smaller splitting, to the two different Au(2+2+2) sites. Three different quadrupole doublets, which should be expected from the crystal structure (Pertlik 1984b), could not be identified. The environments of gold on the two (2+2+2) sites must be sufficiently similar to give rise to indistinguishable Mössbauer patterns. The intensity ratio of the doublets ascribed to the Au(4+2) sites and the two Au(2+2+2) sites is close to 3:1. This result does not agree with the ratio of the gold occupancies of the respective sites. In $Au_{1-x}Ag_xTe_2$ at $x = 0.2$, this ratio should be 5:3. The discrepancy between the intensities of the Mössbauer lines and the occupancy of different Au sites can be attributed to different *f*-factors of the individual sites, as will be discussed in more detail below.

Calaverite

Calaverite $AuTe_2$ contains about 43 wt.% Au. Natural samples of calaverite commonly contain a few wt.% Ag (Cabri 1965; Table 2). The crystal structure of calaverite is monoclinic (pseudo-orthorhombic) *Pc*, and quite similar to the structure of sylvanite (Tunell & Ksanda 1935, Pertlik 1984c). In calaverite, there are two crystallographically different Au sites, which resemble the (4+2) and (2+2+2) sites in sylvanite and krennerite, although they differ less markedly from one another. In particular, the elongation of the distorted octahedra in the (4+2) sites is less pronounced in calaverite than in sylvanite and krennerite (Fig. 2).

Four natural and three synthetic specimens of calaverite were studied. Two of the spectra are shown in Figure 1. As in the case of sylvanite and krennerite, the spectra of calaverite have been fitted with a superposition of two symmetrical quadrupole doublets. The obtained parameters are given in Table 5.

By comparing the Mössbauer parameters of the two doublets with those observed in sylvanite and krennerite (Fig. 3), one can attribute the doublet with the larger isomer shift and quadrupole interaction to Au in the (4+2) site, and the doublet with the smaller isomer shift and quadrupole interaction to Au in the (2+2+2) site. The relative intensity of the (2+2+2) doublet, however, is only about 75% of the intensity of the (4+2) doublet (Fig. 1, Table 5), whereas equal intensities of the two doublets would be expected from the 1:1 occupancy of the two Au sites in stoichiometric calaverite. This situation resembles the one observed in krennerite and can again be attributed to different *f*-factors for Au on the two sites, as will be discussed in detail below.

TABLE 4. MÖSSBAUER PARAMETERS OF KRENNERITE*

SPECIMEN	(mg/cm^2)	IS(mm/s)	QS(mm/s)	W(mm/s)	RI(%)	LATTICE SITE
#1	64	1.54(2)	2.75(2)	2.02(5)	73(1)	(4+2)
		0.14(4)	2.08(6)	"	27(1)	(2+2+2)
M15783	71	1.59(2)	2.75(2)	1.97(6)	75(2)	(4+2)
		0.14(5)	2.21(8)	"	25(2)	(2+2+2)
M23798	67	1.57(1)	2.73(1)	1.89(3)	72(7)	(4+2)
		0.17(2)	2.16(3)	"	28(7)	(2+2+2)

*IS is the isomer shift relative to the source of Au in Pt metal, QS the electric quadrupole splitting, W the full linewidth at half maximum and RI the relative intensity of the individual quadrupole doublets in the Mössbauer spectra. Numbers in parentheses give uncertainty in the last digit reported.

#1. Synthetic specimen prepared by L.J. Cabri from high purity elements in vacuo, annealed for 19 days at 350°C with grinding and pelletizing. The product was confirmed to be krennerite by XRD (Guinier camera) and determined by EPMA to be homogeneous with 37.69% Au; 4.02% Ag; 58.29% Te.

TABLE 5. MÖSSBAUER PARAMETERS OF CALAVERITE*

SPECIMEN	(mg/cm^2)	IS(mm/s)	QS(mm/s)	W(mm/s)	RI(%)	LATTICE SITE
#1	34	1.32(3)	2.36(3)	2.05(5)	56(2)	(4+2)
		0.43(3)	1.75(4)	"	44(2)	(2+2+2)
#2	44	1.32(2)	2.36(2)	2.08(3)	58(2)	(4+2)
		0.44(2)	1.75(3)	"	42(2)	(2+2+2)
#3	42	1.30(2)	2.42(3)	2.18(4)	66(2)	(4+2)
		0.38(4)	1.65(6)	"	34(2)	(2+2+2)
E1924	60	1.35(1)	2.41(1)	2.03(2)	61(1)	(4+2)
		0.39(2)	1.76(2)	"	39(1)	(2+2+2)
M13812	29	1.37(3)	2.43(3)	2.05(5)	63(1)	(4+2)
		0.42(3)	1.77(5)	"	37(1)	(2+2+2)
M41543	31	1.33(3)	2.31(3)	1.97(7)	60(3)	(4+2)
		0.37(4)	1.82(6)	"	40(3)	(2+2+2)
E2569	81	1.45(2)	2.51(1)	2.02(3)	69(1)	(4+2)
		0.40(3)	1.77(3)	"	31(1)	(2+2+2)

*IS is the isomer shift relative to the source of Au in Pt metal, QS the electric quadrupole splitting, W the full linewidth at half maximum and RI the relative intensity of the individual quadrupole doublets in the Mössbauer spectra. Numbers in parentheses give uncertainty in the last digit reported.

#1. Synthetic specimen prepared at CANMET by fusing Au and Te in vacuo. The product was determined by EPMA to be homogeneous with 43.4%Au, 55.9%Te. Calaverite was confirmed by X-ray diffractometer.

#2. Synthetic calaverite containing no silver.

#3. Synthetic specimen prepared by L.J. Cabri from high purity elements in vacuo, annealed for 16 days at 350°C with grinding and pelletizing. The product was confirmed to be calaverite by XRD (Guinier camera) and determined by EPMA to be homogeneous with 41.34% Au; 1.53% Ag; 57.13%Te.

Measurements of the Lamb–Mössbauer factors

In the application of Mössbauer spectroscopy in quantitative analyses of mixtures of gold minerals, it is important to know the Lamb–Mössbauer factors for the constituent compounds. These have, therefore, been measured for a synthetic specimen of calaverite, a specimen of krennerite and a specimen of sylvanite. To this end, Mössbauer spectra of mineral absorbers of a known thickness of about 50 mg/cm^2 of the respective minerals were measured together with a reference absorber consisting of a 1 at.% Au in vanadium. With an isomer shift of +5.61 ± 0.02 mm/s, the single Mössbauer line of this reference absorber is well separated from the patterns of the ditelluride minerals. The relative intensities of the entire ditelluride pattern and the reference line can therefore be determined. The line intensities of the reference absorbers were calibrated against a metallic gold absorber of known thickness in separate measurements. The "reference absorber" technique eliminates influences of the non-resonant background in the γ-ray spectrum and electronic dead-time effects, which modify the intensities of the Mössbauer patterns.

The experiments eventually yield the ratio f(min)/f(Au met.) of the f-factors of the mineral and of metallic gold (Table 6). Using the known f-factor of Au metal, 0.189 ± 0.01 (Erickson *et al.* 1971), absolute values of the Lamb–Mössbauer factors of the gold tellurides can be derived from the measured ratios. Note that the f-factors ratios given in Table 6 were calculated from the total areas of the ditelluride spectra and therefore represent weighted averages over the (4+2) and (2+2+2) type of sites, the weight factors being determined by the respective site-occupancies.

DISCUSSION

Isomer shifts and electric quadrupole interactions

The magnitudes of the observed isomer shifts and electric quadrupole interactions are expected to relate to the local structure of the individual sites in the different minerals. The strongly elongate octahedra associated with the (4+2) gold sites are expected to give rise to larger gradients in electric field than the (2+2+2) sites. This is indeed observed (Fig. 3), although the differences are not very large. Also, note that the (4+2) sites in calaverite are less strongly elongate than those in krennerite and sylvanite. This explains why the quadrupole splitting for these sites is smaller in calaverite than in krennerite and sylvanite.

TABLE 6. SUMMARY OF MÖSSBAUER RESULTS FOR SYLVANITE, KRENNERITE AND CALAVERITE*

	(4+2) sites		(2+2+2) sites		
Mineral	IS (mm/s)	QS (mm/s)	IS (mm/s)	QS (mm/s)	f/f(Au-M)
Sylvanite	1.68(2)	2.78(4)	-0.04(11)	2.19(17)	0.65(3)
Krennerite	1.57(3)	2.74(1)	0.15(2)	2.15(7)	0.58(3)
Calaverite	1.34(8)	2.40(5)	0.40(4)	1.75(8)	0.64(3)

*IS is the average isomer shift relative to the source of Au in Pt metal, QS is the average electric quadrupole splitting, and f/fAu-M) the Lamb-Mössbauer relative to that of metallic gold; these ratios were obtained for the sylvanite specimen M39285, the krennerite specimen M23798 and the synthetic calaverite #2. Numbers in parentheses give uncertainty in the last digit(s) reported. For IS and QS they are derived from the standard deviation of individual values (Tables 3-5).

The isomer shifts in gold compounds are known (Faltens & Shirley 1970, Bartunik *et al.* 1970, Parish 1982) to increase with increasing covalency of the gold–ligand bonds, since increasing covalency transfers *s* electrons from the ligands to the gold. The larger isomer shift of the (4+2) sites (Fig. 3), compared to the (2+2+2) sites, thus shows that the (4+2) sites are the more covalent. This is reflected in the short bond-length of the four close neighbors (Fig. 2). Similarly, the minor differences between the isomer shifts for each type of site indicate that along the series sylvanite – krennerite – calaverite, the covalency decreases for the (4+2) sites, whereas it increases for the (2+2+2) sites (Fig. 3). This can again be explained qualitatively by differences in bond distances among the compounds (Fig. 2). One should keep in mind, however, that the true Au–Te distances for the (2+2+2) sites in krennerite and sylvanite are not known, since the X-ray structure analysis (Pertlik 1984a, b) yielded only averages over the Au–Te and Ag–Te distances for the sites occupied randomly by both elements.

These arguments apply independently of whether the gold is monovalent or trivalent. As has been pointed out by Pertlik (1984b) for krennerite, it is reasonable to consider gold in the (4+2) sites in this compound as Au^{3+}, since the arrangement of four close equatorial and two more distant apical ligands resembles the square planar environment typical of Au^{3+} compounds. For such compounds, there is a nearly linear correlation between the electric quadrupole interaction and the isomer shifts (Bartunik *et al.* 1970, Parish 1982), which is shown in Figure 3. The Mössbauer data for the (4+2) sites in the gold ditellurides fall very well onto the correlation line (Fig. 3) for Au^{3+} compounds, confirming the notion that the (4+2) sites in all gold ditellurides contain trivalent gold, whose bonding resembles that in planar Au^{3+} compounds with a moderate degree of bond covalency.

The situation for the (2+2+2) sites is more intriguing. First of all, the similarity of the Mössbauer parameters for Au on these sites indicates that the nearest-neighbor environment of the gold atoms on (2+2+2) sites is very similar in sylvanite, krennerite and calaverite. The (2+2+2) sites, with two Te neighbors at about 2.7 Å and the other four further away, though not by very much (Fig. 2), could be considered as resembling the linear coordination typical for Au^+ compounds. Such an Au–Te coordination exists, for instance, in petzite, Ag_3AuTe_2, but there the two closest Te neighbors are at 2.54 Å from the gold (Frueh 1959). This short distance can explain why the ^{197}Au Mössbauer spectra of petzite yield a larger quadrupole splitting and isomer shift (Wagner *et al.* 1992; see also Fig. 3) than those observed for the (2+2+2) sites in the ditellurides. An ultimate decision in favor of Au^+ or Au^{3+} for the gold in the (2+2+2) sites of the ditellurides seems to be impossible on the basis of either the crystal structure or the Mössbauer data, particularly since the Mössbauer spectra do not yield the sign of the electric quadrupole splitting, which is expected to be negative for monovalent and positive for trivalent gold. In fact, the gold may be in an electronic state that eludes the simple classification of trivalent or monovalent.

Previous Mössbauer work on synthetic $AuTe_2$ and gold–tellurium alloys with a concentration of gold down to 1 at.% Au (Sham *et al.* 1979) has yielded broad asymmetrical quadrupole patterns resembling those observed in this work for calaverite. These were, however, interpreted in terms of a single quadrupole doublet, whose asymmetry was attributed to the Goldanskii–Karyagin effect (see, *e.g.*, Goldanskii & Makarov 1968). The special nuclear properties of the 77.3 keV transition in ^{197}Au (Prosser *et al.* 1975), however, cause both the Goldanskii–Karyagin effect and asymmetries of quadrupole doublets caused by texture of the absorbers to be very small. Considering the poor solubility of Au in Te metal (Okamoto & Massalski 1984), as well as the poor solubility of Te in $AuTe_2$ (Cabri 1965), it appears probable that all Au–Te alloys studied by Sham *et al.* (1979) were mixtures of $AuTe_2$ and metallic Te, whereas the statistical quality of the spectra was insufficient to reveal the presence of more than one Au site in $AuTe_2$.

Electron-diffraction studies (van Tendeloo *et al.* 1983a, b, 1984) have shown that synthetic calaverite, krennerite and sylvanite exhibit commensurate and incommensurate lattice-distortion waves. The present Mössbauer spectra of gold in these compounds could, however, be interpreted by the two-site model without recourse to the distributions of the hyperfine parameters that would be expected to arise from incommensurate or long-wave commensurate lattice distortions. The most sensitive case for the detection of such effects should be stoichiometric sylvanite, in which only the (4+2) site is populated. The Mössbauer spectrum of the sylvanite specimen closest to stoichiometric composition (ROM M39363, Fig.1, Table 3) could be fitted with a linewidth practically equal to the natural linewidth ($W_0 = 1.88 \pm 0.01$ mm/s, Erickson *et al.* 1971) and only a very weak (2+2+2) doublet. The linewidth obtained for calaverite generally is slightly larger (Table 5), but one cannot rule out that this minor broadening is due to finite thickness of the absorber. We thus conclude that the distortion waves in the structure have no observable influence on the ^{197}Au Mössbauer spectra, which shows that their amplitudes are too small to cause noticeable modulations of the Mössbauer parameters. The distributions of gradients in electric fields previously deduced from Mössbauer spectra of ^{129}I formed in the β^--decay of ^{129}Te in $AuTe_2$ (Langouche *et al.* 1986) may have arisen from the existence of several inequivalent Te sites in the structure of calaverite (Tunell & Ksanda 1935, Pertlik 1984c), rather than the lattice-distortion waves.

Line intensities, Lamb–Mössbauer factors and site occupancy

The relative intensity of the quadrupole doublets attributed to (2+2+2) sites increases along the series sylvanite – krennerite – calaverite (Tables 3–5). In stoichiometric sylvanite, the (2+2+2) sites should be occupied by silver only, and therefore should not appear at all in the Mössbauer spectra. In krennerite of the ideal composition, $Au_{0.8}Ag_{0.2}Te_2$ (Cabri 1965), the intensity ratio of the (2+2+2) and the (4+2) doublets should be 3:5, whereas a 1:1 ratio is expected for stoichiometric calaverite. If a comparison is made of the relative intensities actually observed (Tables 3–5) with these expectations, one should take into account that none of the samples, except the synthetic calaverite, is stoichiometric. Assuming that silver occupies only (2+2+2) sites, the composition of the nonstoichiometric Au–Ag ditellurides can be expressed as $^{(4+2)}Au^{(2+2+2)}[Ag_{1-y}Au_y]Te_2$, with $y = 1$ for stoichiometric calaverite and $y = 0$ for stoichiometric sylvanite. In Figure 4, the ratio $r = I(2+2+2)/I(4+2)$ of the intensities (*i.e.*, areas) of the two quadrupole doublets in the Mössbauer spectra is plotted against the parameter y. The values of y were calculated from the electron-microprobe data for the individual specimens (Table 2). One expects r to be equal to y if the Lamb–Mössbauer factors of the (2+2+2) and the (4+2) sites are equal, and if there is no disorder causing some Ag atoms to occupy (4+2) sites. If the Lamb–Mössbauer factors of the (2+2+2) and (4+2) sites differ, one expects $r = y{\cdot}f(2+2+2)/f(4+2)$, where the ratio $f(2+2+2)/f(4+2)$ could itself depend on the composition of the individual minerals. If $f(2+2+2)/f(4+2)$ is independent of composition, and if the silver occupies only (2+2+2) sites, the data points of all samples of calaverite, krennerite and sylvanite should fall on the straight line connecting the origin and the point for stoichiometric $AuTe_2$ in Figure 4. Within the limits of error, this is indeed the case for all natural minerals except one sample of calaverite, two of krennerite and one of sylvanite, which all fall slightly but not decisively below the straight line. In any case, the data give no indication

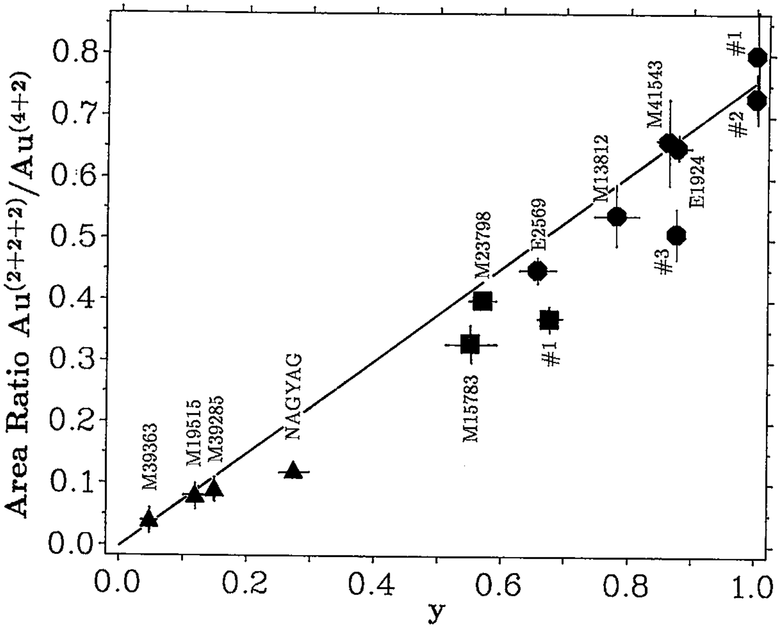

FIG. 4. Relationship between the gold occupancy y of the (2+2+2) sites in $^{(4+2)}Au^{(2+2+2)}[Ag_{1-y}Au_y]Te_2$ and the intensity ratio of the Mössbauer quadrupole doublets attributed to the (2+2+2) and (4+2) sites. Triangles represent sylvanite, dots, krennerite, and squares, calaverite. The sample number is also given for each data point.

that any silver in krennerite or sylvanite occupies (4+2) sites, which would cause the points to lie above the straight line in Figure 4.

From the slope of the straight line in Figure 4, one finds that $f(2+2+2)/f(4+2)$ is equal to 0.75 ± 0.02. Within the limit of error, our data are compatible with the notion that this ratio is the same for all three minerals. The fact that the data points for the non-stoichiometric calaverite, krennerite and sylvanite that lie slightly below the straight line may, however, be taken as an indication that the true correlation between r and y is a slightly sagging curve. This could be explained by a slight decrease of the ratio $f(2+2+2)/f(4+2)$ with decreasing gold and increasing silver content. Only more data could confirm or disprove this notion. The mean f-factors for the three minerals are also nearly equal, with that of calaverite being virtually equal to that of sylvanite (Table 6). This is surprising, since the occupancy of the (2+2+2) sites by half of the Au atoms in calaverite should result in a 15% reduction of the mean f-factor of this mineral with respect to that of sylvanite. That this is not observed indicates a slight increase in the overall stiffness of the structure between sylvanite and calaverite.

The stability of krennerite and sylvanite

The Mössbauer results presented confirm the existence of sylvanite and krennerite as distinctive mineral phases, thus corroborating the previous X-ray crystallographic work. The Mössbauer data shed no light on the question of whether sylvanite and krennerite are truly stable phases, as the studies of Markham (1960), Cabri (1965), Cabri & Rucklidge (1968), Kelly & Goddard (1969), Pertlik (1984a, b, c), van Tendeloo *et al.* (1983a, b, 1984) show, or unstable, since Legendre *et al.* (1980) could not synthesize them in short-term cooling experiments. Indeed, Legendre *et al.* deride the studies of Markham (1960) and Cabri (1965) as follows: "On ne peut manquer d'être frappé par ailleurs par l'état d'esprit de ces travaux, essentiellement "minéralogique" puisque l'existence des composés correspondant aux espèces minéralogiques telle que la sylvanite ou la krennerite est affirmée *a priori* alors que leur synthèse nous a semblé impossible, comme elle l'avait été pour Pellini (1915)" (sic). Had Legendre *et al.* understood the papers of Markham and Cabri, they would have known why they, along with Pellini, had not succeeded in synthetizing krennerite and sylvanite. The Legendre *et al.* synthesis consisted of placing mixtures of lumps or powders of the pure elements in sealed and evacuated quartz tubes in a vertical furnace with the following heat treatment: 48 hours at 500°C, then about 12 hours at 600, 700, 800, and 900°C, then 48 hours at 1000°C and 1 hour at 1100°C, all this followed by cooling to room temperature at a rate of 5°C/min. The samples were then subjected to differential thermal analysis (DTA), and to limited examinations of polished sections and examinations by X-ray diffraction to identify coexisting phases. Cabri (1965), on the other hand, reported that equilibrium takes a long time to achieve at low temperatures, and that samples heated at 270°C for as long as 168 days, with several grinding and pelletizing operations, are still not considered as having attained equilibrium. Cabri also documented experiments on the calaverite – sylvanite join that indicate that grinding and pelletizing operations at intervals during the annealing stage are *essential* to speed up reaction rates. Grinding and pelletizing do help attain reaction, but the mechanical distortion during grinding can lead to metastable starting conditions, which thereby introduces a small possibility for metastable products; but then, so does the strain generated in cooling a multiphase ingot. It is, therefore, quite understandable that Legendre *et al.* did not find traces of krennerite or sylvanite in their DTA diagrams, because these incongruently melting phases (krennerite at 382 ± 2°C; sylvanite at 345 ± 5°C) would not readily form during the rapid descent from the liquidus within the fused solid mass. Note also that van Tendeloo *et al.* (1983a, b, 1984) reported the successful synthesis of all three Au–Ag ditellurides, although they did not elaborate on methods of phase characterization other than mentioning XRD and electron diffraction. We consider it highly likely that their synthetic krennerite and sylvanite consisted of two or more phases, but they were able to detach single phases for their XRD and electron-diffraction studies.

The answer to a question such as "Is sylvanite stable?" might be given by first reviewing the nature of its common occurrence and its mineral associations in Au–Ag telluride deposits (*cf.* Afifi *et al.* 1988). Several mineralogical studies from various ore deposits (*e.g.*, Kelly & Goddard 1969, Porter & Ripley 1985, Ahmad *et al.* 1987) demonstrate by fluid-inclusion thermometry that temperatures of telluride deposition were typically below 250°C, and in keeping with the phase relations of Markham (1960) and Cabri (1965). In addition, Cabri & Rucklidge (1968) reported electron-microprobe data on several samples of calaverite, krennerite and sylvanite, as well as on the composition and homogeneity of sylvanite [in the field sylvanite + Te + L, in a sample synthesized by Cabri (1965)] and krennerite synthesized in 1966. The fact that there is excellent agreement of the sylvanite composition (in the three-phase field above) with what had been previously determined by using the XRD determinative curve (*d*-values *versus* Ag content) for sylvanite is further evidence of the stability of sylvanite. Cabri & Rucklidge in addition documented that some natural Au–Ag tellurides may contain, not unexpectedly, minor quantities of elements such as Cu and Sb, requiring changes in interpretations of phase equilibria, if based on the pure system Au–Ag–Te.

CONCLUSIONS

The gold ditelluride minerals calaverite, krennerite and sylvanite have been found to exhibit distinctive Mössbauer spectra that can be explained by different amounts of gold on the two sites of (4+2) and (2+2+2) type, with the former occupied only by gold, and the latter by gold and silver. In all gold ditellurides, the Lamb–Mössbauer factors of the (2+2+2) sites were found to be only 75% or less of those of the (4+2) sites, whereas the mean Lamb–Mössbauer factors of the ditellurides are all about 60% of those of metallic gold. The Mössbauer results presented contribute to our understanding of the crystal chemistry of the mineral phases of the gold ditellurides, thus corroborating the previous X-ray crystallographic work. The controversial question of the stability of sylvanite and krennerite has also been addressed.

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