1
2
3
4
5 **Stable Te isotope fractionation in tellurium-bearing minerals from precious**
6 **metal hydrothermal ore deposits**
7
8
9
10
11
12
13

14 Andrew P. Fornadel^{a,b}, Paul G. Spry^{a*}, Mojghan A. Haghnegahdar^c, Edwin A. Schauble^c, Simon E.
15 Jackson^d, Stuart J. Mills^e
16

17 ^a*Iowa State University, Dept. of Geological and Atmospheric Sciences, 253 Science I, Ames, IA 50011,*
18 *U.S.A.*

19 ^b*Shimadzu Scientific Instruments, 7102 Riverwood Drive, Columbia, MD 21046, U.S.A.*

20 ^c*University of California, Los Angeles, Dept. of Earth, Planetary, and Space Sciences, 595 Charles Young*
21 *Drive East, Los Angeles, CA 90095-1567, U.S.A.*

22 ^d*Geological Survey of Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada*

23 ^e*Museum Victoria, GPO Box 666, Melbourne, Victoria 3001, Australia*
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40

41 *corresponding author – pgspry@iastate.edu

Abstract

The tellurium isotope compositions of naturally-occurring tellurides, native tellurium, and tellurites were measured by multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-MS) and compared to theoretical values for equilibrium mass-dependent isotopic fractionation of representative Te-bearing species estimated with first-principles thermodynamic calculations. Calculated fractionation models suggest that $^{130/125}\text{Te}$ fractionations as large as 4 ‰ occur at 100° C between coexisting Te(IV) and Te(II) or Te(0) compounds, and smaller, typically < 1 ‰ fractionations occur between coexisting Te(-I) or Te(-II) (Au,Ag)Te₂ minerals (i.e., calaverite, krennerite) and (Au,Ag)₂Te minerals (i.e., petzite, hessite). In general, $^{130/125}\text{Te}$ is predicted to be higher for more oxidized species, and lower for reduced species.

Tellurides in the system Au-Ag-Te and native tellurium analyzed in this study have values of $\delta^{130/125}\text{Te} = -1.54$ to 0.44 ‰ and $\delta^{130/125}\text{Te} = -0.74$ to 0.16 ‰, respectively, whereas those for tellurites (tellurite, paratellurite, emmonsite and poughite) range from $\delta^{130/125}\text{Te} = -1.58$ to 0.59 ‰. Thus, the isotopic composition for both oxidized and reduced species are broadly coincident. Calculations of per mil isotopic variation per amu for each sample suggest that mass-dependent processes are responsible for fractionation. In one sample of coexisting primary native tellurium and secondary emmonsite, $\delta^{130/125}\text{Te}$ compositions were identical. The coincidence of $\delta^{130/125}\text{Te}$ between all oxidized and reduced species in this study and the apparent lack of isotopic fractionation between native tellurium and emmonsite in one sample suggest that oxidation processes cause little to no fractionation.

Because Te is predominantly transported as an oxidized aqueous phase or as a reduced vapor phase under hydrothermal conditions, either a reduction of oxidized Te in hydrothermal liquids or deposition of Te from a reduced vapor to a solid is necessary to form the common tellurides and native tellurium in ore-forming systems. Our data suggest that these sorts of reactions during mineralization may account for a ~3 ‰ range of $\delta^{130/125}\text{Te}$ values. Based on the data ranges for Te minerals from various ore deposits, the underpinning geologic processes responsible for mineralization seem to have primary control on the magnitude of fractionation, with tellurides in epithermal gold deposits showing a narrower range of isotope values than those in orogenic gold and volcanogenic massive sulfide deposits.

1. INTRODUCTION

Stable isotope variability in transition and group 16 (chalcogen) elements can be > 5 ‰ (e.g., O, S, Se, Cu, Fe, and Cr) in terrestrial samples and provide information on their provenance, as well as biological, geochemical, and physical processes responsible for transport and precipitation of the element (e.g., Ohmoto and Rye, 1979; Bullen and Eisenhauer, 2009; Layton-Matthews et al., 2013). Isotope fractionation between phases or species depends on several factors including redox state, relative mass

1 difference, bond strengths, temperature, and reaction kinetics (e.g., Johnson, 2004; Johnson et al., 2004;
2 Schauble et al., 2009).

3 Of the chalcogens, oxygen and sulfur isotope systematics are well established and can vary on the
4 order of 10's of per mil; even at elevated temperatures (e.g., ~350° C), Se isotope fractionation ($\delta^{82/76}\text{Se}$)
5 in ore deposits can vary by up to 11.5 ‰ (e.g., Layton-Matthews et al., 2013). For Se, this fractionation is
6 driven, in part, by changes in oxidation state, with the greatest fractionation produced by microbial or
7 abiotic reduction of Se-oxyanions (Johnson, 2004). Compared to O, S, and Se, modern studies on Te
8 isotope variability in geologic and otherwise naturally-occurring samples are limited in number.

9 Tellurium has eight stable isotopes: ^{120}Te (0.10% nominal abundance), ^{122}Te (2.60%), ^{123}Te
10 (0.91%), ^{124}Te (4.82%), ^{125}Te (7.14%), ^{126}Te (19.0%), ^{128}Te (31.6%), and ^{130}Te (33.7%) and exhibits six
11 oxidation states, -II, -I, 0, +II, +IV, and +VI (Fehr et al., 2004; Fornadel et al., 2014; Hoefs, 2015). The
12 mass difference between the lightest and heaviest isotopes of Te is 8.3%, which is similar to that for S
13 (6.3%) and Se (10.8%). Although the +IV and +VI states are the most common in oxidizing environments
14 at the Earth's surface in tellurites and tellurates, respectively (e.g., Otto Mountain, California; Housely et
15 al., 2011), Te is commonly found in the -II state as metal tellurides and as native tellurium (e.g., Te(0)) in
16 magmatic and hydrothermal ore deposits, including epithermal and orogenic gold deposits (e.g., Cook et
17 al., 2009). Therefore, it is expected that Te should also exhibit resolvable fractionation as its geochemical
18 relatives, O, S, and Se.

19 Tellurium is an unusual element in that its abundance in the universe is greater than that of any
20 other element with atomic number >40 (Anders and Ebihara, 1982); however, it is one of the rarest
21 elements in the Earth's crust (0.4 to 12 ppb; McDonough and Sun, 1995; Reimann and de Caritat, 1998)
22 and seawater (up to 9×10^{-4} ppb; Andreae, 1984). For most unaltered magmatic terrestrial rocks, Te
23 ranges in concentration from a few ppb to 10's of ppb (e.g., volcanic rocks, ultramafic rocks, gabbro,
24 syenite, basalt) (Beaty and Manuel, 1973; Reimann and de Caritat, 1998; Yi et al., 2000; Forrest et al.,
25 2009), but granitoids may contain hundreds of ppb Te (e.g., Beaty and Manuel, 1973). Orogenic and
26 epithermal gold deposits, both of which are commonly associated with alkaline igneous rocks, can contain
27 several percent Te in some ore zones (e.g., Sandaowanzi Au-Te deposit, China, Liu et al., 2013).

28 Early Te isotope studies by Smithers and Krouse (1968) measured Te isotopes with a gas source,
29 as opposed to a plasma source, mass spectrometer, specifically, using thermal ionization mass
30 spectrometers (TIMS) and negative-TIMS (N-TIMS) (e.g., Smith et al., 1978). However, there was
31 appreciable analytical uncertainty with these instruments due to the moderately high first-ionization
32 energy ($869.3 \text{ kJ mol}^{-1}$, ~9 eV) for Te. Smithers and Krouse (1968) focused on the kinetics of Te isotope
33 exchange, while measuring some samples from hydrothermal ore systems, whereas Smith et al. (1978)
34 focused on Te isotope variability within ore systems. From those two studies, Smith et al. (1978) reported

1 the largest fractionation in natural samples, up to 9.4‰ in $^{130/125}\text{Te}$. Nevertheless, mass discrimination due
2 to the use of an electron multiplier coupled to the TIMS instrument by Smith et al. (1978), as well as the
3 overall analytical uncertainty were sufficiently high as to deem that the observed isotopic variability was
4 associated with a large range uncertainty (Lee and Halliday, 1995). Rather, Lee and Halliday (1995)
5 demonstrated far better precision in measuring Te isotope composition with ICP magnetic sector multi-
6 collector mass spectrometry. Indeed, Fehr et al. (2004) demonstrated up to one to two orders of
7 magnitude better precision using multicollector-inductively coupled plasma-mass spectrometry (MC-ICP-
8 MS), with a two-stage liquid chromatographic procedure, compared to TIMS, for Te isotope analysis.
9 Using this technique, Fehr et al. (2004, 2006, 2009) determined the Te isotope composition of various
10 meteorites. Fehr et al. (2004) and Fehr et al. (2005) also determined the Te isotope composition of two
11 unlocated terrestrial samples of pyrite and pyrrhotite, and five samples of Archean sedimentary pyrite,
12 respectively. Note that Fehr et al. (2004, 2006) internally normalized their Te isotope data, which did not
13 provide information relating to mass-dependent Te isotope fractionation of their samples, whereas some
14 data of Fehr et al. (2005, 2009) used different procedures to correct for instrumental mass fractionation.

15 Other more recent Te isotope studies include those of Baesman et al. (2007) and Moynier et al.
16 (2008), the former of which analyzed the isotope ratios of native tellurium crystals formed as a result of
17 the reduction of aqueous Te(IV) by cysteine-HCl. Their study revealed sizable fractionation caused by
18 abiotic reduction, with an enrichment factor of -0.47‰ amu^{-1} . Isotope exchange of Te with
19 dicyclohexano-18-crown-6 as a solvent was shown by Moynier et al. (2008) to produce mass-independent
20 isotope fractionation controlled by nuclear field shift, a process Moynier et al. (2009) argued could
21 explain the Te isotope anomalies measured by Fehr et al. (2006, 2009).

22 Studies of the isotope geochemistry of Te may shed further light on the metallogeny of
23 epithermal and orogenic gold telluride-bearing deposits and, indirectly, the geochemistry of Au, because
24 Te coexists with Au in many ore-related minerals. This study focuses on the most common minerals in
25 the system Au-Ag-Te such as calaverite (AuTe_2), krennerite $[(\text{Au},\text{Ag})\text{Te}_2]$, sylvanite $[(\text{Au},\text{Ag})_2\text{Te}_4]$,
26 petzite (Ag_3AuTe_2), native tellurium, hessite (AgTe_2), and stützite ($\text{Ag}_{5-x}\text{Te}_3$). Analyses of tellurites
27 (TeO_3^{2-}), which form mostly from the oxidation and weathering of tellurides and native tellurium, likely
28 exhibit the effect that changes in redox state have on Te isotope fractionation. Fornadel et al. (2014)
29 demonstrated a range of $\delta^{130/125}\text{Te}$ values of $\sim 1.6\text{‰}$ for the total fractionation for Au-Ag tellurides and
30 native tellurium ($n = 32$) from hydrothermal-magmatic ore systems, relative to a pure, elemental Te
31 standard made from JMC Te metal. They showed that Te isotopes fractionate appreciably at the elevated
32 temperatures of ore-forming conditions (i.e., $150\text{--}400^\circ\text{C}$) and minerals from the same ore district can
33 show disparate $\delta^{130/125}\text{Te}$ values. Furthermore, the Te fractionation reported in Fornadel et al. (2014)
34 showed little evidence for mass independent fractionation.

The present study evaluates the: 1) Abiotic mechanisms that produce mass-dependent Te isotope fractionation in hydrothermal ore deposits; e.g., redox behavior and liquid-vapor separation (because Te is transported in both the liquid and vapor phases), diffusion and exchange kinetics, as well as deposition and transportation processes; 2) Relationship between equilibrium isotope fractionation, determined by theoretical calculations, using vibrational spectra and force-field models for various Te species, and the empirical data derived by MC-ICP-MS analysis; and 3) Implications of Te isotope fractionation for research on the formation of precious metal telluride deposits.

2. SAMPLES

To develop an understanding of Te isotope systematics and the magnitude of total fractionation, tellurides (Te^{2-}) and native tellurium (Te^0) from the hypogene environment were obtained predominantly from museum collections (American Museum of Natural History, Royal Ontario Museum, Denver Museum of Nature and Science, Smithsonian Institution National Museum of Natural History). Additionally, the data obtained here complement 32 isotope analyses from Fornadel et al. (2014). For tellurites (Te^{4+}), samples are secondary accumulations of Te that resulted from the weathering of primary, reduced Te mineral assemblages and were provided by the Museum Victoria, Australia and the Denver Museum of Nature and Science. To assess fractionation factors between coexisting minerals, samples were selected that contain intergrown tellurides and native tellurium. One sample of coexisting native tellurium and a tellurite (emmonsite) was also analyzed. A summary of samples, mineralogy, and sample location is given in Table 1.

Although many of the samples are not precisely spatially located beyond the detail of the general locality of their collection, when possible, multiple samples were collected from the same site (e.g., from within Cripple Creek district, Colorado) to assess isotopic variability within a given ore system. Based on metallogenetic descriptions of many of these deposits, it is likely that the tellurides and native tellurium formed by hypogene processes whereas the tellurates and tellurites are secondary minerals (e.g., Thompson et al., 1985; Ahmad et al., 1987; Richards, 1995; Jensen and Barton, 2000; Kelley and Luddington, 2002; Kampf et al., 2010).

3. SAMPLE PREPARATION, METHODS FOR ISOTOPE ANALYSES, AND POTENTIAL MATRIX EFFECTS

The methodology for sample preparation, ion exchange chromatography and MC-ICP-MS isotope analyses is summarized here but described, in greater detail, in Fornadel et al. (2014). When necessary, samples were mounted in one inch round, polished epoxy mounts for microsampling and petrographic and/or electron microprobe analyses. The mounted materials were sampled using a

micromill for subsequent dissolution. Other samples, typically tellurites, were identified by X-ray diffraction and separated by hand from their matrices. The samples were digested and purified by ion exchange chromatography as described in Fornadel et al. (2014).

Isotopic measurements were made at the Geological Survey of Canada using a Nu Instruments Nu Plasma MC-ICP-MS equipped a Cetac ASX-110FR autosampler. All operating parameters, such as gas flow rates, as well as acceleration and focusing voltages, were optimized daily. Samples were measured under solution nebulization, wet-plasma conditions, three to five times in 2 ppm Te solutions, doped with 1 ppm Cd for mass bias correction. To ensure that Sn was not interfering with Te during isotope analyses, we also monitored for Sn interferences with Te and found that there were no significant concentrations of Sn in any of our samples. Because there is no internationally-recognized standard for Te isotopes, all measurements were made relative to an in-house, gravimetrically prepared Te standard made from 99.9999% Alfa-Aesar Puratronic tellurium metal. It is important to note that our standard is arbitrary in the sense that a comparison of the isotopic composition of the Te in the standard and any given sample reported here has no direct implication for the provenance of terrestrial Te, unlike other standards such as V-CDT for sulfur isotope analysis.

Each reported isotope ratio for Te is presented using standard delta notation (equation 1). Delta values are calculated relative to ^{125}Te because ^{125}Te is the lowest mass of Te that has reasonable natural abundance and no isobaric interferences.

$$\delta_{x/^{125}\text{Te}} = \left[\left(\frac{(^x\text{Te}/^{125}\text{Te})_{\text{sample}}}{(^x\text{Te}/^{125}\text{Te})_{\text{std}}} \right) - 1 \right] \times 1000 \quad (1)$$

where $^x\text{Te}/^{125}\text{Te}_{\text{sample}}$ is the isotope ratio for the sample, $^x\text{Te}/^{125}\text{Te}_{\text{std}}$ the isotope ratio of the standard, and x = the mass of the isotope of interest, 122, 124, 126, 128, or 130.

Uncertainties are reported as two standard deviations from the mean of the analyses for each sample. This is based upon the long term reproducibility of Te isotope data as assessed by repeated analysis of our Te isotope standard against a similar Te solution prepared at the Geological Survey of Canada over a period of 30 months, which yielded reproducibility of $\pm 0.09\%$ for $\delta^{130/125}\text{Te}$ as well as repeated analyses of some samples included as part of the study.

The methodology used here to obtain the Te isotope data for members of the system Au-Ag-Te (Au-Ag tellurides and native tellurium) is the same as that developed by Fornadel et al. (2014). Our column chromatography procedure is similar to the first stage of a two-stage procedure for isolating Te from matrix elements as conducted by Fehr et al. (2004). We also applied the methodology of Fornadel et al. (2014) to obtain Te isotope data for the tellurites emmonsite ($\text{Fe}_2(\text{TeO}_3)_3 \cdot 2\text{H}_2\text{O}$), paratellurite (TeO_2), poughite ($\text{Fe}_2(\text{TeO}_3)(\text{SO}_4)(\text{H}_2\text{O})_2 \cdot \text{H}_2\text{O}$), and tellurite (TeO_2) *sensu stricto*. Although matrix elements other than Au, Ag, and Te elements can alter mass bias and potentially result in erroneous isotope fractionation,

the matrix effect of Fe in the isotopic analyses of Te in emmonsite and poughite was considered negligible since Fe is mostly not retained in the anion-exchange resin when eluted by the 2M HCl solution that was used here (Manuela Fehr, written communication, November 7, 2016).

4. THEORETICAL METHODS

Equilibrium mass-dependent fractionation of tellurium isotopes in crystals and molecules is estimated from the differences in the vibrational energies of isotopically substituted molecules (Urey, 1947). We use first-principles electronic structure calculations to model the vibrational frequencies of gas-phase molecules, solutes, and crystalline species. Molecular and aqueous species are modeled in the gas phase (*in vacuo*). For this purpose, clusters representing the crystal structures including calaverite (Schutte and de Boer 1988) and native tellurium (Bradley, 1924) were created. For calaverite, the average structure was used, and the incommensurate structural modulation was ignored. To account for longer-range effects in crystalline species, model domains are expanded to include nearest neighbors, next-nearest neighbors, and 3rd-nearest neighbor coordination shells, with fixed, partially charged atoms added outside this domain to approximately satisfy dangling bonds at the edge of each cluster; very similar to the truncation method used previously in studies of equilibrium carbon, magnesium, iron and calcium isotope fractionation (e.g., Rustad et al., 2010). The range of substances modeled focuses on the most common and economically significant Te-bearing minerals, molecules, and aqueous species, including tellurides such as calaverite and native tellurium. Aqueous Te(IV) species are modeled because previous thermodynamic studies suggested that aqueous Te(IV) species, for example H_2TeO_3 , might play a role in transporting tellurium to form Te(-II) bearing crystals such as gold-silver tellurides (Grundler et al., 2013). Mass-dependent isotope fractionations are expected to favor high $^{\text{heavy}}\text{Te}/^{\text{light}}\text{Te}$ in oxidized species for most elements, including tellurium (e.g., Smithers and Krouse, 1968).

The electronic structure model results reported here are determined with hybrid density-functional theory (B3LYP; Becke, 1993) and split-valence Def2-SVPD basis sets (Rappoport and Fillip, 2010), which appears to perform reasonably well in the species of interest, matching measured vibrational frequencies and molecular structures in gas-phase molecules such as H_2Te . For cluster models of crystalline species, dangling bonds at the edge of the model domain are terminated with artificial, non-canonically charged hydrogen nuclei, with partial charges set to correspond to the Pauling bond order of each dangling bond. These partial-charge hydrogens are arranged on the outside of each cluster at a distance of 1.5 Å along each truncated bond. Outer-shell and partial-charge hydrogens are modeled with a small basis set (LANL2DZ) (Manchester et al., 1995). Rustad et al. (2010) used a similar-sized 3-21G basis set in their preceding work. The geometry of each molecule was allowed to relax to a minimum-

energy configuration for the B3LYP/Def2-SVPD model electronic structure. For clusters, only the tellurium site and nearest-neighbor sites were allowed to relax; outer-shell atoms and partial-charge hydrogens were held fixed at experimentally determined positions. Vibrational frequencies were determined on relaxed structures.

In general, fractionation factors using medium-sized basis sets (e.g., Def2-SVPD) for molecules and the core regions of crystalline clusters are similar to results from models with larger basis sets (e.g., cc-pVTZ).

Calculations were made with Gaussian09 software (Gaussian 09: EM64L-G09RevD.01, Frisch et al., 2013) on the UCLA Hoffman2 computing cluster.

5. RESULTS

5.1 Theoretical Fractionation

Table 2 presents calculated isotope fractionations for gas-phase molecules and crystals, based on B3LYP/Def2-SVPD models. The values in the parenthesis are from Smithers and Krouse (1968). Calculated fractionations for gas-phase species are in good agreement with previously reported estimates (Smithers and Krouse, 1968). Calculated fractionations also show trends typical for isotope fractionation in other elements (Fig. 1). Equilibrium fractionation between the H₂Te vapor and telluride phases is expected to be small, especially at magmatic-hydrothermal temperatures expected for telluride mineralization, where $\Delta^{130/125}\text{Te}$ equals $\delta^{130/125}\text{Te}$ of a given mineral minus $\delta^{130/125}\text{Te}$ of the H₂Te vapor, and is predicted to be $\approx 0.5\text{‰}$ or less. This approximate value can be shown for the following calculation using the mineral pair calaverite-hessite at T = 373K:

$$\Delta^{130/125}\text{Te} = (\delta^{130/125}\text{Te (calaverite)} - \delta^{130/125}\text{Te (H}_2\text{Te)}) * 1000$$

$$\Delta^{130/125}\text{Te (calaverite)} = (1.00141 - 1.00104) * 1000 \approx 0.4\text{‰}$$

$$\Delta^{130/125}\text{Te} = (\delta^{130/125}\text{Te (hessite)} - \delta^{130/125}\text{Te (H}_2\text{Te)}) * 1000$$

$$\Delta^{130/125}\text{Te (hessite)} = (1.00104 - 1.00104) * 1000 \approx 0.0\text{‰}$$

In contrast, reduction or oxidation of Te is predicted to induce much larger isotope fractionation, especially when the highest oxidation states (IV or VI) are present. Among gas species, the Te(IV) molecules TeF₆ and H₆TeO₆ have the highest $^{130}\text{Te}/^{125}\text{Te}$ at equilibrium, while Te₂ and H₂Te are lowest

with a 6 ‰ difference at 100° C. In general, $^{130}\text{Te}/^{125}\text{Te}$ is higher for more oxidized species, and lower for reduced species. $^{130}\text{Te}/^{125}\text{Te}$ fractionations are expected to be ~3-4 ‰ (at 100° C) between coexisting Te(IV) and Te(-II) compounds (Haghnegahdar et al., 2013). Calculated fractionations decrease with increasing temperature in all models.

5.2 Overall isotopic ranges and trends in natural samples

Tellurium isotope ratios for 61 samples (29 from this study, 32 from Fornadel et al., 2014) were obtained from 36 tellurides, 14 samples of native tellurium, and 11 tellurites. The 29 data obtained in the present study are given in Table 1. The largest isotopic variations are shown for $\delta^{130/125}\text{Te}$ (Fig. 2). Therefore, discussion of the isotope results will focus on values and variations reported in terms of $\delta^{130/125}\text{Te}$. The $\delta^{130/125}\text{Te}$ values for tellurides in the combined studies range from -1.54 to 0.51 ‰, for native tellurium -0.87 to 0.64 ‰, and for tellurites -1.58 to 0.59 ‰ (i.e., emmonsite, paratellurite, tellurite). The $\delta^{130/125}\text{Te}$ values for calaverite span the majority of the entire range of $\delta^{130/125}\text{Te}$ values (-1.54 to 0.51 ‰), whereas values for krennerite are clustered around -0.84 to -0.05 ‰. The isotopic range for stützite is -0.27 to 0.40 ‰, whereas that for sylvanite is -0.78 to 0.44 ‰.

Although the $\delta^{130/125}\text{Te}$ values range from -1.58 to 0.59 ‰ for the oxidized species, with the exception of one sample each of poughite (0.59 ± 0.07 ‰) and emmonsite (0.25 ± 0.11 ‰), the remaining nine samples all have $\delta^{130/125}\text{Te}$ values ranging between -1.59 and -0.12 ‰.

Per mil per amu calculations for all samples show a 1:1 relationship for all isotope pairs within the standard error of the analyses (Fig. 3).

5.3 Te mineral pairs

Samples of intergrown telluride mineral pairs sylvanite-krennerite and two samples of sylvanite-stützite were analyzed to assess isotope partitioning between coexisting phases, with one native tellurium-tellurite pair measured to evaluate the potential effects of oxidation on Te isotope values (Fig. 4). Sylvanite (-0.30 ± 0.06) is isotopically heavier than coexisting krennerite, (-0.55 ± 0.06 ‰). For the two sylvanite-stützite pairs, one pair is isotopically identical within uncertainty with $\delta^{130/125}\text{Te} = -0.37 \pm 0.21$ ‰ for stützite and -0.15 ± 0.10 for sylvanite. The other pair shows sylvanite ($\delta^{130/125}\text{Te} = -0.27 \pm 0.08$ ‰) to be slightly isotopically heavier than stützite (-0.18 ± 0.01 ‰).

The isotopic compositions of the native tellurium-emmonsite pair is of particular interest because native tellurium is considered a primary mineral and emmonsite a secondary weathering product formed by supergene processes. The grains that were sampled were ~4 cm apart from one another in the hand specimen, providing for the opportunity to assess the effects of low-temperature oxidation on Te isotope fractionation, if the emmonsite is assumed to have oxidized from spatially-related tellurides. On the other

hand, it is possible that the oxidized mineral species originated elsewhere and was transported and deposited by supergene processes. The native tellurium and emmonsite have identical isotope compositions with values of $\delta^{130/125}\text{Te}$ of -0.74 ± 0.10 and -0.74 ± 0.07 ‰, respectively.

6. DISCUSSION

6.1 Mass-dependent and mass-independent fractionation

In a plot of $\delta^{128/125}\text{Te}$ versus $\delta^{130/125}\text{Te}$, there is a 1:1 relationship of per mil per amu for this isotope pair (Fig. 3) demonstrating that fractionating processes in these samples are dominated by mass-dependent processes. Although fellow chalcogens oxygen and sulfur (e.g., Thiemens and Heidenreich, 1983; Pavlov and Kasting, 2002) show disequilibrium mass-independent fractionation (MIF) in certain environments, it has not yet been definitively observed in tellurium (see also Fehr et al., 2006; Fehr et al. 2009; Moynier et al., 2009 for discussions of potential Te-MIF in cosmochemical samples). However, it should be noted that Fehr et al. (2005) measured Te isotope compositions of terrestrial pyrite samples that displayed mass-independent S isotope compositions.

6.2 Crystallographic effects on fractionation

Isotope partitioning between two coexisting solids, in large part, depends on the nature and strength of the bonds between the element of interest and the other atoms in the crystal lattice. Some work has been done on the relationship between bond strengths and isotope partitioning in metal-chalcogenide systems (e.g., Bachinski, 1969; Zheng, 1991). In both metal oxides and sulfides, there is a strong correlation between the strength of the bonds in each coexisting mineral and the isotope partitioning between mineral phases. By correlation, it is expected that other metal-chalcogenides would follow a similar relationship.

Calculated isotope fractionations in the simplest Te(-II) telluride crystals appear to show a strong, roughly linear correlation with bond strength. In general, $^{130}\text{Te}/^{125}\text{Te}$ is higher in tellurides with shorter bond lengths, which presumably corresponds to higher bond strength. The calculated isotope value for calaverite is higher than that for hessite (Table 2), which is consistent with the higher bond strength for Au-Te bonds ($237.2 \pm 14.6 \text{ kJ mol}^{-1}$) versus Ag-Te bonds ($195.8 \pm 14.6 \text{ kJ mol}^{-1}$) (Lide and Haynes, 2009), however isotopic values of natural samples of hessite and calaverite overlap and do not show the predicted trend. This should not be surprising since the temperatures of formation for the tellurides in different samples collected here formed at different temperatures. Although *ab initio* calculations can be made for more simple tellurium-bearing species, such as we have done here for calaverite, hessite, and native tellurium, as well as some gases, we have been unable to calculate values for the Au-Ag tellurides,

krennerite, sylvanite, and stützite. Nevertheless, the investigated mineral pair sylvanite-krennerite shows resolvable Te isotope differences (Fig. 4), indicating that there are, in some cases, crystallographic controls on isotope partitioning between coexisting telluride pairs. For two analyzed sylvanite-stützite pairs, their $\delta^{130/125}\text{Te}$ values are coincident within the uncertainty of analysis.

6.3 Isotopic differences among tellurides, native tellurium, and tellurites

The total measured range of fractionation, in terms of $\delta^{130/125}\text{Te}$, between the reduced species (i.e., tellurides and native tellurium) is 2.18 ‰, which is nearly the same as the 2.17 ‰ total fractionation between the oxidized species (i.e., tellurites) (Fig. 2, Table 1). However, whereas the tellurides and native tellurium span the majority of that range, tellurites tend to be isotopically light. Two samples, one of emmonsite (9659-2) and one of poughite (M34162) have positive values of $\delta^{130/125}\text{Te} = 0.25 \pm 0.11$ ‰ and $\delta^{130/125}\text{Te} = 0.59 \pm 0.07$ ‰, respectively. If these samples are considered outliers, the isotopic range of the tellurites is restricted to 1.44 ‰, ranging from $\delta^{130/125}\text{Te} = -1.58$ to -0.14 ‰. Overall, this follows the trend of decreasing fractionation with increasing atomic mass within a group of the periodic table (e.g., Bigeleisen and Mayer, 1947; Urey 1947), because the range of isotopic composition of Te is considerably smaller than the natural isotopic range observed for O, S, and Se (Ohmoto and Rye, 1979; Criss and Taylor, 1986; Layton-Matthews et al., 2013).

The total range of isotopic fractionation of both the oxidized and reduced/neutral Te minerals (i.e., the coincidence of the isotopic composition for reduced, neutral, and oxidized Te minerals), for the minerals studied here, coupled with the isotope data collected from coexisting native tellurium and emmonsite, suggest that reduction-oxidation reactions affect fractionation in only a minor way, if at all. Previous studies have demonstrated the pronounced effects of reduction/oxidation and element transport on elements in ore-forming and weathering environments such as Cu (e.g., Markl et al., 2006) and Se (e.g., Johnson, 2004). These studies highlight that changes in redox state can yield significant isotopic fractionation.

In the case of Se, which we consider a Te analogue because of its position in the same group of the periodic table, Johnson (2004) suggested that abiotic processes could lead to fractionation of Se by up to 12 ‰ during stepwise reduction of Se(VI) to Se(IV), and a further 12 ‰ during reduction from Se(IV) to Se(0). Likewise, bacterial processes may cause up to 5 and 9 ‰ fractionation during these respective reduction reactions. Similarly, Baesman et al. (2007) demonstrated that Se- and Te-fixing bacteria can respire by Te(VI) or Te(IV) reduction to Te(0), leading to 0.4 to 1.0 ‰ amu^{-1} fractionation of Te.

In contrast to Se fractionation during reduction, Johnson et al. (2000) and Johnson (2004) showed that low-temperature, abiotic oxidation reactions, from Se(0) to Se(IV), along with Se(IV) to Se(VI) yield little to no fractionation. Johnson (2004) suggested that the kinetic isotope effect associated with breaking

Se-O bonds during reduction is pronounced, whereas it is relatively insignificant during oxidation. In light of the data from this study, particularly the overlap in isotopic range between primary and secondary Te species as well as the identical delta value of a native tellurium-emmonsite pair, our results suggest that Te displays similar geochemical behavior to Se during oxidation, in that abiotic oxidation during weathering of tellurides may result in little to no discernible isotope fractionation. Further studies of Te fractionation and speciation during oxidation/reduction in a controlled environment are necessary, however, to confirm this suggestion.

There are no experimental or empirical data that can be used to evaluate the isotopic fractionation expected as a result of Te(-II) oxidation. The coincidence of $\delta^{130/125}\text{Te}$ values for tellurides, tellurites, and tellurates, some of which, presumably, formed as a result of oxidation of Te(-II) in telluride minerals, suggests small, if any, fractionation. Small isotopic fractionation of Te(-II) is consistent with the small fractionation in S isotope values during S(-II) oxidation (Fry et al., 1988), and the assumption made by Johnson (2004) that there is only small isotope fractionation associated with the oxidation of Se(-II).

6.4 Comparison of theoretical fractionations to empirical data

The predicted fractionations among various compounds that are likely to be present in these hydrothermal ore systems (Fig. 1) are on the same order (2-3 ‰) as the variations observed in natural samples. However, the theoretical calculations predict appreciable fractionation during oxidation and reduction (e.g., a comparison of beta factors for H_2TeO_3 and native Te), but only minor fractionations are observed in natural samples of coexisting oxidized and reduced/neutral Te species (Fig. 4). In general, measured fractionations and isotope abundance variability are not easily explained by any predicted equilibrium fractionations associated with reduction of oxidized Te-species in hydrothermal solutions. This disparity may reflect isotopic disequilibrium during the oxidation process, but it could also indicate that reduction/precipitation reactions are not widespread in telluride ore genesis. In principle, quantitative or near-quantitative reduction and precipitation of an oxidized species in solution could also lead to muted observed fractionations (as discussed in section 6.5.2 below). In that case, the observed variability would reflect variability in the tellurium source rather than fractionation associated with the mineralization reactions. At present, there is not enough known about variations in the isotopic compositions of tellurium sources, or possible fractionations associated with tellurium mobilization from the source, to evaluate this possibility.

6.5 Factors affecting Te isotopes in hydrothermal ore deposits

Of note are the ranges of Te isotope values in tellurides when discriminated by the locality of sample collection, which is related to the style of hydrothermal mineralization (Fig. 5). Most of the data

presented here originate from epithermal systems related to the relatively shallow emplacement of alkaline igneous rocks (e.g., Cripple Creek, Boulder County, La Plata district, etc.). However, there are other ore styles in which tellurides occur, such as the orogenic/mesothermal mineralization at Kalgoorlie (Australia) and Savodinski (Russia), and the Mattagami Lake volcanogenic massive sulfide (VMS) deposit (Canada). Discriminating the data by deposit type enables the assessment of commonalities in the conditions of mineralization for each deposit and their effect on the isotopic composition. The general characteristics for some of the major ore bodies and districts are listed in Table 3.

6.5.1 Temperature of formation

As the magnitude of equilibrium isotopic fractionation is dependent on temperature (i.e., $1/T^2$), we expected that the range in fractionation within a given deposit would be controlled, in part, by the temperature at which the deposit formed. Temperatures of formation of mineralization were constrained based on fluid inclusion data collected from mineralized quartz veins.

Of the deposits studied here, the majority were epithermal and host veins that were mineralized over a temperature range of 130-270° C (Table 3). The temperatures reported at Mattagami (230-290° C; Costa et al., 1983) are coincident with the higher range of temperatures in the epithermal systems, such as the Boulder County district (Table 3), whereas pressure-corrected temperatures at Kalgoorlie may exceed 400° C (Table 3, Phillips and Groves, 1983). The expected trend of decreasing total fractionation with increasing temperature (i.e., $1/T^2$) was not observed in the samples studied here. In fact, the deposits that formed at the highest temperatures (Kalgoorlie and Mattagami) showed the largest range in overall fractionation, whereas some of those that formed at lower temperatures showed the smallest ranges (e.g., La Plata).

6.5.2 Phase separation (e.g., boiling, effervescence)

Thermodynamic models as well as empirical evidence suggest that Te can be transported in appreciable quantities in the vapor phase (e.g., Grundler et al., 2013). Due to the effects of phase change on the isotopic signature of other elements (e.g., the effect on O isotope composition resulting from the evaporation and condensation of water, as described by, for example Taylor (1979)), it could be expected that phase separation during mineralization could induce larger Te isotope fractionations. However, this is not necessarily the case.

Of the deposits studied here, evidence for phase separation in the ore-forming fluids was deduced by the presence or absence of vapor-rich fluid inclusions coexisting with liquid-rich fluid inclusions as reported in the literature. The ore fluids associated with deposits in the Boulder County and La Plata districts, as well as Mattagami, showed no evidence for boiling, whereas those at Cripple Creek and

Kalgoorlie contained vapor-rich fluid inclusions coexisting with aqueous fluid inclusions, suggesting that phase separation took place during mineralization (Table 3). If the Te vapor condenses into liquid upon cooling in a closed system then the process of phase separation will not produce isotopic fractionation. However, if the hydrothermal system is open and vapor phase migrates away from the liquid and condenses elsewhere this would be conducive to isotope fractionation. Whether or not the lighter isotope preferentially fractionates into the vapor phase remains unclear without experimental studies. However, dramatic isotopic shifts during phase separation have been shown in other isotope systems (e.g., sulfur, McKibben and Eldridge, 1990). Nonetheless, there is little correlation between the magnitude of overall range of Te isotope compositions and the occurrence of boiling during mineralization. Deposits exhibiting phase separation demonstrate both narrow (e.g., Boulder County) and wide (e.g., Kalgoorlie) ranges in Te isotope values, as do the deposits that show no evidence for phase separation (e.g., La Plata, narrow range; and Mattagami, wide range). This suggests that phase separation is not a primary control on the magnitude of isotope fractionation in a given ore system.

6.5.3 Deposit metallogeny

The main trend that discriminates the magnitude of fractionation within a deposit seems to be related to the mode of ore formation. The $\delta^{130/125}\text{Te}$ values for tellurides and native tellurium in epithermal deposits, such as Cripple Creek (with the exception of one light value) and the Boulder County district, are clustered tightly about each other, whereas those measured from orogenic (Kalgoorlie) and VMS-style mineralization (Mattagami) exhibit a larger spread in isotope values.

In the case of the source rocks from which the metals are derived, the mineralization styles differ widely. In epithermal deposits, it is generally accepted that the source of the metals and the heat engine which drives fluid flow is a spatially-related, shallowly-emplaced igneous pluton. In VMS systems, ore fluids are composed of magmatic fluids with a variable seawater input, with metals derived both from igneous rocks and from the extensive leaching of seafloor basalts (e.g., Franklin et al., 2005). It appears that source rocks and the duration of the mineralization process likely affect values of $\delta^{130/125}\text{Te}$ more than the other variables such as T, and phase separation. Models for the formation of orogenic systems invoke the derivation of metals and ore fluids from the devolatilization of upper greenschist facies rocks (or even higher metamorphic grades), with fluids flowing and mineralization occurring along lengthy geologic structures (e.g., Goldfarb et al., 2005). The effects of water-rock interaction have been long-noted for the exchange of elements, including oxygen in bulk rock and metals, such as copper, in acid mine drainage (e.g., Johnson, 2002), as well as in light stable isotopes (e.g., C and O, Banner and Hanson, 1990). The data presented here suggest that increased interaction between host-rocks and ore fluids in orogenic and

VMS deposits may induce a larger fractionation than in epithermal systems where fluids are locally derived from an intrusion.

6.6 Te fractionation during Au-(Ag-) telluride mineralization

Until the recent experiments of Grundler et al. (2013), which were conducted at temperatures from 90 to 250° C, knowledge of the aqueous Te species in the system Te-O-H, and the stability of species in the systems Au-Te-Cl-S-O-H and Ag-Te-Cl-S-O-H up to 300° C, including the “common” precious metal tellurides and native tellurium, relied primarily on the thermodynamic calculations of Saunders and May (1986), Ahmad et al. (1987), Afifi et al. (1988), Jaireth (1991), Zhang and Spry (1994), McPhail (1995), Cook et al. (2009), and Zhao et al. (2009). These thermodynamic studies showed that tellurides form under relatively-reducing conditions (below the magnetite-hematite buffer), and that the stability of native tellurium overlaps the magnetite-hematite buffer (e.g., Grundler et al., 2013). The stability field of calaverite broadly overlaps that of pyrite whereas that for stützite overlaps the pyrite-pyrrhotite join. The aqueous Te species in equilibrium with these tellurides (oxidation state of -II) are $\text{H}_2\text{Te(aq)}$ and HTe^- , which also have an oxidation state of -II. However, thermodynamic modeling, coupled with experimental data, suggest that the dominant Te-bearing species in hydrothermal solutions at elevated temperatures are oxidized, such as H_2TeO_3 and HTeO_3^- , and that the stability of oxidized aqueous Te species increases with temperature (Grunder et al., 2013). Recently, Etschmann et al. (2016) showed that Te (IV) chloride complexes are not important species under most geological conditions and that they are only stable at very low pHs.

On the basis of thermodynamic modeling, McPhail (1995) suggested that Te partitions into the vapor phase rather than the aqueous phase, a conclusion proposed earlier by Symonds (1992). This was later confirmed by thermodynamic modeling of Grundler et al. (2013), which showed a preferential partitioning of Te into the vapor phase at acidic to neutral pHs under moderately reducing conditions. Field based studies of Greenland and Aruscavage (1986), Larocque et al., (2008), and Fulignati and Sbrana (1998) also support the concept that Te can be transported in the vapor phase.

The implication of the current understanding of the geochemical behavior of Te under hydrothermal conditions is that, to precipitate relatively common tellurides under typical temperatures and pressures, either a phase change from a reduced, dominantly vapor Te species to a solid telluride phase, or a reduction reaction from a Te(IV) and/or Te(VI) to Te(-II) species must occur. Furthermore, the differing volatilities of Se and Te account for their release from a subducted epithermal ore source rock at different temperatures and pressures (Saunders and Brueseke, 2012). Based on the isotopic behavior of Se and S reduction reactions are likely to induce fractionation in Te under hydrothermal conditions.

Although Cu isotope values vary between the hypogene and supergene environments (Mathur et al., 2009), leaching and oxidation of tellurides to form tellurites and tellurates may also cause fractionation. However, this did not appear to be the case for the native Te and emmonsite sample studied here where there was no discernible isotopic fraction between the mineral pair.

Grundler et al. (2013) reported that Te and Au concentrations in >200° C, basic, CO₂-rich hydrothermal fluids from the epithermal Lihir Au deposit (Simmons and Brown, 2006), coincided with their predictions from thermodynamic modeling with fluids containing 4 ppb Te and 13 ppb Au. They also noted that elevated Te concentrations, as measured from fluid inclusions from other deposits, develop under highly reducing and highly oxidizing conditions.

If Te is transported in hydrothermal fluids in the oxidized state (e.g., H₂TeO₃) as predicted by Grundler et al. (2013), then reduction to form Au tellurides could occur by fluid mixing or fluid-rock interaction via the following reaction:

or by a modification of another reaction proposed by Grundler et al. (2013):

Grundler et al. (2013) proposed that tellurium transported under reducing conditions is transported as polytelluride complexes (e.g., Te₂²⁻) and that gold telluride is precipitated during cooling of hydrothermal fluids by a reaction of the type:

Calculated ¹³⁰Te/¹²⁵Te ratios in Te(IV) species (TeO₃²⁻) are predicted to be 3-4‰ higher than reduced Te-species such as calaverite (AuTe₂), hessite (Ag₂Te), krennerite ((Au,Ag)Te₂), altaite (PbTe), and petzite (Ag₃AuTe₂) at 100° C, suggesting that strong isotopic fractionation is likely if Te(IV) species play the role of transporter of tellurium to hydrothermal deposits (Haghnegahdar et al., 2013). Kinetic control of fractionation, or quantitative precipitation of aqueous tellurium species, could potentially act to make observed fractionations smaller than would be predicted at equilibrium.

6.7 Comparison to Se isotopes in ore-forming systems

Layton-Matthews et al. (2013) revealed variability of Se isotopes in ore-forming systems, specifically in two VMS deposits and one volcanic sediment-hosted massive sulfide deposit. It is a matter of debate as to whether the Se in these deposits was derived from magmatic sources or assimilated from the host rock during sulfide formation. Layton-Matthews et al. (2013) coupled Se isotope analysis with analyses of stable isotopes of S and Pb to assess the provenance and mechanism for concentration of the Se in the three deposits.

In their study, Layton-Matthews et al. (2013) analyzed the isotopes of Se bound as Se^{2-} within sulfides and found that the three deposits had a rather large range of $\delta^{82/76}\text{Se}$ of -10.2 to 0.7 ‰. Based on the Se concentrations and host geology, they conclude that in two of the systems, Se was sourced primarily from magmatic exsolution or scavenging of Se from magmatic sulfides. In these two systems, $\delta^{82/76}\text{Se}$ values ranged from -3.8 to 0.7 ‰. In the other system, the majority of the Se was scavenged by hot, hydrothermal fluids from a sedimentary source with a minor magmatic input and the $\delta^{82/76}\text{Se}$ values were much more negative $\delta^{82/76}\text{Se} = -10.2$ to -2.3‰ . Thus, the range of Se fractionation observed in magmatic systems is approximately half of that for Se sourced from sedimentary rocks.

The relatively narrow range of Te isotope compositions presented here is similar to that of magmatic Se reported in Layton-Matthews et al. (2013), and possibly reflects a magmatic source of Te in the deposits for which Te isotopes were analyzed. Furthermore, the magnitude of the range of Se isotope values, which is larger in samples for which Se was scavenged from host rock than for those of magmatic origin, may reflect the same processes by which Te isotope values are wider in range in deposits subjected to extensive water-rock interaction.

The $\delta^{130/125}\text{Te}$ values reported here range from -1.54 to 0.64 ‰ ($-0.31 - 0.11 \text{‰ amu}^{-1}$; i.e., 0.42‰ amu^{-1}) for tellurides and native tellurium, which is smaller, but similar in range, than that for magmatic Se at $\delta^{82/76}\text{Se} = -3.8$ to 0.7‰ ($-0.63 - 0.12 \text{‰ amu}^{-1}$; i.e., 0.75‰ amu^{-1}). For a given locality (e.g., Kalgoorlie), the range of fractionation is 1.35‰ for $\delta^{130/125}\text{Te}$. Thus, expected fractionation of tellurides, native tellurium, tellurites, and tellurates is on the order of 2 ‰. The decrease in fractionation magnitude may be caused by an increase in mass between Te and Se. Nevertheless, fractionation of these elements can be on the order of one per mil or greater in ore-forming systems. Note that the observed largest natural range of $\delta^{82/76}\text{Se} = 12.9$ to 7.5‰ for carbonaceous chert and kerogen in the Yutangba Se deposit, China (Wen and Carignan, 2011).

7. CONCLUSIONS

Thermodynamic models demonstrate appreciable Te isotope fractionation between a coexisting mineral or aqueous phase and a hypothetical Te vapor. $^{130}\text{Te}/^{125}\text{Te}$ is predicted to be higher for oxidized species. Calculated isotope fractionations show an apparent correlation between isotopic substitution and

1 bond strength in simple telluride crystals, indicating a strong relationship between crystal structure, bond
2 strength, and isotopic properties.

3 MC-ICP-MS measurements of Te isotopes in tellurides in the system Au-Ag-Te and native
4 tellurium show $\delta^{130/125}\text{Te}$ values ranging from -1.54 to 0.51 ‰ for tellurides, -0.87 to 0.64 for native
5 tellurium, and -1.58 to 0.59 for tellurites. The overlap of these ranges and the isotopic coincidence of the
6 emmonsite-Te pair tentatively suggest that oxidation processes are not responsible for sizable Te isotope
7 fractionation. However, it should be noted here that if the two outliers are removed from this study (i.e.,
8 emmonsite at 0.25 ‰ and poughite at 0.59 ‰), all of the tellurite data are isotopically negative,
9 indicating, perhaps, that fractionation during oxidation is somewhat preferential to the light Te isotopes.

10 Between individual ore deposits containing abundant Te, there does not seem to be a direct
11 correlation between temperature of formation nor the effects of phase separation on the overall magnitude
12 of Te isotope fractionation. There may exist a relationship between the source rocks and the degree of
13 water-rock interaction during the mineralization process that controls overall Te isotope fractionation. In
14 general, epithermal deposits that are genetically related to nearby igneous source rock demonstrated
15 smaller ranges in isotopic values, whereas those deposits that involved extensive water-rock interaction
16 and leaching of host rocks, (i.e., VMS, orogenic) demonstrated larger ranges in $\delta^{130/125}\text{Te}$.

17 The isotope fractionation observed in primary tellurides and native tellurium can be explained by
18 reduction of an oxidized aqueous phase. The range is coincident with that predicted by our models for
19 reduction of H_2TeO_3 to telluride. Reduction fractionation is also observed in bacterial reduction processes
20 as well as abiotic experiments (Smithers and Krouse, 1968; Baesman et al. 2007). However, carefully
21 controlled laboratory experiments involving reduction-oxidation of tellurium and analyzing sequential
22 aliquots for isotope ratios is necessary to confirm this hypothesis.

23 24 **ACKNOWLEDGEMENTS**

25
26 We thank Whitey Hagadorn at the Denver Museum of Natural Science, who graciously allowed
27 us access to the museum's mineral collection, which provided many samples for this study. Others were
28 provided by the American Museum of Natural History, Royal Ontario Museum, the Smithsonian Institute
29 National Museum of Natural History, and Jiajun Lai (China University of Geosciences). Isabelle Girard at
30 the Geological Survey of Canada (Ottawa) is especially thanked for her tireless assistance with all
31 analytical aspects of this project and for discussing matrix effects on isotope compositions. This project
32 was funded by a grant through the National Science Foundation (Award #1047671). The reviews and
33 editorial comments of Manuela Fehr, Frederic Moynier, Jim Saunders, and an anonymous reviewer were
34 greatly appreciated and significantly helped to improve the quality of the manuscript.

Figures

Figure 1 – Calculated fractionation factors for the ^{130}Te - ^{125}Te isotope pair of various molecules and solid Te species with respect to a hypothetical atomic Te vapor. In the figure, the single data points for TeF_6 , TeO_3^{2-} , H_2Te , and Te_2 at 373K are from Smithers and Krouse (1968).

Figure 2 – Range of fractionation for various Te minerals from this study and from Fornadel et al. (2014). In general, oxidized species are at the top of the figure and native tellurium and tellurides are at the bottom. Each point represents an individual sample and the bars represent the two standard deviation analytical uncertainty. Ideal formulas for minerals are given in Table 1.

Figure 3 – Values of $^{130/125}\text{Te}$ and $^{128/125}\text{Te}$ expressed as per mil per amu. Each point represents one sample and two standard deviation error bars are shown for each analysis. The dashed line depicts an ideal 1:1 relationship and is nearly indistinguishable from a linear regression calculated from the data as $y = 1.0048x - 0.0029$, $r^2 = 0.9914$. Includes data from Fornadel et al. (2014).

Figure 4 – Isotope analyses for coexisting Te mineral pairs. Note that the upper-most pair represents an oxidized (emmonsite) and a relatively reduced (native tellurium) pair, whereas the other pairs are for tellurides in the system Au-Ag-Te. Error bars represent two standard deviation of the mean of multiple analyses. Ideal formulas for minerals are given in Table 1.

Figure 5 – Isotope analyses of tellurides and native tellurium discriminated by deposit locality for which more than one sample was analyzed. Deposit descriptions given in Table 3. Error bars represent two standard deviation of the mean of multiple analyses. Data are from this study and from Fornadel et al. (2014). Ideal formulas for minerals are given in Table 1.

REFERENCES

- Afifi A.M., Kelly W.C. and Essene E.J. (1988) Phase relations among tellurides, sulfides, and oxides, Pt. II, Applications to telluride-bearing ore deposits. *Econ. Geol.* **83**, 395-405.
- Ahmad M., Solomon M. and Walsh J.L. (1987) Mineralogical and geochemical studies of the Emperor gold telluride deposit, Fiji. *Econ. Geol.* **82**, 345-370.
- Anders E. and Ebihara M. (1982) Solar system abundances of the elements. *Geochim. Cosmochim. Acta* **46**, 2363-2380.
- Andreae M.O. (1984) Determination of inorganic tellurium species in natural waters. *Anal. Chem.* **56**, 2064-2066.

- Bachinski, D.J. (1969) Bond strength and sulfur isotopic fractionation in coexisting sulfides. *Econ. Geol.* **64**, 56-65.
- Baesman S.M., Bullen T.D., Dewald J., Zhang D., Curran S., Islan F.S., Beveridge T.J. and Oremland R. S. (2007) Formation of tellurium nanocrystals during anaerobic growth of bacteria that use Te oxyanions as respiratory electron acceptors. *Appl. Envir. Microbio.* **73**, 2135-2143.
- Banner J.L and Hanson G.N. (1990) Calculation of simultaneous isotopic and trace element variations during water-rock interaction with applications to carbonate diagenesis. *Geochim Cosmochim Acta* **54**, 3123-3137.
- Beaty R.D. and Manuel O.K. (1973) Tellurium in rocks. *Chem. Geol.* **12**, 155-159.
- Becke A.D. (1993) Density – functional thermochemistry: III the role of exact exchange. *Chem. Phys.* **15**, 261-267.
- Bigeleisen J. and Mayer M.G. (1947) Calculation of equilibrium constants for isotopic exchange reactions. *J. Chem. Phys.* **15**, 261-267.
- Bradley A. (1924) The crystal structures of the rhombohedral forms of selenium and tellurium. *Phil. Mag.* **48**, 285.
- Bullen, T.D. and Eisenhauer, A. (2009) Metal stable isotopes in low-temperature systems. *Elements* **5**, 349-352.
- Cook N.J., Ciobanu C.L., Spry P.G. and Voudouris P. (2009) Understanding gold-(silver)-telluride-(selenide) mineral deposits. *Episodes* **32**, 249-263.
- Costa U.R., Barnett R.L. and Kerrich R. (1983) The Mattagami Lake mine Archean Zn-Cu sulfide deposit, Quebec: Hydrothermal coprecipitation of talc and sulfides in a sea-floor brine pool – evidence from geochemistry, $^{18}\text{O}/^{16}\text{O}$, and mineral chemistry. *Econ. Geol.* **78**, 1144-1203.
- CRC Handbook of Chemistry and Physics 2009-2010 (eds D.R. Lide, and W.M. Haynes), CRC Press, Boca Raton, Florida, USA, 89th edition, 2009.
- Criss R.E. and Taylor H.P., Jr. (1986) Meteoric-hydrothermal systems. *Rev. Mineral.* **16**, 373-424
- Etschmann, B.E., Liu, W., Pring, A., Grundler, P.V., Tooth, B., Borg, S., Testemale, D., Brewe, D., and Brugger, J. (2016) The role of Te(IV) and Bi(III) chloride complexes in hydrothermal mass transfer: An X-ray absorption spectroscopic study. *Chem. Geol.* **425**, 37-51. .
- Fehr M.A., Rehkämper R. and Halliday A.N. (2004) Application of MC-ICPMS to the precise determination of tellurium isotope compositions in chondrites, iron meteorites and sulfides. *Int. J. Mass. Spec.* **232**, 83-94.
- Fehr M.A., Rehkämper R., Halliday A.N., Wiechert U., Hattendorf, B., Günther D., Ono S., Eigenbrode J.L. and Rumble III D. (2005) Tellurium isotopic composition of the early solar system – A search for effects resulting from stellar nucleosynthesis, ^{126}Sn decay, and mass-independent fractionation. *Geochim. Cosmochim. Acta* **69**, 5099-5112.
- Fehr M.A., Rehkämper M., Halliday A.N., Schönbachler M., Hattendorf B. and Günther D. (2006) Search for nucleosynthetic and radiogenic tellurium isotope anomalies in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **70**, 3436-3448.
- Fehr M.A., Rehkämper M., Halliday A.N., Hattendorf B. and Günther D. (2009) Tellurium isotope compositions of calcium-aluminum-rich inclusions. *Meteor. Planet. Sci.* **44**, 971-984.
- Fornadel A.P., Spry P.G., Jackson S.E., Mathur R.D., Chapman J.B. and Girard I. (2014) Methods for the determination of stable Te isotopes variability of minerals in the system Au-Ag-Te by MC-ICP-MS. *J. Anal. Atom. Spec.* **29**, 623-637.
- Forrest A., Kingsley R. and Schilling J-G. (2009) Determination of selenium and tellurium in basalt rock reference materials by isotope dilution hydride generation-inductively coupled plasma-mass spectrometry (ID-HG-ICP-MS). *Geostan. Geoanal. Res.* **33**, 261-269.
- Franklin J.M., Gibson H.L., Jonasson I.R. and Galley A.G. (2005) Volcanogenic massive sulfide deposits. In *Economic Geology 100th Anniversary Volume* (eds J.W. Hedenquist J.W. et al.) pp. 523-560.
- Fry B., Ruf W., Gest H. and Haynes J.M. (1988) Sulfur isotope effects associated with oxidation of sulfide by O_2 in aqueous solution. *Chem. Geol.* **73**, 205-210.

- 1 Fulignati P. and Sbrana, A. (1998) Presence of native gold and tellurium in the active high-sulfidation
2 hydrothermal system of the La Fossa volcano (Vulcano, Italy). *Volcan. Geotherm. Res.* **86**, 187-198
- 3 Frisch, M. J *et al.* (2013) Gaussian 09: EM64L-G09RevD.01, Gaussian, Inc., Wallingford CT.
- 4 Goldfarb R.J., Baker T., Dubé T., Groves D.I., Hart C.J.R. and Gosselin P. (2005) Distribution, character,
5 and genesis of gold deposits in metamorphic terranes. In *Economic Geology 100th Anniversary*
6 *Volume* (eds. J.W. Hedenquist J.W. et al.), pp. 407-450.
- 7 Greenland L.P. and Aruscavage P.J. (1986) Volcanic emissions of Se, Te, and As from Kilauea Volcano,
8 Hawaii. *Volcan. Geotherm. Res.* **27**, 195-201.
- 9 Grundler P.V., Brugger J., Etschmann B.E., Helm L., Liu W., Spry P.G., Tian Y., Testemale D. and Pring A.
10 (2013) Speciation of aqueous tellurium(IV) in hydrothermal solutions and vapors, and the role of
11 oxidized tellurium species in Te transport and gold deposition. *Geochim. Cosmochim. Acta* **120**, 298-325.
- 12 Haghnegahdar M.A., Schauble E.A., Fornadel A.P. and Spry P.G. (2013) First-principles models of
13 equilibrium tellurium isotope fractionation. American Geophysical Union Fall 2013, Abstract V51A-
14 2636
- 15 Hill G.T., Campbell A.R. and Kyle P.R. (2000) Geochemistry of southwestern New Mexico fluorite
16 occurrences: implications for precious metals exploration in fluorite-bearing systems. *J. Geochem.*
17 *Explor.* **68**, 1-20.
- 18 Hoefs, J. (2015) *Stable isotope geochemistry*, 7th edition, Springer Heidelberg, 389 pp.
- 19 Housely R.M., Kampf A.R., Mills S.J., Marty J. and Thorne B. (2011) The remarkable occurrence of rare
20 secondary tellurium minerals of Otto Mountain near Baker, California, including seven new species.
21 *Rocks & Minerals* **86**, 132-145.
- 22 Jaireth S. (1991) Hydrothermal geochemistry of Te, Ag₂Te and AuTe₂ in epithermal precious metal
23 deposits. Econ. Geol. Res. Unit Contrib. **37**, Geology Department, James Cook University, North
24 Queensland, 22 pp.
- 25 Jensen E.P. and Barton, M.D. (2000) Gold deposits related to alkaline magmatism. In *Gold in 2000:*
26 *Reviews in Economic Geology 13* (eds. S.G. Hagemann, and P.E. Brown), pp. 279-314.
- 27 Johnson, C.M., Beard, B.L. and Albarède, F. (2004) Overview and general concepts. In *Geochemistry of*
28 *non-traditional stable isotopes*. Reviews in Mineralogy and Geochemistry 55 (eds. C.M. Johnson,
29 B.L. Beard, B.L., and F. Albarède), pp. 1-24.
- 30 Johnson D.B. (2002) Chemical and microbiological characteristics of mineral spoils and drainage waters
31 at abandoned coal and metal mines. *Water, Air, Soil Poll.* **3**, 47-66.
- 32 Johnson T.M. (2004) A review of mass-dependent fractionation of selenium isotopes and implications for
33 other heavy stable isotopes. *Chem. Geol.* **204**, 201-214.
- 34 Johnson T.M., Bullen T.D. and Zawislanski P.T. (2000) Selenium stable isotope ratios as indicators of
35 sources and cycling of selenium: results from the northern reach of San Francisco Bay. *Env. Sci.*
36 *Tech.* **34**, 2075-2079.
- 37 Kampf, A.R., Housley, R.M., Mills, S.J., Marty, J. and Thorne, B. (2010) Tellurium oxysalts from Otto
38 Mountain near Baker, California: I. The description and crystal structure of the new mineral ottoite,
39 Pb₂TeO₅. *Am. Mineral.* **95**, 1329–1336.
- 40 Kelley K.D. and Luddington S. (2002) Cripple Creek and other alkaline-related gold deposits in the
41 southern Rocky Mountains, USA: influence of regional tectonics. *Mineral. Deposit.* **37**, 38-60.
- 42 Larocque A.C.L., Stimac J.A., Siebe C., Greengrass K., Chapman R. and Melja S.R. (2008) Deposition of
43 high-sulfidation Au assemblage from a magmatic volatile phase, Volcán Popocatepetl, Mexico.
44 *Volcan. Geotherm. Res.* **170**, 51-68.
- 45 Layton-Matthews D., Leybourne M.I., Peter J.M., Scott S.D., Cousens B. and Eglington B.M. (2013)
46 Multiple sources of selenium in ancient seafloor hydrothermal systems: Compositional Se, S, and Pb
47 isotopic evidence from volcanic-hosted and volcanic-sediment-hosted massive sulfide deposits of the
48 Finlayson Lake District, Yukon, Canada. *Geochim. Cosmochim. Acta* **117**, 318-331.
- 49 Lee D-C. and Halliday A.N. (1995) Precise determinations of the isotopic composition atomic weights of
50 molybdenum, tellurium, tin and tungsten using ICP magnetic sector multiple collector mass
51 spectrometry. *Intl. J. Mass Spec. Ion Proc.* **146/147**, 35-46.

- 1 Liu J., Zhao S., Cook N.J., Bai X., Zhang Z., Zhao Z., Zhao H. and Lu J. (2013) Bonanza-grade
2 accumulations of gold tellurides in the Early Cretaceous Sandaowanzi deposit, northeast China. *Ore*
3 *Geol. Rev.* **54**, 110-126.
- 4 Manchester J., Paulsen M. and Ornstein, R. (1995) Calculation of atom – centered partial charges for
5 heme. *Molecular Engineering 01/1995* **5**,135-142
- 6 Markl G., Lahaye Y. and Schwinn, G. (2006) Copper isotopes as monitors of redox processes in
7 hydrothermal mineralization. *Geochim. Cosmochim. Acta* **70**, 4215-4228.
- 8 Mathur R., Titley S., Barra F., Brantley S., Wilson M., Phillips A., Munizaga F., Makshev V., Vervoort J. and
9 Hart G. (2009) Exploration potential of Cu isotope fractionation in porphyry copper deposits. *Geochem.*
10 *Explor.* **102**, 1-6.
- 11 McDonough W.F. and Sun S.-S. (1995) The composition of the Earth. *Chem. Geol.* **120**, 223-254.
- 12 McKibben, M.A. and Eldridge, C.S. (1990) Radical sulfur isotope zonation of pyrite accompanying
13 boiling and epithermal gold mineralization: A SHRIMP study of the Valles caldera, New Mexico.
14 *Econ. Geol.* **85**, 1917-1925.
- 15 McPhail D.C. (1995) Thermodynamic properties of aqueous tellurium species between 25°C and 350°C.
16 *Geochim. Cosmochim. Acta* **59**, 851-866.
- 17 Moynier F., Fujii T., Telouk P. and Albarède F. (2008) Isotope separation of Te in chemical exchange
18 system with Dicyclohexano-18-crown-ether-6. *J. Nucl. Sci. Technology. Suppl.* **5** 10-14.
- 19 Moynier F., Fujii T. and Albarède F. (2009) Nuclear field shift effect as a possible cause of Te isotopic
20 anomalies in the early solar system—An alternative explanation of Fehr et al. (2006 and 2009).
21 *Meteor. Planet. Sci.* **44**, 1735-1742.
- 22 Nash J.T. and Cunningham Jr. C.G. (1973) Fluid-inclusion studies of the fluorspar and gold deposits,
23 Jamestown District, Colorado. *Econ. Geol.* **68**, 1247-1262.
- 24 Ohmoto, H. and Rye, R.O. (1979) Isotopes of sulfur and carbon. In *Geochemistry of hydrothermal ore*
25 *deposits, 2nd ed.* (ed. H.L. Barnes, H.L.), pp. 509-567, Wiley Interscience. New York.
- 26 Pavlov A.A. and Kasting, J.F. (2002) Mass-independent fractionation of sulfur isotopes in Archean
27 sediments: strong evidence for an anoxic Archean atmosphere. *Astrobio* **2**, 27-41.
- 28 Phillips G.N. and Groves D.I. (1983) The nature of Archaean gold-bearing fluids as deduced from gold
29 deposits of Western Australia. *J. Geol. Soc. Aust.* **30**, 25-39.
- 30 Rappoport D. and Fillip F. (2010) Property-optimized Gaussian basis sets for molecular response
31 calculations. *Chem. Phys.* **133**, 134105.
- 32 Reimann C. and de Caritat, P. (1998) *Chemical elements in the environment. Factsheets for the*
33 *geochemist and environmental scientist*. Springer-Verlag, Berlin, 398 pp.
- 34 Richards J.P. (1995) Alkalic-type epithermal gold deposits, a review. *Min. Assoc. Canada Short Course*
35 *Series* **23**, 367-400.
- 36 Rustad J., Casey W., Yin Q., Bylaska E., Felmy A., Bogatko S., Jackson V. and Dixon D. (2010) Isotopic
37 fractionation of $Mg^{2+}(aq)$, $Ca^{2+}(aq)$, and $Fe^{2+}(aq)$ with carbonate minerals *Geochim. Cosmochim. Acta*
38 **74**, 6301-6323.
- 39 Saunders J.A. and May E.R. (1986) Bessie G: A high-grade epithermal gold telluride deposit, La Plata
40 County, Colorado, USA. In *Gold '86* (ed. A.J. MacDonald), pp. 436-444.
- 41 Saunders J.A. and Brueseke M.E. (2012) Volatility of Se and Te during subduction-related distillation
42 and the geochemistry of epithermal ores of the Western USA. *Econ. Geol.* **107**, 165-172.
- 43 Schauble, E.A., Méhaut, M. and Hill, P.S. (2009) Combining metal stable isotope fractionation theory
44 with experiments. *Elements* **5**, 369-374.
- 45 Schutte, W.J., and de Boer, J.L. (1988) Valence fluctuations in the incommensurately modulated structure
46 of calaverite $AuTe_2$. *Acta Crystallograph. B* **44**, 486-494.
- 47 Simmons, S.F. and Brown, K.L. (2006) Gold in magmatic hydrothermal solutions and the rapid formation
48 of a giant ore deposit. *Science* **314** (5797) 288-291.
- 49 Smith C.L., Rosman K.J.R., and de Laeter J.R. (1978) The isotopic composition of tellurium. *Intl. J. Mass*
50 *Spec. Ion Phys.* **28**, 7-17.
- 51 Smithers R.M. and Krouse H.R. (1968) Tellurium isotope fractionation study. *Can. J. Chem.* **46**, 583-591.

- 1 Symonds R.B. (1992) Getting the gold from the gas: how recent advances in volcanic-gas research have
2 provided new insight on metal transport in magmatic fluids. In *Magmatic contributions to*
3 *hydrothermal systems* (ed. J.W. Hedenquist), Geological Survey of Japan Report No. 279, pp. 170-
4 175.
- 5 Taylor H. P. Jr. (1979) Oxygen and hydrogen isotope relationships in hydrothermal ore deposition, In
6 *Geochemistry of hydrothermal ore deposits*, 2nd ed. (ed. H.L. Barnes, H.L.), pp. 236-277, Wiley
7 Interscience. New York.
- 8 Thiemens M.H. and Heidenreich J.E. (1983) The mass-independent fractionation of oxygen: a novel
9 isotope effect and its possible cosmochemical implications. *Science* **219**, 1073-1075.
- 10 Thompson T.B., Trippel A.D., and Dwelley P.C. (1985) Mineralized veins and breccias of the Cripple
11 Creek district, Colorado. *Econ. Geol.* **80**, 1669-1688.
- 12 Urey H.C. (1947) The thermodynamic properties of isotopic substances. *Chem. Soc.* **1947**, 562-581.
- 13 Wen, H. and Carignan J. (2011) Selenium isotopes trace the source and redox processes in the black
14 shale-hosted Se-rich deposits in China. *Geochim. Cosmochim. Acta* **75**, 1411-1427.
- 15 Werle J.L. Ikramuddin M. and Mutschler F.E. (1984) Allard stock, La Plata Mountains, Colorado – an
16 alkaline rock-hosted porphyry copper-precious metal deposit. *Can. J. Earth. Sci.* **21**, 630-641.
- 17 Yi W., Halliday A.N., Alt J.C., Lee D., Rehkämper M., Garcia M.O. and Su Y. (2000). Cadmium,
18 indium, tin, tellurium, and sulfur in oceanic basalts: Implications for chalcophile element
19 fractionation in the Earth. *J. Geophys. Res.* **105**, 18,927-18,948
- 20 Zhang X. and Spry P.G. (1994) Calculated stability of aqueous tellurium species, calaverite, and hessite at
21 elevated temperatures. *Econ. Geol.* **89**, 1152-1166.
- 22 Zhao J., Brugger J., Grundler P.V., Xia F., Chen G. and Pring A. (2009) Mechanisms and kinetics of
23 mineral transformation under hydrothermal conditions: calaverite to metallic gold. *Amer. Mineral.* **94**,
24 1541-1555.
- 25 Zheng Y.F. (1991) Calculation of oxygen isotope fractionation in metal oxides. *Geochim. Cosmochim.*
26 *Acta* **55**, 2299-2307.

Table 1

Table 1. Stable Te isotope compositions of tellurites, native tellurium, and tellurides

Sample	Mineral	Mineral formula	$\delta^{130/125}\text{Te}$ (‰)	2 σ	‰ amu ⁻¹	Analyses	Mine and location
9659-2	Emmonsite	Fe ₂ (TeO ₃) ₃ • 2H ₂ O	0.25	0.11	0.05	5	Bambolla, Moctezuma, Sonora, Mexico
M33434	Emmonsite	"	-0.14	0.07	-0.03	5	Bambolla, Moctezuma, Sonora, Mexico
164335	Emmonsite	"	-0.16	0.22	-0.03	5	Bambolla, Moctezuma, Sonora, Mexico
18834	Emmonsite	"	-0.17	0.04	-0.03	5	Bambolla, Moctezuma, Sonora, Mexico
9664 Em	Emmonsite	"	-0.74	0.07	-0.15	5	Bambolla, Moctezuma, Sonora, Mexico
5806	Emmonsite	"	-1.27	0.13	-0.25	5	Tommy Knocker, Catron County, New Mexico
9658	Paratellurite	TeO ₂ (tetragonal)	-0.46	0.08	-0.09	5	Bambolla, Moctezuma, Sonora, Mexico
M34162	Poughite	Fe ₂ (TeO ₃)(SO ₄)(H ₂ O) ₂ • H ₂ O	0.59	0.07	0.12	5	Bambolla, Moctezuma, Sonora, Mexico
9656	Tellurite	TeO ₂ (orthorhombic)	-1.20	0.19	-0.24	5	Bambolla, Moctezuma, Sonora, Mexico
M19167A	Tellurite	"	-1.36	0.06	-0.27	5	Bambolla, Moctezuma, Sonora, Mexico
164337	Tellurite	"	-1.58	0.13	-0.32	4	Bambolla, Moctezuma, Sonora, Mexico
11206	Native tellurium	Te	0.16	0.07	0.03	5	Mountain Lion, Magnolia District, Colorado
DMNS 15578	Native tellurium	"	-0.14	0.11	-0.03	4	Rex, Gold Hill District, Boulder County, Colorado
9664 Te	Native tellurium	"	-0.74	0.10	-0.15	5	Bambolla, Moctezuma, Sonora, Mexico
11655	Calaverite	AuTe ₂	0.38	0.14	0.08	5	Kalgoorlie, Western Australia
4903	Calaverite	"	0.29	0.08	0.06	5	Cresson, Cripple Creek, Colorado
4141	Calaverite	"	0.21	0.07	0.04	5	Cresson, Cripple Creek, Colorado
13143C	Calaverite	"	-1.54	0.07	-0.31	5	El Paso, Cripple Creek, Colorado
AMNH 837	Hessite	Ag ₂ Te	0.21	0.29	0.04	5	Savodinski, Altai Mtns., Siberia
DMNS 5565	Krennerite	(Au,Ag)Te ₂	-0.05	0.06	-0.01	4	Cresson, Cripple Creek, Colorado
5405B	Krennerite	"	-0.55	0.06	-0.11	5	May Day, La Plata District, Colorado
M33684	Petzite	Ag ₃ AuTe ₂	-0.29	0.08	-0.06	4	Rice Lake, Manitoba
DMNS 473A	Stützite	Ag _{5-x} Te ₃	0.00	0.08	0.00	5	May Day, La Plata District, Colorado
DMNS 492A	Stützite	"	-0.27	0.08	-0.05	5	May Day, La Plata District, Colorado
DMNS 483A	Sylvanite	(Au,Ag) ₂ Te ₄	0.17	0.10	0.03	5	May Day, La Plata District, Colorado
DMNS 473B	Sylvanite	"	-0.14	0.10	-0.03	5	May Day, La Plata District, Colorado
DMNS 492B	Sylvanite	"	-0.19	0.01	-0.04	5	May Day, La Plata District, Colorado
DMNS 5405A	Sylvanite	"	-0.30	0.06	-0.06	5	May Day, La Plata District, Colorado
DMNS 510 ES	Sylvanite	"	-0.36	0.08	-0.07	5	May Day, La Plata District, Colorado

Table 2

Table 2
Calculated isotope fractionation factors for selected gas molecules and crystals at various temperatures*.

Species	298° K	373° K	500° K
TeF ₆	1.01356	1.00904 (1.01070)	1.00522
H ₆ TeO ₆	1.01078	1.00716	1.00413
H ₂ TeO ₃	1.00638	1.00428	1.00249
TeO ₃ ²⁻	1.00609	1.00405 (1.00469)	1.00234
AuTe ₂ (calaverite)	1.00221	1.00141	1.00079
Ag ₂ Te (hessite)	1.00163	1.00104	1.00580
H ₂ Te	1.00140	1.00104 (1.00098)	1.00068
Te ₂	1.00115	1.00074 (1.00079)	1.00041
Native Te	1.00110	1.00070	1.00039

*Data calculated using the Def2-SVPD basis set. The values in the parenthesis are from Smithers and Krouse (1968). Data relative to a hypothetical atomic Te vapor.

Table 3

Table 3
Comparison of geological characteristics of Te-rich deposit.

Deposit	Ore type	Age (Ma)	Associated rocks	Fluid inclusion characteristics	Reference(s)
Cripple Creek, Colorado	Epithermal	27-32	Phonolites, latite-phonolite, syenite, and and alkali basalts brecciated and intruded into Precambrian intrusives and metavocanics	~250° C, H ₂ O rich	Kelley and Luddington (2002), Thompson et al. (1985)
Boulder County, Colorado	Epithermal	44-55	1.7 to 1.4 Ga metamorphics intruded by early Tertiary monzonites and syenite stocks and dikes	205-270°, 4 wt. % NaCl, non-boiling (Jamestown)	Nash and Cunningham (1973)
La Plata district, Colorado	Epithermal	70-85	Monzonite, syenite, and diorite that crosscut Permian to Jurassic metasediments	130-170°, 2-9 wt. % NaCl, some CO ₂ gas hydrates, non-boiling	Saunders and May (1986), Werle et al. (1984)
Organ Mountains, New Mexico	Epithermal	30-33	Alkaline diorites, syenites, latites.	150-187°, 1.6-1.9 wt. % NaCl	Kelley and Luddington (2002), Hill et al. (2000)
Kalgoorlie, Western Australia	Orogenic	2810 +/- 100 Ma	Metabasalts, greenschist - lower amphibolite	>400°, H ₂ O-CO ₂ , neutral to oxidized, <4 wt. % NaCl, OH ⁻ , CO ₃ ²⁻ , and S ²⁻ likely ligands for Te transport	Phillips and Groves (1983)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5