Noble Gases in Tellurium and Associated Minerals and Double-Beta Decay of ^{130}Te

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Tellurobismuthite, quartz and arsenopyrite minerals separated from a specimen of tellurium-bearing ores collected at the Oya mine have been analyzed for noble gas isotopes. The Te minerals released abundant ^4He and ^{40}Ar . Quartz released large amounts of noble gases, which are supposed to have been occluded in fluid inclusions. It contains excess ^{40}Ar inherited from precursor materials. Arsenopyrite released abundant He and Ar. Argon is mostly of atmospheric origin. Definite excesses at ^{129}Xe , ^{130}Xe , and ^{131}Xe isotopes but no excesses at ^{134}Xe and ^{136}Xe are found for the Te minerals. Xe isotopic ratios for the quartz are atmospheric and give no evidence for inherited excess ^{130}Xe . Because the quartz, arsenopyrite and Te minerals were deposited from the same hydrothermal fluids, these indicate that the Te minerals contain inherited excess ^{40}Ar and the isotopic ratios of trapped Xe in the Te minerals is atmospheric. Hence the ^{130}Xe excess found in the Te mineral is attributable to the in-situ double-beta decay of ^{130}Te , and the excesses at ^{129}Xe and ^{131}Xe are to the neutron-captures on ^{128}Te and ^{130}Te , respectively. Besides, a quartz-calcite separate from a Te ore specimen collected at the Suwa mine is enriched in ^4He but the isotopic ratios of Xe is atmospheric, indicating that Xe contained in hydrothermal fluids at Suwa is atmospheric.

In order to decipher the chronological sequence of mineralization of Te ores and solidification of magma, we summarize the occurrences of sample minerals, the geology of sampling sites and their field relationships. Based on noble gas data measured for the Te and associated minerals as well as geological considerations, we prefer $(7.9 \pm 1.0) \times 10^{20}$ years to 3×10^{21} years for the absolute half-life of ^{130}Te double-beta decay. From the excess ratio of ^{129}Xe to ^{131}Xe , we have $710 \text{ n/cm}^2 \text{ y}$ for neutron flux at the Oya mine.

1. Introduction

Double-beta decay (DBD) is a 2nd order process of nuclear weak interaction, by which a nucleus (A, Z) decays to a nucleus $(A, Z \pm 2)$ with spontaneous emissions of two negative (or positive) electrons, where A and Z are a mass number and an atomic number, respectively. Since the first report on the possibility of DBD by Goeppert-Mayer,¹⁾ many experimental as well as theoretical studies have been performed. Isobars ^{130}Te , ^{130}I , and ^{130}Xe belong to a system of nuclides for which successive single-beta decays are energetically forbidden but disintegration through DBD is possible from ^{130}Te to ^{130}Xe . The first experimental result on the ^{130}Te DBD half-life has been given by Inghram and Reynolds.²⁾ Since then, many data on the ^{130}Te half-life have been reported. The ^{130}Te half-life is determined by a geochemical method, where old Te minerals are analyzed for decay product ^{130}Xe by high-sensitivity and high-precision mass spectrometry. The amount of parent ^{130}Te is determined from the chemical composition of the sample mineral and the isotopic abundance of ^{130}Te .

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But there remain discrepancies in the half-life: Experimentally some workers have reported 7 to 9×10^{20} years^{3), 4)} and others 2 to 3×10^{21} years.^{5), 6)} In addition, these experimental half-lives are larger by one to two orders of magnitude than theoretical estimates.⁷⁾ The works reported so far⁸⁾ are solid and without doubt in their analytical results. That the parent to daughter ratio $^{130}\text{Te}/^{130}\text{Xe}$ reported so far by different workers are in good agreement with one another for samples collected from the same locality (*i.e.*, the same mine) indicates that problems are not in analytical techniques for Xe isotopes and Te contents, but in determination of the time interval (*i.e.*, Xe retention age) in which Te minerals accumulated and retained radiogenic ^{130}Xe produced by in-situ decay of ^{130}Te .^{8), 9)}

One possibility to give a short life-time for the ^{130}Te DBD is the existence of excess ^{130}Xe inherited from precursor materials at the time of mineralization.⁹⁾ Noble gas analyses of Te and associated minerals crystallized from the same hydrothermal solution will provide a useful clue to make this problem clear.

This work consists of revisits to the Oya and Suwa mines. One of authors (N.T.) has reported the ^{130}Te half-life using tellurium minerals from Oya³⁾ and Suwa.¹⁰⁾ We will report the result of noble gas analyses on Te and associated minerals separated from Te-bearing ores. We will also give a summary on field relationship between the Te ores and their country rocks and the geology at the Oya and Suwa mines, because they are important to decipher the geochronological sequence in the formation of mineral deposits and to estimate the Xe retention ages for the Te minerals.

2. Experimental

2.1 Samples

Samples used in this work are pure tellurobismuthite (Bi_2Te_3), quartz (SiO_2), and arsenopyrite (FeAsS) separates from a hand specimen of Te-bearing ores collected at the Oya mine, and a quartz-calcite (CaCO_3) separate from a hand specimen of Te-bearing ores collected at the Suwa mine. The ores were carefully crushed to isolate Te and other mineral grains by hand-picking. The Te mineral isolated is flaky and ranges in size typically 1 to 2 mm. The quartz, arsenopyrite and quartz-calcite samples were crushed typically 1 mm in grain size. Arsenopyrite and quartz were separated from the same specimen as the Te mineral, in order to measure the isotopes of noble gases trapped in them, because these minerals are regarded to have crystallized from the same hydrothermal fluids and trapped the same isotopic compositions of noble gases as the Te mineral did. In particular, quartz can provide data on the isotopic ratios of noble gases in the fluids, because it contains usually innumerable fluid inclusions of micron size. Noble gases must have been occluded therein together with the fluids. For the same purpose, the quartz-calcite fraction was prepared from the same specimen of the Te-bearing ores from Suwa that Takaoka¹⁰⁾ had used to measure radiogenic ^{130}Xe produced by DBD.

Arbitrarily selected grains of tellurobismuthite and arsenopyrite were checked for impurity minerals with an electron-probe micro-analyzer (EPMA; JEOL 733) at Department of Earth and Planetary Sciences, Kyushu University. For Te minerals, 23 grains were analyzed for chemical and mineral compositions, using Sb_2Te_3 , Bi_2Se_3 , and CuFeS_2

Fig. 1. (a) Backscattered electron image of tellurobismuthite. A dark patch at middle lower part is tetradymite crystal. (b) Backscattered electron image of arsenopyrite. Small inclusions of tellurobismuthite (gray) and native gold (bright) are found in arsenopyrite (black). White bar = 0.1 mm.

standards. They are almost pure tellurobismuthite with an exception. The Te content is essentially constant (*i.e.*, 47.8 wt%) both in a grain and among grains. The proportion of Te and Bi in tellurobismuthite is almost stoichiometric (3 : 2). These are in good agreement with reported data on Te and Bi contents.^{11), 12)} However, a part of Bi has been replaced by Sb, the content of which was less than 0.5 wt%.

Figure 1(a) exhibits a backscattered electron image of a 0.1 mm-sized patch of tetradymite in tellurobismuthite, and it is only one example found out of 23 grains. Although Takaoka and Ogata³⁾ used tetradymite ($\text{Bi}_2\text{Te}_2\text{S}$) for the terminology of Oya Te mineral, this indicates that the Oya Te mineral is composed mostly of tellurobismuthite and tetradymite is rare.¹²⁾ Figure 1(b) exhibits an example of arsenopyrite grains containing inclusions of tellurobismuthite and native gold. Such inclusions are found in 3 out of 8 arsenopyrite grains examined, indicating contemporaneous crystallization of those minerals.

2.2 Geology of sampling sites

Oya mine. This mine is located near the south-eastern margin of the Kitakama mountainland, one of fundamental, geological blocks in Northeast Japan. Tellurium minerals are embedded in quartz veins, in close genetic relationship with native gold, arsenopyrite and other minerals. The quartz veins, filling fissures, are hosted in the Triassic formation composed mainly of sandstone and slate. According to Watanabe,¹¹⁾ there are two groups of quartz veins: those in the inner zone and those in the outer zone. The veins in the inner zone, called the main veins, are found nearest to the margin of a quartzdiorite body in its metamorphic areole. There sandstone and slate have been

Fig. 2. Geological map near the Oya mine, reproduced after refs. 13, 14, and 15. For simplicity, distribution of main veins in the inner zone is shown, but quartz veins in the outer zone are not shown. Quartz veins are all striking from south to north in parallel arrangement, and a large quartzdiorite body is found in the north near the mine. A small tongue-like cupola is supposed to extend further to south and lie beneath the veins, because bosses regarded as apophyses of the quartzdiorite are found along the line. Triassic sandstone and slate classified as different formations are not distinguished in the figure.

converted into quartzite and hornfels, respectively, and both have been further metamorphosed near the veins. The veins in the outer zone are distributed 1 to 2 km far outside the main veins. They are very rich in pyrite (FeS_2) and arsenopyrite and contain notable amounts of galena (PbS) and spharelite (ZnS), but poor in quartz and gold. No tellurobismuthite is found there.

The main veins are distributed along an extended line of a small tongue-like cupola of the quartzdiorite body that projects toward south (Fig. 2). Some veins are found cut bosses regarded as apophyses of the quartzdiorite, particularly in the northern part of the mine. This indicates that the fissures bearing the veins were formed probably both in circumference hoods of the quartzdiorite cupola and in roof rocks surrounding it (*i.e.*, the Triassic sandstone and slate) after at least part of rims of the quartzdiorite body had

solidified.¹³⁾ At the Oya mine, hydrothermal fluids, enriched in both anions and cations such as Si, Fe, S, As, Te, Bi, and so on, are considered to have originated in connection with quartzdiorite magma and to have filled the fissures at the circumference of quartzdiorite cupola and in the upper Triassic rocks to deposit the quartz veins bearing Te and other minerals. Therefore, the formation age of the quartz veins would be approximated by the formation age of quartzdiorite.

In addition, there are many dykes of porphyrite which outcrop on the south to north-east of the area. Watanabe has reported the field observation that some dykes cut and are cut by the veins.¹¹⁾ Imai has reported the quartz veins accompanied by the porphyrite dykes in the south-eastern margin of the mine.¹³⁾ We would put emphasis on the observation of mutual crosscutting between the porphyrite dykes and the quartz veins, although another geologist supposed that the formation of these dykes may predate the intrusion of quartzdiorite magma.¹⁴⁾ The mutual crosscutting is strong evidence for the contemporaneous formation of the porphyrite dykes and the quartz veins.

In the mineralization sequence inferred for the Oya deposits, after molybdenite (MoS_2) had been first crystallized together with quartz, followed by mineralization of pyrrhotite and pyrite, tellurobismuthite, arsenopyrite and gold were deposited at the middle stage of the sequence, and crystallization of calcite terminated the sequence. Quartz was continuously deposited until immediately before the termination of mineralization.¹⁵⁾ The time interval between the onset and the termination of mineralization is unknown. The veins are typical mesothermal gold deposits from both their occurrence mode and their mineral composition.^{11), 15)} This is consistent with decrepitation temperatures of 270 to 320°C for quartz veins.¹³⁾ These should be regarded as lower limits of the formation temperature of quartz veins because they are not corrected for the pressure effect on conversion of the decrepitation temperature to the formation one.¹⁶⁾ The area in which the Oya mine is located is geologically quiescent since the igneous activities in the late Cretaceous. The Te-bearing ores have not experienced any thermal (igneous) events postdating the quartzdiorite intrusion.³⁶⁾ This implies quantitative retention of radiogenic ^{130}Xe after mineralization.

Suwa mine. The mine is 260 km south to the Oya mine and one of branches of the Hitachi mine, located near the southern margin of the Abukuma plateau. This is also one of fundamental blocks in the geological structure of Northeast Japan. The Hitachi area of the Abukuma plateau consists mainly of granitic rocks, Paleozoic formation and metamorphic rocks. The mine is located in metamorphosed Paleozoic formation (Aka-zawa formation), 4 km south to the Hitachi mine. The ore body is composed mainly of banded cupriferous pyrite deposits in country rocks of quartz-crystalline (or green) schist. A high-grade gold quartz ore, associated with Te minerals, was found locally in an ore tub outside the pit and examined.¹⁷⁾ The Te minerals consist of tellurobismuthite, altaite (PbTe), Te-bearing galena, sylvanite (AuAgTe_4), and petzite (Ag_3AuTe_2). The major mineral is tellurobismuthite (69.9 mol%) and the remaining mostly of altaite (27.5 mol%). The average Te content for the Te minerals has been reported to be 43.7 wt%. The quartz veins bearing Te are several cm to a little above half a meter wide. The veins contain calcite, chlorite, pyrite, native gold, and others. Tellurium minerals were

deposited with gold at the later stage of mineralization, whereas quartz-calcite and chlorite at the early to middle stages.¹⁷⁾

K-Ar age determinations have yielded 90 to 100 Ma for most granitic rocks and 102 to 120 Ma for metamorphic rocks in the Abukuma plateau.^{18), 19)} The K-Ar age of 105 Ma has been determined for muscovite separated from quartz-crystalline schist, the country rocks of the deposits at Suwa.¹⁹⁾ Based on these age data and field relationship, it is reasonable to consider that the intrusion of granitic rocks in the Abukuma plateau took place in the late Cretaceous and the regional metamorphism in the Hitachi area also took place in the same period, in close connection with the granitic intrusion.²⁰⁾ Thus the age for the Xe retention of Suwa Te minerals can be approximated by those metamorphic ages. Difference in retentivity between Ar in silicates and Xe in Te minerals will be discussed later and elsewhere.²⁴⁾

2.3 Mass spectrometry

Helium, Ne, and Ar were measured by an analog mode using a Daly collector followed by a photomultiplier, signals from which are digitized for data acquisition and computation. Xenon and Kr isotopes were measured by a pulse-counting mode with a mass spectrometer (modified VG5400) at the noble gas laboratory of Okayama University, Misasa.²¹⁾ Samples rinsed with ethanol were wrapped in Al foil and mounted in a sample holder of a Ta furnace. A gas-extraction line including the furnace and a gas-purification line are thoroughly degassed. During degassing the lines, the samples were heated overnight approximately at 100°C to desorb atmospheric surface contamination. This temperature was adopted to prevent gas loss in heating because the tellurobismuthite mineral melts at temperature as low as approximately 575°C. Noble gases evolved at blank runs were measured at 850°C for the Te samples and at 1750°C for others. Typical blanks are: $^4\text{He}=2.7\times10^{-10}$, $^{20}\text{Ne}=7.7\times10^{-12}$, $^{40}\text{Ar}=1.5\times10^{-10}$, $^{84}\text{Kr}=7.7\times10^{-15}$, and $^{132}\text{Xe}=4.4\times10^{-15}$ cm³ STP at 850°C for 20 minutes, and $^4\text{He}=3.4\times10^{-10}$, $^{20}\text{Ne}=7.4\times10^{-12}$, $^{40}\text{Ar}=1.1\times10^{-9}$, $^{84}\text{Kr}=1.1\times10^{-13}$, and $^{132}\text{Xe}=2.7\times10^{-14}$ cm³ STP at 1750°C for 15 minutes. Isotopic ratios for 850°C blank Ar were interfered slightly by memory from the mass spectrometer. Blank Ar at 1750°C, Kr and Xe are mostly atmospheric except for ^{124}Xe and ^{126}Xe , for which excesses due to interference and memory from the spectrometer are found. Sensitivity and mass discrimination of the mass spectrometer were determined by measuring known amounts of atmospheric noble gases. Variations in sensitivities are less than 7.5% for He and Ne, less than 5% for Ar and Kr, and 3% for Xe. Mass discrimination for Xe isotopes is 0.38% per mass unit.

3. Results

3.1 Te minerals

Results of noble gas analyses are given in Tables 1 and 2, together with Xe data for the Suwa Te mineral reproduced for comparison.¹⁰⁾ Uncertainties cited include statistical errors (2σ) for isotopic measurements, mass discrimination and blank corrections. Helium and Ne were measured only for elemental abundances. Argon, Kr, and Xe were measured for both elemental and isotopic abundances. However, the isotopic ratios are not listed for Kr because of the atmospheric isotopic ratios. All gases are released from

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Table 1. He, Ne, and Ar in Tellurium and Associated Minerals from Oya and Suwa Mines

Sample	Te-1			Te-2			Quartz	Arsenopyrite	Qz-calcite
Locality	Oya			Oya			Oya	Oya	Suwa
Weight(g)	0.210			0.310			0.0382	0.140	0.0510
T(°C)	850	1020 ^{b)}	total	200	850	total	1750	1750	1750
$^4\text{He}^{\text{a)}}$	585	(0.4) ^{b)}	585	291	171	462	55.8	504	1820
$^{20}\text{Ne}^{\text{a)}}$	0.42	(0.02) ^{b)}	0.42	0.10	0.26	0.36	8.11	4.86	2.0
$^{36}\text{Ar}^{\text{a)}}$	1.02	(0.005) ^{b)}	1.02	0.242	0.664	0.906	8.33	4.95	8.42
$^{38}\text{Ar}/^{36}\text{Ar}$	0.1879	—	0.1879	0.1843	0.1880	0.1870	0.1881	0.1854	0.1861
	± 0.0004	—	± 0.0004	± 0.0078	± 0.0004	± 0.0024	± 0.00012	± 0.0004	± 0.0004
$^{40}\text{Ar}/^{36}\text{Ar}$	324.7	—	324.7	323.2	314.9	317.1	500.6	299.1	316.8
	± 0.2	—	± 0.2	± 2.2	± 0.4	± 0.9	± 1.6	± 0.2	± 0.2

^{a)} Concentrations are given in units of $10^{-9}\text{ cm}^3\text{ STP/g}$.

^{b)} Gases released at 1020°C was assumed to be mostly blank component, and not included in total.

Table 2. Kr and Xe in Tellurium and Associated Minerals ($^{132}\text{Xe}=100$).

Isotopic ratios of Kr is not listed because of atmospheric composition. In calculation of excess Xe, we used the following isotopic ratios for atmospheric Xe: $^{124}\text{Xe}/^{126}\text{Xe}/^{128}\text{Xe}/^{129}\text{Xe}/^{130}\text{Xe}/^{131}\text{Xe}/^{132}\text{Xe}/^{134}\text{Xe}/^{136}\text{Xe}=0.354/0.330/7.136/98.32/15.14/78.90/=100/38.79/32.94$.

Sample	Te-1			Te-2			Quartz	Arsenopyrite	Qz-calcite	Suwa-Te ^{c)}
T(°C)	850	1020 ^{b)}	total	200	850	total	1750	1750	1750	300-800
$^{84}\text{Kr}^{\text{a)}}$	38.2	(0.6) ^{b)}	38.2	10.1	23.4	33.5	324	101	183	—
$^{132}\text{Xe}^{\text{a)}}$	6.07	(0.21) ^{b)}	6.07	2.06	3.00	5.06	30.2	4.54	14.0	19.0
^{124}Xe	0.37	—	0.37	0.40	0.38	0.39	0.35	0.35	0.40	—
	± 0.10	—	± 0.10	± 0.22	± 0.26	± 0.24	± 0.14	± 0.18	± 0.08	—
^{126}Xe	0.35	—	0.35	0.36	0.35	0.35	0.34	0.36	0.42	—
	± 0.06	—	± 0.06	± 0.22	± 0.12	± 0.16	± 0.08	± 0.18	± 0.10	—
^{128}Xe	7.19	7.10	7.19	7.35	7.25	7.29	7.24	7.44	7.33	153 ^{d)}
	± 0.26	± 1.00	± 0.26	± 0.34	± 0.18	± 0.24	± 2.4	± 0.34	± 0.24	± 12
^{129}Xe	117.9	99.5	117.8	102.4	139.1	124.2	99.4	102.4	101.2	98.3
	± 1.2	± 7.6	± 1.2	± 3.4	± 2.4	± 2.8	± 1.8	± 2.4	± 4.0	± 4.4
^{130}Xe	52.3	15.1	52.2	15.92	92.5	61.3	15.17	15.79	15.35	26.3
	± 2.0	± 2.2	± 2.0	± 0.68	± 7.6	± 4.6	± 0.34	± 0.56	± 0.64	± 2.4
^{131}Xe	91.1	78.4	91.1	79.8	104.2	94.3	78.8	79.9	79.1	76.5
	± 2.0	± 3.4	± 2.0	± 1.8	± 3.0	± 1.8	± 1.5	± 1.3	± 2.0	± 3.4
^{134}Xe	39.0	37.7	39.0	39.1	38.93	38.99	38.66	39.01	39.25	39.1
	± 1.0	± 3.8	± 1.0	± 1.0	± 0.88	± 0.92	± 0.56	± 0.94	± 0.86	± 1.6
^{136}Xe	32.8	32.6	32.8	32.9	33.05	32.98	32.74	32.51	33.23	33.4
	± 0.6	± 3.8	± 0.6	± 1.2	± 0.82	± 0.98	± 0.54	± 0.80	± 0.64	± 1.6

^{a)} Concentrations are given in units of $10^{-12}\text{ cm}^3\text{ STP/g}$.

^{b)} Gases released at 1020°C was assumed to be mostly blank component, and not included in total.

^{c)} Reproduced from data on Xe released by step-heating given by ref. 10.

^{d)} ^{128}Xe spike.

the Te samples at 850°C and considerable portions of atmospheric, trapped gases are released at 200°C. In the 850°C fraction of Te samples, there are large isotopic excesses at ^{129}Xe , ^{130}Xe , and ^{131}Xe , compared to the atmospheric Xe. Isotope studies on Xe in Te minerals so far performed have shown that old Te minerals accumulated products from double beta-decays as well as neutron captures on ^{128}Te and ^{130}Te isotopes.^{9, 22)} Therefore, the ^{130}Xe excess determined in the present Te samples is attributable to the ^{130}Te DBD, and both excesses at ^{129}Xe and ^{131}Xe are products of neutron-captures on ^{128}Te and ^{130}Te , respectively. No definite excesses at ^{128}Xe , ^{134}Xe , and ^{136}Xe are found. This indicates negligible contributions from neutron-capture on ^{127}I and from nuclear fission of U. Other nuclear effects by ^{128}Te DBD⁶⁾ and by neutrons, cosmic-ray muons and other particles are minor and obscured by experimental errors, particularly in ores of young ages such as the present case.

The Te minerals released considerable amounts of radiogenic ^4He and ^{40}Ar . As will be discussed in the following section for Ar in the quartz separate, the relevant hydrothermal fluids at Oya contained inherited excess ^{40}Ar . Although we can not give

Fig. 3. Abundance pattern of noble gases for Te and associated minerals from the Oya and Suwa mines. F^m is defined by $F^m = ({}^m\text{X}/^{36}\text{Ar})_S / ({}^m\text{X}/^{36}\text{Ar})_A$, where ${}^m\text{X}$ is noble gas isotope of mass number m . Subscripts S and A represent sample and atmosphere, respectively.

quantitative discussion without data available on the K content, it is very likely that the Te minerals trapped such excess ^{40}Ar at crystallization. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio for the 200°C fraction of sample Oya-2 is significantly higher than the atmospheric ratio (*i.e.*, 295.5). Radiogenic ^{40}Ar appears to reside in low temperature sites. Large amounts of radiogenic ^4He were released from both Oya-1 and -2. But no fissionogenic Xe are detected, as mentioned above. Expected fissionogenic ^{136}Xe is $1 \times 10^{-15} \text{ cm}^3/\text{g}$, if all ^4He are assumed to be in-situ decay products of U and Th. This is within experimental errors. Elemental abundance patterns are given in Fig. 3. Helium is greatly enriched. Enrichments of Kr and Xe are also significant, while depletion of Ne is very small. The great enrichment of ^4He is usually found in emanations from the solid earth.²³⁾ So the Te minerals could have trapped such ^4He at mineralization. In stepped heating of the Te samples, He and Ne were preferentially released at 200°C, together with significant amounts of Kr and Xe. Because of more enrichments in He and Ne compared to the 850°C fraction, they seem to be released from trapping sites, such as grain boundaries, different from those for Kr and Xe that appeared at 200°C, or otherwise the enrichments in He and Ne may be due to large diffusivity for He and Ne in the Te minerals. Great enrichments in Kr and Xe and the Xe isotopic ratios suggest that most of Kr and Xe in the 200°C fraction are attributable to residuals of an atmospheric component adsorbed on samples. However, the $^{130}\text{Xe}/^{132}\text{Xe}$ ratio indicates that small but visible amounts of radiogenic ^{130}Xe are released at 200°C.

3.2 Associated minerals

Oya quartz released 9 and 6 times more ^{84}Kr and ^{132}Xe , respectively, than the Te minerals, while arsenopyrite 3 times more ^{84}Kr and slightly less ^{132}Xe . The isotopic compositions are atmospheric for Kr and Xe from quartz, while arsenopyrite has small excesses at ^{129}Xe and ^{130}Xe . No large isotopic excesses are found. These small excesses can be explained by a small contamination of tellurobismuthite (*i.e.*, 0.6 wt% Te or 1.8 mg tellurobismuthite in 140 mg arsenopyrite). As found in Fig. 1(b), some arsenopyrite grains contain inclusions of tellurobismuthite. Therefore we attribute these small excesses to contaminating tellurobismuthite contained as inclusions. Data on the Xe isotopes indicate that the isotopic ratios of trapped Xe is atmospheric. This implies that the Te minerals have trapped the atmospheric isotopic ratios of Xe when it crystallized, because both Te minerals and arsenopyrite as well as quartz were deposited from the same hydrothermal fluids.

Both quartz and arsenopyrite samples contain abundant Ar. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio is 500.6 for quartz and 299.1 for arsenopyrite. The excess ^{40}Ar for quartz, compared to atmospheric Ar, amounts to $1.71 \times 10^{-6} \text{ cm}^3/\text{g}$. This is too high to be produced by the in-situ decay of ^{40}K because approximately 0.4 wt% K is required to produce it in 100 Ma. Since K content in quartz crystal usually very low (typically less than 100 ppm, for example), K should be contained in fluid inclusions. However, such a high content of K is quite unlikely in fluid inclusions, because it requires that approximately 55% of quartz volume should be shared with the fluid inclusions with an assumption of 10 wt% KCl in NaCl solution of *ca.* 30 wt%; these assumed contents are unreasonably high. Hence most of the excess ^{40}Ar should be inherited Ar from precursor materials at mineralization. This result for Ar suggests that excess ^{40}Ar inherited from precursor

materials was contained in the hydrothermal fluids and the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio was appreciably higher than the atmospheric one. K-Ar dating with Te mineral itself would be dangerous in yielding an erroneous age interfered by inherited excess ^{40}Ar because of low K content in Te minerals.^{9), 30)} Both arsenopyrite and quartz must have acquired Ar of the same isotopic ratio at crystallization. The low $^{40}\text{Ar}/^{36}\text{Ar}$ ratio for arsenopyrite indicates that it was severely contaminated later by atmospheric Ar.

Noble gas abundance pattern plotted in Fig. 3 exhibits that heavy noble gases in the Oya arsenopyrite are atmospheric in elemental composition. This is consistent with the low $^{40}\text{Ar}/^{36}\text{Ar}$ ratio for this sample. On the other hand, the Oya quartz is similar in abundance pattern of heavy gases to water in equilibrium with the atmosphere. However it is not so enriched in ^4He as the arsenopyrite and the Te minerals. The low He in quartz can be assigned to diffusive loss of He because of its high permeability for He.

In addition, in order to know elemental and isotopic compositions of noble gases contained in hydrothermal fluids at the Suwa mine, we have analyzed the quartz-calcite separate from the specimen of Te ores collected at the Suwa mine. With the same Te ore, Takaoka have determined the DBD half-life of ^{130}Te .¹⁰⁾ It is abundant both in ^4He and ^{40}Ar . The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio indicates a significant enrichment of radiogenic ^{40}Ar , though no data are available on the K content. As for the Oya quartz, it may contain inherited excess ^{40}Ar . In contrast, the Xe isotopic ratios are atmospheric and reveal no evidence for radiogenic ^{130}Xe nor fissionogenic ^{136}Xe . Enrichments of Kr and Xe relative to the atmosphere are low compared with the Oya samples, particularly no enrichment in Kr (Fig. 3).

4. Discussion

4.1 Time for accumulation of radiogenic ^{130}Xe

The Te minerals are not adequate for dating samples because of low contents of parent elements and the possible inherited component, as deduced from the noble gas data for the Oya quartz and arsenopyrite. A biotite separate from quartzdiorite and a hornblende-rich separate from porphyrite have been employed for K-Ar dating and the ages of (85.9 ± 1.8) and (104 ± 3) Ma have been given for biotite and hornblende, respectively.²⁴⁾ For biotite from the same quartzdiorite body, a K-Ar age of (88 ± 1) Ma has been reported.³⁴⁾

Usually in conventional K-Ar dating the atmospheric isotopic ratios are assumed to correct for initially trapped Ar. However, as deduced from the Ar data for Oya quartz, the hydrothermal fluids at Oya seem to have contained inherited excess ^{40}Ar . This suggests a possibility that both biotite and hornblende might have trapped initial Ar containing excess ^{40}Ar at crystallization because the quartzdiorite and the porphyrite are considered to be products from the same magma activity that formed the quartz veins. A possible choice of the trapped Ar ratio is the one determined for quartz (that is, 500.6). Considering *in-situ* decay of ^{40}K in quartz, this should be an upper limit of the $^{40}\text{Ar}/^{36}\text{Ar}$ ratio for initial Ar. Because $^{40}\text{Ar}/^{36}\text{Ar}$ for biotite is as high as 5260,²⁴⁾ the biotite age would be decreased only by 4.1% to 82.4 Ma if this initial ratio is used for correction, providing $82.4 < t < 85.9$ Ma for the age of quartzdiorite. The age of porphyrite, for which $^{40}\text{Ar}/^{36}\text{Ar}$ is 2064,²⁴⁾ should be more affected and decreased by 11.5% to

92.0 Ma. Hence we have $92.0 < t < 104$ Ma for the porphyrite age.

Another important issue concerning the Xe retention is of difference in closure temperature between Ar and Xe in different minerals.²⁴⁾ The closure temperature of radiogenic ^{40}Ar is 250 to 350°C for biotite^{25)–27)} and 550°C for hornblende.^{26)–28)} The closure temperature for hornblende is very close to the melting point of tellurobismuthite (*ca.* 575°C). Hence it can bound an upper limit of the age for the onset of Xe retention, if the formation of porphyrite dykes is contemporaneous with¹¹⁾ or predates the intrusion of the quartzdiorite body.^{13), 14)} However, for a lower limit of the age for Xe retention, we are not conclusive because of no quantitative data available on the closure of Xe in tellurobismuthite. Based on the following consideration, we adopt tentatively the K-Ar age for biotite as the lower limit: $t > 82.4$ Ma. This is not a wrong approximation. It represents the age when the rock cooled to 250 to 350°C. As induced from the decrepitation temperature of quartz veins,¹³⁾ the hydrothermal fluids containing silica and Te are supposed to have been introduced into the fissures of sedimentary rocks at temperature higher than the closure temperature for Ar in biotite. The quartz veins deposited therein could grow cold faster than the quartzdiorite. Then the age for quartzdiorite can bound the lower limit. Based on these considerations, we have $82.4 \text{ Ma} < t < 104 \text{ Ma}$, or 93 ± 11 Ma on average, for the Xe retention age in the Oya Te minerals.

4.2 Half-life for ^{130}Te double-beta decay and its effect on geological time-scale of the Japanese Islands

The half-life for ^{130}Te DBD has been determined to be $(7.9 \pm 1.0) \times 10^{20}$ years using $(1.22 \pm 0.04) \times 10^{13}$ for $^{130}\text{Te}/(^{130}\text{Xe})_{\text{DBD}}$ and $(9.3 \pm 1.1) \times 10^7$ years for the age t on average.²⁴⁾ This result agrees well with that by Takaoka and Ogata³⁾ and Missouri group,^{4), 29), 30)} but is distinctly shorter than the half-lives reported by Heidelberg^{5), 22), 31)} and St. Louis^{6), 8), 9)} groups. The present half-life also agrees well with the half-life of 8.6×10^{20} years that has been determined with another Te sample from the Suwa mine (recalculated from data by Takaoka, 1967)¹⁰⁾. Here we used $2.12 \times 10^{-12} \text{ cm}^3 \text{ STP/g}$ for $^{130}\text{Xe}_{\text{DBD}}$, 42.5 wt% for the Te content,¹⁰⁾ and 1.05×10^8 years¹⁹⁾ for the Xe retention age deduced from the formation age of muscovite from country rocks (*i.e.*, quartz-crystalline schist) for calculation of the half-life. The muscovite age is an approximation for the Xe retention age, but based on the geological and geochronological observations on regional metamorphism in the late Cretaceous, mentioned earlier, we believe that it is not a wrong approximation, though it may be overestimated.

The ^{130}Te – ^{130}Xe system can also serve as a geochronometer. If we assume quantitative retention of radiogenic ^{130}Xe in the Te minerals from the Oya and Suwa mines, adoption of such a long half-life of ^{130}Te as 3×10^{21} years^{8), 9)} would require a geological time-scale elongated by 4 times for two fundamental blocks in the geology of Northeast Japan. This implies that the current time-scale in the geology of Japanese Islands should be reformed totally. This would destroy the geological frame of this relatively young islands. Because the geological time-scale is based on accumulation and consistency of a suite of analytical and observational data obtained by radiometric, paleontological and other geological dating methods, it would cause great confusions in earth sciences. Thus, it is quite difficult to accept the half-life as long as 3×10^{21} years for the

¹³⁰Te DBD.

4.3 Neutron-capture products

The Te mineral samples from Oya have definite excesses at ¹²⁹Xe and ¹³¹Xe. These are products from neutron-captures on ¹²⁸Te and ¹³⁰Te. The ratio of ¹²⁹Xe to ¹³¹Xe excesses is 1.64 ± 0.09 on average, in agreement with the previous result,³¹ as listed in Table 3. However, the ratio is different from that of products by thermal neutron-captures on ¹²⁸Te and ¹³⁰Te (1.01 from thermal neutron-capture cross-sections by Walker *et al.*³²⁾ or 0.64 from those by Hughes and Schwartz³³⁾). Considering that approximately 24% of ¹²⁹I is not yet decayed to ¹²⁹Xe, this ratio is 2.16 instead of 1.64. The difference between the measured and the theoretical ratios is attributed to mixing of products by resonance captures of epithermal neutrons, for which the production ratio is 3.98.³⁵⁾

From these data, the mixing ratio of thermal to epithermal neutron-capture ¹³¹Xe is 55 (or 61) % *vs.* 45 (or 39) % with the cross-sections by Hughes and Schwartz³³⁾ (or by Walter *et al.*³²⁾). The mean ¹³¹Xe excess is $7.59 \times 10^{-13} \text{ cm}^3/\text{g}$, or $2.04 \times 10^7 \text{ atom}^S/\text{g}$. The amount of neutron-capture ¹³¹Xe produced in time t is given by

$$N(^{131}\text{Xe})_{nt} = \sigma \phi N(^{130}\text{Te})t, \quad (1)$$

where σ , ϕ , and $N(^{130}\text{Te})$ are the cross-section of neutron-capture on ¹³⁰Te, the mean neutron flux and the amount of target ¹³⁰Te, respectively. From Eq. (1) with $\sigma = 0.22 \text{ b}$ for thermal neutron-capture on ¹³⁰Te,^{32), 33)} we have $\phi(n_{th}) = 7.1$ or $7.9 \times 10^2/\text{cm}^2 \text{ y}$, depending on the cross-section for thermal neutron-capture on ¹²⁸Te. Here we used $N(^{130}\text{Te}) = 7.64 \times 10^{20} \text{ atom}^S/\text{g}$ and $t = 9.3 \times 10^7 \text{ years}$. This flux is significantly high, compared with data given by Bernatowicz *et al.*,⁹⁾ and suggests the existence of a nearby neutron source. The ¹²⁸Xe excess is less than $5 \times 10^{-15} \text{ cm}^3/\text{g}$ (or $1 \times 10^5 \text{ atom}^S/\text{g}$) at face value. The amount of ¹²⁸Xe assigned to ¹²⁸Te DBD^{6), 24)} is $2.0 \times 10^4 \text{ atom}^S/\text{g}$. An upper limit of I content in the Te minerals can be calculated, with the neutron flux determined above and 6.2 and 150 *b* for cross sections of thermal and epithermal neutron-captures on ¹²⁷I, respectively^{32), 33)}, to be less than 2 ppm.

On the other hand, the isotopic excesses at ¹²⁹Xe and ¹³¹Xe is negligibly small for the Suwa Te mineral,¹⁰⁾ as found in Table 2. The ratio of excess ¹²⁹Xe to excess ¹³⁰Xe is less than 0.06 for the Suwa Te mineral, an order of magnitude less compared with 0.53 for the Oya Te. This suggests a neutron flux lower by more than an order of magnitude than that for Oya. The low neutron flux appears to reflect a low U content in the country rocks (*i.e.*, quartz-crystalline schist).

Table 3. Excesses at ¹²⁹Xe and ¹³¹Xe Produced by Neutron-Captures on ¹²⁸Te and ¹³⁰Te, Respectively

Sample	Te (wt%)	¹²⁹ Xe-excess	¹³¹ Xe-excess	$\frac{^{129}\text{Xe-excess}}{^{131}\text{Xe-excess}}$	Remarks
		(10 ⁻¹² cm ³ STP/g)			
Oya Te-1	47.8	1.19 ± 0.04	0.741 ± 0.061	1.61 ± 0.14	This work
Oya Te-2	47.8	1.30 ± 0.04	0.777 ± 0.045	1.68 ± 0.11	This work
Oya Te	24.2 (mean)	(a)		1.58 ± 0.03	Ref. 3

(a) Concentrations of both excesses are low in proportion to the Te content, compared to the present samples.

5. Conclusions

(1) Tellurobismuthite gave definite isotopic excesses at ^{130}Xe , ^{129}Xe , and ^{131}Xe . The ^{130}Xe excess is radiogenic from the ^{130}Te DBD, and the excesses at ^{129}Xe and ^{131}Xe are products by neutron-captures on ^{128}Te and ^{130}Te , respectively. It contains considerable amounts of radiogenic ^4He and ^{40}Ar . Most of radiogenic ^{40}Ar appear to be inherited from precursor materials, as deduced from the analytical result for quartz.

(2) Quartz separated from a specimen of Te-bearing ores from Oya released large amounts of noble gases. They are trapped gases in fluid inclusions. Xenon has the atmospheric isotopic composition and reveals no excesses at ^{130}Xe and other isotopes. This indicates that Xe in the hydrothermal fluids relevant to mineralization was atmospheric and contained no radiogenic ^{130}Xe inherited from precursor materials. On the other hand, abundant Ar of a high $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in quartz is mostly excess ^{40}Ar inherited from precursor materials.

(3) Arsenopyrite separated from Te-bearing ores from Oya contains noble gases similar in the elemental composition to atmospheric ones, except for ^4He . ^4He is greatly enriched. The atmosphere-like $^{40}\text{Ar}/^{36}\text{Ar}$ ratio indicates a heavy contamination by atmospheric gases. The Xe isotopic ratios are atmospheric except at ^{129}Xe and ^{130}Xe . These are consistent with the atmospheric elemental abundance. Small excesses detected at ^{129}Xe and ^{130}Xe are attributable to a small contamination of tellurobismuthite inclusions in arsenopyrite grains.

(4) Quartz-calcite from Suwa contains large amounts of radiogenic ^4He and ^{40}Ar . It released atmospheric Kr and Xe. No excesses are found at ^{130}Xe , ^{134}Xe , and ^{136}Xe . The hydrothermal fluids at Suwa contained atmospheric Xe.

(5) The atmospheric, isotopic composition for trapped Xe implies that the excess ^{130}Xe determined for the Te minerals can be attributed to the in-situ double-beta decay of ^{130}Te . Documents available for the present samples, including the geological relationships and the occurrences of the mineral deposits, enable us to decipher the chronological sequence of the deposits. On the basis of the noble gas data and the field relationships, we prefer $(7.9 \pm 1.0) \times 10^{20}$ to 3×10^{21} years for the absolute half-life of ^{130}Te double-beta decay. Adoption of the latter half-life would destroy the current geological frame of the Japanese Islands totally, when we regard the ^{130}Te – ^{130}Xe system as a geochronometer.

(6) From the excesses at ^{129}Xe and ^{131}Xe , the neutron flux is estimated to be $710 \text{ n/cm}^2 \text{ y}$ at the Oya mine.

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Noble Gases in Tellurium and Associated Minerals and Double-Beta Decay of ^{130}Te

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