



Article Tin (Sn) Geochemical Mapping Based on a Fixed-Value Method: A Case Illustration in Gejiu Area, Southwest China

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Abstract: Geochemical maps play an important role in mineral resource exploration. There are three traditional methods for creating geochemical maps: the cumulative frequency method, the logarithmic interval method, and the Avg \pm k \pm Std (where Avg and Std are the abbreviations of average and standard deviation, and k is a multiple of Std) method. However, with the increasing scope of the study area and cumulative data, the limitations of traditional methods, which depend on the amount of data, are exposed. A fixed-value method for Sn geological mapping is proposed to overcome the limitations of traditional methods. In the fixed-value method, Sn concentrations are divided into 19 levels on 18 fixed values ranging from $1 \,\mu g/g$ (corresponding to the detection limit) to 1000 μ g/g (corresponding to the cut-off grade of Sn in hard rocks). The 19 levels are mapped in six color tones. The first to fifth levels are the lowest background areas in blue tones, which correspond to Sn concentrations ranging from the minimum to $3.4 \,\mu g/g$. The sixth to ninth levels are high background areas in yellow tones corresponding to concentrations less than 10 μ g/g, the 10th to 12th are low anomaly areas in pink tones less than $28 \,\mu g/g$, the 13th to 15th are high anomaly areas in red tones less than 200 μ g/g (corresponding to the placer cut-off grade), the 16th to 18th in gray tones less than 1000 μ g/g, and the 19th level is in black corresponding to Sn ores with Sn concentration not less than $1000 \mu g/g$. The fixed-value method along with three traditional methods was used to contour the Sn geochemical maps in the Gejiu area in Southwest China. The illustration results of the presented fixed-value method and three traditional methods for geochemical mapping of Sn are all feasible for Sn deposit exploration in the Gejiu area, Southwest China. Compared to traditional methods, the presented fixed-value method overcomes the flaws of traditional methods and is also more meaningful in geochemistry.

Keywords: cumulative frequency method; logarithmic-interval method; Avg±k*Std method; fixed-value method; 19 levels of geochemical map

1. Introduction

Geochemical exploration is one of the major means of mineral resource exploration. The basic results of geochemical exploration are geochemical maps and anomaly maps, which have played important roles in the field of resource exploration [1–3] and environmental surveying [4,5]. The Regional Geochemistry National Reconnaissance (RGNR) [6],



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Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). the Multi-Purpose Regional Geochemistry Survey (NMPRGS) [7], and the China Geochemical Baselines (CGB) projects [8,9] have facilitated geochemical map contouring. There are three traditional methods of contouring geochemical maps: the cumulative frequency method, which depends on the cumulative distribution-free percentiles of the data [10–13], the logarithmic interval method, which is based on the range of the data expressed in logarithmic values [12], and the Avg±k*Std (where Avg and Std are the abbreviations of average and standard deviation, and k is a multiple of the Std) method, which relies on the normal (or log-normal) distribution of the data [13]. However, with the increasing scope of the study area and cumulative data, the limitations of traditional methods, which depend on the amount of data, are exposed. To overcome these flaws in traditional methods, An et al. [14] proposed a fixed-value method to contour the geochemical map of Cr.

In the fixed-value method for the Cr geochemical map [14], Cr concentrations were divided into 26 levels on 25 fixed values ranging from 5 μ g/g (corresponding to the detection limit) to 171,000 μ g/g (corresponding to the cutoff grade of 25% for Cr₂O₃ in ores). The 26 levels were mapped in six color tones. However, the fixed-value method was proposed by An et al. [14] can only be applied to the geochemical Cr map as other elements have not been presented.

In this study, three traditional methods were used to contour the Sn geochemical map in the Gejiu area in Southwest China. Then, we proposed and applied a fixed-value method for the Sn geochemical map in this case study. Finally, the geochemical maps contoured by the four methods were compared and discussed.

2. Materials

The Gejiu area in Southwest China was selected as the study area to illustrate the geochemical mapping method for Sn. The Gejiu area is located in Yunnan province, China (Figure 1a), ranging from 102°48′ E to 104°06′ E, and 23°12′ N to 23°30′ N, with an area of ca. 4224 km² [15]. The strata and magmatic intrusions of the Gejiu area are briefly described in Figure 1b after Wu et al. [15].



Figure 1. Location of the Gejiu area in China (**a**) and its geological map with tin deposits (**b**) modified after Wu et al. [15]. Notes for (**b**): (1) Quaternary: sand, sandy clay, clay sandwiched gravel layer; (2) Miocene: sandstone, mudstone; (3) Triassic: shale, dolomite, upper sandstone, calcareous mudstone or phyllite; (4) Upper Triassic: conglomerate, sandstone, slate, intermediate acid volcanic rocks; (5) Middle–Upper Triassic: limestone, dolomitic limestone, siltstone, sandstone, mudstone intercalated with conglomerate, coal; (6) Lower–Middle Triassic: limestone, dolomite, limestone; (7) Upper Permian:

mudstone, sandstone, shale, limestone and basalt; (8) Middle–Upper Permian: limestone, mudstone, siliceous rock, Emeishan basalt, sandstone, shale; (9) Middle Permian: gravel limestone, micrite limestone, chert strip limestone, mudstone, siliceous rocks; (10) Carboniferous-Permian: limestone, lower basalt, tuff; (11) Carboniferous: limestone, sandstone, dolomite; (12) Devonian-Carboniferous: mudstone, sandstone, limestone, argillaceous limestone, and middle and upper sandstone, shale; (13) Devonian: lower sandstone with shale, upper limestone, bioclastic limestone, dolomitic limestone, shale; (14) Upper Devonian: limestone, siliceous limestone, lentil-like limestone, argillaceous strip limestone, dolomite, siliceous mudstone; (15) Middle Devonian: sandstone, limestone; (16) Lower-Middle Devonian: lower mudstone, upper thin limestone, siliceous rock; (17) Lower Devonian: lower argillaceous siltstone, sandstone, mudstone, upper marl, limestone, dolomitic limestone, biogenic limestone; (18) Lower-Middle Ordovician: sandstone, limestone, siltstone; (19) Lower Ordovician: limestone, sandstone, shale; (20) Cambrian–Ordovician: dolomite, limestone, sandstone; (21) Cambrian: shale, limestone, dolomite; (22) Middle Cambrian: argillaceous strip limestone, dolomite; (23) Lower-Middle Cambrian: shale, upper limestone, dolomite; (24) Paleoproterozoic: schist, marble, granulite, marble, graphite schist; (25) Monzogranite; (26) Monzonite; (27) Syenite; (28) Gabbro; (29) lithological boundaries; (30) faults; (31) Sn deposit; (32) main residential place.

The main metal resource in the Gejiu area is tin, and super-large Sn deposit clusters are mainly located in the western part. In the deposit cluster, seven Sn deposits were exploited, including Malage [16], Songshujiao [17], Gaosong [18], Laochang [19], Kafang [20], Niushipo [21], and Zhujingpo Sn-polymetallic deposits. In addition, two super-large Sn deposits in Bainiuchang [22] in the northeast and Guanfang [23] in the southeast were also exploited.

In this study, the Sn concentration data of stream sediments in the Gejiu area were retrieved from the RGNR project database, which has covered >7 million square kilometers of Chinese land surface since its implementation in 1979 [6,10]. In the RGNR project, each composite sample representing 4 km² and corresponding to a scale of 1:20,000 was analyzed for 39 major and trace elements including Sn. The Gejiu area covers approximately 4224 km² with 132 km from west to east and 32 km from north to south. A total of 1170 analytical records were obtained from the RGNR project database to contour the geochemical Sn map.

In the RGNR project, Sn was determined by the AC horizontal electrode emission spectrographic method with a detection limit of 1 μ g/g. The accuracy ($\leq 0.05-0.10 \Delta$ lgC for different concentrations) and the precision ($\leq 10-17\%$ in relative standard deviation for different concentrations) of analyses met the requirements of DZ/T 0167 for the RGNR project.

3. Traditional Geochemical Mapping

The total 1170 lgSn concentrations of stream sediments in the Gejiu area are illustrated in Figure 2a as a histogram with an accompanying box plot [24]. The statistical parameters for Sn and lgSn are listed in Table 1. Furthermore, lgSn data without outliers are illustrated in Figure 2b and their statistical parameters are also listed in Table 1. The outlier data of lgSn were excluded repeatedly when out of the range of Avg \pm 3*Std.

The 1170 Sn concentration data in the Gejiu area range from 0.2 μ g/g to 7760 μ g/g and are close to a log-normal distribution. When the outliers are excluded, the average and standard deviation of 1074 data for lgSn are 0.88 and 0.36, respectively, and the median is 0.83 (Table 1).

Three traditional methods, namely cumulative frequency, logarithmic interval, and $Avg\pm k*Std$, were used to contour Sn geochemical maps in the Gejiu area based on 1170 Sn concentrations.

Parameters	Data Amount	Minimum	Lower Quartile (O1)	Median (Q2)	Upper Quartile (O3)	Maximum	Average (Avg)	Standard Deviation (Std)	
Sn	1170	0.2	4.4	7.4	17	7760	90	468	
lgSn lgSn ⁽¹⁾ Sn ⁽²⁾	1170 1074 1074	$-0.67 \\ -0.15 \\ 0.7$	0.64 0.61 4.1	0.87 0.83 6.7	1.23 1.10 12.5	3.89 1.95 88.4	1.025 0.88 11.2	0.624 0.36 12.4	

Table 1. The statistical parameters of Sn and lgSn in the Gejiu area.

Note: The unit is $\mu g/g$ of Sn concentrations. ⁽¹⁾ without outliers; ⁽²⁾ calculated on the lgSn ⁽¹⁾.



Figure 2. Histograms of Sn concentrations with box plots of stream sediments in the Gejiu area. (a) All data; (b) data without outliers.

3.1. The Cumulative-Frequency Method

The cumulative frequency method is a traditional and mature method to contour geochemical maps using the data of a single index or element. The geochemical map is illustrated in 19 levels with different colors, ranging from blue tones for low values to red tones for high values in 18 cumulative frequencies identified as 0.5, 1.2, 2, 3, 4.5, 8, 15, 25, 40, 60, 75, 85, 92, 95.5, 97, 98, 98.8, and 99.5 in ascending order [10,12].

Based on 1170 data points from Sn concentrations, the 19-level cumulative frequency method was used to contour the Sn geochemical map in the Gejiu area (Figure 3) on GeoExpl 2013 software developed by the Chinese Geological Survey. The 18 contour values of Sn in the Gejiu area correspond to the 18 cumulative frequencies listed in Table 2 along with color information for each level.



0.2 1.1 1.5 2 2.2 2.3 2.9 3.6 4.4 6 10 17 30 100 350 850 1200 1923 3178 7760

Figure 3. Sn geochemical map in the Gejiu area contoured using the cumulative frequency method. Color information is shown in Table 2 and geological legends are the same as those illustrated in Figure 1.

No.	Method Name	Level No.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
1	Cumulative frequency	%	0	0.5	1.2	2	3	4.5	8	15	25	40	60	75	85	92	95.5	97	98	98.8	99.5	100
		Sn	min	1.1	1.5	2.0	2.2	2.3	2.9	3.6	4.4	6.0	10	17	30	100	350	850	1200	1923	3178	max
		lgSn	-	0.041	0.18	0.30	0.34	0.36	0.46	0.56	0.64	0.78	1.00	1.23	1.48	2.00	2.54	2.93	3.08	3.28	3.50	-
		ΔlgSn	-		0.13	0.12	0.04	0.02	0.10	0.09	0.09	0.13	0.22	0.23	0.25	0.52	0.54	0.39	0.15	0.20	0.22	-
2	Logarithmic interval	lgSn	lgmin	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	lgmax
		Sn	min	1.0	1.25	1.6	2	2.5	3.2	4	5	6.3	8	10	12.5	16	20	25	32	40	50	max
		∆lgSn	-	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	-
3	Avg±k*Std	lgSn	lgmin	-0.20	-0.11	-0.02	0.07	0.16	0.34	0.52	0.70	0.88	1.06	1.24	1.42	1.60	1.69	1.78	1.87	1.96	2.05	lgmax
		k	-	-3	-2.75	-2.5	-2.25	-2	-1.5	$^{-1}$	-0.5	0	0.5	1	1.5	2	2.25	2.5	2.75	3	3.25	-
		Sn	min	0.6	0.8	1.0	1.2	1.4	2.2	3.3	5.6	7.6	11	17	26	40	49	60	74	91	112	max
		∆lgSn	-	-	0.09	0.09	0.09	0.09	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.09	0.09	0.09	0.09	0.09	-
-	-	Color	-																			
		R	- '	0	7	17	27	37	52	85	130	176	217	244	255	255	255	249	227	175	146	127
		G	-	0	45	93	136	196	221	244	255	255	255	230	184	138	94	54	22	21	30	7
		В	-	172	215	234	246	255	255	255	221	176	127	81	45	23	17	10	0	44	22	0

Table 2. Sn geochemical map information from the Gejiu area using traditional methods.

Note: The unit is $\mu g/g$ of Sn concentrations. Avg is 0.88 and Std is 0.36 of lgSn with outliers excluded; k is a multiple of Std.

In Figure 3, the highest Sn values are illustrated in red tones and are located in the Gejiu super-large Sn deposit cluster in the west. The Bainiuchang deposit area in the northeast and the Guanfang-Bozhushan area in the east mainly comprise yellow tones, indicating relatively lower values with respect to the Gejiu super-large Sn deposit cluster in the west. The Sn deposits are highlighted in warm color tones (or yellow to red tones) representing higher Sn concentration values in this area.

3.2. The Logarithmic Interval Method

The logarithmic interval method was used for geochemical mapping to contour neighbor lines on a logarithmic interval of 0.1. Within one order of magnitude, the values of 1, 1.25, 1.6, 2, 2.5, 3.2, 4, 5, 6.3, 8, and 10 with an interval of 0.1 logarithmic difference were used to draw contour lines. These values multiplied (or divided) by 10 were used for data in the next (or previous) order of magnitude [12]. With 19 levels classified on the map, the value closest to the logarithm of the median value was used as the ninth level's value. If the data were highly deviating from the normal or log-normal distribution, the data's median value without outliers was referenced to set the ninth level's value. Then, the lower and higher values were set to an interval of 0.1 logarithmic difference [12].

With respect to Sn concentrations in the Gejiu area, which deviate from the log-normal distribution (Figure 2a), the median value of 0.83 for lgSn without outliers (Table 1) was referenced and the 0.8 logarithmic value or 6.3 value in its antilogarithm was adopted as the ninth level's value. Then, the other values were set to a 0.1 logarithmic difference in ascending or descending order. If the minimum and maximum were enough to reach the 19 levels, the 19 levels were contoured, such as the first level ranging from the minimum (or $0.2 \ \mu g/g$) to $1.0 \ \mu g/g$ and the 19th level ranging from 50 $\ \mu g/g$ to the maximum (or 7760 $\ \mu g/g$). If the minimum was too high or the maximum too low, the levels counted in the 0.1 logarithmic difference did not amount to 19. In this case, levels with low or high values were omitted when mapping with the logarithmic interval method.

Based on the 1170 Sn analyses, the 19-level logarithmic interval method was used to contour the Sn geochemical map in the Gejiu area (Figure 4). Table 2 lists the 18 contour values with color information for each level.



0.2 1.0 1.25 1.6 2 2.5 3.2 4 5 6.3 8 10 12.5 16 20 25 32 40 50 7760

Figure 4. Sn geochemical map in the Gejiu area contoured on the logarithmic-interval method. The information of colors is shown in Table 2 and geological legends are the same illustrated in Figure 1.

In Figure 4, the high Sn concentration values are illustrated in red tones and located in the Gejiu super-large Sn deposit cluster in the west, the Bainiuchang deposit area in the northeast, and the Guanfang-Bozhushan area in the east. This illustration shows the geochemical map well of Sn deposits exploration in Gejiu area.

3.3. The $Avg \pm k * Std$ Method

The Avg \pm k*Std method of geochemical mapping relies on the hypothesis that concentration data in background areas are distributed in normal or log-normal patterns. If the data deviate from the normal or log-normal distribution, the outliers should be excluded repeatedly when they are out of the range of Avg \pm 3*Std. Then, the Avg and Std of the re-

maining data are calculated and the $Avg\pm k*Std$ values (or its antilogarithm for log-normal distribution) are used to contour geochemical maps, where k is a multiple of Std and set to 0.5, 1, 1.5, 2, etc. depending on the number of contour levels [13]. For example, if 19 levels are classified on a map, the k values would be set to 0.5, 1, 1.5, 2, 2.25, 2.5, 2.75, 3, and 3.25 depending on the minimum and maximum values, as in Table 2. The Avg would also be set to the ninth level's value. Then, the lower and higher values would be gradually set to $Avg\pm k*Std$ values. If the minimum is too high or the maximum is too low, the level count would not amount to 19. In this case, levels with low or high values are omitted when mapping with the $Avg\pm k*Std$ method.

With respect to the Sn concentration in the Gejiu area, the Avg and Std values of lgSn without outliers of 0.88 and 0.36 were adopted to contour the Sn geochemical map using the Avg \pm k*Std method. The antilogarithm of Avg was 7.6 µg/g and set to the ninth level's value out of 19 levels. Then, the other antilogarithmic values were calculated according to k values in the Avg \pm k*Std method and used to contour the Sn geochemical map in the Gejiu area (Figure 5). Table 2 lists color information for each level.



0.2 0.6 0.8 1.0 1.2 1.4 2.2 3.3 5.6 7.6 11 17 26 40 49 60 74 91 112 7760

Figure 5. Sn geochemical map in the Gejiu area contoured using the $Avg\pm k*Std$ method. Color information is shown in Table 2. Geological legends are the same as those illustrated in Figure 1.

In Figure 5, high Sn concentration values are illustrated in red tones and located in Gejiu's super-large Sn deposit cluster in the west. The Bainiuchang deposit area in the northeast and the Guanfang deposit area in the east are colored in yellow tones, indicating relatively lower values for the Gejiu super-large Sn deposit cluster in the west. The results of this method are consistent with the cumulative frequency method results.

4. The Fixed-Value Method of Sn Geochemical Mapping

Although traditional methods for geochemical maps have played an important role in geochemical exploration, traditional methods' dependence on the amount of data exposes their limitations. In theory, these limitations lead to incomparable results for areas with different amounts of data. We propose a fixed-value method to overcome the limitations of traditional Sn geochemical maps after the fixed-value method proposed by An et al. [14] and the 19 levels illustrated in traditional geochemical maps. In the fixed-value method of Sn geochemical mapping, Sn concentrations are divided into 19 levels on 18 fixed values that range from 1 μ g/g (corresponding to the detection limit) to 1000 μ g/g (corresponding to the cutoff grade of Sn in hard rocks). Table 3 lists 18 fixed values and 19 colors.

The first value is 1 μ g/g, which represents the detection limits of the RGNR [6,10] and NMPRGS projects [7]. However, the Sn detection limit in many laboratories is lower than 1 μ g/g. The second value is 1.3 μ g/g, which is the 0.5% cumulative frequency value of surface soils in China [25].

The third value was set to 1.8 μ g/g after 1.7 μ g/g, corresponding to the 2.5% cumulative frequency value of surface soils in China [25], and 1.96 μ g/g, corresponding to the 25% cumulative frequency value of stream sediments in China [10]. The fourth value was 2.7 μ g/g, which is the 25% cumulative frequency value of surface soils in China [25] and the 50% cumulative frequency value of stream sediments in China [10]. The fifth value

was set to 3.4 μ g/g after 3.2 μ g/g, which is the 50% cumulative frequency value of surface soils in China [25], and 3.7 μ g/g, which is the 75% cumulative frequency value of stream sediments in China [10].

Table 3. The information of Sn geochemical map on the fixed-value method.

Level No.	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Sn	min	1	1.3	1.8	2.7	3.4	4.3	6.0	7.9	10	13	17	28	50	100	200	400	600	1000	max
lgSn	-	0	0.114	0.255	0.431	0.531	0.633	0.778	0.898	1.0	1.114	1.23	1.447	1.699	2.0	2.301	2.602	2.778	3.0	-
∆lgSn		-	0.114	0.141	0.176	0.100	0.102	0.145	0.119	0.102	0.114	0.117	0.217	0.252	0.301	0.301	0.301	0.176	0.222	-
Color																				
R	-	0	9	28	54	128	255	255	255	255	255	255	255	254	249	216	191	135	100	0
G		0	46	140	224	255	230	223	211	198	229	204	153	92	57	35	191	135	100	0
В		170	216	248	255	224	153	127	76	25	255	255	255	18	9	0	191	135	100	0

Note: The unit is $\mu g/g$ of Sn concentrations.

The sixth value was set to $4.3 \,\mu\text{g/g}$ after $4.1 \,\mu\text{g/g}$, corresponding to the 75% cumulative frequency value of surface soils in China [25], and $4.5 \,\mu\text{g/g}$, corresponding to the 85% cumulative frequency value of stream sediments in China [10]. The eighth value is 7.9 $\mu\text{g/g}$, which is the 95% cumulative frequency value of stream sediments in China [10]. Based on the eighth and sixth values, the seventh value is interpolated as 6.0 $\mu\text{g/g}$.

The 10th value is 13 μ g/g, which is the 97.5% cumulative frequency value of surface soils in China [25]. Based on the 10th and 8th values, the ninth value was interpolated to 10 μ g/g. The 11th value was 17 μ g/g, which is the 98.8% cumulative frequency value of stream sediments in China [10]. The 12th value was 28 μ g/g, which is the 99.5% cumulative frequency value of surface soils in China [25]. The 15th value was 200 μ g/g, which is the cutoff grade of the Sn placer [26]. Based on the 15th and 12th values, the 13th and 14th values were interpolated to 50 μ g/g and 100 μ g/g, respectively.

The 16th value is 400 μ g/g which is the minimum industrial tenor [26]. The 18th value was 1000 μ g/g, which corresponds to Sn's cutoff grade in hard rock [27]. Based on the 18th and 16th values, the 17th value was interpolated to 600 μ g/g.

Based on the above 18 fixed values, Sn concentrations can be classified into 19 levels based on the Sn geochemical map. The first level out of 19 levels corresponds to Sn concentration, ranging from the minimum to the first value (or $1 \mu g/g$). The second level out of 19 levels corresponds to Sn concentration, ranging from the first value (or $1 \mu g/g$) to the second value (or $1.3 \mu g/g$). The last level out of 19 levels corresponds to Sn concentration, ranging from the first value (or $1 \mu g/g$) to the second value (or $1.3 \mu g/g$). The last level out of 19 levels corresponds to Sn concentration, ranging from the 18th value (or $1000 \mu g/g$) to the maximum.

To better explain these levels, the 19 levels were mapped in six color tones. The first to fifth levels were low background areas in blue tones corresponding to Sn concentrations ranging from the minimum value of 3.4 μ g/g. The sixth and ninth levels were high background areas in yellow tones corresponding to concentrations less than 10 μ g/g. The 10th to 12th levels are low anomaly areas in pink tones, with less than 28 μ g/g. The 13th to 15th levels are high anomaly areas in red tones, with less than 200 μ g/g. The 16th to 18th levels were in gray tones, with less than 1000 μ g/g corresponding to concentrations of Sn in placers (or Sn mineralization in placer types). The 19th level was in black with Sn concentrations ranging up to the cutoff grade of Sn in hard rock (or Sn mineralization in hard rock types).

The above fixed-value method for Sn geochemical mapping is mainly suggested for Sn concentrations in the RGNR and NMPRGS projects in China [6,7] and cutoff grades of Sn placers and hard rock deposits [27]. The Sn concentrations in this method range from less than detection limits to larger than the cutoff grades. Therefore, the new method is universally applicable to contouring Sn geochemical maps of geological materials. If Sn concentrations in a case study are within a narrow range, its geochemical map may illustrate

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only some of the 19 levels, such as the Cr geochemical map presented by An et al. [14]. In this study of the Gejiu area, Sn concentrations ranged from 0.2 μ g/g to 7760 μ g/g. Therefore, all 19 levels are represented on the Sn geochemical map of this area.

According to the fixed-value method, Sn concentrations of 1170 stream sediments were used to contour a Sn geochemical map of the Gejiu area, as illustrated in Figure 6.



Figure 6. Sn geochemical map in the Gejiu area based on the fixed-value method. Color information is shown in Table 3. The geological legends are the same as those illustrated in Figure 1.

Figure 6 shows the gray and black colors located in the Gejiu super-large Sn deposit cluster in the west. By contrast, the Bainiuchang deposit area in the northeast is in red tones and the Guanfang-Bozhushan area in the east is in pink tones. In other words, Sn deposits in the study area are located in areas with black, gray, red, or pink tones, which correspond to the Sn ore, placer, high-anomaly, and low-anomaly areas. The color tones of the fixed-level method indicate Sn deposits more clearly than traditional methods.

5. Discussion

5.1. Theoretical Comparison of the Employed Methods

Traditional methods of cumulative frequency and Avg±k*Std methods depend on the amount of data. The former is distribution-free, whereas the latter depends on a normal or log-normal distribution. In theory, depending on the data amount limits comparisons between geochemical maps of different areas or the same area with different data amounts.

In addition, the 0.1 value of $\Delta lgSn$ (or difference) is acceptable and meets the requirement of analytical qualities [10–13] for standard samples in labs, indicating that the $\Delta lgSn$ between two neighbor contour levels in geochemical maps should be no less than 0.1. However, the $\Delta lgSn$ between neighbor levels in geochemical maps may be less than 0.1 when the two traditional methods of cumulative frequency and Avg±k*Std methods are used. In the Gejiu area, the minimum of $\Delta lgSn$ in the cumulative frequency method is only 0.02 and the minimum of $\Delta lgSn$ in the Avg±k*Std method is 0.09 depending on the standard deviation value of 0.36 for lgSn data without outliers.

Compared to the cumulative frequency and Avg \pm k*Std methods, the traditional logarithmic interval method and the presented fixed-value method overcome the theoretical limitation of data amount dependence and meet the implicit requirement of the Δ lgSn between neighbor levels no less than 0.1. However, level values in the logarithmic interval method depend on the data's median value and do not have specific geochemical meanings for specific elements such as Sn. The presented fixed-value method's values for Sn geochemical maps were set to the statistical parameters of Sn concentration data derived from the RGNR and NMPRGS projects in China [6,7].

With respect to the classified levels and their colors, the aforementioned four methods were all designed as 19 levels. In the three traditional methods, low and high values were represented by colors ranging from blue to red. The presented fixed-value method, on the other hand, ranged from blue to red and corresponded to low backgrounds and high anomaly values, and from gray to black based on Sn concentrations in placers and ores in hard rocks. The color tones in the newly presented method with six color tones (corresponded)

ing to low background, high background, low anomaly, high anomaly, mineralization in placer type, and mineralization in hard-rock type) are superior to traditional methods with three color tones (from blue to yellow, then to red, corresponding to low, medium, and high values).

5.2. Comparison of Methods in the Gejiu Area

In our case illustration for the Gejiu area, values in the same level of the 19 levels for the four methods may be close or different depending on the case data. For example, the 9th values of 6.0, 6.3, 7.6, and 10 μ g/g for the cumulative frequency, logarithmic interval, Avg±k*Std, and fixed-value methods, respectively, which are relatively close, and the differing values of the 16th level, namely 1200, 32, 74, and 400 μ g/g, respectively.

Furthermore, the geochemical map colors indicating Sn deposits in the Gejiu area may be similar or different. For instance, the Gejiu super-large Sn deposit cluster is located in a high-value area in red tones using the three traditional methods (Figures 3–5) and in gray and black tones using the fixed-value method (Figure 6). The Bainiuchang deposit area and Guanfang-Bozhushan area are located in the yellow-to-red tone and pink-to-red tone areas. For further comparison, the Bainiuchang and Guanfang deposit areas are colored in a way that indicates relatively lower values than the Gejiu super-large Sn deposit cluster using cumulative frequency (Figure 3) and fixed-value methods (Figure 6). However, they may indicate similar values to the logarithmic interval (Figure 4) and $Avg\pm k*Std$ methods (Figure 5). In any case, geochemical map depictions of Sn deposits in the Gejiu area are basically consistent with all four methods. These similar results indicate that all four methods are feasible for geochemically mapping Sn in this case illustration. However, the presented fixed-value method is superior to the other three traditional methods.

6. Conclusions

- To overcome the limitations of traditional methods, which depend on the amount of data, a fixed-value method was proposed with 18 fixed Sn concentration values ranging from the detection limit to the cutoff grade to contour a geochemical Sn map with 19 levels and six color tones;
- (2) With six color tones corresponding to low backgrounds, high backgrounds, low anomalies, high anomalies, mineralization in placer types, and mineralization in hard-rock types, the fixed-value method is superior to traditional methods, which are usually represented by three colors (from blue to yellow, then to red) that correspond to low, medium, and high values;
- (3) Although the four discussed methods of Sn geochemical mapping are all feasible for Sn deposit exploration in the Gejiu area, the presented fixed-value method is more meaningful.

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