# Discriminating geodynamical regimes of tin ore formation using trace element composition of cassiterite: the *Sikhote'Alin* case (Far Eastern Russia)

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Abstract: A possible interpretation of the Sikhote'Alin accretion system (Asian margin of the Pacific Ocean) assumes that this region underwent an alternation of subduction and transform tectogenesis (here called the tectogenetic switch hypothesis). This palaeotectonic model fits well with the observed complexity of ore districts and deposits of the region. In this contribution, several statistical analyses are applied to a compositional dataset of trace elements in cassiterite obtained from this area. The goal is to assess the reliability of the tectogenetic switch hypothesis, based solely on cassiterite compositional information. First, biplots are used to get an insight into the variability of the data. Secondly, cluster analysis is applied to detect the existence of natural groups of samples, without using the existing geological information. Finally, discriminant analysis uncovers the main differences in the composition of cassiterite from the different groups obtained. Results highlight the contrast between areas formed under different tectogenetic environments, being subduction-related cassiterite richer in siderophile elements (In, Fe, Sc, W, Cr) and transform-related cassiterite richer in lithophile elements (Mn, Zr). Further natural groups discriminate cassiterite samples depending on their V/Be ratio, which might be related to the age of the deposit. These results suggest that sources of ore magmas and fluids within the region might have a mixed or varied mantle-crust origin and support the tectogenetic switch assumption.

The Sikhote'Alin accretion folded system is located in the easternmost part of Asian Russia, north to the city of Vladivostok. It is a very complex system, containing several terranes of ages ranging from the Jurassic to the Neogene (Fig. 1) and its formation is open to debate. Some authors (e.g. Faure et al. 1995) consider this area as the result of a series of collisions of island-arc systems on the Asian main foreland. A newer interpretation of this area, following Khanchuk (2000), suggests that a better explanation of the observed characteristics of this structure is achieved by considering a switch between geodynamic regimes. According to this model of geodynamic evolution, a shift in the tectogenetic conditions occurred in the interval 100-45 Ma in this part of the Asian margin of the Pacific Ocean (Khanchuk et al. 2003). From a transform continental margin of Californian type (between the Early Cretaceous and the beginning of the Late Cretaceous), the margin changed to an active regime of Andean type (from the Late Cretaceous to the Paleocene), and switched back to a transform margin type again (during Eocene). Such a process is called here **tectogenetic switch**.

Under continental transform margin conditions, active magmatism is connected with the asthenospheric diapiric penetration into slab-windows of the subducted lithosphere, able to produce the formation of major tin deposits with polymineral compositions. The magmatism over slab-window zones is characterized by an evolution of the fluids in the magmatic chamber from basic to acid compositions, by low partial pressure of H<sub>2</sub>O and H<sup>+</sup> and high partial pressure of B and F, and also by the prolonged development of these magmatic chamber systems. This might give rise to large polygenetic deposits of tin and tungsten. On the contrary, subduction-related magmatism within active margins is characterized by the inverse sequence of magmatic series (from acid to basic), by high partial pressure of  $H_2O$  and  $H^+$  and by tin-polymetal mineralizations

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Fig. 1. Geological map of the Russian Far East (after Khanchuk & Kemkin 2003). Tin regions: 1, Komsomol'sk  $(35 \times 25 \text{ km}^2)$ ; 2, Kavalerovo  $(35 \times 50 \text{ km}^2)$ .



**Fig. 2.** Geodynamic model of ore-magmatic systems for the Russian Far East. Legend: 1, volcanics of *Sikhote' Alin* belt; 2, accretion complex; 3, suboceanic complex; 4, turbidite complex; 5, accretion complex; 6, accretion prism; 7, basalt layer of the 'transition' crust; 8, basalt layer of the oceanic crust; 9, upper mantle; 10, lower mantle (asthenosphere); 11, mantle diapirs.

(Khanchuk *et al.* 2003) (Fig. 2). This Andean-type environment is related to poly-formational systems, which may have undergone many periods of magmatic activity.

Some experimental evidence supports the tectogenetic switch hypothesis. Isotope geochemical data (Gonevchuk 2002), for example, show that sources of magmas and associated fluids within the region have a heterogeneous mantle-crust origin. Moreover, this model offers a natural explanation for the observed multi-stage character of the polymineral ore bodies present in this region, as well as for the geochemical differences observed in their several stages: the formation of some deposits occurred during several (2-3) mineralization stages connected with different geodynamic settings. In fact, the proposed model was suggested primarily by Khanchuk (2000) to explain the complexity of the many tin- and tungsten-bearing deposits of this region, which are of capital economic importance. The goal here is to search for statistical evidence for this theory, by studying the compositional differences in cassiterite from some of the tin-bearing deposits of the region.

Why cassiterite? This choice is determined by two factors: (1) cassiterite, being the main mineral of various genetic groups of tin deposits, crystallizes during an ore-forming stage and therefore reflects physico-chemical conditions of mineralization – providing the most important genetic information; (2) geochemical trace element associations in cassiterite are studied in 46

#### N. GORELIKOVA ET AL.

detail for many tin deposits, thus the approach may be extended easily in the future to other tin districts. Using trace element paragenesis on a mineral species to complement classical petrologic mineral paragenesis is an old idea (Fersman 1953; Shcheka et al. 1987), since both are considered essential indicators of metallogenic provinces and of its genetic type. In this line, this work focuses on the trace element composition of cassiterite, instead of on the mineral paragenesis accompanying it. The studied database involves 600 analyses of trace elements (In, Sc, W, Nb, Zr, Be, Fe, Ti, Cr, V, Mn). To obtain them, cassiterite grains were selected from tin ores under binocular microscope - possible because of the coarse-grained nature of both cassiterite and the accompanying minerals. Cassiterite grains were powdered in an agate mortar and leached with acids to remove other mineral traces. Samples of cassiterite were analysed by quantitative spectral analysis using spectrograph Qu-24 Zeiss Jena and Adam Hilger with quartz optics (Harrison 1949). For the analysis, samples weighting up to 10 mg were admitted into coal electrodes and burnt down. Spectra of atoms were recorded on photo plates and spectrograms were deciphered using atlases of analytical lines (Gossler 1942; Brode 1943; Crook 1935). Spectral response is 1-3 ppm, duplication is characterized by rms. error in the 10-25% area. Accuracy of an analysis is represented by a relative error in the 10-20% area.

Based on a classical multivariate statistical analysis of an extended version of this dataset, Gorelikova & Tchijova (1997) argued that the available trace elements appear to give reliable criteria for genetic type identification and mineralization productivity assessment. According to them, the trace element paragenesis is conditioned by different factors, such as the deep crust structure, the associated magmatism type and the genetic type of the deposit. Their results indicate that the geochemical associations of minerals formed in the continental basement are characterized by a predominant lithophile composition (Be, Nb, Zr, Mn), while siderophile trace elements (Fe, Ti, V, Cr, Ni) are preferentially linked to potassic series. Such potassic series are typical for intermediate zones between ocean and continent (Gorelikova 1988). Using classical factor analysis, the authors found that: (1) W-Be-Sc or Be-W-In-Fe associations appear to be typical for cassiterite from rare-metal ores; (2) Ti-V-Cr association might be typical for cassiterite-quartz ores; (3) the Sc-Nb-Ti-V association might be typical in cassiterite-tourmaline and cassiterite-chlorite ores; and (4) cassiterite-sulphide ores would behave in a way similar to the silicate paragenesis, showing a preferential enrichment in Ti-V-Nb-Cr.

## Setting

Within the Sikhote'Alin accretion folded system, there are several metallogenic belts: from them, the Khingan-Okhotsk and the Sikhote'Alin (Fig. 1) belts were selected for this study. Within the Khingan-Okhotsk metallogenic belt, the Komsomol'sk ore-magmatic system was considered and, within this system, the present study analyses the deposits of Festival'noe and Pereval'noe. Within the Sikhote'Alin metallogenic belt, the Kavalerovo ore region was selected, represented by the tin deposits of Vysokogorskoe and Arsen'evskoe. These regions and deposits, jointly with the zones in which they are divided, are included in Table 1, which describes their main geological characteristics.

According to the Khanchuk (2000) model, the formation of the tin deposits of the whole Komsomol'sk ore region (Cretaceous) and Vysokogorskoe deposit (Eocene) in Kavalerovo is connected to a Californian-type environment, and Arsen'evskoe deposit (Late Cretaceous–Paleocene), also in the Kavalerovo region, to an active continental Andean margin. These differences in the assumed tectonic environment justify the choice of these deposits. Moreover, Arsen'evskoe is one of the most complex, largest and most important deposits from an economic point of view.

The main characteristics of these regions and deposits, as well as their internal zones, are described in Table 1. It includes the geodynamic regime assumed to govern the formation of each ore body, the ages of the mineralization and of the associated magmatic complex, and the main mineral paragenesis. An extended description of the ore bodies is compiled in Appendix A, due to the lack of references outside the Russian literature.

#### **Dataset description**

For each sample of cassiterite a composition of trace elements included in the crystalline structure of this mineral is recorded, and they are reported in percentages. Once complemented with the rest up to 100 (approximately representing the amount of tin), they form a closed vector and fall within the scope of compositional data analysis. Therefore, log-ratio techniques, introduced by Aitchison (1986) and described in section three of this volume, are applied. First, the clr coefficients of the compositional vectors  $\mathbf{x} = [x_1, x_2, \dots, x_{12}]$  are computed using the clr transformation,

$$\operatorname{clr}(\mathbf{x}) = \left[ \ln \frac{x_1}{g(\mathbf{x})}, \ln \frac{x_2}{g(\mathbf{x})}, \dots, \ln \frac{x_{12}}{g(\mathbf{x})} \right],$$
  
where  $g(\mathbf{x}) = \sqrt[12]{x_1 \cdot x_2 \cdots x_{12}},$  (1)

Region	Deposit	Zone	Geodynamic regime (stage)	Age of magmatic complex (Ma)	Age of mineralization (Ma)	Parageneses
Komsomol'sk	Festival'noe	Geophysicheskaya	C	102-85; 103-75	95-84	Quartz, tourmaline, cassiterite, sulphides
	Pereval'noe	Severnaya	C	102-85	95 - 84	Quartz, tourmaline, sulphides
Kavalerovo	Arsen'evskoe	Fel'zitovayal	C (3rd)	60-48	25 - 23	Quartz, micas, sulphides
		Fel'zitovava2	C (3rd)	60-48	25-23	Quartz, cassiterite, micas, sulphides
		Induktzionnava	A (2nd)	80 - 76	60 - 55	Quartz, chlorite, cassiterite, sulphides
		Podruzhka	C (1st)	115-95	93-95	Tourmaline, Mn-minerals, stannite, sulphides
		Yuzhnaya	A (2nd)	80-76	60 - 55	Quartz, chlorite, cassiterite, sulphides
		Tourmalinovaya	C (1st)	115-95	93–95	Tourmaline, Mn-minerals, stannite, sulphides
	Vysokogorskoe	8th Vostok	ັ ບ	105-50	45	Quartz, cassiterite, tourmaline, sulphides
	0	Kulisnaya	C	105 - 50	45	Quartz, cassiterite, tourmaline, sulphides
		Tektonicheskaya	C	105 - 50	45	Quartz, cassiterite, tourmaline, sulphides
Abbreviations used	in the geodynamic regi	mes correspond to California	an and Andean margi	n types.		

Table 1. Summary of relevant geological information regarding the studied regions, deposits and zones

given that the dataset has 12 parts (11 trace elements and the rest). Using the clr-transformed observations, some descriptive statistics can be computed, and those which are interpretable in terms of the original parts can be back-transformed. This is the case of the mean, computed first as the average of the clr-transformed dataset, taking then exponentials of each component and finally closing it to 100%. Table 2 brings the global mean and the means by zones, including also the number of samples in each zone and other global descriptive statistics.

To explore the dataset in more detail, the biplot is used (Gabriel 1971; Aitchison & Greenacre 2002; Daunis-i-Estadella et al. 2006). It is a joint graphical representation of both variables and individuals projected onto the plane of the two first principal components obtained from the clr-transformed variables. Being a projection, this plot displays only part of the variability of the data, here 68% of the total variability (Fig. 3). Therefore, conclusions based on visual perceptions should be considered with care. To assess visual differences between the zones, in Figure 3 each sample is plotted using a different symbol for its ore body. At first sight, there is a clear separation to the right of the plot of most of the samples in the Yuzhnaya zone. Following a circular pattern clockwise, the mixture of some samples of Yuzhnaya and Induktzionnava can be recognized. The next group of samples is a mixture of 8th Vostok, Kulisnaya, Severnaya, Tektonicheskaya, and the two Fel'zitovaya zones. Finally, the last group of samples corresponds to a sequence going from Podruzhka through Tourmalinovaya to Geophysicheskaya. However, there is no clear separation of the two regions, Komsomol'sk and Kavalerovo. Nevertheless, at the level of the deposits, and considering the regions separately, some trends can be recognized. For example, the two deposits in the Komsomol'sk region, Festival'noe and Pereval'noe, are quite well separated. Within Vysokogorskoe separating from Kavalerovo, Arsen'evskoe, the separation of the 8th Vostok and Kulisnaya from the Tektonicheskaya samples can be recognized. But it is the overlapping of some zones, such as the similarity of the latitudinal zones (Tourmalinovaya and Podruzhka) with those of the Komsomol'sk region, which suggests that the geodynamic environment exerts a primary control over the mineralization regime. At least, the pure geographical control appears not to be sufficient to define different groups.

# Methodology

Using the clr-transformed dataset, Ward cluster analysis, binary logistic discriminant analysis and

Table 2.	. Summary	of statistical characteris	tics (sample	e size, maximum, n	vinimum and compo	sitional mean) for 1	the studied regions,	deposits and zones	
ы	D	Zone	u	II	Sc	M	Nb	Λ	c
K'sk	F P	Geophysicheskaya Severnaya	12	$1.05 \times 10^{-2}$ $5.00 \times 10^{-4}$	$1.05 \times 10^{-3}$ $4.44 \times 10^{-4}$	$\frac{1.76 \times 10^{-1}}{6.15 \times 10^{-2}}$	$3.42 \times 10^{-3}$ $9.13 \times 10^{-3}$	$\frac{8.91 \times 10^{-4}}{2.29 \times 10^{-3}}$	$\frac{2.10\times10^{-3}}{5.00\times10^{-4}}$
Kvo	A	Fel'zitovayal Fel'zitovaya2	∞ ∞	$6.84 \times 10^{-4}$ $5.00 \times 10^{-4}$	$7.63 \times 10^{-4}$ $4.06 \times 10^{-4}$	$4.93 \times 10^{-2}$ 5.46 × 10^{-2}	$1.88 \times 10^{-2}$ 2.16 × 10^{-3}	$1.26 \times 10^{-3}$ $1.18 \times 10^{-2}$	$8.40 \times 10^{-4}$ $1.69 \times 10^{-3}$
		Induktzionnaya Podruzhka Yuzhnava	6 80 80	$5.79 \times 10^{-4}$ $5.35 \times 10^{-4}$ $5.01 \times 10^{-4}$	$3.00 \times 10^{-4}$ $3.00 \times 10^{-4}$ $3.00 \times 10^{-4}$	$8.61 \times 10^{-2}$ $5.20 \times 10^{-2}$ $6.55 \times 10^{-2}$	$1.50 \times 10^{-3}$ $2.77 \times 10^{-3}$ $1.25 \times 10^{-3}$	$2.73 \times 10^{-3}$ $2.66 \times 10^{-3}$ $3.33 \times 10^{-3}$	$7.73 \times 10^{-4}$ $7.99 \times 10^{-4}$ $8.70 \times 10^{-4}$
		Tourmalinovaya	4	$5.00 \times 10^{-4}$	$4.05 \times 10^{-4}$	$7.29 \times 10^{-2}$	$1.08 \times 10^{-3}$	$6.85 \times 10^{-3}$	$2.66 \times 10^{-3}$
	4	8-th Vostok	r 7	$5.00 \times 10^{-4}$	$2.71 \times 10^{-4}$	$1.06 \times 10^{-1}$	$2.43 \times 10^{-3}$	$1.14 \times 10^{-2}$	$2.00 \times 10^{-3}$
		Kuusnaya Tektonicheskaya	n vn	$3.88 \times 10^{-4}$	$3.00 \times 10^{-4}$ $3.82 \times 10^{-4}$	$5.96 \times 10^{-2}$	$1.80 \times 10^{-5}$ 9.84 × $10^{-3}$	$7.51 \times 10^{-4}$	$6.01 \times 10^{-4}$ $6.07 \times 10^{-4}$
		Global mean	144	$2.79 \times 10^{-3}$	$6.89 \times 10^{-4}$	$1.09 \times 10^{-1}$	$3.83 \times 10^{-3}$	$1.37 \times 10^{-3}$	$1.47 \times 10^{-3}$
		Global raw		$5.0 \times 10^{-5}$	$2.00 \times 10^{-4}$	$9.00 \times 10^{-3}$	$1.00 \times 10^{-4}$	$3.0 \times 10^{-5}$	$4.00 \times 10^{-4}$
		Global raw maximum		$6.10 \times 10^{-2}$	$9.60 \times 10^{-3}$	$6.30 \times 10^{-1}$	$4.30 \times 10^{-1}$	$2.40 \times 10^{-2}$	$6.90 \times 10^{-1}$
R	D	Zone	u	Be	П	Zr	Fe	Mn	Rst
K'sk	r d	Geophysicheskaya Severnaya	12	$1.07 \times 10^{-4}$ 9.31 × 10^{-6}	$7.90 \times 10^{-2}$ 2.08 × 10^{-1}	$2.53 \times 10^{-3}$ $1.53 \times 10^{-2}$	1.80 $3.47 \times 10^{-1}$	$1.68 \times 10^{-3}$ $1.62 \times 10^{-2}$	97.9 99.3
Kvo	А	Fel'zitovaya1	8	$5.61 \times 10^{-5}$	$1.11 \times 10^{-1}$	$1.35 \times 10^{-2}$	$4.96 \times 10^{-1}$	$9.66 \times 10^{-3}$	99.3
		Fel'zitovaya2 Induktrionnova	∞ vc	$1.77 \times 10^{-5}$	$3.36 \times 10^{-1}$ $6.50 \times 10^{-2}$	$1.72 \times 10^{-2}$ 1 83 $\times 10^{-3}$	$7.21 \times 10^{-1}$ 4.03 $\times 10^{-1}$	$2.25 \times 10^{-2}$ $1.44 \times 10^{-3}$	98.8 00 3
		Podruzhka	o vo	$9.75 \times 10^{-6}$	$1.96 \times 10^{-1}$	$1.47 \times 10^{-2}$	$6.13 \times 10^{-1}$	$1.48 \times 10^{-2}$	99.1
		Yuzhnaya Tourmalinovava	80 4	$6.18 \times 10^{-6}$ $1.12 \times 10^{-5}$	$2.53 \times 10^{-1}$ $2.60 \times 10^{-1}$	$2.19 \times 10^{-2}$ $1.70 \times 10^{-2}$	$4.01 \times 10^{-1}$ $5.73 \times 10^{-1}$	$1.28 \times 10^{-2}$ $1.24 \times 10^{-2}$	99.2 99.1
	Λ	8-th Vostok	7	$9.40 \times 10^{-6}$	$3.22 \times 10^{-1}$	$1.93 \times 10^{-2}$	$3.69 \times 10^{-1}$	$9.55 \times 10^{-3}$	99.2
		Kulisnaya	5	$2.38 \times 10^{-5}$	$5.65 \times 10^{-2}$	$1.14 \times 10^{-2}$	$2.69 \times 10^{-1}$	$9.35 \times 10^{-3}$	9.66
		Tektonicheskaya	5	$1.05 \times 10^{-4}$	$1.02 \times 10^{-1}$	$6.77 \times 10^{-3}$	$3.87 \times 10^{-1}$	$8.22 \times 10^{-3}$	99.4
		Global mean	144	$4.75 \times 10^{-5}$	$1.09 \times 10^{-1}$	$5.10 \times 10^{-3}$	$9.83 \times 10^{-1}$	$3.75 \times 10^{-3}$	98.8
		Global raw		$5.00 \times 10^{-6}$	$1.40 \times 10^{-2}$	$1.00 \times 10^{-3}$	$1.30 \times 10^{-1}$	$5.00  imes 10^{-4}$	96.1
		Global raw		$1.20 \times 10^{-3}$	$5.20 \times 10^{-1}$	$1.63 \times 10^{-1}$	3.63	$1.30 imes10^{-1}$	2.66
		Inaximum							

48

N. GORELIKOVA ET AL.

Regions and deposits are abbreviated from Table 1.



**Fig. 3.** Biplots of cassiterite trace elements from the studied tin deposits (Far Eastern Russia), distinguishing samples according to their zone of origin (variables use the upper and right scales, data use the lower and left scales; horizontal scale is the first principal component direction, and vertical scale the second principal component one).

classical linear regression were applied (Fahrmeir & Hammerle 1984; Krzanowsky 1988). Cluster analysis works with a measure of similarity and looks for an optimal splitting of the sample according to a given criterion (Fahrmeir & Hammerle 1984). It looks for existing natural groups without using information about existing groups. Ward's method takes as similarity measure the homogeneity (computed as the sum of distances between the centre of a group and all individuals within the group) and looks for the splitting which produces a smaller loss of homogeneity. Generally, it results in compact, spherical clusters. Martín-Fernández (2001) discussed drawbacks and advantages of several clustering techniques applied to compositional data, as well as the influence of the distance used. Here, a Ward cluster analysis is applied to the standardized, clr-transformed 12-part compositional dataset.

Binary logistic discriminant analysis looks for a linear function which predicts the log-odds of allocation of an individual over two groups. This linear function is constructed as a projection of the available explicative variables onto a direction, which is obtained by regressing a binary variable (valued 0 for one group, and 1 for the other) against the explicative variables (Krzanowsky 1988). Barceló-Vidal (1996) introduced and discussed equivalent parametric discrimination techniques for compositional data. Here, the logistic technique is applied to the clr-transformed dataset. A classical measure of goodness of discrimination is obtained by computing **misclassification rates**: the proportion of samples from each group which are classified erroneously by the discrimination rule.

# Results

As a first approach, discriminant analysis was applied to existing groups defined by regions, deposits and zones (Table 1). In spite of the small number of samples (Table 2) compared with the number of variables, misclassification rates were clearly unsatisfactory (more than 20% of samples are classified badly), thus supporting the idea that the formation process of these ore bodies was

**Table 3.** Misclassification rates of groups, defined according to regions, deposits and zones, as well as the several discrimination analyses performed with groups defined by the Ward clustering method

Criterion	Global misclassification rate (%)	Highest misclassification rate in a group (%)	Worse classified group
Region	22	31	Komsomol'sk
Deposit	22	100	Vysokogorskoe
Zone	35	87.5	Fel'zitovava1
Ward groups (full)	3	17	group 3
Ward groups (simplified)	5	14	group 2

Note: 'Full' uses the discrimination rules defined in Table 5, whereas 'simplified' uses the discrimination rules of equations (2)-(4).

highly complex. Global misclassification rates and maximal misclassification rate for a single group are included in Table 3.

Given this unsuccessful direct approach, the Ward clustering technique was applied to the standardized clr-transformed dataset to look for natural associations between observations, independently of the original geotectonic information. Results suggested the existence of, at most, four different groups, which were a posteriori crosstabulated with the existing zones of the dataset (Table 4). The first group is identified with the Vysokogorskoe deposit, Fel'zitovaya zones (Arsen'evskoe deposit) and Pereval'noe deposit (Komsomol'sk district). The second group includes Tourmalinovaya and Podruzhka zones from the Arsen'evskoe deposit, as well as the Festival'noe deposit from Komsomol'sk district. The third group corresponds to a subgroup of samples of Yuzhnaya zone and to Induktzionnaya zone from the Arsen'evskoe deposit, while the remaining samples of Yuzhnaya zone form group 4. The distribution pattern in the original biplot (Fig. 4) shows a clear visual difference between groups 1-2 versus groups 3-4. Such a difference can be related to the fact that both groups 1 and 2 are considered to be formed under a transform margin regime, whereas formation of groups 3 and 4 is regarded to be linked to an active margin (Table 1).

The good separation of the obtained groups suggests that a hierarchical binary logistic discriminant analysis could be applicable. First, zones from Andean versus Californian regimes were discriminated (groups 1 and 2 vs. groups 3 and 4). Afterwards, discrimination inside these regimes was conducted. The obtained discriminating rules among the groups produce misclassification rates below 4%. The coefficients in Table 5 correspond to the discriminating directions expressed as compositions. Table 3 reports misclassification rates of this hierarchical discriminating system.

The obtained discriminating functions were not easy to interpret. Therefore, the next step was to

		Zone	Ward clusters				E'
Region	Deposit		1	2	3	4	group
Komsomol'sk	Festival'noe	Geophysicheskaya	2	10			2
	Pereval'noe	Severnaya	4				1
Kavalerovo	Arsen'evskoe	Fel'zitovaya1	8				1
		Fel'zitovaya2	8				1
		Induktzionnaya	1		5		3
		Podruzhka	1	4			2
		Yuzhnaya	1		10	69	3 and 4
		Tourmalinovaya		4			2
	Vysokogorskoe	8-th Vostok	7				1
		Kulisnaya	5				1
		Tektonicheskaya	5				1

Table 4. Classification of tin deposits by Ward's cluster analysis

The number of samples of each zone falling in each group obtained by cluster analysis is reported. The final column reports to which group the whole zone was finally attached. For example, for the rest of the analysis, *Geophysicheskaya* was considered wholly in group 2.



**Fig. 4.** Biplots of cassiterite trace elements from the studied tin deposits (Far Eastern Russia), distinguishing samples to the groups obtained from Ward's cluster analysis. Note that groups tend to have a similar spread (as expected from a Ward cluster) and that the biplot is the same as in Figure 3 (since grouping does not change the covariance structure of the variables).

	Discrin	Discriminating loadings			Correlation coefficients			
	1&2 vs. 3&4	3 vs. 4	1 vs. 2	1&2 vs. 3&4	3 vs. 4	1 vs. 2		
clr(In)	0.567	1.956	-0.043	0.863*	0.801*	0.706*		
clr(Sc)	0.195	0.315	0.459	0.610*	0.540	0.431		
clr(W)	0.432	-0.045	-0.030	0.678*	0.283	0.373		
clr(Nb)	-0.093	0.099	0.604	-0.237	0.135	0.035		
clr(V)	-0.149	-1.381	-0.147	-0.384	$-0.782^{*}$	-0.608*		
clr(Cr)	0.121	0.120	0.020	0.477	0.074	0.200		
clr(Be)	-0.251	0.988	0.316	0.558	0.845*	0.702*		
clr(Ti)	0.049	0.527	-2.199	-0.552	-0.604*	-0.871*		
clr(Zr)	-0.375	0.121	-0.080	-0.813*	-0.461	-0.572		
clr(Fe)	0.243	-1.948	0.469	0.756*	0.314	0.495		
clr(Mn)	-0.539	-0.217	-0.383	$-0.817^{*}$	-0.544*	-0.568*		
clr(Rst)	-0.200	-0.536	1.014	-0.568	-0.613	-0.219		

**Table 5.** Coefficients of the linear discriminating rules between groups, following a hierarchical scheme: Andean (3-4) vs. Californian (1-2) margin type, main Yuzhnaya (4) vs. Induktionnaya (3) zones in Arsen'evskoe deposit, and Geophysicheskaya, Podruzhka and Tourmalinovaya zones (2) vs. the rest (1)

Highest correlation coefficients have been marked with an asterisk (\*).

look for balances with the highest correlation with each discriminating rule. Balances are log-ratios of the geometric mean of the parts of two subcompositions, multiplied by a normalizing constant (Egozcue & Pawlowsky-Glahn 2005, 2006). To determine these balances, those elements which had clr-transformed values with the highest correlation with each discrimination function (Table 5) were selected first, afterwards all balances between these elements were computed, and finally those with the highest correlation with the discriminating functions were selected. The first discriminating functions, expressed as a linear function of a balance and afterwards rounding the coefficients, resulted in

$$f_{1} \approx 0.96 \ln \frac{(\text{In} \cdot \text{Fe} \cdot \text{Sc} \cdot \text{W} \cdot \text{Cr})^{2}}{(\text{Mn} \cdot \text{Zr})^{5}} - 0.115$$
$$\approx \ln \frac{(\text{In} \cdot \text{Fe} \cdot \text{Sc} \cdot \text{W} \cdot \text{Cr})^{2}}{(\text{Mn} \cdot \text{Zr})^{5}} - 0.12, \quad (2)$$

which has positive values in groups 3 and 4 (Andean regime) and negative values in groups 1 and 2 (Californian regime). Inside the Andean group, groups 3 and 4 are discriminated using the

simplified second rule,

$$f_2 \approx 3.91 \ln \frac{\operatorname{Be} \cdot \operatorname{In}}{\operatorname{V}^2} + 1.16$$
$$\approx 4 \ln \frac{\operatorname{Be} \cdot \operatorname{In}}{\operatorname{V}^2} + 1.2, \qquad (3)$$

characterized by negative values in group 4 and positive values in group 3. Finally, discrimination inside the Californian group is based on using the simplified third rule,

$$f_3 \approx 1.06 \ln \frac{\mathrm{Be} \cdot \mathrm{Nb}}{\mathrm{V}^2} + 0.07 \approx \ln \frac{\mathrm{Be} \cdot \mathrm{Nb}}{\mathrm{V}^2},$$
 (4)

with negative values in group 2 and positive values in group 1. The similarity between the simplified second and third functions suggests that the ratio Be/V is very informative. The scatter-plot (Fig. 5) of the first simplified discriminant function (1) and ln(Be/V) clearly separates the four groups. Note that in this figure, the borders between the groups in the vertical directions do not coincide with the zero level. This is due to the means of ln(In/V) and ln(Nb/V), which were subtracted from equations (3) and (4), respectively. Misclassification rates of this balance discriminating system are also reported in Table 3.



Fig. 5. Scatter-plot of the linear discriminating functions approximated by balances among groups defined by Ward cluster analysis, with indication of mean values for each group. The legend is the same as in Figure 4.

## Discussion

Balance (2) compares two groups of parts: (In, Fe, Sc, W, Cr) vs. (Mn, Zr). The ratio of the first against the second group is greater in those samples from the Andean type vs. the Californian type. These groups have a relative resemblance to the siderophile (Fe, Ti, V, Cr, Ni) and lithophile (Be, Nb, Zr, Mn) associations of Gorelikova & Tchijova (1997). They suggest that Andean-regime fluids have a higher proportion of siderophile trace elements, while Californian-regime fluids are relatively richer in lithophile trace elements. Another interesting difference between groups 1-2 vs. 3-4 is the presence/absence of tourmaline (Table 1).

In the Californian group, group 1 (Fel'zitovaya zones in the Arsen'evskoe deposit, jointly with Vysokogorskoe and Pereval'noe deposits) is characterized by higher Be/V ratios than group 2 (an early stage represented by Tourmalinovaya, and Podruzhka in the Arsen'evskoe deposit, plus Geophysicheskaya). In general terms, group 2 zones are older than those integrated in group 1, and intense metamorphism is reported for some of these older zones. Therefore, one could tentatively relate equation (4) with age. Thus, this rule discriminates zones formed during the early Cretaceous episode from those formed during the Eccene. Alternatives would be to relate equation (4) with the influence or superposition of metamorphism, as well as with a balance between tourmaline parageneses, dominant in group 2 (Table 1), against sulphide and quartz parageneses, dominant in group 1.

Under an Andean regime, group 4 (main part of the Yuzhnaya zone in the Arsen'evskoe deposit) is characterized by higher V (or lower Be and In) content than group 3 (formed by a small part of the Yuzhnaya zone, and the whole Induktzionnaya zone, both in the Arsen'evskoe deposit). No mineral difference may be associated with these groups, according to Table 1.

Finally, note that the results of Gorelikova & Tchijova (1997) are not inconsistent with those obtained here, although theirs were obtained using a classical approach and those presented here using a log-ratio one, showing that they obtained a reasonable approximation. Here, siderophile fluids would be indicated by the association (In, Fe, W, Sc, Cr), whereas lithophile fluids would be linked to the association (Mn, Zr). Mineral parageneses are not so clearly linked to trace element parageneses.

# Conclusions

Geochemical associations in cassiterite from tinbearing zones of Far Eastern Russia allow the classification of the zones in groups corresponding to probable geodynamic settings: an early Cretaceous transform margin (Pereval'noe deposit and some metamorphized zones of the Arsen'evskoe deposit), an active margin (zones Yuzhnaya and Induktzionnaya from the Arsen'evskoe deposit) and, finally, a late Eocene transform margin (Vysokogorskoe deposit and more recent zones of Arsen'evskoe). On the basis of these results, it is admissible that the differences in cassiterite compositions are governed primarily by the fluids involved, which are eventually determined by the geodynamic regime. Geochemical differences could then be used to identify tin deposits formed under various settings and to give additional support to the geodynamic model of ore deposits of Khanchuk (2000).

Complementary results show that those deposits or zones formed under a Californian regime are almost always marked by the presence of tourmaline in their mineral paragenesis, whereas this silicate does not appear in those ore bodies formed under an Andean regime. A further division of both the Californian and the Andean groups is achieved by the ratio Be/V. In the Californian group, this ratio separates acceptably well ore bodies formed in the Cretaceous and those formed in the Eocene. The interpretation of this division within the Andean group needs further investigation.

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# Appendix A: Geological characterization of studied ore bodies

#### Komsomol'sk region

The formation of the Khingan-Okhotsk metallogenic belt, including the Myao-Chan zone from the Cretaceous stage - to which the tin mineralization is related - happened under both the early transform margin regime and the subduction margin (Gonevchuk et al. 2000; Khanchuk 2000; Khanchuk & Kemkin 2003), covering the whole Cretaceous. In the Myao-Chan zone (Komsomol'sk ore region) tin deposits are represented by mineral associations of cassiterite-silicate-sulphide type composed of thick quartz-tourmaline zones. The main tin-bearing magmatic association of this region is dated in the interval 102-85 Ma (Gonevchuk 2002). The most probable age of tin mineralization is 95-84 Ma, and some isotope dating fixes it at 103-75 Ma. Petrochemical and geochemical features of magmatic and ore assemblages define the Komsomol'sk ore-magmatic system as a heterogeneous

#### 54

#### N. GORELIKOVA ET AL.

mantle-crust one. From the several deposits of this region, *Festival'noe* and *Pereval'noe* are included in the study.

Festival'noe deposit. The Festival'noe deposit is located in the southern linear Perevalnensk ore structure within the Jurassic terrigenous-volcanic rocks of Mesozoic age. The main ore zones are Yagodnaya and Geophysicheskaya, dominated by copper-tin-sulphide paragenesis. Hosting structures are south-strike fractures, with related quartz-feldspar metasomatites regarded as an early mineralization stage. Mineralization of quartz-cassiterite, quartz-sulphide and quartz-carbonate composition occurred in the following stages. The mineral composition of these ore stages is rather complex: cassiterite, arsenopyrite, wolframite, scheelite, chalcopyrite, pyrrhotite, stannite, magnetite, galena, sphalerite and pyrite, among others. Besides, there are mainly: guartz, tourmaline, chlorite, micas, fluorite, calcite and siderite, with an accessory presence of wolframite and arsenopyrite (particularly with quartz). Sulphides are distributed widely in thick mineralization veins. Chalcopyrite and pyrrhotite are widespread. Cassiterite is represented by meso-crystalline and coarse-crystalline varieties and its maximal abundance is related to the structural discordance between sedimentary and volcanic rocks. The formation of ore zones from the Festival'noe deposit occurred over a long period under the influence of intensive tectonic deformations. This study considers the mineralization of the zone Geophysicheskaya.

Pereval'noe deposit. The Pereval'noe deposit is located in the northern part of the Komsomol'sk region within the large Amut syncline composed of the thick volcanic Choldamy and Amut series of Cretaceous age. The strata of the Early Cretaceous volcanic-sedimentary rocks is represented by conglomerates, breccia, sands, gritstone, tuffs, and tuff breccia of quartz porphyrys which are placed above pyroxene-plagioclase porphyrites. Intrusive rocks of the Amut syncline are dykes and stocks of diorites and gabbro-diorites, intruded within the Jurassic sedimentary rocks with a sharp angle. Severnaya zone is the most important one in this deposit. It is composed of quartztourmaline-sulphide ores. It has a complicated morphology: a thick vein of quartz-tourmaline metasomatites is cut by cassiterite-quartz veins with sulphides, among which arsenopyrite, pyrrotite, chalcopyrite and pyrite prevail. In the upper part of the porphyrite section there are series of imbricate zones and veins with a Pb-Zn mineralization stockwork. In the deposit, a mineralogical zonation is observed as a change in the quartz-sulphide mineralization at the upper horizons by the cassiteritequartz one at the middle level, and the quartz-tourmaline at the lower horizons. Based on a study of the structuralmorphological features of ores, it is believed that the Severnaya zone was formed in several stages: (1) the quartz-tourmaline stage; (2) the quartz-cassiterite stage, with formation of wolframite, arsenopyrite and sericite; (3) the quartz-carbonate-sulphide stage, with formation of chlorite, pyrrhotite, chalcopyrite, sphalerite, galena and bournonite; and (4) the calcite stage, with formation of chalcedony, pyrite and marcasite.

#### Kavalerovo region

Within the Sikhote-Alin' metallogenic belt tin deposits from the Kavalerovo ore region are considered, the largest and most studied. In accordance with the 'tectogenetic switch' hypothesis, the Kavalerovo region is located within the Taukhinsky terrane of the Early Cretaceous accretion prism and the Zhuravlevsky terrane of the Jurassic-Early Cretaceous turbidite basin accreted to the continent in the Late Alb time (Golozubov & Khanchuck 1995). The tinbearing magmatism of this region is dated in the interval 115-45 Ma and, according to Khanchuk (2000, Khanchuck et al. 2003), it is related to both the geodynamic regimes of transform margin (Early Cretaceous) and subduction (Middle-Late Cretaceous), although the Paleocene transform margin significantly altered it. Most deposits of this region suffered two stages of tin mineralization, namely, the Late Cretaceous and the Paleocene ones, both with a varied composition (Finashin 1986; Tomson et al. 1996). This work considers tin zones of the Vysokogorskoe and Arsen'evskoe deposits.

Vysokogorskoe deposit. The Vysokogorskoe deposit (Kokorin et al. 2001) is located in the eastern part of the region and is related to a tectonic block of terrigenouscarbonaceous rocks of the Taukhinsky terrane (Cretaceous-Paleocene volcanic materials). Isotope dating shows that the ore-magmatic association of this deposit was formed in the interval 95-45 Ma. However, some results fix the age of the early granodiorites at 105 Ma. In the opinion of most researchers, three different mineralization stages related to several magmatic stages occurred in this deposit. About one hundred ore veins have been identified, as well as stockwork zones and mineralizations in explosion breccia. The main age of mineralization is 55-45 Ma, using K/Ar data (Finashin et al. 1978), and the formation of the main ore zones corresponds to the regime of a young transform margin.

The main mineralization stage is a tin ore, formed by metasomatic veins of complex morphology and mineralization, as well as breccia zones of about 1 km width, related to the *Silinsky* jointing zone. At approximately 500 m depth, mineralization in explosive breccia replaces the veins. These explosive breccia, made of fragments of siltstones and silica, are cemented by tourmaline, sericite, chlorite, quartz, cassiterite and sulphides. The early formation stage of this explosive breccia is dominated by a quartz-tourmaline paragenesis, with fragments of microquartzites cemented by a fine-grained aggregate. The later quartz-sulphide assemblage is formed by quartz, pyrrhotite, pyrite, sphalerite, chalcopyrite and Ag-galena. The final stage is characterized by a quartz-fluorite-carbonate

paragenesis, with accessory pyrite, galena and sphalerite. The vein series of quartz-tourmaline-chlorite ores, according to Khanchuk & Kemkin (2003), essentially corresponds to the late Cretaceous-Paleocene mineralization stage. The present study considers ore associations of vein zones *Tectonicheskaya*, *Kulisnaya* and *8th Vostok*.

Arsen'evskoe deposit. The Arsen'evskoe deposit is located in the western part of the ore region in rocks of the Zhuravlevsky turbidite terrane. It is related to the central Sikhote' Alin fault, a major tectonic structure controlling some large intrusions in the region. Magmatic rocks are represented by trachymonzonites and andesitediorites formed during the Alb-Turonian, the Cenomanian and the Paleocene periods (Popovichenko 1989). From the Alb-Turonian, there are stocks of monzonite-porphyries and rare dykes of trachyandesite-basalts of the Ararat-Beresovsky complex (114–90 Ma), characterized in detail by Gladkov (1982, 1988) and Gonevchuk (2002).

At the Cenomanian period, formation of widespread dykes of granodiorite–porhyry and rare granites and rhyolites occurred. Granodiorites and granites are present as fragments in explosive breccia of the Paleocene period. Their age, using K/Ar dating, is  $80 \pm 5$  Ma (Gonevchuk 2002; using biotites) and  $76 \pm 4$  Ma (Tomson *et al.* 1996; using the bulk rock). This igneous complex might be related to the *Uglovsky* volcanic–plutonic complex (100–80 Ma), which is traditionally related in this region with ore mineralization of the Late Cretaceous stage (predominant within the central part of the deposit). The Paleocene magmatic stage is present as highly aluminiferous andesites and andesite– basalts in dykes and subvolcanic bodies of ultrapotassic rhyolites.

Most researchers distinguish two stages of tin mineralization within this deposit: the earliest Early-Late Cretaceous one  $(95-93 \pm 8 \text{ Ma}; \text{Tomson et al. } 1996)$  is represented by the so-called latitudinal zones; the later Upper Cretaceous stage is characterized by the formation of the main vein series from the economically interesting tin ores (60-70 Ma), dipping approximately to the south. There are different views about the formation of Fel'zitovaya 1 and Fel'zitovaya 2 zones, both connected with felsite dykes from the final stage. Some researchers connect these zones with the main ore stage, considering felsite dykes as intrametalliferous (Nekrasov & Popov 1990), others consider it as an independent stage (Khanchuk et al. 2004). The early stage (Tourmalinovaya zone) is characterized by metasomatic tourmaline-cassiterite-sulphosalt ores. It is related to the Late Cretaceous Berezovsky-Ararat volcanic-plutonic complex. Ore bodies of this stage are linked with biotite metasomatites, and are represented by zones of fine-grained tourmalinites and streakydisseminated sulphide-sulphosalt ores (Tourmalinovava and Podruzhka zones, aka latitudinal zones). They cut porphyry dykes and they are, in turn, cut and metamorphized by other felsitic porphyry dykes and cassiterite-chloritesilicate-sulphide veins. The mineralization of the early

stage, in vein-shaped bodies with unclear contacts, was formed as a result of metasomatic substitution of tectonic jointing zones. Ore zones are composed of silicified rocks, together with sericite-quartz paragenesis and quartztourmaline metasomatites (Finashin 1986). Ore textures are massive, compact breccia and disseminated veins.

The zones of the second stage form thick vein series of cassiterite-quartz composition (Yuzhnaya and Induktzionnaya zones). Both Fel'zitovaya zones are formed by a thick fracture structure of substitution, which occurred after the felsite dyke intrusion, and have a dominant quartz-cassiterite composition, with calcite and fine impregnation of sulphides. Metasomatic ores present segregations of massive sulphides involving pyrrhotite, chalcopyrite, sphalerite, stannite and impregnation of Bi-Ag-galena, arsenopyrite, pyrite, marcasite, wolframite, tetrahedrite, freibergite, sulphosalts of Pb and Sb, minerals of the series lillianite-gustavite, and native Bi and Sb. Non-metalliferous minerals are: quartz, tourmaline, chlorite, sericite and Mn-bearing carbonates.

The main vein series of the second stage is represented by thick quartz-cassiterite-sulphide ore bodies placed along NW-SE fractures. They occur in low metamorphized sedimentary rocks of the Jurassic-Early Cretaceous stage. The age of intrametalliferous dykes and metasomatites is 58-53 Ma, using K/Ar dating (Tomson et al. 1983). Filling veins have banded and zonal textures, resulting from successive deposition of cassiterite, chlorite and quartz. The deposition of the main mass of cassiterite occurred at the early stage of the ore process, associated with early quartz and chlorite. In zones of the main vein series, the following mineralization stages have been identified: (1) quartz-chlorite-cassiterite, (2) quartz-sulphidesulphosalt, (3) quartz-fluorite-carbonate. Each stage cuts all the preceding stages. Samples were collected from the cassiterite-chlorite-quartz vein zones called Yuzhnaya and Induktzionnaya.

The mineralization of the third stage is represented by quartz-cassiterite-sulphide ores, connected with potassic rhyolitic dykes posterior to the basic magmatic rocks (Nekrasov & Popov 1990). They might be related to a young transform margin of Eocene age. The spatiotemporal association of these K-rhyolitic dykes with high-aluminiferous basalts suggests that they should be interpreted as a genetic association, of age 60-48 Ma (Finashin 1986). These rhyolites can be considered as a subvolcanic analogue of the leucogranites of the Uglovsky complex. The mineralization is composed of two veins, Fel'zitovaya, which forms a thick fracture structure with a vertical dip parallel to the main vein series, going from the volcano Samovar to the Intermontane fault. Fel'zitovaya is observed at 800 m depth and it crops out poorly as quartz-sulphide veins. Veins form a stock-shaped substitution deposit, and essentially have a quartz-cassiterite composition, with calcite and fine impregnation of arsenopyrite, pyrrhotite, galena, chalcopyrite and pyrite.

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56

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